

Synthesis of ammonia by the Haber-Bosch process

Aims of the experiment

- To carry out the synthesis of ammonia at atmospheric pressure
- To detect ammonia in the reaction mixture based on the change in pH value (acids and bases)
- To understand the Haber-Bosch process as an example of a significant large-scale technical process
- To understand how chemical equilibria can be influenced by pressure, temperature and concentration (the Le Chatelier principle, the law of mass action, Gibbs energy, enthalpy and entropy).
- To understand the reaction kinetics (activation energy, temperature dependence of the reaction rate)

Principles

The Haber-Bosch process is named after its developers, the chemists Fritz Haber and Carl Bosch. Fritz Haber developed the synthesis on a laboratory scale between 1903 and 1909, after which Carl Bosch converted the process to large-scale production in 1913. For this work, both received the Nobel Prize independently from one another and at different times (Haber in 1918, Bosch in 1931). Alwin Mittasch must also be mentioned, who from 1909 as an assistant to Carl Bosch developed and optimised the catalyst used in the synthesis.

The synthesis of ammonia is significant above all for the production of food, as the ammonia produced is mainly used for the manufacture of artificial fertilisers. It is the starting

material for the fertilisers ammonium nitrate, ammonium sulphate and potassium nitrate. Further uses are in the production of explosives without sodium nitrate and the manufacture of nitric acid.

Before introduction of the Haber-Bosch process, the main source of nitrogen used for these purposes was so-called "Chile saltpeter". Here we are dealing with sodium nitrate which has resulted from the deposition and weathering of bird droppings. The main place where this natural occurrence of nitrate is found is in the Atacama Desert in Chile.

The synthesis of ammonia is the only process of technical significance in which inert nitrogen from the air is made to react. In the Haber-Bosch process, hydrogen and nitrogen react exothermically to produce ammonia.





This is an equilibrium reaction in which the equilibrium under standard conditions is to more than 95 % on the side of ammonia. Because of the high activation energy of c. 400 kJ/mol that is required, the reaction rate at 25 °C and 1.013 bar is so low, however, that practically no reaction takes place. The reaction can be accelerated by increasing the temperature or by the use of a suitable catalyst. Using the Mittasch catalyst, the activation energy is reduced to about 100 kJ/mol. In spite of this, a temperature of about 500 °C is needed in order to achieve an adequate reaction rate.

The Le Chatelier principle can help here. By placing a constraint on a system that is in equilibrium through a change in pressure, temperature or concentration, the equilibrium will move in a direction that will remove or reduce the constraint. This means that, in the case of an exothermic reaction in which heat is released into the surroundings, an increase in temperature will favour the backward reaction.

A further factor which has an influence on the position of the equilibrium is the entropy. Reactions in which the number of gas particles is reduced take place with a reduction of the entropy of the system. Apart from this, the nature of the particles plays a role. A mixture of two different particles is in a more chaotic state compared with a pure substance. According to the Gibbs-Helmholtz equation, the state with the higher entropy is favoured by increasing the temperature.

$$\Delta G = \Delta H - T \cdot \Delta S$$

In the case of the synthesis of ammonia, both effects lead to the fact that at 500 °C the reaction equilibrium lies almost completely on the side of the reactants. At normal pressure only about 0.1 % of ammonia is present.

In order nevertheless to obtain ammonia, the ammonia synthesis is carried out at an increased pressure. We make use of the fact that in the reaction to produce ammonia, the number of gas molecules per conversion according to formula is reduced from four to two. By increasing the pressure from 1.013 bar to 200 bar, a constraint is applied which is balanced out by a reduction in the number of particles. For this reason, the equilibrium is moved in the direction of ammonia.

In this way, a yield of 17.6 % ammonia can be achieved using the Haber-Bosch process. This is then removed continuously from the reaction equilibrium.

The experiment which now follows is conducted at atmospheric pressure. For this reason, it will not be possible to achieve this yield. However, the 0.1 % ammonia in the reaction mixture will be sufficient to identify it on the basis of the colour of an indicator paper.

Risk assessment

When heating the catalyst, be sure not to hold the test tube in the flame for too long to prevent it from cracking.

The greatest potential hazard in the synthesis of ammonia originates from the hydrogen gas. It forms a combustible detonation gas mixture with oxygen from the air which explodes on heating. It must be ensured that the apparatus is air-tight. Before introducing hydrogen, the apparatus must be flushed out with nitrogen in order to ensure that it no longer contains air. In this way, no detonation gas mixed can be formed.

Before commencing with the heating, all gas bottles must be removed from the vicinity of the heat source, as these

could explode on heating! Also ensure that the valve on the metal hydride storage cartridge (HydroStik PRO) is closed. To do this, unscrew the storage cartridge from the valve.

Under no circumstances must a reaction tube be used for this experiment which is not made from quartz glass. These melt on prolonged heating and leak. Oxygen could then enter the apparatus, resulting in a detonation gas reaction.

Calcium oxide



Hazard statements

H315+H318+H335 Causes skin irritation and serious eye damage. May cause respiratory irritation.

Precautionary statements

P261 Avoid breathing dust/fume/gas/mist/vapours/spray
P305+351+338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

Iron, powder



Hazard statements

H228 Flammable solid.

Precautionary statements

P370+378 In case of fire: Use metal fire powder for extinction.

Potassium nitrate



Hazard statements

H272 May intensify fire; oxidizer

Precautionary statements

P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking.
P221 Take any precautions to avoid mixing with combustibles

Hydrogen



Hazard statements

H220+280 Extremely flammable gas. Contains gas under pressure; may explode if heated.

Precautionary statements

P210 Keep away from heat/sparks/open flames/hot surfaces – No smoking.
P377 Leaking gas fire – Do not extinguish unless leak can be stopped safely.
P381 Eliminate all ignition sources if safe to do so.
P403 Store in a well ventilated place.

Keep gas bottles away from heat. Danger of explosion!

Equipment and chemicals

1	Reaction tube, quartz	664 0772
1	Panel frame C100, two-level, for CPS.....	666 428
2	Adhesive magnetic board 300 mm.....	666 4660
2	Adhesive magnetic board 500 mm.....	666 4659
2	Silicone stopper, 16 x 21 x 25 mm,	667 286
1	HydroStik PRO, CPS	666 4795
2	Spring clip, magnetic, size 7a,30 ... 32 mm...	666 4665
3	Spring clip, magnetic, size 2, 9 ... 11 mm.....	666 4661
1	Combustion boat, glazed	666 9881
1	Silicone tubing 7 mm diam., 1 m	667 194
1	Silicone tubing 4 mm diam., 1 m	667 197
1	Silicone tubing 2 mm diam., 1 m	667 198
1	Connector, straight PP, 4 ... 15 mm diam.	604 510
2	Gas syringe 100 ml with three-way stopcock	665 914
1	Cartridge burner, DIN type	666 714
1	Gas igniter, mechanical.....	666 731
1	Three-way valve, ST, capillary tap, T-shape .	602 711
1	Glass connector, 2 x GL 18.....	667 312
1	Laborboy II (laboratory jack-stand).....	300 76
1	HydroFill PRO	666 4798
1	Fine regulator valve for Minican gas cans	660 980
1	Minican gas can, nitrogen	661 000
1	Tweezers, blunt, stainless steel, 200 mm	667 034
1	Double-sided spatula, steel, 210 mm	604 5662
1	Pocket balance JE500, 500 : 0.1 g.....	667 7933
1	Universal indicator paper pH 1 ... 11, roll	MA90201
1	Test tube DURAN, 16 x 160 mm.....	602 002
1	Test tube holder, wooden, 40 mm diam.	667 032
1	Mortar, 50 ml	608 350
1	Pestle 52 mm	608 360
1	Watch glass dish, 80 mm diam.	664 154
1	Beaker, DURAN, 150 ml, tall.....	602 032
1	Wash bottle, PE, 500 ml.....	661 243
1	Flip-flap glass tube, 20 ml	661 251
1	Iron powder, reduced, 50g	671 8300
1	Aluminium oxide, 250 g.....	670 2900
1	Calcium oxide, powder, 100 g.....	671 3200
1	Potassium nitrate, 100 g.....	672 6800

Construction and preparation of the experiment

Note: Instead of the Mittasch catalyst used here, iron wool can also be used if necessary. The quantity of ammonia that results will be just sufficient to allow a slight colouration of the indicator paper to be seen. However, the Mittasch catalyst is more suitable, as more ammonia is produced and a more distinct colour can be seen.

Preparation of the Mittasch catalyst

In a mortar, homogenise 2 g of iron powder together with 0.5 g of aluminium oxide, 0.25 g of calcium oxide and 0.75 g of potassium nitrate. Place the mixture into a test tube and carefully heat it with a Bunsen burner under the fume cupboard. Do not hold the test tube in the flame for too long. The occurrence of a reaction can be recognised by the development of gas. Continue heating for a short time. Transfer the product back to the mortar and grind it to a powder.

For the following experiment, about 1 g of the prepared catalyst will be needed. The rest can be stored in a glass tube with a snap-on lid for further experiments.

The hydrogen source

The hydrogen is provided from a HydroStik PRO metal hydride storage cartridge. This is loaded with hydrogen which

has previously been produced by electrolysis. The electrolysis takes place in a HydroFill PRO system, from which the HydroStik PRO is filled at the same time.

1. Open the cover of the water tank and carefully pour in distilled or deionised water up to the inner ridge. Close the cover.

2. Connect the AC-DC adaptor and plug it into an AC mains socket. The status indicator will now flash green.

3. Screw the HydroStik PRO into the HydroFill PRO. The status indicator will now change from green to red to show that the connection has been made. Firmly screw in the HydroStik PRO.

4. The HydroStik PRO is filled automatically, which is shown by the red status indicator. Charging takes about 4 to 6 hours. An occasional hissing sound indicates that the system is rinsing. The oxygen produced can be seen in the form of bubbles.

5. When the status indicator changes to green, the HydroStik PRO is fully charged and can be removed. A brief hissing sound will occur at this time.

6. When charging is complete, disconnect the HydroFill PRO from the mains and empty the water tank.

Setup of the apparatus

Weigh 1 g of the Mittasch catalyst into a combustion boat. Fasten both gas syringes to the magnetic wall each with a small and a large spring clip (see picture). Place the combustion boat into the centre of the reaction tube and close the reaction tube with silicone stoppers.

Connect the reaction tube between the gas syringes by pushing the ends of the gas syringes into the holes in the silicone stoppers. Mount an additional three-way stopcock above the left gas syringe. Connect this to the three-way stopcock of the gas syringe using a glass connector.

Test the apparatus for air-tightness by setting the three-way stopcocks such that the gas syringes and the reaction tube form a system closed to the atmosphere. The apparatus is air-tight if the pistons can only be pulled away from one another under great force and then spring back into their original positions.

Preparation

Shorten the silicone tubes to the required length. About 50 cm of the 2 mm diameter tube, 55 cm of the 4 mm diameter tube and about 10 cm of the 7 mm diameter tube are needed. Connect the 2 mm diameter tube to the valve of the HydroStik PRO. Attach the HydroStik PRO CPS module to the upper left corner of the panel frame and insert the other end of the silicone tube into the three-way stopcock. Connect the other two tubes together using a tube connector. Insert the end of the 4 mm diameter tube over the valve of the nitrogen gas can and the other end over the three-way stopcock of the right-hand gas syringe.

Fold the indicator paper in the middle and moisten it with a little water. Then push it into the free opening of the additional three-way stopcock.

Place the cartridge Bunsen burner onto a laboratory jack-stand beneath the reaction tube.

Performing the experiment

Tip: Operating the apparatus can be made easier by marking the opening direction of the three-way stopcocks on the stopcocks.

Flushing out the apparatus

Before starting the experiment, the apparatus must be flushed out with nitrogen. This is to ensure that no more oxygen is present and that no detonation gas reaction can occur when it is heated. For this purpose, pass 50 ml of nitrogen into the right-hand gas syringe. Turn the three-way stopcock to allow the nitrogen to be forced into the apparatus such that the air contained within it is pressed into the other gas syringe. Allow the air to pass to the outside via the three-way stopcock of the left-hand gas syringe. Repeat this procedure with a further 50 ml of nitrogen.

Comparison experiment with nitrogen

To conduct a comparison experiment, pass another 100 ml of nitrogen into the apparatus. Adjust the three-way stopcocks of both gas syringes such that the gas in the apparatus can be moved back and forth by moving the syringe pistons. Put the gas bottle aside, as compressed gas bottles can explode on heating.

Now heat the catalyst. As soon as it is glowing red, begin to move the gas back and forth by moving the pistons. Repeat this several times before turning the gas off. Then force the gas into the left-hand gas syringe and pass it over the indicator paper. Immediately close the three-way stopcock again so that no oxygen can enter the apparatus.

There should be no colouration visible on the indicator paper.

Synthesis of ammonia

For the synthesis of ammonia, 100 ml of hydrogen are now passed into the left-hand gas syringe. Discard the first 100 ml by passing it over the indicator paper. One can see that hydrogen also does not colour the indicator paper.

Once again pass 100 ml of hydrogen into the left-hand gas syringe and mix it with the nitrogen that is still present in the apparatus by moving the pistons back and forth. Proceed with the hydrogen-nitrogen mixture in the same way as was done previously with the pure nitrogen.

After passing the gases out over the indicator paper, it should be possible to observe a green-blue colouration on it.

Observations and result of the experiment

The comparison experiment is performed to ensure that when pure nitrogen is heated together with the catalyst, it does not produce a basic gas. Also pure hydrogen does not lead to a colouration of the indicator. Only when both together are heated with the catalyst does a reaction take place. Ammonia is generated in very small amounts, which can be demonstrated by a green-blue colouration of the indicator paper.

As only two molecules of ammonia result from four molecules of hydrogen and nitrogen in the reaction, the reaction is associated with a reduction in volume. However, no substantial volume reduction should be observed with the reaction, as only a very small amount of ammonia is produced. If a large volume change has nevertheless taken place, this is probably due to the fact that hydrogen, a highly volatile gas, has escaped through exerting pressure on the syringe pistons.

This is also the reason why it is not possible with this apparatus to shift the equilibrium in the direction of ammonia by increasing the pressure, as is the case in the Haber-Bosch process. The system is also able to avoid the constraint of a pressure increase through pressure on the pistons by reducing the number of particles. However, this is not effected through a reaction to produce ammonia, but through hydrogen escaping to the outside.

Cleaning and disposal

Tip: When cleaning the gas syringes, ensure the pistons and syringe barrels that belong together are not mixed up. As these parts differ only minimally from one another, this could result in leaks. Differentiation can be made easier by marking parts that belong together accordingly.

Residues of catalyst remaining in the combustion boat can be dissolved by the addition of concentrated nitric acid under the fume cupboard. Dilute the resulting solution and place it in the container for inorganic solvent waste (G4).

Unused catalyst can be stored in a glass tube with a snap-on lid for later experiments. Place the spent catalyst in the collecting container for solid inorganic waste material.