GROUP-16 ELEMENTS
OR
OXYGEN FAMILY

Introduction :-

→ The Group-16 consists of 5 numbers of elements i.e. oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te) and polonium (Po)

→ These are called as Chalcogens as these are Ore forming elements.

→ Oxygen and Sulphur are non-metals, selenium and tellurium are metalloid and Polonium is a radioactive metal.

Electronic Configuration :-

Group-16 elements contain 6 electrons in their outermost shell. Therefore the general electronic configuration is $ns^2 np^4$

Elements	Atomic Number	Electronic Configuration
O	8	$1s^2 2s^2 2p^4$ or [He] $2s^2 2p^4$
S	16	[Ne] $3s^2 3p^4$
Se	34	[Ar] $3d^{10} 4s^2 4p^4$
Te	52	[Kr] $4d^{10} 5s^2 5p^4$
Po	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$

General trends in the physical properties of oxygen family :-

1. **Atomic Radii :-**

→ If we move down the group from Oxygen to polonium, the atomic radii gradually increases due to the addition of new shell or orbit.

→ The atomic radii of group-16 elements are smaller than the corresponding group-15 elements, due to the greater nuclear charge of group-16 elements.

2. Density :)

If we move down the group from 'O' to 'Po', density gradually increases due to increase in atomic mass.

3. Ionisation Energy :)

→ Group-16 elements have high ionisation energy due to greater nuclear charge and small size.

→ If we move down the group, the ionisation energy gradually decreases due to increases in atomic size.

4. Electronegativity :)

→ It is defined as the ability to attract shared pair of e⁻s towards itself.

→ If we move down the group, the electronegativity value decreases due to increase in atomic size.

→ Oxygen is the most electronegative element in this group.

5. Electron affinity :)

→ It is the amount of energy released when an electron is added to neutral gaseous atom.

→ The elements of group-16 being very close to noble gas have greater tendency to accept e^-. Hence have high electron affinity value.

→ Electron affinity value decreases down the group.

$$S > Se > Te > O$$

→ Electron affinity of oxygen is less than that of Sulphur due to smaller size of oxygen and more $e^- - e^-$ repulsion.

6. Melting Point & Boiling point :)

If we move down the group melting point & boiling point increases due to the increase in atomic mass of element.

7. Oxidation State

These elements have six electrons in their valence shell. Oxygen has no vacant d-orbital but others have vacant d-orbital. So, they show variable oxidation state.

Elements	Oxidation state
Oxygen	$-2, -1, 0, +1, +2$
Sulphur	$-2, +2, +4, +6$
Selenium	$+2, +4, +6$
Tellurium	$+2, +4, +6$
polonium	$+2, +6$

Oxygen shows +1 & +2 oxidation state only its compound with fluorine. For example ÷ oxidation state of oxygen in O_2F_2 is +1 and OF_2 is +2.

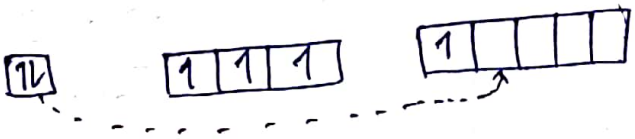
Oxygen atom (Ground state) — $1s^2$ $2s^2$ $2p^4$

Oxygen is divalent since it has two half filled 2p-orbitals. Since its valence shell has no vacant d-orbital, it is impossible to excite an electron into higher energy d-orbital. Therefore, oxygen shows divalency.

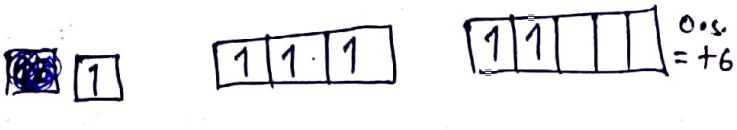
Sulphur atom. [Ne] 3s 3p 3d

(Ground state)

Sulphur atom (1st excited state)



Sulphur atom (2nd Excited state)



Similarly other members of oxygen family show oxidation state +2, +4, +6.

8. Allotropy :-

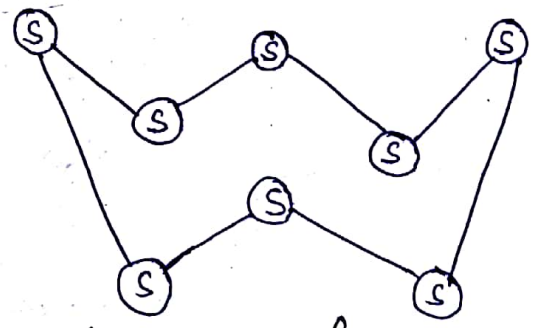
Elements	Allotropes
Oxygen	oxygen, ozone
Sulphur	Rhombic, Monoclinic, plastic
Selenium	Red, grey
Tellurium	Metallic, Non-metallic
Polonium	α, β

9. State :- (OR) Q. Explain why O_2 is a ~~diamagnetic~~ diatomic gas where as S, Se, Te are octaatomic solid ?

O_2 is a diatomic gas. S, Se, and Te are octaatomic solid i.e. S_8, Se_8, Te_8.

Reason :- → 'O' is small in size due to which it can form both sigma and $p\pi - p\pi$ bonds with one another. So, O_2 is formed as a stable diatomic molecule.

→ 'S' being large in size can not form $p\pi - p\pi$ bond. It only form σ bonds, and eight 'S' atoms are linked by σ bonds forming a puckered ring structure. Due to closeness of 'S' atoms it forms a solid.



(Structure of S_8 molecule)

10. Catenation :-

The property of self-linkage among identical atoms is called as Catenation.

Sulphur has strong tendency to catenation.

The order of catenation is S-S > O-O > Se-Se > Te-Te.

The bond energy of S-S & O-O are 213 KJ mole^{-1} & 138 KJ mole^{-1} respectively.

Chemical properties :-

1. Hydride Formation :-

All the elements of oxygen family forms hydrides such as H_2O, H_2S, H_2Se, H_2Te, H_2Po.

(i) **Thermal Stability :-**

If we move down the group, the thermal stability of hydrides decreases due to size of central atom increases.

order $\boxed{H_2O > H_2S > H_2Se > H_2Te > H_2Po}$

Stability of hydrides is inversly properetional to the bond length.

(ii) **Acidity :-**

If we move down the group, the acidic strength of hydrides increases due to size of central atom increases.

order $\boxed{H_2O < H_2S < H_2Se < H_2Te < H_2Po}$

(iii) **Van-der waals forces of Attraction :-**

If we move down the group, the van-der waall's force of attraction of hydrides increases due to increase in surface area with increase in molecular size.

order $\boxed{H_2O < H_2S < H_2Se < H_2Te < H_2Po}$

$\boxed{\text{Vander waals force} \propto \text{molar mass}}$

(iv). **Hydrogen Bonding :-**

→ Hydrogen bonding depends on Electronegativity.

→ Oxygen atom is small atom with high electronegativity. Thus, it forms strong H-bonding in water.

→ If we move down the group electronegativity decreases. Sothat no hydrogen bonding takes place in case of H_2S, H_2Se, H_2Te, H_2Po.

(V) **Boiling point & Melting point :-**

The order of M.P. & B.P. of hydrides :-

$\boxed{H_2O > H_2Te > H_2Se > H_2S}$

If we move down the group from H_2S to H_2Te the B.P. & M.P increases due to increase in Vanderwaals forces of attraction.

The B.P. & M.P. of H_2O is high due to H-bonding.

(vi) The reducing nature increases down the group.

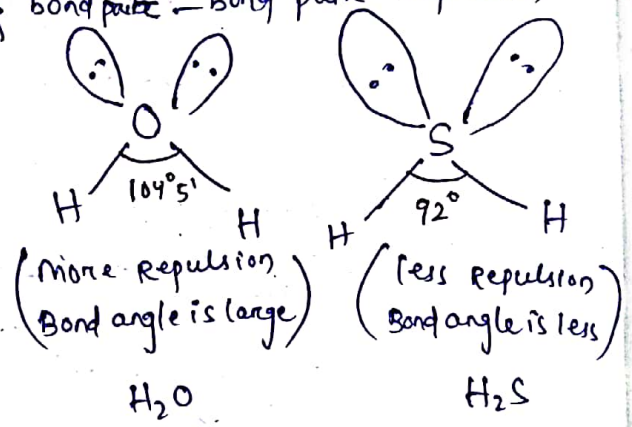
$$H_2O < H_2S < H_2Se < H_2Te$$

(vii). Bond angle :-)

If we move down the group, the bond angle of hydrides gradually decreases. order

$$H_2O > H_2S > H_2Se > H_2Te$$

Down the group, the electronegativity of central atom decreases. As a result lone pair - lone pair & bond pair - bond pair repulsion decreases.



2. Oxide Formation :-)

All the elements of group-16 forms the following binary oxides.

Elements	Monoxide	Dioxide	Trioxide	Heptoxide
Sulphur	SO	SO_2	SO_3	S_2O_7
Selenium	—	SeO_2	SeO_3	—
Tellurium	TeO	TeO_2	TeO_3	—
polonium	PoO	PoO_2	—	—

→ As we move down the group, the acidic nature of oxides of group-16 elements decreases

$$SO_2 > SeO_2 > TeO_2$$

→ As we move down the group, the stability of oxides of group-16 elements decreases.

→ The dioxide & trioxide are soluble in water to form oxoacids.

Dioxide:
- $SO_2 + H_2O \longrightarrow H_2SO_3$ (Sulphurous Acid)
- $SeO_2 + H_2O \longrightarrow H_2SeO_3$ (Selenous Acid)

Trioxide:
- $SO_3 + H_2O \longrightarrow H_2SO_4$ (Sulphuric acid)
- $SeO_3 + H_2O \longrightarrow H_2SeO_4$ (Selenic acid)

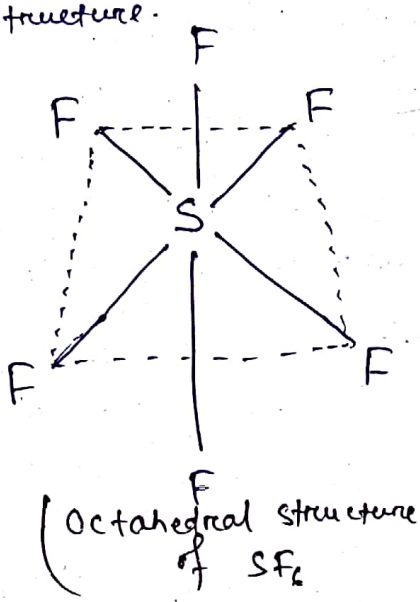
3. Halide Formation :-

→ The elements of group-16 combines with halogen to form halides.

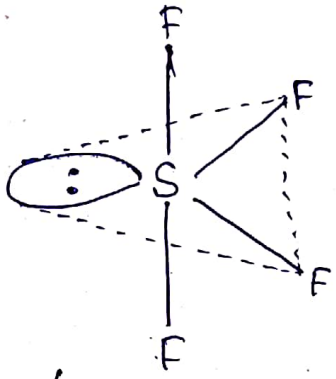
→ The elements of group-16 in their halides show +2, +4, +6 oxidation state.

→ S, Se, Te form hexafluorides such as SF_6, SeF_6, TeF_6. Hexafluorides are sp^3d^2 hybridised and octahedral in shape.

→ Tetrafluorides (SF_4, SeF_4, TeF_4) are sp^3d hybridised and has See-Saw structure.



(Octahedral structure of SF_6)



(Trigonal bipyramidal structure of SF_4)

→ Except Selenium, all other elements form dihalide. Dihalides are sp^3 hybridised and has bent structure.

4. Oxoacid Formation

→ 'S' has a number of oxoacids i.e. H_2SO_3 (Sulphurous Acid)
$H_2S_2O_2$ (Thiosulphurous Acid)
$H_2S_2O_4$ (Hypo sulphurous Acid)
$H_2S_2O_5$ (Pyrosulphurous Acid)
H_2SO_4 (Sulphuric Acid)
H_2SO_5 (Caro's Acid)
$H_2S_2O_8$ (Marshall's Acid)

→ 'Se' has two oxoacids such as H_2SeO_3, H_2SeO_4.

→ 'Te' has two oxoacids such as H_2TeO_3, H_2TeO_4.

→ The acidic strength of oxoacids decreases down the group.

$$H_2SO_4 > H_2SeO_4 > H_2TeO_4$$

Anomalous Behaviour of Oxygen :-

Oxygen is differ from other elements of group-16 due to its

i. Small size
ii. High Ionisation Energy.
iii. High Electronegativity.
iv. Non-availability of d-orbitals.
v. Oxygen is a gas whereas other elements are exists as Solids.
vi. Molecular oxygen is diatomic whereas other members exists as S_8, Se_8, with puckered ring structure.
vii. Molecular oxygen is paramagnetic whereas ~~other~~ molecules of other elements are diamagnetic.

DIOXYGEN

→ Oxygen is the most essential constituent of air. It constitutes about 21% by volume and 23% by mass of the atmosphere.
→ Oxygen is present in all minerals, vegetables and animals.
→ Oxygen is present in the atmosphere ~~is~~ and to be formed by the process of photosynthesis.

Methods of preparation :-

1. By Heating oxides of Less reactive metals :-

Oxygen is liberated when oxides of less reactive metals are heated.

$$2HgO \xrightarrow{\Delta} 2Hg + O_2\uparrow$$

$$2PbO_2 \xrightarrow{\Delta} 2PbO + O_2\uparrow$$

$$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2\uparrow$$

2. Electrolysis of Water :-

Electrolysis of water leads to release of hydrogen gas at cathode and dioxygen at anode.

$$2H_2O_{(l)} \xrightarrow{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$$

9. Laboratory Method :)

From chlorates, nitrates, permanganates of potassium :)
Oxygen gas is liberated by heating oxygen containing salts.

$$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2\uparrow$$

(potassium chlorate)

$$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2\uparrow$$

(potassium nitrate)

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2\uparrow$$

(potassium permanganate) (potassium manganate)

Physical properties :)

1. Dioxygen is a colourless, odourless and tasteless gas.
2. It is slightly soluble in water.
3. It is heavier than air.
4. It is pale blue in liquid & solid state.

Chemical properties :)

1. Reaction with Metals :)

Dioxygen combines with most of the metals except noble metals (gold, platinum) to form metal oxides.

$$4Na_{(s)} + O_{2(g)} \xrightarrow[Temp.]{Room} 2Na_2O_{(s)}$$

$$2Na + O_2 \xrightarrow{575K} Na_2O_2$$

(sodium peroxide)

$$2Mg + O_2 \longrightarrow 2MgO$$

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$

2. Reaction with Non-metals :-
Dioxygen combines with non-metals to form their respective oxides.

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$$

$$S_{(s)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)}$$

$$P_{4\,(s)} + 5O_{2\,(g)} \longrightarrow 2P_2O_{5\,(g)}$$

$$N_{2\,(g)} + O_{2\,(g)} \xrightarrow{3273K} 2NO_{(g)}$$

3. Reaction with Compounds :-
It oxidises a number of compounds under suitable condition to form useful products.

$$SO_{2\,(g)} + O_{2\,(g)} \xrightarrow[700K]{Pt/V_2O_5} SO_{3\,(g)}$$] → Contact process

$$4HCl_{(g)} + O_{2\,(g)} \xrightarrow[700K]{CuCl_2} 2H_2O_{(g)} + 2Cl_{2\,(g)}$$

Uses.

1. Dioxygen is an essential component for the process of respiration, and combustion.
2. Oxygen cylinders are used in hospitals, mountaineering.
3. Liquid oxygen is used as rocket fuel and in the launching of satellite.
4. Liquid oxygen sometimes used as explosive along with coal.
5. It is used as an oxidising agent & bleaching agent.

Classification of Oxides

Oxygen forms a variety of oxides when it combines with other elements. These are classified as follows :-

1. **Acidic Oxides :-**

These are the oxides which dissolved in water to form acid. Thus such oxides are called as acid anhydride.

Examples :- SO_3, P_2O_5, CO_2, CrO_5, Mn_2O_7 etc.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

2. **Basic Oxides :-**

These are the oxides which dissolved in water to form alkali.

Examples :- Na_2O, CaO, MgO. etc.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

3. **Amphoteric oxides :-**

→ It behaves both as an acid and base.

Ex :- ZnO, SnO, Al_2O_3.

→ Such oxides react with acid as well as base to form salt.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

(Sodium zincate)

4. **Neutral oxides :-**

These are the oxides which neither give acid nor base with water.

Example :- CO, N_2O, NO

Trends in periodic table :-

As we move from left to right in a period the nature of oxides changes.

Na_2O MgO Al_2O_3 SiO_2 P_2O_5 SO_3 Cl_2O_7

(Strongly basic) (Strongly Acidic)

As we move down the group the acidic character gradually decreases and basic character increases.

Ex Group-13 B_2O_3 (Strongly Acidic)

Al_2O_3

Ga_2O_3

In_2O_3

Tl_2O_3 (Strongly Basic)

L.Q. 9MP

OZONE

Molecular Formula = O_3 Molecular Mass = 48

Occurence :-

Ozone is mostly present in the upper layer of the atmosphere. When fluorine reacts with water OR when oxygen is exposed to ultra-violet light, we get ozone.

$$3H_2O + 3F_2 \longrightarrow 6HF + O_3$$

$$3O_2 \xrightarrow{\text{UV-Light}} 2O_3$$

Preparation of Ozone :-

When oxygen is subjected to silent electric discharge, we get ozone.

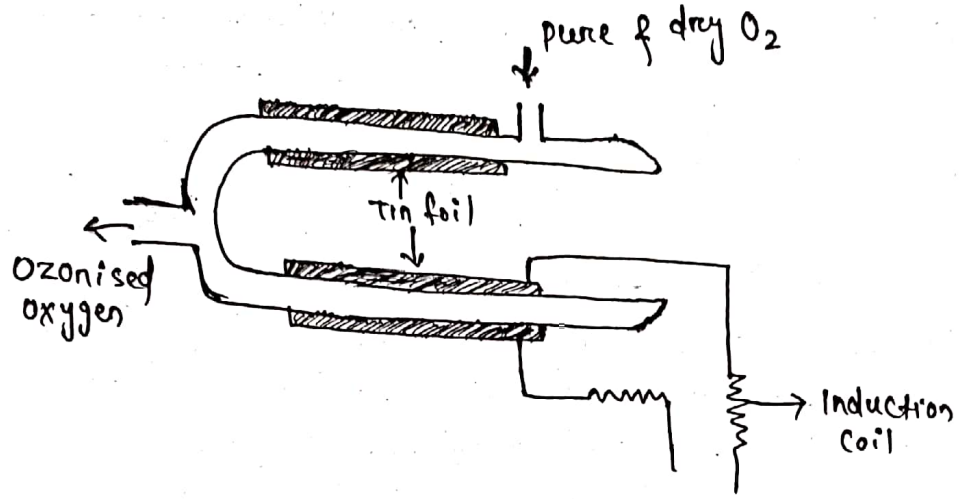
$$3O_2 \xrightarrow[\text{discharge}]{\text{Electric}} 2O_3$$

The apparatus used to prepare ozone by the passage of silent electric discharge is called as Ozoniser.

There are two types of ozoniser-

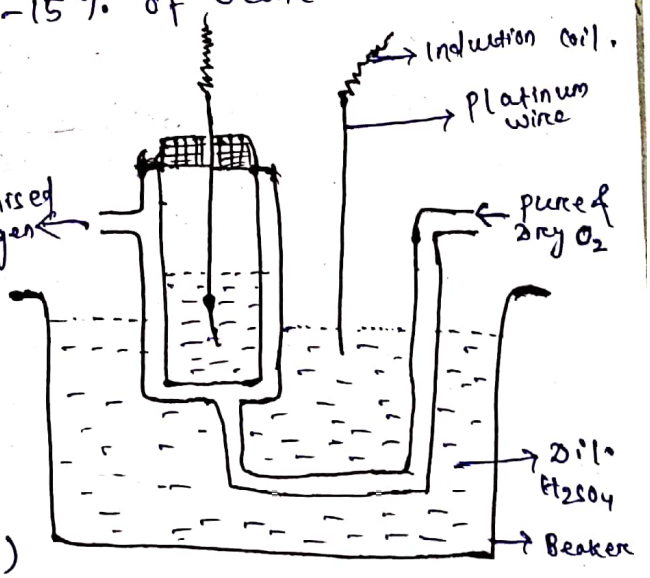
1. Siemen's Ozoniser
2. Brodie's Ozoniser

1. Siemen's Ozoniser :-



(i) It consists of two co-axial glass tubes, which fused together.
(ii) The inner side of the inner tube & outer side of the outer tube are cotted with tin foil.
(iii) The inner and outer sides of the tin foil are connected to induction coil which produces current of high voltage
(iv). A pure and dry O_2 is passed through the annular space of ozoniser as shown in the figure. Thus, on subjecting it to electric discharge, ozonised oxygen will be formed.
(v) Ozonised oxygen contains 10-15 % of ozone.

2. Brodie's Ozoniser :-



i. It is a U-shaped co-axial glass tube, which fused together.
ii. In place of tin foil, dil. H_2SO_4 is taken in it. The ozoniser also kept in beaker containing dilute H_2SO_4.
iii. Two platinum wires (electrodes) are dipped, one in beaker and other in co-axial glass tube.
iv. The Pt wires are connected with induction coil.
v. A pure & dry O_2 is passed through annular space. Then passing electric current Oxygen is converted into ozonised oxygen

Preparation of pure Ozone :-

pure ozone is obtained by cooling ozonised oxygen in liquid air. and subjecting the condensed blue liquid to fractional distillation. Finally pure ozone is formed.

Better yield for Ozone :-

Conditions ⇒ 1. pure & dry O_2 should be used.
2. Electric discharge should be sparkless.
3. Low temperature 0-5°C should be maintained.
4. The ozoniser should be dry & clean.

Physical properties :-

1. Ozone is a pale blue gas having pungent smell.
2. It is diamagnetic in nature.
3. It is slightly soluble in water.
4. It is heavier than air.

Chemical properties :-

A. Oxidising Nature :-

Ozone is a powerful oxidising agent, ~~It is~~ because it has tendency to give up nascent oxygen.
It is stronger than oxygen.

$$O_3 \longrightarrow O_2 + [O]$$
(Nascent oxygen)

1. Reaction with Mercury :-

Imp Ozone oxidises mercury to give mercurous oxide, which sticks on the glass surface and changes the shape of mercury. So, it is called as Tailing of Mercury.

$$O_3 \longrightarrow O_2 + [O]$$

$$2Hg + [O] \longrightarrow Hg_2O$$

$$O_3 + 2Hg \longrightarrow Hg_2O + O_2$$
(Mercurous oxide)

2. Reaction with PbS

It oxidises lead sulphide (black ppt.) to lead sulphate (white ppt.).

gmp

$$[\, O_3 \longrightarrow O_2 + [O] \,] \times 4$$

$$PbS + 4[O] \longrightarrow PbSO_4$$

$$4O_3 + PbS \longrightarrow PbSO_4 + 4O_2$$

(Black) (White)

3. Reaction with potassium Iodide (KI) :-

Ozone oxidises potassium iodide solution to give Iodine.

gmp

$$O_3 \longrightarrow O_2 + [O]$$

$$2KI + H_2O + [O] \longrightarrow 2KOH + I_2$$

$$O_3 + 2KI + H_2O \longrightarrow 2KOH + O_2 + I_2$$

4. Reaction with Halogen acids :-

Ozone oxidises halogen acids to give halogens.

$$O_3 \longrightarrow O_2 + [O]$$

$$2HCl + [O] \longrightarrow H_2O + Cl_2$$

$$O_3 + 2HCl \longrightarrow Cl_2 + H_2O + O_2$$

5. Reaction with Sulphur dioxide :-

Ozone oxidises sulphur dioxide to give sulphur trioxide.

$$O_3 \longrightarrow O_2 + [O]$$

$$SO_2 + [O] \longrightarrow SO_3$$

$$O_3 + SO_2 \longrightarrow SO_3 + O_2$$

6. Ozone oxidises H_2S to give sulphur.

$$O_3 + H_2S \longrightarrow S + H_2O + O_2$$

7. Reaction with moist Iodine :-

It oxidises moist iodine to give iodic acid.

$$[\, O_3 \longrightarrow O_2 + [O] \,] \times 5$$

$$I_2 + H_2O + 5[O] \longrightarrow 2HIO_3$$

$$5O_3 + I_2 + H_2O \longrightarrow 2HIO_3 + 5O_2$$

(Iodic acid)

8. Reaction with moist phosphorous :-

It oxidises moist phosphorous to give phosphoric acid.

$$[\, O_3 \longrightarrow O_2 + [O] \,] \times 10$$

$$P_4 + 6H_2O + 10[O] \longrightarrow 4H_3PO_4$$

$$10O_3 + P_4 + 6H_2O \longrightarrow 4H_3PO_4 + 10O_2$$

(phosphoric acid)

9. Reaction with stannous chloride :- *

gmp Ozone oxidises acidified stannous chloride to give stannic chloride. In this reaction no oxygen gas is liberated.

$$O_3 \longrightarrow O_2 + [O]$$

$$[\, SnCl_2 + 2HCl + [O] \longrightarrow SnCl_4 + H_2O \,] \times 3$$

$$O_3 + 3SnCl_2 + 6HCl \longrightarrow 3SnCl_4 + 3H_2O$$

(stannic chloride)

10. Reaction with potassium Ferrocyanide :-

gmp Ozone oxidises potassium ferrocyanide to potassium ferricyanide.

$$O_3 \longrightarrow O_2 + [O]$$

$$2K_4[Fe(CN)_6] + H_2O + [O] \longrightarrow 2K_3[Fe(CN)_6] + 2KOH$$

$$O_3 + 2K_4[Fe(CN)_6] + H_2O \longrightarrow 2K_3[Fe(CN)_6] + 2KOH + O_2$$

11. Reaction with ferrous Sulphate :-

Ozone oxidises acidified ferrous sulphate to give ferric sulphate.

ymp

$$O_3 \longrightarrow O_2 + [O]$$

$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$O_3 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O + O_2$$

(Ferric sulphate)

12. Ozone oxidises nitrite to nitrate, sulphite to sulphate, arsenite to arsenate, manganate to permanganate.

$$NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2$$

(Sodium Nitrite) (Sodium nitrate)

$$Na_2SO_3 + O_3 \longrightarrow Na_2SO_4 + O_2$$

(Sodium sulphite) (Sodium sulphate)

$$Na_3AsO_3 + O_3 \longrightarrow Na_3AsO_4 + O_2$$

(Sodium arsenite) (Sodium arsenate)

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

(Potassium Manganate) (Potassium permanganate)

B. Reducing Nature

Ozone also acts as a reducing agent. It reduces hydrogen peroxide to give water.

$$H_2O_2 \longrightarrow H_2O + [O]$$

$$O_3 + [O] \longrightarrow 2O_2$$

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

Ozone reduces Barium peroxide to Barium oxide.

$$BaO_2 \longrightarrow BaO + [O]$$

$$O_3 + [O] \longrightarrow 2O_2$$

$$BaO_2 + O_3 \longrightarrow BaO + 2O_2$$

3. Bleaching agent :-

→ Ozone acts as a bleaching agent. It bleaches colouring matter into colourless matter in presence of nascent oxygen.

→ The bleaching property is due to its oxidising nature and it is permanent.

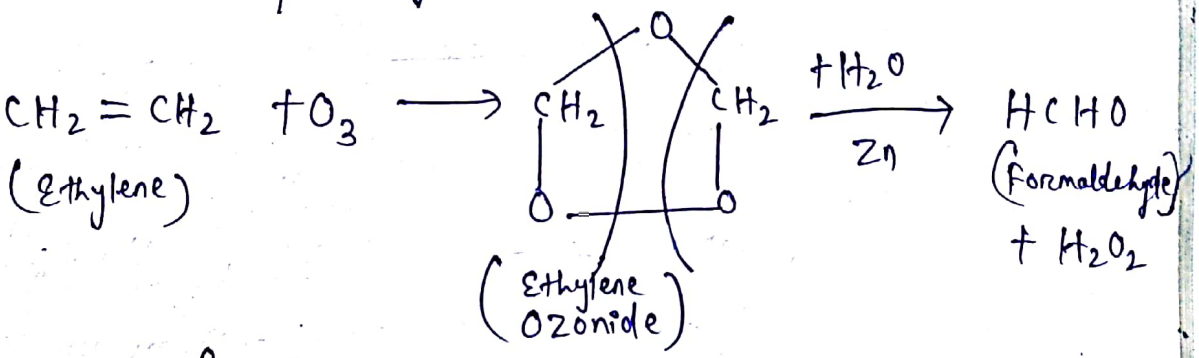
$$O_3 \longrightarrow O_2 + [O]$$

Colouring matter + $[O] \longrightarrow$ Colourless matter.

Ozonolysis :- (or) Formation of ozonides

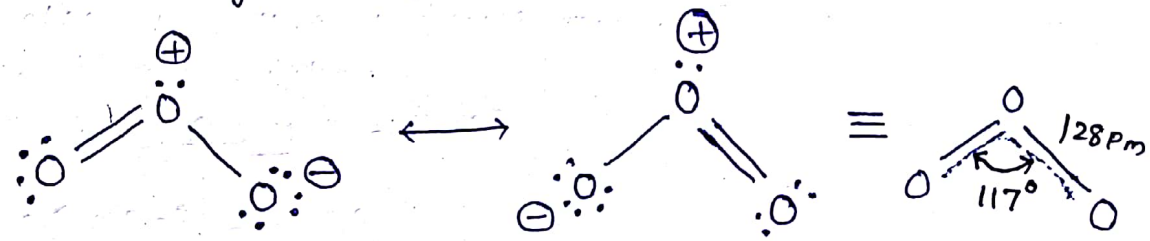
→ Ozone reacts with unsaturated compounds containing double bonds such as ethylene to form addition products called ozonides.

The ozonides are decomposed by water in presence of Zinc to form H_2O_2 & aldehyde or ketone.



Structure of Ozone :-

Ozone has angular structure. The O–O–O bond angle is 117° and the bond length is 128 pm.



Uses :-

1. It is used as germicide.
2. It is used for the manufacture of artificial silk.
3. It bleaches vegetative matter, oils, ivory, silk.
4. It is used for improving the atmosphere of crowded place like mines, cinema halls, restaurants.
5. It is used as an oxidising agent.

SULPHUR DIOXIDE

Molecular formula = SO_2 Molecular Mass = 64

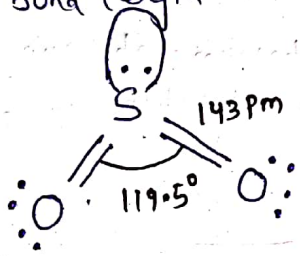
Occurrence :-

→ SO_2 gas is more stable and is found in the gases coming out of Volcanic erruptions.

→ Air around big factories where coal is burnt is found to be contaminated with sulphur dioxide. Since coal contains a large number of sulphur compound.

Structure :-

SO_2 has bent or angular structure, having bond angle 119.5° and bond length 143 pm.



Methods of preparation

1. **By burning of Sulphur in Air :-**

When sulphur is burnt in air or oxygen, Sulphur dioxide is formed.

$$S + O_2 \longrightarrow SO_2$$

2. **By roasting of metal sulphide**

When iron pyrite is roasted in air or oxygen, Sulphur dioxide is formed.

$$4FeS_2 + 11O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 8SO_2$$

(Iron pyrites)

3. **From sulphuric acid :-**

When Carbon or sulphur is heated with Conc. H_2SO_4, sulphur dioxide is formed.

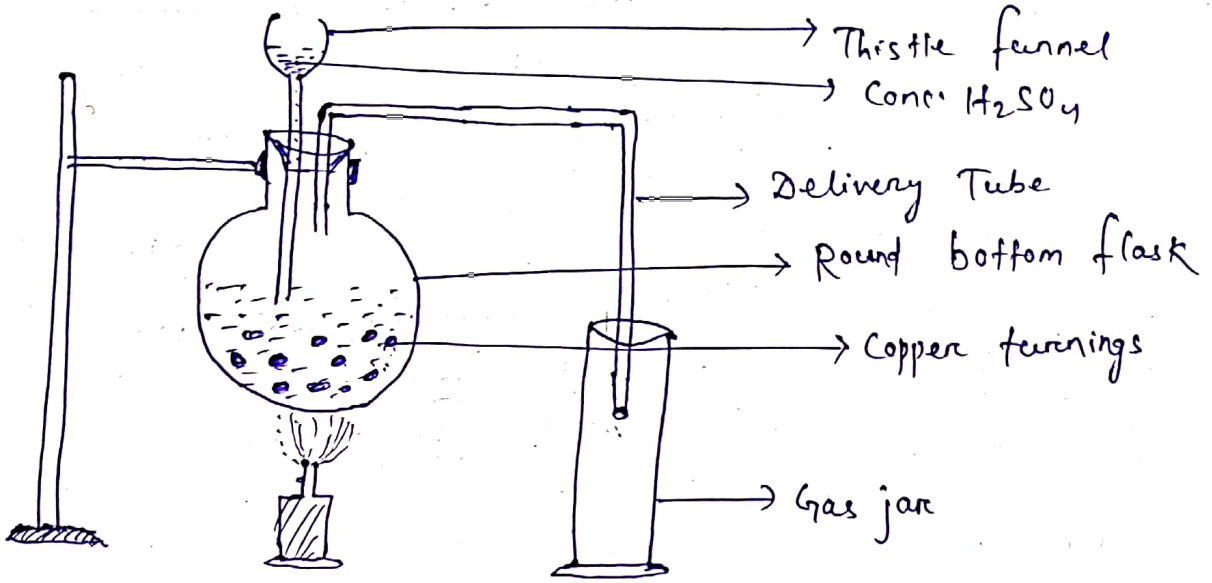
$$C + 2H_2SO_4 \longrightarrow 2H_2O + CO_2 + 2SO_2$$

$$S + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$$

4. Laboratory Methods of Preparation :-

gmp principle :- Sulphur dioxide is prepared in the laboratory by heating conc. H_2SO_4 with copper turnings / chips.

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



(Laboratory preparation of SO_2)

Experiment

→ Copper turnings are taken in a round bottom flask, which is fitted with thistle funnel and a delivery tube by an air tight cork.

→ Concentrated H_2SO_4 is added to the flask through the thistle funnel and heated.

→ SO_2 gas is collected in the gasjar by the upward displacement of air.

Drying of gas

The prepared SO_2 gas may contain H_2O. So, it is dried by passing through Conc. H_2SO_4.

Quick lime (CaO) can not be used as drying agent for SO_2.

$$CaO + SO_2 \longrightarrow CaSO_3$$
(Basic) (Acidic) (Salt)

Physical properties :-

i. It is a colourless gas with suffocating and pungent smell.
ii. It is highly soluble in water
iii. It is heavier than air.
iv. Its boiling point is $-10^{\circ}C$.
v. It is an acidic oxide.
vi. It is a reducing gas.

Chemical properties :-

1. **Thermal stability :-**
SO_2 is thermally very stable.
It dissociates into sulphur trioxide and sulphur by strong heating or electric spark.

$$3SO_2 \xrightarrow[\text{(or) Electric spark}]{\text{Strong Heating}} 2SO_3 + S$$

2. **Combustibility :-**
SO_2 is neither combustible nor a supporter of combustion.

3. **Acidic Nature :-**
(a) **Litmus paper Test :-** SO_2 is a lewis acid which turns blue litmus paper to red due to the formation of H_2SO_3.

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

(b) **Reaction with lime water :-**
When SO_2 gas is passed through lime water, a milky white ppt of $CaSO_3$ is formed.

$$Ca(OH)_2 + SO_2 \longrightarrow \underset{\text{(calcium sulphite)}}{CaSO_3} \downarrow + H_2O$$
(Lime water) (milky color)

By passing excess SO_2 gas milkiness disappear due to the formation of soluble calcium bisulphite.

$$CaSO_3 + H_2O + SO_2 \longrightarrow \underset{\text{(calcium Bisulphite)}}{Ca(HSO_3)_2}$$
(soluble)

(c) Reaction with Basic oxide :-

SO_2 reacts with basic oxides and alkali to form salts.

$$CaO + SO_2 \rightarrow CaSO_3$$
(Calcium sulphite)

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$
(Sodium sulphite)

$$Na_2CO_3 + H_2O + 2SO_2 \rightarrow 2NaHSO_3 + CO_2$$
(Sodium Bisulphite)

4. Reducing property :-

SO_2 acts as a reducing agent in presence of moisture or in aqueous medium. Because it has tendency to give up nascent hydrogen and sometimes take up nascent oxygen.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2[H]$$
(Nascent Hydrogen)

OR

$$SO_2 + H_2O + [O] \rightarrow H_2SO_4$$

(a) Reaction with Ferric salt :-

SO_2 reduces ferric salt into ferrous salt.

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

$$Fe_2(SO_4)_3 + 2[H] \rightarrow 2FeSO_4 + H_2SO_4$$

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$
(Ferric sulphate) (Ferrous sulphate)

(b) Reaction with Acidified potassium dichromate solution :-

SO_2 reduces and changes the orange colour of $K_2Cr_2O_7$ to green colour.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$[SO_2 + H_2O + [O] \rightarrow H_2SO_4] \times 3$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
(Orange) (Green)

(c) Reaction with Acidified potassium permanganate solution (KMnO4):
It reduces and decolourises pink colour of potassium permanganate solution.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$[SO_2 + H_2O + [O] \longrightarrow H_2SO_4] \times 5$$

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(pink) (colourless)

(d) With Halogens :
SO_2 reduces halogens to halogen acid in presence of moisture.

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

$$Cl_2 + 2[H] \longrightarrow 2HCl$$

$$SO_2 + Cl_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$$

(e) With potassium Iodate :
It reduces potassium iodate into iodine.

$$2KIO_3 + 5SO_2 + 4H_2O \longrightarrow 2KHSO_4 + 3H_2SO_4 + I_2$$

5. Oxidising property :
SO_2 also acts as an oxidising agent.
SO_2 oxidises magnesium, HI and H_2S to give MgO, I_2 & sulphur.

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

(magnesium oxide)

$$4HI + SO_2 \longrightarrow 2H_2O + 2I_2 + S$$

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

6. Bleaching Agent :)

SO_2 acts as bleaching agent. It bleaches colouring matter into colourless matter in presence of nascent hydrogen.

In the presence of moisture, SO_2 gives nascent Hydrogen.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$
(Nascent hydrogen)

$$\text{Vegetative colouring matter} + [H] \longrightarrow \text{colourless matter.}$$

* Bleaching property of SO_2 is due to its Reducing property.
* Bleaching action of SO_2 is ~~temporary~~. temporary. Because again colourless matter regain its original colour in presence of air due to oxidation.

$$\text{Colourless matter} + [O] \xrightarrow{\text{Air}} \text{Colouring matter.}$$

7. Addition Reaction :)

(a) Reaction with chlorine :)

SO_2 reacts with chlorine in presence of sunlight to give Sulphuryl chloride.

$$SO_2 + Cl_2 \xrightarrow{\text{Sunlight}} SO_2Cl_2$$
(Sulphuryl chloride)

(b) Reaction with oxygen :)

SO_2 reacts with oxygen in presence of catalyst platinised asbestos or V_2O_5 to give Sulphur trioxide.

It is a reversible reaction & occurs at 450°C.

$$2SO_2 + O_2 \underset{450^\circ C}{\overset{Pt}{\rightleftharpoons}} 2SO_3$$
(Sulphur trioxide)

Uses :)

1. It is used in the manufacture of sulphuric acid.
2. It is used as bleaching agent.
3. It is used as germicide and disinfectant.
4. Liquid SO_2 is used in refrigerators.

Allotropic forms of Sulphur :-

Allotropic forms of sulphur are Rhombic sulphur, Monoclinic sulphur and plastic sulphur.

Rhombic Sulphur :-

- It is also called as α-sulphur, or ortho rhombic sulphur.
- It is the most stable form of sulpur.
- It is a yellow color crystalline solid.
- It is soluble in Carbon disulphide & insoluble in water.

Monoclinic Sulphur :-

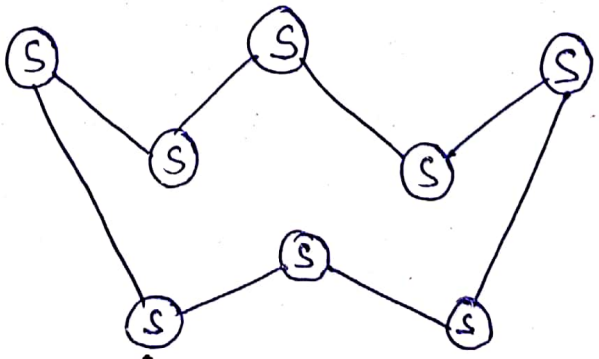
- It is also called as β-sulphur.
- It is less stable than rhombic sulphur.
- It is a dull yellow colour crystalline solid.
- It is also soluble in Carbon disulphide & insoluble in water.

Rhombic sulphur (α-Sulphur) $\xrightarrow{\text{Above 369K}}$ Monoclinic Sulphur (β-sulphur)

Monoclinic Sulphur (β-sulphur) $\xrightarrow{\text{Below 369K}}$ Rhombic sulphur (α-Sulphur)

* Above 369K α-sulphur changes to β-sulphur. Below 369K β-Sulphur changes to α-sulphur. This particular 369K temperature is called transition temperature. because both α-sulphur & β-sulphur co-exist at that temperature.

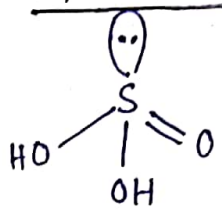
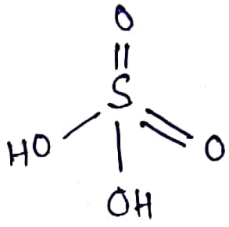
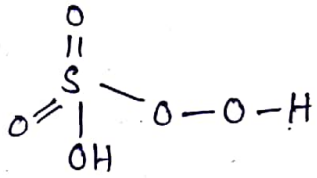
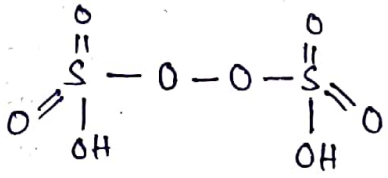
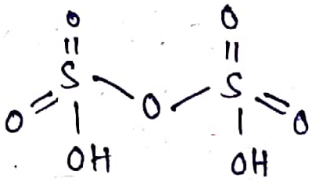
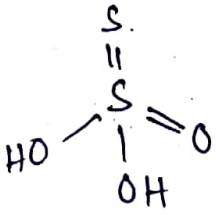
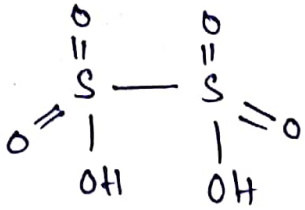
* Both Rhombic & monoclinic sulphur exist as S_8 molecule which has puckered ring structure (or) Crown shaped.



(puckered ring structure of S_8 molecule (or) Crown shaped)

Oxoacids of Sulphur :-)

Sulphur forms a number of oxoacids.
Structure of oxoacids of sulphur are discussed below.

Name	molecular formula	Structure
1. Sulphurous acid	H_2SO_3	
2. Sulphuric acid	H_2SO_4	
3. peroxo monosulphuric acid or Caro's acid	H_2SO_5	
4. peroxodisulphuric acid or Marshall's acid.	$H_2S_2O_8$	
5. pyrosulphuric acid.	$H_2S_2O_7$	
6. Thiosulphuric acid	$H_2S_2O_3$	
7. Dithionic acid	$H_2S_2O_6$	

SULPHURIC ACID

Molecular formula = H_2SO_4 molecular mass = 98 amu.

It is also known as oil of Vitriol.

preparation of H_2SO_4 :-

Sulphuric acid can be prepared by **Contact process**.

Contact process involves 3 steps.

Step-1 (Formation of SO_2)

When sulphur burns with oxygen the sulphur dioxide is formed or it is also prepared by roasting of iron pyrites (FeS_2).

$$S + O_2 \longrightarrow SO_2$$
(Sulphur dioxide)

(or)

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$
(Iron pyrites) (Sulphur dioxide)

Step-2 (Formation of SO_3)

SO_2 is oxidised with oxygen in presence of catalyst like V_2O_5 or platinum asbestos to give Sulphur trioxide (SO_3)

→ It is a reversible reaction & exothermic in nature.

$$2SO_2 + O_2 \underset{450^\circ C}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3$$
(Sulphur Trioxide)

→ The temperature must be 450°c.

Step-3 (Formation of H_2SO_4)

(i) SO_3 is dissolved in conc. H_2SO_4 to produce Oleum or fuming Sulphuric acid.

$$SO_3 + H_2SO_4 \text{ (conc.)} \longrightarrow H_2S_2O_7$$
(Oleum)

(ii) Oleum is diluted with water to give sulphuric acid, of any concentration. (or (fuming sulphuric acid))

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$
(Oleum) (Sulphuric acid)

physical properties :-

1. It is a colourless, odourless and syrupy liquid.
2. It is highly corrosive to the skin.
3. It is soluble in water with evolution of heat.
4. It is good conductor of electricity.
5. It is hygroscopic in nature.
6. It fumes in moist air.

Chemical properties :-

1. **Acidic property :-** It is a dibasic acid.

Sulphuric acid is a strong acid. It ionises in solution to give hydrogen ions, bisulphate ion & sulphate ion.

$$H_2SO_4 \xrightleftharpoons{aq} H^+ + HSO_4^-$$

(Bisulphate ion)

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

(Sulphate ion)

(a) **Action with metal hydroxide or Base :-**

Sulphuric acid reacts with metal hydroxide (Base) to give salt and water.

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$$

(Sodium Bisulphate)

$$\underset{\text{(Base)}}{2NaOH} + \underset{\text{(Acid)}}{H_2SO_4} \longrightarrow \underset{\text{(Salt)}}{Na_2SO_4} + 2H_2O$$

(Sodium sulphate)

(b) **Action with Metal Carbonate :-**

Sulphuric acid reacts with metal carbonate to give salt, water & CO_2 gas is libereated.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2\uparrow$$

(Sod. Carbonate) (Sodium sulphate)

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2\uparrow$$

(Calcium sulphate)

(c) Action with Metal oxide :-
Sulphuric acid reacts with metal oxide to give salt and water.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$
(Zinc sulphate)

$$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$
(Magnesium sulphate)

(d) Action with Metals :-
Dilute Sulphuric acid reacts with more electropositive metals (Na, Zn, Mg, Fe etc.), H_2 gas is liberated.

$$2Na + H_2SO_4 \longrightarrow Na_2SO_4 + H_2\uparrow$$
(Sodium sulphate)

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2\uparrow$$

2. Dehydrating property :-
Concentrated H_2SO_4 removes water from compounds, due to its greater affinity for water. So, it acts as a good dehydrating agent.

(a) $C_{12}H_{22}O_{11} \xrightarrow{Conc.\ H_2SO_4} 12C + 11H_2O\uparrow$
(Sucrose) or Sugar — (Black ppt.)

(b) $C_6H_{12}O_6 \xrightarrow{Conc.\ H_2SO_4} 6C + 6H_2O\uparrow$
(Glucose)

(c) $H-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Conc.\ H_2SO_4} CO + H_2O\uparrow$
(Formic acid)

(d) $COOH-COOH \xrightarrow{Conc.\ H_2SO_4} CO + CO_2 + H_2O\uparrow$
(Oxalic acid)

(e) $CH_3-CH_2-OH \xrightarrow{Conc.\ H_2SO_4} CH_2=CH_2 + H_2O\uparrow$
(Ethyl alcohol) (Ethylene)
or $CH_2(H)-CH_2(OH)$

(f) $CuSO_4 \cdot 5H_2O \xrightarrow{\text{conc. } H_2SO_4} CuSO_4 + 5H_2O$

(Blue) (white)

3. **Oxidising property** :- Dilute H_2SO_4 is not a oxidising agent. Concentrated Sulphuric acid (H_2SO_4) is a good oxidising agent because it has tendency to give up nascent oxygen.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$

(a) **Reaction with H_2S** :-

Sulphuric acid oxidises hydrogen sulphide (H_2S) to give Sulphur.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$

$$H_2S + [O] \longrightarrow H_2O + S$$

$$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$$

(b) **Reaction with moist phosphorous** :-

Sulphuric acid oxidises moist phosphorous to give phosphoric acid.

$$[\ H_2SO_4 \longrightarrow H_2O + SO_2 + [O]\ ] \times 10$$

$$P_4 + 6H_2O + 10[O] \longrightarrow 4H_3PO_4$$

$$10H_2SO_4 + P_4 \longrightarrow 4H_2O + 10SO_2 + 4H_3PO_4$$

(phosphoric acid)

(c) **Reaction with halogen acid (HX)**

Sulphuric acid oxidises halogen acid (HBr, HI) to give halogen.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$

$$2HBr + [O] \longrightarrow H_2O + Br_2$$

$$H_2SO_4 + 2HBr \longrightarrow 2H_2O + SO_2 + Br_2.$$

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$

$$2HI + [O] \longrightarrow H_2O + I_2$$

$$H_2SO_4 + 2HI \longrightarrow 2H_2O + SO_2 + I_2$$

(d). Reaction with Nonmetals (Carbon & Sulphur)

Sulphuric acid oxidises Carbon to give Carbon dioxide.

$$[H_2SO_4 \longrightarrow H_2O + SO_2 + [O]] \times 2$$

$$C + 2[O] \longrightarrow CO_2$$

$$2H_2SO_4 + C \longrightarrow CO_2 + 2H_2O + 2SO_2$$

(Carbon dioxide)

Sulphuric acid oxidises Sulphur to give Sulphur dioxide.

$$[H_2SO_4 \longrightarrow H_2O + SO_2 + [O]] \times 2$$

$$S + 2[O] \longrightarrow SO_2$$

$$2H_2SO_4 + S \longrightarrow 3SO_2 + 2H_2O$$

(Sulphur dioxide)

(e) Reaction with metals (Cu, Ag, Hg, Pb)

Concentrated H_2SO_4 oxidises Copper to give Copper sulphate.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$

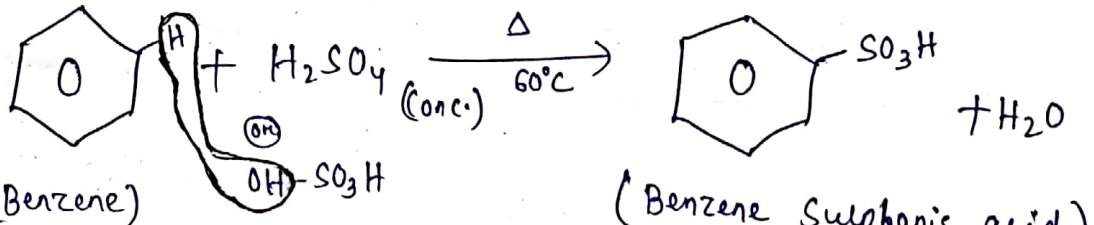
$$Cu + [O] + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

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

~~$Cu + 2H_2SO_4$ (conc.) $\longrightarrow CuSO_4 + 2H_2O + SO_2\uparrow$~~

4. Sulphonation (in / As Sulphonating agent)

When benzene is heated with Conc. H_2SO_4 to give benzene sulphonic acid.



(Benzene) (Benzene Sulphonic acid)

Conc. H_2SO_4 is used in the sulphonation of benzene.

5. Reaction with Salts ($NaCl$, KNO_3)

conc. H_2SO_4 reacts with salt to give corresponding acids

(i) With NaCl :-

$$NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + HCl$$

(Sodium sulphate)

(ii) With KNO_3 :-

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

(Potassium Nitrate) (Potassium bisulphate) (Nitric acid)

6. Precipitation Reaction

When H_2SO_4 reacts with salt of barium and strontium to give white ppt.

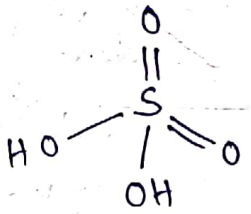
$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2HCl$$

(Barium chloride) (Barium sulphate)

$$Sr(NO_3)_2 + H_2SO_4 \longrightarrow SrSO_4 \downarrow + 2HNO_3$$

(Strontium sulphate)

Structure of H_2SO_4 :-



(Tetrahedral structure of H_2SO_4) Hybridisation = sp^3

→ The oxidation state of sulphur in H_2SO_4 is +6.

→ It is a dibasic acid due to the presence of two basic group (-OH).

Uses :- 1. It is a very important laboratory reagent.

2. It is used in the manufacture of dyes, drugs, paints, medicines, insecticides, explosives.

3. It is used in petroleum refining.

4. It is used in coal tar industry & leather industry.

5. It is used in the manufacture of nitric acid, hydrochloric acid etc.

Due to this wide applications, H_2SO_4 is called as King of Chemicals.