THE PRODUCTION OF SULFURIC ACID

9.5.3 – Present information to describe the steps and chemistry involved in the industrial production of sulfuric acid and analyse the process to predict ways in which the output of sulfuric acid can be maximized.

Sulfuric Acid – An Overview:

Sulfuric acid is the most widely industrially synthesised chemical in the world. The yearly global output of this colourless, corrosive substance ranges in the hundreds of millions of tonnes, and the demand for sulfuric acid is slowly increasing as the world's population increases.

Sulfuric acid has a wide range of uses, the most important of which is fertilizer production, which supports the Earth's massive population. Sulfuric acid is used to create superphosphate, ammonium sulfate and other fertilizers. Other uses include the production of lead-acid batteries, explosives, dyes, polymers and as an industrial dehydrating agent.

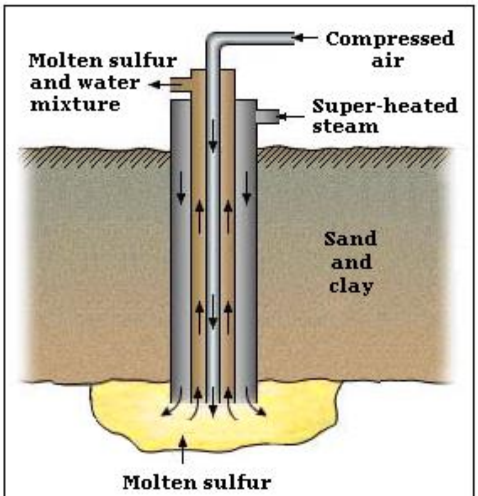
The production of sulfuric acid involves the extraction of elemental sulfur deposits, the combustion of this sulfur into sulfur dioxide, the conversion of sulfur dioxide into sulfur trioxide, the dissolution of sulfur trioxide in sulfuric acid to form oleum, and the dilution of oleum to form sulfuric acid.

The Extraction of Sulfur:

The Frasch Process:

The raw materials sulfuric acid production are SULFUR, OXYGEN and WATER. Oxygen is derived from the air and water from freshwater bodies such as lakes and reservoirs, but sulfur must be mined. Sulfur is mined from elemental deposits, *not* from minerals containing sulfur compounds.

The extraction of these deposits is called the *Frasch Process*. In this process, three concentric pipes are forced down to the underground sulfur deposits. Superheated steam (which is pressurised to 160°C) is inserted into the outer-most pipe, directly into the sulfur, causing it to melt. Pressurised air is forced down the inner-most tube, which then pushes the molten sulfur & water foam through the middle-tube, back to the surface. The mixture is then cooled, and the sulfur readily separates from the water.



(Frasch Process)

The low melting point of sulfur (113°C) as well as its insolubility in water allows this process to yield a highly pure sulfur product. Approximately 99.5% purity is achieved.

The Contact Process:

The chemical process for synthesising sulfuric acid is called the *Contact Process*. It is composed of a number of chemical reactions, or steps, each occurring under different conditions and in different industrial chambers.

Sulfur Combustion:

The first step in the Contact Process is the synthesis of sulfur dioxide through the combustion of the mined sulfur. Sulfur is liquefied, and sprayed into a combustion furnace containing an excess of dry air at atmospheric pressure. The liquefaction of the sulfur greatly increases its surface area, and the excess of air promotes the reaction. The resulting reaction is strongly exothermic:

$$\underset{\text{sulfur}}{S_{(l)}} + \underset{\text{oxygen}}{O_{2\,(g)}} \xrightarrow{\Delta} \underset{\text{sulfur dioxide}}{SO_{2\,(g)}}$$

It is a reaction that goes to completion. Alternatively, and much more cheaply, sulfur dioxide can be sourced from waste gases produced by the smelting of metal sulfide ores.

Conversion To Sulfur Trioxide:

The conversion of sulfur dioxide (SO_2) into sulfur trioxide (SO_3) is the most difficult step of the process. This is because the conversion is an equilibrium reaction, and as such yield and rate considerations must be made:

$$\underset{\text{sulfur dioxide}}{2SO_{2\,(g)}} + \underset{\text{oxygen}}{O_{2\,(g)}} \rightleftharpoons \underset{\text{sulfur trioxide}}{2SO_{3\,(g)}}$$

$$\Delta H = -99\ \text{kJ/mol}$$

Equilibrium Considerations:

According to the *predictions* of Le Chatelier's Principle, the output can be **maximised** by:

- Using an EXCESS of *oxygen*; this forces the equilibrium to the right, creating more product.
- Using a LOW *temperature*; lower temperatures encourage the counter-acting heating effect of the endothermic forward reaction, to re-establish equilibrium with a higher yield.
- Using HIGH *pressure*; there are 2 moles of product gas, compared to 3 moles of reactant gas, so a higher pressure will encourage the *pressure-reducing* forward reaction, as it produces less moles of gas.

However, these are PURELY equilibrium considerations, which only relate to yield. In an industrial process, the yield, as well as the rate of reaction, are extremely economically significant. A large yield, which takes weeks to form, is not economically viable.

Rate Considerations:

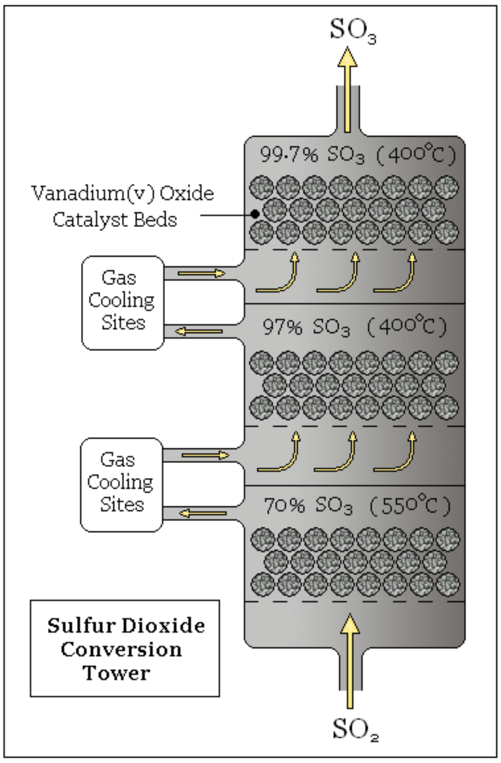
For any chemical reaction, the rate of reaction increases as temperature increases. This is because greater thermal energy means greater kinetic energy, which leads to more collisions between reactant molecules, and hence more reactions can occur. So, purely in terms of rate of reaction:

- A HIGH temperature favours fast reaction.
- A CATALYST is used to speed up the reaction.

Compromise Conditions:

Through considering all of the above, industrial chemists have decided on compromise conditions for this step of the contact process, in order to maximise the yield of sulfur trioxide, and hence the yield of sulfuric acid. The conditions are:

- A pressure of a little above atmospheric (100 kPa; large pressures, are not used, even though it would increase the yield, because high pressure equipment is expensive and dangerous to build and maintain).
- A small excess of oxygen.
- A catalyst of vanadium(V) oxide is used.
- Moderate temperature ranging from 400-550°C.



The Reaction Beds:

The sulfur dioxide from the combustion furnace is extremely hot, at more than 1000°C, due to the exothermic nature of combustion. Before this gas is fed into the conversion tower, it is cooled to the required temperature of 550°C. This cooled gas is then passed over a catalyst bed of vanadium(v) oxide in porous silica pellets.

At the temperature of 550°C, a yield of 70% SO_3 is rapidly achieved. This mixture of 70% SO_3 is removed from the tower, and cooled to 400°C to increase the yield. It is re-fed into the tower, and 97% conversion is achieved. The process is repeated until the resultant mixture of SO_2 and SO_3 achieves 99.7% conversion.

The remaining 0.3% SO_2 is released into the atmosphere; its concentration is low enough to satisfy environmental considerations.

Oleum Production:

When sulfur trioxide is dissolved in water, it forms sulfuric acid. However, the reaction is extremely exothermic, reacting explosively and spraying sulfuric acid mist in all directions. This is not suitable for industrial production, as the separation of the mist from the air is expensive.

Alternatively, the high purity sulfur trioxide that leaves the conversion tower is dissolved into a stream of concentrated sulfuric acid, forming *oleum* ($H_2S_2O_7$). The sulfur trioxide dissolves very easily into sulfuric acid, and the reaction is stable:

$$\underset{\text{sulfur trioxide}}{SO_{3\,(g)}} + \underset{\text{sulfuric acid}}{H_2SO_{4\,(l)}} \longrightarrow \underset{\text{oleum}}{H_2S_2O_{7\,(l)}}$$

The oleum is then diluted with water to form 98% sulfuric acid:

$$\underset{\text{oleum}}{H_2S_2O_{7\,(l)}} + \underset{\text{water}}{H_2O_{(l)}} \longrightarrow \underset{\text{sulfuric acid}}{2\,H_2SO_{4\,(l)}}$$

This product is common “concentrated” sulfuric acid. It is then collected and shipped off to be sold.

Conclusion:

Hence, the industrial production of sulfuric acid is a complex chemical reaction that takes place in a series of steps. At each step, the chemical reactions must be monitored and adjusted in order to produce the highest yield, in the shortest time possible, to form a pure product. From the above analysis of the reactions, it is clear that in all industrial processes, compromises must be made in order to create an economically viable product.

Bibliography:

Printed Material:

Farrelly, R., Garnett, P., Irwin, D., Vitlin, D. 2002, *Chemistry Contexts 2,*
Pearson Education Australia, Sydney.

Roebuck, C. M. 2000, *Excel HSC: Chemistry*,
Pascal Press, Singapore.

Smith, R. 2005, *Conquering Chemistry: HSC Course* (4th edn.),
McGraw Hill Australia, Sydney, pp. 330-336.

The New Encyclopædia Britannica, 1987, Vol. 16, *Sulphuric Acid* (15th edn.),
Encyclopædia Britannica, **Inc**, Chicago.

Electronic Data:

Encyclopædia Britannica, 2007, *Sulfuric Acid*,
Britannica Concise Encyclopedia, viewed August 15, 2007,
<http://concise.britannica.com/ebc/article-9379847/sulfuric-acid >

Encarta® 99 Encyclopedia, 1999, *Sulphuric Acid,*
© 1993-1998 **Microsoft Corporation**. All rights reserved.

Encarta® 99 Encyclopedia, 1999, *Contact Process,*
© 1993-1998 **Microsoft Corporation**. All rights reserved.

194.200.130.xxx, et al. 2001, *Sulfuric Acid*,
Last updated 00:57, 16 August 2007, by 202.61.139.34
The Wikipedia Foundation, viewed 16 August, 2007.
<http://en.wikipedia.org/wiki/Sulfuric_acid>