Manufacture, Properties and Uses of Ammonia [Case Study]

Explain how an industrial process such as the Haber process for manufacturing ammonia (NH_3) involves a compromise of rate, equilibrium yield and economic considerations.

Manufacture of ammonia (NH_3) by the Haber Process

Raw Materials.

Nitrogen is easily obtained from air by fractional distillation, (Air is almost 80% nitrogen).
Hydrogen is obtained from methane (natural gas) or naphtha. The hydrocarbons reacted with steam.

methane + steam $\rightarrow$ carbon dioxide + hydrogen.

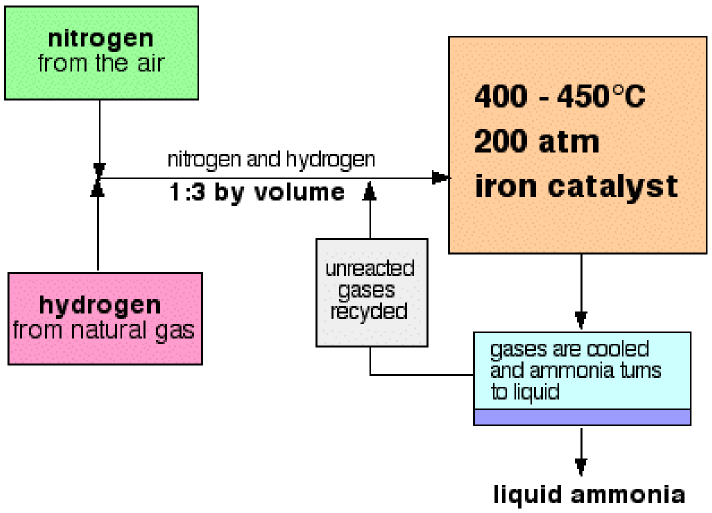
$$CH_{4(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 4H_{2(g)}$$

The raw materials are therefore air - for nitrogen, and methane and water - for hydrogen

The Haber Process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia. The reaction is reversible and the production of ammonia is exothermic.

$$N_{2(g)} + 3H_{2(g)} \qquad 2NH_{3(g)} \qquad \Delta H = -92\ kJmol^{-1}$$

A flow scheme for the Haber Process looks like this:



Industrial conditions for the Haber Process

(i) Temperature between 450 °C and 500°C.

(ii) Pressure of 200 atm (atmospheres)

(iii) An Iron (Fe) catalyst is used. This lowers the E_a (energy of activation) and allows the equilibrium to be established more quickly. The presence of a catalyst has no effect on the position of equilibrium.

(iv) Removal of NH_3

(iv) Recycling the unreacted nitrogen (N_2) and hydrogen (H_2). At each pass of the gases through the reactor, only about 15% of the nitrogen and hydrogen converts to ammonia. (This figure also varies from plant to plant.) By continual recycling of the unreacted nitrogen and hydrogen, the overall conversion is about 98%.

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Some notes on the conditions

The catalyst

The catalyst is actually slightly more complicated than pure iron. It has potassium hydroxide added to it as a promoter - a substance that increases its efficiency.

The pressure

The pressure varies from one manufacturing plant to another, but is always high. You can't go far wrong in an exam quoting 200 atmospheres.

Recycling

At each pass of the gases through the reactor, only about 15% of the nitrogen and hydrogen converts to ammonia. (This figure also varies from plant to plant.) By continual recycling of the unreacted nitrogen and hydrogen, the overall conversion is about 98%.

Explaining the conditions

The nitrogen triple bond is very stable and so a catalyst helps to break this bond in stages. As the process is exothermic, increasing the heat will favour the reverse reaction. However Collision Theory favours a higher temperature to ensure both the correct activation energy as well as the orientation. A 15% yield is achieved in a short time and the ammonia is liquefied (bp-33) to start the process again.

$$N_{2(g)} + 3H_{2(g)} \qquad 2NH_{3(g)} \qquad \Delta H = -92\ kJmol^{-1}$$

Effect of temperature

Equilibrium considerations

You need to shift the position of the equilibrium as far as possible to the right in order to produce the maximum possible amount of ammonia in the equilibrium mixture.

The forward reaction (the production of ammonia) is exothermic.

$$N_{2(g)} + 3H_{2(g)} \qquad 2NH_{3(g)} \qquad \Delta H = -92\ kJmol^{-1}$$

According to Le Chatelier's Principle, this will be favoured if you lower the temperature. The system will respond by moving the position of equilibrium to counteract this - in other words by producing more heat.

In order to get as much ammonia as possible in the equilibrium mixture, you need as low a temperature as possible. However, 400 - 450°C isn't a low temperature!

Rate considerations

The lower the temperature you use, the slower the reaction becomes. A manufacturer is trying to produce as much ammonia as possible per day. It makes no sense to try to achieve an equilibrium mixture which contains a very high proportion of ammonia if it takes several years for the reaction to reach that equilibrium. You need the gases to reach equilibrium within the very short time that they will be in contact with the catalyst in the reactor..

The compromise

400 - 450°C is a compromise temperature producing a reasonably high proportion of ammonia in the equilibrium mixture (even if it is only 15%), but in a very short time.

Effect of pressure

Equilibrium considerations

$$N_{2(g)} + 3H_{2(g)} \qquad 2NH_{3(g)} \qquad \Delta H = -92\ kJmol^{-1}$$

Notice that there are 4 molecules on the left-hand side of the equation, but only 2 on the right. According to Le Chatelier's Principle, if you increase the pressure the system will respond by favouring the reaction which produces fewer molecules. That will cause the pressure to fall again. In order to get as much ammonia as possible in the equilibrium mixture, you need as high a pressure as possible. 200 atmospheres is a high pressure, but not amazingly high.

Rate considerations

Increasing the pressure brings the molecules closer together. In this particular instance, it will increase their chances of hitting and sticking to the surface of the catalyst where they can react. The higher the pressure the better in terms of the rate of a gas reaction.

Economic considerations

Very high pressures are very expensive to produce on two counts. You have to build extremely strong pipes and containment vessels to withstand the very high pressure. That increases your capital costs when the plant is built. High pressures cost a lot to produce and maintain. That means that the running costs of your plant are very high.

The compromise

200 atmospheres is a compromise pressure chosen on economic grounds. If the pressure used is too high, the cost of generating it exceeds the price you can get for the extra ammonia produced.

Effect of concentration

Equilibrium considerations

$$N_{2(g)} + 3H_{2(g)} \qquad 2NH_{3(g)} \qquad \Delta H = -92\ kJmol^{-1}$$

Separating (removal) the ammonia

When the gases leave the reactor they are hot and at a very high pressure. Ammonia is easily liquefied under pressure as long as it isn't too hot, and so the temperature of the mixture is lowered enough for the ammonia to turn to a liquid. The nitrogen and hydrogen remain as gases even under these high pressures, and can be recycled.

The catalyst

Equilibrium considerations

The catalyst has no effect whatsoever on the position of the equilibrium. Adding a catalyst doesn't produce any greater percentage of ammonia in the equilibrium mixture. Its only function is to speed up the reaction.

Rate considerations

In the absence of a catalyst the reaction is so slow that virtually no reaction happens in any sensible time. The catalyst ensures that the reaction is fast enough for a dynamic equilibrium to be set up within the very short time that the gases are actually in the reactor.

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Properties of Ammonia (NH_3)

Ammonia is a basic gas. It turns red litmus blue. It is extremely soluble in water with which it reacts forming hydroxide ions

Ammonia reactions:

Ammonia is a weak base with a lone pair of electrons which allows it to accept protons from acids to form the ammonium ion, NH_4^+.

$$NH_{3(g)} + H_2O_{(l)} \qquad NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$NH_{3(g)} + H^+{}_{(aq)} \qquad NH_4^+{}_{(aq)}$$

The basic character is evident in its reaction with acids to form ammonium salts.

ammonia + sulfuric acid → ammonium sulfate

$$2NH_{3(g)} + H_2SO_{4(aq)} \rightarrow (NH_4)_2SO_{4(s)}$$

Dense white fumes of ammonium chloride, NH_4Cl, are formed from the reaction of ammonia gas with hydrogen chloride gas.

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

Uses of Ammonia (NH_3)

Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food (amino acids in protein) and fertilisers.

- Ammonia is used to manufacture fertilisers (e.g. ammonium sulfate $(NH_4)_2SO_4$, ammonium nitrate NH_4NO_3 and urea, $(NH_2)_2CO$)
- Ammonia is used to make nitric acid (HNO_3), which in turn reacts with ammonia to form ammonium nitrate. Ammonium nitrate is a very important fertiliser and explosive.
- Ammonia is used in the synthesis of sodium carbonate (Na_2CO_3). Sodium carbonate has many uses from manufacturing glass and paper to wool processing.
- Synthesis of numerous organic compounds used as dyes, drugs, and in plastics; and in various metallurgical processes.
- Used in many commercial cleaning products (cloudy or household ammonia).

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Nitric acid synthesis

Once ammonia has been produced by the Haber process, it can be converted into nitric acid through a multi-step procedure known as the Ostwald process. In the first step in this reaction, ammonia and oxygen gas catalytically react to form nitrogen monoxide:

(1) $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$ $\Delta H = -906$ kJ

The reaction is quite exothermic. In the commercial reaction, the catalyst used is a platinum-rhodium metal gauze that is heated to about 900 ^{0}C. However, even a hot copper wire can catalyze the reaction in the laboratory. Once the reaction has started, the energy it produces is enough to keep the catalyst hot enough to sustain the reaction.

In the next step, the NO reacts with oxygen to produce NO_2. No catalyst is required for this reaction, as it will occur in air at room temperature.

(2) $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

The NO_2 can be compressed and cooled which will make it dimerize into N_2O_4, which can then be used as an oxidizer for rocket fuel.

(3) $2NO_{2(g)}$ $N_2O_{4(g)}$ + 58 kJ (i.e. $\Delta H = -$ve)

From le Châtelier's principle we can predict that at high pressures the equilibrium will be shifted to the right, since there are less molecules of gas in the products. Similarly, at lower temperatures the reaction will shift to the right.

Instead of storing the NO_2, we can use it to produce nitric acid. The $NO_{2(g)}$ reacts with water to produce nitric acid (HNO_3) and NO. The nitric acid is separated by distillation, and the NO can be recycled through reaction (2).

(4) $3NO_{2(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(aq)} + NO_{(g)}$

The nitric acid can then be used in the manufacture of countless numbers of different nitrogen containing compounds. For example, ammonia will react with the nitric acid to produce ammonium nitrate, one of the most important forms of nitrogen fertilizers.

(5) $3NH_{3(g)} + HNO_{3(l)} \rightarrow 2NH_4NO_{3(s)}$

Urea ($(NH_2)_2CO$) synthesis

Urea is made from ammonia and carbon dioxide. The ammonia and carbon dioxide are fed into the reactor at high pressure and temperature, and the urea is formed in a two-step reaction

$2NH_3 + CO_2$ NH_2COONH_4 (ammonium carbamate)

NH_2COONH_4 $H_2O + NH_2CONH_2$ (urea)

The urea contains unreacted NH_3 and CO_2 and ammonium carbamate. As the pressure is reduced and heat applied the NH_2COONH_4 decomposes to NH_3 and CO_2. The ammonia and carbon dioxide are recycled. The urea solution is then concentrated to give 99.6% w/w molten urea, and granulated for use as a fertiliser (slow release) and a chemical feedstock.

Sodium carbonate (Na_2CO_3) synthesis

Sodium carbonate, Na_2CO_3, has a number of uses but its most common use is in the production of glass. Since the 1860's, sodium carbonate has been produced using the Solvay Process, which is a continuous process using limestone ($CaCO_3$) to produce carbon dioxide (CO_2) which reacts with ammonia (NH_3) dissolved in brine (concentrated $NaCl_{(aq)}$) to produce sodium carbonate.