



## Reversible Reactions & Equilibrium

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# Reversible reactions

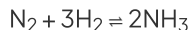
- Some reactions go to **completion**, where the reactants are used up to form the product molecules and the reaction stops when all of the reactants are used up
- In **reversible reactions**, the product molecules can themselves react with each other or decompose and form the reactant molecules again
- It is said that the reaction can occur in **both directions**:
  - The **forward** reaction forming the products
  - The **reverse** reaction forming the reactants
- If the forward reaction is **exothermic**, then the reverse reaction will be **endothermic**
  - The same amount of heat is transferred in both directions

## Chemical equations for reversible reactions

- When writing chemical equations for reversible reactions, the following symbol is used:



- An example is, the reaction for the **Haber process** which produces ammonia from nitrogen and hydrogen

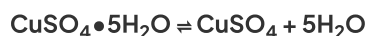


- The forward reaction, producing ammonia, is exothermic
- So, the reverse reaction is endothermic

## Hydrated and anhydrous salts

- Hydrated** salts are salts that contain **water of crystallisation** which affects their molecular shape and colour
  - Water of crystallisation is the water that is stoichiometrically included in the structure of some salts during the crystallisation process
- One example is copper(II) sulfate:

**hydrated copper(II) sulfate  $\rightleftharpoons$  anhydrous copper(II) sulfate + water**

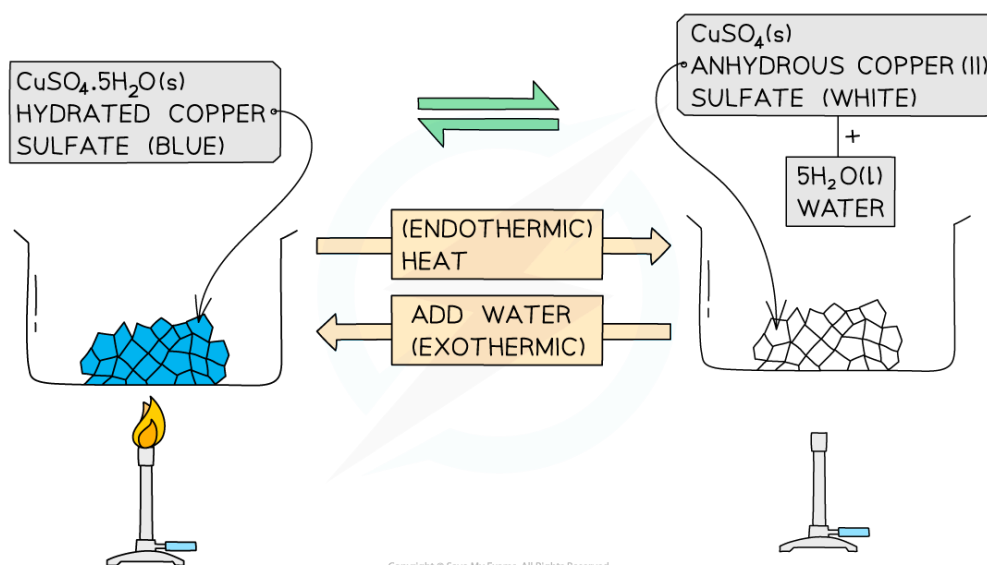


- The hydrated salt is copper(II) sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 
  - These are usually seen as blue crystals
  - The hydrated salt can be heated / dehydrated to form anhydrous copper(II) sulfate,  $\text{CuSO}_4$



Your notes

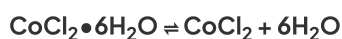
- This reaction is endothermic as energy is taken in to remove the water
- The anhydrous salt is copper(II) sulfate
  - This is usually seen as white crystals / powder
  - Adding water to the anhydrous salt forms the hydrated copper(II) sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
  - This reaction is highly exothermic



**The forward reaction is exothermic and the reverse reaction is endothermic**

- Another example is cobalt(II) chloride:

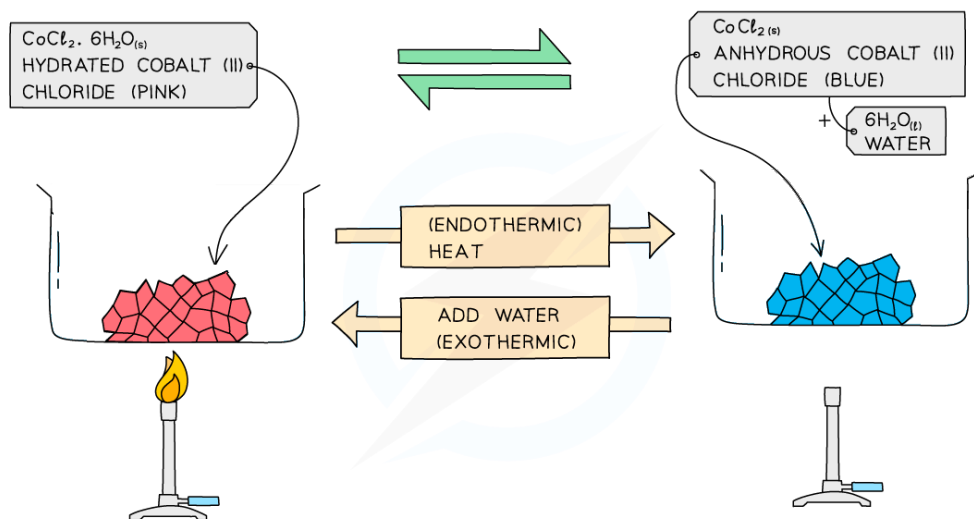
**hydrated cobalt(II) chloride  $\rightleftharpoons$  anhydrous cobalt(II) chloride + water**



- The hydrated salt is cobalt(II) chloride hexahydrate,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 
  - These are usually seen as pink crystals
  - The hydrated salt can be heated / dehydrated to form anhydrous cobalt(II) chloride,  $\text{CoCl}_2$
  - This reaction is endothermic as energy is taken in to remove the water
- The anhydrous salt is cobalt(II) chloride,  $\text{CoCl}_2$ 
  - This is usually seen as blue crystals
  - Adding water to the anhydrous salt forms the hydrated cobalt(II) chloride hexahydrate,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
  - This reaction is highly exothermic



Your notes



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*The forward reaction is exothermic and the reverse reaction is endothermic*



### Examiner Tips and Tricks

The hydration of  $\text{CoCl}_2$  and  $\text{CuSO}_4$  are chemical tests used to detect the presence of water.

You should remember the equations and colour changes:

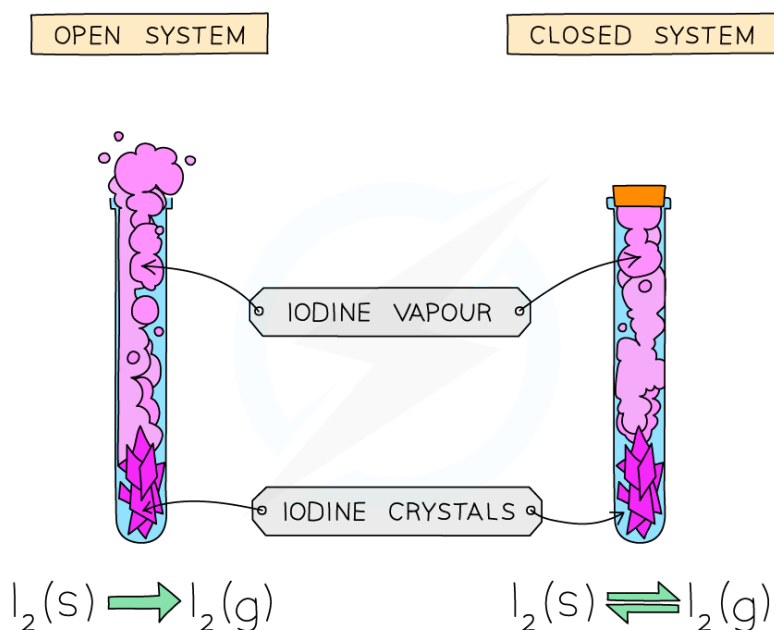
- $\text{CoCl}_2 + 6\text{H}_2\text{O} \rightleftharpoons \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  **Blue to pink**
- $\text{CuSO}_4 + 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  **White to blue**



# The concept of equilibrium

## Extended tier only

- Reversible reactions occur in **both** the forward and backward directions
- A reversible reaction can reach **equilibrium** in a **closed system**
  - This is so none of the participating chemical species can leave the reaction vessel and nothing else can enter



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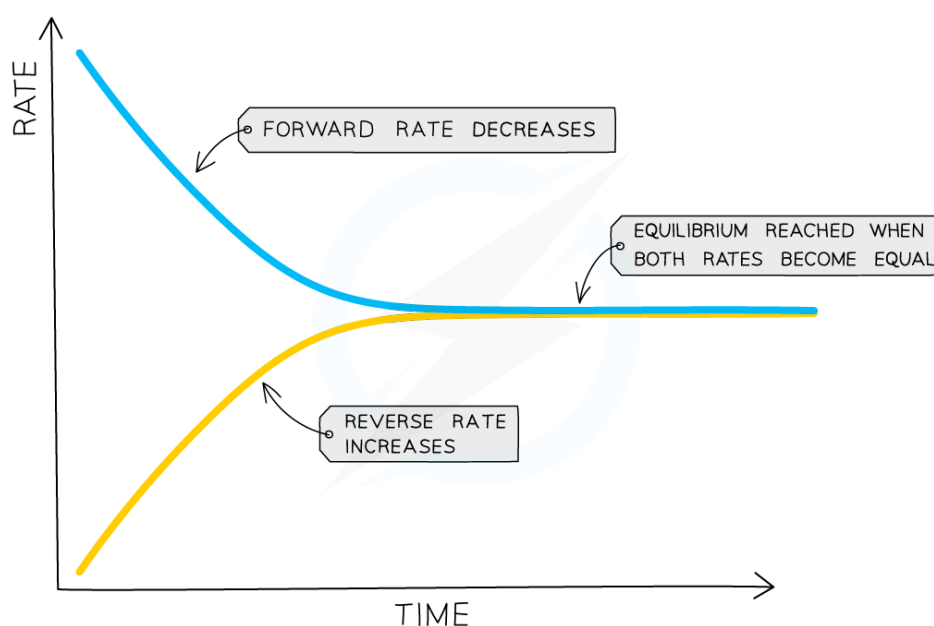
**Equilibrium can only be reached in a closed vessel which prevents reactants or products from escaping the system**

- At equilibrium:
  - The rate of the forward reaction is **equal** to the rate of the reverse reaction
  - The **concentration** of reactants and products remains **constant** (given there is no other change to the system such as temperature and pressure)
- Equilibrium is **dynamic**
  - This means that the molecules on the left and right of the equation are **changing** into each other by chemical reactions constantly and at the same rate



Your notes

- An example of a reaction reaching equilibrium is the reaction between  $\text{H}_2$  and  $\text{N}_2$  in the [Haber process](#):
  - At the start of the reaction, only nitrogen and hydrogen are present
    - This means that the rate of the forward reaction is at its **highest**, since the **concentrations** of hydrogen and nitrogen are at their **highest**
  - As the reaction proceeds, the **concentrations** of hydrogen and nitrogen gradually **decrease**
    - So, the rate of the forward reaction will **decrease**
  - However, the concentration of ammonia is gradually increasing and so the rate of the **backward** reaction will increase
    - Ammonia will decompose to reform hydrogen and nitrogen
  - In a closed system, the two reactions are interlinked and none of the gases can escape
  - So, the rate of the forward reaction and the rate of the backward reaction will eventually become **equal** and equilibrium is reached:



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*At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction*

## Le Chatelier's principle

Extended tier only



- The relative amounts of all the reactants and products at equilibrium depend on the **conditions** of the reaction
  - This balance is framed in an important concept known as Le Chatelier's Principle,
- This principle states that when a change is made to the conditions of a system at equilibrium, the system automatically moves to **oppose** the change
- The principle is used to predict changes to the position of equilibrium when there are changes in:
  - **Temperature**
  - **Pressure**
  - **Concentration**
- Knowing the energy changes, states and concentrations involved allows us to use the principle to manipulate the outcome of reversible reactions
- For example, if pressure is increased, the position of equilibrium moves in the direction which has the smallest amount of gaseous molecules
- The position of equilibrium is said to shift to the **right** when the **forward** reaction is favoured
  - This means that there is an increase in the amount of **products** formed
- The position of equilibrium is said to shift to the **left** when the **reverse** reaction is favoured
  - So, there is an increase in the amount of **reactants** formed

## How temperature affects equilibrium

- We can predict the effect of changes in temperature on systems in equilibrium
  - To make this prediction it is necessary to know whether the reaction is exothermic or endothermic
- If the temperature is **raised**:
  - The yield from the endothermic reaction increases
  - The yield from the exothermic reaction decreases
- If the temperature is **lowered**:
  - The yield from the endothermic reaction decreases
  - The yield from the exothermic reaction increases
- When a change in temperature is made to a system, the system will **oppose** the change
  - E.g. If the temperature is increased, the system will oppose the change by decreasing the temperature
  - It will do this by favouring the endothermic reaction

## The effects of temperature on equilibrium



Your notes

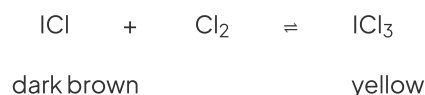
Change	How the equilibrium shifts
Increase in temperature	Equilibrium moves in the <b>endothermic</b> direction to reverse the change
Decrease in temperature	Equilibrium moves in the <b>exothermic</b> direction to reverse the change



### Worked Example

Iodine monochloride reacts reversibly with chlorine to form iodine trichloride.

The forward reaction is exothermic:



What colour will the mixture turn when heated? Explain your answer.

**Answer:**

- The system will oppose the increase in temperature
  - Increasing the temperature of an equilibrium reaction favours the endothermic reaction
- If the forward reaction is exothermic, then the backward reaction must be endothermic
- Therefore, the equilibrium will move to the left and produce more of the reactants
- This means that the colour of the mixture will become increasingly brown as the temperature increases

## How pressure affects equilibrium

- Changes in pressure only affect reactions where the reactants or products are gases
- We can predict the effect of changes in pressure on systems in equilibrium
  - To make this prediction, the balanced symbol equation must be known

## The effects of pressure on equilibrium

Change	How the equilibrium shifts
Increase in pressure	Equilibrium shifts in the direction that produces the <b>least</b> number of molecules

Decrease in pressure

Equilibrium shifts in the direction that produces the **greatest** number of molecules

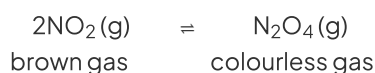


Your notes



### Worked Example

Nitrogen dioxide molecules can dimerise and form dinitrogen tetroxide in the following equilibrium reaction:



What will the colour change be if the pressure is increased? Explain your answer.

**Answer:**

- The number of gas molecules produced by the forward reaction = 1
- The number of gas molecules produced by the reverse reaction = 2
- An **increase** in pressure will cause equilibrium to shift in the direction that produces the **least** number of molecules of gas
  - This is the forward reaction
- So, the equilibrium shifts to the right
- This means that:
  - The mixture will become increasingly colourless
  - The concentration of  $\text{N}_2\text{O}_4$  will increase

## How concentration affects equilibrium

- The effect of changing concentration can be thought of as a balance, with the reactants on the left and the products on the right
  - If the concentration of a reactant increases, then the equilibrium shifts to the right to balance this balance

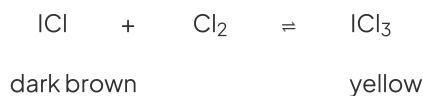
### The effects of concentration on equilibrium

Change	How the equilibrium shifts
Increase in concentration of a reactant	Equilibrium shifts to the right
Decrease in concentration of a reactant	Equilibrium shifts to the left
Increase in concentration of a product	Equilibrium shifts to the left
Decrease in concentration of a product	Equilibrium shifts to the right



### Worked Example

Iodine monochloride reacts reversibly with chlorine to form iodine trichloride



Explain what happens when:

1. The concentration of  $\text{ICl}_3$  increases
2. Some  $\text{Cl}_2$  is removed

**Answers:**

1. The concentration of  $\text{ICl}_3$  increases
  - There are more molecules of  $\text{ICl}_3$  on the products side
  - So, the position of the equilibrium moves **to the left**
  - This produces more  $\text{ICl}$  and  $\text{Cl}_2$ 
    - So, the reaction mixture gets darker / turns dark brown
2. Some  $\text{Cl}_2$  is removed
  - There are less molecules of  $\text{Cl}_2$  on the reactants side
  - So, the position of the equilibrium moves **to the left**
  - This produces more  $\text{Cl}_2$  (and  $\text{ICl}$ )
    - So, the reaction mixture gets darker / turns dark brown



Your notes

## How catalysts affects equilibrium

- The presence of a catalyst:
  - Does **not** affect the position of equilibrium
  - Increases the rate at which equilibrium is reached
- This is because the catalyst increases the rate of **both** the forward and backward reactions by the same amount by providing an alternative pathway requiring lower activation energy
- As a result, the equilibrium **concentration** of reactants and products is the **same** as it would be without the catalyst



Your notes

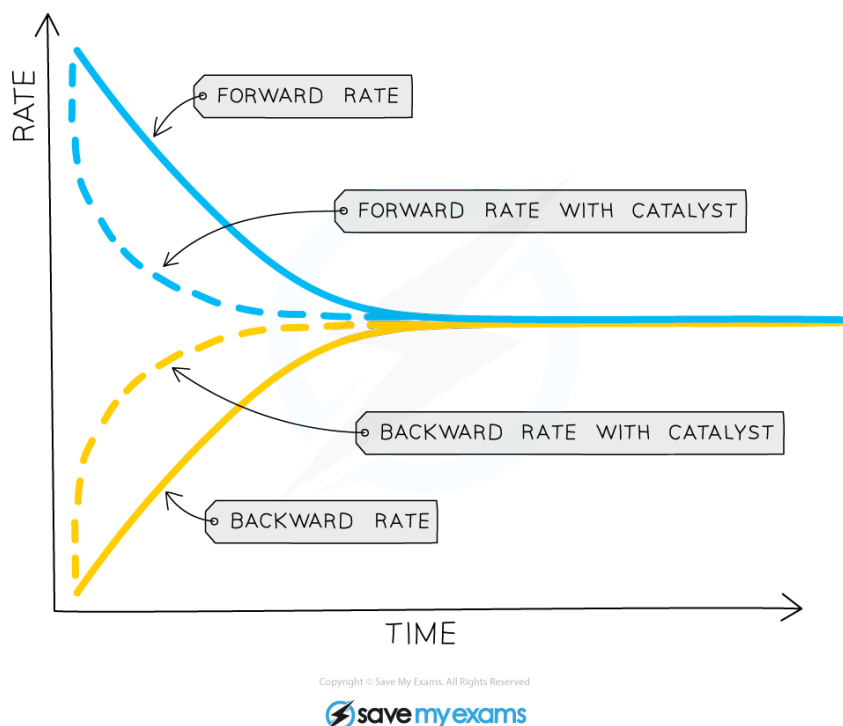


Diagram showing the effect of a catalyst on the time taken for equilibrium to be established



### Examiner Tips and Tricks

When the conditions at equilibrium are changed, the system always responds by doing the **opposite**.

For example if the concentration is increased the system tries to reduce it by changing the direction of the reaction or if the temperature is increased the system will try to reduce the temperature by absorbing the extra heat.



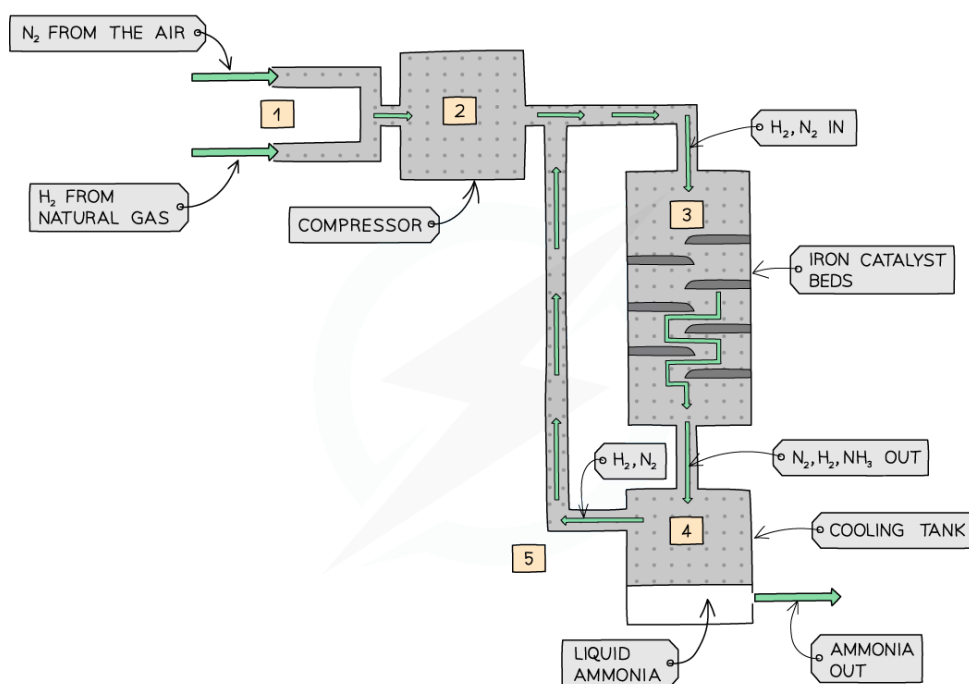
# The Haber process

### Extended tier only

- Ammonia is manufactured in an **exothermic** reaction called the **Haber process** which occurs in five stages:
- **Stage 1**
  - H<sub>2</sub> is obtained from methane
  - N<sub>2</sub> is obtained from the air
  - They are pumped into the compressor through a pipe
- **Stage 2**
  - Inside the compressor, the gases are compressed to around **20 000 kPa** or **200 atmospheres**
- **Stage 3**
  - The pressurised gases are pumped into a tank containing layers of an **iron catalyst** at a temperature of **450 °C**
  - Some of the hydrogen and nitrogen react to form ammonia:
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- **Stage 4**
  - Unreacted H<sub>2</sub> and N<sub>2</sub> and the ammonia product pass into a cooling tank
  - The ammonia is liquefied and removed to pressurised storage vessels
- **Stage 5**
  - The unreacted H<sub>2</sub> and N<sub>2</sub> gases are recycled back into the system and start over again



Your notes



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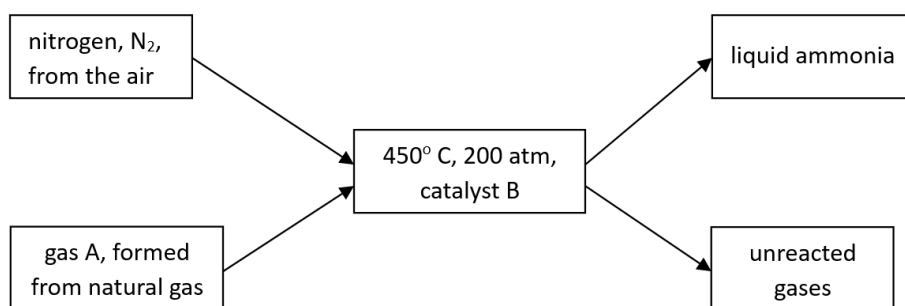


### The production of ammonia by the Haber process



#### Worked Example

Ammonia is produced during the Haber Process. The reaction is summarised in the diagram below.



1. Name gas **A**.
2. Name catalyst **B** used and state why it is used

**Answer:**

1. Gas **A** is hydrogen /  $H_2$ .

2. Catalyst **B** is iron, which is used to speed up the reaction / increase the rate of reaction.



Your notes



### Examiner Tips and Tricks

Examiners often comment that while many students can state the overall reaction, they frequently lose marks by not knowing the specific details.

To secure top marks, make sure you can recall:

- The **sources of the raw materials**:
  - **Nitrogen** from the fractional distillation of liquid **air**
  - **Hydrogen** from **natural gas** (methane)
  - This is a specific syllabus point and is often tested
- The **name of the catalyst**:
  - **Iron**
  - Do not confuse it with catalysts from other industrial processes, like 'vanadium oxide' and 'enzymes'

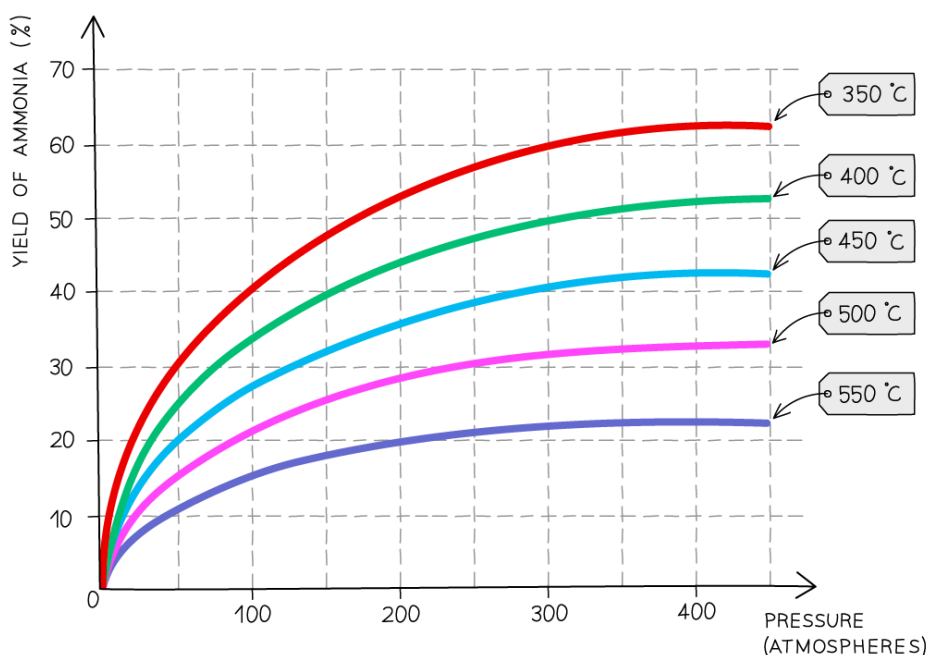
## Explaining the conditions in the Haber process

### Extended tier only

- Chemists' knowledge of the energy changes and factors affecting reaction rates can be used to predict the best possible conditions to make the most ammonia in the fastest possible time
- However, sometimes those conditions are contradictory and choices have to be made between factors that improve the yield of ammonia and those that speed up the reaction
- The graph below illustrates the effects of changing temperature and pressure on the yield of ammonia obtained



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**The yield of ammonia produced changes with changes made to temperature and pressure**

- From the graph:
  - As the **pressure increases**, the percentage yield increases
    - This is shown by following any of the curved lines
  - As the temperature **decreases**, the percentage yield increases
    - This is shown by following any vertical line upwards from the x-axis that
- The actual conditions used must be chosen depending on a number of economical, chemical and practical considerations

## Economic considerations

- Like all industries, companies that manufacture and sell chemical goods do so to make a profit
- Part of the industrial process is the economic decision on how and where to design and implement a manufacturing site
- The availability and cost of **raw materials** is a major consideration which must be studied well before any decisions are taken
- In the Haber Process the raw materials are readily available and inexpensive to purify:
  - Nitrogen** - from the **air**
  - Hydrogen** - from **natural gas**



- If the cost of extraction of raw materials is too high or they are unavailable then the process is no longer **economically viable**
- Many industrial processes require huge amounts of **heat** and **pressure** which is very expensive to maintain
- Production energy costs are also a factor to be considered carefully and alongside the raw materials issue

## Temperature: 450°C

- **High** temperature favours the reverse reaction as it is endothermic
  - So, a higher yield of **reactants** will be made
- **Low** temperature favours the forward reaction as it is exothermic
  - So, a higher yield of **products** will be made
- However, at low temperature the rate of reaction is very **slow**
- So, 450 °C is a compromise temperature between having a **lower yield** of products but being made more quickly

## Pressure: 200 atm

- **Low** pressure favours the reverse reaction as there are more moles of gaseous reactant
  - So, a higher yield of **reactants** will be made
- **High** pressure favours the forward reaction as there are **fewer** moles of gaseous product
  - So, a higher yield of **products** will be made
- However, high pressure can be dangerous and very expensive equipment is needed
- So, 200 atmospheres is a **compromise** pressure between a lower yield of products being made **safely** and **economically**

## Catalyst: Iron

- The presence of a catalyst does **not** affect the position of equilibrium but it does increase the **rate** at which equilibrium is reached
- This is because the catalyst increases the rate of **both** the forward and backward reactions by the same amount (by providing an alternative pathway requiring **lower activation energy**)
- As a result, the **concentration** of reactants and products is nevertheless the **same** at equilibrium as it would be without the catalyst.

So a catalyst is used as it helps the reaction reach equilibrium quicker
- It allows for an acceptable yield to be achieved at a **lower temperature** by lowering the activation energy required
- Without it the process would have to be carried out at an even **higher temperature**, increasing **costs** and decreasing **yield** as the higher temperature **decomposes** more of

the  $\text{NH}_3$  molecules



### Examiner Tips and Tricks

The reaction conditions chosen for the Haber process are not ideal in terms of the yield but do provide balance between product yield, reaction rate and production cost.

These are called **compromise conditions** as they are chosen to give a good compromise between the yield, rate and cost.



Your notes



# The Contact process

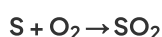
### Extended tier only

- Sulfuric acid is synthesised by the **Contact process**
- Concentrated sulfuric acid is used in car batteries, making **fertilisers, soaps** and **detergents**

## Stage 1

- The first stage is the production of sulfur dioxide
- The oxygen for this stage is obtained from the air
- The sulfur for this stage is obtained by:
  - Burning sulfur to oxidise the sulfur

**sulfur + oxygen → sulfur dioxide**



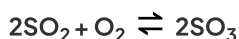
- Roasting sulfide ores

**metal sulfide + oxygen → metal oxide + sulfur dioxide**

## Stage 2

- The main stage is the oxidation of sulfur dioxide to sulfur trioxide using a **vanadium(V) oxide,  $\text{V}_2\text{O}_5$ , catalyst**

**sulfur dioxide + oxygen ⇌ sulfur trioxide**



- The oxygen used in this stage is obtained from air
- The conditions for this main stage of production are:
  - A temperature of **450 °C**
  - A pressure of **2 atm (200 kPa)**
- Once sulfur trioxide is formed, it undergoes more processes to produce sulfuric acid

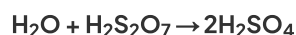
## Stage 3

- The sulfur trioxide is absorbed into a solution of 98% sulphuric acid to produce a thick liquid called **oleum** (disulfuric acid):



**sulfur trioxide + sulfuric acid → disulfuric acid**

- It is not absorbed into water because a fine mist of sulfuric acid would be produced and this would be difficult to condense and is also highly dangerous
- Oleum is added to water to form concentrated sulfuric acid:



**water + disulfuric acid → sulfuric acid**



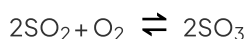
### Examiner Tips and Tricks

You need to recall the temperature, pressure and catalyst needed for the Contact process and the equation for stage 2 only.

## Explaining the conditions in the Contact process

### Extended tier only

- Similar to the Haber process, the pressure and temperature used need to be considered
- The equation for the main stage of the Contact process is:



### Temperature: 450 °C

- High** temperature favours the reverse reaction as it is endothermic
  - So, a higher yield of **reactants** will be made
- Low** temperature favours the forward reaction as it is exothermic
  - So, a higher yield of **products** will be made
- However, at low temperature the rate of reaction is very **slow**
- So, 450 °C is a compromise temperature between having a **lower yield** of products but being made more quickly

### Pressure: 200 kPa / 2 atm

- Low** pressure favours the reverse reaction as there are more moles of gaseous reactant
  - So, a higher yield of **reactants** will be made
- High** pressure favours the forward reaction as there are **fewer** moles of gaseous product
  - So, a higher yield of **products** will be made
- However, the position of equilibrium lies far to the right
  - The equilibrium mixture contains about 96% sulfur trioxide



Your notes

- So, the reaction is carried out at just above atmospheric pressure because:
  - High pressures can be dangerous and very expensive equipment is needed
  - A higher pressure causes the sulfur dioxide to liquify



### Examiner Tips and Tricks

**Remember:** These conditions are a **compromise** between yield, rate, safety and cost.



Your notes