Edexcel International AS Chemistry

Your notes

Introduction to Kinetics & Equilibria

Contents

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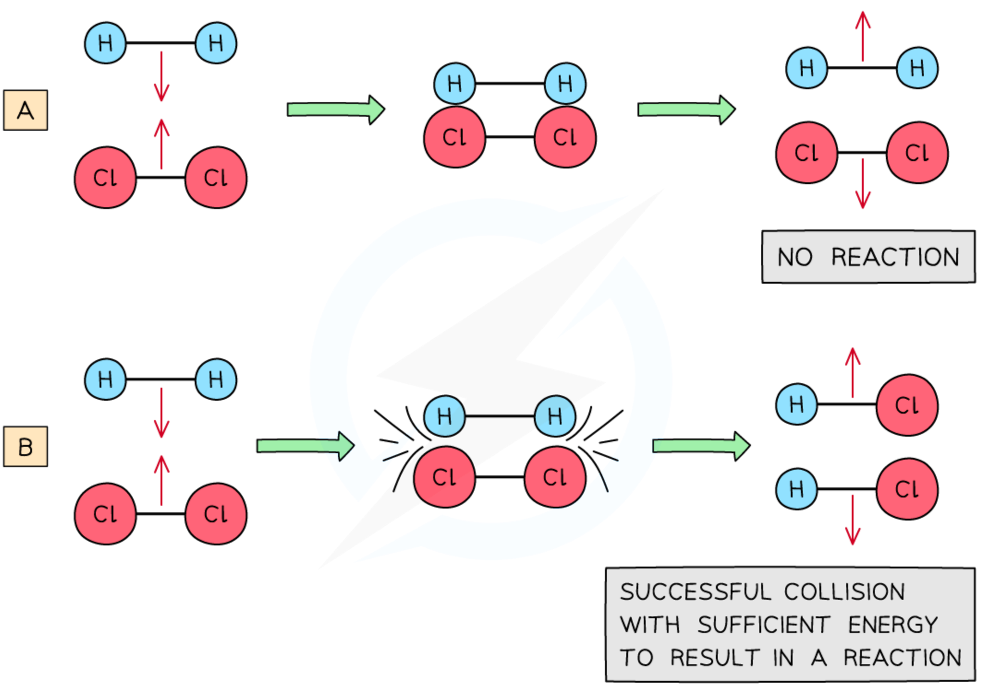
Changing Reaction Conditions

Collision Theory

- When reactants come together the kinetic energy they possess means their particles will collide and some of these collisions will result in chemical bonds being broken and some new bonds being formed
- The rate of a chemical reaction depends on factors including:
  - **collision frequency**
  - **collision energy**
  - **activation energy**
- Ultimately, the rate of reaction depends on the number of successful / effective collisions that happen per unit time
  - A **successful / effective collision** is where the particles collide in the correct orientation and with sufficient energy for a chemical reaction to occur
  - An **unsuccessful / ineffective collision** is when particles collide in the wrong orientation or when they don't have enough energy and **bounce off** each other without causing a chemical reaction



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(a) shows an ineffective collision due to the particles not having enough energy whereas (b) shows an effective collision where the particles have the correct orientation and enough energy for a chemical reaction to take place

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Collision frequency

- If a chemical reaction is to take place between two particles, they must first collide
- The number of collisions between particles per unit time in a system is known as the **collision frequency**
- The **collision frequency** of a given system can be altered by:
  - Changing the **concentration** of the reactants
    - Increasing the concentration will mean that there are more particles available to react in the same volume / amount of space leading to more frequent, successful collisions
  - Changing the total **pressure**
    - Increasing the pressure means that there will be the same number of particles but in a smaller volume leading to more frequent, successful collisions
  - Changing the **temperature**
    - This will increase the kinetic energy of the reacting particles, ultimately, resulting in more frequent, successful collisions
  - Changing the **size** of the reacting particles
    - This is achieved by increasing the **surface area** which means that there are more particles available to react in the same volume / amount of space leading to more frequent, successful collisions

Collision energy

- Not all collisions result in a chemical reaction
  - Most collisions just result in the colliding particles bouncing off each other
  - Collisions which do not result in a reaction are known as **unsuccessful collisions**
- **Unsuccessful collisions** happen when the colliding species do not have enough energy to break the necessary bonds
- If they do not have sufficient energy, the collision will not result in a chemical reaction
- If they have sufficient energy, they will react, and the collision will be successful

Activation Energy

- For a reaction to take place, the reactant particles need to overcome a minimum amount of energy
- This energy is called the **activation energy (E_a)**
- In **exothermic reactions,** the reactants are higher in energy than the products

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- In **endothermic reactions,** the reactants are lower in energy than the products
- Therefore, the E_a in **endothermic reactions** is relatively larger than in exothermic reaction

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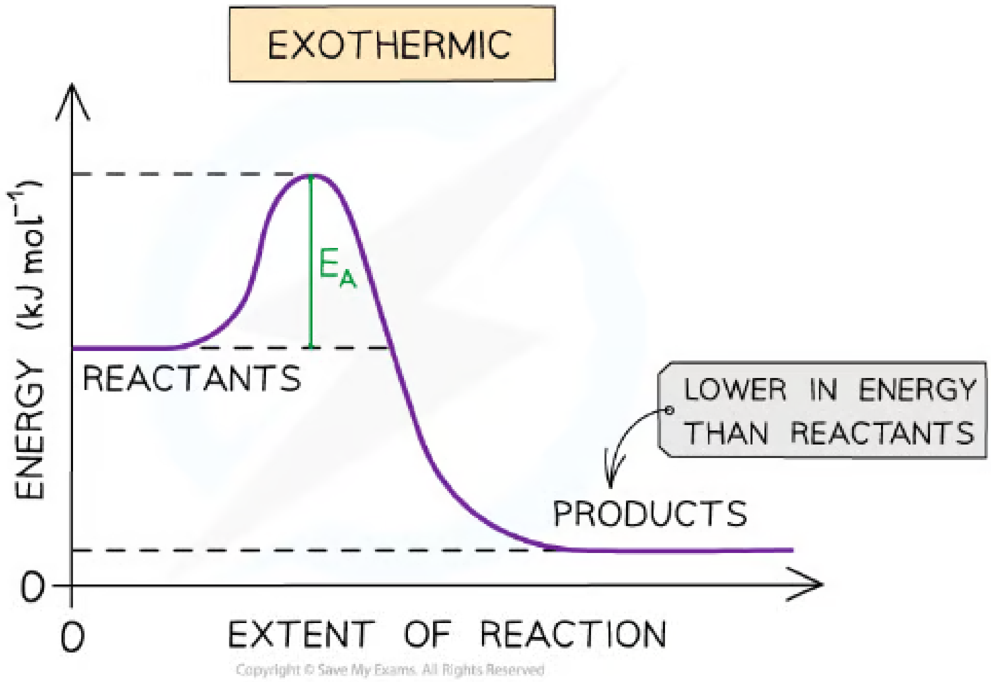
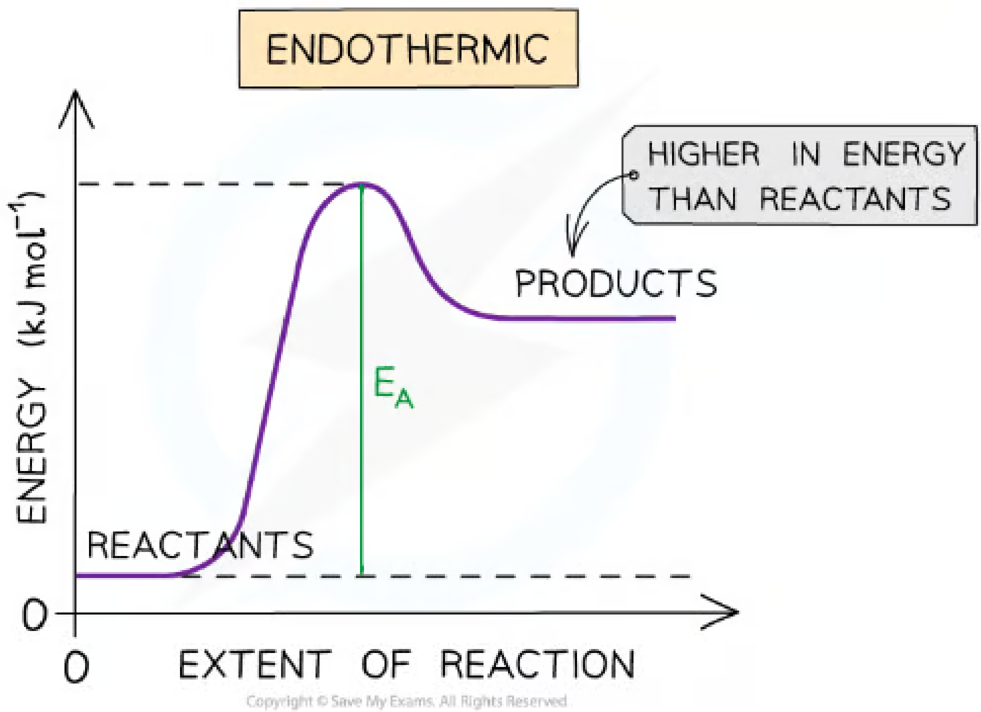


The diagram shows that the reactants are higher in energy than the products in the exothermic reaction, so the energy needed for the reactants to go over the energy barrier is relatively small



The diagram shows that the reactants are lower in energy than the products in the endothermic reaction, so the energy needed for the reactants to go over the energy barrier is relatively large

Your notes

- Even though particles collide with each other in the same orientation, if they don't possess a minimum energy that corresponds to the E_a of that reaction, the reaction will **not** take place
- Therefore, for a collision to be **effective** the reactant particles must collide in the correct orientation **AND** possess a minimum energy equal to the E_a of that reaction
- The success of a reaction can be measured using the rate of reaction, which could be achieved by measuring:
  - The amount of reactant lost
  - The amount of product formed
  - The time it takes for a specific colour change to happen
  - The time it takes for a certain amount of precipitate to form

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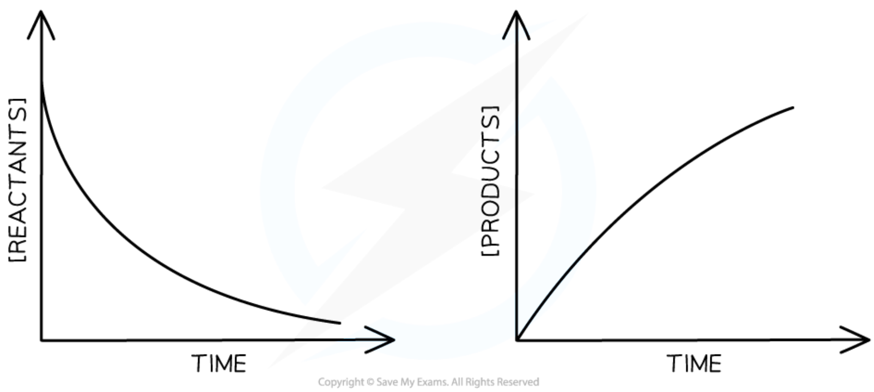
Rates of Reaction – Graphs & Calculations

- Some reactions take place instantly, but most are much slower and it is possible to measure how long these reactions take to reach a certain stage
- As a chemical reaction proceeds, the concentration of the reactants decreases and the concentration of the products increases
- The **rate of a reaction** is the speed at which a chemical reaction takes place and has units **mol dm^{-3} s^{-1}**
- The rate of a reaction can be calculated by:

$$\text{Rate of reaction} = \frac{\text{change in amount of reactants or products }(\text{mol dm}^{-3})}{\text{time (s)}}$$

- Graphically we can represent the rate of reaction as:



Rate of reaction graphs

Worked Example

Iodine and methanoic acid react in aqueous solution.

$$I_2\,(aq) + HCOOH\,(aq) \rightarrow 2I^-\,(aq) + 2H^+\,(aq) + CO_2\,(g)$$

The rate of reaction can be found by measuring the volume of carbon dioxide produced per unit time and plotting a graph as shown

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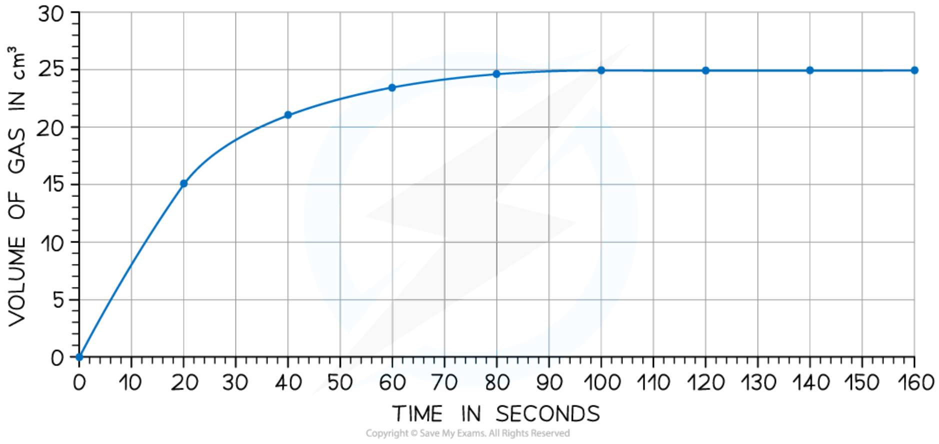
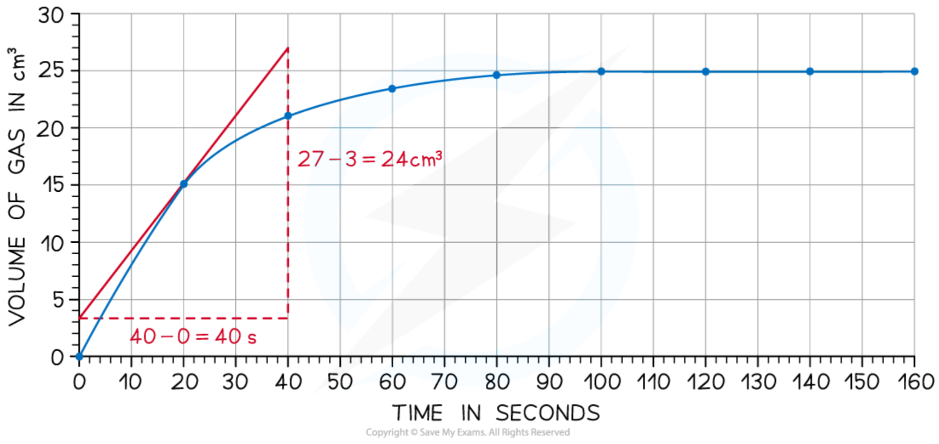


Calculate the rate of reaction at 20 seconds

Answer:

- Draw a tangent to the curve at 20 seconds:



- Complete the triangle and read off the values of x and y
  - Determine the gradient of the line using Δy / Δx
  - Rate of reaction = 24 ÷ 40 = **0.60 $cm^3 s^{-1}$**

Examiner Tips and Tricks

When drawing the tangent to a curve make the triangle large and try to intersect with gridlines if you can. This minimises errors of precision and reduces the chance you will accidently misread the graph values

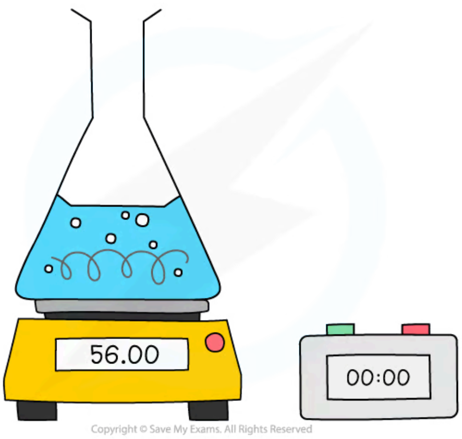
- To measure the **rate of a reaction**, we need to be able to measure either how quickly the reactants are used up or how quickly the products are formed
- The method used for measuring depends on the substances involved

Your notes

- There are a number of ways to measure a reaction rate in the lab; they all depend on some property that changes during the course of the reaction
- That property is taken to be **proportional** to the concentration of the reactant or product, e.g., colour, mass, volume
- Some reaction rates can be measured as the reaction proceeds (this generates more data);
  - faster reactions can be easier to measure when the reaction is over, by averaging a collected measurement over the course of the reaction
- Commonly used techniques are:
  - **mass loss**
  - **gas production**

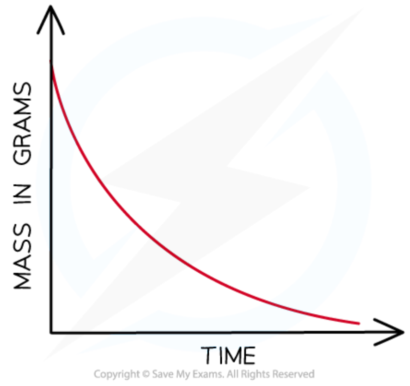
Changes in mass

- When a gas is produced in a reaction it usually escapes from the reaction vessel, so the mass decreases
  - This can be used to measure the rate of reaction
  - For example, the reaction of calcium carbonate with hydrochloric acid produces CO_2
  - The mass is measured every few seconds and change in mass over time is plotted as the CO_2 escapes



Measuring changes in mass using a balance

- The mass loss provides a measure of the amount of reactant, so the graph is the same as a graph of amount of reactant against time

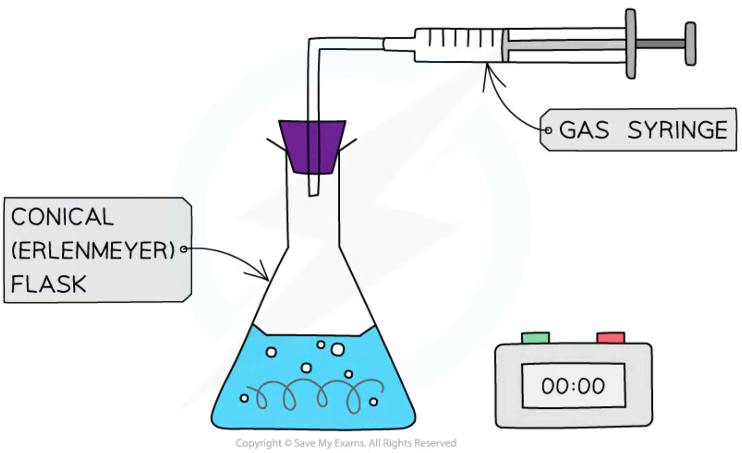


Mass loss of a product against time

- However, one limitation of this method is the gas must be sufficiently dense or the change in mass is too small to measure on a 2 or 3 d.p. balance
  - So carbon dioxide would be suitable (M_r = 44.0) but hydrogen would not (M_r = 2.0)

Volumes of gases

- When a gas is produced in a reaction, it can be trapped and its volume measured over time
  - This can be used to measure the rate of reaction.
  - For example, the reaction of magnesium with hydrochloric acid produces hydrogen



Collecting gases experimental set up

- An alternative gas collection set up involves collecting a gas through water using an inverted measuring cylinder (as long as the gas is not water soluble)

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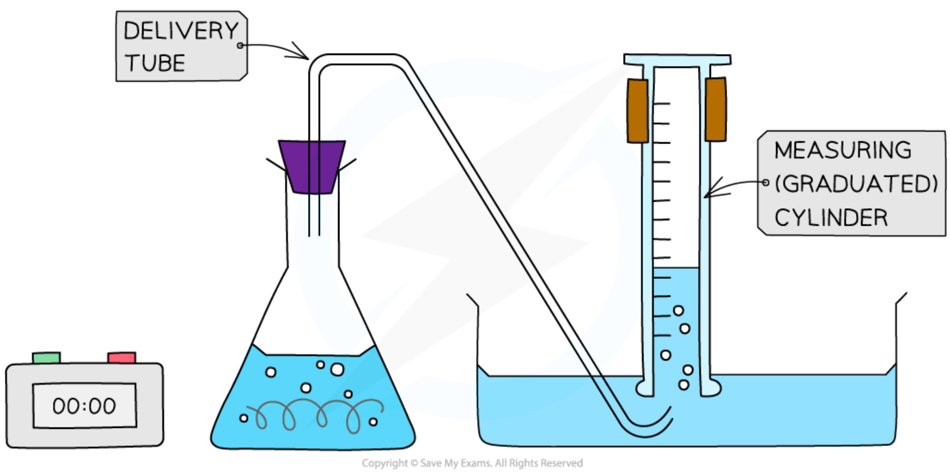
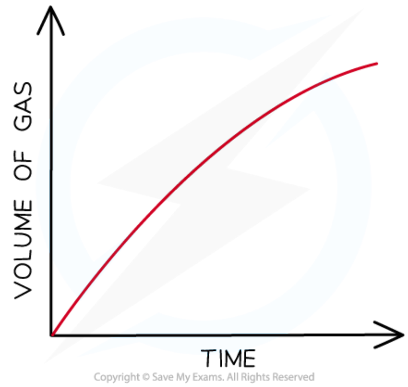


Alternative gas collection set up

- The volume can be measured every few seconds and plotted to show how the volume of gas varies with time
- The volume provides a measure of the amount of product, so the graph is a graph of amount of product against time

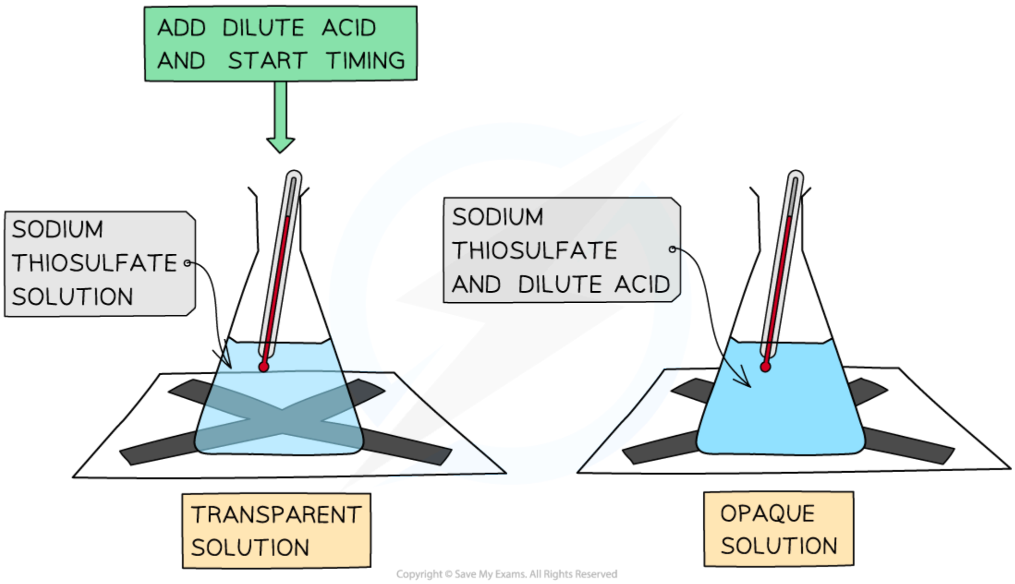


Graph of gas volume evolved against time

Measuring concentration changes

- Measuring concentration changes during a reaction is not easy; the act of taking a sample and analysing it by **titration** can affect the rate of reaction (unless the reaction is deliberately stopped- this is called **quenching**).
- Often it is more convenient to 'stop the clock' when a specific (visible) point in the reaction is reached
  - For example when a piece of magnesium dissolves completely in hydrochloric acid
  - Another common rate experiment is the reaction between sodium thiosulfate and hydrochloric acid which slowly produces a yellow precipitate of sulfur that obscures a cross when viewed through the solution:

$Na_2S_2O_3 (aq) + 2HCl (aq) \rightarrow 2NaCl aq) + SO_2 (g) + H_2O (l) + S(s)$



The disappearing cross experiment

- The main limitation here is that often it only generates one piece of data for analysis

Worked Example

Using the results shown below, calculate the initial rate of reaction for the reaction using 2.0 mol dm^{-3} HCl (aq)

$Mg (s) + 2HCl (aq) \rightarrow MgCl_2 (aq) + H_2 (g)$

	Volume of gas / cm³		
Time / seconds	2.0 mol dm^{-3}	1.0 mol dm^{-3}	0.5 mol dm^{-3}
0	0	0	0
10	10	6	3
20	20	11	6
30	28	15	9
40	34	19	12
50	40	21	14
60	44	22	15

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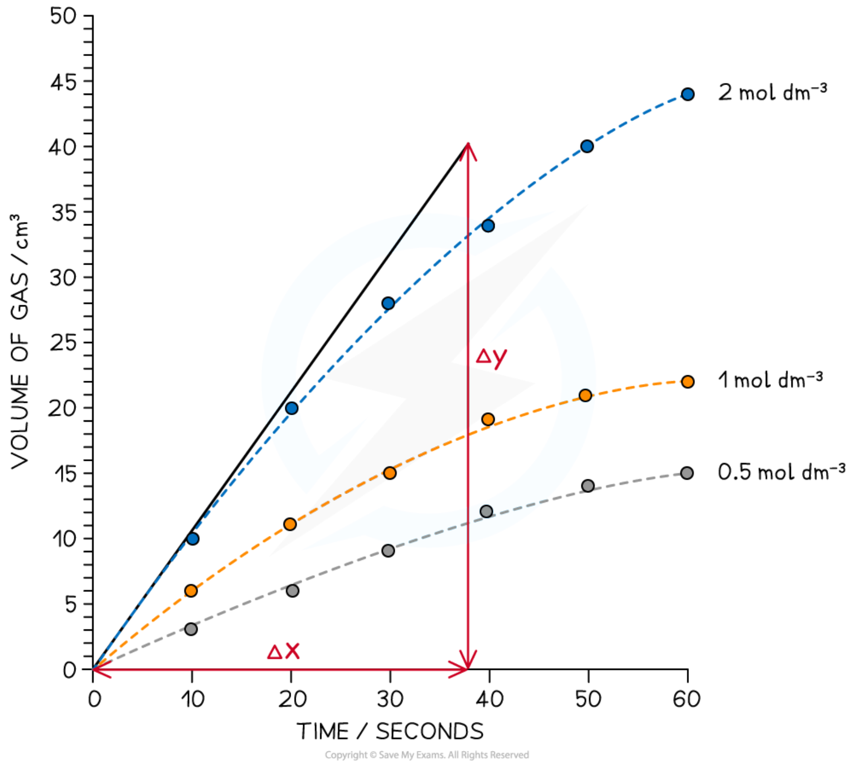
Answer

Step 1: Draw a graph of the results



- The gradient can be used to give the rate of reaction, however, the graph has produced a curve

Step 2: Draw a tangent to the curve at time = 0 seconds

Step 3: Calculate the gradient

- Gradient $= \dfrac{\Delta y}{\Delta x} = \dfrac{40}{38} =$ 1.05 mol dm^{-3} s^{-1}

Examiner Tips and Tricks

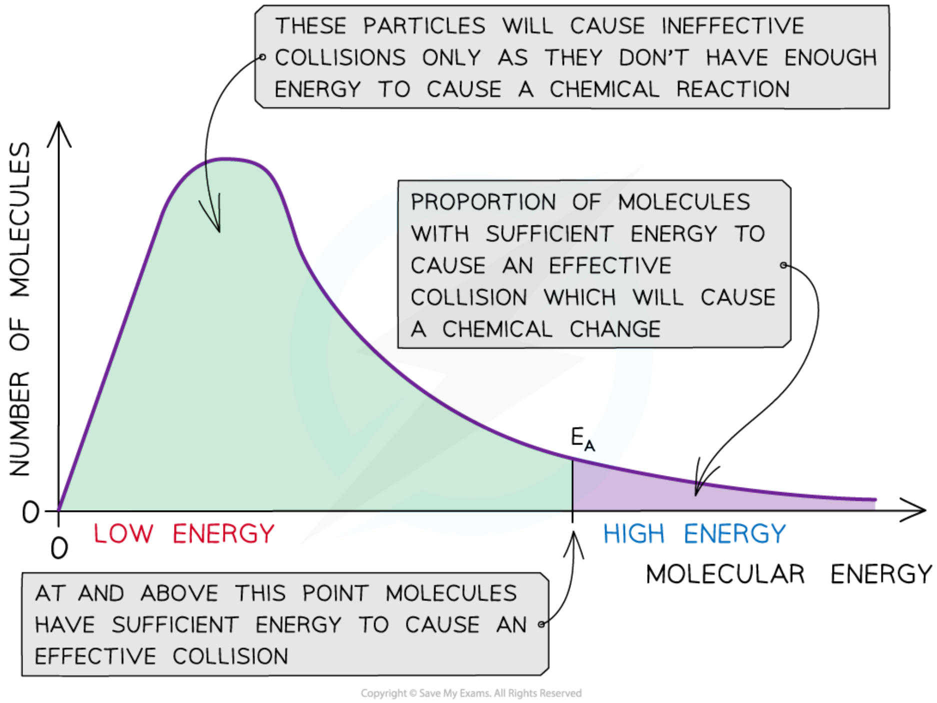
You should be familiar with the interpretation of graphs of changes in concentration, volume or mass against time and be able to calculate a rate from a tangent to the graph

Your notes

Maxwell-Boltzmann & Temperature

Maxwell-Boltzmann distribution curve

- A **Maxwell-Boltzmann distribution curve** is a graph that shows the distribution of **energies** at a certain **temperature**
- In a sample of a gas, a few particles will have very low energy, a few particles will have very high energy, but most particles will have energy in between



The Maxwell-Boltzmann distribution curve shows the distribution of the energies and the activation energy

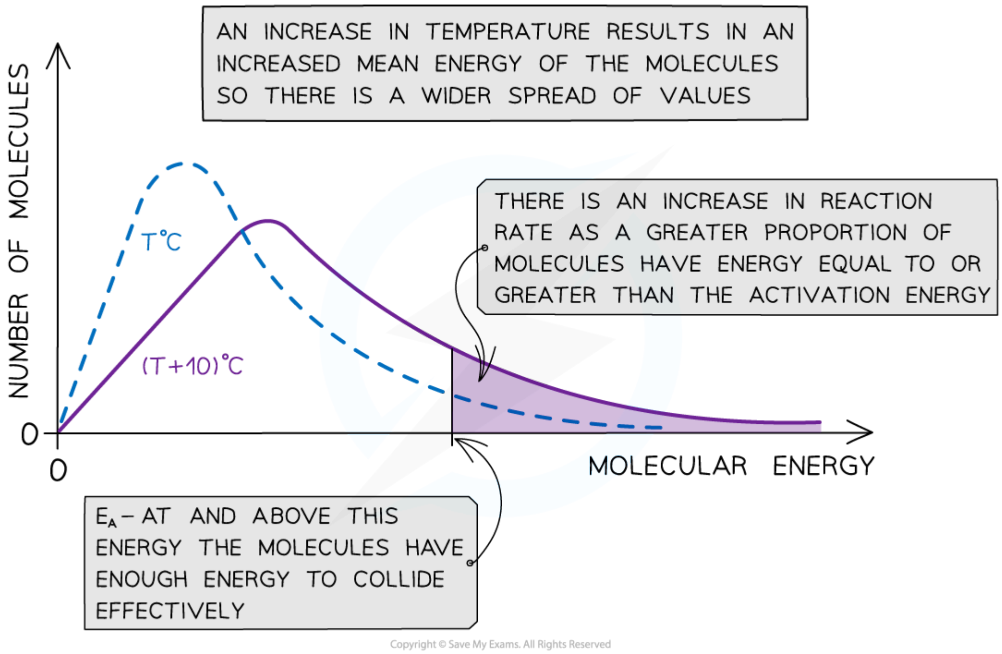
- The graph shows that only a small proportion of molecules in the sample have enough energy for an **effective collision** and for a **chemical reaction** to take place

Changes in temperature

- When the temperature of a reaction mixture is increased, the particles gain more kinetic energy
- This causes the particles to move around faster resulting in more **frequent collisions**
- Furthermore, the proportion of **successful collisions** increases, meaning a higher **proportion** of the particles possess the minimum amount of energy (activation energy) to cause a chemical reaction

Your notes

- With higher temperatures, the Boltzmann distribution curve **flattens** and the peak **shifts** to the right



The Maxwell-Boltzmann distribution curve at T °C and when the temperature is increased by 10 °C

- Therefore, an increase in temperature causes an increased rate of reaction due to:
  - There being **more effective collisions** as the particles have **more kinetic energy**, making them move around faster
  - A **greater proportion** of the molecules having **kinetic energy** greater than the **activation energy**

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Reaction Profiles & Maxwell-Boltzmann

- **Catalysis** is the process in which the rate of a chemical reaction is increased, by adding a **catalyst**
- A catalyst increases the rate of a reaction by providing the reactants with an **alternative reaction pathway** which is **lower in activation energy** than the uncatalysed reaction
- There are three main advantages to using catalysts in chemical reactions:
    1. They increase the rate of reaction which means that more product is potentially made in a given amount of time
    2. They reduce energy costs as the reaction can happen at lower temperatures and pressures
    3. They can increase atom economy as the alternative reaction pathway that they provide can reduce the unwanted reactions and, in some cases, even reduce the amount of other products, e.g. the use of zeolites in the synthesis of phenol
- Catalysts can be divided into two types:
    - Homogeneous catalysts
    - Heterogeneous catalysts
- **Homogeneous** means that the catalyst is in the **same phase** as the reactants
    - For example, the reactants and the catalysts are all in solution
- **Heterogeneous** means that the catalyst is in a **different phase** to the reactants
    - For example, the reactants are gases but the catalyst used is a solid
    - This type of catalyst is the most common in industry

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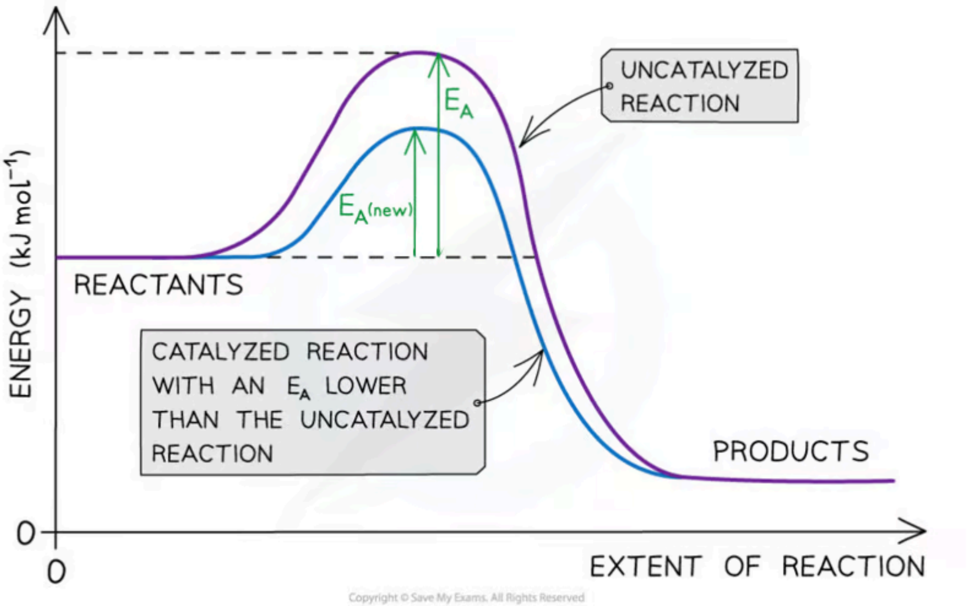
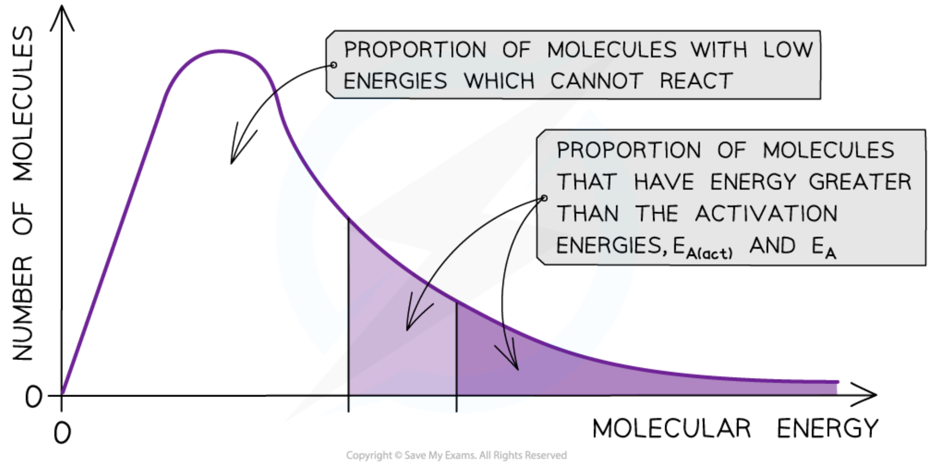


The diagram shows that the catalyst allows the reaction to take place through a different mechanism, which has a lower activation energy than the original reaction

Maxwell-Boltzmann distribution curve

- **Catalysts** provide the reactants another pathway which has a lower activation energy
- On the graph below, the original number of successfully reacting particles is shown by the dark shaded area
- By lowering E_a, a **greater proportion** of molecules in the reaction mixture have the activation energy, and therefore have sufficient energy for an **effective collision**
  - This is shown by the combined number of particles in the light and dark shaded areas
- As a result of this, the rate of the catalysed reaction is increased compared to the uncatalysed reaction



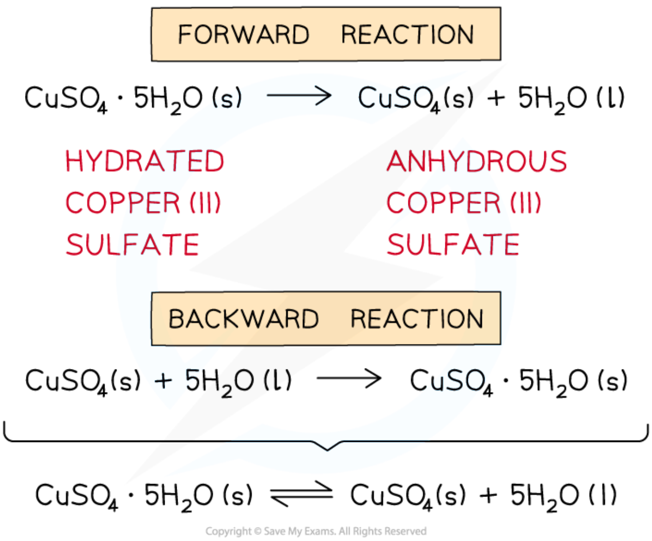
The diagram shows that the total shaded area (both dark and light shading) under the curve shows the number of particles with energy greater than the E_a when a catalyst is present. This area is much larger than the dark shaded area which shows the number of particles with energy greater than the E_a without a catalyst

Your notes

Dynamic Equilibrium in Reversible Reactions

Reversible reaction

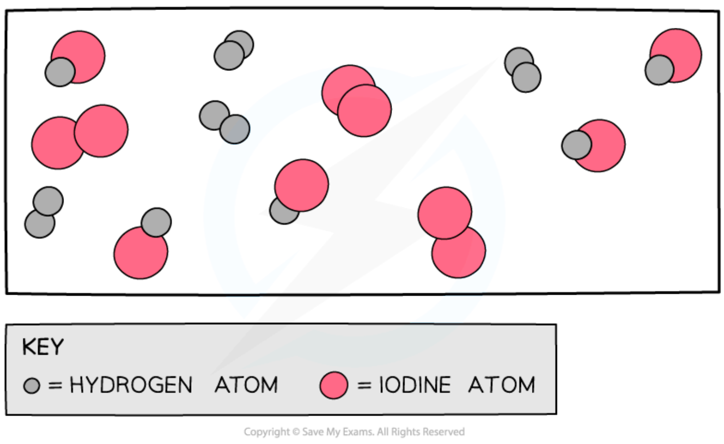
- Some reactions go to completion where the reactants are used up to form the products
  - The reaction stops when all of the reactants are used up
- In **reversible reactions**, the products can react to reform the original reactants
  - To show a reversible reaction, two opposing half arrows are used: ⇌



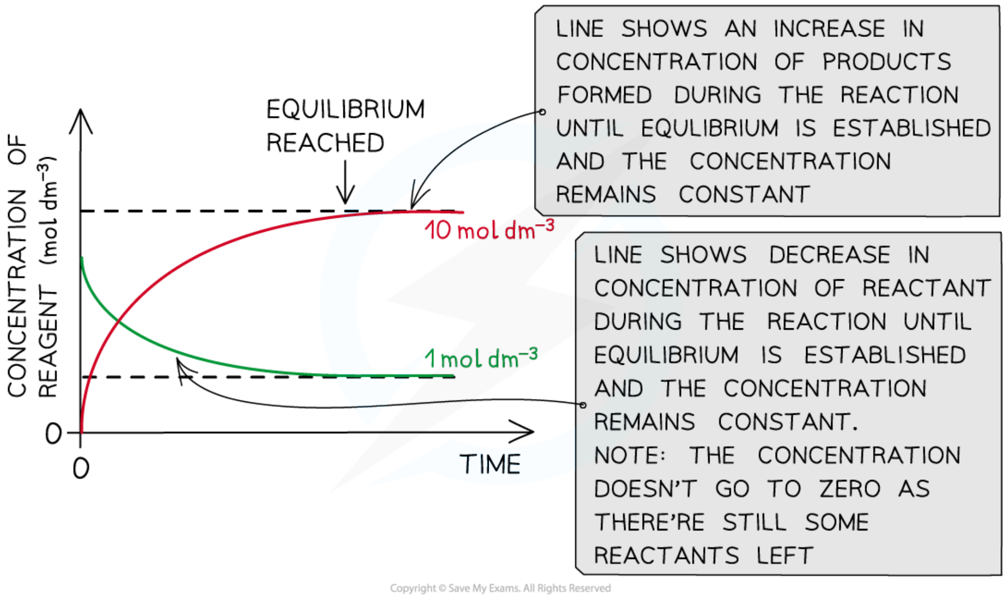
The diagram shows an example of a forward and backward reaction that can be written as one equation using two half arrows

Dynamic equilibrium

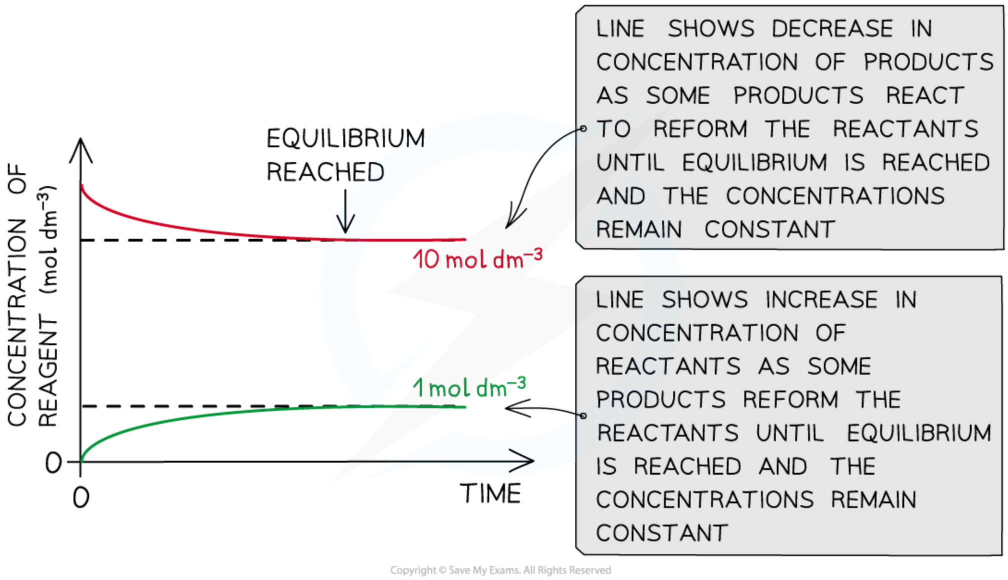
- In a **dynamic equilibrium**, the reactants and products are **dynamic** (they are constantly moving)
- In a dynamic equilibrium, the **rate** of the **forward** reaction is the same as the rate of the **backward** reaction in a **closed system**, and the **concentrations** of the **reactants** and **products** are **constant**



The diagram shows a snapshot of a dynamic equilibrium in which molecules of hydrogen iodide are breaking down to hydrogen and iodine at the same rate as hydrogen and iodine molecules are reacting together to form hydrogen iodide

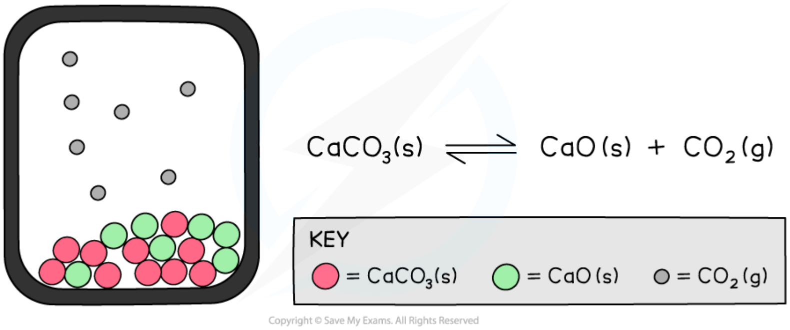


The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using reactants)

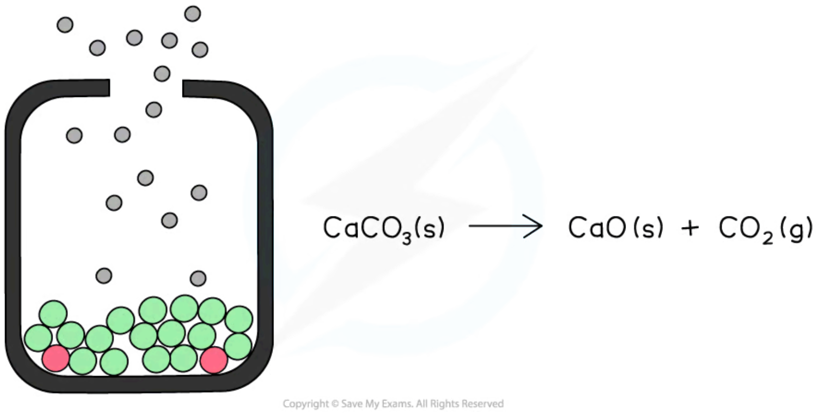


The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using products)

- A **closed system** is one in which none of the reactants or products escape from the reaction mixture
- In an **open system**, matter and energy can be lost to the surroundings
- When a reaction takes place entirely in solution, equilibrium can be reached in open flasks as a negligible amount of material is lost through evaporation
- If the reaction involves gases, equilibrium can only be reached in a closed system



The diagram shows a closed system in which no carbon dioxide gas can escape and the calcium carbonate is in equilibrium with the calcium oxide and carbon dioxide



The diagram shows an open system in which the calcium carbonate is continually decomposing as the carbon dioxide is lost causing the reaction to eventually go to completion

Examiner Tips and Tricks

A common misconception is to think that the concentrations of the reactants and products are equal.

They are not equal but they **remain constant** at dynamic equilibrium (i.e. the concentrations are not changing).

The concentrations will change as the reaction progresses, only until the equilibrium is reached.

Your notes

The Position of Equilibrium

Position of the equilibrium

- The **position of the equilibrium** refers to the relative amounts of products and reactants in an equilibrium mixture
- When the position of equilibrium shifts to the **left**, it means the concentration of **reactants** increases
- When the position of equilibrium shifts to the **right**, it means the concentration of **products** increases

Le Chatelier's principle

- **Le Chatelier's principle** says that if a change is made to a system in dynamic equilibrium, the position of the equilibrium moves to counteract this change
- The principle is used to predict changes to the position of equilibrium when there are changes in temperature, pressure or concentration

Effects of concentration

How the Equilibrium Shifts with Concentration Changes

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN CONCENTRATION	EQUILIBRIUM SHIFTS TO THE **RIGHT** TO REDUCE THE EFFECT OF INCREASE IN THE CONCENTRATION OF A REACTANT
DECREASE IN CONCENTRATION	EQUILIBRIUM SHIFTS TO THE **LEFT** TO REDUCE THE EFFECT OF A DECREASE IN REACTANT (OR AN INCREASE IN THE CONCENTRATION OF PRODUCT)

Worked Example

Changes in equilibrium position

Using the reaction below:

$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$

Explain what happens to the position of equilibrium when:

1. **More $CH_3COOC_2H_5$ is added**

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2. **Some C_2H_5OH is removed**

Using the reaction below:

$Ce^{4+}(aq) + Fe^{2+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq)$

Explain what happens to the position of equilibrium when

3. **Water is added to the equilibrium mixture**

Answer 1:

- The position of the equilibrium moves to the left and more ethanoic acid and ethanol are formed
    - The reaction moves in this direction to oppose the effect of added ethyl ethanoate, so the ethyl ethanoate decreases in concentration

Answer 2:

- The position of the equilibrium moves to the left and more ethanoic acid and ethanol are formed
    - The reaction moves in this direction to oppose the removal of ethanol so more ethanol (and ethanoic acid) are formed from ethyl ethanoate and water

Answer 3:

- There is no effect as the water dilutes all the ions equally so there is no change in the ratio of reactants to products

Effects of pressure

- Changes in pressure only affect reactions where the reactants or products are gases

How the Equilibrium Shifts with Pressure Changes

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN PRESSURE	EQUILIBRIUM SHIFTS IN THE DIRECTION THAT PRODUCES THE **SMALLER** NUMBER OF MOLECULES OF GAS TO DECREASE THE PRESSURE AGAIN
DECREASE IN PRESSURE	EQUILIBRIUM SHIFTS IN THE DIRECTION THAT PRODUCES THE **LARGER** NUMBER OF MOLECULES OF GAS TO INCREASE THE PRESSURE AGAIN

Worked Example

Changes in pressure

Predict the effect of increasing the pressure on the following reactions:

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1. $N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$

2. $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$

Predict the effect of decreasing the pressure on the following reaction:

3. $2NO_2 (g) \rightleftharpoons 2NO (g) + O_2 (g)$

Answer 1:

- The equilibrium shifts to the left as there are fewer gas molecules on the left
    - This causes a decrease in pressure

Answer 2:

- The equilibrium shifts to the left as there are no gas molecules on the left but there is CO_2 on the right
    - This causes a decrease in pressure

Answer 3:

- The equilibrium shifts to the right as there is a greater number of gas molecules on the right
    - This causes an increase in pressure

Effects of temperature

How the Equilibrium Shifts with Temperature Changes

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **ENDOTHERMIC** DIRECTION TO REVERSE THE CHANGE
DECREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **EXOTHERMIC** DIRECTION TO REVERSE THE CHANGE

Worked Example

Changes in temperature

Using the reaction below:

$H_2 (g) + CO_2 (g) \rightleftharpoons H_2O (g) + CO (g) \quad \Delta H = +41.2 \text{ kJ mol}^{-1}$

1. Predict the effect of increasing the temperature on this reaction

Using the reaction below:

$Ag_2CO_3 (s) \rightleftharpoons Ag_2O (s) + CO_2 (g)$

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2. **Increasing the temperature increases the amount of CO_2(g) at constant pressure. Is this reaction exothermic or endothermic?**

Explain your answer

Answer 1:

- The reaction will absorb the excess energy and since the forward reaction is endothermic, the equilibrium will shift to the right

Answer 2:

- The reaction will absorb the excess energy and since this causes a shift of the equilibrium towards the right (as more CO_2(g) is formed) this means that the reaction is endothermic

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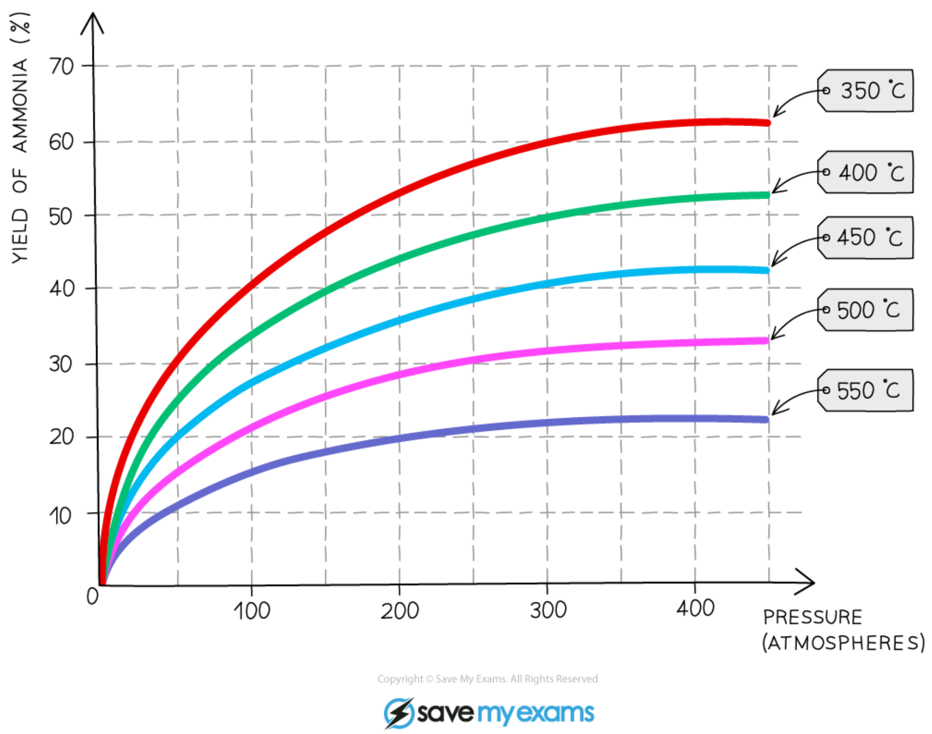
The Yield-Rate Compromise

- The Haber Process is, once again, a good example of the need for a compromise of reaction conditions in industrial processes

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

- The reaction is exothermic in the forward direction
  - Therefore, an increase in temperature may increase the rate of reaction but it will decrease the overall yield as the equilibrium shifts to the left
- An increase in pressure will increase the yield
  - This is because there are 4 moles of reactant compared to only 2 moles of product
- The overall effect of changing the pressure at different temperatures can be seen:



The yield of ammonia with varying conditions for the Haber Process

- Temperature is the first compromise in conditions
- 450 °C is used as this still produces an acceptable yield of ammonia (roughly 35%) but also within an acceptable time frame
  - Higher temperatures are not used because of the lower yields combined with the increased costs to achieve these temperatures

- Lower temperatures are not used because the rate is too slow despite an increased yield

Your notes

Examiner Tips and Tricks

In very simplistic terms, this temperature compromise can be thought of as the following question:

Is it better to produce 100 g per hour or 1000 g per day?

- For 100 g per hour, less product is being made but it is being made more quickly
- For 1000g per day, more product is being made but it is being made much more slowly
- Overall, 100 g per hour is better as this results in a total of 2400 g per day

- The second compromise in conditions is pressure
- A pressure of around 20 MPa (or 200 atmospheres) is used, which produces an acceptable yield (around 35%)
  - Doubling the pressure to around 40 MPa (roughly 400 atmospheres, only increases the yield by around 7%
  - However, this comes with the financial and energy costs of producing the pressure requires along with the health and safety considerations of working at such high pressure
- While industry aims for a high yield where possible, sometimes this is balanced and compromised by:
  - Financial and profit considerations - is the cost of altered reaction conditions balanced out by a sufficient increase in yield and, therefore, profit?
  - Energy and environmental considerations - will altering the reaction conditions have an effect on the energy needs (linking back to finance) and will there be an increased use of fossil fuels resulting from the change of conditions?
  - Health and safety considerations - are the proposed reaction conditions actually safe to work with? What potential harm to workers and the manufacturing plant could happen? Is this balanced out by the increase in yield and, therefore, profit?

Examiner Tips and Tricks

The Haber Process has been used as the example for industrial considerations as you should be relatively familiar with this process

However, you can be expected to apply the ideas shown here to any potential industrial reaction

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