Group 16 Elements

Oxygen family: Group 16 of periodic table consists of five elements –

oxygen (O),

sulphur (S),

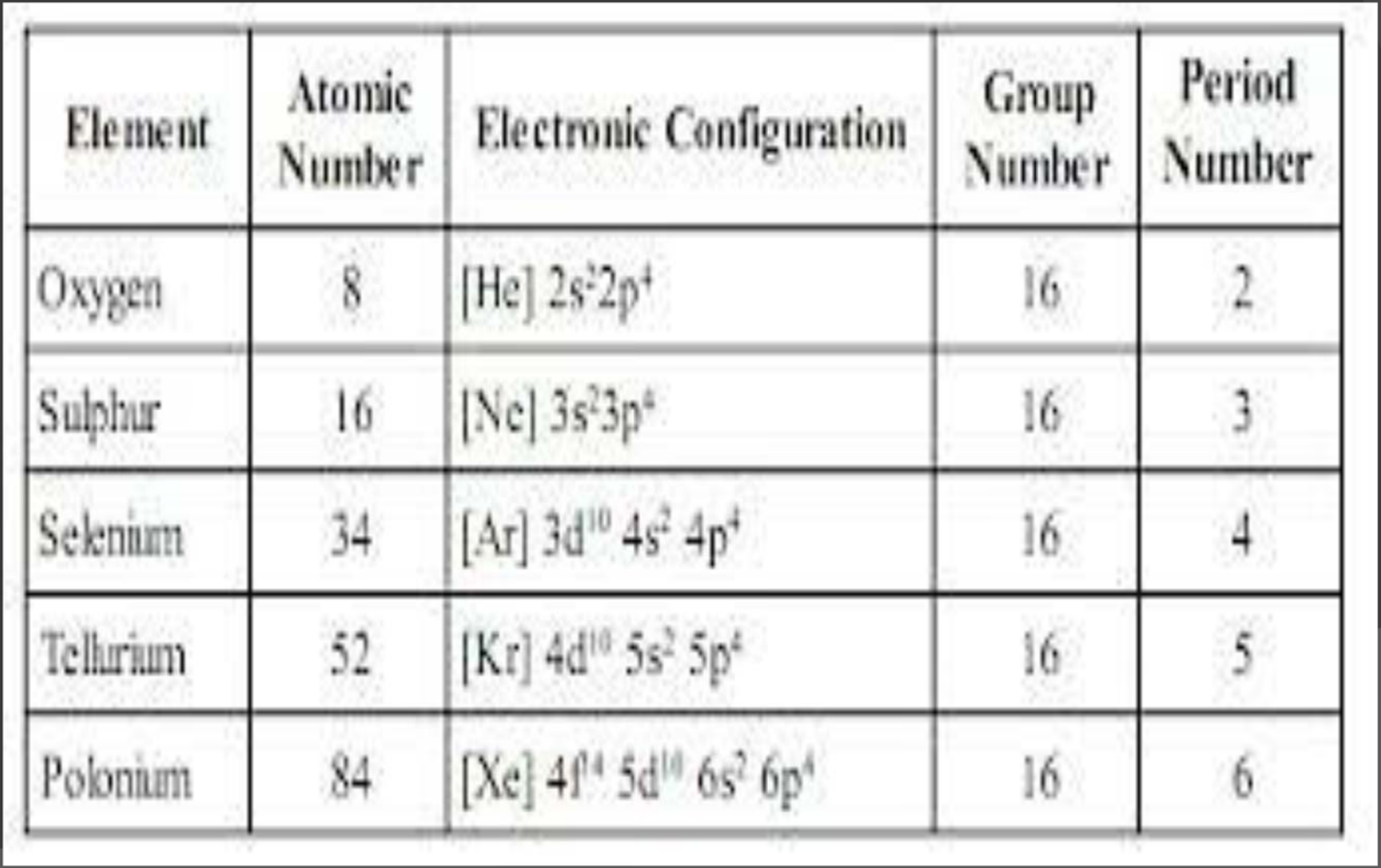
selenium (Se),

tellurium (Te) and

polonium (Po).

Their general electronic configuration is ns2np4.

Electronic configuration



Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Oxygen	8	[He] $2s^2 2p^4$	16	2
Sulphur	16	[Ne] $3s^2 3p^4$	16	3
Selenium	34	[Ar] $3d^{10}\ 4s^2\ 4p^4$	16	4
Tellurium	52	[Kr] $4d^{10}\ 5s^2\ 5p^4$	16	5
Polonium	84	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$	16	6

general periodic trends:

Periodic properties	Trends
Atomic Radii (the radius of the atom)	increases
Electronegativity:(the atom's ability of attracting electrons)	Decreases down the group
Ionization Enthalpy (the amount of energy required to remove an electron from the atom in it's gaseous phase)	decreases
Electron Affinity (ability of the atom to accept an electron)	decreases
Melting Point (amount of energy required to break bonds to change a solid phase substance to a liquid phase)	increases going down the group
Boiling Point (amount of energy required to break bonds to change a liquid phase substance to a gas)	increases going down the group

Oxidation state

Their general electronic configuration is ns2np4

The most common oxidation state is – 2.

The most common oxidation state for the chalcogens are −2, +2, +4, and +6.

Chemical properties

Reaction with air:

- $S + O_2 \longrightarrow SO_2$

$\longrightarrow$

with acid[only oxidizing acids]

- $s + 6hno_3 \quad h_2so_4 + 6no_2 + 2h_2o \quad \longrightarrow$

With alkali

- $3S + 6\,NaOH \quad Na_2SO_3 + 2$

reactions

with non - metals

- $2S + C \rightarrow CS2$
- $S + H2 \rightarrow H2S$
- $S + 3F2 \rightarrow SF6$

reactivity

1. The **metallic character** increases as we descend the group. Oxygen and sulphur are typical nonmetals. Selenium (Se) and Te are metalloids and are semiconductors. Polonium is a metal.

2. Tendency to form **multiple bond** decreases down the group.

Example $O=C=O$ is stable, $S=C=C$ is moderately stable, $Se=C=Se$ decomposes readily and $Te=C=Te$ is not formed

Formation of Hydrides

All the elements of group 16 form hydrides of the type H2M (where M= O, S, Se, Te or Po).

The stability of hydrides decreases as we go down the group.

Except H2O, all other hydrides are poisonous foul smelling gases.

Their acidic character and reducing nature increases down the group. [less energy to break M – H bond]

All these hydrides have angular structure and the central atom is in sp3 hybridised.

H – M – H Bond angle decreases.

BP also decreases from H2O TO H2S then increases.

Formation of Halides

Element of group 16 form a large number of halides. The compounds of oxygen with fluorine are called oxyfluorides because fluorine is more electronegative than oxygen (example OF2).

Formation Of Oxides

Group 16 elements mainly form three types of oxides.

1. Monoxides: Except Selenium (Se), all other elements of the group form monoxides of the type MO (Example SO)

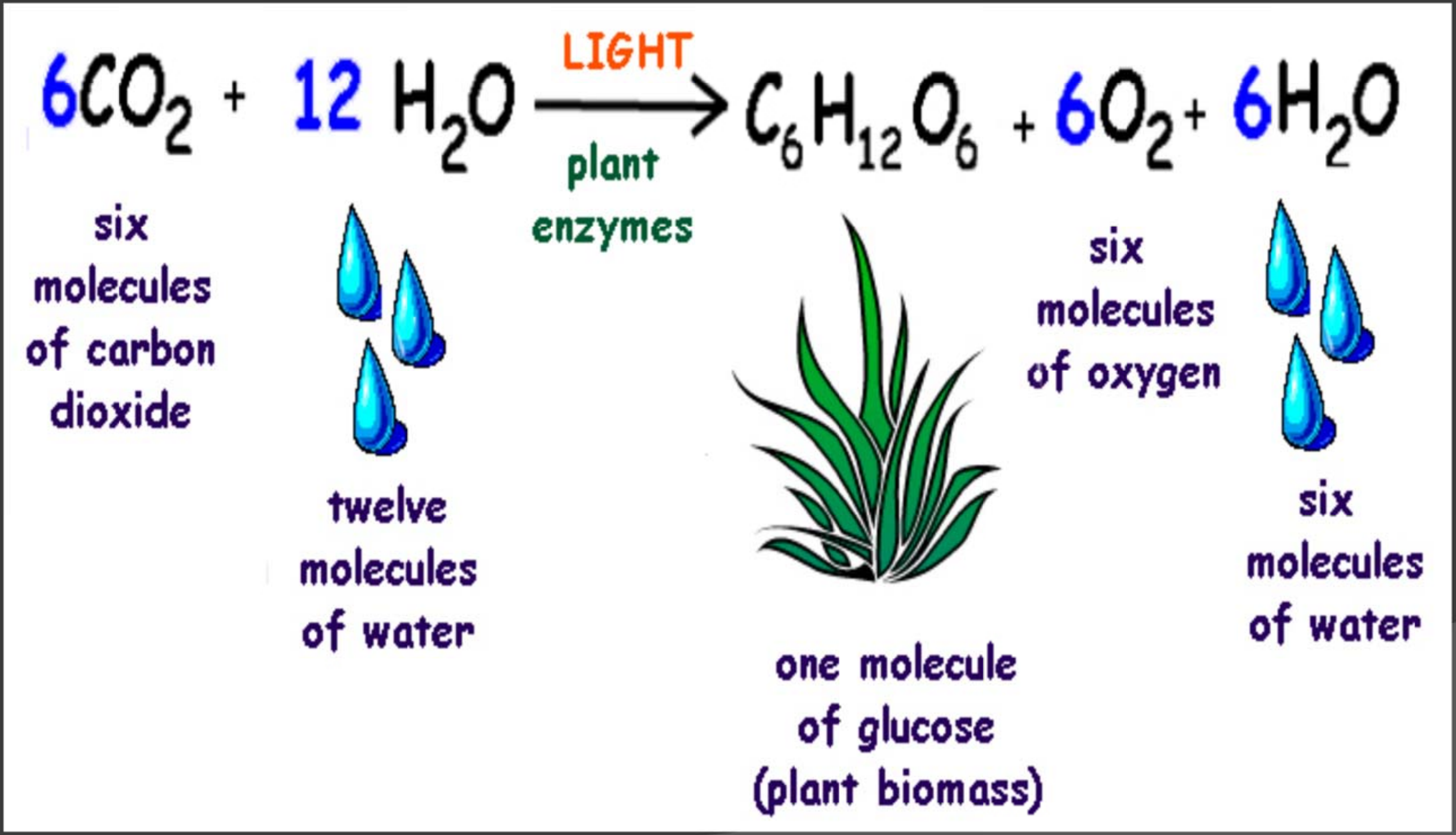
2. Dioxides: All the elements of group 16 form dioxides of the type $MO2$ (Example $SO2$)

3. Trioxides: All the elements of the group form trioxides of the type $MO3$

Anomalous behaviour of oxygen

- O is gas all are solids.
- O diatomic others poly atomic.
- O2is paramagnetic others diamagnetic.
- Forms H bonds in hydrides, alcohols and carboxylic acids.
- forms p∏ - p∏ multiple bonds.
- oxidation states -2 and +2 only with F others +2 and +6.
- Forms ionic compounds.

dioxygen



$$6CO_2 + 12\,H_2O \xrightarrow[\text{plant enzymes}]{\text{LIGHT}} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

Preparation of o2

thermal decomposition of oxygen rich compounds

Potassium chlorate will readily decompose if heated in contact with a catalyst, typically manganese (IV) dioxide (MnO_2) .

$$2\,KClO_3(s) \xrightarrow{\triangle} 3\,O_2(g) + 2KCl(s)$$

$$2\,KNO_3 \xrightarrow{\triangle} 2\,KNO_2 + O_2$$

Oxides

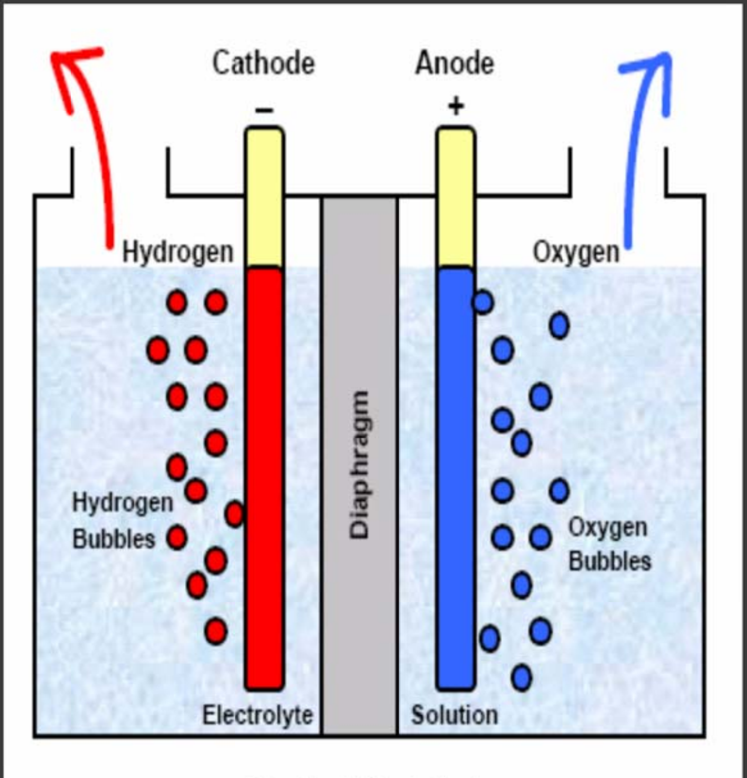
- **Preparation of oxygen using hydrogen peroxide**

The decomposition of hydrogen peroxide using manganese dioxide as a catalyst also results in the production of oxygen gas.

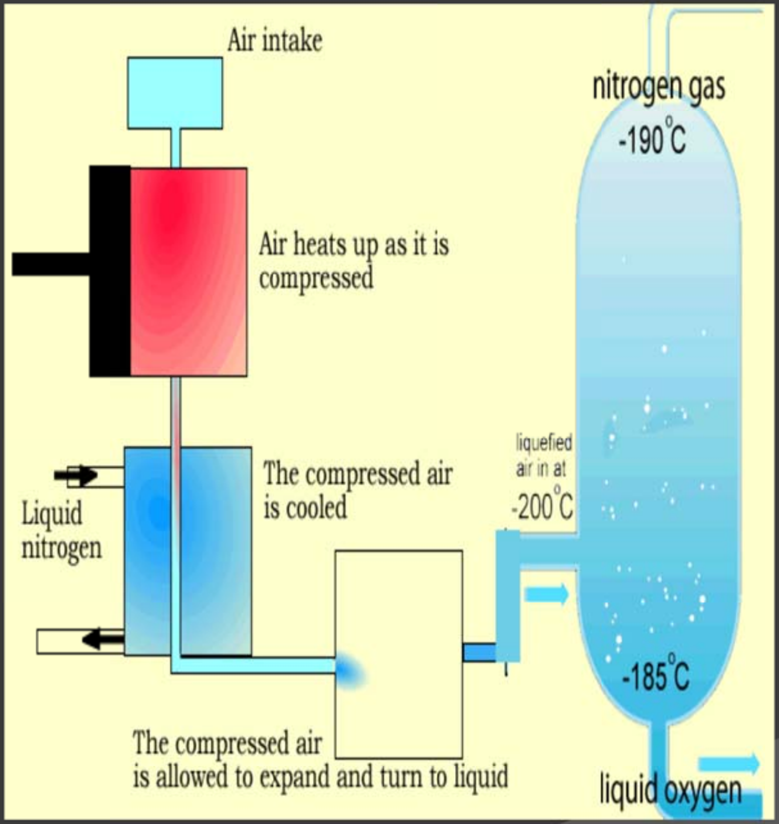
$$2\ H_2O_2 \implies 2\ H_2O + O_2$$

- $2\ BaO_2 \implies 2\ BaO + O_2$
- $6\ MnO_2 \implies Mn_3O_4 + O_2$

Manufacture of oxygen



Standard Electrolysis



- 1.electrolysis of
- 2.Fractional

properties

- Oxygen is a colourless gas, without smell or taste,
- is slightly heavier than air,
- is sparingly soluble in water,
- is difficult to liquefy, boiling point 90.2K, and the liquid is pale blue in colour and is appreciably magnetic.
- At still lower temperatures, light-blue solid oxygen is obtained, which has a melting point of 54.4K.

reactions

- With metals

Potassium, sodium, lithium, calcium and magnesium →
react with oxygen and burn in air.

$4Na(s) + O2(g) \rightarrow 2Na2O(s)$

- $2Ca(s) + O2(g) \rightarrow 2CaO(s)$

Metals in the reactivity series from aluminium to copper
react with oxygen in the air to form the

reactions

- When carbon reacts with oxygen, carbon dioxide is formed along with production of heat.

$$\underset{Carbon}{C(s)} + \underset{Oxygen}{O_2} \longrightarrow \underset{Carbon\ dioxide}{CO_2(g)} + Heat$$

When carbon is burnt in insufficient supply of air, it forms carbon monoxide. Carbon monoxide is a toxic substance. Inhaling of carb

$$\underset{Carbon}{2C(s)} + \underset{Oxygen(insufficient)}{O_2} \longrightarrow \underset{Carbon\ monoxide}{CO(g)} + Heat$$

reactions

- Sulphur gives sulphur dioxide on reaction with oxygen. Sulphur catches fire when exposed to air.

$$\underset{\text{Sulphur}}{S(s)} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Sulphur dioxide}}{SO_2(g)}$$

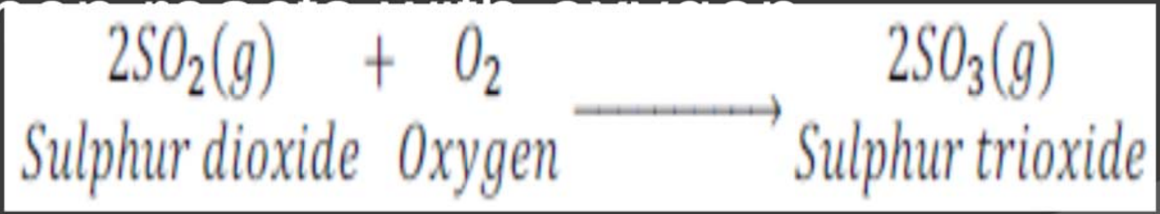
- (3) When hydrogen reacts with oxygen it giv

$$\underset{\text{Hydrogen}}{2H_2} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Water}}{2H_2O}$$

- With ammonia :react with oxygen in excess air, and platinum catalyst to form nitrogen monoxide

  $4NH3(g) + 5O2(g) \rightarrow 4NO(g) + 6H2O(l)$

Sulphur dioxide gives sulphur trioxide wh



$$\underset{\text{Sulphur dioxide}}{2SO_2(g)} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Sulphur trioxide}}{2SO_3(g)}$$

reactions

- Reacts with metal sulphides forming metal oxides and sulphur dioxide.
- Reacts with hydrocarbons forming carbon dioxide and water.

uses

- Oxygen is essential for life and it takes part in processes of combustion, its biological functions in respiration make it important. Oxygen is sparingly soluble in water, but the small quantity of dissolved oxygen in is essential to the life of fish.
- Oxygen gas is used with hydrogen or coal gas in blowpipes and with acetylene in the oxy-acetylene torch for welding and cutting metals.
- Oxygen gas is also used in a number of industrial processes.
- Medicinally, oxygen gas is used in the treatment of pneumonia and gas poisoning, and it is used as an anesthetic when mixed with nitrous oxide, ether vapour, etc..
  Carbon Dioxide is often mixed with the oxygen as this stimulates breathing, and this mixture is also used in cases of poisoning and collapse for restoring respiration.
- Liquid oxygen mixed with powdered charcoal has been used as an explosive.

Types of oxides : basic

- Reaction of sodium oxide with water: Sodium oxide gives sodium hydroxide when reacts with water.

$$\underset{\text{Sodium oxide}}{Na_2O} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Sodium hydroxie}}{2NaOH}$$

Sodium hydroxide is a strong base.

- (2) Reaction of magnesium oxide with water: Magnesium o

$$\underset{\text{Magnesium oxide}}{MgO} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Magnesium hydroxie}}{Mg(OH)_2}$$

- (3) Reaction of potassium oxide with water: Potassium oxide giv water.

$$\underset{\text{Potassium oxide}}{K_2O} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Potassium hydroxie}}{2KOH}$$

Types of oxides : acidic

- Examples include:
- Carbon dioxide which reacts with water to produce carbonic acid.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

- Sulfur dioxide, which does not form the non-existent sulfuric acid.

$$SO_3 + H_2O + \rightarrow H_2SO_4$$

- Phosphorus pentoxide (P_2O_5) reacts with water and forms phosphoric acid (H_3PO_4)

Types of oxides:amphoteric

- Aluminium oxide and zinc oxide are insoluble in water. Aluminium oxide and zinc oxide are amphoteric in nature.
- An amphoteric substance shows both acidic and basic character. It reacts with base like acid and reacts with acid like a base.

$$\underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Hydrochloric acid}}{2HCl} \longrightarrow \underset{\text{Zinc chloride}}{ZnCl_2} + \underset{\text{Water}}{H_2O}$$

- When zinc oxide reacts with sodium hydroxide, it behaves like an acid. In this reaction, sodium zicate and water are formed.

$$\underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Sodium zincate}}{2Na_2ZnO_2} + \underset{\text{Water}}{H_2O}$$

Types of oxides : amphoteric

- In similar way aluminium oxide behaves like a base when reacts with an acid and behaves like an acid when reacts with a base.
- Aluminium oxide gives sodium aluminate along with water when reacts with sodium hydroxide.

$$\underset{\text{Alumium oxide}}{Al_2O_3} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Sodium aluminate}}{2NaAlO_2} + \underset{\text{Water}}{H_2O}$$

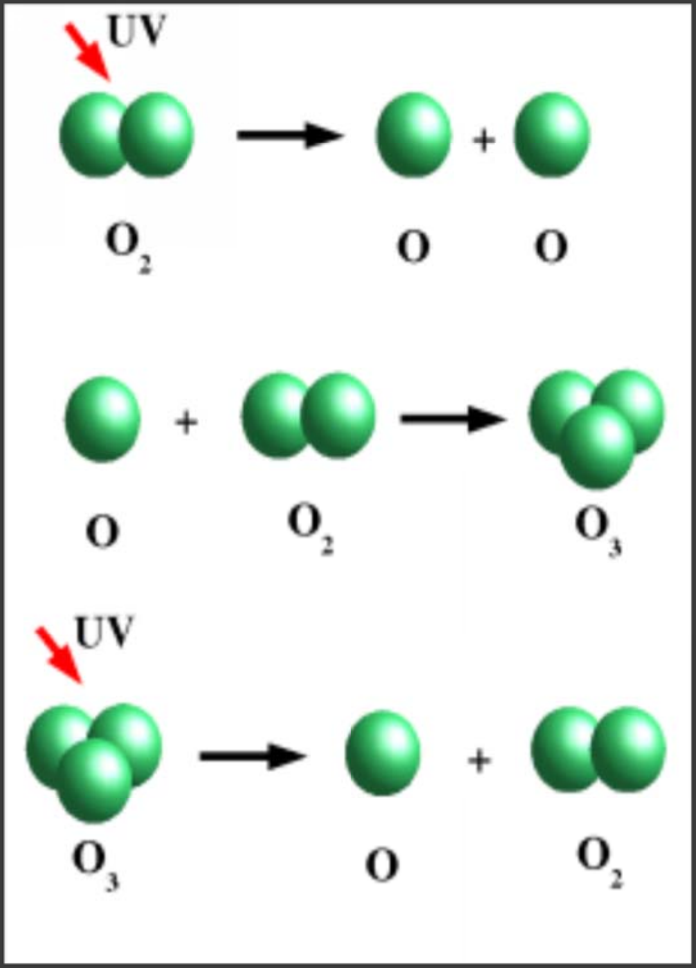
Alu
wh

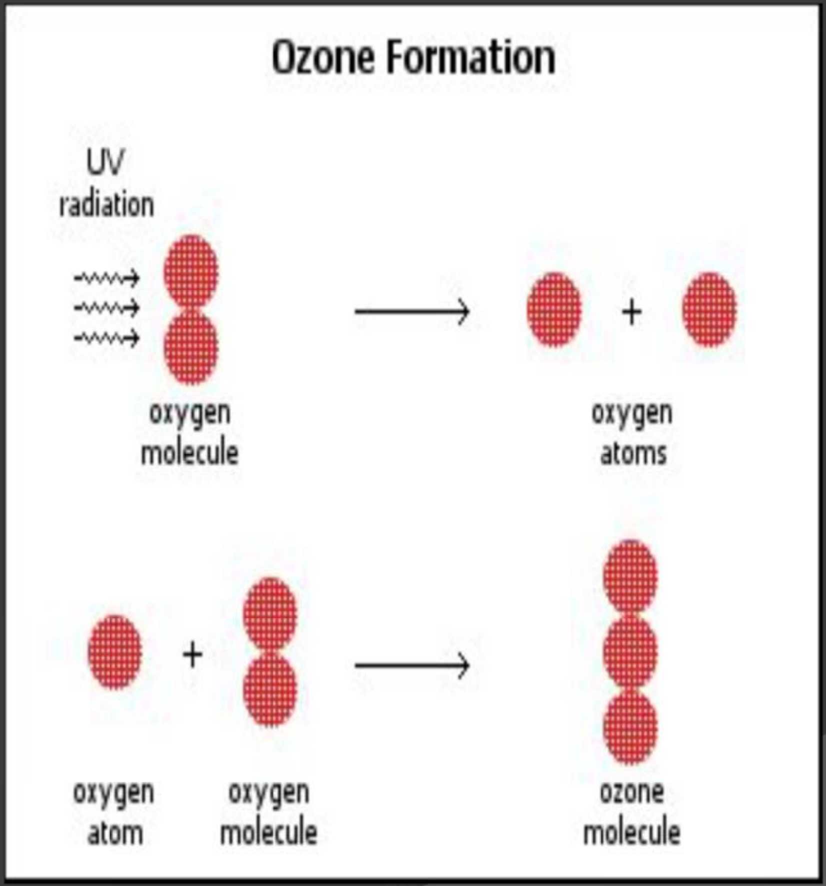
$$\underset{\text{Alumium oxide}}{Al_2O_3} + \underset{\text{Hydrochlorice acid}}{6HCl} \longrightarrow \underset{\text{Aluminium chloride}}{2AlCl_3} + \underset{\text{Water}}{H_2O}$$

ozone

- **Ozone** (**O3**), or **trioxygen**, is a triatomic molecule, consisting of three oxygen atom.
- It is an allotrope of oxygen that is much less stable than the diatomic allotrope (O2), breaking down in the lower atmosphere to normal dioxygen.
- Ozone is formed from dioxygen by the action of ultraviolet light and also atmospheric electrical discharges, and is present in low concentrations throughout the Earth's atmosphere.
- In total, ozone makes up only 0.6 parts per million of the atmosphere.

Formation of ozone





ozone

- Ozone is a pale blue gas, slightly soluble in water and much more soluble in inert non-polar solvents such as carbon tetrachloride or fluorocarbons,
- where it forms a blue solution. At 161 K (−112 °C; −170 °F), it condenses to form a dark blue liquid.
- At temperatures below 80 K (−193.2 °C; −315.7 °F), it forms a violet-black solid.

- Ozone is a powerful oxidizing agent, far stronger than O2.
- It is also unstable at high concentrations, decaying to ordinary diatomic oxygen (with a half-life of about half an hour in atmospheric conditions):

$$2\ O3 \quad \rightarrow \quad 3\ O2$$

- Ozone also oxidizes nitric oxide to nitrogen dioxide:

$$NO + O3 \rightarrow NO2 + O2$$

reactions

- Reducing action with BaO_2 and H_2O_2

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

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

- Reacts with KI to liberate iodine

uses

- Ozone is a reagent in many organic reactions in the laboratory and in industry.
- Ozonolysis is the cleavage of an alkene to carbonyl compounds.
- Many hospitals around the world use large ozone generators to decontaminate operating rooms between surgeries. The rooms are cleaned and then sealed airtight before being filled with ozone which effectively

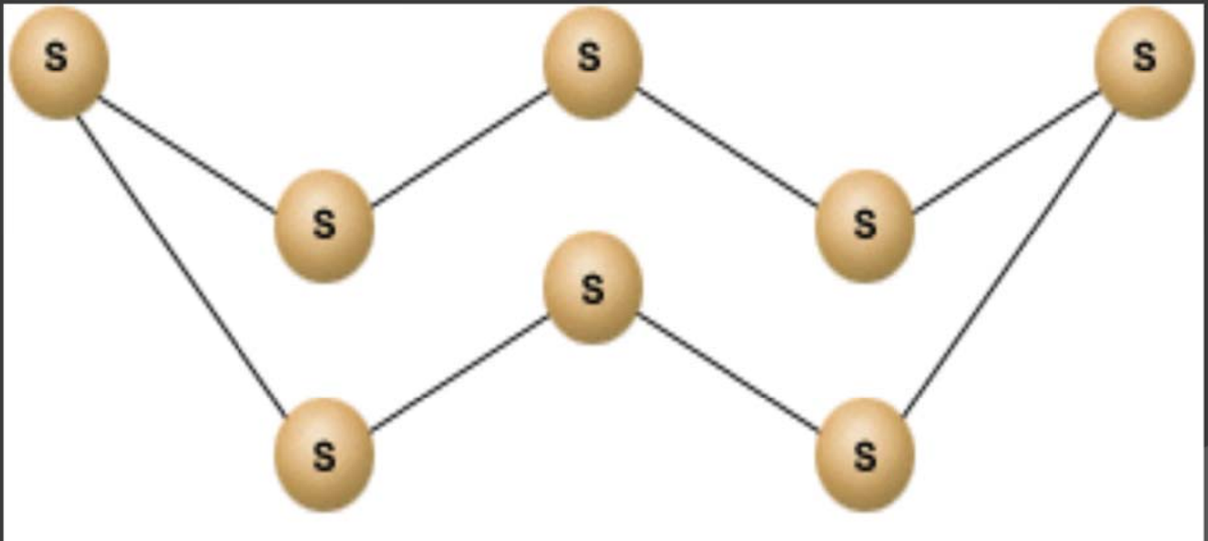
sulphur

1) sulphides : pyrites : Cu2S , FeS
Blende ZnS ,
cinnabar HgS and
galena PbS

2) Sulphates : gypsum CaSO4 .2H2O
epsum MgSO4 .7H2O
burytes BaSO4

allotropes

- Rhombic 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.



Structure of a sulphur molecule, S_8

Allotropes

- Monoclinic sulphur (β-sulphur) cyclo 6
- Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS2

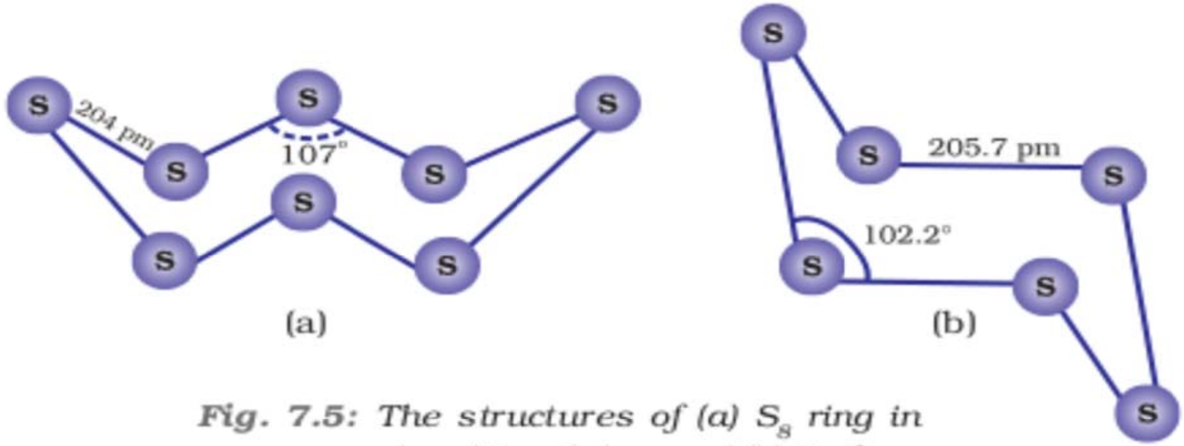
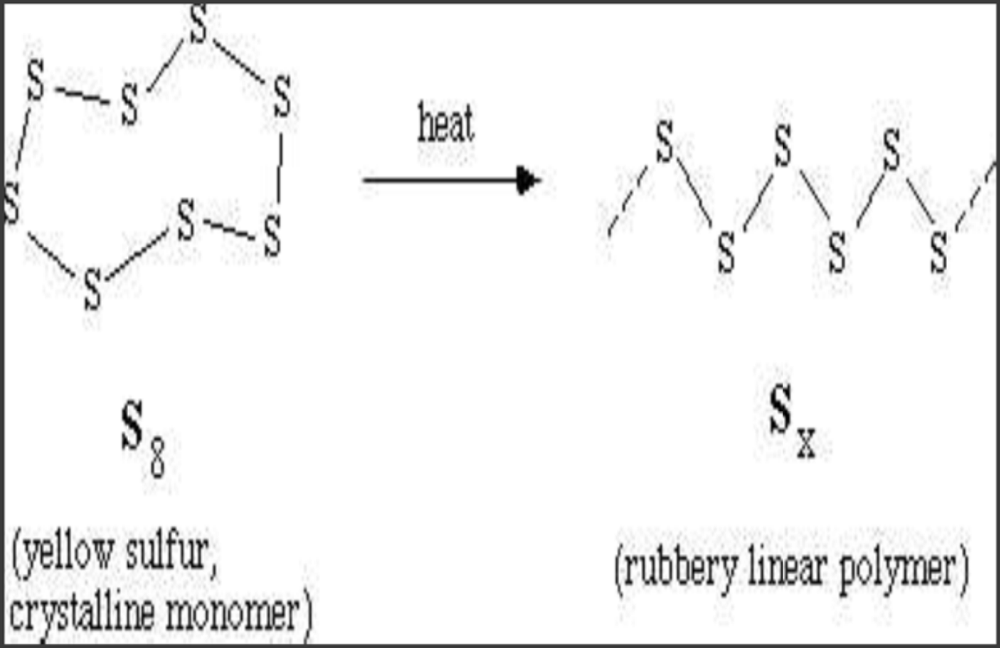


Fig. 7.5: The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

allotropes

- Plastic or γ - sulphur



allotropes

- ## Milk of sulphur

Prepared by boiling of sulphur with milk of lime, a mixture of Ca penta sulphide and thiosulphate are formed which on treatment with HCl give milk of sulphur

→

$3Ca(OH)_2 + 12S + 6HCl$

$3CaCl_2 + 12S + 2H_2O$

- ## Colloidal sulphur

- Thiosulfate react with dilute acids to produce sulfur, sulfur dioxide and water.
- $Na_2S_2O_3 + 2\,HCl \rightarrow 2\,NaCl$

$+ S + SO_2 + H_2O$

Action of H_2S on SO_2

→

$2H_2S$ on SO_2 3 S + $2H_2O$

so2

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

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

- Industrially, it is produced as a by-product of the roasting of sulphide ores. $4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$
- Action of sulphuric acid on Cu turnings

properties

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

properties

- Treatment of basic solutions with sulfur dioxide affords sulfite salts:

$SO_2 + 2\ NaOH \rightarrow Na_2SO_3 + H_2O$

It is oxidized by halogens to give the sulfuryl halides, such as sulfuryl chloride :

$SO_2 + Cl_2 \rightarrow SO_2Cl_2$

properties

- With iodine

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

With dichromate

Potassium dichromate paper can be used to test for sulfur dioxide, as → it turns distinctively from orange to green

- $K_2Cr_2O_7(aq) + 3SO_2(g) + H_2SO_4(aq)$ $Cr_2(SO_4)_3(aq) +$

$K_2SO_4(aq)$

properties

- When moist, sulphur dioxide behaves as a reducing agent. For example,
- it converts iron(III) ions to iron(II) ions

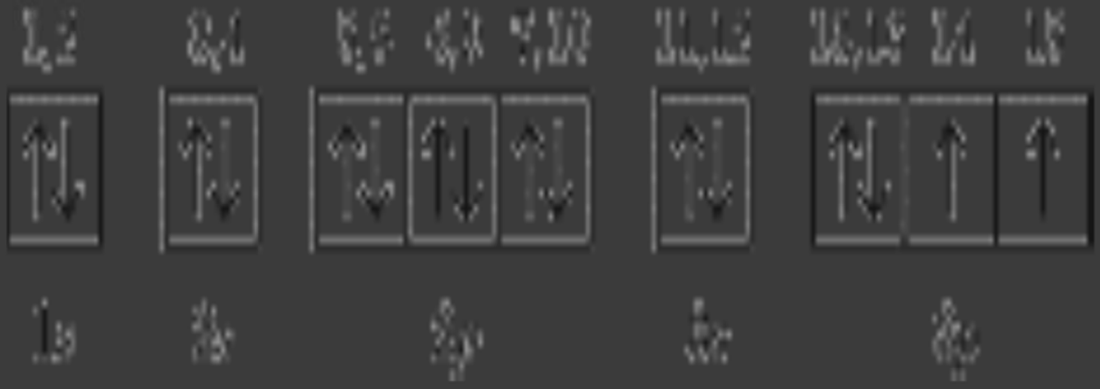
$2Fe3+ + SO2 + 2H2O \rightarrow 2Fe2+ + SO2$
$-4 + 4H+$

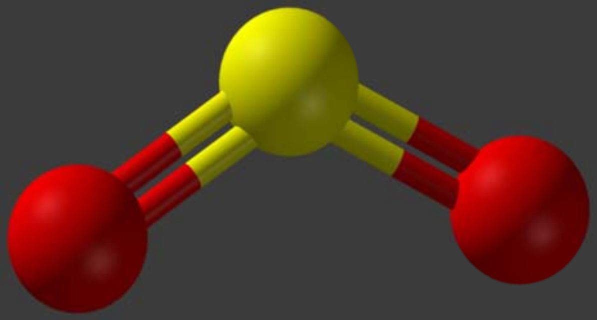
- and decolourises acidified potassium permanganate(VII) solution;

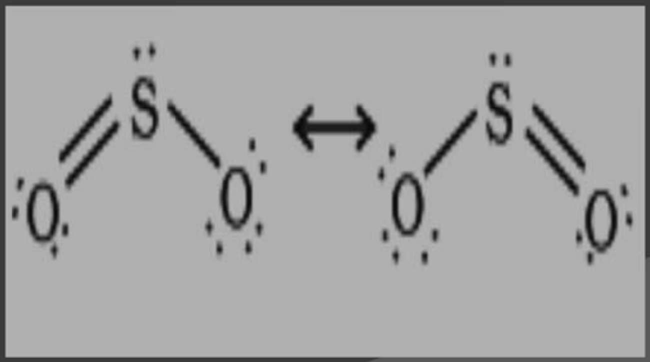
this reaction is a convenient test for the gas.

Structure
sp2 hybrized

- Sp2 hybridization in sulphur







uses

- Sulphur dioxide is a reducing agent and is used for bleaching and as a fumigant and food preservative.
- Large quantities of sulphur dioxide are used in the contact process for the manufacture of sulphuric acid.
- Sulphur dioxide is used in bleaching wool or straw, and as a disinfectant.
- Liquid sulphur dioxide has been used in purifying petroleum products

Contact process

- The process can be divided into five stages:
- combining of sulfur and oxygen;
- purifying sulfur dioxide in the purification unit;
- adding excess of oxygen to sulfur dioxide in presence of catalyst vanadium oxide;
- sulfur trioxide formed is added to sulfuric acid which gives rise to oleum (disulfuric

Contact process

Sulphur or iron pyrites burnt in air

$$S(s) + O2(g) \rightarrow SO2\ (g)$$

- Sulfur dioxide and oxygen then react as follows:

$$2\ SO2(g) + O2(g) \rightleftharpoons 2\ SO3(g)$$

- Hot sulfur trioxide passes through the heat exchanger and is dissolved in concentrated H2SO4 in the absorption

Contact process

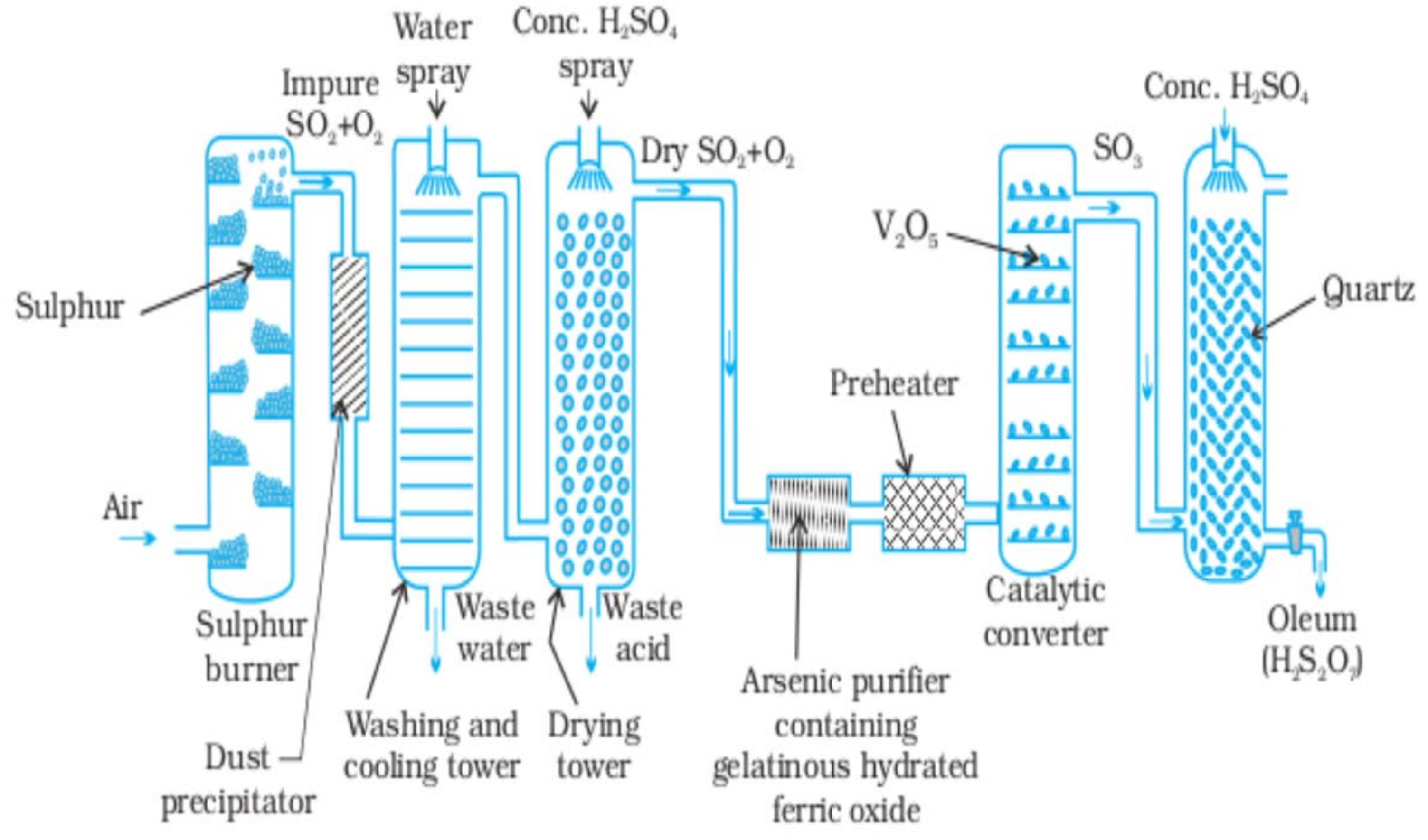


Fig. 7.7: Flow diagram for the manufacture of sulphuric acid

Lead chamber process

- Mixture of SO2 , NO and air is treated to steam to obtain sulphuric acid. NO ,nitric oxide acts as a catalyst.

$$2SO_2 + O_2(g) + 2H_2O \xrightarrow{NO} 2H_2SO_4$$

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.

reactions

- In aqueous solution, sulphuric acid ionises in two steps.
- H2SO4(aq) + H2O(l) → H3O+ (aq) + HSO4− (aq);

  Ka1 = very large (Ka1>10)

HSO4 (aq) + H2O(l) → H3O+ (aq) + SO42− (aq) ;

Ka2> = 1.2 × 10−2

Dehydrating agent

- Action on cane sugar

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

- Action on formic acid

$HCOOH \longrightarrow CO + H_2O$

Action on alcohol

$C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O$

Oxidising agent

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

$3S + 2H_2SO_4(conc.) \rightarrow 3SO_2 + 2H_2O$

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

dilute acid reacts with metals liberating H_2 gas.

Reaction with benzene

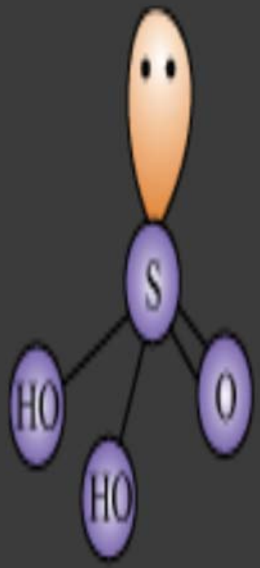
uses

- Sulphuric acid is a very important industrial chemical. 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

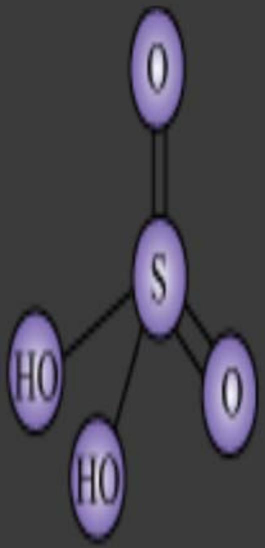
Oxyacids of sulphur

- Sulphoxylic acid H2SO2
- Sulphurous acid H2S2O2 ,H2SO3 H2S2O4, H2S2O5
- sulphuric acid H2SO4, H2S2O3 ,H2S2O7
- peroxy sulphuric acid H2SO5, H2S2O8 .
- Thionic acid series : dithionic acid H2S2O6 poly thionic acid H2SnO6 (n = 3 to 6)

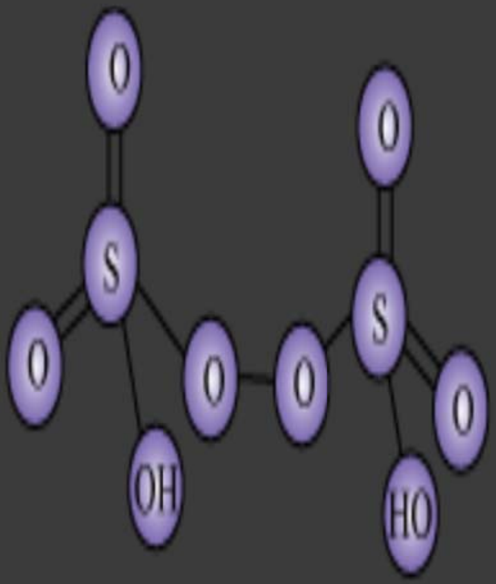
Oxyacids of sulphur



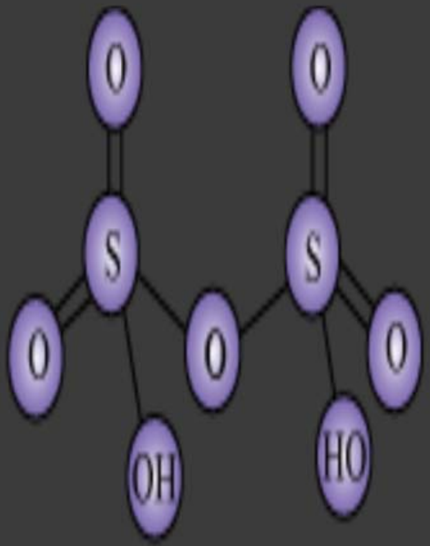
Sulphurous acid
(H_2SO_3)



Sulphuric acid
(H_2SO_4)



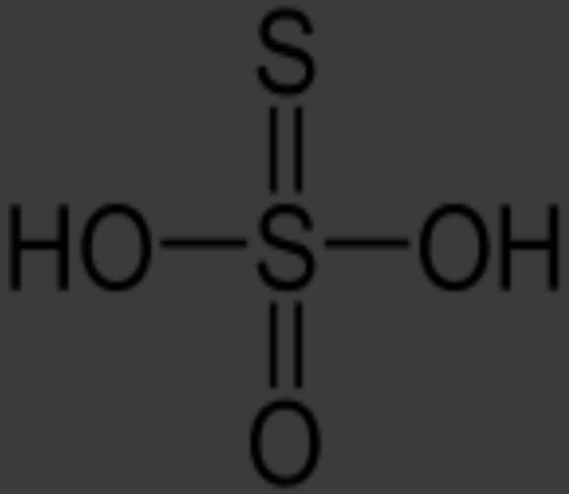
Peroxodisulphuric acid
($H_2S_2O_8$)



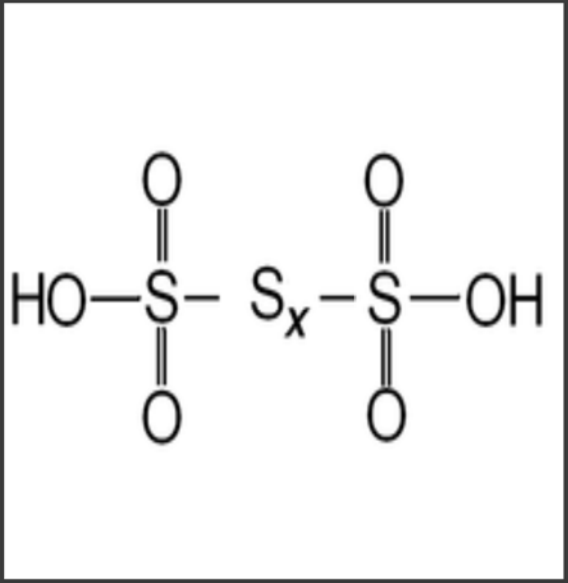
Pyrosulphuric acid (Oleum)
($H_2S_2O_7$)

Oxyacids of sulphur

- Thiosulphuric acid



- Polythionic acid



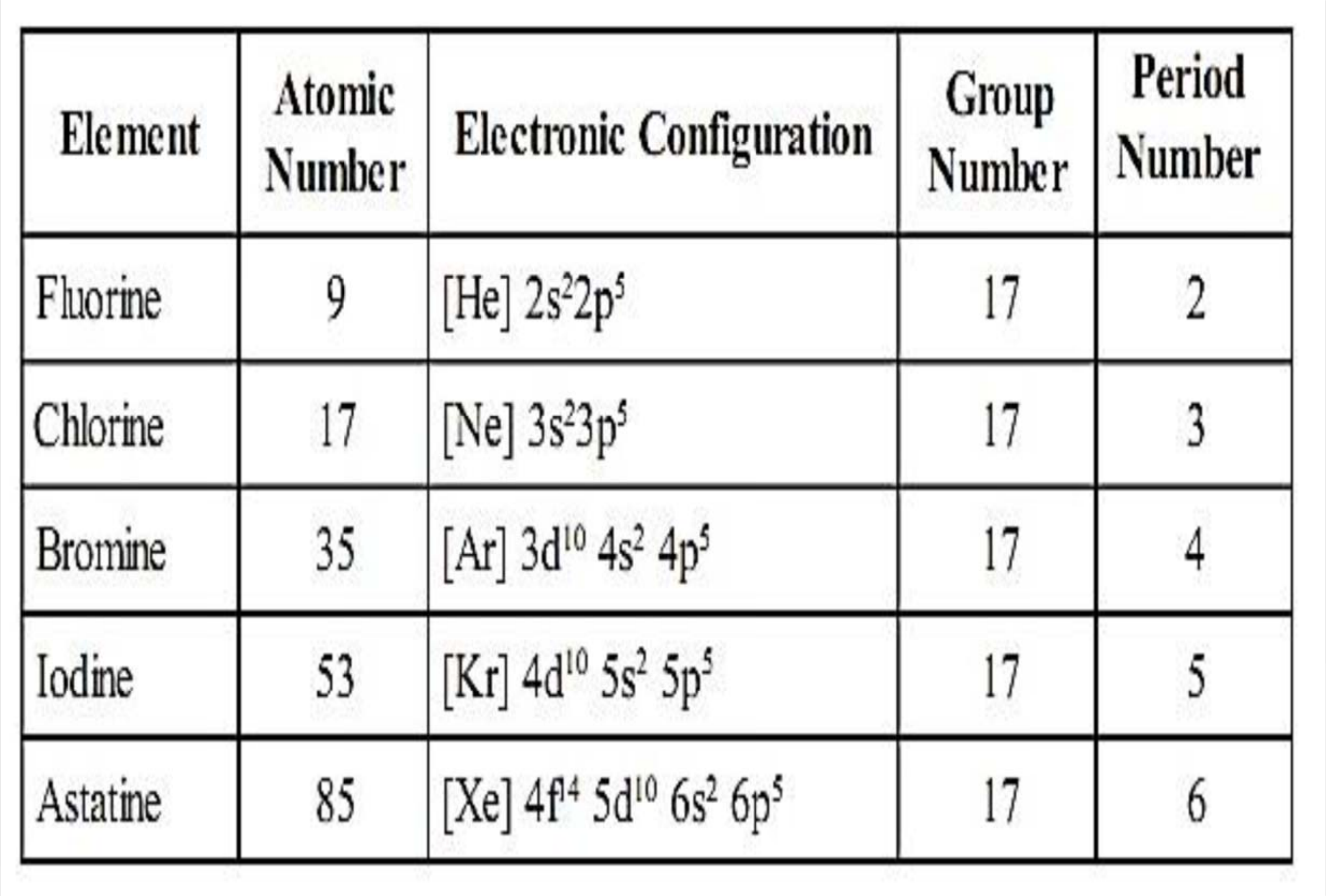
Group 17 Elements

- **The halogen family: Group 17 elements, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At), belong to halogen family. Their general electronic configuration is ns2np5.**

Group 17 Elements

- Fluorine and chlorine are fairly abundant while bromine and iodine less so.
- Fluorine is present mainly as insoluble fluorides (fluorspar CaF2, cryolite Na3AlF6 and fluoroapatite 3Ca3(PO4)2.CaF2)
- small quantities are present in soil, river water plants and bones and teeth of animals.
- Sea water contains chlorides, bromides

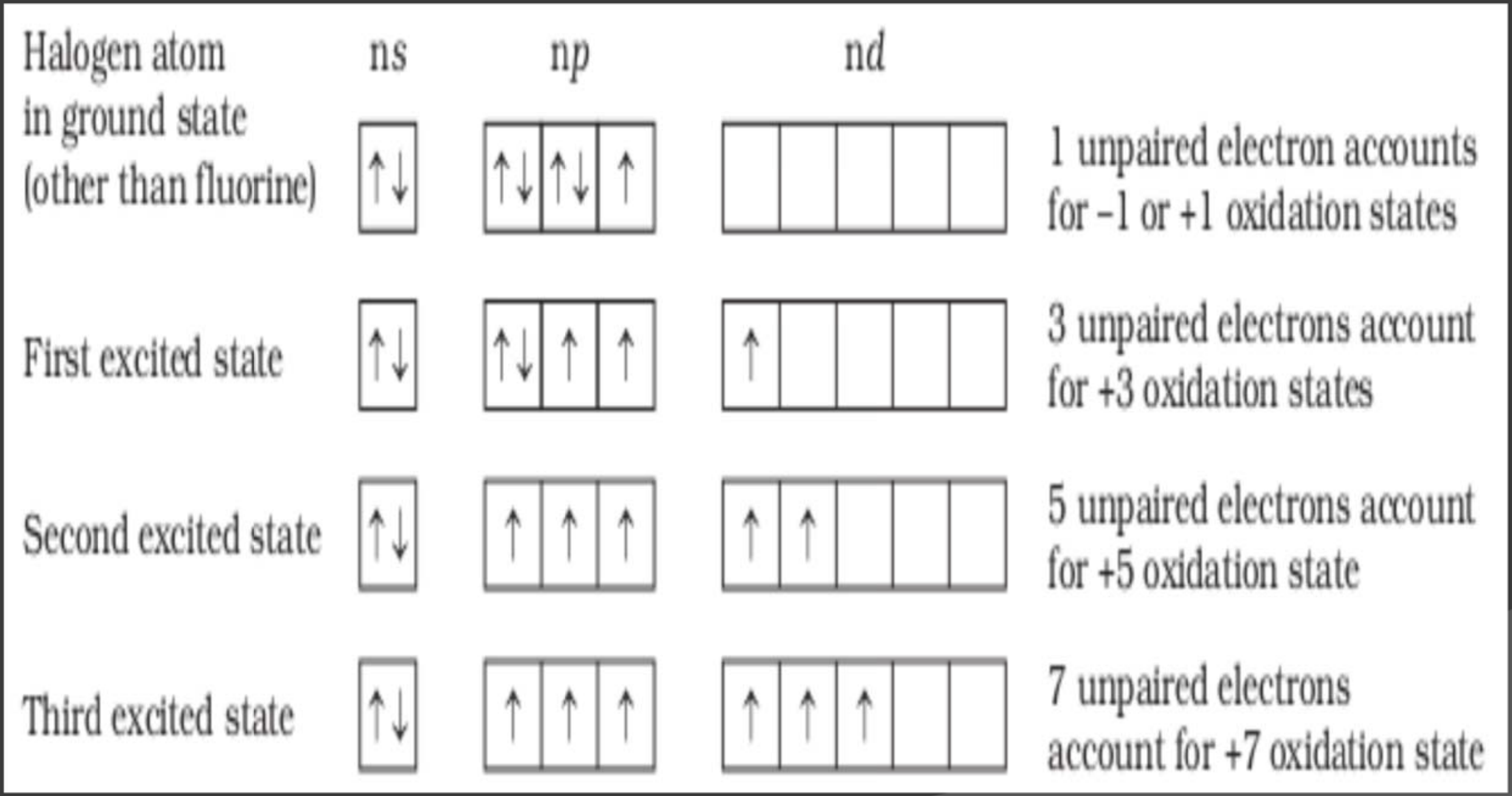
Electronic configuration



Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Fluorine	9	[He] $2s^2 2p^5$	17	2
Chlorine	17	[Ne] $3s^2 3p^5$	17	3
Bromine	35	[Ar] $3d^{10}\ 4s^2\ 4p^5$	17	4
Iodine	53	[Kr] $4d^{10}\ 5s^2\ 5p^5$	17	5
Astatine	85	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$	17	6

Oxidation states and trends in chemical reactivity

- All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states



Halogen atom	ns	np	nd	
in ground state (other than fluorine)	↑↓	↑↓ ↑↓ ↑		1 unpaired electron accounts for –1 or +1 oxidation states
First excited state	↑↓	↑↓ ↑ ↑	↑	3 unpaired electrons account for +3 oxidation states
Second excited state	↑↓	↑ ↑ ↑	↑ ↑	5 unpaired electrons account for +5 oxidation state
Third excited state	↑↓	↑ ↑ ↑	↑ ↑ ↑	7 unpaired electrons account for +7 oxidation state

reactivity

- The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.
  F2 + 2X– → 2F– + X2 (X = Cl, Br or I)
  Cl2 + 2X– → 2Cl– + X2 (X = Br or I)
  Br2 + 2I– → 2Br– + I2

Reaction with metals and non - metals

- Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.
  $Mg (s) + Br_2 (l) \rightarrow MgBr_2 (s)$
- The ionic character of the halides decreases in the order MF > MCl > MBr > MI

Reaction with hydrogen

- Reactivity towards hydrogen: They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids

.

Reactivity towards oxygen:

- Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF2 and O2F2. However, only OF2 is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents

oxides

- Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones.
- Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising

oxides

- The bromine oxides, Br_2O, BrO_2 , BrO_3 are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents.
- The iodine oxides, I_2O_4 , I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

- Reactivity of halogens towards other halogens:
- Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX ′ , XX3′, XX5′
- and XX7′ where X is a larger size halogen and X’ is smaller size halogen.

fluorine is anomalous in many properties

- ionisation enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens.
- Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected.
- The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond

Chlorine

- Chlorine was discovered in 1774 by Scheele by the action of HCl on MnO_2.
- In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, chloros = greenish yellow

Group 16 Elements

- . **Oxygen family: Group 16 of periodic table consists of five elements –**

  oxygen (O),

  sulphur (S),

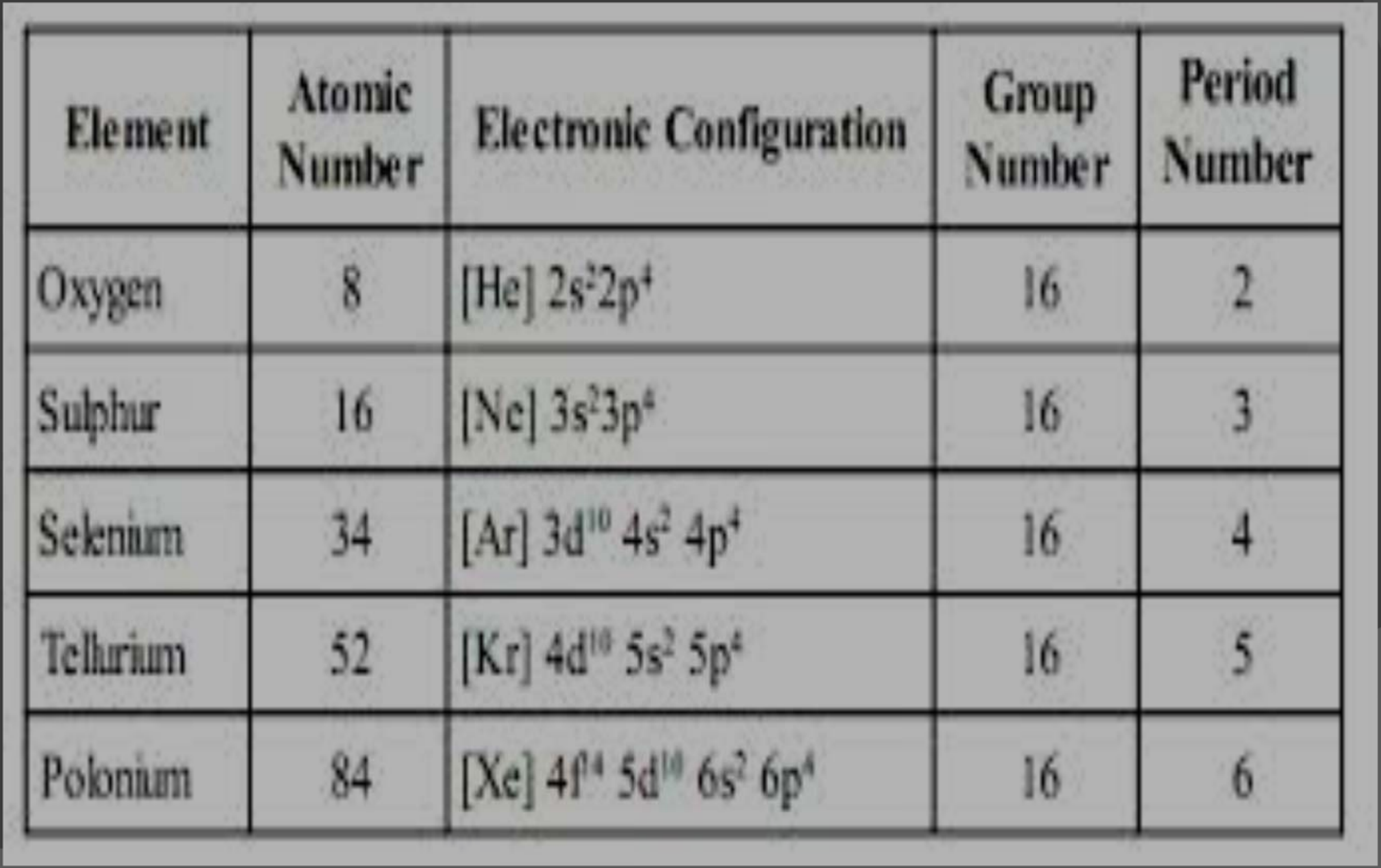
  selenium (Se),

  tellurium (Te) and

  polonium (Po).

Their general electronic configuration is ns2np4.

Electronic configuration



Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Oxygen	8	[He] $2s^2 2p^4$	16	2
Sulphur	16	[Ne] $3s^2 3p^4$	16	3
Selenium	34	[Ar] $3d^{10}\ 4s^2\ 4p^4$	16	4
Tellurium	52	[Kr] $4d^{10}\ 5s^2\ 5p^4$	16	5
Polonium	84	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$	16	6

general periodic trends:

Periodic properties	Trends
Atomic Radii (the radius of the atom)	increases
Electronegativity:(the atom's ability of attracting electrons)	Decreases down the group
Ionization Enthalpy (the amount of energy required to remove an electron from the atom in it's gaseous phase)	decreases
Electron Affinity (ability of the atom to accept an electron)	decreases
Melting Point (amount of energy required to break bonds to change a solid phase substance to a liquid phase)	increases going down the group
Boiling Point (amount of energy required to break bonds to change a liquid phase substance to a gas)	increases going down the group

Oxidation state

- Their general electronic configuration is ns2np4

The most common oxidation state is – 2.

The most common oxidation state for the chalcogens are −2, +2, +4, and +6.

Chemical properties

Reaction with air:

- $S + O_2 \rightarrow SO_2$

with acid[only oxidizing acids]

- $s + 6hno_3 \rightarrow h_2so_4 + 6no_2 + 2h_2o$

With alkali

- $3S + 6\,NaOH \rightarrow Na_2SO_3 + 2$

reactions

with non - metals

- $2S + C \rightarrow CS_2$
- $S + H_2 \rightarrow H_2S$
- $S + 3F_2 \rightarrow SF_6$

reactivity

- **1.** The **metallic character** increases as we descend the group. Oxygen and sulphur are typical nonmetals. Selenium (Se) and Te are metalloids and are semiconductors. Polonium is a metal.

  2. Tendency to form **multiple bond** decreases down the group. Example O=C=O is stable, S=C=C is moderately stable, Se=C=Se

Formation of Hydrides

All the elements of group 16 form hydrides of the type H2M (where M= O, S, Se, Te or Po).

The stability of hydrides decreases as we go down the group.

Except H2O, all other hydrides are poisonous foul smelling gases.

Their acidic character and reducing nature increases down the group. [less energy to break M – H bond]

All these hydrides have angular structure and the central atom is in sp3 hybridised.

H – M – H Bond angle decreases.

Formation of Halides

Element of group 16 form a large number of halides. The compounds of oxygen with fluorine are called oxyfluorides because fluorine is more electronegative than oxygen (example OF2).

The main types of **halides** are
1. Monohalides of the type M2X2
2. Dihalides of the type MX2
3. Tetrahalides of the type MX4
4. Hexahalides of the type MX6

Formation Of Oxides

Group 16 elements mainly form three types of oxides.

1. Monoxides: Except Selenium (Se), all other elements of the group form monoxides of the type MO (Example SO)

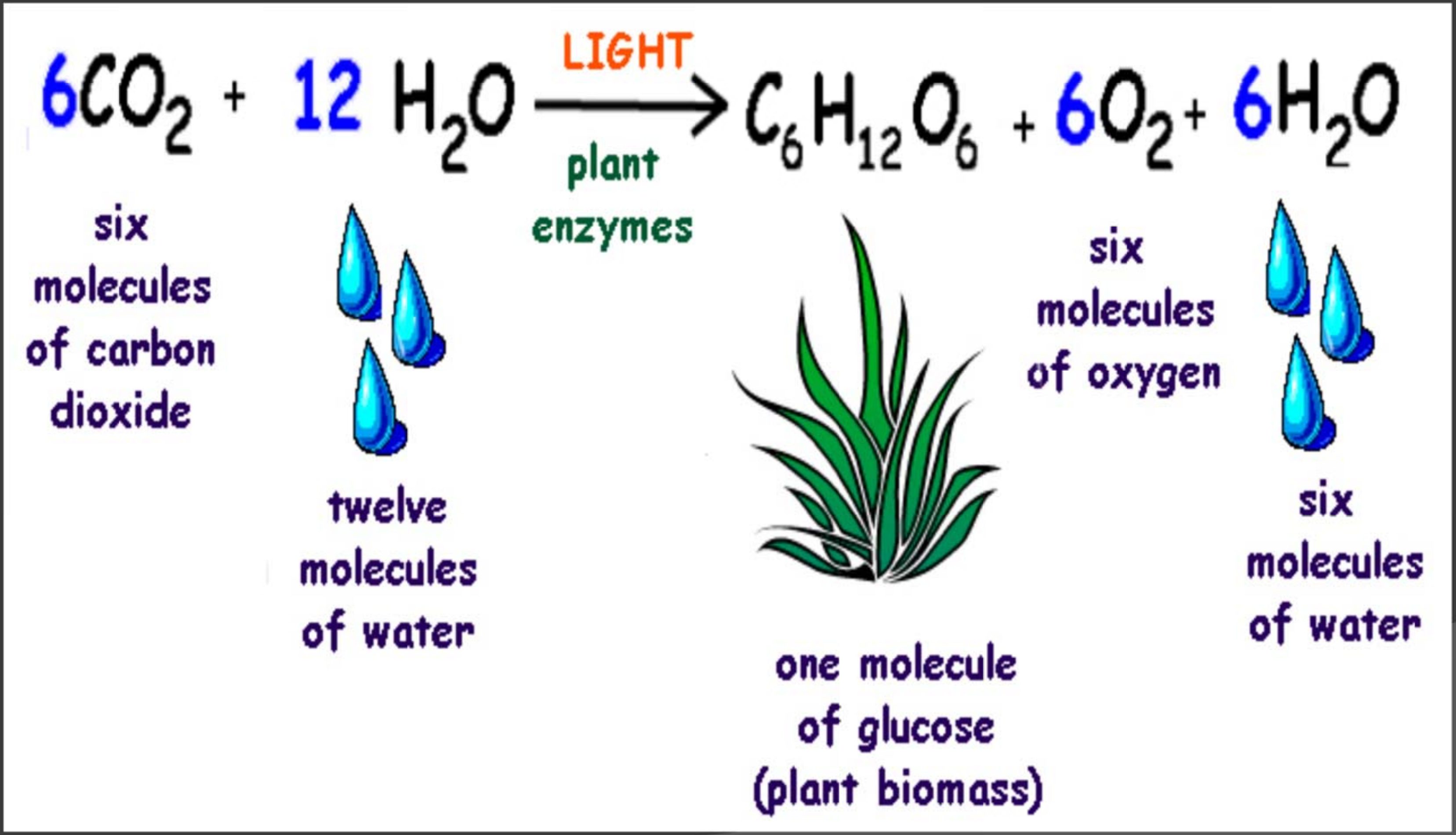
2. Dioxides: All the elements of group 16 form dioxides of the type MO2 (Example SO2)

3. Trioxides: All the elements of the group

Anomalous behaviour of oxygen

- O is gas all are solids.
- O diatomic others poly atomic.
- O2is paramagnetic others diamagnetic.
- Forms H bonds in hydrides, alcohols and carboxylic acids.
- forms p∏ - p∏ multiple bonds.
- oxidation states -2 and +2 only with F others +2 and +6.
- Forms ionic compounds.

dioxygen


$6CO_2 + 12\,H_2O \xrightarrow[\text{plant enzymes}]{\text{LIGHT}} C_6H_{12}O_6 + 6O_2 + 6H_2O$
six molecules of carbon dioxide
twelve molecules of water
one molecule of glucose (plant biomass)
six molecules of oxygen
six molecules of water

Preparation of o2

thermal decomposition of oxygen rich compounds

Potassium chlorate will readily decompose if heated in contact with a catalyst, typically manganese (IV) dioxide (MnO_2) .

$$2\,KClO_3\overset{\triangle}{(s)} \rightarrow 3\,O_2(g) + 2KCl(s)$$

△

$$2\,KNO_3 \rightarrow 2\,KNO_2 + O_2$$

oxides

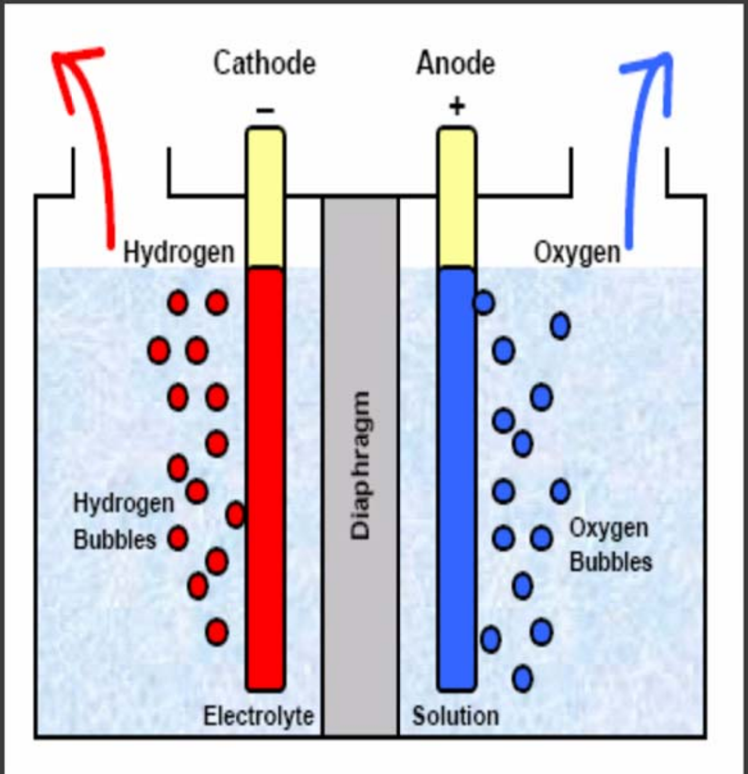
- **Preparation of oxygen using hydrogen peroxide**

The decomposition of hydrogen peroxide using manganese dioxide as a catalyst also results in the production of oxygen gas.

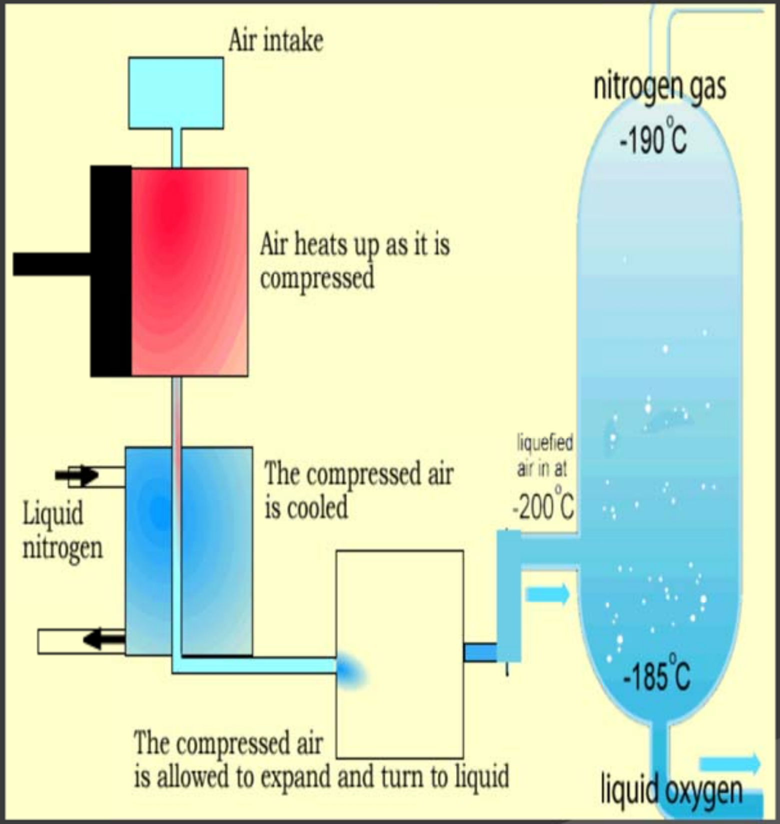
$$2\ H_2O_2 ==> 2\ H_2O + O_2$$

- $2\ BaO_2 ==> 2\ BaO + O_2$
- $6\ MnO_2 ==> Mn_3O_4 + O_2$

Manufacture of oxygen



Standard Electrolysis



- 1.electrolysis of

- 2.Fractional

properties

- Oxygen is a colourless gas, without smell or taste,
- is slightly heavier than air,
- is sparingly soluble in water,
- is difficult to liquefy, boiling point 90.2K, and the liquid is pale blue in colour and is appreciably magnetic.
- At still lower temperatures, light-blue solid oxygen is obtained, which has a melting point of 54.4K.

reactions

- With metals

Potassium, sodium, lithium, calcium and magnesium
react with oxygen and burn in air.

$4Na(s) + O2(g) \rightarrow 2Na2O(s)$

- $2Ca(s) + O2(g) \rightarrow 2CaO(s)$

Metals in the reactivity series from aluminium to copper
react with oxygen in the air to form the

reactions

- When carbon reacts with oxygen, carbon dioxide is formed along with production of heat.

$$\underset{Carbon}{C(s)} + \underset{Oxygen}{O_2} \longrightarrow \underset{Carbon\ dioxide}{CO_2(g)} + Heat$$

When carbon is burnt in insufficient supply of air, it forms carbon monoxide. Carbon monoxide is a toxic substance. Inhaling of carb

$$\underset{Carbon}{2C(s)} + \underset{Oxygen(insufficient)}{O_2} \longrightarrow \underset{Carbon\ monoxide}{CO(g)} + Heat$$

reactions

- Sulphur gives sulphur dioxide on reaction with oxygen. Sulphur catches fire when exposed to air.

$$\underset{\text{Sulphur}}{S(s)} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Sulphur dioxide}}{SO_2(g)}$$

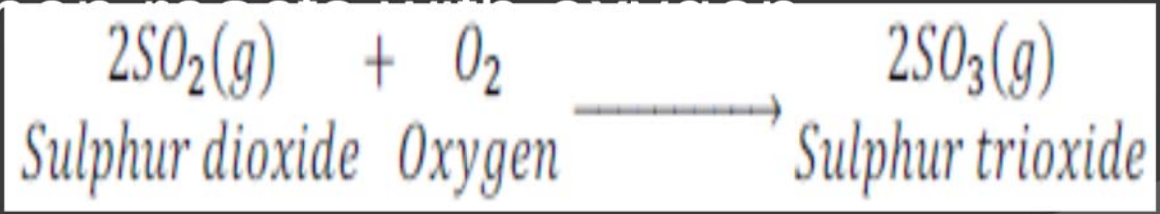
- (3) When hydrogen reacts with oxygen it giv

$$\underset{\text{Hydrogen}}{2H_2} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Water}}{2H_2O}$$

- With ammonia :react with oxygen in excess air, and platinum catalyst to form nitrogen monoxide

$$4NH3(g) + 5O2(g) \rightarrow 4NO(g) + 6H2O(l)$$

Sulphur dioxide gives sulphur trioxide wh



$$\underset{\text{Sulphur dioxide}}{2SO_2(g)} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Sulphur trioxide}}{2SO_3(g)}$$

reactions

- Reacts with metal sulphides forming metal oxides and sulphur dioxide.
- Reacts with hydrocarbons forming carbon dioxide and water.

uses

- Oxygen is essential for life and it takes part in processes of combustion, its biological functions in respiration make it important. Oxygen is sparingly soluble in water, but the small quantity of dissolved oxygen in is essential to the life of fish.
- Oxygen gas is used with hydrogen or coal gas in blowpipes and with acetylene in the oxy-acetylene torch for welding and cutting metals.
- Oxygen gas is also used in a number

Types of oxides : basic

- Reaction of sodium oxide with water: Sodium oxide gives sodium hydroxide when reacts with water.

$$\underset{\text{Sodium oxide}}{Na_2O} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Sodium hydroxie}}{2NaOH}$$

Sodium hydroxide is a strong base.

- (2) Reaction of magnesium oxide with water: Magnesium c

$$\underset{\text{Magnesium oxide}}{MgO} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Magnesium hydroxie}}{Mg(OH)_2}$$

- (3) Reaction of potassium oxide with water: Potassium oxide giv water.

$$\underset{\text{Potassium oxide}}{K_2O} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Potassium hydroxie}}{2KOH}$$

Types of oxides : acidic

- Examples include:
- Carbon dioxide which reacts with water to produce carbonic acid.

$$CO2 + H2O \rightarrow H2CO3$$

- Sulfur dioxide, which does not form the non-existent sulfuric acid.

$$SO3 + H2O + \rightarrow H2SO4$$

- Phosphorus pentoxide (P2O5) reacts with water and forms phosphoric acid (H3PO4)

Types of oxides:amphoteric

- Aluminium oxide and zinc oxide are insoluble in water. Aluminium oxide and zinc oxide are amphoteric in nature.
- An amphoteric substance shows both acidic and basic character. It reacts with base like acid and reacts with acid like a base.

$$\underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Hydrochloric acid}}{2HCl} \longrightarrow \underset{\text{Zinc chloride}}{ZnCl_2} + \underset{\text{Water}}{H_2O}$$

- When zinc oxide reacts with sodium hydroxide, it behaves like an acid. In this reaction, sodium zicate and water are formed.

$$\underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Sodium zincate}}{2Na_2ZnO_2} + \underset{\text{Water}}{H_2O}$$

Types of oxides : amphoteric

- In similar way aluminium oxide behaves like a base when reacts with an acid and behaves like an acid when reacts with a base.
- Aluminium oxide gives sodium aluminate along with water when reacts with sodium hydroxide.

$$\underset{\text{Alumium oxide}}{Al_2O_3} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Sodium aluminate}}{2NaAlO_2} + \underset{\text{Water}}{H_2O}$$

Alu

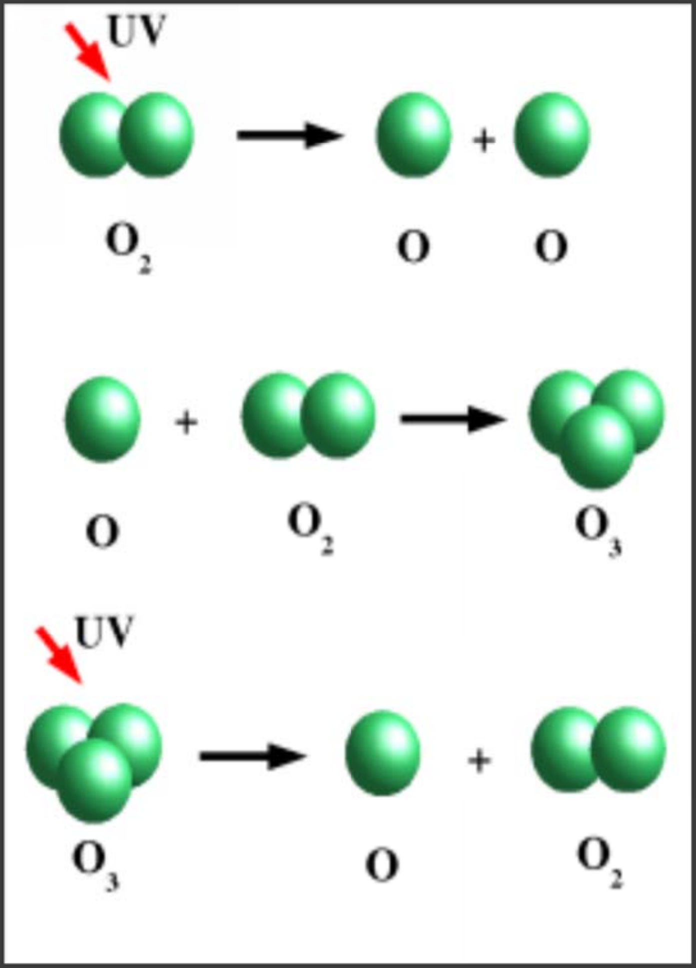
wh

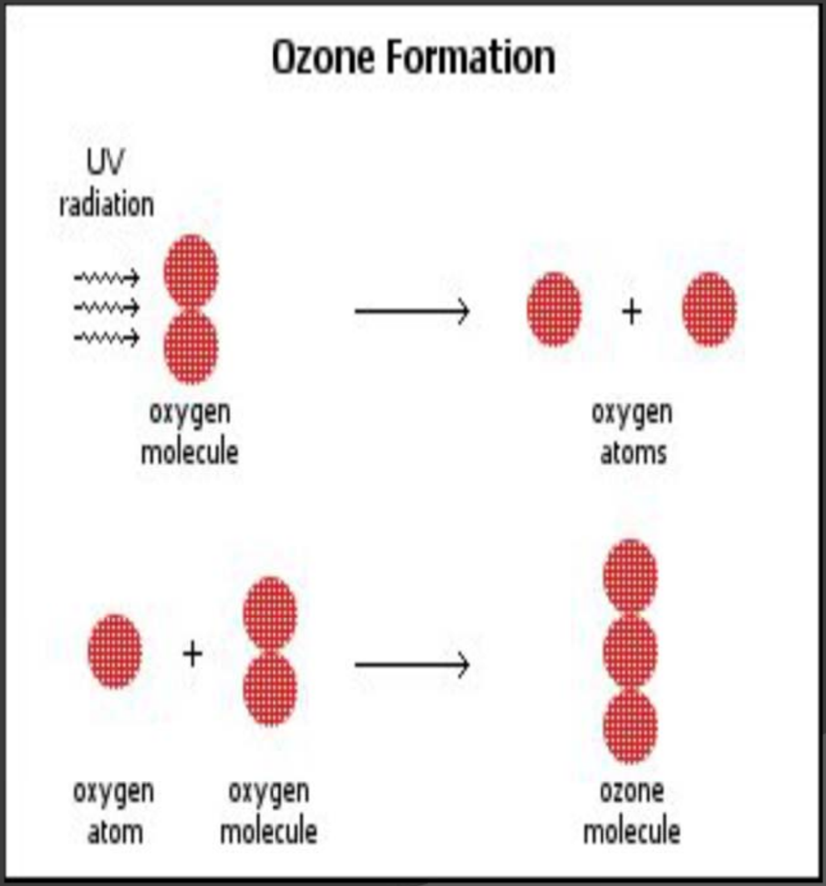
$$\underset{\text{Alumium oxide}}{Al_2O_3} + \underset{\text{Hydrochlorice acid}}{6HCl} \longrightarrow \underset{\text{Aluminium chloride}}{2AlCl_3} + \underset{\text{Water}}{H_2O}$$

ozone

- **Ozone** (**O3**), or **trioxygen**, is a triatomic molecule, consisting of three oxygen atom.
- It is an allotrope of oxygen that is much less stable than the diatomic allotrope (O2), breaking down in the lower atmosphere to normal dioxygen.
- Ozone is formed from dioxygen by the action of ultraviolet light and also atmospheric electrical discharges, and is present in low concentrations throughout the Earth's atmosphere.
- In total, ozone makes up only 0.6 parts per million of the atmosphere.

Formation of ozone





ozone

- Ozone is a pale blue gas, slightly soluble in water and much more soluble in inert non-polar solvents such as carbon tetrachloride or fluorocarbons,
- where it forms a blue solution. At 161 K (−112 °C; −170 °F), it condenses to form a dark blue liquid.
- At temperatures below 80 K (−193.2 °C; −315.7 °F), it forms a violet-black solid.

- Ozone is a powerful oxidizing agent, far stronger than O_2.
- It is also unstable at high concentrations, decaying to ordinary diatomic oxygen (with a half-life of about half an hour in atmospheric conditions):

$$2\,O_3 \rightarrow 3\,O_2$$

- Ozone also oxidizes nitric oxide to nitrogen dioxide:

$$NO + O_3 \rightarrow NO_2 + O_2$$

reactions

- Reducing action with BaO_2 and H_2O_2

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

$$\longrightarrow$$

$$H_2O_2 \quad + \quad O_3 \qquad\qquad H_2O$$
$$+ \; 2O_2$$

$$\longrightarrow$$

- Reacts with KI to liberate iodine

uses

- Ozone is a reagent in many organic reactions in the laboratory and in industry.
- Ozonolysis is the cleavage of an alkene to carbonyl compounds.
- Many hospitals around the world use large ozone generators to decontaminate operating rooms between surgeries. The rooms are cleaned and then sealed airtight before being filled with ozone which effectively

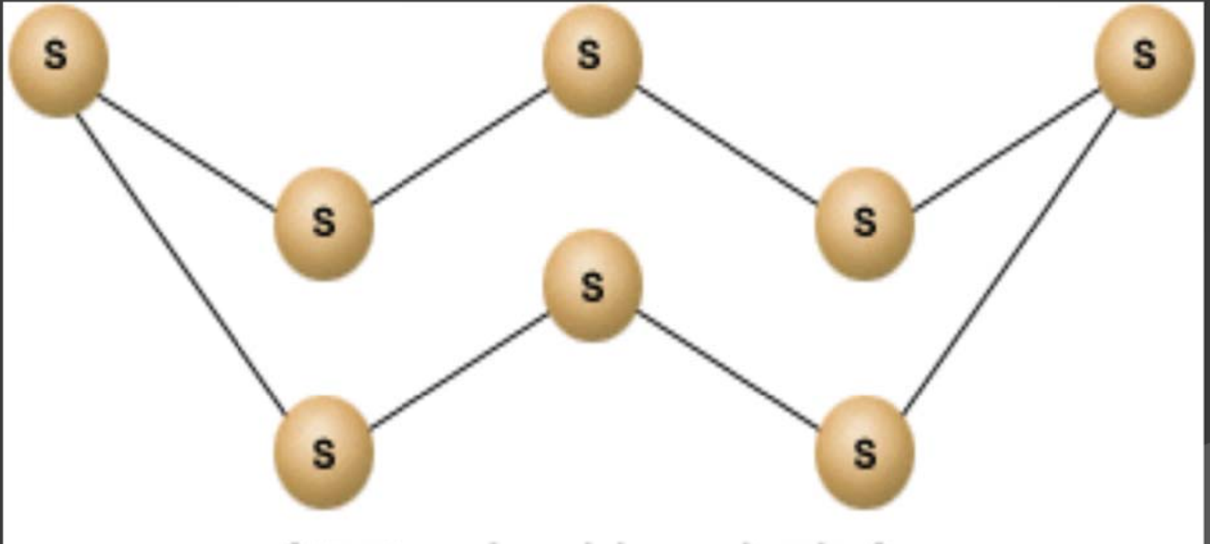
sulphur

1) sulphides : pyrites : Cu_2S , FeS
Blende ZnS ,
cinnabar HgS and
galena PbS

2) Sulphates : gypsum $CaSO_4 . 2H_2O$
epsum $MgSO_4 . 7H_2O$
burytes $BaSO_4$

allotropes

- Rhombic 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.



Structure of a sulphur molecule, S_8

Allotropes

- Monoclinic sulphur (β-sulphur) cyclo 6
- Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS2

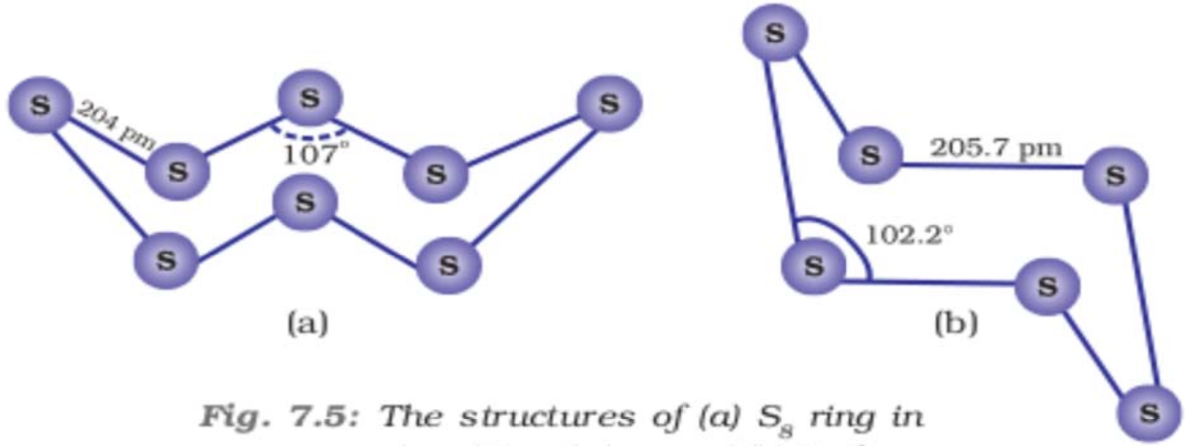
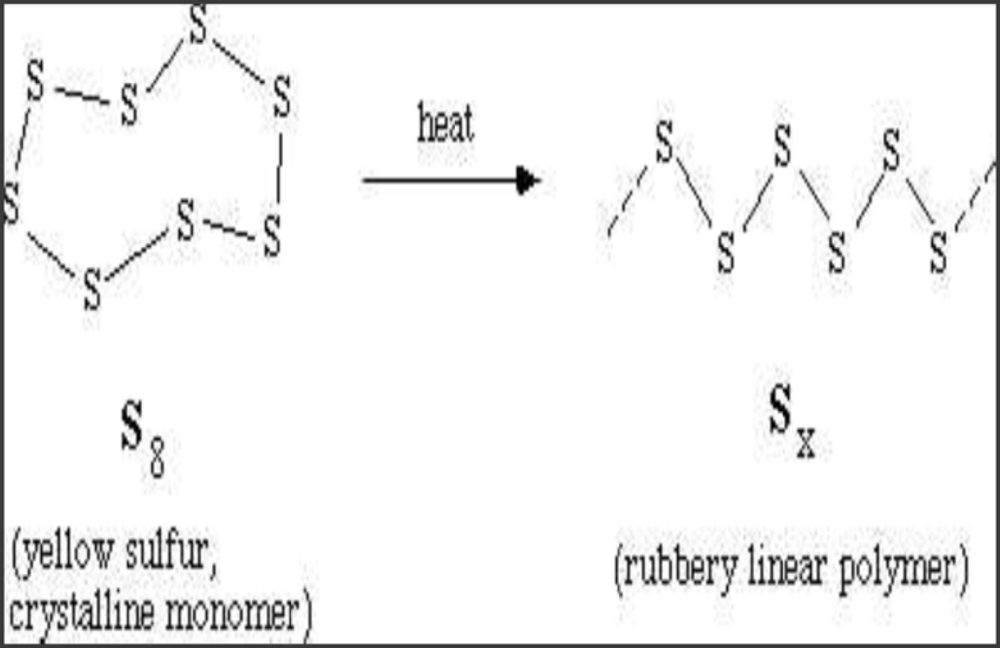


Fig. 7.5: The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

allotropes

- Plastic or γ - sulphur



allotropes

- Milk of sulphur

Prepared by boiling of sulphur with milk of lime, a mixture of Ca penta sulphide and thiosulphate are formed which on treatment with HCl give milk of sulphur

→

$3Ca(OH)_2 + 12S + 6HCl$

$3CaCl_2 + 12S + 2H_2O$

- Colloidal sulphur
  - Thiosulfate react with dilute acids to produce sulfur, sulfur dioxide and water.
  - $Na_2S_2O_3 + 2\ HCl \rightarrow 2\ NaCl$

    $+ S + SO_2 + H_2O$

Action of H_2S → on SO_2

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

so2

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

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

- Industrially, it is produced as a by-product of the roasting of sulphide ores.
$4FeS_2\ (s) + 11O_2\ (g) \rightarrow 2Fe_2O_3\ (s) + 8SO_2\ (g)$

- Action of sulphuric acid on Cu turnings

properties

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

properties

- Treatment of basic solutions with sulfur dioxide affords sulfite salts:

$$SO2 + 2\ NaOH \rightarrow Na2SO3 + H2O$$

It is oxidized by halogens to give the sulfuryl halides, such as sulfuryl chloride :

$$SO2 + Cl2 \rightarrow SO2Cl2$$

properties

- With iodine

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

With dichromate

Potassium dichromate paper can be used to test for sulfur dioxide, as → it turns distinctively from orange to green

- $K_2Cr_2O_7(aq) + 3SO_2(g) + H_2SO_4(aq)$ $Cr_2(SO_4)_3(aq) +$ $K_2SO_4(aq)$

properties

- When moist, sulphur dioxide behaves as a reducing agent. For example,
- it converts iron(III) ions to iron(II) ions

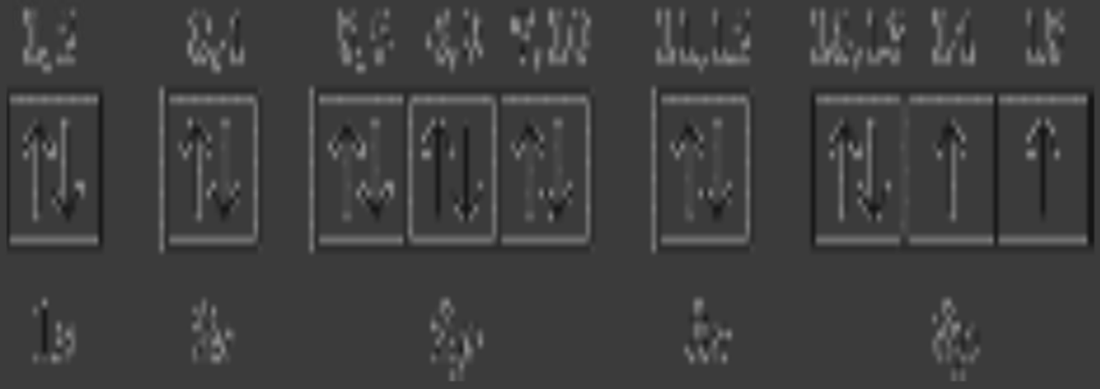
$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

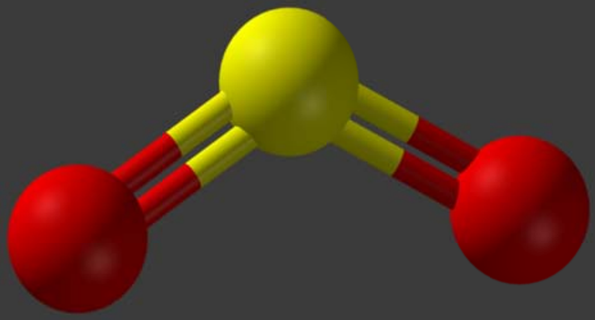
- and decolourises acidified potassium permanganate(VII) solution;

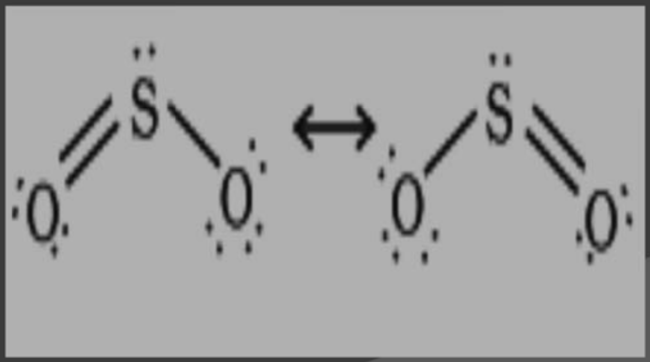
this reaction is a convenient test for the gas.

Structure
sp2 hybrized

- Sp2 hybridization in sulphur







uses

- Sulphur dioxide is a reducing agent and is used for bleaching and as a fumigant and food preservative.
- Large quantities of sulphur dioxide are used in the contact process for the manufacture of sulphuric acid.
- Sulphur dioxide is used in bleaching wool or straw, and as a disinfectant.
- Liquid sulphur dioxide has been used in purifying petroleum products

Contact process

- The process can be divided into five stages:
- combining of sulfur and oxygen;
- purifying sulfur dioxide in the purification unit;
- adding excess of oxygen to sulfur dioxide in presence of catalyst vanadium oxide;
- sulfur trioxide formed is added to sulfuric acid which gives rise to oleum (disulfuric

Contact process

Sulphur or iron pyrites burnt in air

$$\mathrm{S(s) + O2(g) \rightarrow SO2\ (g)}$$

- Sulfur dioxide and oxygen then react as follows:

$$\mathrm{2\ SO2}(g) + \mathrm{O2}(g) \rightleftharpoons \mathrm{2\ SO3}(g)$$

- Hot sulfur trioxide passes through the heat exchanger and is dissolved in concentrated H2SO4 in the absorption

Contact process

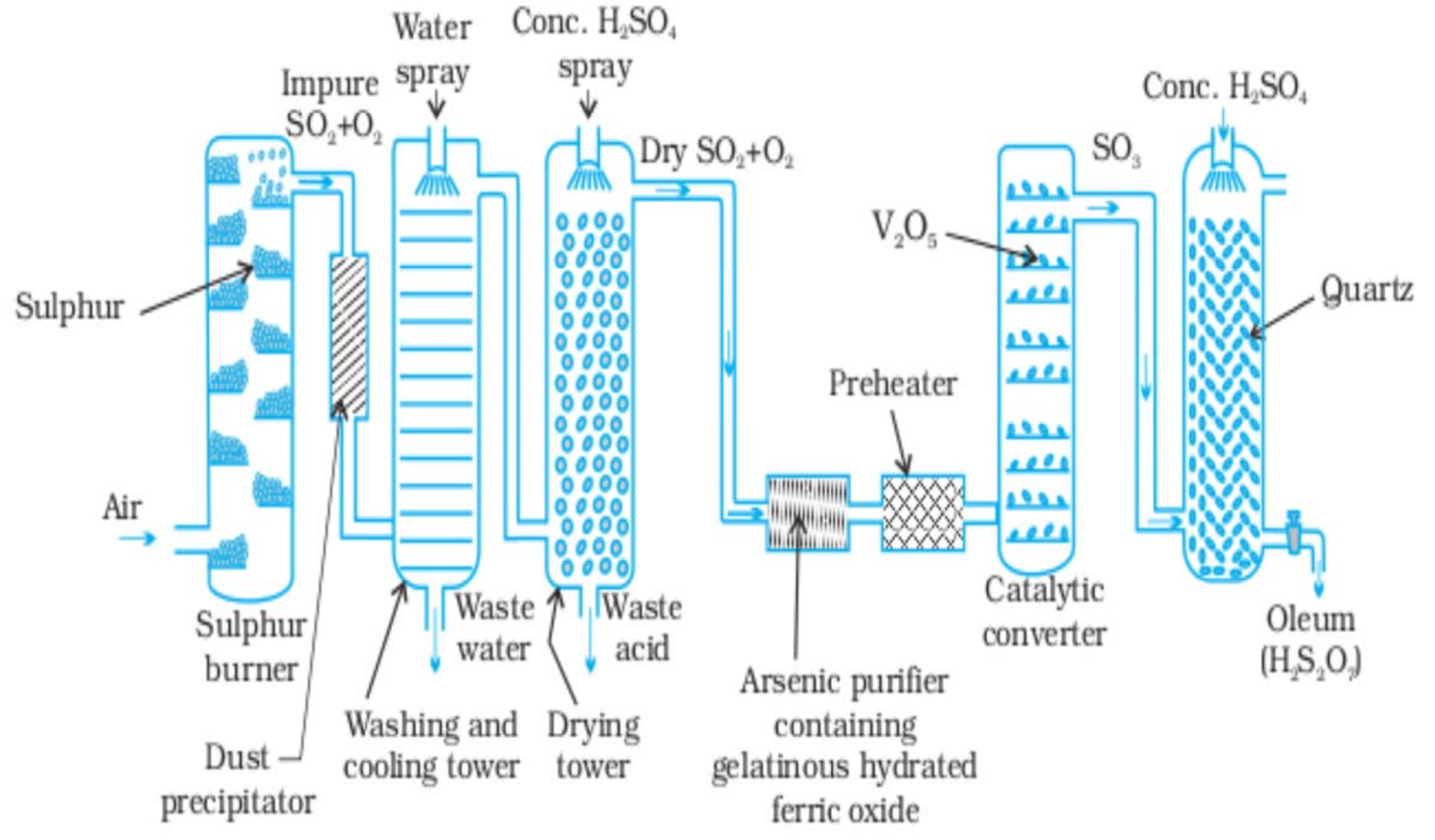


Fig. 7.7: Flow diagram for the manufacture of sulphuric acid

Lead chamber process

- Mixture of SO_2 , NO and air is treated to steam to obtain sulphuric acid. NO ,nitric oxide acts as a catalyst.

$$2SO_2 + O_2(g) + 2H_2O \xrightarrow{NO} 2H_2SO_4$$

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.

reactions

- In aqueous solution, sulphuric acid ionises in two steps.
- $H2SO4(aq) + H2O(l) \rightarrow H3O+ (aq) + HSO4- (aq);$

  Ka1 = very large (Ka1>10)

$HSO4 (aq) + H2O(l) \rightarrow H3O+ (aq) + SO42- (aq) ;$

Ka2> = 1.2 × 10−2

Dehydrating agent

- Action on cane sugar

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

- Action on formic acid →

$HCOOH$ $CO + H_2O$

→

Action on alcohol

C_2H_5OH $C_2H_5OC_2H_5$ +
H_2O

Oxidising agent

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

3S + 2H2SO4(conc.) → 3SO2 + 2H2O

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

dilute acid reacts with metals liberating H2 gas.

Reaction with benzene

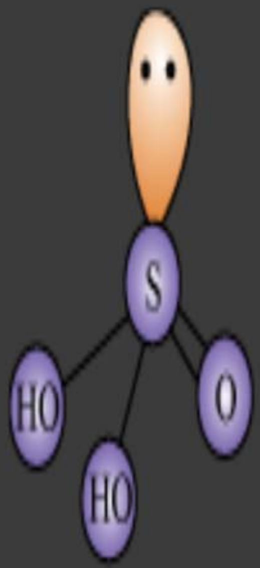
uses

- Sulphuric acid is a very important industrial chemical. 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

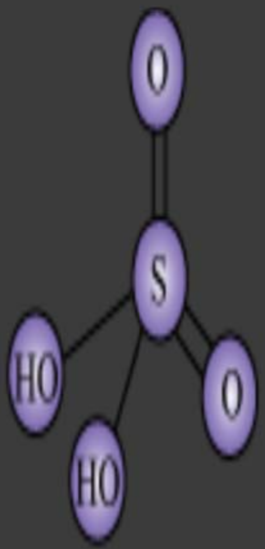
Oxyacids of sulphur

- Sulphoxylic acid H_2SO_2
- Sulphurous acid $H_2S_2O_2$,H_2SO_3 $H_2S_2O_4$, $H_2S_2O_5$
- sulphuric acid H_2SO_4, $H_2S_2O_3$,$H_2S_2O_7$
- peroxy sulphuric acid H_2SO_5, $H_2S_2O_8$.
- Thionic acid series : dithionic acid $H_2S_2O_6$ poly thionic acid $H_2S_nO_6$ (n = 3 to 6)

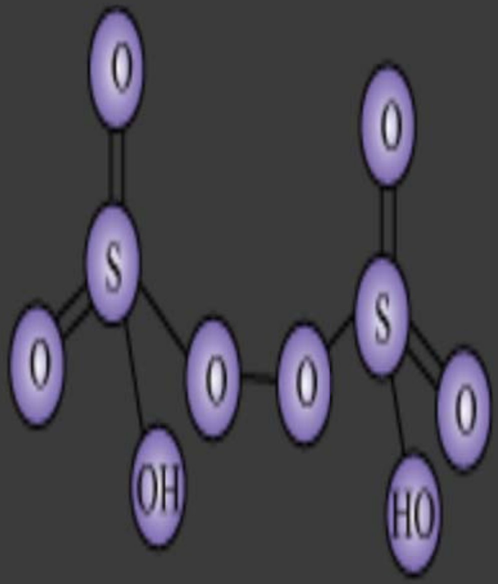
Oxyacids of sulphur



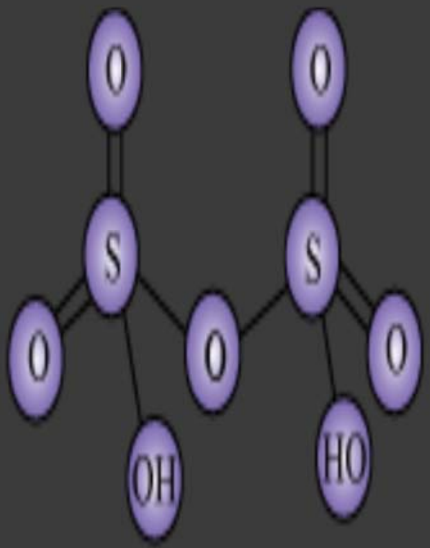
Sulphurous acid
(H_2SO_3)



Sulphuric acid
(H_2SO_4)



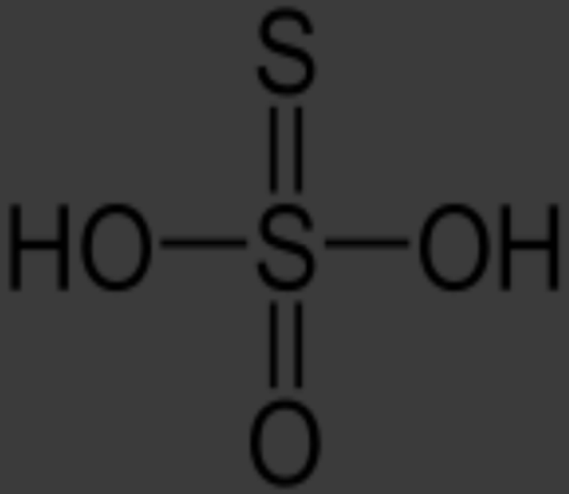
Peroxodisulphuric acid
($H_2S_2O_8$)



Pyrosulphuric acid (Oleum)
($H_2S_2O_7$)

Oxyacids of sulphur

- Thiosulphuric acid



- Polythionic acid