

Group 16 Elements

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

Occurrence:Oxygen is the most abundant of all the elements on earth. Oxygen forms about 46.6% by mass of earth’s crust. Dry air contains 20.946% oxygen by volume.

However, the abundance of sulphur in the earth’s crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as gypsum CaSO₄.2H₂O, epsom salt MgSO₄.7H₂O, baryte BaSO₄ and sulphides such as galena PbS, zinc blende ZnS, copper pyrites CuFeS₂. Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur. Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals.

The important atomic and physical properties of Group16 along with electronic configuration are discussed below.

Electronic Configuration: The elements of Group16 have six electrons in the outermost shell and have ns²np⁴ general electronic configuration.

Atomic and Ionic Radii: Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.

Ionisation Enthalpy: Ionisation enthalpy decreases down the group. It is due to increase in size. However, the elements of this group have lower ionisation enthalpy values compared to those of Group15 in the corresponding periods. This is due to the fact that Group 15 elements have extra stable halffilled p orbitals electronic configurations.

Electron Gain Enthalpy: Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative upto polonium.

Electronegativity: Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decreases with an increase in atomic number. This implies that the metallic character increases from oxygen to polonium.

Physical Properties: Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). All these elements exhibit allotropy. The melting and boiling points increase with an increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as diatomic molecule (O₂) whereas sulphur exists as polyatomic molecule (S₈).

Chemical Properties:

Oxidation states and trends in chemical reactivity:

The elements of Group 16 exhibit a number of oxidation states . The stability of -2 oxidation state decreases down the group. Polonium hardly shows –2 oxidation state. Since electronegativity of oxygen is very high, it shows only negative oxidation state as –2 except in the case of OF₂ where its oxidation state is + 2. Other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation state in their compounds with oxygen and + 6 with fluorine. The stability of + 6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in +4 and +6 oxidation states is primarily covalent.

Anomalous behaviour of oxygen: The anomalous behaviour of oxygen, like other members of p-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H₂O which is not found in H₂S.

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

(i) Reactivity with hydrogen: All the elements of Group 16 form hydrides of the type H₂E (E = O, S, Se, Te, Po). Their *acidic character* increases from H₂O to H₂Te. The increase in acidic character can be explained in terms of decrease in bond enthalpy for the dissociation of H–E bond down the group. Owing to the decrease in enthalpy for the dissociation of H–E bond down the group, the thermal stability of hydrides also decreases from H₂O to H₂Po. All the hydrides except water possess reducing property and this character increases from H₂S to H₂Te.

(ii) Reactivity with oxygen: All these elements form oxides of the EO₂ and EO₃ types where E = S, Se, Te or Po. Ozone (O₃) and sulphur dioxide (SO₂) are gases while selenium dioxide (SeO₂) is solid. Reducing property of dioxide decreases from SO₂ to TeO₂; SO₂ is reducing while TeO₂ is an oxidising agent. Besides EO₂ type, sulphur, selenium and tellurium also form EO₃ type oxides (SO₃, SeO₃, TeO₃). Both types of oxides are acidic in nature.

(iii) Reactivity towards the halogens: Elements of Group 16 form a large number of halides of the type, EX₆, EX₄ and EX₂ where E is an element of the group and X is a halogen. The stability of the halides decreases in the order F⁻ > Cl⁻ > Br⁻ > I⁻. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride, SF₆ is exceptionally stable for steric reasons. Amongst tetrafluorides, SF₄ is a gas, SeF₄ a liquid and TeF₄ a solid. These fluorides have sp³d hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry.

All elements except oxygen form dichlorides and dibromides. These dihalides are formed by sp³ hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are S₂F₂, S₂Cl₂, S₂Br₂, Se₂Cl₂ and Se₂Br₂. These dimeric halides undergo disproportionation as given below:

2Se₂Cl₂ → SeCl₄ + 3Se

Dioxygen

Preparation:

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

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

2KClO₃ $\xrightarrow[\text{MnO}_2]{\text{Heat}}$ 2KCl + 3O₂

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

2Ag₂O(s) → 4Ag(s) + O₂(g); 2Pb₂O₃(s) → 6PbO(s) + O₂(g)

2HgO(s) → 2Hg(l) + O₂(g); 2PbO₂(s) → 2PbO(s) + O₂(g)

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

2H₂O₂(aq) → 2H₂O(l) + O₂(g)

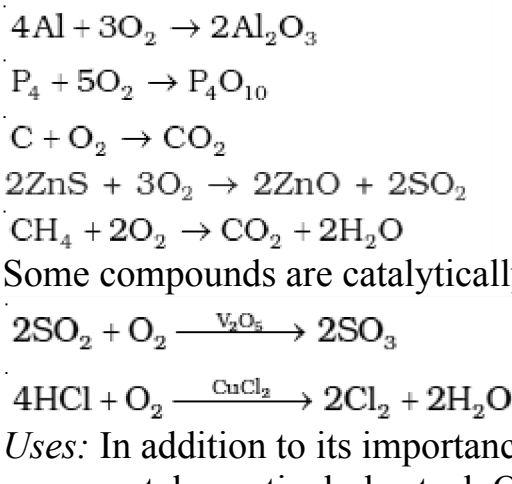
On large scale it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode. Industrially, dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

Properties:

Dioxygen is a colourless and odourless gas. Its solubility in water is to the extent of 3.08 cm³ in 100 cm³ water at 293 K which is just sufficient for the vital support of marine and aquatic life. It liquefies at 90 K and freezes at 55 K. Oxygen atom has three stable isotopes: ¹⁶O, ¹⁷O and ¹⁸O. Molecular oxygen, O₂ is unique in being paramagnetic inspite of having even number of electrons .

Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. Its combination with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of oxygen-oxygen double bond is high (493.4 kJ mol⁻¹).

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



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.

Simple Oxides

A binary compound of oxygen with another element is called oxide. As already stated, oxygen reacts with most of the elements of the periodic table to form oxides. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties. Oxides can be simple (e.g., MgO, Al₂O₃) or mixed (Pb₃O₄, Fe₃O₄). 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., SO₂, Cl₂O₇, CO₂, N₂O₅). For example, SO₂ combines with water to give H₂SO₃, an acid.

SO₂ + H₂O → H₂SO₃

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., Mn₂O₇, CrO₃, V₂O₅). The oxides which give a base with water are known as basic oxides (e.g., Na₂O, CaO, BaO). For example, CaO combines with water to give Ca(OH)₂, a base.

CaO + H₂O → Ca(OH)₂

In general, metallic oxides are basic.

Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalis. For example, Al₂O₃ reacts with acids as well as alkalis.

Al₂O₃ (s) + 6HCl (aq) + 9H₂O (l) → 2[Al(H₂O)₆]³⁺ (aq) + 6Cl⁻ (aq)

Al₂O₃ (s) + 6NaOH (aq) + 3H₂O (l) → 2Na₃ [Al(OH)₆] (aq)

There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N₂O.

Ozone:

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

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.

3O₂ → 2O₃ ΔH° (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 per cent 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 a pale blue gas, dark blue liquid and violet-black solid. Ozone has a characteristic smell and in small concentrations it is harmless. However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (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 can be dangerously explosive.

Due to the ease with which it liberates atoms of nascent oxygen (O₃ → O₂ + O), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

PbS(s) + 4O₃(g) → PbSO₄(s) + 4O₂(g)

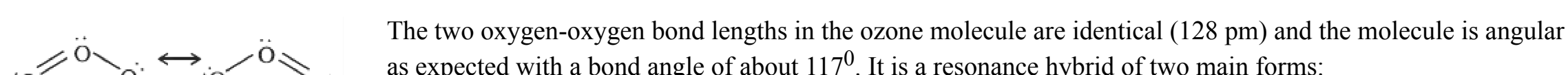
2I⁻(aq) + H₂O(l) + O₃(g) → 2OH⁻(aq) + I₂(s) + O₂(g)

When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O₃ gas.

Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

NO (g) + O₃ (g) → NO₂ (g) + O₂ (g)

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



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

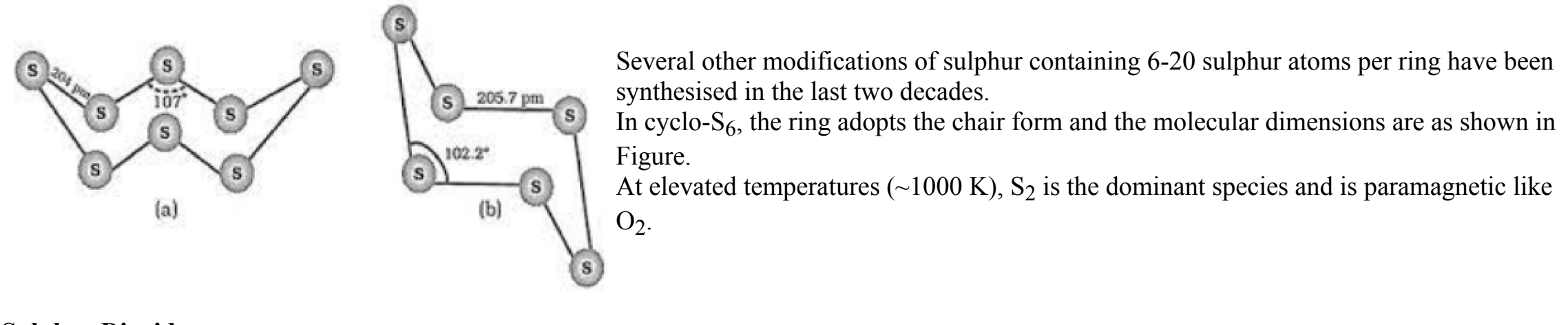
Sulphur

Allotropic Forms: Sulphur forms numerous allotropes of which the yellow rhombic (α-sulphur) and monoclinic (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

Rhombic sulphur (α-sulphur): This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS₂. It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS₂.

Monoclinic sulphur (β-sulphur): Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS₂. This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β-sulphur are formed. It is stable above 369 K and transforms into α-sulphur below it. Conversely, α-sulphur is stable below 369 K and transforms into β-sulphur above this. At 369 K both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have S₈ molecules. These S₈ molecules are packed to give different crystal structures. The S₈ ring in both the forms is puckered and has a crown shape.



Sulphur Dioxide

Preparation:

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

S(s) + O₂(g) → SO₂ (g)

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

SO₃²⁻(aq) + 2H⁺ (aq) → H₂O(l) + SO₂ (g)

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

4FeS₂ (s) + 11O₂ (g) → 2Fe₂O₃ (s) + 8SO₂ (g)

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

Properties:

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

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

SO₂(g) + H₂O(l) → H₂SO₃(aq)

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

2NaOH + SO₂ → Na₂SO₃ + H₂O

Na₂SO₃ + H₂O → 2NaHSO₃

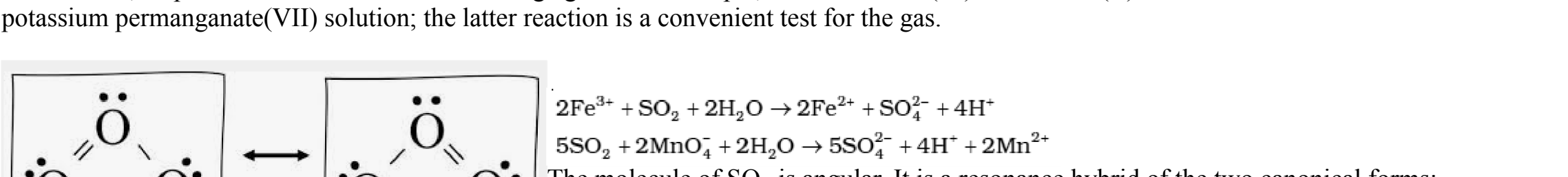
In its reaction with water and alkalis, the behaviour of sulphur dioxide is very similar to that of carbon dioxide.

Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride, SO₂Cl₂. It is oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.

SO₂(g) + Cl₂ (g) → SO₂Cl₂(l)

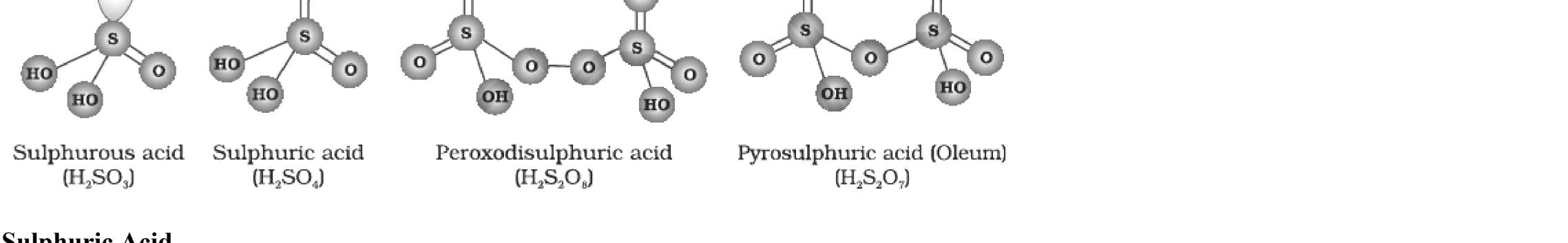
2SO₂ (g) + O₂ (g) $\xrightarrow{\text{V}_2\text{O}_5}$ 2SO₃ (g)

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



Uses: Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO₂ is used as a solvent to dissolve a number of organic and inorganic chemicals.

Oxoacids of Sulphur: Sulphur forms a number of oxoacids such as H₂SO₃, H₂S₂O₃, H₂S₂O₄, H₂S₂O₅, H₂S_xO₆ (x = 2 to 5), H₂SO₄, H₂S₂O₇, H₂SO₅, H₂S₂O₈. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in the following Figure.



Sulphuric Acid

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

(i) burning of sulphur or sulphide ores in air to generate SO₂.

(ii) conversion of SO₂ to SO₃ by the reaction with oxygen in the presence of a catalyst (V₂O₅), and

(iii) absorption of SO₃ in H₂SO₄ to give Oleum (H₂S₂O₇).

The SO₂ produced is purified by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of H₂SO₄ is the catalytic oxidation of SO₂ with O₂ to give SO₃ in the presence of V₂O₅ (catalyst).

2SO₂ (g) + O₂ (g) $\xrightarrow{\text{V}_2\text{O}_5}$ 2SO₃ (g) Δ_rH° = -196.6 kJmol⁻¹

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

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO₃ gas from the catalytic converter is absorbed in concentrated H₂SO₄ to produce oleum. Dilution of oleum with water gives H₂SO₄ of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

SO₃ + H₂SO₄ → H₂S₂O₇ (Oleum)

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

Properties:

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

The chemical reactions of sulphuric acid are as a result of the following characteristics:

(a) low volatility

(b) strong acidic character

(c) strong affinity for water and

(d) ability to act as an oxidising agent.

In aqueous solution, sulphuric acid ionises in two steps.

H₂SO₄(aq) + H₂O(l) → H₃O⁺(aq) + HSO₄⁻(aq); K_a = very large (K_a >10)

HSO₄⁻(aq) + H₂O(l) → H₃O⁺(aq) + SO₄²⁻(aq) ; K_a = 1.2 × 10⁻²

The larger value of K_{a1} (K_{a1} >10) means that H₂SO₄ is largely dissociated into H⁺ and HSO₄⁻. Greater the value of dissociation constant (K_a), the stronger is the acid.

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

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

2 MX + H₂SO₄ → 2 HX + M₂SO₄ [X = F, Cl, NO₃] (M = Metal)

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

C₁₂H₂₂O₁₁ $\xrightarrow{\text{H}_2\text{SO}_4}$ 12C + 11H₂O

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO₂.

Cu + 2 H₂SO₄(conc.) → CuSO₄ + SO₂ + 2H₂O

S + 2H₂SO₄(conc.) → 3SO₂ + 2H₂O

C + 2H₂SO₄(conc.) → CO₂ + 2 SO₂ + 2 H₂O

Uses:

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