INTRODUCTION OF SULPHUR

Sulphur is the second member of VI-A group of the periodic table. Its atomic number is 16 and atomic mass is 32 a.m.u. In 1787 Lavoiser recognized it as an element.

OCCURRENCE OF SULPHUR:

Sulphur is non metal and makes up about 0.19% of the earth's crust. It is found in Free State in Mexico, USA, Japan and Newzealand.

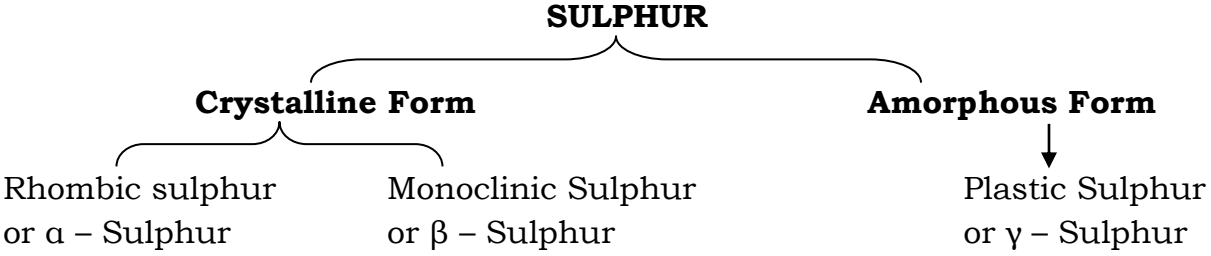
In combined state it is largely found as sulphides of Fe, Zn, Pb Cu and Hg also as sulphates of Mg, Ca and Ba e.g., FeS, ZnS, $MgSO_4$, $CaSO_4$ etc. Sulphur is an essential constituent of many organic substances such as protein, eggs, onion, garlic and mustard etc.

ALLOTROPIC FORMS OF SULPHUR

DEFINITION:

Different forms of one element due to different arrangement of atoms in crystal lattice which have same chemical properties but different physical properties are called Allotropic forms or Allotropes and the phenomenon is called "Allotropy".

The main Allotropic forms of sulphur and given below.



1. RHOMBIC SULPHUR OR ALPHA (α) – SULPHUR:

Properties:

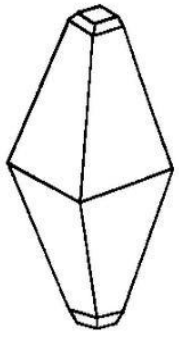
i. It is stable crystalline form of sulphur at ordinary temperature which exists up to 96°C.
ii. It is insoluble in water but soluble in carbon disulphide (CS_2), petroleum and benzene.
iii. It is of lemon yellow in color.
iv. Its melting point is 113°C and its density is 2,08 g/cm^3 at 20°C.

Preparation:

It is prepared by slow evaporation of solution of ordinary sulphur in carbon disulphide (CS_2)

Structure:

Rhombic sulphur consists of S_8 molecules in which eight atoms of sulphur are arranged in two planes to form octahedral puckered ring as shown in figure.



2. MONOCLINIC SULPHUR OR BETA(β) OR PRISMATIC SULPHUR:

Properties:

i. It is another crystalline form of sulphur.
ii. It is stable between 96°C to 119°C.
iii. It changes slowly to rhombic sulphur at ordinary temperature.
iv. It consists of dark yellow transparent needle like crystals.
v. It is soluble in CS_2 but insoluble in water.
vi. Its melting point is 119°C and density is 1.96 g/cm^3.

Preparation:

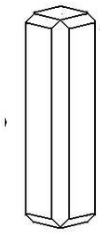
When rhombic sulphur is heated above 96°C then it is changed into monoclinic sulphur. The transformation of monoclinic sulphur to rhombic sulphur is reversible.

Rhombic sulphur ⟷ Monoclinic sulphur
(Below 96°C) (Above 96°C)

The temperature 96°C is called **transition temperature**.

Structure:

The crystal of monoclinic sulphur is long, thin and needle like in shape in figure. Its molecule also consists of eight atoms of sulphur (S_8) similar to rhombic sulphur.



3. PLASTIC SULPHUR OR GAMA (γ) – SULPHUR

Properties:

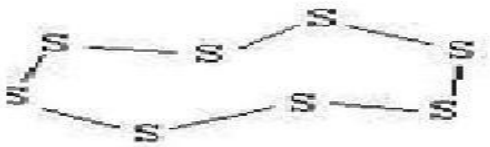
i. It is non crystalline form of sulphur.
ii. It is soft, sticky and rubber likes material.
iii. It is insoluble in CS_2.
iv. It is unstable form of sulphur and converted into rhombic sulphur on standing at room temperature.

Preparation:

When molten sulphur is heated up to its boiling point about 444.6°C and poured with thin stream into cold water then sulphur is changed into soft, sticky and rubber like material called plastic sulphur.

Structure:

It contains long chain of sulphur atoms in which S – atoms are arranged in zic – zag manner as shown in figure.

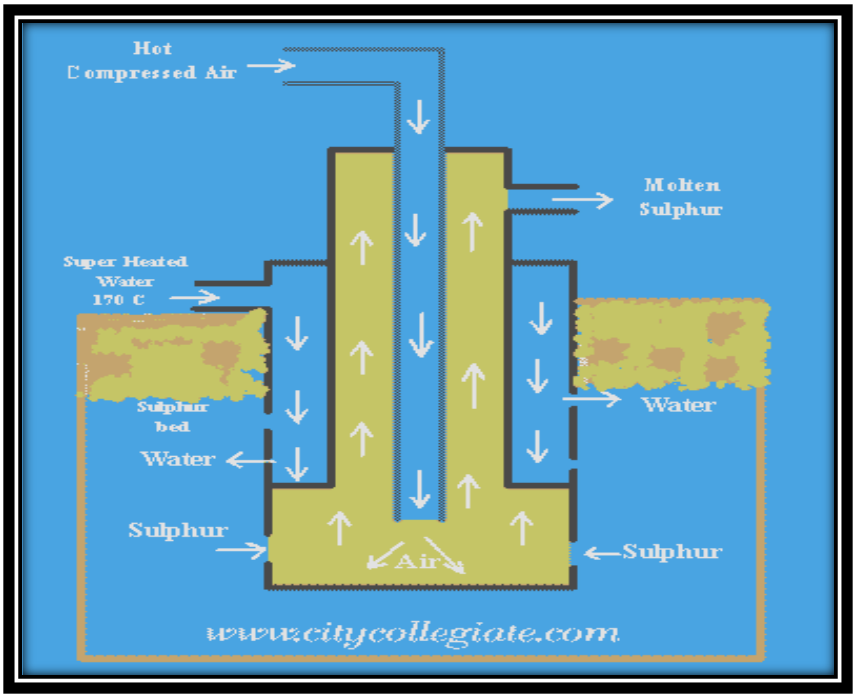


EXTRACTION OF SULPHUR BY HERMAN FRASCH PROCESS

An American engineer Herman Frasch gave a method to obtained sulphur from its underground deposits. In this method sulphur is melted the earth surface by introducing hot water and then molten sulphur is pumped at the surface of the earth.

PROCESS:

1. A hole or bore of about 30cm in diameter is made to the deposits of sulphur. Three concentric iron pipes of different diameters are introduced into the bore as shown in fugure. These pipes are about 20cm, 15cm and 10cm in diameter.
2. Through the outermost pipe, super heated water at about 140°C and 100 atmospheric pressure is forced down. It melts the sulphur beds and forms an emulsion.
3. Through the innermost pipe the hot compressed air at 15 atmospheric pressure is blown down. It forces the molten sulphur up through the middle pipe.
4. When molten sulphur reaches to the surface of the earth, it is collected in wooden tanks and allowed to solidify. The sulphur so obtained is about 99.5% pure.



PHYSICAL PROPERTIES:

1. Sulphur is a yellow solid.
2. It is insoluble in water but soluble in carbon disulphide (CS_2).
3. It is non metallic element.
4. It is bad conductor of electricity and heat.
5. Its boiling point is about 444°C.

CHEMICAL PROPERTIES:

1. Reaction With Metals:

Sulphur combines with many, metals directly to form their respective sulphides. Na, K may even reacts sulphur without much more heating, when both are in finely divided form.

i. $2Cu + S \xrightarrow{\Delta} Cu_2S$

ii. $Fe + S \xrightarrow{\Delta} FeS$

iii. $Zn + S \xrightarrow{\Delta} ZnS$

iv. $Pb + S \xrightarrow{\Delta} PbS$

v. $2Na + S \xrightarrow{\Delta} Na_2S$

2. Reactions With Nonmetals:

a. With Oxygen

$S + O_2 \xrightarrow{\text{ignition}} SO_2$

b. With Hydrogen

$H_2 + S \xrightarrow{600\text{-}650^\circ C} H_2S$

c. With Chlorine

$2S + Cl_2 \xrightarrow{\Delta} S_2Cl_2$

d. With Carbon

$C + 2S \xrightarrow{\text{electricity}} CS_2$

e. With Fluorine

$3F_2 + S \xrightarrow{\Delta} SF_6$

3. <u>Reaction With Concentrated Acid:</u>

Sulphur is readily oxidized when warmed with concentrated sulphuric acid to produce SO_2 gas and also with concentrated nitric acid to produce NO_2 gas.

i. $S + 2H_2SO_4 \xrightarrow{hot} 3SO_2 + 2H_2O$

ii. $S + 6HNO_3 \xrightarrow{hot} H_2SO_4 + 6NO_2 + 2H_2O$

USES OF SULPHUR:

1. It is used in the manufacture of sulphuric acid, sulphur dioxide and carbon disulphide.
2. It is used for the manufacture of calcium and magnesium hydrogen sulphate and also used for bleaching wood pulp.
3. Sulphur is used in vulcanizing rubber.
4. It is used for disinfecting houses and for dirty vines.
5. It also helps to kill fungi and insects.

SULPHURIC ACID (H_2SO_4)

On large scale sulphuric acid is prepared by two processes.

1. Lead chamber process
2. Contact process

In Pakistan it is manufactured by contact process.

CONTACT PROCESS:

This process involves the following steps.

1ST STEP: PREPARATION OF SO_2 GAS:

In the 1st step sulphur or iron pyrite (FeS_2) is burnt with air in pyrite burner to produce sulphur dioxide gas (SO_2).

i. $S + O_2 \longrightarrow SO_2$

ii. $4FeS_2 + 11O_2 \longrightarrow 2FeS_3 + 8SO_2$

2ND STEP: PURIFICATION OF SO_2 GAS:

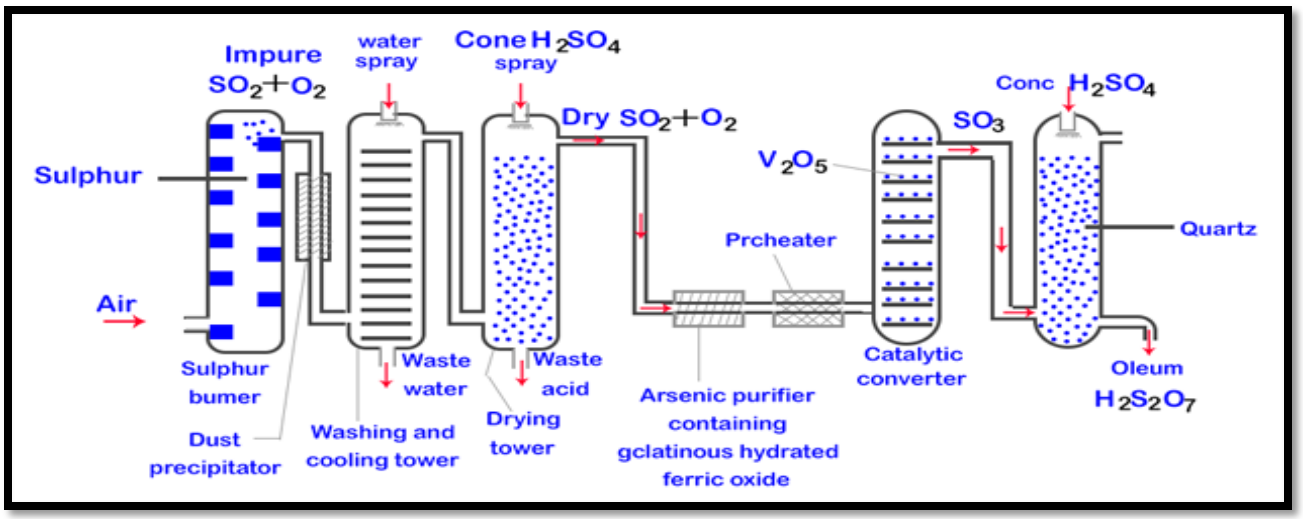
SO_2 gas obtained from pyrite burner contains many impurities such as a sulphur, dust particles, arsenic oxides (As_2O_3) etc which make the catalyst ineffective. To remove these impurities, mixture of SO_2 and air is passed through special dust filter chamber, washing tower and then drying tower as shown in figure.

3RD STEP: PREPARATION OF SO_3 GAS:

Mixture of purified SO_2 gas and air is heated at 450°C under 1.5 – 1.7 atmospheric pressure in the presence of vanadium pentaoxide (V_2O_5) or platinum (Pt) as catalyst in contact tower. In this tower SO_2 gas is oxidized to SO_3 gas.

$$2SO_2 + 3O_2 \longleftrightarrow 2SO_3 \quad \Delta H\ (-ve)$$

This reaction is slow, reversible and exothermic.



4TH STEP: PREPARATION OF OLEUM ($H_2S_2O_7$):

Sulphur trioxide gas (SO_3) produced in contact tower is absorbed in 97% sulphuric acid and in absorption tower to form very thick liquid called oleum or pyrosulphuric acid.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

5TH STEP: PREPARATION OF H_2SO_4:

The oleum or pyrosulphuric acid is dissolved in calculated amount of water to obtained sulphuric acid of any desired concentration.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

100% pure sulphuric acid can be obtained by this process.

PHYSICAL PROPERTIES OF H_2SO_4:

1. Pure sulphuric acid is a colorless, odorless and viscous oily liquid often known as oil of vitriol.
2. When concentrated sulphuric acid is mixed with water, it produces large amount of heat energy.
3. Its melting point is 10.5°C, boiling point is 338°C and specific gravity is 1.84.

CHEMICAL PROPERTIES OF H_2SO_4:

Sulphuric acid is very reactive compound. It reacts in three different ways.

i. As an acid
ii. As an oxidizing agent
iii. As a drying or dehydrating agent.

i. Acidic Properties Or H_2SO_4 As An Acid:

a. Sulphuric acid is strong diprotic acid as one molecule of H_2SO_4 produces two hydrogen ions ($2H^+$) in aqueous solution.

$$H_2SO_4 \longleftrightarrow 2H^+ + SO_4^{-2}$$

Or $$H_2SO_4 + 2H_2O \longleftrightarrow 2H_3O^+ + SO_4^{-2}$$

b. It reacts with alkalis to form salt and water. It is dibasic acid as one molecule of H_2SO_4 neutralizes two molecules of bases.

For Example:

$$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$$
$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

c. It reacts with metal carbonates and bicarbonates to produce corresponding salts, CO_2 gas and H_2O.

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + CO_2 + H_2O$$
$$H_2SO_4 + NaHCO_3 \longrightarrow Na_2SO_4 + CO_2 + H_2O$$

ii. Oxidizing Properties Or H_2SO_4 As An Oxidizing Agent:

Concentrated as well as diluted sulphuric acid acts as strong oxidizing agent. It oxidizes many metals or non metals when they are heated with it. The degree of oxidation depends upon.

a. Concentration of H_2SO_4
b. Temperature
c. Nature of reducing substances.

A. Reaction With Metals:

i. $Cu + 2H_2SO_4 \xrightarrow{cold} CuSO_4 + SO_2 + 2H_2O$
ii. $Zn + H_2SO_4 \xrightarrow{hot} ZnSO_4 + H_2$
iii. $Pb + 2H_2SO_4 \xrightarrow{hot} PbSO_4 + SO_2 + 2H_2O$
iv. $2Al + 3H_2SO_{4(dil)} \xrightarrow{hot} Al_2(SO_4)_3 + 3H_2$
v. $2Al + 6H_2SO_{4(conc)} \xrightarrow{hot} Al_2(SO_4)_3 + 3SO_2 + 2H_2O$

B. Reaction With Non Metals:

i. $C + 2H_2SO_4 \xrightarrow{hot} CO_2 + SO_2 + 2H_2O$

ii. $S + 2H_2SO_4 \xrightarrow{hot} 3SO_2 + 2H_2O$

iii. $2P + 3H_2SO_4 \xrightarrow{hot} 2H_3PO_4 + 3SO_2$

iii. Dehydrating Properties Or H_2SO_4 As A Dehydrating Agent:

"That substance which can remove the water molecules from other compounds during chemical reaction is known as dehydrating agent."

Sulphuric acid has strong attraction towards water hence it extracts water molecules from other compounds. Thus it acts as dehydrating and drying agent.

i. $C_{12}H_{22}O_{11} + H_2SO_{4(conc)} \longrightarrow 12C + 11H_2O$

ii. $HCOOH + H_2SO_{4(conc)} \longrightarrow CO + H_2O$

iii. $CuSO_4.5H_2O + H_2SO_{4(conc)} \longrightarrow CuSO_4 + 5H_2O$

USES OF SULPHURIC ACID(H_2SO_4):

i. It is used in the manufacture of fertilizers specially in ammonium sulphate $[(NH_4)_2SO_4]$ and calcium super phosphate$[Ca(H_2PO_4)_2]$
ii. It is very useful chemical in dyeing, paper, iron and steel, leather and textile industries.
iii. It is used in the manufacture of rayon, plastics detergents, paints and pigments.
iv. It is used for refining of petroleum and in the preparation of all kinds of man-made fabrics.
v. It is used in the manufacture of highly explosive materials and as drying agent.