

Introduction

Most of the world's nitrogen in found in the air as nitrogen gas. In this chapter, the chemistry of the conversion of this nitrogen into ammonia by the Haber Process is investigated together with uses of ammonia.

Chapter Opener (page 260)

1. To open the chapter, the following questions could be discussed. Precise answers are not needed at this stage.

How useful is ammonia to us?

Answer: Ammonia is used in the manufacture of fertilisers and in window cleaners.

How is ammonia manufactured?

Answer: Ammonia is produced commercially by the reaction of nitrogen and hydrogen in the Haber Process. The equation for the reaction is:

 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Ammonia can be used to make explosives. Should scientists use their knowledge for war?

Answer: Refer to the discussion in Additional Worksheet 1 at the end of this chapter.

2. Carry out an 'Inquiry Preview.'

Learning Outcomes

After completing this chapter, students should be able to:

- > state the major uses of ammonia
- describe the use of nitrogen and hydrogen in the manufacture of ammonia
- state that some chemical reactions are reversible
- describe the essential conditions for the manufacture of ammonia by the Haber Process
- describe the displacement of ammonia from its salts

Teaching pointers

17.1 What are Some Uses of Ammonia? (page 261)

Stimulation

Bring into the classroom some products made from ammonia, such as some of those mentioned in Figure 17.2. Discuss these uses, especially in the production of fertilisers needed to grow the food crops needed to feed the world. Introduce the production of ammonia from nitrogen in the air. Students can also carry out an Inquiry Preview by preparing a lost of questions that they can answer as the chapter is studied.

Notes for Teachers

Production and uses for ammonia

The annual production of ammonia has increased from about 5 million tonnes in 1950 to over 130 million tonnes today. The reason for the increase is due to an increase in the usage of fertilisers to support the growth of the world's population.

Uses for ammonia include the following:

| Textiles fibre processing | To "relax" cotton fibres during manufacture, reducing the tendency to shrink in use. | | | |
|---------------------------|--|--|--|--|
| Explosives | Nitric acid, made from ammonia, is used to manufacture explosives. | | | |
| Refrigeration | The refrigerant used for the refrigeration for bulk food storage often uses ammonia. | | | |
| Water purification | Used to manufacture a chloramine (monochloramine NH_2Cl), a more effective anti-bacterial compound than chlorine. | | | |
| Food production | Ammonium hydrogencarbonate is a raising agent for biscuits. | | | |
| Rubber production | Ammonia and ammonium laurate are used to preserve raw latex. | | | |
| Photography | Ammonium thiosulfate is used in fixers for film processing. | | | |
| Metal plating | Ammonium carbonate is used in chrome plating; ammonium methanoate and ethanoate are used in other plating processes. | | | |
| Other uses | Pulp/paper manufacture, household cleaners, pharmaceuticals and chemical intermediates. | | | |

Teaching pointers

17.2 How is Ammonia Manufactured? (page 262)

- In discussing the Haber Process reaction, refer back to Avogadro's law and the volume ratios of the gases in the reaction (Section 10.3 on page 178 of the Textbook). To enhance students' understanding of the process, discuss the process itself first before introducing the ideas of reversible reaction, equilibrium and reaction conditions.
- 2. Hydrogen for the Haber Process can be obtained by the cracking of petroleum fractions. As cracking is not introduced until Chapter 25, just give the class a general idea without any details or equations. Today, the reaction of natural gas (methane) with steam is more commonly used to produce the hydrogen needed.
- **3.** An iron catalyst is used in the Haber Process. In industrial practice, magnetite Fe_3O_4 , is used instead of iron. This is reduced by the hydrogen feedstock to form fine particles of metallic iron which then catalyse the reaction.
- **4.** Emphasise the efficiency of the Haber Process as discussed on page 263 of the Textbook.
- **5.** When discussing the conditions for the manufacture of ammonia, discuss temperature and pressure separately to see how they affect the yield. Then discuss the idea of optimum conditions which are a compromise between yield, time and costs. Chemists have to strike a balance between temperature and pressure to get the most economical yield, i.e. a good yield in a reasonable time and at a reasonable cost.
- 6. Additional Exercise 1 raises the issue of the potential of scientific knowledge to be used for harm as well as for good, and the dilemmas that scientists sometimes have to face in deciding how to use their knowledge. The exercise looks at Haber's active participation in the development of poison gases for warfare. Reference could also be made to the toxic properties of chlorine that made it useful for use in chemical warfare. Note too, that in contrast to Haber, Linus Pauling (Chapter 6, Additional Exercise 6.3) was a peace activist.
- 7. Most of the ammonia from the Haber Process is used in the production of ammonia fertilisers, the three most important being ammonium nitrate NH_4NO_3 , ammonium sulfate $(NH_4)_2SO_4$ and urea $CO(NH_2)_2$.

Chemistry Inquiry (page 264)

Group Discussion

- (a) The amount of product that is actually obtained in a reaction (usually less than the theoretical amount calculated using the equation for the reaction).
 - (b) Because as products form, some of them are changed back into the reactants again.
- 2. The conditions of 400 °C and 300 atmospheres give 50% ammonia at equilibrium. These conditions are not used because the pressure is too high and will result in extra expense and safety risk. The conditions of 300 °C and 100 atmospheres also give 50% ammonia at equilibrium. These conditions are not used as the reaction would be far too slow and it would take a very long time to reach equilibrium.

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Skills Practice (page 265)

- (a) The yield is almost 100%.
 (b) The yield is high.
 (c) At 100 °C, the reaction would be too slow. The pressure is 400 atmospheres: it is expensive to make metal chambers that can withstand high pressures.
- 2. This is to recycle the unreacted gases in order to save money and to prevent pollution which results from releasing hydrogen into the air.
- 3. At a 98% yield, the theoretical amount of ammonia produced = $7000 \div 98 \times 100$ = 7143 tonnes

 $N_{2}(g) + 3H_{2}(g) = 2NH_{3}(g)$

From the balanced equation, 34 g of NH_3 is produced from 28 g N_2 and 6 g H_2 . Therefore 7143 tonnes of NH_3 is produced from (a) 5882 tonnes N_2 and (b) 1261 tonnes H_2 .

- 4. Most ammonia from a Haber Process plant is converted into fertilisers. As Singapore does not have enough land for agricultural purposes, there is little need for fertilisers and thus a Haber Process plant is not needed. Also, it is cheaper to import other products made with ammonia than to build a Haber Process plant and related industries to produce them.
- 5. (a) $NH_3(g) + HNO_3(aq) \longrightarrow NH_4NO_3(aq)$
 - (b) The NH₃ comes out as ammonia gas from a reaction between the ammonium nitrate and calcium hydroxide. The equation for this reaction is:

 $2NH_4NO_3(s) + Ca(OH)_2(s) \longrightarrow Ca(NO_3)_2(aq) + 2NH_3(g) + 2H_2O(l)$

Notes for Teachers

The conversion of nitrogen gas into nitrogen compounds

There are few practical ways of converting nitrogen gas into nitrogen compounds. This is due to a lack of reactivity of nitrogen (nitrogen has very strong N≡N triple bond). In nature, lightning causes nitrogen gas to react with oxygen in the air to form nitrogen compounds. When it rains, the nitrogen oxides react with water to become nitric acid which reacts with oxides in the soil to form nitrate compounds. This process was duplicated at the beginning of the 20th Century in Norway using cheap electricity from hydroelectric power stations. However, the process was very expensive and is no longer used. The Haber Process is the only economic large-scale method of making nitrogen compounds from nitrogen gas.

Chemistry in **Society** (page 265)

The Development of the Haber Process

The sodium nitrate obtained from rocks was also converted into nitric acid by reacting and distilling a mixture of sodium nitrate and concentrated sulfuric acid as shown in the following equation:

 $NaNO_{3}(s) + H_{2}SO_{4}(aq) \longrightarrow NaHSO_{4}(aq) + HNO_{3}(g)$

The nitric acid was used to make explosives, such as nitroglycerine and trinitrotoluene (TNT). But during World War I, the British Navy cut off the supplies of sodium nitrate needed in Germany to make nitric acid. As a result, chemists in Germany developed a process to convert the ammonia from the recently invented Haber process into nitric acid as summarised by the following equations: $\begin{array}{l} 4NH_{3}(g) + 5O_{2}(g) \longrightarrow 4NO(g) + 6H_{2}O(g) \\ 2NO(g) + O_{2}(g) \longrightarrow 2NO_{2}(g) \\ 4NO_{2}(g) + O_{2}(g) + 2H_{2}O(g) \longrightarrow 4HNO_{3}(aq) \end{array}$

This process is now known as the Ostwald Process. Successful production of concentrated nitric acid on a large scale began in 1915. Some historians believe that because Germany was able to produce nitric acid, the war was prolonged by as much as one year.

Exercise

- Supplies of sodium nitrate rock and guano that were used to produce ammonia were running out. As the world population increased, the production of food crops need to keep up with this population growth. Thus it became necessary to find a new way to produce ammonia.
- 2. This is necessary so as to find out first if the reaction will occur and subsequently the best design for the process. If changes need to be made, this is more easily and cheaply done with small-scale apparatus. Once all the design problems have been solved, the large industrial plant can be built.

17 Chapter Review

Self-Management

Misconception Analysis (page 266)

- 1. **False** As reversible reactions also involve a backward reaction, some of the products always change back into reactants.
- 2. **False** At equilibrium, the forward and backward reactions continue. But as they occur at the same speed, we observe no change in the amounts of the reactants and products.
- 3. **False** As the Haber reaction is a reversible reaction, the reaction does not go to completion.
- 4. **True** As a result, conditions are chosen to give the most economical amount of ammonia in a given time.
- 5. **True** Some ammonia is used in window cleaning solutions but this is only a tiny fraction of the total amount of ammonia produced.

Practice

Structured Questions (page 266)

- 1. (a) $N_2(g) + 3H_2(g) \implies 2NH_3(g)$
 - (b) (i) Nitrogen is obtained from the air. Hydrogen is obtained from cracking compounds in petroleum or from the reaction of natural gas (methane) with steam.
 - (ii) The shortage of petroleum/natural gas will result in a shortage of hydrogen gas. This will affect the amount of ammonia and fertilisers produced. The decrease in the amount of fertilisers will affect the yield of food crop and will result in a shortage of food.
 - (c) (i) Iron
 - (ii) Iron is used as a catalyst in the Haber Process.
- 2. (a) **A**-nitrogen
 - ${\bm B}-\text{hydrogen}$
 - C sodium hydroxide (or another base/alkali)
 - (b) (i) Sodium chloride and water
 - (ii) $NH_4Cl(s) + NaOH(aq) \longrightarrow NaCl(s) + NH_3(g) + H_2O(l)$
- (a) The Haber Process is a reversible reaction. Thus, as ammonia is formed, some of it decomposes into nitrogen and hydrogen again.
 - (b) The yield increases.
 - (c) The reaction is faster/reaches equilibrium more quickly.
 - (d) The yield decreases.
 - (e) (i) About 40%

- (ii) In the Haber Process, unreacted nitrogen and hydrogen are passed over the catalyst again to form more ammonia.
- 4. (a) (i) The reaction is faster and there is a greater percentage of ammonia at equilibrium.
 - (ii) It is more expensive as thick tanks and pipes are needed to contain the pressure. It is also more dangerous.
 - (b) In high wage countries, it saves labour costs if the process is faster. It would be more economical in countries with cheap steel tanks and pipes.
 Note: Students may come up with other reasonable answers.

Free Response Questions (page 267)

Responses to this question may include the following points:

Some reasons why an ammonia plant is important:

- It is used to manufacture (nitrogen) fertilisers which are needed to grow food/increase crop yields, especially in developing countries.
- Ammonia is a raw material for many other products needed by developing countries, e.g. production of paper, nylon and household cleaning solutions.
- The ammonia plant will require other factories/industries to be set up, e.g. fertiliser plants, thus providing many jobs.
- The products from these industries can be exported to other countries and this helps to boost the economy.

Extension: Answers/Notes

Calculations with a spreadsheet

Remind students that 1 mole of N_2 gives 2 moles of NH_3 while 1 mole of NH_3 gives ½ mole of $(NH_4)_2SO_4$. It is assumed that students have had some practice in the use of spreadsheets.

The following is an example of a spreadsheet using the following masses of nitrogen: 1 kg, 1000 kg and 50 000 kg.

| Α | В | C | D | E | F | G | H |
|---------------|----------------|---------------------------------------|---------------------|-------------------------|------------------------|------------------------|---|
| Mass of N_2 | Moles of N_2 | $\frac{\text{Moles of}}{\text{NH}_3}$ | Yield of $\rm NH_3$ | Moles of $(NH_4)_2SO_4$ | Mass of $(NH_4)_2SO_4$ | Mass of $(NH_4)_2SO_4$ | Yield of (NH ₄) ₂ SO ₄ |
| kg | moles | moles | moles | moles | g | kg | kg |
| 1 | 35.714286 | 71.428571 | 70 | 35 | 4620 | 4.62 | 4.5276 |
| 1000 | 35714.286 | 71428.571 | 70000 | 35000 | 4620000 | 4620 | 4527.6 |
| 50 000 | 1785714.3 | 3571428.6 | 3500000 | 1750000 | 231000000 | 231000 | 226380 |

The spreadsheet formulae for the cells are:

B3: =A3*1000/28

C3: =B3*2 D3: =C3*98/100

E3: =D3/2

F3: =E3*132

G3: =F3/1000

H3: =G3*98/1000

Additional Teaching Material

Additional Exercise 1: Ammonia for Peace and War

Objective

- To further appreciate that scientific knowledge can be used to benefit or to harm society
- To discuss whether scientific knowledge should be used for war

Key Competencies

- CL: use and abuse of scientific knowledge
- CIT: creativity [generate ideas], sound reasoning [decision-making]
- ICS: openness, communication effectively [collaboration with others, short talk] presentation]

Science can be used to benefit society and to cause harm. Ammonia can be used to sustain or destroy life.

Ammonia from the Haber Process is used to make fertilisers (Figure 1). Fertilisers have enabled farmers to increase the yield of food crops needed to feed the world's population. Ammonia is also used to make explosives (Figure 2). The Haber Process became very important when the First World War started in 1914, as Germany needed explosives.

During this period, Haber also developed poison gases for use in chemical warfare (Figure 3). These include chlorine and mustard gas. In April 1915, the German army first used chlorine gas, with horrifying results. Over 5000 soldiers were killed and many others seriously injured.

Haber said 'Yes' when his country asked him to develop poisons for war. This was in contrast to Michael Faraday, the 19th Century English scientist, who said 'No' when his government asked him to do the same. Interestingly, Haber's first wife also believed that science should be used for constructive purposes, and not to make weapons of mass destruction.



Figure 1 Ammonia is used to make fertilisers.



Figure 2 Many explosives, such as those used in hand grenades, are derived from ammonia.



Figure 3 Chlorine being released from cannisters during a gas attack in World War I.

Question for Discussion

Should scientists use their knowledge for war?

1. Haber said 'Yes', whereas Faraday said 'No'. In the table below, list some points 'for' and 'against' the use of scientific knowledge for war.

| 'For' the use of scientific knowledge for war | 'Against' the use of scientific knowledge for war |
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- **2.** In your groups, discuss the above question.
- **3.** (Optional) Prepare a short talk to present the points in your group discussion together with the conclusion, if any.

The website below provides more information on the life and work of Fritz Haber, his contribution to the development of chemical warfare, and the contrasting views of Haber and his wife on the use of scientific knowledge.

http://world.std.com/-jlr/doom/haber.htm