Topic 23 – Ammonia

Subject content

(a)	describe the use of nitrogen, from air, and hydrogen, from the cracking of crude oil, in the manufacture of ammonia
(b)	state that some chemical reactions are reversible, e.g. manufacture of ammonia
(c)	describe the essential conditions for the manufacture of ammonia by the Haber process
(d)	describe the displacement of ammonia from its salts

23.1 Reversible Reactions

Reversible reaction: can go both <u>forward + backward</u> at <u>same time</u>

- **forward reaction**: left to right
- **backward reaction**: right to left

forward reaction

$$\mathbf{A+B \rightleftharpoons C+D}$$

backward reaction

Decomposition of ammonium chloride:

NH_4Cl (s) ⇌ NH_3 (g) + HCl (g)	
<u>Forward reaction</u> NH_4Cl (s) → NH_3 (g) + HCl (g) Ammonium chloride decomposes to form ammonia and hydrogen chloride gas	<u>Backward reaction</u> NH_3 (g) + HCl (g) → NH_4Cl (s) Ammonium chloride reforms upon cooling

Formation of ammonia:

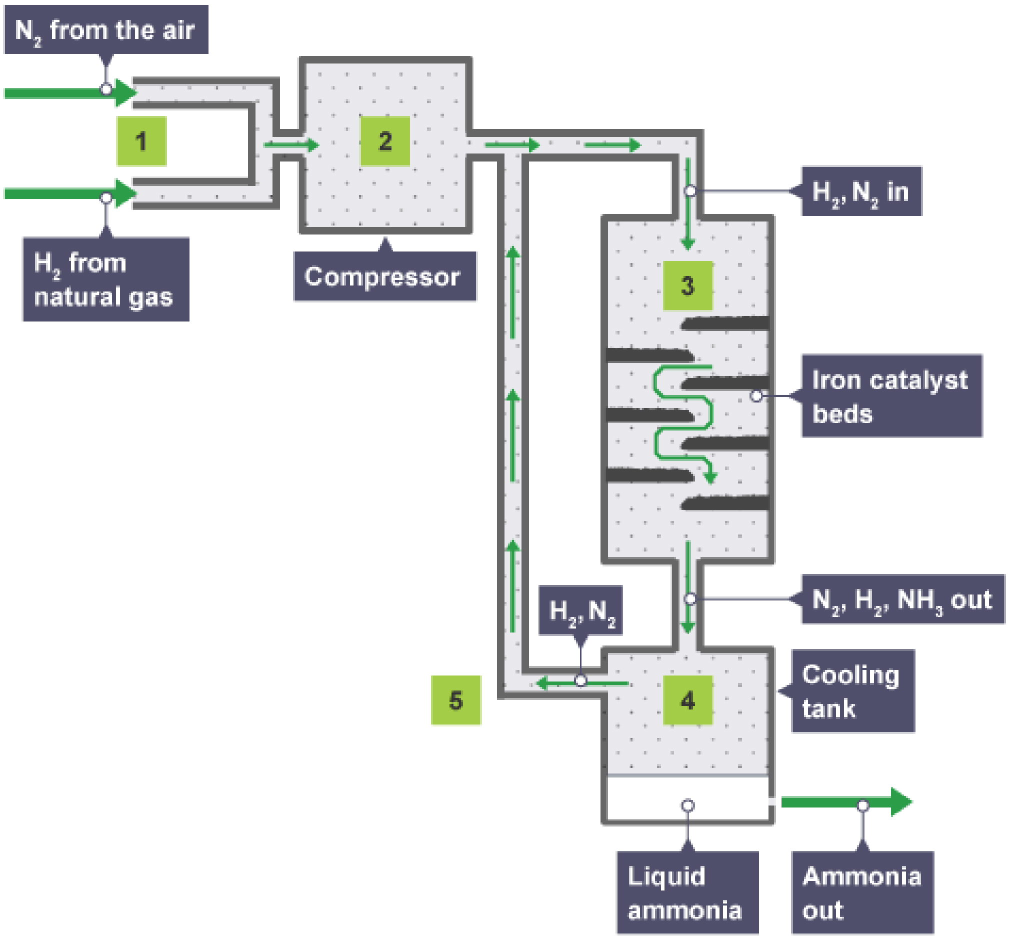
N_2 (g) + 3 H_2 (g) ⇌ 2 NH_3 (g)	
<u>Forward reaction</u> N_2 (g) + 3 H_2 (g) → 2 NH_3 (g)	<u>Backward reaction</u> 2 NH_3 (g) → N_2 (g) + 3 H_2 (g)

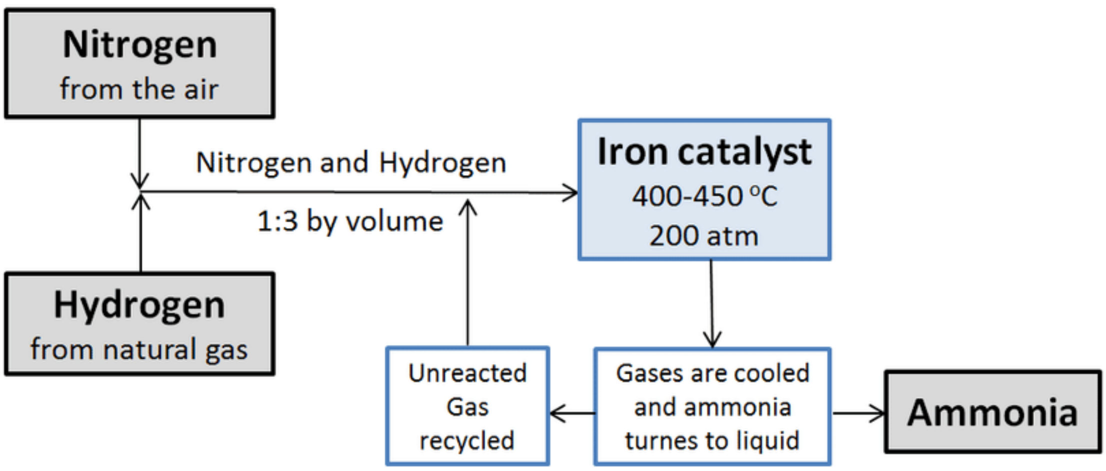
Nitrogen: obtained from <u>fractional distillation of liquid air</u>
Hydrogen: produced from <u>cracking of petroleum</u>

23.2 Haber Process

nitrogen + hydrogen ⇌ ammonia

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



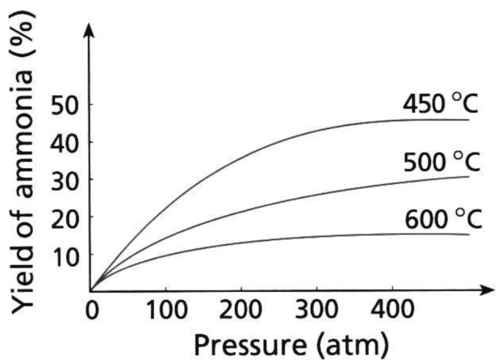


Step	Description
1. **Gases**	● Mixed in proportion 1:3 by volume 1) nitrogen 2) hydrogen
2. **Compressor**	● Compressed to 250 atm
3. **Catalyst chamber**	● Heated to 450°C ● Passed over finely divided iron catalyst ● 10 ~ 15% nitrogen + hydrogen → ammonia
4. **Resulting gas**	● Mixture of ammonia + nitrogen + hydrogen ● Cooled
5. **Cooling chamber**	● Ammonia gas: condense → liquid ammonia ● Unreacted nitrogen + hydrogen: pumped into converter for further reaction (recycled)

<u>**Conditions**</u>

Carefully control conditions

- Reaction is reversible → ammonia decompose & convert back to nitrogen + hydrogen
- Achieve max yield of ammonia + minimum cost



Rxn condition	Change	Description	Optimal
1. **Pressure**	Pressure ↑ yield ↑ Pressure ↑ rate ↑	● Costly to maintain high pressure → expensive equipment ● special pumps ● stronger pipes ● Limit to amt of pressure applied	250 atm
2. **Temperature**	Temp ↓ yield ↑ Temp ↓ rate ↓	● Reduce decomposition of ammonia	450°C
3. **Catalyst**	Catalyst ✓ rate ↑	● Rxn slow at high pressure + relatively high pressure	iron catalyst

23.3 Displacement of Ammonia from its Salts

Ammonium salt heated with alkali, ammonia is displaced from salt

Examples:

Alkali	Equation
sodium hydroxide	NH_4Cl (s) + NaOH (aq) → **<u>NH_3 (g)</u>** + H_2O (*l*) + NaC*l* (aq)
calcium hydroxide	2 NH_4C*l* (s) + $Ca(OH)_2$ (aq) → **<u>2 NH_3 (g)</u>** + 2 H_2O (*l*) + CaC*l*$_2$ (aq)

Loss of nitrogen from fertilisers
- Calcium hydroxide + calcium oxide → neutralise excess acidity in soil
- React with ammonium / nitrogenous → ammonia gas, escape into atm
- X add both at same time

Note: examples of nitrogenous fertilisers
(a) liquid ammonia (<u>**N**</u>H_3)
(b) ammonium nitrate (<u>**N**</u>H_4<u>**N**</u>O_3)
(c) ammonium sulfate [(<u>**N**</u>H_4)$_2$$SO_4$]
(d) urea [CO(<u>**N**</u>H_2)$_2$]

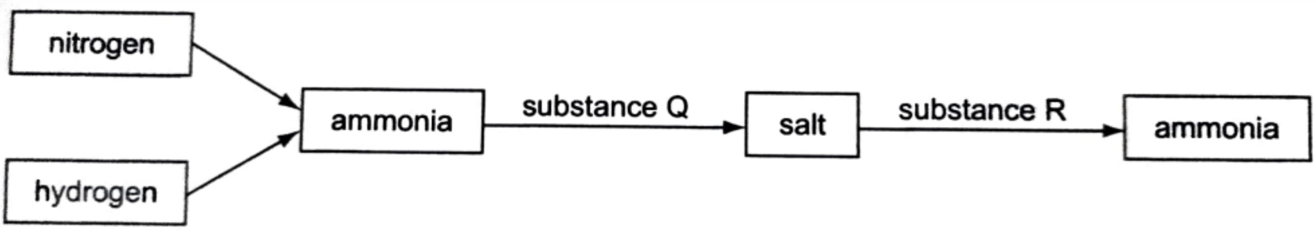
Typical questions

Multiple choice questions

1 A reversible reaction is exothermic in the forward direction and the heat given off is 196 kJ/mol. The activation energy for the forward reaction is 75 kJ/mol.
What is the activation energy of the **reverse** reaction? (2020 P1 Q14)

A 75 kJ/mol
B 121 kJ/mol
C 196 kJ/mol
D 271 kJ/mol

2 Ammonia is produced by the reaction of the elements hydrogen and nitrogen in the Haber process. One of these elements is obtained from crude oil.
The ammonia formed can be reacted with substance Q to form a salt. Ammonia can be displaced from this salt by reacting with substance R.



Which row correctly shows the element obtained from crude oil and the types of substances corresponding to Q and R? (2013 P1 Q26)

	element obtained from crude oil	substance Q	substance R
A	hydrogen	acid	base
B	hydrogen	base	acid
C	nitrogen	acid	base
D	nitrogen	base	acid

3 Ammonia is produced by the Haber process.
Which statement is **not** correct? (2012 P1 Q24)

A A catalyst of iron is used.
B Each hydrogen molecule reacts with three nitrogen molecules to form two molecules of ammonia.
C Hydrogen for the process can be obtained by the cracking of oil.
D The reaction is reversible.

4 In which reaction is ammonia gas not produced?

A Haber Process
B Reacting ammonium sulfate with dilute sulfuric acid
C Reacting ammonium chloride with magnesium hydroxide
D Reacting ammonium phosphate with calcium hydroxide

5 In the Haber process, what is the source of hydrogen?

A Hydrochloric acid
B Water
C Crude oil
D Air

6 Ammonium salts react with sodium hydroxide to produce ammonia gas. Which of the following will give the greatest mass of ammonia upon reaction with sodium hydroxide?

A 0.5 mol of $(NH_4)_2SO_4$
B 0.5 mol of $(NH_4)_2CO_3$
C 0.5 mol of $(NH_4)_3PO_4$
D 1.0 mol of NH_4Cl

Structured questions

1 Ammonium sulfate is a fertiliser.

The table shows some information about two industrial processes that are used to make ammonium sulfate. In each process, ammonium sulfate is the useful product.

process	equation	atom economy
1	$2\ NH_3(g) + H_2SO_4(aq) \rightarrow (NH4)_2SO_4(aq)$	100%
2	$(NH_4)_2CO_3(aq) + Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow (NH_4)_2SO_4(aq) + CaCO_3(s)$	> 50%

The atom economy of a process is a measure of the percentage by mass of the products that are useful.

$$\textbf{atom economy} = \frac{M_r \text{ of useful product}}{\text{total } M_r \text{ of products}} \times 100\%$$

(2020 P1 B9 OR)

(a) The table says that the atom economy for process 2 is > 50%.
Calculate the actual atom economy of process 2. [2]

Mr of $(NH_4)_2SO_4$ = 2(14+4) + 32 + 4(16) = 132

M_r of $CaCO_3$ = 40 + 12 + 3(16) = 100

Atom economy = $\frac{132}{132 + 100} \times 100\%$ = **<u>56.9%</u>** (3 s.f.)

(b) Suggest reasons why the atom economies of the two processes are different. [2]

<u>In process 1, $(NH_4)_2SO_4$ is the only product and thus has an atom economy of 100%.</u>

<u>In process 2, $CaCO_3$ is produced as a by-product with $(NH_4)_2SO_4$, thus its atom economy will be lower.</u>

(c) In process 1, 1000 dm^3 of ammonia, measured at room temperature and pressure, is added to the reactor.
What mass of sulfuric acid is needed to completely react with 1000 dm^3 of ammonia? [3]
(One mole of gas occupies 24 dm^3 at room temperature and pressure.)

No. of moles of NH_3 = 1000/24 = 41.667 mol

No. of moles of H_2SO_4 = 1/2 × 41.667 = 20.833 mol

Mass of H_2SO_4 = 20.833 × [2(1) + 32 + 4(16)] = **<u>2040 g</u>** (3 s.f.)

(d) Ammonium sulfate is sold as a solid fertiliser.

(i) Describe how solid ammonium sulfate can be separated from the reaction mixture formed in process 2. [2]

- Filter the mixture. Remove the residue which is calcium carbonate solid and obtain ammonium sulfate solution as the filtrate.
- Heat the solution to saturation and allow to cool for ammonium sulfate crystals as residue. Press dry with filter paper to obtain solid ammonium sulfate crystals.

(ii) The percentage yield of ammonium sulfate in process 2 is lower than in process 1. Suggest a reason why. [1]

More reactants are involved in process 2. More impurities will be present and thus will have a lower percentage yield.

2 The process of making ammonia from raw materials has several stages.
The equations show two stages in the process.

Stage 1: Methane reacts with steam to make hydrogen.

$CH_4(g) + H_2O(g) \rightleftharpoons CO_2(g) + 3\ H_2(g)$	$\Delta H = +210$ kJ/mol	**Conditions:** 30 atm nickel oxide catalyst 800°C

Stage 2: Hydrogen formed reacts with nitrogen to make ammonia in a reactor.

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$	$\Delta H = -92$ kJ/mol	**Conditions:** 25 – 150 atm iron catalyst 450°C

(2018 P2 A6)

(a) Less energy is needed to maintain the temperature for stage 2 than is needed for stage 1. Suggest two reasons why the reaction in stage 2 requires less energy. [2]

- The temperature required in stage 2 is 450°C which is lower than the 800°C required in stage 1.
- Reaction in stage 2 is exothermic while the reaction in stage 1 is exothermic.

(b) The gases from stage 1 are separated. The waste gas produced in stage 1 is burned as a fuel. Explain why it is important that this gas is collected and burned. [2]

- Carbon monoxide is a poisonous gas that is colourless and odourless.
- It prevents the haemoglobin in blood to transport oxygen to the rest of the body and causes headaches, breathing difficulties or even death.

(c) In stage 2, nitrogen and hydrogen are mixed in definite proportions before they enter the reactor.
The table shows the percentages of each gas in the mixture by volume and by mass.

	nitrogen	hydrogen
percentage by volume	25	75
percentage by mass	82	18

(i) Explain why these percentages by volume are chosen. [2]

The percentages by volume used is similar to the molar ratio of nitrogen to hydrogen (1 : 3) to minimise excess.

(ii) Explain why the percentages of the gases are different when they are measured by volume and when they are measured by mass. [1]

A mole of any gas has the same volume (at the same conditions of temperature and pressure). However, gases do not have the same molar mass.

(iii) The gases leaving the reactor contain unreacted nitrogen and about 15% ammonia by volume. Unreacted nitrogen and hydrogen are fed back into reactor in stage 2.
Give **two** reasons why the unreacted gases are fed back into the reactor. [2]

- Unreacted gases are recycled to minimise the cost of raw materials.
- A higher percentage of the reactants is eventually changed into ammonia.

3 Ammonia is used to manufacture nitric acid using a two-stage process.
In stage 1, ammonia is converted to nitrogen(II) oxide by heating it to a high temperature of 300°C.

$$4\ NH_3\ (g) + 5\ O_2\ (g) \rightarrow 4\ NO\ (g) + 6\ H_2O\ (g);\ \triangle H = -ve$$

In stage 2, nitrogen(II) oxide is converted to nitric acid.

$$4\ NO\ (g) + 2\ H_2O\ (g) + 3\ O_2\ (g) \rightarrow 4\ HNO_3\ (aq)$$

(a) Describe what happens when the temperature in the reacting system in stage 1 is increased.

When the temperature is increased, the reacting gas molecules gain kinetic energy.
Hence, they tend to collide more frequently,
resulting in an increased rate of reaction.

(b) During stage 1, the ammonia and oxygen are passed through a powdered platinum catalyst.

(i) Explain, with the help of an energy graph, how a catalyst aids in speeding up a chemical reaction.

A catalyst works by providing an alternative pathway with lower activation energy necessary for the initiation of the reaction. This increases the chance of the formation of new products.

(ii) What will happen to it at the end of the reaction?

The platinum catalyst remains unreacted at the end of the reaction. It will also become hotter because the reaction between ammonia and oxygen is exothermic where heat is given out.

(iii) Explain why powdered rather than a lump of platinum catalyst is used.

To provide a larger surface area for the reaction to occur.

(iv) The pH of the reacting solution is measured. Explain how and why the measured pH changes throughout stage 1 of the reaction.

Ammonia from the reactants is soluble in water to form aqueous ammonia which is an alkali. Hence, as the reaction progresses, the pH in the solution will drop until it is neutral, indicating that all of the ammonia has been used up.

(c) Using the equation in stage 2, calculate the maximum mass of nitric acid which is produced from 500 dm^3 of NO at r.t.p.

No. of moles of NO used = 500 / 24 = 20.83 mol
Mass of HNO_3 = 20.83 × [1+14+3(16)] = 20.83 × 63 = **1312.3 g**