Manufacture of sulfuric acid by the contact process

Aims of the experiment

- To manufacture sulfuric acid through the contact process
- To detect synthesis gases using appropriate indicators (dyes, solubility products)
- To understand the contact process as an example of a significant large-scale technical process
- To understand how chemical equilibria can be influenced through pressure, temperature and concentration
- To understand reaction kinetics (reaction rate, catalysts, activation energy)

Principles

The significance of the contact process

The contact process is a process for the manufacture of sulfuric acid. The basic principle of the process was patented as long ago as 1831 by the English vinegar manufacturer, Peregrine Phillips. However, it took over 50 years for the process to be implemented on a large scale and replace the lead chamber process for the production of sulfuric acid that was prevalent at that time.

The disadvantage of the lead chamber process was that it was only possible to produce sulfuric acid at a maximum concentration of 78%. Sulfuric acid with a higher concentration as well as oleum (sulfuric acid with an excess of SO_3) had to be obtained from this through multiple distillation.

In contrast to the lead chamber process, the contact process is a heterogeneous catalytic process in which the catalyst is present in a different phase from the reactants. The term "contact process" stems from the fact that the usually solid catalyst is also called a "contact" in a heterogeneous catalysis.

As the demand for sulfuric acid could be met by the lead chamber process in the middle of the 19th century, there was initially no incentive to develop the process further. Only with the rise of the dyes industry was sulfuric acid needed in larger quantities for the manufacturing process. It therefore became of interest to implement the contact process on a large industrial scale.

One of the most important steps in this process was to develop suitable systems for cleaning the synthesis gases to prevent poisoning of the catalyst through "contact poisons" such as arsenic compounds, and to develop a cheap catalyst. This is because the platinum catalyst originally used was too ex-

pensive for use in large industrial plants. Instead of platinum, vanadium pentoxide is used today mixed with potassium pyrosulfate as an activator on porous SiO_2.

Sulfuric acid is to date one of the most important chemicals for industry and in chemical laboratories. The largest proportion of the world's production is used for the manufacture of fertilisers. As one example, ammonium sulfate can be produced through conversion of ammonia with sulfuric acid. As another, the insoluble phosphate salt $Ca_3(PO_4)_2$ can be converted to the soluble salt $Ca(H_2PO_4)_2$. Furthermore, inorganic acids can be manufactured from their salts through conversion with sulfuric acid.

Theoretical consideration of the contact process

The contact process can be divided into several stages. Initially, the SO_2 gas must be manufactured that is needed for the conversion. This is achieved either by burning elemental sulfur which accumulates in large amounts from the desulfurisation of crude oil and natural gas, or by the roasting of sulfide ores.

$$\frac{1}{8} S_8 + O_2 \rightarrow SO_2 \qquad \Delta H = -297{,}03\ kJ/mol$$

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$$

The previously cleaned SO_2/air mixture is led into the contact vessel where it is converted to SO_3 by the catalyst.

$$2\ SO_2 + O_2 \leftrightarrows 2\ SO_3 \qquad \Delta H = -98{,}08\ kJ/mol$$

For controlling the reaction equilibrium, pressure and temperature are of decisive importance. As the activation energy for this reaction is very high, the rate of the reaction at room temperature is too low. For this reason, the reaction has to be carried out at an elevated temperature.

The Le Chatelier principle states that the equilibrium of a system under a constraint (changes in pressure, temperature or concentration) will move in a direction that reduces the constraint. In the case of an exothermic reaction, such as the synthesis of SO_3, the reaction equilibrium shifts towards the educts with increasing temperature.

One must therefore choose a temperature that on the one hand permits an adequate reaction rate, and on the other hand does not move the equilibrium too far in the direction of the educts. The catalyst reduces the activation energy such that the reaction can be carried out at a temperature of 420 °C – 620 °C.

By increasing the pressure to 5 – 10 bar, the equilibrium can be pushed further in the direction of the products, as the system will evade the constraint of increased pressure through a reduction in the number of particles. This occurs here because three gas particles of SO_2 and O_2 react to produce two gas particles of SO_3.

To further increase the reaction conversion, the reaction mixture is repeatedly led over the catalyst in four sequential cycles. So that at every catalytic stage the optimal temperature is maintained, the heat of reaction must be transported away in heat exchangers. The heat removed can be used in other technical processes.

In the so-called "double contact process", the remaining SO_2 is separated from the resulting SO_3 before going through the fourth cycle. This makes a yield of more than 99.5 % SO_3 possible.

In the final stage, the resulting SO_3 is led into concentrated sulfuric acid. This results in the formation of oleum, also called fuming sulfuric acid. This is sulfuric acid with an excess of SO_3 in which so-called disulfuric acid as well as more highly condensed sulfuric acids form. The 98 % sulfuric acid that is available commercially is obtained by diluting this mixture with water.

Risk assessment

As vanadium pentoxide is a highly poisonous substance, a platinum catalyst will be used in this experiment.

The substances produced in this experiment, sulfur dioxide and sulfur trioxide, are poisonous and/or corrosive gases. For this reason, particular attention must be paid at the start of the experiment to ensure that the apparatus is air tight. If possible, a water-jet pump should be connected up in the fume cupboard to ensure that no SO_2 can escape.

It is imperative that protective gloves, protective glasses and a lab coat are worn when carrying out the experiment.

Before filling the gas scrubber bottles with sulfuric acid, these should be removed from the magnetic board, as sulfuric acid will attack the metal of the spring clamps.

Barium chloride

Signal word: Hazard

Hazard statements

H332 Harmful if inhaled.

H301 Toxic if swallowed.

Precautionary statements

P301+P310 IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.

Fuchsine solution

Signal word: Hazard

Hazard statements

H351 Suspected of causing cancer.

Precautionary statements

P201 Obtain special instructions before use.

P202 Do not handle until all safety precautions have been read and understood.

P281 Use personal protective equipment as required.

P308+P313 If exposed or concerned: Get medical advice/attention.

P405 Store locked up.

P501 Dispose of contents/container according to local/regional/national/ international regulations.

Sulfur

Signal word: Caution

Hazard statements

H315 Causes skin irritation.

Precautionary statements

P302+P352 IF ON SKIN: Wash with soap and water

Sulfur dioxide

Signal word: Hazard

Hazard statements

H331 Toxic if inhaled.

H314 Causes severe skin burns and eye damage.

H280 Contains gas under pressure; may explode if heated.

EUH071 Corrosive to the respiratory tract.

Precautionary statements

P260 Do not breathe dust/fume/ gas/mist/vapours/spray.

P280 Wear protective gloves/protective clothing/eye protection/face protection.

P304+P340 IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.

P303+P361+P353 IF ON SKIN (or hair): Immediately remove/take off all contaminated clothing. Rinse skin with water/shower.

P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

P315 Get medical advice/attention.

P405 Store locked up.

P403 Store in a well-ventilated place.

Sulfuric acid

Signal word: Hazard

Hazard statements

H314 Causes severe skin burns and eye damage.

H290 May be corrosive to metals.

Precautionary statements

P280 Wear protective gloves/protective clothing/eye protection/face protection.

P301+ P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

P309 + P310 IF exposed or you feel unwell: Immediately call a POISON CENTER or doctor/physician.

P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

Sulfur trioxide

Signal word: Hazard

Hazard statements

H314 Causes severe skin burns and eye damage.

H335 May cause respiratory irritation.

Equipment and chemicals

1	Catalytic converter	666 360
1	Panel frame C100, two-level, CPS	666 428
6	Adhesive magnetic board 300 mm	666 4660
6	Magnetic holder, size 2, 11...14 mm	666 4662
3	Magnetic holder, size 4, 27...29 mm	666 4664
1	Funnel for gas collection	665 001
1	Evaporating dish, 80 mm diam.	664 442
3	Gas scrubber bottle, lower section	664 800
3	Glass tube insert with straight handle	664 805
1	Joint clip, ST 29/32, from set	665 392ET10
2	Glass connector, 1 x GL 18, 1 x olive	667 313
2	Glass connector, 2 x GL 18	667 312
1	Woulff's bottle with manometer	665 9351
1	Rubber stopper, one hole, 25-31 mm	667 261
1	Mobile-CASSY 2	524 005
1	Temperature probe, NiCr-Ni, type K	529 676
2	Laboratory stand	300 76
1	Stand base, V-shaped, small	300 02
1	Stand rod 75 cm, 12 mm diam.	300 43
1	Universal clamp 0...120 mm	301 72
2	Cartridge burner, DIN type	666 714
1	Water-jet pump	375 56
1	Vacuum rubber tubing, 8 mm diam.	667 186
1	Rubber tubing 6 mm diam.	307 64
1	Connector, straight, 6...8 mm	665 226
1	Four-legged stand	608 020
1	Heat protection cover plate	666 686
1	Micro double-ended spatula	666 961
1	Measuring cylinder, 100 mL	665 754
1	Wash bottle, PE, 500 mL	661 243
1	Beaker, Boro3.3, 150 mL, squat	602 023
1	Droppers, 150 x 7 mm, set of 10	665 953
1	Rubber bulbs, set of 10	665 954
1	Electronic precision balance	OHSPU401
1	Sulfur, crystalline, 250 g	674 7510
1	Sulfuric acid, 95-98%, 500 mL	674 7860
1	Fuchsine solution, 50 mL	672 0820
1	Barium chloride, 100 g	670 7200
1	Stopcock grease, 60 g	661 082

Set-up and preparation of the experiment

Preparation of the experiment

To prepare the indicator solution, weight 1 g of barium chloride into a beaker (150 mL) and dissolve it in 100 mL of distilled water. Then add about five drops of fuchsine solution and stir well with a spatula.

Have the crystalline sulfur and the concentrated sulfuric acid ready for the experiment.

Connect the 6 mm diameter tubing to the 8 mm diameter tubing using a tubing connector. If necessary, the tubings can be shorted to the required length at a later time.

Before commencing to set up the experiment, grease the ground glass joints of the gas scrubber bottles, reassemble them and secure each joint with a joint clip. Unscrew the GL caps with the seals from the glass connectors and the funnel for gas collection and place them onto the openings of the gas scrubber bottles. A spatula can be used as an aid for this.

Construction of the experiment

The apparatus is set up from left to right. Locate the four-legged stand with the heat protection plate in the bottom left corner of the apparatus (see illustration). Screw the funnel for gas collection onto the gas delivery tube of the gas scrubber bottle. Screw a glass connector with olive onto the other side of the gas scrubber bottle. Using two small and one large

magnetic holders, attach this part of the apparatus to the magnetic board so that the opening of the funnel is as close as possible to the heat protection cover plate on the four-legged stand. However, it should still be possible later to place the evaporating dish with the sulfur beneath the funnel by turning it.

As a next step, push the temperature probe through the pre-drilled hole in the left silicone stopper of the reaction tube containing the exhaust gas catalyst. Try to push the tip of the temperature probe as far as possible under the edge of the catalyst. Replace the other silicone stopper of the reaction tube with a rubber stopper, as SO_3 will attack plastics and rubber is more resistant to SO_3 than silicone. This stopper will not be used again after this experiment. Push the other glass connector with olive into this stopper. Attach this part of the apparatus to the magnetic board using two small magnetic holders and then connect it to the other part of the apparatus. Pass the cable behind the wall and connect it to the Mobile-CASSY 2.

With each of the two remaining gas scrubber bottles, screw a glass connector to the side facing away from the dip tube. Attach the glass connectors one after the other to the magnetic board using a small magnetic holder and screw them onto the apparatus (see illustration). Attach the gas scrubber bottles to the magnetic board using large magnetic holders.

Place a stand next to the panel frame. Attach a Woulff's bottle to the stand using a large universal clamp. Screw the dip tube of the Woulff's bottle to the apparatus using the glass connector. Push the prepared tube over the other tube of the Woulff's bottle and connect it to the water-jet pump.

Finally, place the burner on a jack-stand under the reaction tube containing the catalyst. Raise a further jack-stand until it can just be pushed under the four-legged stand then put it to one side within reach.

Filling the apparatus

Place about two spatula tips of crystalline sulfur onto an evaporating dish. Place the evaporating dish under the funnel by turning the funnel forwards.

Remove the lower sections of the gas scrubber bottles one after the other from the magnetic board, fill them with the appropriate solutions and mount them again on the board. It is recommended to remove the lower section of the gas scrubber bottle together with the magnetic holder.

Into each of the first two gas scrubber bottles, as seen from the left, pour 50 mL of indicator solution. Into the last gas scrubber bottle, carefully pour 50 mL of sulfuric acid.

Check that all screw connectors are screwed up firmly.

Performing the experiment

Before turning on the water-jet pump, ensure that all dip tubes are pointing away from the water-jet pump, as otherwise the liquid would be aspirated out of the gas scrubber bottles.

Turn on the water-jet pump and adjust it so that a distinct bubble formation can be seen in all gas scrubber bottles.

Now heat the catalyst. Regulate the temperature to about 400 °C to 500 °C by means of the air supply to the burner and the distance from the catalyst. When the stated temperature has been reached, start the reaction. For this, heat the sulfur on the evaporating dish using a second burner until smoke development can be seen. As soon as this is the case, extinguish the burner flame by turning off the gas, replace the burner with the prepared jack-stand and raise the jack-stand (see illustration) until there is only a small opening between the heat protection cover plate and the funnel, sufficient to allow air to enter.

If vapours should rise outside of the funnel, the water-jet pump needs to be turned up a little.

Now allow the reaction to take place and observe what happens. When the sulfur has completely burned away, continue to heat the catalyst for a further 30 minutes, as the porous material which surrounds the catalyst absorbs SO_2 and continues to release SO_3 for a long time after when heated.

Observation

1. The indicator solution in the gas scrubber bottle before the catalyst discolours first.
2. After a while, the indicator solution in the gas scrubber bottle after the catalyst becomes cloudy, while the first one remains clear.
3. In the right-hand part of the apparatus, a white fog can be seen after the gas has passed through the catalyst.
4. A blackening of the stopper to the right of the catalyst can be identified.
5. After some time, the second indicator also discolours.

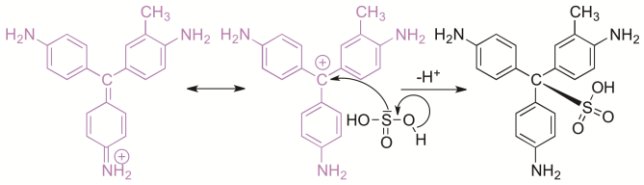
Result of the experiment

When sulfur is burned, the sulfur initially reacts with oxygen from the air to form SO_2.

$$\frac{1}{8} S_8 + O_2 \rightarrow SO_2 \qquad \Delta H = -297{,}03 \text{ kJ/mol}$$

The SO_2 gas is led into the solution containing fuchsine and barium chloride. It can be observed that the fuchsine solution discolours. This discolouring is an indicator for the formation of SO_2. SO_2 forms sulfurous acid in water which reacts with the fuchsine dye to produce colourless fuchsine-sulfurous acid.

$$SO_2 + H_2O \leftrightarrows 2\ H_2SO_3$$



Barium chloride is an indicator for sulfate ions, which react with barium chloride to produce insoluble barium sulfate.

$$Ba^{2+} + SO_4^{2-} \leftrightarrows BaSO_4\downarrow$$

The cloudiness in the second gas scrubber bottle shows that SO_3 has been formed, which dissolves in water to form sulfate ions and H_3O^+.

$$SO_3 + 3H_2O \leftrightarrows SO_4^{2-} + 2H_3O^+$$

The observation that no cloudiness is to be seen in the first gas scrubber bottle is a sign that the reaction gas before passing through the catalyst does not contain SO_3.

The fog in the right-hand part of the apparatus results from the fact that SO_3 together with water droplets present in the apparatus forms sulfuric acid vapours.

The right-hand stopper of the catalyst module blackens because SO_3 attacks plastics. If a silicone stopper had been used here it would have disintegrated. The blackening is therefore also evidence for the formation of SO_3.

The fuchsine solution in the second gas scrubber bottle also discolours after a time, as the SO_2 is not fully converted in the

reaction, and for this reason a small amount of SO_2 is still present in the reaction gas.

When the reaction gas passes through the concentrated sulfuric acid, oleum is formed, as previously described, in which the SO_3 and sulfuric acid are in equilibrium with higher condensed sulfuric acids.

$$SO_3 + H_2SO_4 \leftrightarrows H_2S_2O_7$$

The increase in the concentration of the self-prepared fuming sulfuric acid could be proven by titration, if required.

Cleaning and disposal

Begin dismantling the apparatus by disposing of the solutions in the gas scrubber bottles. Pour the indicator solutions with fuchsine and barium chloride into the collecting container for solutions containing heavy metals.

The highly concentrated sulfuric acid produced can be stored in a chemicals bottle. It can be used for experiments that require concentrated sulfuric acid or for cleaning. If the sulfuric acid is nevertheless to be disposed of, it must first be diluted with water and then neutralised with sodium hydroxide before it can be placed in the collecting container for inorganic waste.

In the further course of dismantling and cleaning the apparatus, proceed with care, as there are still residues of sulfuric acid in the apparatus.