OXYGEN FAMILY

1. INTRODUCTION

These are called chalcogen. Beacuse these are ore forming elements {Chalco = ore}

$$\left.\begin{matrix}\text{O}\\\text{S}\\\text{Se}\\\text{Te}\\\text{Po}\end{matrix}\right\}ns^2np^4 \text{ (electronic configuration)}$$

2. IMPORTANT POINT

Po is radioactive element

3. GENERAL PROPERTIES

(i) State and Nature :

(a) Only O_2 in gaseous state and rest all are solid.

∴ Only form pπ – pπ bond.

(b) O and S both non metal

(c) Se and Te are metalloids.

(d) Po is metallic.

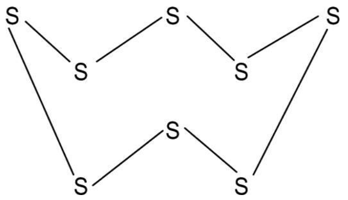
(ii) Atomicity :

(a) Atomicity of O is 2 or 3 (O_3)

(b) S_8, Se_8 (octa atomic molecules)

These exist as puckered ring structure where all atoms are not on same plane.

[Crown form of S.]



(c) Te and Po are mono atomic.

(d) Tellurium exists in two form alpha and Beta.

(iii) Atomic Radii, Ionic Radii, Density and Electropositive : ↓ Increases down the group.

(iv) Ionic Potential and Electron Negativity :

↓ Decreases down the group

C.Q. Most reactive among VIth group elements

Ans. O

C.Q. Least reactive among VIth group elements.

Ans. Te.

(v) Physical State :

Existence of oxygen as a diatomic molecule is due to ability of oxygen atom to form stable pπ-pπ multiple bond where as sulphur and other elements of the group are incapable of pπ - pπ overlap.

(vi) Melting Point and Boiling Point :

From oxygen to tellurium melting and boiling points go on increasing. The M.P. of polonium is less than tellurium.

(vii) Allotropy and Allotropic Forms :

Oxygen has two allotropes O_2 and O_3. The type of allotropy is called as monotropy. Sulphur has number of allotropic forms. The most common are Rhombic sulphur, monolinic sulphur, plastic sulphur, colloidal sulphur etc.

4.CHEMICAL PROPERTIES

4.1 Formation of Hydraides :

(a) Hydrides which are formed have H_2Y formula where Y is the VIth group elements and O.S. +2.

Eg. $H_2O \longrightarrow$ Neutral hydrides {liquid state}

$$\left.\begin{matrix}H_2S\\H_2Se\\H_2Te\end{matrix}\right\}\rightarrow \text{Acidic Nature (Gaseous)}$$

(b) H_2O undergoes strong intermolecular H-bonding so exist in liquid state.

(c) The least boiling Hydrides is H_2S. Because no H-bonding.

(d) The B.P. of these hydrides vary as $H_2O > H_2S < H_2Se < H_2Te$

(e) Properties :

(1) Volatility : $\left.\begin{matrix}H_2O\\H_2S\end{matrix}\right\downarrow$ increases

$\left.\begin{matrix}H_2S\\H_2Te\end{matrix}\right\downarrow$ decreases.

So H_2S is most volatile in between these.

(2) Thermal Stability : $\left.\begin{matrix}H_2O\\H_2Te\end{matrix}\right\downarrow$ decreases.

(3) Acidic character : $\left.\begin{array}{l} H_2O \\ H_2Te \end{array}\right\downarrow$ increases

∴ Charge density decreases and increases size.

(4) Reducing Character :

(a) All hydraides except water are reducing agents

(b) $\left.\begin{array}{l} H_2S \\ H_2Te \end{array}\right\downarrow$ increases.

(c) Only on reaction with F, H_2O is reducing agent and releases O_2 because F is more E.N. than O.

(5) Bond Angle : ↓ Decreases

∴ Decreasing electronegativity of central atom.

4.2 Formation of Halides :

(a) YX_2 Y_2X_2 YX_4 YX_6

(b) Oxygen forms halides with F only

	OF_2	O_2F_2
O.S. of O	+2	+1

Shape and structure of O_2F_2 is same as H_2O_2.

(c) SCl_2 S_2Cl_2 SCl_4 SF_6.

S_2Cl_2 used in preparation of mustard gas.

(d) Same for Se

(e) Te_2Cl_2 and PO_2Cl_2 are not known. This is due to weaker Te – Te and Po - Po bonds

(f) Thermal stability of halides F > Cl > Br > I

(g) All elements form exahalide but only hexafluorides because size of fluorine is small.

4.3 Formation of Oxides :

Only S, Se and Te form two types of oxides

(a)	YO_2	and	YO_3
O.S.	+4		+6
(b)	Eg. $O.O_2 \cong O3$		X
	SO_2		SO_3
	SeO_2		SeO_3
Amphoteric	TeO_2		TeO_3

C.Q. Most acidic oxide among oxides of VIth group.

Ans. SO_3.

4.4 Formation of Oxyacids :

S, Se and Te form two types of oxyacids - our and –ic acids.

Sulphur	H_2SO_3	H_2SO_4
Selenium	H_2SeO_3	H_2SeO_4
Tellurium	H_2TeO_3	H_2TeO_4

- ic acids are stronger acids than - ous acids. Among - ous acids of different elements acidic strength is

$H_2SO_3 > H_2SeO_3 > H_2TeO_3$.

5. FAMILY MEMBERS OF VITH GROUP

5.1 Oxygen : (O)

(i) Oxygen Molecule (O_2) :

(1) In air as O_2 to the entent of 21% by volume or 23% by weight.

(2) Lab method to produce O_2 is.

$$2NaO_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

(3) Air is liquefied by use of joule - thomson effect {cooling by expansion of gas}.

(4) Reaction with compounds :

(a) Contact Process :

$$2SO_2 + O_2 \xrightarrow{\text{Pt. asbestos}} 2SO_3$$

(b) Ostwald Process :

$$4NH_3 + 5O_2 \xrightarrow{\text{Pt. Gauze}} 4NO + 6H_2O$$

(c) Deacon's Process :

$$4HCl + O_2 \xrightarrow[\text{Chloride}]{\text{Cupric}} 2Cl_2 + 2H_2O.$$

(5) Uses :

(a) Oxy-Acetylene flame is used for cutting process and welding process.

(b) Liquid oxygen is a constituents of fuels used in rockets.

5.1.1 Oxides :

A binary compound of oxygen with another element is called an oxide.

(a) Oxygen combined nearly with all other elements except inert gases, noble metals and halogens.

(b) The binary compounds of oxygen with other element are called oxides. Hence, the compounds of oxygen and fluorine (OF_2, O_2, F_2) are not called as oxides.

Classification of oxides

(1) **Acidic oxides** → $H_2O + CO_2 \rightarrow H_2CO_3$.

e.g. CO_2, B_2O_3, SiO_2, N_2O_3, NO_2, N_2O_5, P_4O_6

Note: Mixed anhydrides → Those oxides which form two oxy acids.

e.g. $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

$P_4O_8 + 6H_2O \rightarrow 2H_3PO_3 + 2H_3PO_4$

$SiO_2 + 2NaOH \rightarrow \underset{\text{salt}}{Na_2SiO_3} + \underset{\text{water.}}{H_2O}$

(2) **Basic oxides :**

Oxide + $H_2O \rightarrow$ alkali ; e.g. $Na_2O + H_2O \rightarrow 2NaOH$

Oxide + acid $\rightarrow$ salt + H_2O ;

e.g. $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$

Oxide + Acidic oxide $\rightarrow$ salt ;

e.g. $PbO + SO_3 \rightarrow PbSO_4$.

(3) **Neutral Oxide** -

Oxide + Acid $\rightarrow$ No reaction

Oxide + Base $\rightarrow$ No reaction

e.g. CO, H_2O, N_2O, NO etc.

(4) **Amphoteric oxides** $\rightarrow$ React with acid & base both to form salts.

e.g. ZnO, Al_2O_3, BeO, Sb_2O_3, Cr_2O_3, PbO, PbO_2 etc.

$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$;

$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$

$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$;

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$;

$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$

$Cr_2O_3 + 2NaOH \rightarrow Na_2Cr_2O_7 + H_2O$;

$Cr_2O_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2O$

(5) **Compound or mixed oxides** $\rightarrow$ Oxides which behaves as mixture of two simple oxides.

e.g. Pb_3O_4 ($2PbO + PbO_2$)

Fe_3O_4 ($FeO + Fe_2O_3$)

Mn_3O_4 ($2MnO + MnO_2$)

(6) **Peroxides** $\rightarrow$ Oxides + dil acids $\rightarrow H_2O_2$

e.g. $Na_2O_2 + H_2SO_4(dil) \rightarrow Na_2SO_4 + H_2O_2$

$BaO_2 + H_2SO_4.(dil) \rightarrow BaSO_4 + H_2O_2$

(7) **Dioxides** $\rightarrow$ Like peroxides, these also contain excess of oxygen but do not form H_2O_2 with dilute acids. They evolve chlorine with conc. HCl and oxygen with conc. H_2SO_4.

e.g. $\rightarrow$ PbO_2, MnO_2

$MnO_2 + 4HCl$ conc. $\rightarrow MnCl_2 + Cl_2 + 2H_2O$

$2MnO_2 + 2H_2SO_4(conc.) \rightarrow 2MnSO_4 + O_2 + 2H_2O$

(8) **Suboxides** $\rightarrow$ The oxides which contain less oxygen than expected from the normal valency of the elements are termed sub-oxides.

e.g. Carbon suboxide - C_3O_2

Lead suboxide - Pb_3O

Nitrous oxides - N_2O

(9) **Superoxides** $\rightarrow$ These oxides contain O_2^- ion.

e.g. KO_2, RbO_2, CsO_2.

These react with water to give hydrogen peroxide and oxygen.

$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$

5.2 Sulphur (S) :

5.2.1 Allotropic forms of Sulphur :

(i) Rhombic octahedral or α-sulphur :

(ii) Monoclinic Prismatic or β-sulphur :

(a) These two sulphur are called as enantiatropic substances

α - sulphur $\rightleftharpoons$ β - sulphur.

(b) α and β sulphur are crystalline and rest being amorphous and exist as S_8 cyclic molecule.

(iii) Plastic or γ sulphur :

It is obtained by quenching of boiling sulphur in a thin stream to cold water.

(iv) Milk of sulphur :

It is obtained by boiling milk of lime with sulphur and decomposing the products with HCl.

$\Rightarrow$ $3Ca(OH)_3 + 12S \longrightarrow 2CaS_5 + CaS_2O_3 + 3H_2O$

$\Rightarrow$ $2CaS_5 + CaS_2O_3 + 6HCl \longrightarrow 3CaCl_2 + 3H_2O + 12S$

Milk of sulphur is soluble in CS_2 and is mainly used in medicine

(v) Colloidal or δ-sulphur :

It is prepared by passing H_2S through a solution of an oxidising agent

Eg. $HNO_3 + H_2S \longrightarrow 2NO_2 + 2H_2O + S$

$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$

5.2.2 Uses of Sulphur :

(a) In manufacture of H_2SO_4, CS_2 gun powder etc.

(b) Vulcanisation of rubber.

5.2.3 Compounds of sulphur :

5.2.3.1 Hydrogen sulphide (H_2S) :

(i) Also known as sulphuratted hydrogen.

(ii) Lab method : Kipps apparatus

$FeS + Conc.\ 2HCl \longrightarrow FeCl_2 + H_2S$

In this reaction conc. HNO_3 cannot be employed because HNO_3 is a oxidising agent and converts H_2S into colloidal sulphur.

(iii) $Sb_2S_2 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S$.

Antimony sulphide

Here H_2S is rotten egg smelling gas. If conc. HNO_3 or H_2SO_4 is added the rotten smell of H_2S disappears.

(iv) Properties :

(1) $H_2S + Pb(CH_3COO)_2 \longrightarrow PbS\ (Black) + 2CH_3COOH$

This would be confirmatory test for H_2S.

(2) It bums in air with a blue flame.

$2H_2S + O_2 \longrightarrow 2H_2O + S$

If the air supply is in excess.

$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_3$

(3) It reduces moist chlorine to HCl

$H_2S + Cl_2 \text{ (moist)} \longrightarrow 2HCl + S$

(4) It is a mild acid

$H_2S \rightleftharpoons S^{-2} + 2H^+$

$H_2S \rightleftharpoons SH^- + H^+$

(5) Ferric salts reduced to ferrous salts

$H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + S$

(6) Acidified $KMnO_4$ gets decoloured by H_2S.

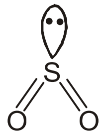
$$2KMnO_4 + 5H_2S + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

(7) Acidified $K_2Cr_2O_7$ becomes green in colour.

$$3H_2S + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{green colour}}{Cr_2(SO_4)_3} + 8H_2O + 3S$$

5.2.3.2 SO_2 Sulphur di-oxide :

(i)



S^{+4} :

↑↓	↑	↑	↑	↑

- * π bond for nuclei $d\pi$ - $p\pi$ bond.
- * v - shape or trigonal planar.

(ii) Bleaching Property : SO_2 acts as a bleaching agent in following two ways.

(1) In the presence of H_2O, it is oxidised with the liberation of nascent hydrogen which reduces the colouring matter to colourless.

$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$

Colouring matter + 2[H] $\rightleftharpoons$ Colourless compound.

(2) $\underset{\text{Coloured}}{X - OH} + SO_2 \longrightarrow \underset{\text{Colourless}}{X - HSO_3}$

(iii) Preparations :

(1) **Lab Method :** By heating copper turnings with conc. H_2SO_4.

$$Cu + 2H_2SO_4 \text{ (conc.)} \xrightarrow{\Delta} CuSO_4 + SO_2 + 2H_2O$$

(2) By roasting ZnS or iron pyrities.

$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

$4FeS_2 + HO_2 \longrightarrow 2FeO_3 + 8SO_2$.

(3) Reaction of anhydride with coke :

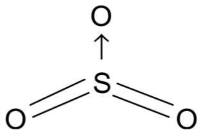
$2CaSO_4 + C \longrightarrow 2CaO + CO_2 + 2SO_3$.

(iv) Physical Properties :

(1) It is pungent smelling suffocating gas.

(2) It is soluble in H_2O.

5.2.3.3 Sulphur trioxide (SO_3) :



triagonal planar molecule.

(1) Preparation :

1. Action of heat on Ferric sulphate

$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3$

2. Commercial Method :

By the oxidation of dry SO_2 with dry oxygen.

$2SO_2 + O_2 \xrightleftharpoons{Pt} 2SO_3$.

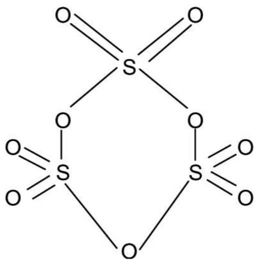
SO_2 and O_2 are first dried by passing through conc. H_2SO_4 and then passed over heated (400°C) platinsed asbestos contained in a hard glass tube.

(2) Physical Properties :

It exists in atleast three forms α-sulphur, β - sulphur and γ - sulphur

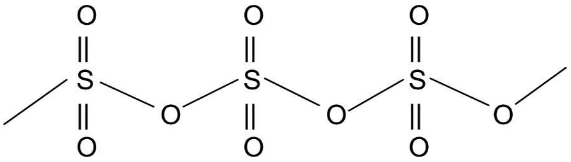
Thes structure of solid SO_3 is complex. It possesses cyclic trimer (α form) structure.

(a) α form



(b) β and γ forms :

It possesses an infinite helical chain made up of linked SO_4 tetrahedron.



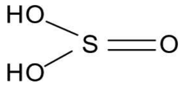
(3) Chemical Reactions :

1. It dissolves in conc. H_2SO_4 to form pyrosulphuric acid (oleum)
   $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$.
2. $SO_3 + 2HBr \longrightarrow H_2O + Br_2 + SO_2$. In this SO_3 is used as an oxidising agent.

5.2.3.4 Oxy Acids of Sulphur :

(a) Sulphurous Acid (H_2SO_3) :

(i) Structure :



(b) Sulphuric Acid (H_2SO_4) or oil of vitrol :

(i) Preparation : Mainly two process used

(A) Lead Chamber Process :

$S + O_2 \longrightarrow SO_2$

$FeS_2 + \frac{1}{2}O_2 \longrightarrow Fe_2O_3 + 4SO_2$

$SO_2 + NO_2 \longrightarrow SO_3 + NO$

$SO_3 + H_2O \longrightarrow H_2SO_4$.

Note :

1. NO (Nitric Oxide) produced takes oxygen from air and gets converted back to nitrogen dioxide. Thus oxide of nitrogen take oxygen from air and pass it to SO_2 and thus act as oxygen carrers.
   $2NO + O_2 \longrightarrow 2NO_2$
2. It is seen that in the presence of an insufficient quantity of steam or water spray, lead chamber crystals of the composition $SHSO_4$. No are obtained.

(B) Contact Process :

$S + O_2 \longrightarrow SO_2$

$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$

$2SO_2 + O_2 \longrightarrow 2SO_3$ + Energy

Initially Pt. was employed as catalyst but how V_2O_5 is used because Pt is poisonous.

SO_3 + conc. $H_2SO_4 \longrightarrow H_2S_2O_7$ Oleum

$\xrightarrow{H_2O} 2H_2SO_4$

(1) To get the appropriate amount of H_2SO_4 contact process is utilised.

(2) If bottle of H_2SO_4 is opened, it absorbs unlimited amount of moisture and H_2SO_4 overflows to conc. H_2SO_4 is deliquescent liquid which is highly viscous and has high density.

(3) When H_2SO_4 is done dilute by adding water the reaction being highly exothermic so temp increases to 120°C and thus along with water vapour the energy released when conc is contact with skin, causing burning.

(4) Conc. H_2SO_4 + Glucose $\longrightarrow 6C + 6H_2O$

The white sugar changes to black and this is called charring of sugar (Blackening of sugar). this is the conformation test of H_2SO_4 .

5.2.3.5 Chemical Reaction of H_2SO_4 :]

(1) It has greater affinity for water. Hence is used for drying of all gases except ammonia. It is also employed as dehydrating agent.

(a) $C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$

This called as charing of sugars.

(b) $\begin{array}{c}\text{COOH}\\|\\\text{COOH}\end{array} \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2 + H_2O$

(c) Chloro benzene + Chloral $\xrightarrow{\text{conc. } H_2SO_4}$ DDT.

2 : 1

(2) Action with potassium ferrocyanide:

$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

5.2.3.6 Uses :

(a) It is regarded as king of chemical.

(b) In manufacture of explosives (T.N.T, gun cotton) etc.

(c) As a pickling agent : Pickly is an industrial process for removing layers of basic oxides from metals like Fe and Cu. before electroplating, galvanizing and soldering.

5.2.3.7 Hypo, or Sodium Thiosulphate ($Na_2S_2O_3 . 5H_2O$) :

(i) It is used in photography for removing unaffected silver bromide (halides). during fixing of negatives.

$2Na_2S_2O_3 + AgCl \longrightarrow Na_3[Ag(S_2O_3)_2] + NaCl$.

(ii) It is used an antichlor (To remove excess Cl_2 from bleached fabrics).

$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + S + 2HCl$