ATOMIC ENERGY CENTRAL SCHOOL 3, TARAPUR

MODULE-2

p- BLOCK ELEMENTS

Group -16- elements : The Oxygen family (Chalcogens)

O
S
Se
Te
Po

p- BLOCK ELEMENTS

16- Group elements

- The Oxygen family (Chalcogens)
- These are called as chlcogens due to their ore forming tendency.
- **Occurrence**: Oxygen is most abundant of all the elements. It occurs in the free state as O_2 , 23% by mass of the atmosphere. It also occurs in the form of ozone(O_3), In the form of mineral as silicate minerals.
- Other elements of this group are less abundant in the earth crust.

Electronic configuration: Their general electronic configuration is ns^2np^4.

Trends in atomic & physical properties :

(1**) Atomic and ionic radii** : The atomic and ionic radii of group 16 elements are smaller than 15 group elements. The atomic and ionic radii increases down the group.

(2) **Ionization enthalpy**: The first ionization enthalpy (I_1) of group 16 elements is lower than group 15 elements. (because electronic configuration of group 15 elements is symmetrical and more stable).

(3**) Electron gain enthalpy** : The electron gain enthalpy decreases down the group but exceptionally the electron gain enthalpy of oxygen is less than the other elements of the group this is due to the smaller size of oxygen atom, smaller size of p-orbital, high electron density, greater repulsion felt by the incoming electron.

(4) **Electronegativity :** The elements of this group have higher values of E.N. than Group 15, due to the smaller size of atoms. Oxygen is the second most electronegative element.

(5) **Non-metallic character** / Metallic character: Oxygen and sulphur are non-metallic where as Se and Te are metalloids , Polonium is however metallic in nature but it is a radioactive.

(6) **Melting and boiling points** : The m.p. and b.p. increases down the group, due to the increase in atomic size, increase in van der Waals forces of attraction

Trends in chemical properties

(1)**Oxidation states**: these elements can show positive and negative both types of o.s. For ex: oxygen can show -2 in H_2O, -1 in H_2O_2 and +2 in F_2O, The highest o.s. of this group is +6. The stability of +6 oxidation state decreases down the group due to inert pair effect.

(2) **Chemical reactivity**: Oxygen is most reactive in the group, S is also very reactive at high temperature. The reactivity decreases down the group.

(3) **Reactivity towards hydrogen** : All the elements of this group form hydrides of general formula H_2E, Where E = O, S, Se, Te, Po.

The **thermal stability** of hydrides decreases down the group, because as the size of central atom increases, the
E-H bond becomes weaker and thus breaks on heating.

$H_2O > H_2S > H_2Se > H_2Te$.

Reducing character : Reducing character increases down the group, because as the size of central atom increases bond strength of E-H bond dereases.

$H_2O < H_2S < H_2Se < H_2Te$.

Acidic character : It is increases down the group, due to decrease in bond strength of E-H bond.

$H_2O < H_2S < H_2Se < H_2Te$.

(4) **Reactivity towards Halogens** :

The elements of this group form number of halides in the oxidation states +1, +2,+3,+4 and +6.

Hexahalides : Only fluorine forms hexahalides, their relative stability decreases down the group, because size of central atom increases, electronegativity decreases, bond polarity increases leading to increase in reactivity or decrease in stability.

$SF_6 > SeF_6 > TeF_6$

Here TeF_6 is less stable therefore undergo hydrolysis readily.

Dioxygen

Preparation : Dioxygen is prepared by the following methods :

(1). By decomposition of oxygen-rich compounds :

$2KMnO_4$ ----------> $K_2MnO_4 + MnO_2 + O_2$

$2BaO_2$ ----------> $2BaO + O_2$

(2) Laboratory method :

In the laboratory, dioxygen is produced by heating a mixture of potassium chlorate and manganese dioxide in the ratio 4:1 in a hard glass test tube at 147^0C.

$2KClO_3$ (s) -----------------> 2KCl (s) + $3O_2$(g).

It can also be prepared in the laboratory by the action of water on sodium peroxide.

2 Na_2O_2 (s) + 2 H_2O (l) ---------> 4 NaOH (aq) + O_2(g)

Dioxygen

(3) Industrial or commercial method :

(i)The most economical method for the commercial preparation of dioxygen is liquefaction of air followed by fraction distillation.

(ii) Dioxygen can also be prepared by the electrolysis of water containing a small amount of a mineral acid or an alkali.

$2H_2O$ (l) ------------------> $2H_2$ (g) + O_2 (g).D

Dioxygen

Properties and uses :

(1) **Physical properties** :

Dioxygen is a colourless and odourless and tasteless gas.

It is slightly soluble in water, sustain marine and aquatic life.

It liquefies at -183^{0}C and freezes at -218^{0}C.

(2) Chemical properties :

(i) **Action on litmus** : Dioxygen is neutral to litmus.

(ii) **Supporter of combustion** : It is not combustible but supports combustion.

(iii) **Oxidation** : It is a powerful oxidizing agent can oxidize metals, non-metals and other compounds to their respective oxides.

(a) reaction with metals :

$4Na + O_2$ -------> $2Na_2O$, $2Na + O_2$ -------> Na_2O_2

$2Ca + O_2$ ------> $2CaO$

(b) Reaction with non-metals :

$2H_2 + O_2$ ------> $2H_2O$

$N_2 + O_2$ --------> $2NO$

$S + O_2$ ---------> SO_2

$2C + O_2$ ----------> $2CO$, $C + O_2$ (excess) --------> CO_2

(c **) Reaction with compounds** :

(i) 2 SO_2(g) + O_2(g) ----------------------> 2SO_3(g)

This reaction forms the basis of **Contact process** for the manufacture of sulphuric acid.

(ii) With hydrocarbons:

CH_4(g) + 2O_2(g----> CO_2 (g)+ 2H_2O(g), ΔH = - 890 kJ mol^{-1}.

CH_2 = CH_2(g) + 3O_2(g) ---->2CO_2(g) + 2H_2O(g), ΔH = - 1411 kJ mol^{-1}

These reactions are called combustion reactions and are highly exothermic in nature. That is why hydrocarbons are used as fuels.

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.

Oxides : A binary compound of oxygen with another element is called oxide. As already stated, oxygen reacts with most of the elements to form 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.

(i) Acidic oxides : An oxide that combines with water to give an acid is known as acidic oxide (e.g., SO_2, Cl_2O_7, CO_2, N_2O_5).

For example,

SO_2 (g)+ H_2O(l) ----> 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).

(ii) Basic oxides : The oxides which give a base with water are known as basic oxides (e.g., Na_2O, CaO, BaO). For example,

Na_2O(s) + H_2O (l) ------> 2NaOH(aq)

In general, metallic oxides are basic.

(iii) Amphoteric oxides: 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 alkalies.

For example, Al_2O_3 , ZnO, PbO reacts with acids as well as alkalies.

(iv) **Neutral oxides** : 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 N_2O.

Ozone

Ozone is an allotropic form of oxygen. 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 :

Ozone is obtained when silent electric discharge is passed through pure, cold and dry oxygen in a apparatus called the ozoniser.

During this reaction, conversion of O_2 to ozone is 10% and therefore the product is called ozonised oxygen.

$3O_2$ (g) -----------------------------> $2O_3$(g), $\Delta H^0 = + 142$ kJ mol^{-1}

Since the reaction is endothermic ,silent discharge produce less heat and thus prevent the decomposition of ozone back to oxygen.

Structure of ozone : The central oxygen in ozone is sp^2 hybridized containing a lone pair of electrons. As a result, ozone has an angular structure with a bond angle of 117^0.

Physical 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.

Chemical properties :

(i) **Oxidising agent** : Due to the ease with which it liberates atoms of nascent oxygen (O_3 ----> O_2 + O), it acts as a powerful oxidising agent. For example, it
oxidises lead sulphide to lead sulphate and iodide ions to iodine.

$PbS(s) + 4O_3(g) \text{ ---> } PbSO_4(s) + 4O_2(g)$

$2I^-(aq) + H_2O(l) + O_3(g) \text{ ----> } 2OH^-(aq) + I_2(s) + O_2(g)$

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 O_3 gas.

Uses : Ozone 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.

compounds of sulphur : (1) Sulphur dioxide (SO_2) :

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

$S(s) + O2(g) \text{-->} SO2\ (g)$

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

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

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

$4 FeS (s) + 11 O_2 (g) \text{------>} 2 Fe_2O_3(s) + 8SO_2(g)$

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.

$SO_2(g) + H_2O(l)$ --------> H_2SO_3.

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

$2NaOH + SO_2$ -----> $Na_2SO_3 + H_2O$

$Na_2SO_3 + H_2O + SO_2$ ------> $2NaHSO_3$

In its reaction with water and alkalies, 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, SO_2Cl_2. It is oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.

$SO_2(g) + Cl_2\ (g)$ ---------> $SO_2Cl_2(l)$

$2\ SO_2(g) + O_2(g)$ --------> $2\ SO_3(g)$

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.

$2Fe^{3+} + SO_2 + 2\,H_2O \text{ --------> } 2Fe^{2+} + SO_4^{2-} + 4H^+$

$5SO_2 + 2MnO_4^- + 2\,H_2O \text{ -----> } 5SO_4^{2-} + 4H^+ + 2\,Mn^{2+}$

The molecule of SO_2 is angular.

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

This is an oxoacid of S, having molecular formula H_2SO_4.

Industrial process of manufacture of sulphuric acid :

These days sulpuric acid is mostly prepared by the contact process. The acid produced by this method is free from arsenic impurities.

Sulphuric acid is manufactured by the Contact Process which involves

three steps:

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

(ii) conversion of SO_2 to SO_3 by the reaction with oxygen in the presence

of a catalyst (V_2O_5), and

(iii) absorption of SO_3 in H_2SO_4 to give Oleum ($H_2S_2O_7$).

Properties and uses :

(1) Acidic character : In aqueous solution, H_2SO_4 ionizes in two steps :

$$H_2SO_4\ (aq) \text{ ----------->} H^+\ (aq) + HSO_4^-\ (aq)\ \ ;\ \ K_{a1} = 1 \times 10^3$$

$$HSO_3^-\ (aq) \text{ ----------->} H^+(aq) + SO_4^{2-}(aq)\ \ ;\ \ K_{a2} = 1.2 \times 10^{-2}$$

Thus H_2SO_4 acts as a strong diprotic or dibasic acid and forms tow series of salts, sulphates and bisulphates.

(2) **Dehydrating agent** : Conc. H_2SO_4 has a strong affinity for water and hence it acts as a strong dehydrating agent. For example,

$$C_{12}H_{22}O_{11} \xrightarrow[H_{2SO4}]{\text{Conc.}} 12\,C + 11\,H_2O \quad \text{(charring of sugar)}$$

(3) **Oxidising agent** : Hot concentrated sulphuric acid is a moderately strong oxidizing agent. In this respect, it is intermediate between phosphoric and nitric

Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

$Cu + 2\ H_2SO_4(conc.)$ ------>$CuSO_4 + SO_2 + 2H_2O$

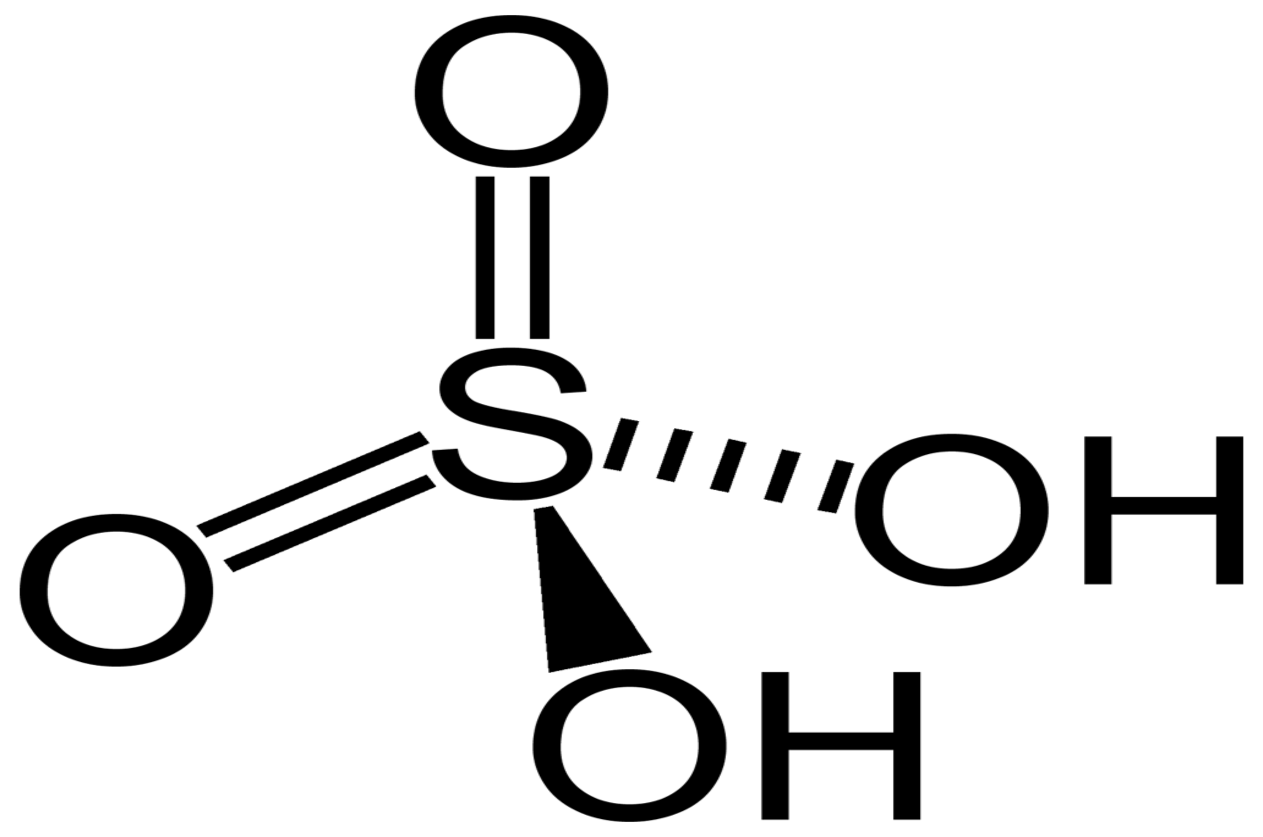
$3S + 2H_2SO_4(conc.)$ -------> $3SO_2 + 2H_2O$

$C + 2H_2SO_4(conc.)$ -------->$CO_2 + 2\ SO_2 + 2\ H_2O$

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.

Oxoacids of sulphur (structures only) :

Sulphur forms a number of oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$ etc. For structure kindly go through NCERT text book.

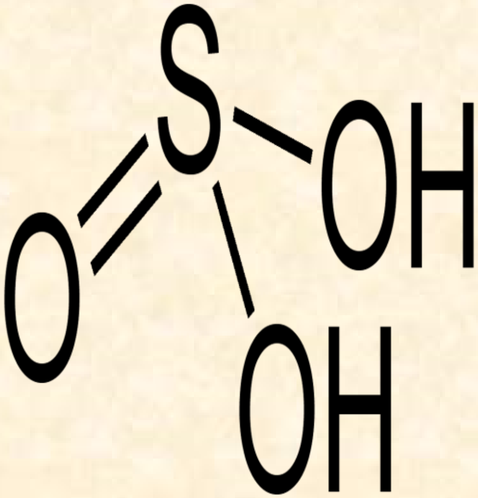


Structure of Sulphuric acid

It is a dibasic acid means it can donate to protons in aqueous medium the H atoms those are directly bonded with oxygen atom are metal replaceable & come as H^+ in water

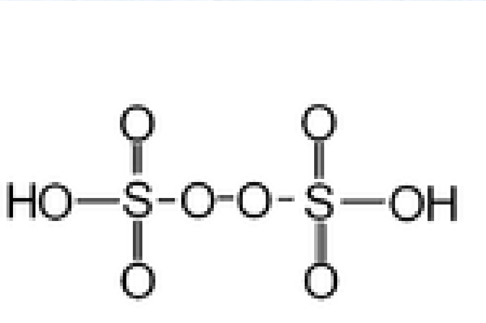
Structure of sulphurous acid

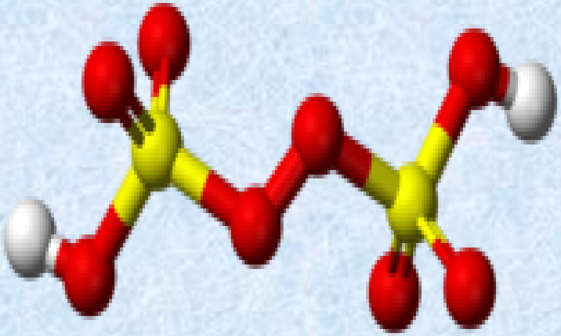
It is also dibasic acid like sulphuric acid but it has one lone pair of electrons on the S atom, due to this it can act as a reducing agent. it



Peroxydisulphuric acid

It is also known as Marshall’s acid. It has one peroxide linkage. It a power ful oxidising agent.





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