Y4 DHP CHEMISTRY
AMMONIA (HABER PROCESS)

Learning Objectives

(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.

Introduction to Reversible Reactions

Many chemical reactions can proceed in one direction only, i.e. they cannot be reversed.

For example, a neutralization reaction:

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

However, some chemical reactions are **reversible.**

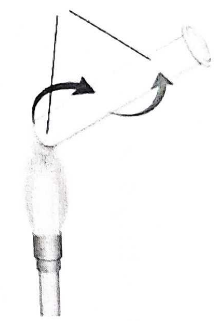
For example,

Solid ammonium chloride decomposes upon heating to form ammonia gas and hydrogen chloride gas.

$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

Upon cooling, the two gases recombine to form back solid ammonium chloride.

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$



A reversible reaction can go both forward and backward at the same time, depending on the conditions under which the reaction is occurring.

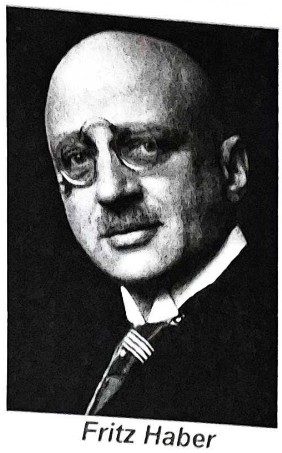
A **double arrow sign**, ⇌, is used to indicate a **reversible reaction.**

The above reaction can be rewritten as such:

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

- The reaction from **left to right** is called the **forward reaction.**
- The reaction from **right to left** is called the **backward reaction.**

Introduction to Ammonia and the Haber Process



Fritz Haber

Ammonia is one of the most important chemicals because it is used in making fertilisers, nitric acid, explosives, and other important chemicals. It is produced from the reaction between nitrogen and hydrogen. However, the reaction does not occur readily as nitrogen is quite unreactive.

During World War I, German chemist Fritz Haber developed a way to convert nitrogen from the air into ammonia for the production of explosives. Later, Carl Bosch, another German chemist, improved the technique to produce ammonia on a larger scale.

This process of making ammonia is called the **Haber Process**, or sometimes the Haber-Bosch Process, named after the two scientists. Both men were awarded the Nobel Prize in 1918.

The Raw Materials

The raw materials for the Haber Process are nitrogen and hydrogen. Nitrogen is obtained by fractional distillation of liquid air. Hydrogen is made by the cracking of alkanes from crude oil or reacting methane (natural gas) and steam.

Reaction A: cracking of C_{18} alkane to make hydrogen.

$$C_{18}H_{38} \rightarrow C_{18}H_{36} + H_2$$

Conditions:
high pressure
catalyst
high temperature

Reaction B: methane reacts with steam to make hydrogen.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +210\ kJ$$

Conditions:
30 atm
nickel oxide catalyst
800°C

Optimal Conditions for The Haber Process

In the Haber Process, a mixture of nitrogen and hydrogen, in the volume ratio of 1 : 3, is sent to a compressor where they are subjected to a pressure of **200 atmospheres**. The pressurized gases are then passed over a finely divided **iron catalyst** (to speed up reaction) in a converter at a temperature of **450°C**. The nitrogen and hydrogen react on the iron's surface to form ammonia.

Reaction C : nitrogen reacts with hydrogen to make ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\ kJ$$

Conditions:
200 atm
Finely divided iron catalyst
450°C

As the reaction is reversible, not all the nitrogen and hydrogen are converted to ammonia. Approximately 10 – 15% of the hydrogen and nitrogen become ammonia at this point.

The next stop is the cooling chamber where ammonia, hydrogen, and nitrogen are cooled. Only ammonia gas condenses to form liquid ammonia and it is removed from the other two gases. The unreacted nitrogen and hydrogen are pumped back into the converter and recycled for further reaction. Eventually, about 98% of nitrogen and hydrogen is converted into ammonia.

Selecting the Conditions for the Manufacture of Ammonia

The reaction for the manufacture of ammonia is **reversible** under the same conditions.

$$N_2(g) + 3H_2(g) \underset{\textit{backward reaction}}{\overset{\textit{forward reaction}}{\rightleftharpoons}} 2NH_3(g)$$

The forward and backward reactions take place simultaneously when nitrogen, hydrogen and ammonia are present in a closed container. This means that as nitrogen and hydrogen combine to form ammonia, some ammonia formed decomposes into nitrogen and hydrogen again. Hence, the reaction does not go to completion, it will reach a state of dynamic equilibrium **(reactions are still happening)** but the speed of forward reaction is equal to the speed of backward reaction. At equilibrium, the amount of reactants and products in the container **remain unchanged (constant)**.

The amount of reactants and products at equilibrium in a reversible reaction can be altered by changing the conditions of the reaction such as temperature and pressure as shown in **Diagram 1.**

To achieve the **maximum yield of ammonia** at the **minimum cost**, the reaction conditions are very carefully controlled.

Diagram 1 shows how the percentage yield of ammonia at equilibrium varies under different temperatures and pressures.

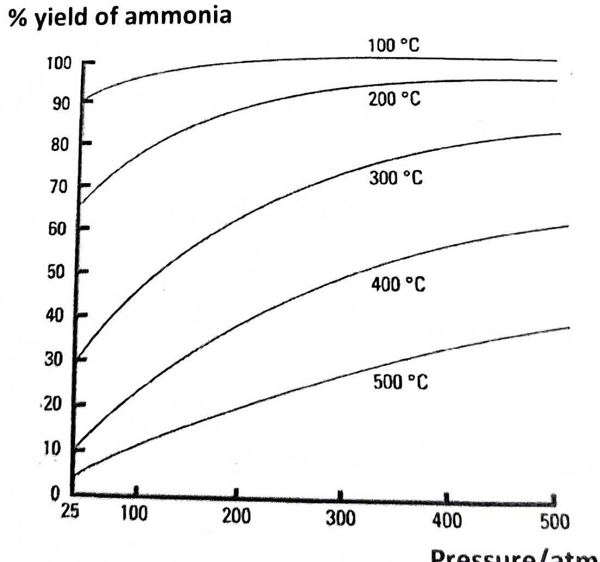


Diagram 1

As pressure increases, percentage yield of ammonia increases.

Le Chatelier's Principle and the Selection of Conditions (Temperature and Pressure) for the Manufacture of Ammonia

Le Chatelier's Principle states that:

> *If a system in equilibrium is subjected to a* **change** which disturbs the equilibrium, the system *responds in such a way as to* **counteract the effect** of the change.

Applying Le Chatelier's Principle to explain how percentage yield of ammonia varies with pressure and temperature

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92$ kJ

a) Pressure

If the pressure of the equilibrium mixture of N_2, H_2 and NH_3 is increased, by Le Chatelier's Principle, the reaction mixture will try to decrease the pressure (to counteract the effect of the change). It can do so by decreasing the number of moles of gas present (the less the gas, the lower is the pressure). Hence, the forward reaction is favoured as it produces fewer molecules and causes the pressure to fall.

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

1 + 3 = 4 moles → 2 moles

High pressure is required for large percentage of ammonia (percentage yield) in the equilibrium mixture. However, **expensive equipment such as a special pump and stronger pipes that can withstand high pressures would be needed**. Hence, a pressure of **200 atm** is selected as a compromise.

b) Temperature

The forward reaction is exothermic, so heat is given out when ammonia is formed. According to Le Chatelier's Principle, when the temperature of the equilibrium mixture is lowered, the reaction mixture will try to release heat to raise the temperature of the equilibrium mixture. It does this by favouring the forward reaction to produce more ammonia in the equilibrium mixture.

To get the maximum percentage yield of ammonia, the temperature needs to be as low as possible. However, a **lower temperature results in a slower reaction**. It will take a very long time for the reaction to reach equilibrium if a low temperature is used.

Hence, a moderate temperature of **450°C** is selected as a compromise.

Le Chatelier's Principle and the Selection of Conditions (Temperature and Pressure) for the Manufacture of Ammonia

Le Chatelier's Principle states that:

> If a system in equilibrium is subjected to a change which disturbs the equilibrium, the system responds in such a way as to counteract the effect of the change.

Applying Le Chatelier's Principle to explain how percentage yield of ammonia varies with pressure and temperature

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Displacement of Ammonia from Its Salts

Recall from Acids, Bases and Salts topic, whenever an ammonium salt is heated with an alkali, ammonia is displaced from the salt.

For example:

$$NH_4Cl(s) + NaOH(aq) \rightarrow NH_3(g) + H_2O(l) + NaCl(aq)$$

Examples of ammonium salts: ammonium nitrate, ammonium sulfate

Examples of alkalis: sodium hydroxide, calcium hydroxide

This reaction is usually used for laboratory preparation of ammonia.

Quick Check

Complete all the clues *Across*, to find *11 Down*, which describes the type of reaction the Haber process is.

	1 h	y	d	11 r	o	g	e	n				
2 t	e	m	p	e	r	a	t	u	r	e		
	3 c	o	n	v	e	r	t	e	r			
			4 f	e	r	t	i	l	i	s	e	r
	5 n	i	t	r	o	g	e	n				
6 p	r	e	s	s	u	r	e					
				7 i	r	o	n					
		8 H	a	b	e	r						
9 c	a	t	a	l	y	s	t					
			10 r	e	c	y	c	l	e	d		

Across

1. This is a raw material for the Haber Process and is produced from the cracking of petroleum. (8 letters)
2. The speed of the Haber process can be changed by controlling its pressure and temperature. (11 letters)
3. In the manufacture of ammonia, this is where the chemical reaction takes place. (9 letters)
4. Ammonia is used in the manufacture of this. (10 letters)
5. This is a raw material for the Haber process and is extracted from the air. (8 letters)
6. 200 atmospheres of this helps to increase the yield of ammonia. (8 letters)
7. The catalyst used in the Haber process (4 letters)
8. The inventor of the large-scale manufacture of ammonia. (5 letters)
9. The general name for a chemical which speeds up a chemical reaction. (8 letters)
10. In the Haber process, unreacted hydrogen and nitrogen gases will be recycled. (8 letters)

Self-Check Exercise

1 A mixture of nitrogen and hydrogen, in a mole ratio of 1:3, is heated in the presence of a suitable catalyst.

Which are correct about the reaction?

I All the nitrogen and hydrogen will combine completely to form ammonia if the reaction is allowed to proceed for a long enough period.
II Only a certain percentage of the nitrogen and hydrogen will react to form ammonia, no matter how much time the reaction is given.
III The chemical equation for the reaction is $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.
IV The chemical equation for the reaction is $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

A I and III only
B II and III only
C II and IV only
D I, II and IV only

(C)

2 The Haber process is used to manufacture ammonia gas. The reaction is exothermic and the chemical equation for the process is:

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

What is the effect of increasing the pressure inside the reaction vessel on the rate of production and the yield of ammonia gas?

	rate	yield
A	decrease	decrease
B	increase	unchanged
C	increase	decrease
D	increase	increase

(D)

3 Which statement is **not** true of the Haber process?

A The raw material nitrogen gas is obtained from the cracking of petroleum.
B Liquid ammonia is the product of the Haber process.
C Nitrogen and hydrogen gases are compressed at 200 atm during the process.
D Unreacted nitrogen and hydrogen are recycled and transferred back into the converter.

(A)

4 When 1 mol of nitrogen is reacted with 3 mol of hydrogen at 200 atm and 450 °C in the presence of an iron catalyst, less than 2 mol of ammonia is formed.

Which best explains this observation?

A The pressure used was too low.
B The temperature used was too low.
C The nitrogen and hydrogen used in the reaction contained impurities.
D The reaction of nitrogen and hydrogen to form ammonia is reversible.

(D)

5 Which reactant would produce ammonia gas when heated with ammonium chloride?

A calcium carbonate
B nitric acid
C aqueous potassium hydroxide
D water

C

Qn	Ans	Explanation
1	C	I & II – The reaction between nitrogen and hydrogen is reversible. The reaction does not go to completion and there would not be a 100% yield of ammonia. It will reach a state of dynamic equilibrium where the speed of forward reaction is equal to the speed of backward reaction. Some of the product will revert back to the reactants and the **amount** of reactants and products remain **unchanged (constant)** at equilibrium. III & IV – The reaction between nitrogen and hydrogen to form ammonia is *reversible*. The single arrow → in the equation indicates that the reaction proceeds to 100% completion. The double arrow ⇌ in the equation indicates that the reaction is *reversible*.
2	D	Increasing the pressure of the gas would increase the number of reacting particles per unit volume. The frequency of effective collision between reacting particles increases. Hence, **speed of reaction increases.** **$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$** According to Le Chatelier's Principle, increasing the pressure of the gas causes the equilibrium to shift to the right (**favouring the forward reaction**). This is because forward reaction decreases the number of gas molecules and lowers the gas pressure in the system. Hence, the **yield** of ammonia increases.
3	A	Cracking of petroleum produces hydrogen gas (not nitrogen gas) as one of the possible products.
4	D	A, B – Optimal conditions for the manufacturing process are used. C – Question did not mention that impurities are present. Iron is used as a catalyst to speed up the reaction and remains chemically unchanged at the end of the reaction. D – A reversible reaction does not go to completion as products can be converted back into reactants, so less than 2 mol of ammonia product is formed. Both the forward and backward reactions occur at the same time.
5	C	Whenever an **ammonium salt** is heated with an **alkali**, **ammonia** is displaced from the salt.