

# CHAPTER

# 2



# GROUP 16 ELEMENTS

- \* General Characteristics
- \* Oxy Acids of Sulphur
- \* Hydrides, Halides and Oxides
- \* Ozone and Sulphuric Acid

## GENERAL CHARACTERISTICS

### 2.1.1

#### Position in periodic table

*VIA elements are called chalcogens because they form minerals*

IA	IIA											0
		IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	
												N
												O
												F
												P
												S
												Cl
												As
												Se
												Br
												Sb
												Te
												I
												Bi
												Po
												At

Table 2.1 Position of group VIA elements


*General electronic configuration of group VIA is  $ns^2np^4$*

Each of the group VIA elements has six electrons in the valence shell. Two electrons are filled in the s sub-shell and the remaining four in the p sub-shell. The general electronic configuration of these elements is  $ns^2np^4$ . Configuration of these elements is given in the box method in Fig 2.1 and summarized in Table 2.2.

Configuration	$ns^2$	$np_x^2$	$np_y^1$	$np_z^1$
in the ground state	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$

Fig 2.1 Electronic configuration of group VIA elements

Table 2.2 Atomic numbers and electronic configuration of the group VIA elements

Element	Symbol	Atomic Number	Configuration
Oxygen	O	8	[He] 2s <sup>2</sup> 2p <sup>4</sup>
Sulphur	S	16	[Ne] 3s <sup>2</sup> 3p <sup>4</sup>
Selenium	Se	34	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>
Tellurium	Te	52	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>
Polonium	Po	84	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>

In accordance with the Hund's rule, the fourth electron will be paired up in the p-sub shell. Therefore the number of unpaired electrons in an atom of each of these elements is 2.

Only two electrons are present in the penultimate shell of oxygen, eight electrons in sulphur, eighteen electrons each in selenium, tellurium and polonium. This shows why oxygen differs in some of its properties from sulphur and these two elements differ from the remaining elements of the group.

### 2.1.2

#### Occurrence

Oxygen and sulphur occur widely in nature as oxides, sulphides and sulphates. The important minerals are :

##### Sulphides

Galena : PbS

Zinc blende : ZnS

Copper pyrites : CuFeS<sub>2</sub>

##### Sulphates

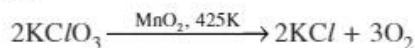
Gypsum : CaSO<sub>4</sub>·2H<sub>2</sub>O

Epsom : MgSO<sub>4</sub>·7H<sub>2</sub>O

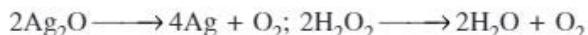
Barytes : BaSO<sub>4</sub>

Oxygen is also available in free state as dioxygen. Oxygen comprises about 21% of the earth's atmosphere by volume. Oxygen is the most abundant element of the earth's crust. It makes up 46 percent of earth by weight.

Oxygen is prepared by the fractional distillation of liquid air. It is also prepared by thermal decomposition of potassium chlorate in the presence of manganese dioxide as catalyst, decomposition of KMnO<sub>4</sub> and nitrates of alkali metals, except lithium.



Oxygen is also available by the decomposition of higher oxides of some metals, oxides of relatively lower electropositive metals and peroxides.



On large scale oxygen is obtained at anode by the electrolysis of acidulated water. Oxygen has three stable isotopes : <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O. Molecular oxygen is also called dioxygen and it is unique in being paramagnetic.

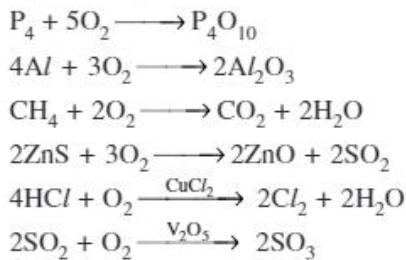
Dioxygen is colourless, odourless gas, liquifies at 90 K and freezes at 55K. It's solubility in water is less, about 3.08 cc in 100 cc of water at 293 K, which is just sufficient, as dissolved oxygen, for vital marine life.

Oxygen is the  
most abundant  
element of earth's  
crust (46%w/w)

  
**Combination of oxygen with elements is often exothermic**  

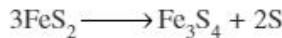

  
**Oxygen is important in respiration and combustion**  


Oxygen directly reacts with nearly all non-metals and metals, except metals like Au, Pt, etc., and noble gases. Combination of oxygen is often exothermic. However, to overcome the double bond dissociation, the reactions are initiated by external heating.



Oxygen is important in normal respiration, oxyacetylene welding, manufacture of steel, combustion process and constituent in rocket fuels.

Sulphur is the sixteenth most abundant element in the earth's crust. Abundance of sulphur is 340 ppm. Organic materials such as wool, hair, proteins, egg, garlic, onion and mustard contain sulphur. In vapour state, S partially exists as  $S_2$  and exhibits paramagnetism. Though native sulphur is also available, sulphur is usually recovered by the distillation of iron pyrites.



$H_2S$  and  $SO_2$  are present in volcanic gases. These gases react to give sulphur.



Selenium and tellurium are very less abundant in the earth's crust. Polonium is radioactive and short lived. It was isolated by Curie from the mineral, pitchblende.

### 2.1.3

**General properties** The similarities and gradation in the general physical properties of the group VIA elements are summarised in Table 2.3.

**Table 2.3 Gradation in the physical constants of the group VIA elements**

Property	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Atomic weight	15.99	32.06	78.96	127.6	210
Covalent radius ( $\text{\AA}$ )	0.74	1.04	1.14	1.42	1.59
Density in solid state ( $\text{gc. c}^{-1}$ )	1.13	2.08	4.79	6.24	9.2
Melting point ( $^{\circ}\text{C}$ )	-229	119	221	452	254
Boiling point ( $^{\circ}\text{C}$ )	-183	445	685	990	962
Electron affinity ( $\text{kJ mol}^{-1}$ )	-141	-200	-195	-190	-174
Ionisation potential ( $\text{kJ mol}^{-1}$ )	1314	999	941	863	813
Electronegativity (Pauling scale)	3.5	2.6	2.4	2.1	2.0
M-M bond energy ( $\text{kJ mol}^{-1}$ )	213	422	271	217	--
Common oxidation states	-2 +2	-2 +2, +4, +6	-2 +2, +4, +6	+2, +4, +6	+2, +4

**Atomic radius :** From oxygen to polonium the atomic radius and the atomic weight gradually increase. The differentiating electron enters into the next higher energy shell, suggesting an increase in the atomic radius. However, the increase in the radius is less predominant beyond sulphur. This is due to the shielding effect by inner d-orbitals.

Oxygen is a gas and other elements of group 16 are solids



Selenium and tellurium are metalloids



**Physical state :** Oxygen is a gas at room temperature. Other elements of the group 16 are solids. The melting and boiling points gradually increase from oxygen to tellurium. The smaller values of polonium are attributed to a different crystal structure.

**Metallic nature :** The electronegativity values on Pauling's scale gradually decrease from oxygen to polonium. The metallic nature increases gradually with an increase in the atomic size. Oxygen and sulphur are non-metals. Selenium and tellurium are metalloids. Polonium, though radioactive and least abundant, is clearly a metal.

**Ionisation potential :** The ionisation potential values decrease gradually on descending the group as the atomic number increases.

Ionisation potential values of the group VIA elements are relatively low compared to the corresponding elements of adjacent groups. Higher ionisation potential value of the group VA elements is attributed to the stable half-filled p-orbitals in group VA. The higher values of ionisation potential of the group VIIA elements is attributed to the larger nuclear charge of these elements. The decrease in ionisation potential values after sulphur is less predominant, which is attributed to shielding effect of inner d-orbitals.

**Electron affinity :** The electron gain enthalpy of oxygen is less negative than that of sulphur. This is because of compact nature of oxygen. Oxygen is the element with least electron affinity among chalcogens.

**Atomicity :** The oxygen is a diatomic molecule with a double bond between two bonded atoms. The double bond contains one sigma and one pi-bond. Double bond of oxygen molecule based on orbital overlap is shown in Fig 2.2.

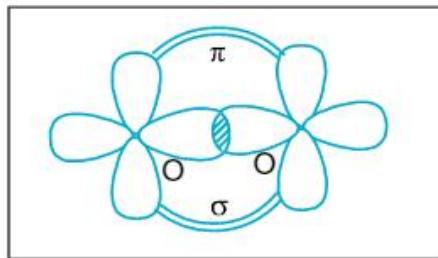


Fig 2.2 Orbital overlaps in  $\text{O}_2$  molecule

Oxygen is a paramagnetic molecule due to the presence of two unpaired electrons. The magnetic behaviour of oxygen is explained by molecular orbital theory.

Atomicity of sulphur, selenium and tellurium is eight each. They form crown shaped molecules. The structure of these molecules is referred as puckered ring. In the sulphur molecule the S-S bond length is 2.05 Å and SSS bond angle is 105°, as shown in Fig 2.3.

Atomicity of sulphur is 8.  
 $\text{S}_8$  has puckered ring structure



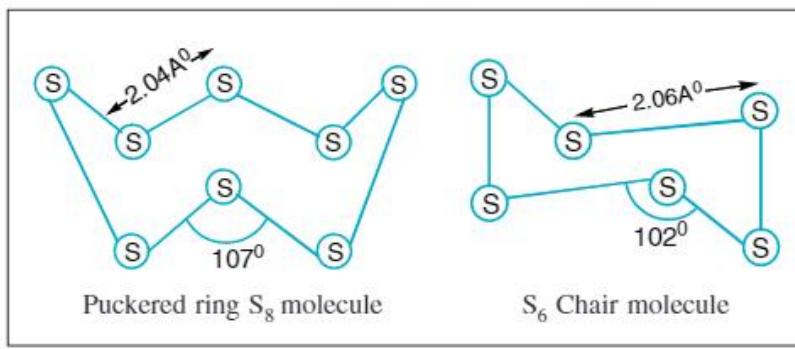


Fig 2.3 Structure of sulphur molecules

The large difference between melting and boiling points of oxygen and sulphur is due to the difference in atomicity.

**Catenation :** Tetra-atomic molecule of oxygen with four oxygen atoms has been reported. Catenation ability is second highest for sulphur, after carbon. Catenation ability of sulphur is much evidenced in its compounds with hydrogen. The tendency of self-linkage of atoms of same element gradually decreases from sulphur to polonium. This decrease in the catenation ability is attributed to the decrease in M-M bond energies.

**Allotropy :** All the group 15 elements exhibit allotropy. The only gaseous element that exhibits allotropy is oxygen. Its allotrope is triatomic oxygen, called ozone.

Sulphur exhibits two types of allotropes, crystalline and amorphous. Rhombic sulphur and monoclinic sulphur are the crystalline forms of sulphur. At room temperature, the most stable form of sulphur is rhombic. It is the most common form of sulphur and stable up to 95.6°C. Above this temperature monoclinic sulphur is stable. Rhombic sulphur is most stable thermodynamically. It is yellow, melts at 386 K with specific gravity 2.06. It is insoluble in water, readily soluble in carbondisulphide and dissolves to some extent in benzene, ether and alcohol. Monoclinic sulphur is insoluble in carbon tetrachloride.

Temperature at which both allotropes of sulphur are at equilibrium is called transition temperature. The transition temperature of crystalline forms of sulphur is 95.5°C or 368.5 K. The two forms are also called enantiotropic substances. Rhombic sulphur is called  $\alpha$ -sulphur. Monoclinic sulphur has two forms  $\beta$ - and  $\gamma$ . All  $\alpha$ -,  $\beta$ - and  $\gamma$ - are crystalline forms and differ in their densities.

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. Engle's sulphur has  $S_6$  rings in chair forms. On heating sulphur melts at 119°C and forms a mobile liquid. On further heating at 160°C, the octaatomic rings break to give  $S_6$ ,  $S_4$  and  $S_2$  units. Molten sulphur on quenching in water gives plastic sulphur. This is called  $\psi$  form. At elevated temperature (about 1000K),  $S_2$  is the dominant species and is paramagnetic like dioxygen.

Selenium has six allotropes, in which four are red and two are grey varieties. Most stable form is the metallic selenium of grey variety. Tellurium also has red and grey varieties. Crystalline tellurium is isomorphous with grey selenium. Crystalline tellurium is strongly metallic and is a good conductor.

All elements of group 15 exhibit allotropy

Transition temperature of  $\alpha$ - and  $\beta$ -sulphurs is 368.5 K

  
**Oxygen cannot be hexavalent, due to lack of valence d-orbitals**  


**Bonding and valency :** Each element of the group VIA has six valence electrons and requires two more for attaining stable octet configuration. The usual valency of chalcogen is thus two. The maximum valency of these elements is however, is the group number 6.

Oxygen cannot exhibit tetravalency and hexavalency like the other elements of this group. This is due to lack of valence d-orbitals in oxygen. In hydronium ion, the maximum covalency of oxygen is three. Due to its high electronegativity and small size, oxygen can form ionic compounds with metals. By gaining 2 electrons, it forms metal oxides. Sulphur also has the tendency of forming metal sulphides.

### 2.1.4

#### Oxidation numbers

  
**Oxygen exhibits positive oxidation states in fluorides**  


The general oxidation numbers of the group VIA elements are -2, +2, +4 and +6. The negative oxidation state (-2) is predominant for oxygen. This is due to its non-metallic nature and higher electronegativity value.

Oxygen exhibits positive oxidation numbers in fluorides, +1 in  $O_2F_2$  and +2 in  $OF_2$ . Oxygen exhibits -1 state in peroxides. Oxygen also exhibits fractional oxidation state, -1/2 in superoxides.

The importance of -2 oxidation state decreases from oxygen to sulphur and then almost vanishes for tellurium and polonium. The tendency of exhibiting +6 oxidation state by the group VIA elements decreases from oxygen to polonium. This is due to inert pair effect.

The common oxidation states of sulphur in its compounds are -2, +2, +4 and +6. These are all even numbers. Two unpaired electrons can form two bonds in the ground state of sulphur. Electronic configuration of sulphur in different states is shown in Fig 2.4.

  
**Oxidation numbers of sulphur are all even numbers**  


Configuration in the ground state	3s <sup>2</sup>	3p <sup>4</sup>	3d <sup>0</sup>
Configuration in the first excited state	3s <sup>2</sup>	3p <sup>3</sup>	3d <sup>1</sup>
Configuration in the second excited state	3s <sup>1</sup>	3p <sup>3</sup>	3d <sup>2</sup>

**Fig 2.4 Electronic configuration of sulphur in different states**

With four unpaired electrons, sulphur forms four bonds in the first excited state. With six unpaired electrons, six bonds are formed in the second excited state.

In the ground state, sulphur exhibits -2 oxidation state. eg :  $H_2S$ ,  $ZnS$ , etc. In the first excited state, sulphur may undergo  $sp^2$  or  $sp^3d$  hybridisation. The oxidation state exhibited is +4. eg :  $SO_2$ ,  $SF_4$ ,  $SCl_4$ , etc. In the second excited state, sulphur may undergo  $sp^2$  or  $sp^3d^2$  hybridisation. The oxidation state exhibited is +6. eg :  $SO_3$ ,  $SF_6$ , etc.

S and Se are more stable in their +4 or +6 states than +2 state. Te is stable in its +4 and +6 states, though +2 state is also considerably stable.



**P.2.1** What is the percentage make up of most abundant element in the most abundant liquid of the earth's crust?

**Solution** Most abundant liquid in earth's crust is water. Most abundant element is oxygen.

16 grams of oxygen is present in 18 grams of water,  $\text{H}_2\text{O}$ .

$$\text{Weight percentage of oxygen} = (16/18) \times 100 = 88.89\%$$



**P.2.2** Oxygen is a gas, but other elements of group 16 are solids at room temperature. Why ?

**Solution** Oxygen exists as isolated diatomic molecules. Between atoms of oxygen molecule the attractions are strong, but inter molecular attractions are very weak. Hence oxygen is a gas.

Other elements of group 16, have complex states. The tendency to form multiple bonds between identical atoms decreases with an increase in atomic weight. Bonding ability between many atoms of same element increases. Molecular complexity and van der Waals forces increase. Hence, they are solids.



**P.2.3** First and second electron gain enthalpies of oxygen are  $-141$  and  $+ 702 \text{ kJ mol}^{-1}$ . How is large number of oxides accounted for ?

**Solution**  $\text{O(g)} + \text{e}^- \rightarrow \text{O}^-(\text{g}) ; \Delta H = -141 \text{ kJ mol}^{-1}$ ;  $\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g}) ; \Delta H = + 702 \text{ kJ mol}^{-1}$ .

Formation of  $\text{O}^-$  is exothermic and  $\text{O}^{2-}$  is endothermic. However, oxygen is divalent and forms oxide with stable  $\text{ns}^2\text{np}^6$  configuration. Further, the lattice energies of oxides are very high on account of greater electrostatic forces of attraction.



**P.2.4** Viscosity of sulphur increases when molten sulphur is heated from  $120^\circ\text{C}$  to  $160^\circ\text{C}$ . Why ?

**Solution** At  $119^\circ\text{C}$ , sulphur forms a clear mobile liquid.

When this liquid is further heated, the cleavage of octaatomic ring structure occurs. Zig-zag open chains are formed, which get interwound and tangled together. Hence sulphur becomes more viscous.



**P.2.5** Comment on the catenation capacity of sulphur.

**Solution** Catenation ability of sulphur is highest among chalcogens. Sulphur is next to carbon in the tendency to catenate. Catenation ability of sulphur is observed in polysulphids and polythionic acids.

Among M-M bonds of chalcogens, S-S bond is stronger and hence higher catenation ability.



**P.2.6** What is the maximum covalency of oxygen? Give examples.

**Solution** Oxygen usually forms two bonds. Its valency cannot be expanded due to lack of valence d-orbitals. However, the maximum covalency of oxygen is three, due to an additional dative bond formed by oxygen using one of its lone pairs.

Hydronium ion,  $\text{H}_3\text{O}^+$  has two covalent bonds and one coordinate covalent bond formed by oxygen atom. Oxonium ion,  $(\text{C}_2\text{H}_5)_2\text{OH}^+$  also has three bonds formed by oxygen.

### EXERCISE - 2.1.1

1. Discuss the electronic configuration of group 16 elements.
2. What are chalcogens? Why are they so called?
3. Write the trends in atomic radius, ionisation potential and metallic nature of group VIA elements.
4. Write on the allotropy of sulphur.
5. Discuss the valency and bonding in oxygen and sulphur molecules.
6. Why oxidation states of sulphur are all even numbers?

## HYDRIDES, OXIDES AND HALIDES

### 2.2.1

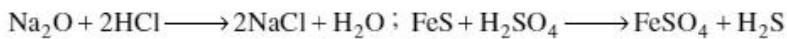
#### Hydrides

The binary compounds of hydrogen with chalcogens are called hydrides. Their general formula is  $MH_2$ , also represented as  $H_2M$ . General characteristics of hydrides of group VIA are given in Table 2.4.

**Table 2.4 Characteristics of hydrides of group VIA elements**

Hydride	Name	M-H bond length	M-H bond energy	Bond angle	Enthalpy of formation	Melting point	Boiling point	Decomposition temperature
$H_2O$	Water	$0.97\text{\AA}$	$464 \text{ kJ mol}^{-1}$	$104.5^\circ$	$-286 \text{ kJ mol}^{-1}$	273K	373K	2273 K
$H_2S$	Hydrogen sulphite	$1.33\text{\AA}$	$348 \text{ kJ mol}^{-1}$	$92.5^\circ$	$-20 \text{ kJ mol}^{-1}$	188K	213K	773 K
$H_2Se$	Hydrogen selenide	$1.48\text{\AA}$	$276 \text{ kJ mol}^{-1}$	$91^\circ$	$73 \text{ kJ mol}^{-1}$	208K	231K	433 K
$H_2Te$	Hydrogen telluride	$1.73\text{\AA}$	$238 \text{ kJ mol}^{-1}$	$90^\circ$	$99 \text{ kJ mol}^{-1}$	222K	270K	Room temperature

Water is formed by the combination of hydrogen and oxygen in the presence of a catalyst. It is the neutralisation product of a protonic acid with a base.  $MH_2$  type hydrides of chalcogens are usually prepared by the action of acid on a binary compound with metal.



The shape of  $MH_2$  type hydride is angular. The hybridisation of oxygen in water molecule is  $sp^3$ . It has tetrahedral geometry with two lone pairs on the central atom. Water is a bent molecule with 'V' shape. The bond angle in water is  $104.5^\circ$ . The decrease in the bond angle from the tetrahedral angle is due to greater repulsions between two lone pairs.

In the hydrides of other elements also, the central atom has two bond pairs and two lone pairs. The bond angles are almost equal to  $90^\circ$ . This is due to the use of unhybridised pure p-orbitals for bonding.

All these hydrides, except water, are gases. They are highly volatile substances, foul smelling and poisonous. Hydrogen sulphide is most volatile. Abnormal high boiling point of water and its low volatility are attributed to intermolecular hydrogen bonding. Only van der Waals forces of attractions are present in other hydrides.

Moving down from  $H_2O$  to  $H_2Te$ , the M-H bond length increases bond energy decreases and as a result of which thermal stability decreases. Water is most stable and its reactivity is very less.

The order of volatility is :  $H_2S > H_2Se > H_2Te > H_2O$ .

The order of stability is :  $H_2O > H_2S > H_2Se > H_2Te$ .

The order of boiling points is :  $H_2O > H_2Te > H_2Se > H_2S$ .

The order of  $K_a$  values is :  $H_2O < H_2S < H_2Se < H_2Te$ .

**Water and other  $MH_2$  hydrides are angular**

Water is practically a neutral liquid. These hydrides dissolve in water and ionise to produce proton.



*Water is a very weak acid.*

*Hence OH<sup>-</sup> is a strong base*



The dissociation constants are low, but the value increases from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{Te}$ , due to decrease in bond energy. These hydrides are weak dibasic acids and form two types of salts. e.g.  $\text{NaHS}$  and  $\text{Na}_2\text{S}$ . The conjugate base of weak acid water is hydroxyl ion,  $\text{OH}^-$  and is a strong base.  $\text{H}_2\text{Te}$  is relatively more acidic and  $\text{TeH}^-$  is relatively a weaker base.

Oxygen has two binary compounds with hydrogen,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ . Sulphur has many binary compounds with hydrogen  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{S}_2$  and polysulphides like  $\text{H}_2\text{S}_3$ ,  $\text{H}_2\text{S}_4$ ,  $\text{H}_2\text{S}_5$ , etc.  $\text{H}_2\text{S}_5$  is called hydrogen pentasulphide and also as hydrogen polysulphide. As the number of sulphur atoms increases, the stability of hydride decreases.

### 2.2.2

#### Oxides



*$\text{Fe}_3\text{O}_4$  and  $\text{Pb}_3\text{O}_4$  are examples of mixed oxides*



Binary compounds of oxygen with another element are called oxides. Oxygen reacts with most of the elements to form oxides. Ozone may be treated as dioxide of oxygen. In many cases one element forms two or more oxides.

Oxides can be simple, where rules of valency and stoichiometry are not violated eg:  $\text{MgO}$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CO}_2$ , etc. If the content of oxygen is high, it is called a superoxide (eg:  $\text{KO}_2$ ,  $\text{CsO}_2$ , etc.) and less is called a suboxide (eg:  $\text{C}_3\text{O}_2$ ,  $\text{S}_2\text{O}$ , etc.). Magnetic oxide ( $\text{Fe}_3\text{O}_4$ ), red lead ( $\text{Pb}_3\text{O}_4$ ), etc., are called mixed oxides.

Simple oxides can be classified, based on their acid-base behaviour into 4 types. These four types of oxides are listed in Table 2.5.

**Table 2.5 Four types of oxides based on nature**

Types of oxides	Reactivity of oxides	Examples of oxides
Basic oxide	Neutralises hydrochloric acid	$\text{Na}_2\text{O}$ , $\text{K}_2\text{O}$ , $\text{MgO}$ , $\text{CaO}$ , $\text{CrO}$ , $\text{CuO}$ , $\text{Ti}_2\text{O}$ , $\text{Fe}_2\text{O}_3$
Acidic oxide	Neutralises caustic soda solution	$\text{B}_2\text{O}_3$ , $\text{CO}_2$ , $\text{NO}_2$ , $\text{P}_4\text{O}_{10}$ , $\text{SO}_2$ , $\text{SO}_3$ , $\text{Cl}_2\text{O}$ , $\text{Cl}_2\text{O}_7$ , $\text{Mn}_2\text{O}_7$ , $\text{CrO}_3$
Amphoteric oxide	Neutralises hydrochloric acid as well as caustic soda solution	$\text{Ge}_2\text{O}_3$ , $\text{Sb}_4\text{O}_6$ , $\text{TeO}_2$ , $\text{Al}_2\text{O}_3$ , $\text{BeO}$ , $\text{ZnO}$ , $\text{SnO}_2$ , $\text{PbO}_2$ , $\text{V}_2\text{O}_5$ , $\text{Cr}_2\text{O}_3$
Neutral oxide	Neutralises neither hydrochloric acid nor caustic soda solution	$\text{CO}$ , $\text{N}_2\text{O}$ , $\text{NO}$ , $\text{H}_2\text{O}$



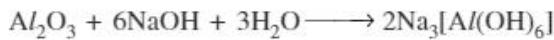
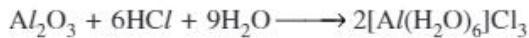
*Metallic oxides are generally basic*



*Non-metallic oxides are generally acidic*



In general metallic oxides are basic. Some of the metallic oxides and oxides of some metalloids are amphoteric. Alumina reacts with acids as well as alkalies, exhibiting dual nature.



In general non-metallic oxides are acidic. Some of the non-metallic oxides are neutral. Neutral oxides do not react with acids as well as bases. If an element is forming two or more binary oxides, that oxide with more oxygen content is generally more acidic.

Oxygen reacts with other elements of group VIA to form dioxides and trioxides. These oxides are listed in **Table 2.6**. The acidic nature of the oxides decreases down the group. The stability and solubility also decreases.

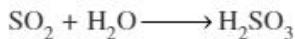
**Table 2.6 Oxides of group VIA elements**

Element	Dioxide	Trioxide	Other oxides
Sulphur	$\text{SO}_2$	$\text{SO}_3$	$\text{S}_2\text{O}$ , $\text{S}_6\text{O}$ , $\text{S}_8\text{O}$
Selenium	$\text{SeO}_2$	$\text{SeO}_3$	—
Tellurium	$\text{TeO}_2$	$\text{TeO}_3$	$\text{TeO}$
Polonium	$\text{PoO}_2$	—	$\text{PoO}$

**Sulphurdioxide :** Sulphur dioxide is obtained by the burning of sulphur or by roasting of sulphide mineral.



Sulphur dioxide is easily liquifiable gas and the liquid is used as non-aqueous solvent. Sulphur dioxide is the anhydride of sulphurous acid.



Sulphur dioxide is a reducing agent in neutral and acid media. In the presence of moisture it liberates nascent hydrogen and bleaches vegetable colouring matter. Schiff's reagent is prepared based on the bleaching action of sulphur dioxide.



Sulphur dioxide reduces ferric salts to ferrous salts, acidified dichromate to green coloured chromic salts and acidified permanganate to colourless manganous salts in solutions



$\text{SO}_2$  reacts readily with caustic soda solution forming sodium sulphite, which then reacts readily with more  $\text{SO}_2$  to form sodium hydrogensulphite.



Sulphur dioxide forms addition compounds. In the presence of sun light or camphor it adds with chlorine to give sulphuryl chloride.



All dioxides are solids, except sulphur dioxide. All trioxides are solids. Reducing property of dioxides decreases from  $\text{SO}_2$  to  $\text{TeO}_2$ .

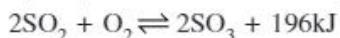
*$\text{SO}_2$  is the anhydride of  $\text{H}_2\text{SO}_3$*

*$\text{Moist SO}_2$  is a bleaching agent based on reduction*

*$\text{Sulphur dioxide forms addition compounds}$*

*$\text{Sulphur dioxide forms addition compounds}$*

**Sulphur trioxide :** Sulphur trioxide is obtained by the oxidation of sulphur dioxide in the presence of a catalyst. Platinised asbestos, vanadium pentoxide, nitric oxide, etc., are some of the catalysts used.



At room temperature sulphur trioxide is a solid. It exists in three distinct forms:  $\alpha$  – and  $\beta$  – forms are linear polymeric forms and  $\gamma$  – form is a cyclic trimer. Among these forms,  $\alpha$  – is the most stable form as it has crossed links.

Sulphur trioxide is called sulphuric anhydride. But it is not possible commercially to dissolve it in water. It is dissolved in sulphuric acid to form oleum, also called pyrosulphuric acid. Sulphur trioxide is more acidic than sulphurdioxide. Sulphur trioxide is a strong oxidant.

**Structures of gaseous  $\text{SO}_2$  and  $\text{SO}_3$  :** Sulphur forms  $\text{SO}_2$  in the first excited state and  $\text{SO}_3$  in the second excited state. Sulphur undergoes  $\text{sp}^2$  hybridisation in both oxides with planar trigonal geometry. These structures are given in Fig 2.5. A molecule of  $\text{SO}_2$  has two double bonds and a lone pair at vertex. It is angular, hybrid of two canonical forms and the bond angle is  $119.5^\circ$ . A molecule of  $\text{SO}_3$  has three double bonds. The bond angle in the planar structure is  $120^\circ$ . One  $\text{p}\pi-\text{p}\pi$  and one  $\text{p}\pi-\text{d}\pi$  bonds are present in  $\text{SO}_2$  molecule. One  $\text{p}\pi-\text{p}\pi$  and two  $\text{p}\pi-\text{d}\pi$  bonds are present in  $\text{SO}_3$  molecule. Because of the difference in  $\pi$  – bonds, both sulphur dioxide and sulphur trioxide are denoted by resonance.

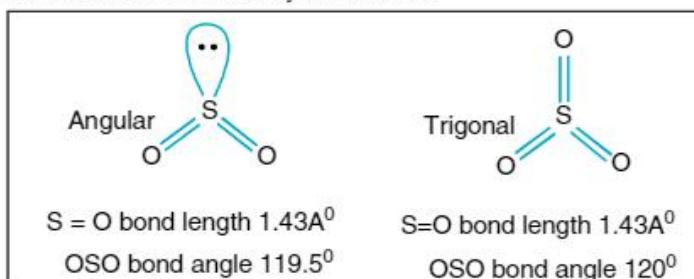


Fig 2.5 Structures of  $\text{SO}_2$  and  $\text{SO}_3$  molecules

### 2.2.3

#### Halides

Oxygen forms only one type of halides known as fluorides.

Oxygen difluoride,  $\text{OF}_2$  is prepared by passing fluorine gas through a very dilute solution of caustic soda. It is a pale yellow coloured poisonous gas. It does not form any oxyacid, but dissolves in water with evolution of oxygen.

Oxygen monofluoride is dimeric,  $\text{O}_2\text{F}_2$ . It is prepared by the silent electric discharge of a mixture of oxygen and fluorine at low pressure and temperature. It is a reddish–brown gas. It is a powerful oxidant as well as fluorinating agent.

Binary halides of various compositions of other chalcogens are known. Some of them are listed in Table 2.7. Sulphur has four important types of halides. The stability of the halides decreases in the order :  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

**Monohalides :** Dimeric monohalides of sulphur,  $\text{S}_2\text{F}_2$  and  $\text{S}_2\text{Cl}_2$  are known. Sulphur monochloride is prepared by treating excess sulphur with dry chlorine. It hydrolyses slowly and undergoes disproportionation.

Selenium monochloride itself disproportionates to selenium and selenium tetrachloride.



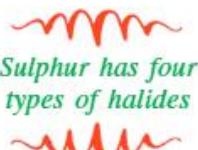
  
*Sulphur has four types of halides*

Table 2.7 Binary halides of chalcogens

Element	$M_2X_2$ type	$MX_2$ type	$MX_4$ type	$MX_6$ type	Other types of halides
Sulphur	$S_2F_2$ $S_2Cl_2$	$SF_2$ $SCl_2$	$SF_4$ $SCl_4$	$SF_6$	$S_2F_4$ , $S_2F_{10}$ , $S = SF_2$
Selenium	$Se_2Cl_2$ $Se_2Br_2$	$SeCl_2$	$SeF_4$ , $SeCl_4$	$SeF_6$	$Se_2F_4$
Tellurium	$Te_2Cl_2$	$TeCl_2$ , $TeBr_2$ , $TeI_2$	$TeF_4$ , $TeBr_4$ , $TeI_4$	$TeF_6$ $TeBr_4$ ,	-
Polonium	-	$PoCl_2$ , $PoBr_2$	$PoCl_4$ $PoBr_4$	-	-

  
*Sulphur dichloride is angular with bond angle 103°*

  
*Sulphur tetrahalide has distorted tetrahedral structure*

**Dihalides :** Dichloride of sulphur is best known dihalide. It is formed by saturating molten  $S_2Cl_2$  with dry chlorine at room temperature. Sulphur dichloride is a dark red liquid with foul smell. It has water molecule like angular structure with  $sp^3$  hybridisation of central sulphur atom.

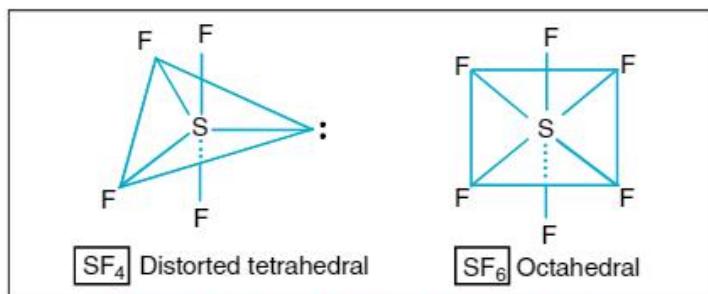
**Tetrahalides :** Tetrafluorides are difficult to prepare because fluorine is best oxidising agent and hexafluorides are more stable. However, tetrachlorides are obtained by the direct combination of chlorine with elements.

Sulphur undergoes  $sp^3d$  hybridisation in its tetrahalide. Geometry of tetrahalides is trigonal bipyramidal with 4 bond pairs and 1 lone pair. Due to the presence of a lone pair, sulphur tetrachloride has distorted tetrahedral structure. This structure as shown in Fig 2.6.

**Hexahalides :** Among the hexahalides, only hexafluorides are stable. They are formed by the direct oxidation of the element with fluorine.

Sulphur hexafluoride is a colourless gas. It does not undergo hydrolysis. Due to its stability it is used in high voltage electrical gadgets.

Sulphur undergoes  $sp^3d^2$  hybridisation in its hexafluoride. The structure is regular octahedral with 6 bond pairs and no lone pair. The S–F bond length is 115pm and bond angle in sulphur hexafluoride molecule is 90°. The structure of  $SF_6$  is shown in Fig 2.6.

Fig 2.6 Structure of  $SF_4$  and  $SF_6$  molecules



**P.2.7** The dissociation constants of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$  are  $1.8 \times 10^{-16}$ ,  $1.4 \times 10^{-7}$ ,  $1.3 \times 10^{-4}$  and  $2.2 \times 10^{-3}$ , respectively. What do these values denote?

**Solution** Dissociation of hydride is given as,  $\text{H}_2\text{M} \rightleftharpoons \text{H}^+ + \text{MH}^-$

For this dissociation equilibrium, a lower value of  $K_a$  denotes that the acid is weak.

As the  $K_a$  values increase from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{Te}$ , their acidic strength also increases.  $\text{H}_2\text{Te}$  is relatively a stronger acid. The  $K_a$  values also denote that  $\text{OH}^-$  is a stronger base and  $\text{TeH}^-$  is a weaker base.



**P.2.8** Tellurium forms oxides of the formula  $\text{TeO}$ ,  $\text{TeO}_2$  and  $\text{TeO}_3$ . What is the nature of these tellurium oxides?

**Solution**  $\text{TeO}$  (oxidation number of Te is +2) is basic.

$\text{TeO}_2$  (oxidation number of Te is +4) is amphoteric.

$\text{TeO}_3$  (oxidation number of Te is +6) is acidic.

As the oxidation number of the element forming oxide increases, the acidic nature also increases.



**P.2.9** Oxygen forms only fluorides, but other chalcogens form different halides. Why?

**Solution** The binary compound of oxygen and fluorine is called fluoride, but not oxide.

$\text{OF}_2$  and  $\text{O}_2\text{F}_2$  are the fluorides of oxygen, with oxidation state of 'O', respectively +2 and +1.

The binary compounds of oxygen with other halogens are known. e.g.  $\text{Cl}_2\text{O}_6$ ,  $\text{Cl}_2\text{O}_7$ ,  $\text{BrO}_3$ ,  $\text{I}_2\text{O}_5$ ,  $\text{I}_4\text{O}_9$ , etc. But they are called oxides of halogens.



**P.2.10** A and B are elements with atomic numbers 16 and 17. Write different combinations of binary compounds known from them.

**Solution** Atomic number of A = 16. It is sulphur. Atomic number of B = 17. It is chlorine.

Excess sulphur reacts with chlorine to give dimeric monochloride. Sulphur reacts with excess chlorine to give tetrachloride. Molten dimeric monochloride on saturation with chlorine gives dichloride.



**P.2.11** Dry sulphur dioxide does not bleach dry flowers. Explain.

**Solution** Sulphur dioxide acts as a bleaching agent only in moist conditions. Nascent hydrogen responsible for reduction is produced



Coloured flower + (H)  $\longrightarrow$  Colourless flower

### EXERCISE - 2.1.2

1. Write on the stability and acidic nature of hydrides of chalcogens.
2. Water is a liquid and abnormally has low volatility. Explain.
3. How are oxides of sulphur prepared? What are their properties?
4. Discuss the structures of sulphur dioxide and sulphur trioxide molecules.
5. Mention the preparation and discuss the structures of  $\text{SCl}_4$  and  $\text{SF}_6$ .

## OXY ACIDS

### 2.3.1

#### Oxyanions

Oxygen itself is a constituent element in the ternary compounds called oxyacids. Sulphur, selenium and tellurium form generally two types of oxyacids (Table 2.8). Polonium is not known to form oxyacids.

Table 2.8 Oxyacids of group VIA elements

Element	-ous acid	-ic acid
Sulphur	$\text{H}_2\text{SO}_3$ Sulphurous acid	$\text{H}_2\text{SO}_4$ Sulphuric acid
Selenium	$\text{H}_2\text{SeO}_3$ Selenous acid	$\text{H}_2\text{SeO}_4$ Selenic acid
Tellurium	$\text{H}_2\text{TeO}_3$ Tellurous acid	$\text{H}_6\text{TeO}_6$ Telluric acid

Dioxide is the anhydride of -ous acid and trioxide of -ic acid. The -ic acid is more acidic than the -ous acid of a given element. The strength of the oxyacids of a given type decreases with a decrease in the electronegativity of element forming the acid. Acidic strength:  $\text{H}_2\text{SO}_3 > \text{H}_2\text{SeO}_3 > \text{H}_2\text{TeO}_3$  and  $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4 > \text{H}_2\text{TeO}_4$ .

The -ous acids are generally reducing agents and the -ic acids are stronger oxidising agents. The salts of -ous acids are called -ites and -ic acids are called -ates. Structures of sulphite, sulphate and thiosulphate are given in Fig 2.7. In all these anions, sulphur undergoes  $\text{sp}^3$  hybridisation. While sulphite is pyramidal, sulphate and thiosulphate are tetrahedral. Sodium thiosulphate pentahyphate is called hypo, which is used in volumetry and photography.

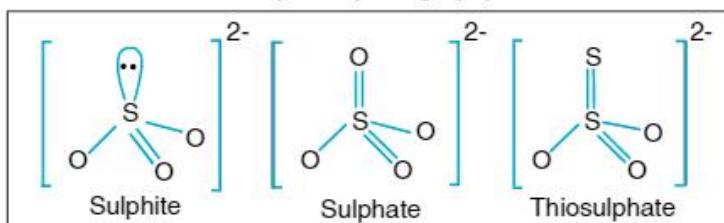


Fig 2.7 Structures of important oxyanions of sulphur

### 2.3.2

#### Oxyacids of sulphur

The element known to have maximum number of oxyacids is sulphur. Oxyacids of sulphur are divided into four types.

- (a) Sulphurous acid series,
- (b) Sulphuric acid series,
- (c) Thionic acid series and
- (d) Peroxy acid series.

Some of the oxyacids have more than one structure. But generally it is observed that the central sulphur atom undergoes  $\text{sp}^3$  hybridisation with tetrahedral geometry around it. Each oxyacid of sulphur has two -OH groups and basicity is 2. The structural information of the oxyacids of sulphur is listed in Table 2.9.

### 2.3.3

#### Anomalous behaviour of oxygen

Oxygen differs from rest of the chalcogens. The important points of difference between oxygen and other elements of group VIA are :

1. Oxygen is a gas, other elements are solids at room temperature.
2. Oxygen is simple diatomic, other elements have puckered ring octaatomic structures.
3. Oxygen is a non-metallic element and forms oxides of different nature.
4. The valency of oxygen is only 2. Other elements exhibit even hexavalency.
5. Though all molecules of chalcogens have even number of electrons, oxygen is paramagnetic.

*Sulphur is known to form maximum number of oxyacids*

*Oxygen molecule has even number of electrons, but paramagnetic*

Table 2.9 Oxyacids of sulphur and their structural aspects

Oxyacid	Formula of acid	Oxidation state of S	Structure	Other information
<b>a) Sulphurous acid series</b>				
Sulphurous acid	H <sub>2</sub> SO <sub>3</sub>	+4	HO— $\overset{\cdot\cdot}{S}$ —OH    O	Tautomeric structures are possible
Thiosulphurous acid	H <sub>2</sub> S <sub>2</sub> O <sub>2</sub>	-2, +4	HO— $\overset{\cdot\cdot}{S}$ —OH    S	p π-d π bond between sulphur atoms
Dithionous acid	H <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	+3, +3	HO— $\overset{\cdot\cdot}{S}$ — $\overset{\cdot\cdot}{S}$ —OH    O O	Unstable and is known as hyposulphurous form
Pyrosulphurous acid	H <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	+3, +5	HO— $\overset{\cdot\cdot}{S}$ — $\overset{\cdot\cdot}{S}$ —OH    O O	Average oxidation state of sulphur is +4
<b>b) Sulphuric acid series</b>				
Sulphuric acid	H <sub>2</sub> SO <sub>4</sub>	+6	HO— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —OH	Has 2 p π-d π bonds
Thiosulphuric acid	H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	-2, +6	HO— $\overset{\text{S}}{\underset{\text{O}}{\text{S}}}$ —OH	Hydrated thiosulphate is familiar as hypo.
Pyrosulphuric acid	H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	+6, +6	HO— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —O— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —OH	It is called oleum or fuming sulphuric acid
<b>c) Thionic acid series</b>				
Dithionic acid	H <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	+5, +5	HO— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ — $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —OH	Has 2 p π-d π bonds on each sulphur atom
Polythionic acid (x = n + 2)	H <sub>2</sub> S <sub>x</sub> O <sub>6</sub>	+5, +5	HO— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ — $\overset{\text{O}}{\underset{\text{O}}{\text{S}}_n}$ — $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —OH	Middle sulphur atoms have zero oxidation state
<b>d) Peroxy acid series</b>				
Peroxymono-sulphuric acid	H <sub>2</sub> SO <sub>5</sub>	+6	HO— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —O—OH	Called Caro's acid. Fairly stable
Peroxydi-sulphuric acid	H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	+6, +6	HO— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —O—O— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —OH	Called Marshall's acid. Persulphates are well known

- The hydride of oxygen is a liquid. While hydrides of other elements are foul odoured gases.
  - Water is neutral. Hydrides of other elements act as weak acids in aqueous solutions.
  - Oxygen forms only fluorides, while other elements form numerous halides.

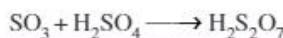
The anomalous behaviour of oxygen is attributed to the small atomic size, high electronegativity and lack of vacant valence d-orbitals.



- P.2.12** Which oxyacid of sulphur has S–O–S link? How is it prepared?

**Solution**  $\text{H}_2\text{S}_2\text{O}_7$  oleum (or) fuming (or) pyrosulphuric acid has S–O–S link.

Pyrosulphuric acid is prepared by dissolving sulphur trioxide in concentrated sulphuric acid.



- P.2.13** Oxygen is divalent in its compounds, but sulphur is even hexavalent. Why?

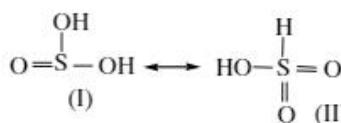
**Solution** Ground state configuration of oxygen has two orbitals with unpaired electrons. It forms two bonds. Oxygen cannot expand its valencies due to absence of valence d-orbitals.

Sulphur forms 4 bonds in the first excited state and 6 bonds in the second excited state.



- P.2.14** Write the tautomerism in sulphurous acid.

**Solution** Sulphurous acid has two tautomeric forms.



Structure I is preferred as the sulphite ( $\text{SO}_3^{2-}$ ) salts are familiar for sulphurous acid.



- P.2.15** Justify that peroxymono and peroxydisulphuric acids have a peroxy linkage. How are they structurally different?

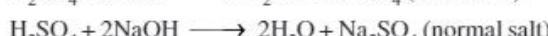
**Solution** The peroxymono and peroxydisulphuric acid may be considered to have been derived from  $\text{H}_2\text{O}_2$  by replacing one H and both H by  $\text{HSO}_4^-$  groups respectively.

$\text{H}_2\text{SO}_5$  the monoacid and  $\text{H}_2\text{S}_2\text{O}_8$  the peroxydisulphuric acid, both on hydrolysis yield  $\text{H}_2\text{O}_2$ . Both permno and perdi sulphuric acids contain  $-\text{O}-\text{O}-$  linkage in their molecular structure.



- P2.16** Proticity of sulphuric acid is two. Explain?

**Solution** Sulphuric acid forms two series of salts. Hence it is a dibasic acid. It forms two types of salts.



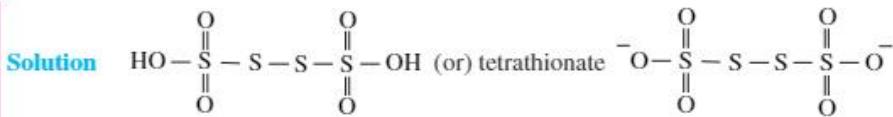
- B2.17** Mention the principle in iodometry.

**Solution** Even mild oxidants can oxidise iodide to iodine. The iodine liberated is titrated using sodium thiosulphate in volumetry, using starch indicator. Starch - iodine is blue and at the end point blue colour disappears.





**P.2.18** Write the structure and oxidation numbers of sulphur in tetrathionic acid.



Tetrathionic acid or its salt tetrathionate has persulphide link, S–S.

The oxidation states of sulphur are : +5, 0, 0 and +5.

The average oxidation state of S is +2.5.

### EXERCISE - 2.1.3

1. Mention the four types of oxyacids of sulphur and give examples.
2. Write the oxidation states of sulphur in its oxyacids.
3. Draw the structures of sulphite sulphate and thiosulphate.
4. Write the peroxy acids and polythionic acids of sulphur.
5. How is oxygen different from other elements of the same group? What are the reasons?

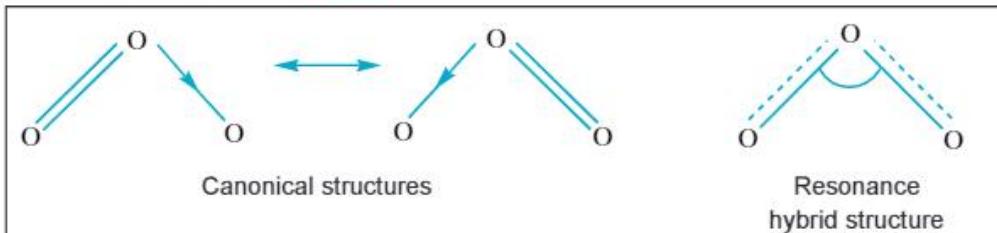
## OZONE AND HYDROGEN SULPHIDE

### 2.4.1

#### Ozone

Ozone is trioxygen with atomicity 3. It is an allotrope of oxygen. Marum observed the characteristic odour in the silent electric discharge of oxygen and Schonbein named it as ozone. Soret determined its formula. Ozone is present in the stratosphere and prevents the harmful ultraviolet radiations coming from the sun reaching the earth.

**Structure :** Ozone is an angular molecule. The 'V' shaped molecule can be represented with two canonical structures. The actual structure of ozone is a resonance hybrid of these two canonical forms. It has a pair of delocalised pi electrons. The experimental O–O bond length in  $\text{O}_3$  is 1.27 Å, which is shorter than a O–O single bond (1.48 Å), but longer than O=O double bond (1.2 Å) length. The bond angle in ozone is  $116^\circ 49'$ . The canonical structures and the resonance hybrid structure of ozone is shown in Fig 2.8. The bond order in ozone is 1.5.



**Fig 2.8 Structures of ozone**

Ozone is produced from oxygen by silent electric discharge. The instrument used for such an allotropic conversion is called ozoniser.

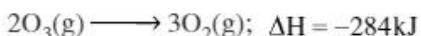


Ozone is prepared from oxygen by silent electric discharge

Ozonised oxygen is collected finally with about 5 to 10% ozone. When the ozonised oxygen is passed through a packed silica gel column, ozone is adsorbed by silica gel leaving oxygen gas. The ozone gas can be desorbed by passing nitrogen into the column.

**Ozone** is a pale blue coloured and pungent odoured poisonous gas. It is heavier than air. It readily dissolves in terpine oil, carbon tetrachloride or acetic acid. It is practically not soluble in water. It kills bacteria and causes respiratory problems when inhaled.

**Stability :** Ozone is thermodynamically less stable. It decomposes into oxygen slowly at room temperature, but rapidly over 200°C. The decomposition of ozone is catalysed by the presence of platinum, silver and manganese dioxide. Upon decomposition, its volume is increased by 1.5 times.



The decomposition of ozone into oxygen results in the liberation of heat and increase in entropy ( $\Delta H$  is negative and  $\Delta S$  is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change. It may be noted that high concentrations of ozone can be dangerously explosive.



**Oxidation ability :** Ozone is a powerful oxidant. Among elements, it is the next best oxidising agent to fluorine. Ozone readily decomposes to give nascent oxygen. This is the reason for its oxidation ability.

- i) Ozone oxidises black lead sulphide to white lead sulphate.



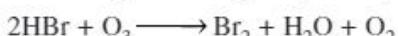
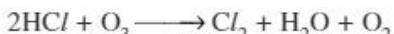
- ii) Ozone oxidises green potassium manganate solution to pink potassium permanganate solution.



- iii) Ozone oxidises acidified ferrous sulphate into ferric sulphate.



- iv) Ozone oxidises hydrohalic acids (except HF) to the respective halogens.



- v) Ozone oxidises hydrosulphide to sulphur.

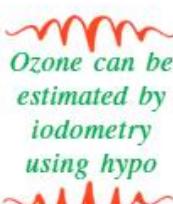


- vi) Ozone oxidises moist potassium iodide to give violet coloured iodine.



When ozone reacts with an excess of potassium iodide solution in a borate buffer at pH 9.2, iodine is liberated. The iodine can be titrated against a standard hypo solution. This is a method for the quantitative estimation of ozone.

- vii) Ozone oxidises ferrocyanide to ferricyanide.



viii) When ozone gas is passed over mercury, the metal is oxidised to mercurous oxide. Mercury loses its meniscus and the oxide formed sticks to the inner walls of the glass container. The phenomenon is called tailing of mercury.



ix) Ozone oxidises moist non-metals to their respective oxyacids with higher oxidation state, iodine to iodic acid, phosphorus to phosphoric acid, etc.

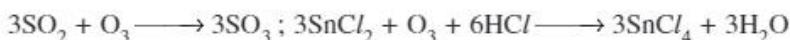


x) Ozone oxidises nitric oxide to nitrogen dioxide. Thus ozone layer is depleting in the upper atmosphere causing environmental problem. Another threat to the ozone layer is by the use of freons used in aerosol sprays and as refrigerants.



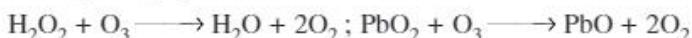
In all these examples, each ozone molecule is involved in a two electron change, through the involvement of only one oxygen atom. However, in few cases, all atoms of ozone molecule are involved in the oxidation and  $\text{O}_2$  is not evolved.

Oxidation of sulphur dioxide and oxidation of stannous chloride in hydrochloric acid medium are examples of the six electron change reactions by each ozone molecule.



Ozone bleaches the vegetable matter. Bleaching ability of ozone is based on its oxidation reaction. It is a dry bleach.

**Reduction ability :** Ozone acts as reductant too. Ozone takes up an oxygen atom from some substances to reduce them. These reduction reactions are sometimes referred as mutual reduction reactions with ozone. Ozone reduces silver oxide to metallic silver, hydrogen peroxide to water and lead dioxide to a stable lead monoxide (litharge).



**Ozonide formation :** Ozone adds with unsaturated hydrocarbons to form ozonides. These ozonides are less stable and can be decomposed by water in the presence of zinc to give carbonyl compounds. This process is known as ozonolysis. Ozonolysis of ethylene gives formaldehyde, Ozonolysis of acetylene gives glyoxal and benzene also gives glyoxal.

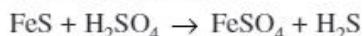
#### Uses of ozone

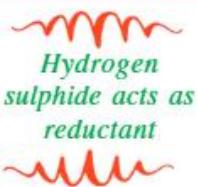
Ozone is a germicide, fungicide and disinfectant. It is used for sterilisation of water. Ozone is used to purify drinking water and for the purification of air in crowded halls, mines, zoo and metro railways. Ozone is a mild bleaching agent and a dry bleach. It is used to decolourise silk, ivory, starch, oil, etc. Ozone is used in the detection of unsaturation in the hydrocarbons and particularly to locate the position of multiple bonds. Ozone is used in the manufacture of synthetic camphor, potassium permanganate and artificial silk.

#### 2.4.2

#### Hydrogen Sulphide

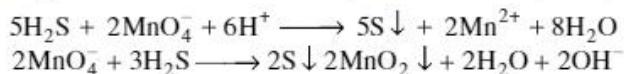
Hydrogen sulphide is prepared in the laboratory by reaction of Ferrous sulphide, on dilute sulphuric acid





Hydrogen sulphide is soluble in water. It burns in air with a blue flame. It is a weak dibasic acid and forms two series of salts.

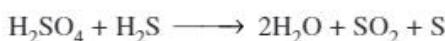
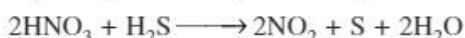
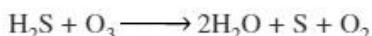
Hydrogen sulphide decolourises acidified permanganate. In alkaline medium permanganate is reduced to manganous dioxide (black).



Hydrogen sulphide turns acidified potassium dichromate green.



Hydrogen sulphide reduces hydrogen peroxide to water, ozone to oxygen, nitric acid to nitrogendioxide and sulphuric acid to sulphurdioxide.



Hydrogen sulphide is an important laboratory reagent for the detection of basic radicals in qualitative analysis. It is used as a reducing agent. Hydrogen sulphide has unpleasant rotten eggs smell. It can be tested as it turns lead acetate paper black and gives violet colouration with sodium nitroprusside solution.



- P.2.19** The magnetic properties of oxygen and ozone are different. Explain.



**Solution** Oxygen is a molecule with even number of electrons. But it is paramagnetic. Its magnetic moment is 2.83BM corresponding to two unpaired electrons. Molecular orbital theory explains the presence of unpaired electrons.

Ozone is diamagnetic. Its magnetic moment is zero. Ozone molecule has no unpaired electrons.



- P.2.20** Both ozone and hydrogen peroxide act as oxidants as well as reductants. What main differences are noticed in their reactions?

**Solution**

	Reaction	Ozone	Hydrogen peroxide
With starch iodide in the presence of ferrous sulphate	Does not give blue complex of starch-iodine	Gives blue coloured starch-iodine	
With acidified KMnO <sub>4</sub>	Does not decolourise	Decolourise	
With aciditied titanium sulphate pertitanate	Does not react	Gives orange coloured	
With alcholoic benzidine solution	Turns brown	Does not react	



- P.2.21** In the manufacture of sulphuric acid by the contact process, sulphur trioxide is not directly dissolved in water. Why?



**Solution** SO<sub>3</sub> reacts with water to form H<sub>2</sub>SO<sub>4</sub> which is not easily condensed. It escapes in the atmosphere. It is, therefore, absorbed in conc. H<sub>2</sub>SO<sub>4</sub> to from oleum which may be diluted to form H<sub>2</sub>SO<sub>4</sub>.



- P.2.22** Ozone is used in improving the atmosphere of crowded places. Why?

**Solution**

Ozone easily decomposes to give O<sub>2</sub> and thus improves the percentage of oxyten at crowded places, such as tube railways, cinema halls, etc.



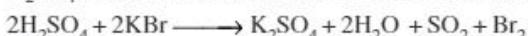
**P.2.23** How does  $\text{H}_2\text{SO}_4$  react with  $\text{KCl}$  and  $\text{KBr}$ ?

**Solution**  $\text{H}_2\text{SO}_4$  is weaker oxidant than  $\text{Cl}_2$ , but stronger oxidant than  $\text{Br}_2$ .

$\text{H}_2\text{SO}_4$  liberates  $\text{HCl}$  with  $\text{KCl}$ , but does not give  $\text{Cl}_2$ .



$\text{H}_2\text{SO}_4$  liberates  $\text{HBr}$  with  $\text{KBr}$ , which is finally oxidised to  $\text{Br}_2$ .



**P.2.24** Hydrogen sulphide is important in cation analysis. Explain.

**Solution** Group 2 and Group 4 cations are precipitated as their respective sulphides.

Group 2 cations have lower solubility. Hence they are precipitated in dilute acid medium.

### EXERCISE - 2.1.4

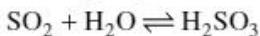
- Discuss the structure of ozone.
- Write four examples of properties of ozone acting as oxidant.
- Write the uses of ozone.
- How is hydrogen sulphide prepared?
- Hydrogen sulphide can be used as reducing agent. Support with three examples.

## SULPHUROUS, SULPHURIC AND THIOSULPHURIC ACIDS

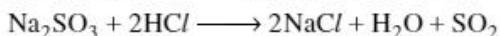
### 2.5.1

#### Sulphurous Acid

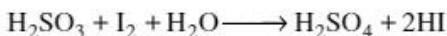
Sulphurous acid is obtained by dissolving sulphur dioxide gas in water. It actually exists as  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and this acid is known only in solution.



Sulphurous acid is a strong diprotic acid. It forms two types of salts.  $\text{NaHSO}_3$  is thus an acid salt and  $\text{Na}_2\text{SO}_3$  is normal salt and both liberate  $\text{SO}_2$  gas on reaction with acid.



Sulphurous acid is a good reducing agent. It reduces halogens to hydrogen-halides and ferrous salts to ferric salts.



Sulphurous acid reduces permanganate and dichromate.



Sulphurous acid behaves as a good bleaching agent. This action is based on its reduction ability and is due to nascent hydrogen.



### 2.5.2

#### Sulphuric acid

Sulphuric acid is one of the most important industrial chemicals world wide. It is called 'oil of vitriol' or 'king of chemicals'.

Sulphuric acid was prepared earlier by lead chamber process, which is an example of homogeneous catalysis. Sulphur dioxide is oxidised with oxygen in the

*Contact process  
is an example of  
heterogeneous  
catalysis*

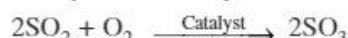
*Excess pure  
oxygen is used  
in modern plants  
of contact process*

presence of nitric oxide as catalyst. The method is out dated now. It is manufactured by contact process in the present times. Contact process is an example of heterogeneous catalysis. Three main aspects of contact process are :

1. Sulphur dioxide required for the process is obtained by roasting of iron pyrites.



2. Sulphur dioxide is oxidised catalytically with atmospheric air to sulphur trioxide. The catalyst commonly used is vanadium pentoxide.



3. Sulphur trioxide formed is absorbed in conc. sulphuric acid to get oleum, which is diluted with water to obtain sulphuric acid.



Catalysts are often poisoned in contact process. Hence gases used must be pure. In modern plants, excess pure oxygen is used. Various parts of the plant used in the manufacture of sulphuric acid is as shown in Fig 2.9.

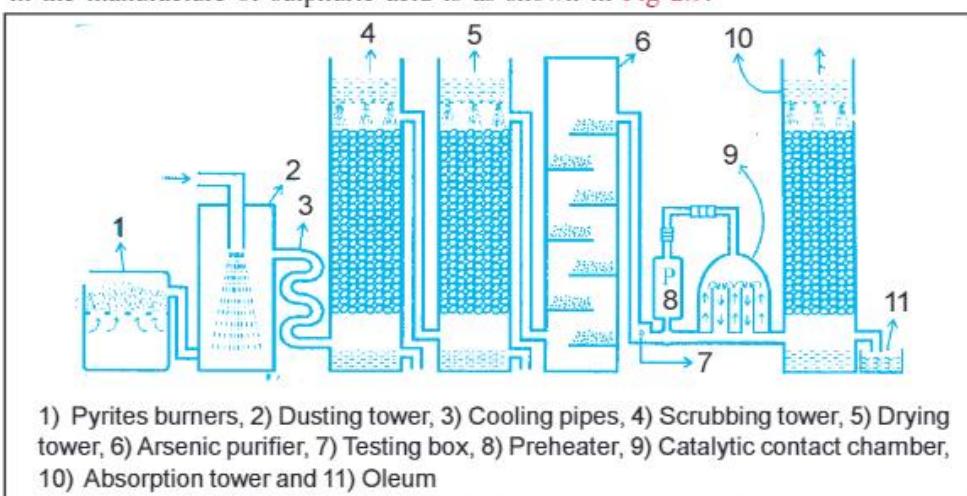


Fig 2.9 Manufacture of sulphuric acid by contact process

The  $\text{SO}_2$  to  $\text{SO}_3$  is reversible, exothermic and leads to a decrease in volume in forward direction. Hence low temperature and high pressure are favourable. In practice, the plant is operated at 2 bar pressure and a temperature of 720K.

Sulphuric acid is dense, colourless oily liquid with a specific gravity 1.84 at room temperature. It freezes at 283 K and boils at 610 K. It is soluble in water, but the dissolution is largely exothermic. Hence care is to be taken in preparing an aqueous solution; the concentrated acid must be added slowly into water with constant stirring. Sulphuric acid is less volatile and hence it is used to prepare volatile acids from their corresponding salts.



Sulphuric acid is a strong diprotic acid ( $\text{K}_{\text{a}1} > 10$  and  $\text{K}_{\text{a}2}$  is  $1.2 \times 10^{-2}$ ). It forms two types of salts upon neutralisation.

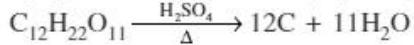
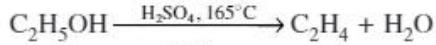


*Volatile acids  
from their salts  
are prepared  
using  $\text{H}_2\text{SO}_4$*

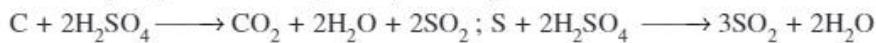
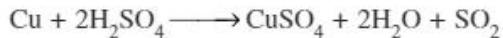
*Sulphuric acid  
is a strong  
diprotic acid*

**Concentrated sulphuric acid is a strong dehydrating agent**

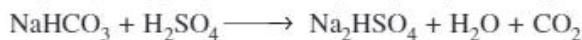
Concentrated sulphuric acid is a strong dehydrating agent. It removes water from organic compounds and chars carbohydrates.



Hot concentrated sulphuric acid is a moderately strong oxidant. It is less powerful than  $\text{HNO}_3$ , but more powerful than  $\text{H}_3\text{PO}_4$  in its oxidation ability. It oxidises metals and non-metals and is reduced to sulphur dioxide.



Sulphuric acid decomposes carbonates and bicarbonates into carbondioxide.



Sulphuric acid evolves hydrogen with electropositive metals. It decomposes more volatile acids to from their metal salts.



Bulk of sulphuric acid is used in manufacturing fertilisers. It is also used in petroleum refining, detergent industry, manufacture of paints and pigments, manufacture of nitrocellulose, storage batteries and also as a laboratory reagent.

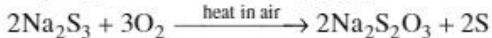
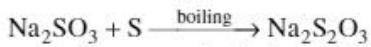
Sulphuric acid is used as pickling agent (removing basic oxide layer from metal surface like iron and copper before electroplating, enamalins, galvanising and solderins.

### 2.5.3

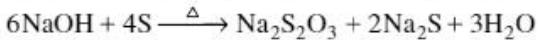
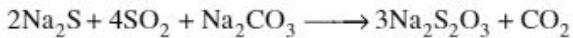
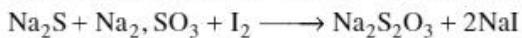
#### Sodium thiosulphate

Thiosulphuric acid can not be prepared because of its low stability. However,

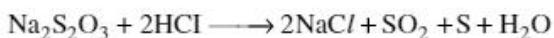
its salts called thiosulphates can be prepared.



The following reactions are called Spring's reactions. These are also used to convert sodium sulphide or sulphur into sodium thiosulphate.



Hydrated sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , is called 'hypo'. It forms very large colourless hexagonal crystals, melting point  $48^\circ\text{C}$ . It is highly soluble in water. Hypo is an efflorescent substance and at  $215^\circ\text{C}$ , it is completely dehydrated to  $\text{Na}_2\text{S}_2\text{O}_3$ . Dilute acids like  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  decompose hypo into sulphurdioxide and colloidal sulphur and gives yellowish-white turbidity. This is a disproportionation reaction.

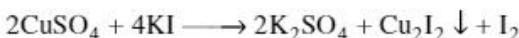


Iodine oxidises sodium thiosulphate to sodium tetrathionate.

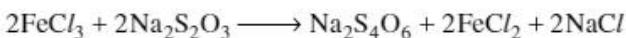
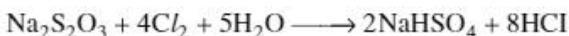


**Hydrated sodium thiosulphate is called hypo**

This reaction is used for the iodometric estimation of oxidising agents like  $\text{CuSO}_4$ ,  $\text{CaOCl}_2$ ,  $\text{MnO}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$  etc., which on reaction with KI liberate iodine. The liberated iodine is estimated using hypo and starch as indicator.



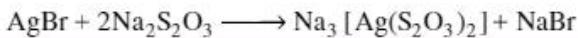
Sodium thiosulphate is used in the bleaching industry to destroy any excess chlorine on fabrics. Thus it is used as antichlor in textiles.



Silver nitrate reacts with thiosulphate giving white precipitate of silver thiosulphate, which changes to yellow, then to brown and finally black silver sulphide.



Hypo is used in photography for ‘fixing’ films and prints. Aqueous sodium thiosulphate dissolves unreacted silver bromide from the photographic emulsion by complexation reaction.



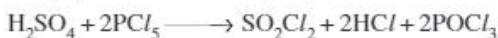
**P.2.25** How is dilute sulphuric prepared?

**Solution** Dissolution of sulphuric acid with water is highly exothermic. Hence care is taken in preparing dilute sulphuric acid. Concentrated acid is added slowly into water with stirring.

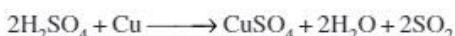


**P.2.26** How are  $\text{SO}_2\text{Cl}_2$  and  $\text{SO}_2$  obtained from sulphuric acid?

**Solution**  $\text{SO}_2\text{Cl}_2$  is formed from  $\text{H}_2\text{SO}_4$  by treating with excess of phosphorus pentachloride.

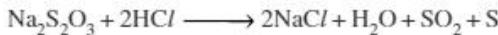


$\text{SO}_2$  is obtained from  $\text{H}_2\text{SO}_4$ , when heated with copper metal.



**P.2.27** How is thiosulphate distinguished from sulphate?

**Solution** Thiosulphate gives yellow precipitate of sulphur on reaction with a dilute mineral acid.



Sulphate, however, does not react with dilute mineral acids.

### EXERCISE - 2.1.5

1. Sulphurous acid is a bleaching agent base on sodium. Explain.
2. Comment on the manufacture of sulphuric acid by contact method.
3. Sulphuric acid acts as dehydrating agent. Substantiate.
4. Hypo is used as ‘anti chlor’ and for ‘fixing films’. Discuss with suitable equations.



1. Oxygen, sulphur, selenium, tellurium and polonium are the elements of group 16 and are called chalcogens.
2. The general electronic configuration of group VIA elements is  $ns^2 np^4$ .
3. Oxygen is a gas at room temperature, while other elements of the group are solids.
4. Oxygen is the most abundant element of the earth's crust.
5. Oxygen is commonly available as oxide, sulphur as sulphide and both are available as sulphates.
6. Oxygen is diatomic, while sulphur, selenium and tellurium are octaatomic.
7. Oxygen and sulphur are non-metals. Selenium and tellurium are metalloids.
8. All elements of group VIA exhibits allotropy. The only gaseous element with allotropes is oxygen.
9. Sulphur molecule has puckered ring structure.
10. The maximum covalency of oxygen is 3, but that of sulphur is 6.
11. Oxygen exhibits -2 oxidation state in oxides, -1 in peroxides, -1/2 in superoxides and positive oxidation states in fluorides.
12. Water has angular 'V' shape. The central atom undergoes  $sp^3$  hybridisation. The bond angle is  $104.5^\circ$ , due to greater repulsions between two lone pairs.
13. Water is the stable hydride of group VIA, due to relatively stronger O-H bond.
14. Water is a liquid at room temperature and less volatile due to intermolecular hydrogen bonding.
15. Hydrogen sulphide is most volatile hydride of chalcogens.
16.  $SO_2$  is angular and  $SO_3$  is trigonal.  $SO_2$  is anhydride of  $H_2SO_3$  and  $SO_3$  is anhydride of  $H_2SO_4$ .
17. In the presence of moisture,  $SO_2$  acts as a bleaching agent. The bleaching action is due to reduction.
18. Oxygen forms only fluorides, but sulphur usually forms dimeric mono, di, tetra and hexahalides.
19. Among hexahalides, only hexafluorides are known.  $SF_6$  is very inert and does not undergo hydrolysis.
20. Sulphur forms four types of oxyacids. Polythionic acids denote catenation ability of sulphur.
21. Ozone is angular molecule with two delocalised electrons and a lone pair on central atom. Bond angle in ozone is  $117^\circ$ .
22. Ozone is prepared from oxygen by silent electric discharge, using ozoniser.

23. Ozone acts as oxidant, reductant and bleaching agent. It tails mercury and forms ozonides with unsaturated hydrocarbons.
24. Sulphuric acid is commercially prepared in contact process, an example for heterogeneous catalysis.
25. Sulphuric acid is a strong dibasic acid. It forms two types of salts, bisulphates and sulphates.
26. Sulphuric acid is used in the manufacture of fertilisers, paints, nitrocellulose and in storage battery. It is also used as pickling agent in fertilisers and in metallurgy.
27. Thiosulphuric acid can not be prepared because of its lower stability. Its salts can be prepared.

### EXERCISE - 2.2

1. Oxygen is a blue gas, but sulphur is yellow solid. Explain.
2. Discuss the structure and bonding in  $S_8$  molecules.
3. Radius of sulphur atom is 102 pm. SSS angle is  $105^\circ$ . What is the diameter of the sphere from the centre of  $S_8$  molecule? (Ans : 260 pm)
4. Why is sulphur paramagnetic in vapour state?
5. Write on the valency, bonding and catenation of sulphur.
6. Oxygen is divalent, but sulphur is tetravalent as well as hexavalent in its compounds. Explain.
7. Among rhombic, monoclinic and plastic forms of sulphur, which form has highest heat of combustion. Why? (Ans : plastic)
8. Liquid oxygen stick to magnetic poles but not liquid nitrogen. Why?
9. Comment on the stability of hydrogen sulphide and polysulphides.
10. Write on the trends of bond energy, bond angle, volatility and boiling points of  $MH_2$  hydrides.
11. Write the preparation of hydrogen sulphide. How is it used in qualitative analysis?
12. Tetrafluorides of sulphur are not prepared directly from elements. Why?
13. How are fluorides of oxygen prepared? Draw their structures.
14. Discuss the bonding and structures of  $SF_6$ ,  $SCl_4$ ,  $SCl_2$  and  $S_2Cl_2$  molecules.
15. Nitric acid can not be used to prepare hydrogen sulphide. Why?
16. In the Lassaigne's test of organic sulphur, sulphide plays an easy role of detection. Explain.
17. The bond angle in water molecule is nearer to tetrahedral angle, but in hydrogen sulphide it is nearer to right angle. Why?
18. Discuss the structures of sulphite and sulphate ions.
19. What is ozonolysis? Write the significance of ozonotysis
20. Ozone acts as oxidising agent as well as reducing agent. Substantiate.
21. Hydrogen sulphide can not be dried over conc.  $H_2SO_4$ . Why?

22. How many sulphur atoms in  $H_2S_nO_6$  has sulphur linked to only its atoms? (Ans :  $n - 2$ )
23. Turbidity is obtained when hydrogen sulphide is passed through aqueous solution of sulphur dioxide. Explain.
24. Compared to water, hydrogen sulphide is thermally less stable, stronger acid and better reductant. Substantiate.
25. Supar turns black on adding with sulphuric acid. Why?
26. Ozone destroys mercury meriscus. Why?
27. Water should not be added to cone acid while preparing dilute sulphuric acid. Why?
28. Chlorination of a gas X with chlorine gives a substance Y. Y is used to prepare anhydrous ferric chloride from its hexahydrated salt and also used to convert ethanol to ethylchloride. Identify Y and write necessary equations. (Ans :  $Y = SO_2Cl_2$ )
29. Sulphuric acid is manufactured in contact process, but some amount of sulphuric acid is used in contact process. Justify.
30. In the reaction of ozone with potash an orange red solid is formed. What is characteristic about the solid?
31. Sulphurous acid turns pink permanganate colourless and turns acidified dichromate green. Explain.
32. An aqueous solution of a gas (G) decolourises acidified permanganate and pararosanilide. On boiling G with hydrogen peroxide, an acid X is formed, which gives a white precipitate Y with barium chloride solution. Y is insoluble in dilute hydrochloric acid. Identify the compounds G and Y. (Ans :  $G = SO_2$ ;  $Y = BaSO_4$ )
33. With aqueous silver nitrate, sodium thiosulphate gives a white precipitate, which finally turns black. Why?
34. An inorganic solid (A) dissolve in water to give acid B and acid C. A also reacts with aqueous alkali to form two salts in solution. The salt solution gives white precipitates with both  $AgNO_3$  and  $BaCl_2$  solutions. What is A? (Ans :  $SO_2Cl_2$ )
35.  $Na_2CO_3 + SO_2 \xrightarrow{A} A + B ; B + S \longrightarrow C$  and  $C + 2AgNO_3 \longrightarrow 2NaNO_3 + D$ .  
When compound D on exposure to moisture gives black precipitate silver sulphide. What are the substances A and C? (Ans :  $CO_2$ ;  $C = Na_2S_2O_3$ )

