

Sulphur dioxide (SO₂)

- ❖ **Preparation:** The following reactions can be used for the preparation of sulphur dioxide.

- ❖ By burning sulphur in air or oxygen.



- ❖ (b) By heating sulphur with concentrated sulphuric acid.



- ❖ (c) By heating copper or silver with conc. sulphuric acid

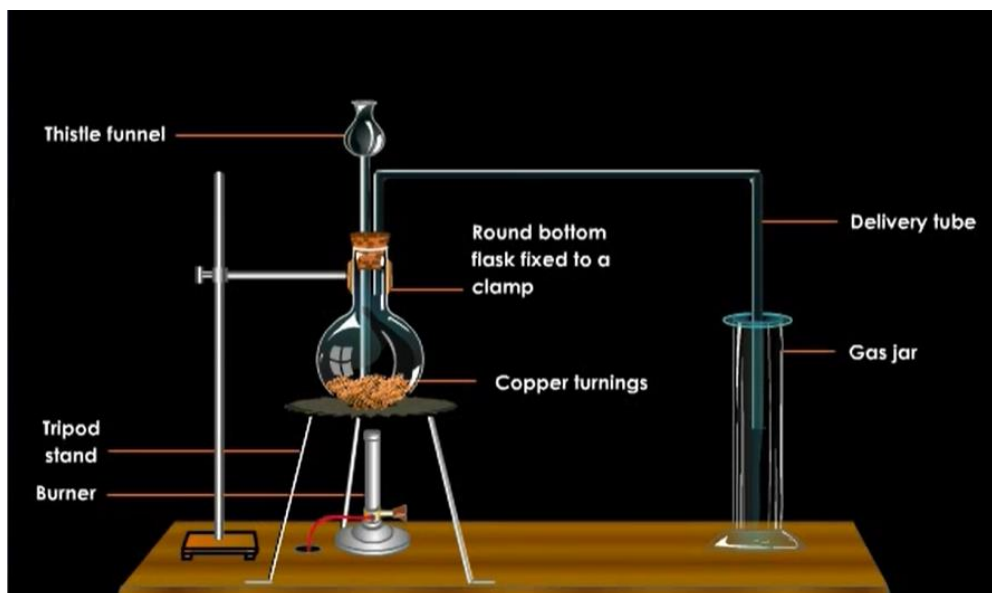
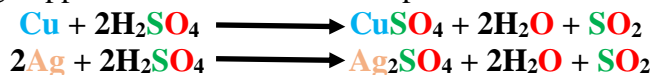


Fig: Laboratory preparation of SO₂.

- ❖ (d) By reacting sodium sulphite or sodium hydrosulphite with dil. HCL

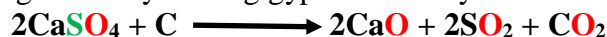


- ❖ (e) By roasting of sulphides.



- ❖ The reactions (b), (c) and (d) can be used for the preparation of SO₂ in the laboratory while the reactions (a) and (e) are used in industry to obtain SO₂.

- ❖ In places where gypsum or anhydrite are found in abundance, sulphur dioxide can be obtained on a large scale by heating gypsum or anhydrite with carbon at about 1000°C.



- ❖ **Properties:**

- ❖ **Physical properties:** (a) It is a colourless gas with a pungent, suffocating odour.

- ❖ (b) It is heavier than air.

- ❖ (c) It is highly soluble in water.

- ❖ (d) It can be easily liquefied to a colourless liquid at -10°C and into a snow like solid at -76°C.

- ❖ **Uses:**

- ❖ It is used in the manufacture of sulphuric acid and paper from wood pulp (use of bisulphites).

- ❖ (ii) It is used as a bleaching agent for delicate articles like wool, silk and straw.

- ❖ (iii) It is used in refining of petroleum and sugar.
- ❖ (iv) As a disinfectant for killing disease germs, fungi and certain moulds.
- ❖ (v) As a refrigerant in the form of liquid SO₂.
- ❖ (vi) It is used as an antichlor for removing chlorine from a fabric after bleaching.

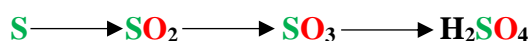
❖ **Sulphuric Acid (oil of vitriol) H₂SO₄**

Sulphuric acid is considered as the *King of chemicals*. The prosperity of any country is measured by the amount of sulphuric acid it consumes. Sulphuric acid is, thus, a substance of very great commercial importance as it is used practically in every important industry.

- ❖ In ancient days, it was called *oil of vitriol* as it was prepared by distilling ferrous sulphate (Green vitriol).

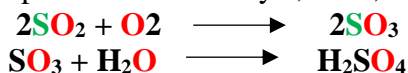


Native sulphur is the starting material for the preparation of sulphuric acid. Sulphur is burnt and easily converted into sulphur dioxide. The conversion of sulphur dioxide into sulphur trioxide is a matter of difficulty. It requires either a catalyst or a strong oxidising agent. The trioxide dissolves in water to form sulphuric acid. The whole process may be summarised as:

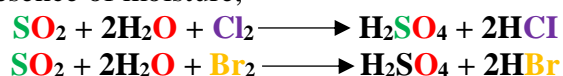


- ❖ For the oxidation of sulphur dioxide into sulphur trioxide, the following reactions may be used:

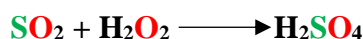
- (i) By atmospheric oxygen in presence of a catalyst, V₂O₅, at 400 °C,



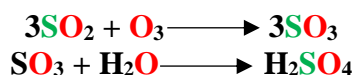
- (ii) By Cl₂ or Br₂ in presence of moisture,



- (iii) By H₂O₂,



- (iv) By ozone (O₃)



- (v) By conc. HNO₃



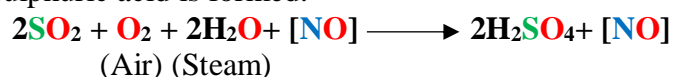
❖ **Manufacture:**

- ❖ Sulphuric acid is manufactured these days by the following two processes :

- ❖ Lead chamber process
- ❖ (b) Contact process

❖ **Lead Chamber Process**

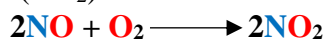
- ❖ **Principle:** The mixture containing sulphur dioxide, air and nitric oxide when treated with steam, sulphuric acid is formed.



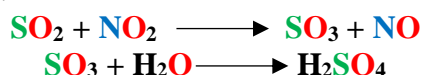
Nitric oxide acts as a catalyst in this reaction.

Various mechanisms have been proposed for this reaction.

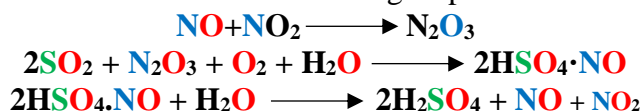
- ❖ **Berzelius mechanism:** Nitric oxide, NO combines with oxygen of the air and is oxidised to nitrogen dioxide (NO₂)



- ❖ SO₂ is oxidised by nitrogen dioxide into sulphur trioxide which reacts with steam forming sulphuric acid.

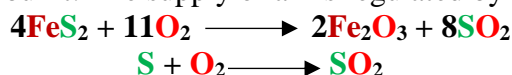


- ❖ NO formed reacts again with oxygen of air and is oxidised to NO₂. Thus, NO and NO₂ act as oxygen carriers.
- ❖ **Davy and Longe mechanism:** Nitroso-sulphuric acid is first formed as an intermediate product which then reacts with water forming sulphuric acid.



- ❖ **Working and Plant:**

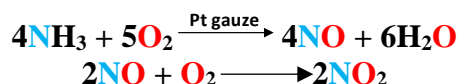
- ❖ The plant used for the manufacture of H₂SO₄ in lead chamber process is shown diagrammatically in figure 2.
- ❖ The various parts of the plant and their functions are described below:
- ❖ Pyrites or sulphur burners: These are specially designed brick furnaces where iron pyrite or sulphur is burnt. The supply of air is regulated by sliding doors.



- ❖ (b) **Dust chamber:** The dust chamber is provided with baffle walls where dust particles in the gaseous mixture coming from the burners separate due to gravity. This can also be done by using Cottrell electrostatic dust precipitator.
- ❖ (c) **Nitre pots:-** Burner gases through a nitre oven in which potassium nitrate is heated with sulphuric acid. The nitric acid is decomposed by SO₂.

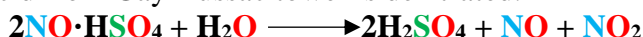


- ❖ In modern plants, oxides of nitrogen are produced by the catalytic oxidation of ammonia.



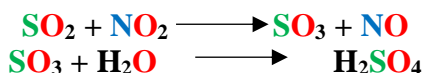
- ❖ (d) **Glover's tower:** The tower is made of steel. It is lined inside with sheet of lead or acid resisting bricks. It is packed with flint stone or quartz. There are two tanks at the top. One tank contains the dilute chamber acid and other the nitrated acid from the base of the Gay-Lussac tower. Both these acids are mixed and then allowed to flow down slowly in Glover's tower. The gases are allowed to enter from the base of the tower. The following four functions occur in this tower:

- ❖ The gases are cooled down from about 400°C to 80°C,
- ❖ Dilute chamber acid is concentrated.
- ❖ The nitrated acid from Gay-Lussac tower is denitrated.

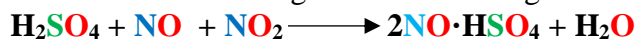


- ❖ Some SO₂ is converted into H₂SO₄. The sulphuric acid is collected at the bottom of the tower and is about 80%.

- ❖ (e) **Lead chambers:** The gaseous mixture (SO₂, air, oxides of nitrogen) is then allowed to enter three or more large chambers made of lead and supported in wooden frames. Steam is admitted into these chambers from the top when dilute sulphuric acid is formed.



- ❖ The acid is collected at the bottom of the chambers in a common receiver. This is known as chamber acid and contains 65-70% H₂SO₄. It is pumped to the top of Glover's tower for the concentration.
- ❖ (f) **Gay-Lussac tower:** The residual gases mainly air and oxides of nitrogen from the lead chambers are allowed to enter another tower called Gay-Lussac tower. This tower is lined with sheet lead packed with coke. A stream of cold concentrated sulphuric acid pumped from the base of Glover's tower flows down when it absorbs oxides of nitrogen from residual gases.



- ❖ This acid is pumped on the top of the Glover's tower. The waste gases are allowed to escape through a chimney on the extreme right of the plant.
- ❖ **Removal of impurities:** The chief impurities present in the sulphuric acid manufactured by lead chamber process are:
 - Arsenious-oxide (from-pyrites),
 - Lead sulphate from the action of H₂SO₄ on lead chamber.
 - Oxides of nitrogen.

- ❖ These are removed as follows :

(a) The acid-is diluted with-water when lead-sulphate is precipitated which is filtered off.

(b) Hydrogen sulphide is passed through dilute sulphuric acid which combines with arsenious oxide to form arsenious sulphide.



Arsenious sulphide is filtered off.

- ❖ (c) The acid is now distilled over-ammonium sulphate when oxides of nitrogen are reduced to nitrogen.



- ❖ Usually, the chamber acid is not purified and is used as such for most of the purposes. Whenever pure H₂SO₄ is needed, the acid manufactured by the contact process is used.

- ❖ **Concentration of chamber acid:** The acid obtained from Glover's tower contains about 80% H₂SO₄ and is known as brown oil of vitriol (B.O.V.) due to its colour. It can be further concentrated and the concentrated acid is called rectified oil of vitriol (R.O.V.). The concentration is done by evaporation of water present in the acid with the help of hot gases. Two methods are used for this purpose :

Cascade process and Gaillard process.

- ❖ (a) **Cascade process:** A series of ferrosilicon dishes are arranged, one below the other, on a slope. The heating is done by means of hot gases playing below the dishes (Fig.). As the acid flows downwards, it is subjected to stronger heat, so that when it reaches the lowermost dish it has been concentrated to the maximum. Addition of ammonium sulphate during concentration helps to remove any dissolved oxides of nitrogen.

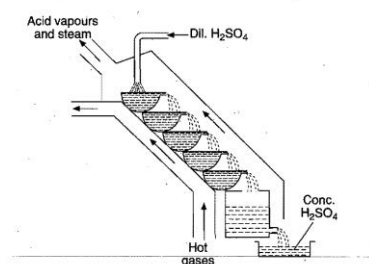


Fig: Cascade process for concentration of H₂SO₄.

- ❖ (b) **Gaillard process:** The dilute acid is allowed to flow down in the form of a spray in a tower lined with acid resisting stone. Hot air enters from the base of the tower. The dilute acid comes in contact with hot air and loses water content. By the time the acid reaches the bottom, it becomes concentrated to about 95% (Fig.).

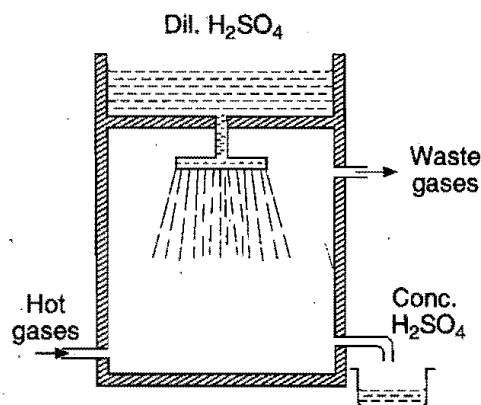


Fig: Gaillard process for concentration of H₂SO₄.

Contact Process

- ❖ Principle: This process involves the oxidation of sulphur dioxide by air in the presence of a catalyst. $2\text{SO}_2 + \text{O}_2 \xrightleftharpoons{\text{Catalyst}} 2\text{SO}_3$
- ❖ Sulphur trioxide is dissolved in 98% sulphuric acid when oleum is formed. .

$$\text{H}_2\text{SO}_4 + \text{SO}_3 \longrightarrow \text{H}_2\text{S}_2\text{O}_7 \text{ (Oleum)}$$
- ❖ Sulphuric acid of any desired concentration can be obtained from oleum by dilution with water.

$$\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{SO}_4$$
- ❖ The oxidation of sulphur dioxide is reversible and exothermic.

$$2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3 + 46.98 \text{ kcal}$$
- ❖ According to Le-Chatelier principle, the favourable conditions for the greater yield of sulphur trioxide are:
- ❖ (a) **An excess of air:** Best results are obtained when SO₂ and oxygen are present in molecular proportion of 2 : 3. .
- ❖ (b) **A low temperature:** The optimum temperature is 450°C. Even at this temperature, the rate of reaction is slow and to accelerate the rate of reaction a catalyst is required. The commonly used catalysts are platinum, ferric oxide or vanadium. Out of these best yield is obtained by the use of platinum. But it is very expensive and is easily poisoned by impurities. The purification of gases is done carefully when platinum is used as the catalyst. Nowadays, vanadium pentoxide (V₂O₅) is preferred as it is cheaper and not poisoned by impurities. However; it cannot be recovered after use .
- ❖ (c) **A higher pressure:** The optimum pressure for carrying the oxidation of sulphur dioxide is kept about one atmosphere.
- ❖ **Working and Plant**
- ❖ The manufacture of sulphuric acid involves three steps :
 - (i) Production of sulphur dioxide
 - (ii) Conversion of SO₂ into SO₃
 - (iv) Absorption of SO₃ in H₂SO₄

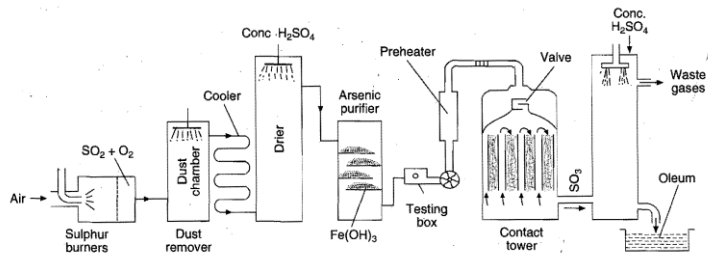
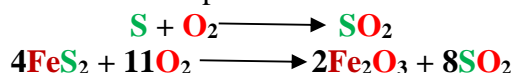


Fig: Manufacture of H₂SO₄.

❖ The plant used has been shown diagrammatically in Fig. The various parts of the plant and their functions are described below:

❖ (a) **Pyrite burners or sulphur burners:** It is a kind of furnace in which sulphur or iron pyrite is burnt to sulphur dioxide.



❖ The gases leaving the furnace contain SO₂, air, dust particles and arsenious oxide.

❖ (b) **Purification unit:** The gases are passed into dust chamber in which heavy dust particles are removed by mechanical precipitation aided by steam or electrically by using the Cottrell precipitator. The gases are now passed through cooling pipes and cooled to 100°C. The gases are led to steam scrubber where these are washed with steam or spray of water. The dust particles and impurities soluble in water are removed. If the catalyst is vanadium pentoxide, the gases should be made completely free from chlorine by using lime water in the scrubber.

❖ The gases are dried by passing through the drying tower packed with coke or flint stone. A steam of concentrated acid flows down in this tower. Finally, the gases are allowed to arsenic purifier which contains shelves holding ferric hydroxide. Ferric hydroxide absorbs arsenious oxide. The dry and pure mixture of SO₂ and air is then sent to the testing box in order to test the purity of the gas mixture.

❖ (c) **Preheater and contact tower:** The dry and pure mixture of SO₂ and air is preheated to about 400°C are allowed to enter contact chamber (Fig.). It consists of iron cylinder containing a number of vertical pipes packed with platinised asbestos heated to about 450°C. SO₂ is oxidised to SO₃ by O₂ of the air. As this conversion is an exothermic reaction, the heat evolved maintains the temperature of the catalyst.

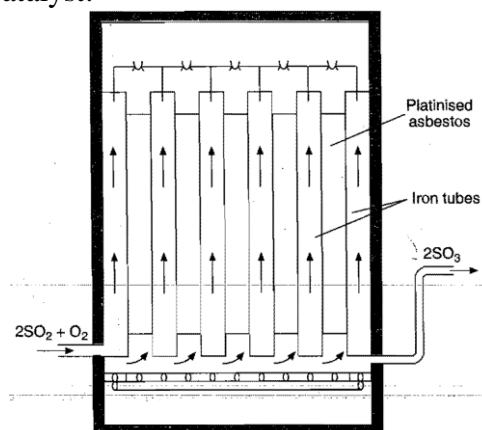


Fig: Contact tower

❖ (d) **Absorption tower:** The SO_3 formed is passed up an absorption tower where it meets a descending stream of conc. H_2SO_4 . The acid absorbs sulphur trioxide forming oleum (fuming sulphuric acid). The SO_3 cannot be absorbed in water because it produces a dense fog which does not easily condense.

❖ **Properties**

❖ **Physical properties:** (a) It is a colourless syrupy liquid. It contains 98.3% sulphuric acid. Its specific gravity is 1.84 at 15°C . It has high viscosity because its molecules are associated due to hydrogen bonding.

❖ (b) It boils at 338°C (constant boiling mixture containing 98.3% H_2SO_4 and 1.7% water). It freezes into colourless crystals at 10.5°C .

❖ (c) It fumes strongly in moist air and is highly corrosive in nature.

❖ (d) It is a conductor of heat and electricity.

❖ (e) It is highly soluble in water. Various hydrates such as $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$, are known. Heat is evolved when dissolved in water, usually bumping occurs. Due to this reason, water should be not added to concentrated sulphuric acid for dilution but concentrated sulphuric acid should be added slowly to cold water with constant stirring. Due to its great affinity for water, it is used as a dehydrating substance.

❖ **Uses**

❖ It is used:

❖ For the manufacture of fertilizers such as ammonium sulphate and superphosphate of lime.

❖ In the manufacture of other acids such as hydrochloric acid, orth-phosphoric acid, nitric acid, etc.

❖ In the manufacture of explosives such as, nitroglycerine, gun cotton, TNT (trinitro-toluene), picric acid, etc.

❖ In the manufacture of important chemicals such as sodium carbonate, alums, metal sulphates etc.

❖ In the refining of petroleum.

❖ In the manufacture of coal-tar dyes and a number of drugs and disinfectants.

❖ In the textile, paper and dyeing industries.

❖ In the leather industry for tanning.

❖ For cleansing metals before electroplating, enameling, galvanising, etc. (Pickling).

❖ In storage batteries.

❖ In manufacturing paints and pigments.

❖ As an important laboratory reagent. In organic chemistry it is used for synthesis of various organic compounds and sulphonation reactions. It is also used as an oxidising and a dehydrating agent.

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