Module: 4
Lecture: 18

SULFURIC ACID (continued)

2. The contact process for sulfuric acid

Almost all sulfuric acid is manufactured by the contact process.

Raw Materials

<table>
<thead>
<tr>
<th>Basis: 1000kg sulfuric acid (100%)</th>
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<tbody>
<tr>
<td>Sulfur dioxide or pyrite (Fe$\text{S}_2$) = 670kg</td>
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<tr>
<td>Air = 1450-2200Nm$^3$</td>
</tr>
</tbody>
</table>

Sources of raw material

- Sulfur from mines
- Sulfur or hydrogen sulfide recovered from petroleum desulfurization
- Recovery of sulfur dioxide from coal or oil-burning public utility stack gases
- Recovery of sulfur dioxide from the smelting of metal sulfide ores
  \[2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2\]
- Isolation of SO$_2$ from pyrite

Reactions

- \[\text{S} + \text{O}_2 \rightarrow \text{SO}_2\] $\Delta H = -71.2$kcals
- \[2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3\] $\Delta H = -46.3$kcals
- \[\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4\] $\Delta H = -31.1$kcals

Manufacture

- Block diagram of manufacturing process
- Diagram with process equipment
- Animation
Steps in the Contact Process

The steps in this process are as follow.

1. Burning of sulfur
2. Catalytic oxidation of SO$_2$ to SO$_3$
3. Hydration of SO$_3$

1. Burning of sulfur

Burning of sulfur in presence of dry air is carried out in sulfur pyrite burner. As SO$_2$ is needed for the catalytic oxidation and prevention of corrosion, dry air is used in the combustion process. If sulfur contains carbonaceous impurities, the molten material has to be filtered to avoid poisoning the catalyst and forming water from burning hydrogen.

2. Catalytic oxidation of SO$_2$ to SO$_3$

When using sulfur from sources 1 and 2, purification of the SO$_2$ gas is normally not needed. Other sources of SO$_2$ require wet scrubbing followed by treatment of the gas with electrostatic precipitators to remove fine particles. The catalyst used is vanadium pentoxide ($V_2O_5$) and the pressure is 1.2-1.5 atmospheres. The temperature has to be kept around 450°C. If it rises above 450°C, the equilibrium is displaced away from SO$_3$. Temperature should reach around 450°C for the catalyst to be activated. This process is strongly exothermic. The catalytic reactor is designed as a four-stage fixed-bed unit. The gas has to be cooled between each step. Four passes, together with “double absorption, described below, are necessary for overall conversion of 99.5-99.8% (three passes, 97-98%). The temperature rises to over 600°C with the passage of the gas through each catalyst bed. The doubled absorption consists of cooling the gases between each bed back to the desired range by sending them through the heat exchanger and then back through the succeeding beds. Between the third and fourth beds, the gases are cooled and sent to an...
absorption tower. This is to shift the equilibrium to the right by absorbing SO$_3$. The gases are then sent to the heat exchanger to warm them to 410-430°C and then on to the fourth catalyst bed.

3. Hydration of SO$_3$

After the catalytic oxidation process, the resulting SO$_3$ is hydrated by absorption in packed towers filled with 98-99% sulfuric acid. This is the H$_2$SO$_4$ azeotrope of minimum total vapour pressure. The catalytic oxidation has to proceed in high yield to avoid air pollution problems. SO$_2$ has a low solubility in 98% H$_2$SO$_4$. At lower acid concentrations, sulfuric acid and SO$_3$ form a troublesome mist and at higher concentrations emissions of SO$_3$ and H$_2$SO$_4$ vapour become significant. The absorption acid concentration is kept within the desired range by exchange as needed between the H$_2$SO$_4$ in the drying acid vessel that precedes the combustion chamber with the H$_2$SO$_4$ in the absorption tower. The acid strength can be adjusted by controlling the streams of H$_2$SO$_4$ to give acid of 91 to 100% H$_2$SO$_4$ with various amounts of added SO$_3$ and water. The conversion of sulfur to acid is over 99.5%.

Kinetics and thermodynamics

The crucial step is the oxidation of SO$_2$ to SO$_3$. At normal conditions, the equilibrium lies far to the left and the amount of SO$_3$ formed is very small. To improve the yield of SO$_3$, the reaction is carried out at around 450°C and 1.5-1.7 atm pressure in presence of V$_2$O$_5$ or Pt as catalyst.

$$2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 \quad \Delta H = -46.98 \text{kcal}$$

These conditions are chosen by applying Le Chatelier's principle as explained below.

Effect of temperature

Since the forward reaction is exothermic, at higher temperatures the backward reaction i.e., the dissociation of SO$_2$ is more favoured. However, at very low temperature, the rate of combination of SO$_2$ and O$_2$ is very slow and at higher temperature of about 450°C, the rate of formation of SO$_3$ is high and rate of decomposition of SO$_3$ is minimum. Hence, the temperature range which best meets kinetics and thermodynamics requirements for high yield in the synthesis of SO$_3$ is located in between 400°C to 500°C, with optimum temperature at about 450°C.

Effect of pressure

In the forward reaction i.e. formation of sulfur trioxide, the number of moles of gaseous components is decreasing.

$$\Delta n_g = (2) - (2+1) = -1$$
The formation of SO$_3$ takes place with decrease in volume and hence increase in pressure is expected to increase the rate of formation of SO$_3$, i.e., rate of forward reaction. However, it has been observed that there is no appreciable change in the yield at higher pressures. Also, higher pressure will increase the rate of corrosion of iron tower used in the process. Hence pressure of 1.5-1.7 atm is usually satisfactory.

The equilibrium constant in terms of partial pressure is given by

$$\text{Kp} = \frac{p^2\text{SO}_3}{p^2\text{SO}_2p\text{O}_2}$$

The amount of SO$_3$ at various concentrations of SO$_2$ and O$_2$ can be estimated by using partial pressures of the gases. If $a$ and $b$ are the moles of SO$_2$ and O$_2$ respectively and $X$ is the mole of SO$_3$ formed at equilibrium, then Kp is given by,

$$\text{Kp} = \frac{4X^2(a+b-X)}{(a-2X)^2(b-X)p}$$

**Rate of contact reactions**

The main steps involved in the rate of contact reactions in heterogeneous catalyst are as follows:

- Diffusion of the reacting gases to the catalyst
- Adsorption of the gases on the surface of the catalyst
- Chemical reactions taking place on the surface of the catalyst
- Desorption of the reaction products from the surface of the catalyst
- Diffusion of the reacted molecules away from the catalyst

It has been observed that the rate of oxidation of SO$_2$ on the surface of platinum catalyst is proportional to the pressure of SO$_2$ and inversely proportional to the square root of the pressure of SO$_3$. The rate is independent of the pressure of oxygen. The energy of activation on platinum surface is about 10 kcal/mole as against an activation energy of about 23-34 kcal/mole for the promoted vanadium catalyst. Maximum value of 34 kcal/mole has actually been observed for pure V$_2$O$_5$ catalyst. The rate of oxidation of SO$_2$ to SO$_3$, on the surface of vanadium catalyst largely depends upon the pressure of oxygen and weakly upon the pressure of SO$_2$.

The rate of oxidation is determined by the following three steps.

- Rate of absorption of reacting gases (SO$_2$ and O$_2$) on the surface of the catalyst
- Chemical reactions between absorbed SO$_2$ and O$_2$ on the surface of the catalyst
- The rate of desorption of SO$_2$ from the surface
The actual reactions are very complicated, as they involve a series of reactions between the gas, the catalyst, the promoters and the carriers.

**Comparison of vanadium and platinum catalyst**

<table>
<thead>
<tr>
<th>Aspect</th>
<th>Vanadium catalyst</th>
<th>Platinum catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>Higher</td>
<td>Lower and decrease with use</td>
</tr>
<tr>
<td>Investment</td>
<td>Initially less, 5% replacement is required per year</td>
<td>High, Lower life and highly fragile</td>
</tr>
<tr>
<td>Catalyst poisoning</td>
<td>Relatively immune to poison</td>
<td>Poisoned, especially by arsenic</td>
</tr>
<tr>
<td>Handling of SO₂</td>
<td>Less (7-8%)</td>
<td>High (8-10%)</td>
</tr>
<tr>
<td>Requirement per 1000kg (100% acid)/day</td>
<td>14kg catalyst mass containing 7-8%V₂O₅</td>
<td>189gms</td>
</tr>
</tbody>
</table>

**Operation of multistage convertor**

**Figure: Multistage reactor for the conversion of SO₂ into SO₃**
The apparatus in which $\text{SO}_2$ is converted into $\text{SO}_3$ is as shown in figure. It is designed so as to achieve high rate of conversion along with highest possible thermodynamic yields. The convertor is subdivided into several compartments having separate layers of catalytic mass supported by meshes.

In four compartment reactor, upon entering the reactor from top, the sulfurous gases have been heated to about $400^\circ\text{C}$ by heat exchange carried out earlier on the sulfurous gases themselves, the added air or the mixture of them are heated up to about $600^\circ\text{C}$ where upon they react. The rate of reaction is high but the yield does not exceed 75%.

Upon leaving the first compartment the temperature of the partially converted gases is lowered by $100^\circ\text{C}$ in the gas-gas heat exchanger (HE-1), and they are returned to the convertor where, in correspondence with the temperature of the catalytic bed in the second compartment, they are brought up to about $500^\circ\text{C}$ and react to form further $\text{SO}_3$ from $\text{SO}_2$. The rate of reaction is lower but the yield goes up to 85%.

The gases are again sent out of the reactor and their temperature is reduced again by $100^\circ\text{C}$ by means of heat exchanger (HE-2). Then returned to third compartment where yields raised up to 95% by passing through the catalytic bed at $480^\circ\text{C}$. The rate of reaction is further lowered, but now only small amounts of gas to be converted into $\text{SO}_3$.

After lowering the temperature third time by external heat exchange (HE-3), the gases are passed back to the reactor where they undergo on the catalytic bed in the fourth compartment, final conversion at about $450^\circ\text{C}$, which gives yield of 98-99%.

**Major engineering problems**

- Design of multistage catalytical convertor for highly exothermic reaction. Earlier two stage convertor is used but nowadays the design of three or four stages rather than conventional two stage operation are developed.
- To optimize space velocity in catalyst chamber because it deals with pumping cost or fixed charges of reactor
- Thin catalyst beds of 30-50cm height used to avoid above difficulties. Yield can drop due to longitudinal mixing if the convective gas velocity through the bed is low
- Removal of heat of absorption of $\text{SO}_3$ in acid. Pipe coolers with water dripping over external surface have been replaced by cast iron pipe with internal fins to promote better heat transfer.
- Pressure drop must be low, so, 8cm stacked packing is often used.
PROPERTIES

Physical Properties

- **Molecular formula**: $\text{H}_2\text{SO}_4$
- **Molecular weight**: 98.08 gm/mole
- **Appearance**: Water white slightly viscous liquid
- **Boiling point**: 290$^\circ$C
- **Melting point**: 10$^\circ$C
- **Density**: 1.840 gm/mL (liquid)
- **Solubility**: Miscible with water in all proportions
- **Viscosity**: 26.7 cP (20$^\circ$C)
- Aqueous sulfuric acid solutions are defined by their H$_2$SO$_4$ content in weight-
  percent terms.
- Anhydrous (100%) sulfuric acid sometimes referred to as “monohydrate,”
  which means that it is the monohydrate of SO$_3$.
- Dissolve any quantity of SO$_3$, forming oleum (“fuming sulfuric acid”).
- The physical properties of sulfuric acid and oleum are dependent on H$_2$SO$_4$
  and SO$_3$ concentrations, temperature, and pressure.

Chemical Properties

1. **Dehydrating agent**
   - Has a great affinity for water and the reaction is extremely exothermic.
   - A large amount of heat is produced due to formation of mono and dehydrates
     (H$_2$SO$_4$.H$_2$O and H$_2$SO$_4$.2H$_2$O) on mixing acid with water. So while preparing
     dilute solutions of H$_2$SO$_4$, the acid should be added to water slowly with
     constant stirring. Never add water to the acid.
   - Used for drying almost all gases, except NH$_3$ and H$_2$S.
   - Its corrosive action on skin is also due to dehydration of skin which then burns
     and produces itching sensation.
   - Due to dehydrating property, it chars sugar to give carbon.
     \[ \text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow 12\text{C} + 11\text{H}_2\text{O} \]
   - Also, paper, starch, wood etc. are charred by conc. H$_2$SO$_4$ due to the
     removal of water. It is also used in removing water from various substances
     such as oxalic acid and formic acid.
     \[ \text{COOH-COOH} \rightarrow \text{H}_2\text{O} + \text{CO} + \text{CO}_2 \]

2. **Oxidising agent**
   - Gives O$_2$ on strong heating, hot conc. H$_2$SO$_4$ also acts as an oxidising agent.

3. **Pickling agent**
   - Finds application in pickling in which layers of basic oxides are removed
     before electroplating, enameling, galvanizing and soldering.
4. Acidic nature

- Strong dibasic acid and forms two series of salts with alkalis. These are bisulfates (HSO₄⁻) and sulfates (SO₄²⁻).

USES

- The largest single use is in the fertilizer industry.
- Mostly in production of phosphoric acid, which in turn used to manufacture fertilizers such as triple superphosphate, mono and diammonium phosphates.
- Used for producing superphosphate and ammonium sulfate.
- Used as an acidic dehydrating reaction medium in organic chemical and petrochemical processes involving such reactions as nitration, condensation, and dehydration, as well as in oil refining, in which it is used for refining, alkylation, and purification of crude-oil distillates.
- In the inorganic chemical industry e.g. in the production of TiO₂ pigments, hydrochloric acid, and hydrofluoric acid.
- In the metal processing industry e.g. for pickling and descaling steel, for leaching copper, uranium, and vanadium ores in hydrometallurgical ore processing, and in the preparation of electrolytic baths for nonferrous-metal purification and plating.
- Certain wood pulping processes in the paper industry require sulfuric acid, used in textile and chemical fiber processes and leather tanning.
- In manufacture of explosives, detergents and plastics.
- In production of dyes, pharmaceuticals.