

Module: 4

Lecture: 17

SULFURIC ACID

INTRODUCTION

Sulfuric acid (H_2SO_4) is a highly corrosive strong mineral acid. It is a colorless to slightly yellow viscous liquid which is soluble in water at all concentrations. It is one of the most important heavy industrial chemicals due to it has a number of large-scale uses particularly in the phosphate fertilizer industry. About 60 % of the sulfuric acid produced is utilized in fertilizer manufacture.

Sulfuric acid was called "oil of vitriol" by Medieval. The study of vitriol began in ancient times. Sumerians had a list of types of vitriol that classified according to substance's colour.

Johann Glauber prepared sulfuric acid by burning sulfur together with saltpeter (potassium nitrate, KNO_3), in the presence of steam in the 17th century. Decomposition of saltpeter followed by oxidation produces SO_3 , which combines with water to produce sulfuric acid. Joshua Ward used the method for the first large-scale production of sulfuric acid in 1736.

John Roebuck, produce less expensive and stronger sulfuric acid in lead-lined chambers in 1746. The strength of sulfuric acid by this method is 65%. After several refinements, this method, called the "lead chamber process" or "chamber process", remained the standard for sulfuric acid production for almost two centuries.

The process was modified by Joseph Louis Gay-Lussac and John Glover which improved concentration to 78%. However, the manufacture of some dyes and other chemical processes require a more concentrated product. Throughout the 18th century, this could only be made by dry distilling minerals in a technique similar to the original alchemical processes.

Pyrite (iron disulfide, FeS_2) was heated in air to yield iron(II) sulfate, FeSO_4 , which was oxidized by further heating in air to form iron(III) sulfate, $\text{Fe}_2(\text{SO}_4)_3$, which, when heated to 480°C , decomposed to iron(III) oxide and sulfur trioxide, which could be passed through water to yield sulfuric acid in any concentration. But the production expenses are very high.

More economical process i.e. the contact process was patented by Peregrine Phillips in 1831. Today, nearly all of the world's sulfuric acid is produced using this method.

MANUFACTURE

The Industrial manufacture of sulfuric acid is done mainly by two processes

1. The Lead Chamber process
2. The Contact process

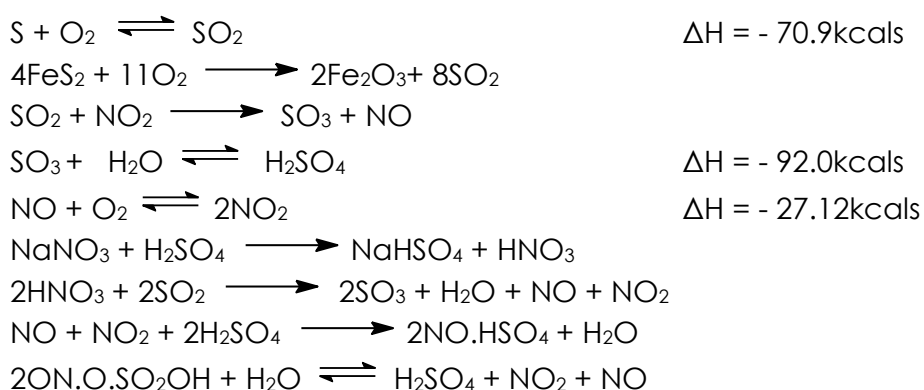
1. The lead chamber process

The Lead Chamber process for the manufacture of sulfuric acid dates back about 200 years. Although less efficient than the contact process, it is still of considerable commercial importance.

Raw Materials

Basis: 1000kg Sulfuric acid (98% yield)
 Sulfur = 400kg
 Air = 399kg

Reaction



Manufacture

[Block diagram of manufacturing process](#)

[Diagram with process equipment](#)

[Animation](#)

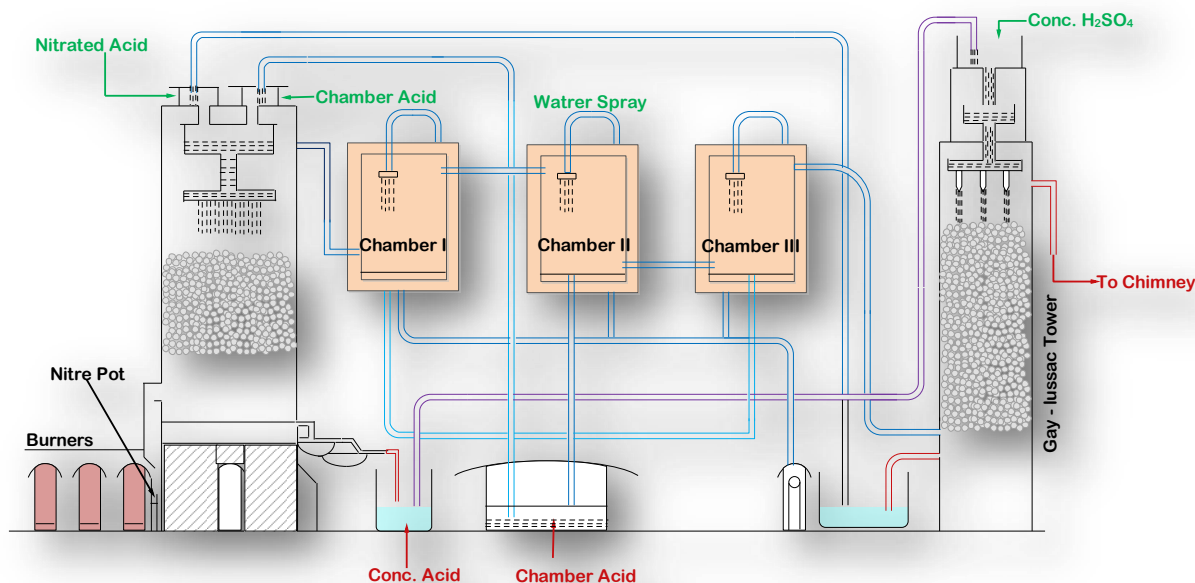


Figure: Manufacturing of Sulfuric acid by Chamber process

Sulfur dioxide is obtained by burning sulfur or by roasting pyrites. There are two function of burner

1. To oxidize sulfur to maximum extent
2. To produce and constant supply of gas containing maximum concentration of SO_2

The burner of the furnace should expose large surface of melted sulfur and should be provided secondary air in order to burn sublimed burner. This is necessary due to low heat of combustion and high vapour pressure of sulfur. At about 400°C , pyrite (FeS_2) decompose in to FeS and sulfur vapour, the later oxidized to SO_2 in presence of excess air. The residual FeS also oxidizes to Fe_2O_3 and SO_2 . Iron oxide (Fe_2O_3) slightly catalyzed oxidation of SO_2 to SO_3 . Burner gas should contain sufficient oxygen for carry out further oxidation of SO_2 to SO_3 .

The burner gases which contain SO_2 , N_2 , O_2 and dust or fine particle of pyrites are passed through dust chamber followed by Cottrell electrical precipitator or centrifugal separator in order to remove dust or fine particle of ore. Dust chambers are provided with horizontal shelves or baffles followed by filtration through crushed coke or similar material.

Now, burner gases are passed through niter oven made of cast iron in which equimolecular proportion of NaNO_3 and H_2SO_4 is heated. Resulting nitric acid reacts with SO_2 to give mixture of nitric oxide (NO) and nitrogen dioxide (NO_2) which are carried with burner gases.

In modern plant oxides of nitrogen are produced by passing mixture of ammonia and air through heated platinum gauze acting as catalyst (same as manufacture of HNO₃ by ammonia oxidation process)

After passing burner gases to dust chamber and niter oven, they pass through 5 meter square and 10 -15meter high Glover tower which is packed with flint stone, quartz, tile or acid resisting bricks. The packing in the tower is loosely stacked at the bottom to facilitate mixing of hot gases. The hot burner gases passes up this tower is at 450 - 650°C and dilute H₂SO₄ from the lead chamber and nitrosyl sulfuric acid from Gay-Lussac tower are made to trickle down the Glover tower by means of sprayers. Here, burner gases are cooled down to 70-80°C, dilute chamber acid is concentrated up to 78% and nitrosyl sulfuric acid (nitrous vitriol) is denitrated by action of water.

The tower acid is drawn off from the bottom of the tower and collected in the container called acid egg. The acid from base of Glover tower is cooled to 40°C by air coolers.

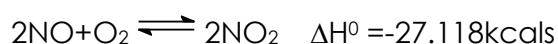
The mixture of SO₂, Oxides of nitrogen and air is then passed to series of rectangular vessels made of lead (lead chamber) having 15-45 meter length, 6-7 meter width and 7 meter length. The number of chambers depends upon the size of plant, but usually they are 3 to 6 in number. The chambers are arranged in two parallel rows. Steam from low pressure boiler or pure filtered water is sprayed from top of the chamber. Mixture of gases is converted into H₂SO₄ having 65-70%v strength is collected at the bottom of the chamber. Dilute sulfuric acid obtained in any of the chamber is called chamber acid. A part of chamber acid is pumped to Glover tower, and the rest is sent for concentration.

The unabsorbed remaining gases contain oxides of nitrogen and SO₂ from lead chamber are then passed through Gay-Lussac tower at the top of which Glover acid is sprayed to recover oxides of nitrogen.

The oxides of nitrogen recovered in the form of nitroso sulfuric acid are pumped to Glover tower to again regenerate oxides of nitrogen.

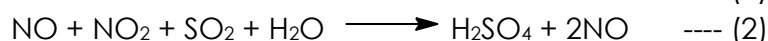
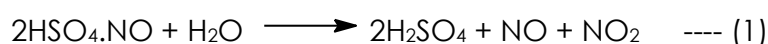
When pyrite is used as raw material, the chamber acid may contain arsenious oxide (from pyrite), lead sulfate from lead chamber are removed by treatment of H₂S and dilution of acid respectively. Dilute acid may be further concentrated into Glover tower.

Kinetics and thermodynamics

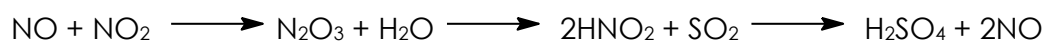


Above reaction is rate controlling step in the chamber process. The exothermic forward reaction is favoured by decrease in temperature. As the reaction proceeds with decrease in volume, the formation of NO_2 would be favoured by increase in pressure. It has been observed that the rate of oxidation is slow at ordinary temperature and rate is proportional to the square of the absolute pressure. At lower temperature, the production of chamber acid has been found to be greater. All these facts are in good agreement with the fact that the oxidation of NO to NO_2 is the rate controlling step in this process.

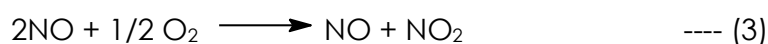
The dilution of nitrosyl sulfuric acid within the Glover tower leads to its decomposition and nitrous fumes produced catalyze the synthesis of sulfuric acid when they come in contact with sulfur dioxide and water.



Reaction (2) can be shown in chain as follow

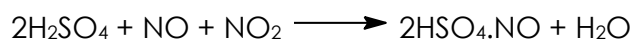


Reaction (2) can be repeated cyclically by the partial reoxidation of the nitric oxide produced by excess air which forms part of the sulfurous gas coming from the combustion chamber.

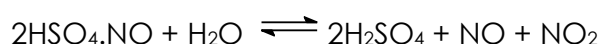


Reaction (2) and (3) mainly occur in chambers following the Glover tower until the SO_2 has been exhausted.

The recovery of nitrous gases is important task of Gay Lussac towers but it is difficult. A reverse reaction of reaction (1) is taking place here. This is in effect, a typical equilibrium reaction which is particularly sensitive to the mass action effect by water



or reversible reaction



Above reaction is displaced to the right in the Glover tower where water is relatively abundant and to the left in the Gay Lussac tower which is supplied with sulfuric acid which is transformed into nitrosyl sulfuric acid by absorbing equimolecular mixture of NO and NO_2 on account of its high concentration (78%).

Reason for obsolescence

As discussed above, overall reaction consisting of number of partial reactions which takes place in liquid phase, the development of surfaces which are covered in this liquid is a factor of fundamental importance in promoting the synthesis of sulfuric acid. Maximum strength of sulfuric acid obtained by chamber process is 78%.

However, in manufacture of some dyes and chemical processes require more concentrated H_2SO_4 . There so, the process is largely replaced by contact process.