The *p*-block Elements (Group 16 elements) - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following:

- Anomalous behavior of oxygen
- Hydrides, oxides and halides of group 16 elements and their properties
- Preparation and properties of dioxygen
- Preparation and properties of ozone
- Allotropic forms of sulphur
- Preparation and properties of sulphur dioxide
- Structure of oxoacids of sulphur
- Preparation and properties of sulphuric acid

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- Introduction
- General Properties of Group 16 Elements
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- Binary Compounds of Group 16 Elements with Hydrogen (Hydrides)
- Oxides of Group 16 Elements
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- Allotropes of Oxygen Dioxygen - Preparation and Properties
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- Sulphur Dioxide
- Oxoacids of Sulphur
- Summary

Introduction

The elements of Group 16 are oxygen, sulphur, selenium, tellurium and polonium which are known as groups of *chalcogens (pronounced as kal-ke-jens meaning ore forming elements)*. The name is derived from the Greek word for brass and points to the association of sulphur and its congeners with copper. Most copper minerals contain either oxygen or sulphur.

Group 16

8
O
Oxygen
16.0

16
S
Sulfur
32.1

34
Se
Selenium
79.0

52
Te
Tellurium
127.6

84
Po
Polonium
(209)

OCCURENCE

Oxygen is the most abundant of all the elements on earth. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume. However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. It is the sixteenth most abundant element. Combined sulphur exists primarily as sulphates such as *gypsum* $CaSO_4.2H_2O$, *epsom salt* $MgSO_4.7H_2O$, *baryte* $BaSO_4$ and sulphides such as *galena* PbS, *zinc blende* ZnS, *copper pyrites* $CuFeS_2$. Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur. Selenium and tellurium are less abundant than sulphur (0.05 ppm Se and 0.002 ppm Te) and found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals.

General Properties of Group 16 Elements

- **Electronic Configuration**

  The valence shell electronic configuration of these elements is ns^2np^4.

- **Atomic and Ionic Radii**

  Atomic size increases down the group 16 as a result of addition of valence shells. These elements have smaller radii than the corresponding elements of group 15.

- **Ionization Enthalpy**

  Due to increase in size down the group Ionization enthalpy decreases. However, the elements of this group have lower first ionization enthalpy values as compared to those of Group 15 in the corresponding periods. The difference can be explained on the basis of valence shell configuration. Group 15 elements have stable half filled valence orbital configuration of ns^2np^3 which gets disturbed when one electron is removed. The loss in this stability accounts for high ionization enthalpy. Group 16 elements with ns^2np^4 configuration however are not associated with any extra stability. The removal of one valence electron though leads to stable half filled orbital configuration and this accounts for their low ionization enthalpy.

- **Electronegativity**

In general electronegativity decreases down the group because of increased atomic size and decreasing effective nuclear charge on valence orbitals. Oxygen is second amongst all elements to have highest electronegativity next to fluorine.

- **Electron Gain Enthalpy**

  From sulphur onwards the electron gain enthalpy decreases as a regular group trend. Oxygen however is an exception in having lower electron gain enthalpy than sulphur. The 2*p* valence orbital present in the oxygen is too small to accommodate additional electrons without significant interelectronic repulsions.

- **Physical State and Metallic Character**

  Oxygen exists as a gas while all other elements of this group are solids at room temperature. Oxygen and sulphur are non-metals, selenium and tellurium are metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived ($t_{½}$ = 13.8 days). All these elements exhibit allotropy.

- **Melting and Boiling Points**

  Melting and boiling points of elements increase down the group because of increasing atomic size.. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as a diatomic molecule (O_2) whereas sulphur exists as a polyatomic molecule (S_8). The size dependent *van der waals* forces are therefore stronger in sulphur than in oxygen.

- **Oxidation States**

  Being a group of electronegative elements, -2 oxidation state is commonly observed for these elements, the stability of which, however, decreases down the group because of decreasing electronegativity. Polonium does not show –2 oxidation state. The other oxidation states observed for group 16 elements are +1, +2, +4 and +6. Oxygen displays only two positive oxidation states +1 and +2 only when it is bonded to the most electronegative atom F in compounds O_2F_2 and OF_2. Oxygen lacks *d* orbitals in its valence shell and hence can’t show higher positive oxidation states (greater than two) though it can have a maximum covalency of four (rarely observed). For other elements of this group, +4 and +6 are quite common oxidation states. Like group 15 elements, the inert pair effect is quite visible in the heavier members of the group 16 as well. Since electronegativity of oxygen is very high, it shows only negative oxidation state i.e –2 except in the case of OF_2 where its oxidation state is + 2. The stability of + 6 oxidation state decreases down the group and stability of + 4 oxidation state increases.

Compounds containing -2 oxidation states of these elements can be ionic or covalent depending on the electronegativity of other bonded atoms. The compounds containing positive oxidation states are however all covalent.

Anomalous Properties of Oxygen

Oxygen being the first member of the group has small atomic size, high Ionization enthalpy, high electronegativity and lacks d orbitals in the valence shell. These factors contribute to some anomalous properties observed for oxygen. These are:

- ***Oxygen exists in the gaseous form as a stable diatomic molecule***

  Oxygen forms extremely stable $p\pi$-$p\pi$ multiple bonds with other oxygen atoms through its small 2*p* orbitals. The stable diatomic molecules generated have only weak *van der waals forces between them and thus* exist in gaseous state. It forms similar stable $p\pi - p\pi$ multiple bonds with C and N also (C=O, N=O). Other elements in this group do not form stable $p\pi - p\pi$ multiple bonds because of large orbital size.

- ***Oxygen lacks catenation property***

  Oxygen does not form stable O-O single bonds because of large inter electronic repulsions between non bonding electron pairs on each bonded oxygen atom. O=O double bond however is quite stable and results in valency satisfaction for each oxygen. Oxygen thus does not catenate. For sulphur and other elements however, single bonds are stable. Their large atomic size results in reduced lone pair – lone pair repulsions resulting in a large number of atoms linking to each other. Sulphur exists as S_8 in its most common allotrope. For this reason also, other elements exist in the solid state.

- Oxygen lacks d orbitals in its valence shell and hence can have a *maximum covalency of four* though rarely it exceeds two.

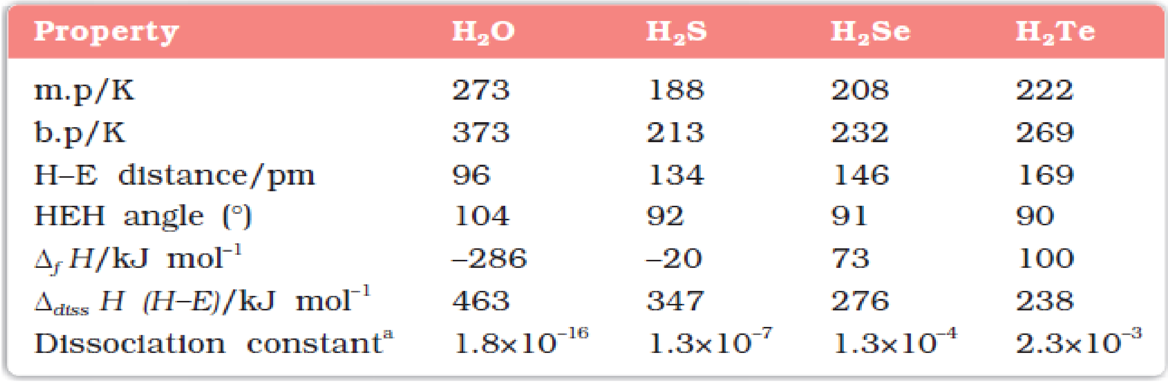
Binary Compounds of Group 16 Elements with Hydrogen (Hydrides)

All the elements of group 16 react with hydrogen to form compounds of the type H_2E (E = O, S, Se, Te, Po). Some properties of these compounds are given in Table 3.1.

- **Thermal stability of these compounds decreases down the group** due to decrease in H–E bond enthalpy down the group.
- These compounds contain ionisable hydrogen and hence act as acids. **The acidic character increases down the group** because of decreasing H-E bond dissociation enthalpy down the group.

- Except water (H_2O) all these compounds are gaseous at room temperature. **Melting and boiling point of these compounds increases from H_2S onwards** due to increase in vanderwaal interaction with increasing size. *Water has exceptionally high melting and boiling point* due to strong intermolecular hydrogen bonding resulting from high O-H bond polarity.
- All these compounds have sp^3 hybridisation of the central atom in H_2E and thus have tetrahedral geometry with two non bonding electron pairs and two E-H bond pairs. The shape of the molecule is thus v shape. The lone pair bond pair repulsions make the bond angle lower than tetrahedral bond angle values (table 3.1) Bond angle H-M-H decreases down the group. With increase in atomic size of the central atom, the size of orbital carrying the lone pair increases and lone pair-bond pair repulsions increase, forcing the bond angle to decrease.

Table 3.1 - Physical properties of hydrides



Property	H_2O	H_2S	H_2Se	H_2Te
m.p/K	273	188	208	222
b.p/K	373	213	232	269
H–E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H$/kJ mol^{-1}	–286	–20	73	100
$\Delta_{diss} H$ (H–E)/kJ mol^{-1}	463	347	276	238
Dissociation constant^a	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

Oxides of Group 16 Elements

All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. Sulphur dioxide (SO_2) is a gas while SeO_2 and TeO_2 are solids. This is because Se and Te can not form stable π bonds and thus polymerise through Se-O or Te-O single bonds. The stability of +4 oxidation state increases down the group and thus reducing the property of dioxides decreases from SO_2 to TeO_2. All these dioxides are acidic in nature.

The trioxides EO_3 (SO_3, SeO_3, TeO_3) contain group 16 elements in +6 oxidation state and are stronger acids than dioxides.

Halides of Group 16 Elements

Elements of Group 16 form a large number of halides of the type, EX_6, EX_4 and EX_2 where E is an element of the group 16 and X is a halogen. Oxygen forms only mono and di fluorides. The stability of the halides decreases in the order *fluoride* > *chloride* > *bromide* > *iodide*. This is due to decreasing E-X bond strength with increasing atomic size of halogen.

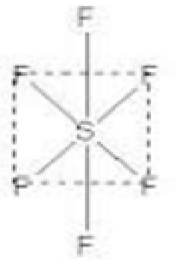
Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral geometry with sp^3d^2 hybridisation (Fig 3.1). Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons. Six fluorine atoms surround the sulphur atom completely and provide steric hindrance to any attacking reagent. For this reason SF_6 is resistant towards hydrolysis.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid. These fluorides have sp^3d hybridisation (Fig 3.1) and thus, have trigonal bipyramidal geometry with lone pair occupying one of the equatorial positions. This shape of the tetrahalides appears as a see-saw. SF_4 which is sterically less hindered is more reactive than SF_6.

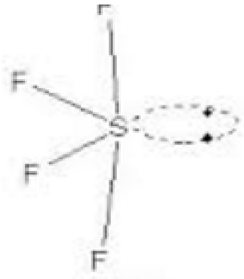
All elements except oxygen form dichlorides and dibromides. These dihalides have sp^3 hybridisation of group 16 elements and thus have tetrahedral geometry. The presence of two lone pairs and two bond pairs gives rise to a V-shaped molecule.

The well known monohalides are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as follows

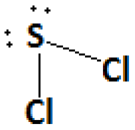
$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$



SF_6
Geometry : Octahedral
Shape : Octahedral



SF_4
Geometry : Trigonal bipyramidal
Shape : See-Saw



Geometry: Tetrahedral
Shape: V shape (bent)

Fig 3.1: Shapes of Sulphur Halides

Allotropes of Oxygen

Oxygen exists in two allotropic forms both of which are in the gaseous form at room temperature - dioxygen (O_2) and ozone (O_3).

- **<u>Dioxygen (O_2)</u>**

  Dioxygen, the diatomic allotrope of oxygen, is also known as 'molecular oxygen'.

Preparation

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

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

$$2KClO_3\,(s) \xrightarrow[MnO_2]{heat} 2KCl(s) + 3O_2\,(g)$$

Potassium chlorate oxygen gas

$$2KMnO_4 \xrightarrow{488-508\,K} K_2MnO_4\,(s) + MnO_2(s) + O_2\,(g)$$

Potassium permanganate Oxygen gas

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

$$2Ag_2O(s) \rightarrow 4Ag\,(s) + O_2(g)$$

$$2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$$

$$2HgO(s) \rightarrow 2Hg\,(l) + O_2(g)$$

$$2PbO_2(s) \rightarrow 2PbO\,(s) + O_2(g)$$

iii. Catalytic decomposition of 30% Hydrogen peroxide into water and dioxygen.

$$2H_2O_2(\text{aq}) \xrightarrow{\text{MnO}_2} 2H_2O(l) + O_2(g)$$

On a commercial scale it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode. Industrially, dioxygen is obtained from air by first removing carbon dioxide and water vapour and then fractional distillation of the remaining liquefied gasses at 90 K to give dinitrogen and dioxygen.

Properties

- Dioxygen is a colorless, odourless and tasteless gas.
- It is soluble in water and acts as vital support of marine and aquatic life. The solubility in water is to the extent of 3.08 cm^3 in 100 cm^3 water at 293 K .
- Its boiling point is 90 K and freezing point is 55 K. Oxygen condenses to a paramagnetic pale blue liquid.
- Oxygen atom has three stable isotopes: ^{16}O, ^{17}O and ^{18}O.
- Molecular oxygen, O_2 is unique, It is paramagnetic in spite of having an even number of electrons. The unpaired electrons present in the antibonding pi orbitals of oxygen molecules give rise to paramagnetism in dioxygen.
- Dioxygen is not combustible but a supporter of combustion. It is a powerful oxidizing agent and can oxidize metals, non-metals and other compounds to their respective oxides. Its reaction with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of oxygen-oxygen double bond is high (493.4 KJ mol^{-1}).

  $2Ca\,(s) + O_2(g) \rightarrow 2CaO\,(s)$

  $4Al\,(s) + 3O_2(g) \rightarrow 2Al_2O_3\,(s)$

  $P_4\,(s) + 5O_2\,(g) \rightarrow P_4O_{10}\,(s)$

  $C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$

  $2ZnS + 3O_2(g) \rightarrow 2ZnO\,(s) + 2SO_2\,(g)$

  $CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$

Oxidation of some compounds takes place in the presence of a catalyst only. For example

$$2SO_2\ (g)\ +\ O_2\ (g)\ \xrightarrow{V_2O_5}\ 2SO_3\ (g)$$

$$4HCl\ (g)\ +\ O_2\ (g)\ \xrightarrow{CuCl_2}\ 2Cl_2(g)\ +\ 2\,H_2O\ (l)$$

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

Oxides can be simple (e.g., MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4). Simple oxides can be classified on the basis of their acidic, basic or amphoteric character. An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO_2, Cl_2O_7, CO_2, N_2O_5). For example, SO_2 combines with water to give H_2SO_3, an acid.

$$SO_2\,(g)\ +\ H_2O\ (l)\ \rightarrow H_2SO_3\,(aq)$$

As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn_2O_7, CrO_3, V_2O_5). The oxides which give a base with water are known as basic oxides (e.g., Na_2O, CaO, BaO). For example, CaO combines with water to give $Ca(OH)_2$, a base.

$$CaO\ (s)\ +\ H_2O\ (l)\ \rightarrow Ca(OH)_2\,(aq)$$

In general, metallic oxides are basic. Some metallic oxides exhibit a dual behavior. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies. For example, Al_2O_3 reacts with acid as well as alkali.

$$Al_2O_3\,(s)\ +\ 6\,HCl\,(aq)\ +\ 9\,H_2O\ (l) \rightarrow 2[Al(H_2O)_6]^{3+}\ (aq)\ +\ 6Cl^-\ (aq)$$

$$Al_2O_3\,(s)\ +\ 6\,NaOH\ (aq)\ +\ 3\,H_2O\ (l) \rightarrow 2Na_3[Al(H_2O)_6]\ (aq)$$

Uses

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

Ozone (O_3)

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

Preparation

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

$$3O_2 \rightleftharpoons 2O_3;\ \Delta H_v\ (298\,K) = +\ 142\ kJ\ mol^{-1}$$

Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a **silent electrical discharge in its preparation to prevent its decomposition.** If concentrations of ozone greater than 10 percent are required, a battery of ozonisers can be used, and pure ozone (b.p. 101.1K) can be condensed in a vessel surrounded by liquid oxygen.

Properties

Pure ozone is an unstable diamagnetic pale blue gas, dark blue liquid (b.pt. 161.1K) and violet-black solid (m.pt. 80.5 K).

Ozone has a characteristic smell and in small concentrations it is harmless. Infact, it was first detected by means of its smell (Greek word, *ozein,* to smell). The permissible limit for safe exposure to ozone is 0.1 ppm however the concentrations upto 1 ppm are tolerable and tend to be non toxic if the exposure time does not exceed 8-10 minutes.

Gaseous Ozone is thermodynamically unstable with respect to decomposition to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative

Gibbs energy change (ΔG) for its conversion into oxygen. It is not really surprising; therefore, high concentrations of ozone, liquid and solid ozone are dangerously explosive.

$3O_2 \rightleftharpoons 2O_3$ $\quad \Delta H_f^\circ = +142.7$ KJ mol^{-1}, $\quad \Delta G_f^\circ = +163.2$ KJ mol^{-1}

Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidizing agent. It oxidizes lead sulphide to lead sulphate and iodide ions to iodine.

$$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$

$$2I^-(aq) + H_2O(l) + O_3(g) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

Ozone has a unique ability to absorb ultraviolet radiations in the region 220-290 nm because of which it is able to provide earth and its inhabitants, a shield from UV radiations of the sun.

Ozone tends to combine very rapidly with nitric oxide (NO). The increased concentrations of NO in air emitted from the exhaust systems of supersonic jet airplanes and from the burning of fossil fuels in automobiles results in depleting the concentration of the ozone layer in the upper atmosphere.

$$NO\,(g) + O_3(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

$$O_3(g) + sunlight \rightarrow O_2\,(g) + O\,(oxygen\,free\,radical)$$

$$NO_2\,(g) + O \rightarrow NO\,(g) + O_2\,(g)$$

Overall reaction: $2O_3(g) \rightarrow 3O_2(g)$

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

In the stratosphere Freons decompose with exposure to ultraviolet light

$$CCl_2F_2\,(g) \xrightarrow{\text{UV radiation}} CF_2Cl(g) + Cl(g)\ \text{(atomic chlorine)}$$

Freon

$Cl\,(g) + O_3\,(g) \rightarrow ClO\,(g) + O_2\,(g);$

$O_3(g) + ClO(g) \rightarrow Cl\,(g) + 2O_2\,(g)$

So every chlorine atom destroys two molecules of ozone and is regenerated. The cycle goes on till Cl atom combines irreversibly with any other free radical present in the atmosphere.

Quantitative Estimation of Ozone Gas in Gas Mixture

The gas mixture is passed through an excess of potassium iodide solution buffered with a borate buffer (pH 9.2). The liberated iodine is titrated against a standard solution of sodium thiosulphate. The amount of sodium thiosulphate consumed is then equated with the concentration of iodine present in the titration mixture and hence concentration of ozone in the gas mixture.

$O_3\,(g) + 2\,KI\,(aq) + H_2O\,(l) \rightarrow I_2\,(aq) + O_2\,(g) + 2KOH\,(aq)$

(gas mixture/air)

$2Na_2S_2O_3\,(aq) + I_2\,(aq) \rightarrow Na_2S_4O_6\,(aq) + 2NaI\,(aq)$

Sodium thiosulphate

Structure

The molecule of ozone has a bent structure with central oxygen atom *sp*^{2} hybridized. Central oxygen atom is double bonded to the second oxygen atom and coordinated to the third oxygen atom. The molecule is resonance stabilized and hence the two oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the OOO bond angle of about 117°. The actual structure is a resonance hybrid of two resonating forms (Fig 3.2)

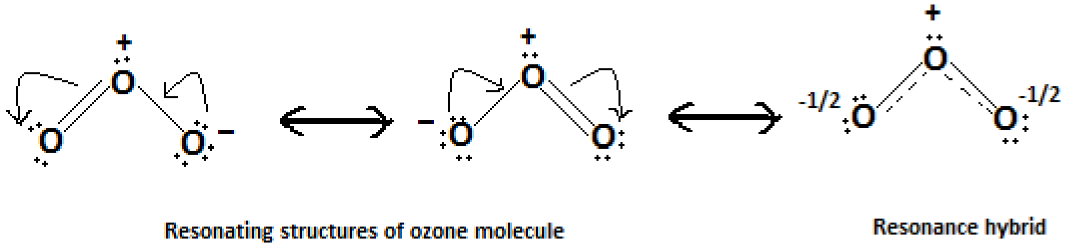


Fig 3.2 Structure of ozone molecule

Uses

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

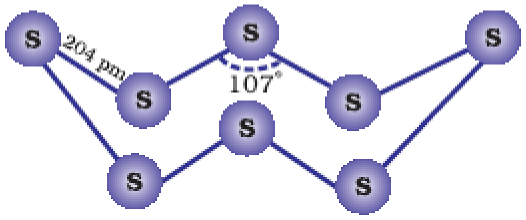
Allotropes of Sulphur

Sulphur forms a large number of allotropes with variable S-S bond lengths and a range of S-S-S bond angles. Two important allotropes and sulphur are discussed below in table 3.2.

Table 3.2. Properties of α and β Sulphur

Rhombic Sulphur (α-sulphur)	***Monoclinic Sulphur (β-sulphur)***
This allotrope is thermodynamically the most stable form and is yellow in color with m.pt. 385.8 K and specific gravity 2.06 g cm^{-3}.	It is colorless form with m.pt. 393 K and specific gravity 1.98g cm^{-3}.
Rhombic sulphur crystals are formed by evaporating the solution of sulphur in CS_2.	This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colorless needle shaped crystals of β-sulphur are formed.
α-sulphur transforms into β-sulphur above 368.5 K. This temperature is called transition temperature.	It is stable above 368.5 K and transforms into α-sulphur below it.
It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS_2.	It is readily soluble in CS_2.

Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape.



(a)

Several other modifications of sulphur containing 6 to 20 sulphur atoms per ring have been synthesized in the last two decades. The rhombohedral sulphur is also called cyclo-S_6. This is prepared by addition of conc HCl to a solution of sodium thiosulphate at -10°C. In cyclo-S_6, the ring adopts the chair conformation and the molecular dimensions are as shown in Fig 3.3. At elevated temperatures (~1000 K), S2 is the dominant species and is paramagnetic. The S_2 molecule in the vapour phase is similar to O_2 molecules and contains two unpaired electrons in antibonding π orbitals which gives rise to paramagnetism.

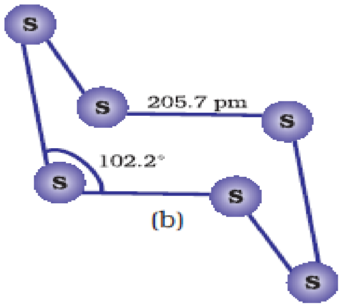


Fig 3.3. Cyclo – S_6 sulphur in chair conformation

<u>Sulphur Dioxide (SO_2)</u>

Preparation

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

$$S(s) + O_2(g) \rightarrow SO_2\,(g)$$

In the laboratory it is readily generated by acidifying a sulphite salt

$$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O\,(l) + SO_2\,(g)$$

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

$$4FeS_2\,(s) + 11O_2(g) \rightarrow 2Fe_2O_3\,(s) + 8SO_2\,(g)$$

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

Properties

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

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

$$SO_2(g) + H_2O\,(l) \rightarrow H_2SO_3\,(aq)$$

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

$$2NaOH\,(aq) + SO_2\,(g) \rightarrow Na_2SO_3\,(aq) + H_2O\,(l)$$

$$Na_2SO_3\,(aq) + H_2O\,(l) + SO_2\,(g) \rightarrow 2NaHSO_3\,(l)$$

Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride, SO_2Cl_2. It is oxidized to sulphur trioxide by oxygen in the presence of vanadium pentoxide catalyst.

$$SO_2\,(g) + Cl_2(g) \xrightarrow{\text{charcoal}} SO_2\,Cl_2(l)$$

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{V_2O_5} 2SO_3\,(g)$$

When moist, sulphur dioxide behaves as a reducing agent. It is a weak reducing agent in acid solution and a much stronger reducing agent in basic solutions. It reduces Fe^{3+} ions to Fe^{2+} ions, decolourises $KMnO_4$ by reducing the purple MnO_4^- to colorless Mn^{2+} and turns acidified $K_2Cr_2O_7$ solution from orange to green .

$$2Fe^{3+}\ (aq) + SO_2\ (g) + 2H_2O\ (l) \rightarrow 2Fe^{2+}\ (aq) + SO_4^{2-}\ (aq) + 4H^+\ (aq)$$

$$2\,MnO_4^-\ (aq) + 5\,SO_2\ (g) + 2H_2O\ (l) \rightarrow 5SO_4^{2-}\ (aq) + 4H^+\ (aq) + 2\,Mn^{2+}\ (aq)$$

Purple colourless

$$Cr_2O_7^{2-}\ (aq) + 3SO_2\ (g) + 2\,H^+\ (aq) \rightarrow 3SO_4^{2-}\ (aq) + H_2O\ (l) + 2\,Cr^{3+}\ (aq)$$

Orange green

Structure

The S atom in SO_2 is *sp*^{2} hybridized and the molecule is angular. It is a resonance hybrid of canonical form as shown in Fig 3.4

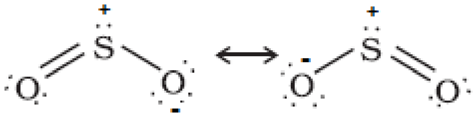


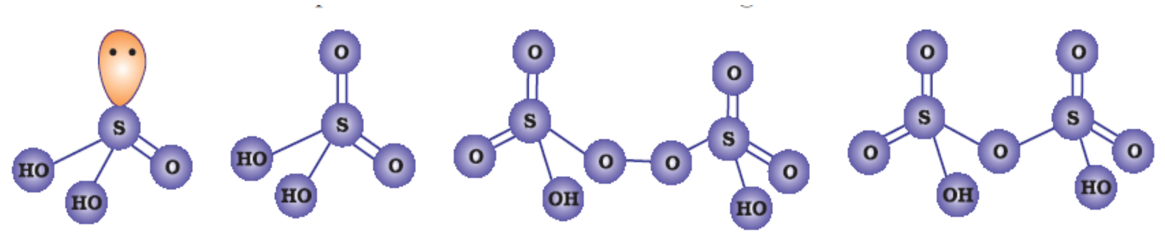
Fig 3.4. Resonating structures of sulphur dioxide

Uses

Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative. It is used as an important industrial chemical to synthesize sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite. Liquid SO_2 is used as a non aqueous solvent to dissolve a number of organic and inorganic compounds.

Oxoacids of Sulphur

Sulphur forms a large number of oxoacids. Not all these acids can be isolated in a pure state. Some oxoacids of sulphur are known in aqueous solution and some in the form of their salts. Name and oxidation states of some important oxoacids are given in table 3.3 and Structures are shown in Fig 3.5.


Sulphurous acid (H_2SO_3) Sulphuric acid (H_2SO_4) Peroxodisulphuric acid ($H_2S_2O_8$) Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Structures of some important oxoacids of sulphur

Fig 3.5

Table 3.3. Oxoacids of Sulphur - Names, Formula and Oxidation States

Name of the oxoacid	**Formula**	**Oxidation state of S**
Sulphurous acid	H_2SO_3	+4
Thiosulphuric acid	$H_2S_2O_3$	+2
Dithionous acid	$H_2S_2O_4$	+3
Disulphurous acid	$H_2S_2O_5$	+4
Dithionic acid	$H_2S_2O_6$	+5
Polythionic acid	$H_2S_nO_6$	+5 (for terminal S atoms)
Sulphuric acid	H_2SO_4	+6
Pyrosulphuric acid (oleum)	$H_2S_2O_7$	+6
Peroxomonosulphuric acid (Caro's acid)	H_2SO_5	+6
Peroxodisulphuric acid (Marshall's acid)	$H_2S_2O_8$	+6

Sulphuric Acid

Preparation

Sulphuric acid is one of the most important industrial chemicals worldwide. Sulphuric acid is manufactured by the **Contact Process** which involves three steps:

i) Roasting of sulphur or sulphide ores in air to generate SO_2.

ii) Catalytic oxidation of SO_2 to SO_3 in the presence of a V_2O_5

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{V_2O_5} 2SO_3\,(g)$$

$$\Delta H_f^0 = -196.6\text{KJ/mol}$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favorable conditions for maximum yield. But the temperature should not be very low otherwise the rate of reaction will become slow. In practice, the plant is (fig 3.6) operated at a pressure of 2 bars and a temperature of 720 K.

iii) Absorption of SO_3 in H_2SO_4 to give *Oleum* ($H_2S_2O_7$)

a) $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7\ (Oleum)$

iv) Hydrolysis of oleum.

Direct hydrolysis of SO_3 to give H_2SO_4 is avoided because of the violent exothermic nature of this hydrolysis reaction. Hydrolysis of oleum is comparatively less exothermic and hence safe.

$$H_2S_2O_7\ (Oleum) + H_2O\ (l) \rightarrow 2\,H_2SO_4\ (aq)$$

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

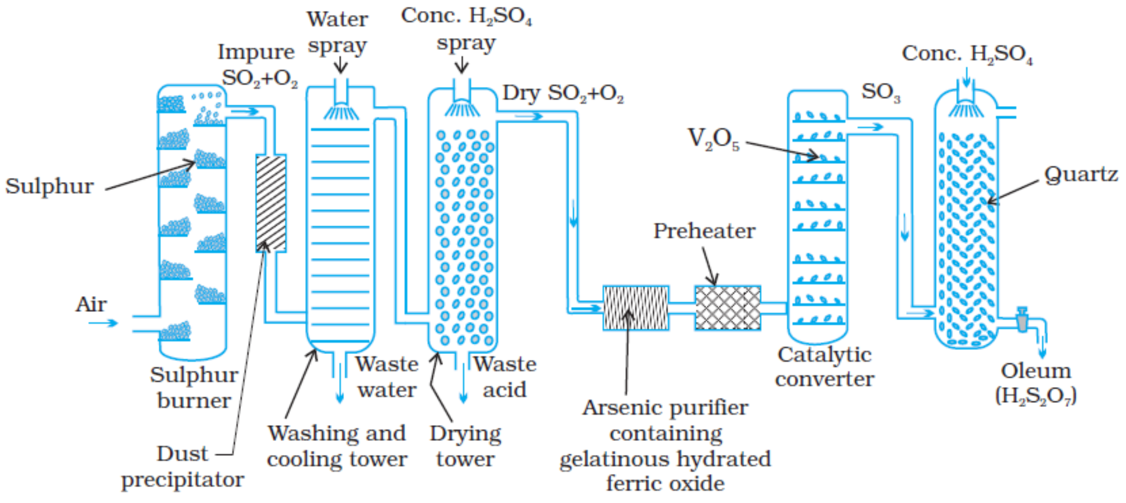


***Fig 3.6*- Flow Diagram for the manufacturing of sulphuric acid**

Properties

Sulphuric acid is a colourless, dense, oily liquid (boiling point 611 K and freezing point 283 K) and a specific gravity of 1.84g/cm^3 at 298 K.

It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into bulk water with constant stirring.

It is used to manufacture other acids from their corresponding salts.

$BaX_2\,(aq) + H_2SO_4\,(conc.) \rightarrow BaSO_4\,(s) + HX\,(aq)$ where X = F^-, Cl^- and NO_3^-

Concentrated sulphuric acid is a strong acid.

In aqueous solution, sulphuric acid ionizes in two steps

$$H_2SO_4\,(aq) + H_2O\,(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq);\; K_{a_1} = very\ large\ (K_{a_1} > 10)$$

$$HSO_4^-(aq) + H_2O\,(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)\,;\; K_{a_2} = 1.2 \times 10^{-2}$$

The higher value of K_{a_1} means that H_2SO_4 is largely dissociated into H^+ and HSO_4^-. Greater the value of dissociation constant (K_a), the stronger the acid. The second ionization is also strong though weaker than the first ionization.

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

Conc. Sulphuric acid has a strong affinity towards water and thus act as a very strong **dehydrating agent.** It can dehydrate organic compounds completely for e.g.;

Charring of sugar: $C_{12}H_{22}O_{11}\ (s) \xrightarrow{H_2SO_4(conc)} 12C\ (s) + 11H_2O\ (l)$

Dehydration of alcohol to alkene, $C_2H_5OH\ (l) \xrightarrow{H_2SO_4(conc)} C_2H_4\ (g) + H_2O(l)$

Removes water of crystallization from hydrated salts such as blue vitriol.

$$CuSO_4.5H_2O \xrightarrow{H_2SO_4(conc)} CuSO_4\ (anhydrous) + 5H_2O$$

(the water molecules are absorbed by sulphuric acid)

Hot conc. H_2SO_4 acts as an **oxidizing agent** of moderate strength. It is a stronger oxidizing agent than H_3PO_4 but weaker than HNO_3

$$Cu\,(s) + 2H_2SO_4\,(conc.) \rightarrow CuSO_4 + SO_2\,(g) + 2H_2O\,(l)$$

$$S\,(s) \quad + \quad 2H_2SO_4\,(conc.) \rightarrow 3SO_2\,(g) \quad + \quad 2H_2O\,(l)$$

$$C\,(s) \quad + \quad 2H_2SO_4\,(conc.) \rightarrow CO_2 \quad + \quad 2\,SO_2\,(g) \quad + \quad 2\,H_2O\,(l)$$

Structure of sulphuric acid

The central S atom in H_2SO_4 is sp^3 hybridized and the molecule has a tetrahedral geometry. There are two S=O double bonds and two S-OH single bonds.

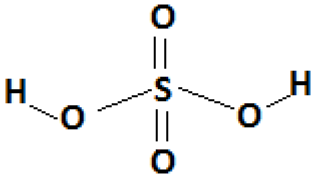


Fig. 3.7. Structure of Sulphuric acid

Uses

Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk sulphuric acid produced is used in the manufacture of fertilizers (e.g., ammonium sulphate, superphosphate). Other uses are in:(a) petroleum refining (b) manufacture of pigments, paints and dyestuff intermediates (c) detergent industry (d) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanizing(e) storage batteries (f) in the manufacture of nitrocellulose products and (g) as a laboratory reagent.

Health Hazards/ Health Effects: Concentrated H_2SO_4 is more dangerous than the other mineral acids. Being a strong dehydrating agent and a strong acid, it causes severe chemical burns upon skin contact. It dehydrates skin and even flesh beneath and the heat generated on hydrolysis of sulphuric acid leads to further irreparable damage. Contact with eyes can lead to permanent damage and blindness.

Summary

Chalcogens, the group 16 elements have general electronic configuration ns^2np^4. They show variable oxidation states ranging from -2,+2, +4, to +6. Being the smallest member, oxygen shows many anomalous properties. Oxygen has two allotropes –dioxygen and ozone – both of which sustain life on earth. Oxygen combines with all other elements of the periodic table to form oxides. It forms a number of oxides with metals. Ozone is a strong oxidizing agent. Sulphur also has a number of allotropes. Sulphur combines with oxygen to give oxides such as SO_2 and SO_3. SO_2 is prepared by catalytic oxidation of sulphur. Sulphur dioxide acts as a reducing agent. It is used in the manufacture of H_2SO_4. Sulphur forms a large number of oxoacids. Amongst them, the most important is H_2SO_4. It is a dehydrating and oxidizing agent and is used in the manufacture of several compounds of industrial use.