HL IB Chemistry

How Fast? The Rate of Chemical Change

Contents

Rate of Reaction

Rate of Reaction

What is rate of reaction?

- 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
  - Reversible reactions are an exception to this, where the concentration of reactants and products remains constant once dynamic equilibrium has been achieved
- The **rate of a reaction** is the speed at which a chemical reaction takes place and can be expressed as the change in concentration of a particular reactant or product per unit time
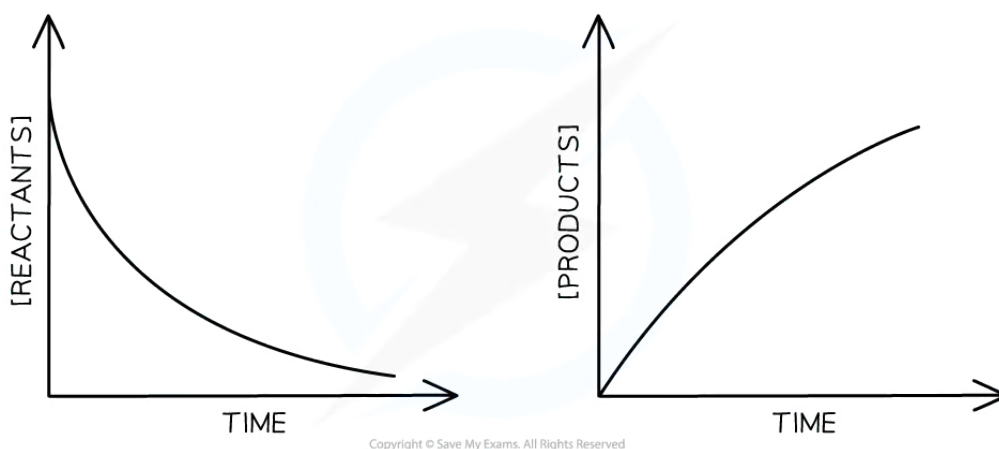- The rate of reaction typically has the units **$mol \ dm^{-3} \ s^{-1}$**

How to calculate rate of reaction

- The rate of reaction formula is:

$$\text{rate of reaction } (mol \ dm^{-3} \ s^{-1}) = \frac{\text{change in concentration of reactants or products } (mol \ dm^{-3})}{\text{time } (s)}$$

- Experimental data from reactions can be shown graphically and used to calculate the rate of reaction

Rate of reaction graphs

As the reaction proceeds, the concentration of reactants and products change with time

- The steeper the gradient, the quicker the rate of reaction
- The rate of reaction at a particular time can be found by calculating the gradient of the curve at that time

Your notes

- To find the gradient of a curve, draw the tangent to the curve and calculate the gradient of the tangent by using the equation:

$$\text{gradient} = \frac{\Delta y}{\Delta x}$$

> 💡 **Examiner Tip**
>
> - The rate of reaction is a positive value
> - The graph of the reactants' concentration over time shows a negative gradient
>   - So, the sign of the rate should be altered to be a positive value
>   - E.g. gradient = –20.6 mol dm^{-3} s^{-1} → rate = 20.6 mol dm^{-3} s^{-1}
> - The graph of the products' concentration over time shows a positive gradient
>   - So, the sign of the rate will already be a positive value and not need altering

✏️ Worked example

Iodine and methanoic acid react in aqueous solution.

$$I_2 \, (aq) + HCOOH \, (aq) \rightarrow 2I^- \, (aq) + 2H^+ \, (aq) + CO_2 \, (g)$$
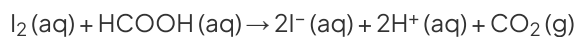
The rate of reaction can be found by measuring the volume of carbon dioxide produced per unit time and plotting a graph as shown:
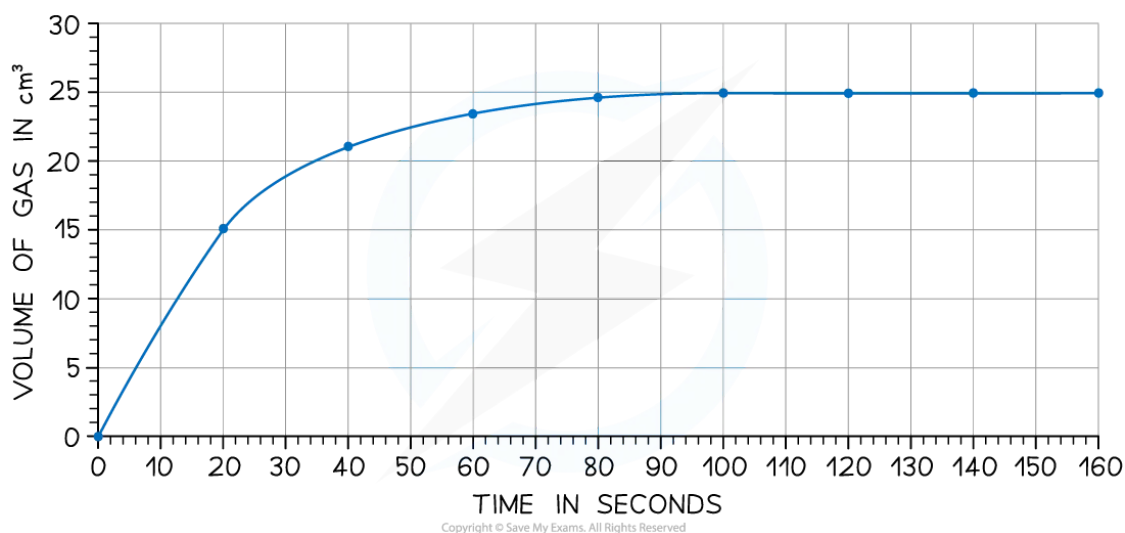
Calculate the rate of reaction at 20 seconds.

Answer:

- Draw a tangent to the curve at 20 seconds:
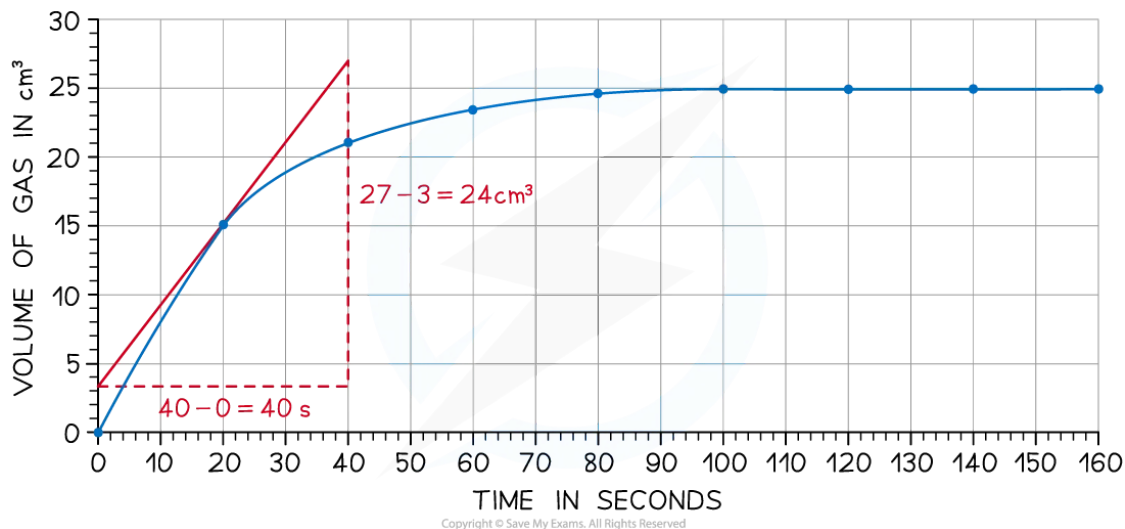
Your notes

- 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 Tip

- When drawing the tangent to a curve, you should:
  - Make the triangle large
  - Try to intersect with gridlines if you can
- These points should minimise errors of precision and reduce the chance you will accidentally misread the graph values

Measuring Rates of Reaction

Measuring Rates of Reaction

Measuring rate of reaction

- 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
- 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
- Three commonly used techniques are:
  - **Mass loss**
  - **Gas production**
  - **Colorimetry**

Measuring the rate of reaction using colorimetry

- A colorimeter or spectrophotometer measures the amount of light that passes through a solution
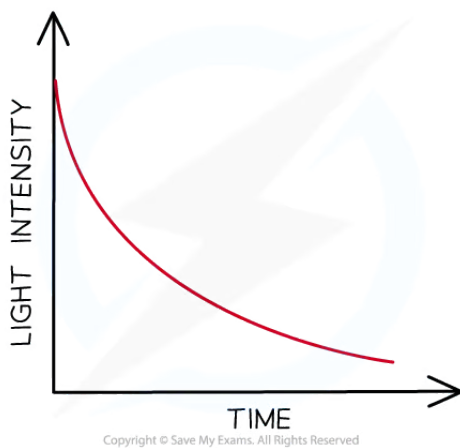
Colorimetry Set Up

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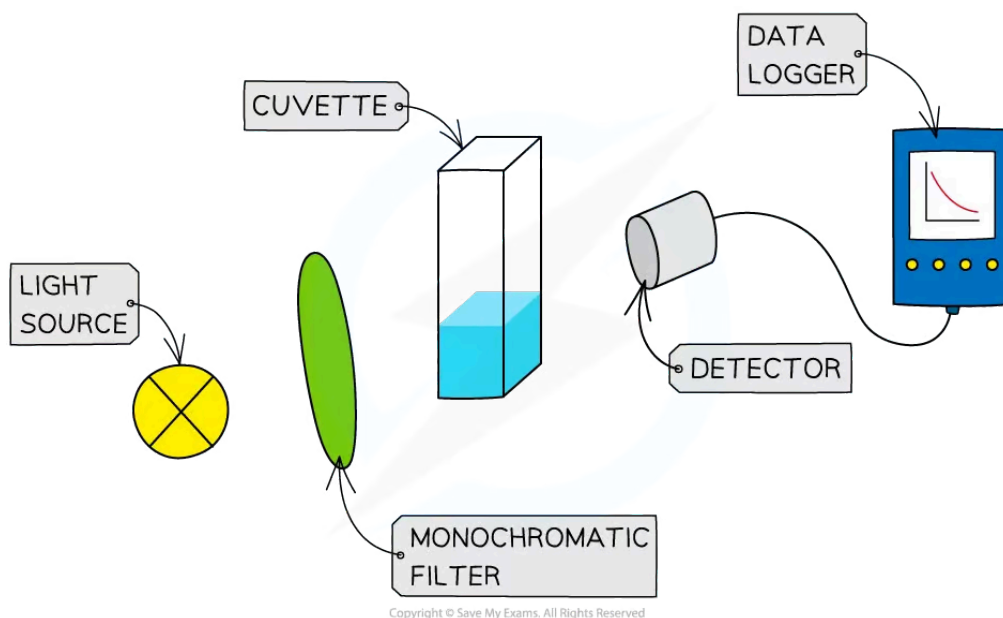
Colorimetry measures the light intensity of light passing through a sample

- If a solution changes colour during a reaction, this can be used to measure the rate
- The intensity of light reaching the detector is measured every few seconds and the data is plotted to show how the concentration of the reactants or products changes with time
- The light intensity is related to the concentration, so the graph represents a graph of concentration of products or reactants against time

Examples results from a colorimeter

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Sketch graph of colour intensity against time (the coloured species is a reactant in this case)

- **Note:** Colorimetry cannot be used to monitor the formation of coloured precipitates as the light will be scattered or blocked by the precipitate

> 💡 **Examiner Tip**
>
> - A colorimeter / spectrophotometer can also measure how much light is absorbed by the sample and the corresponding results show a plot of absorbance against time.

Measuring the rate of reaction using changes in mass

- When a gas is produced in a reaction it usually escapes from the reaction vessel, so the mass of the vessel 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 the change in mass over time is plotted as the CO_2 escapes

Equipment used to measure the loss of mass

Your notes
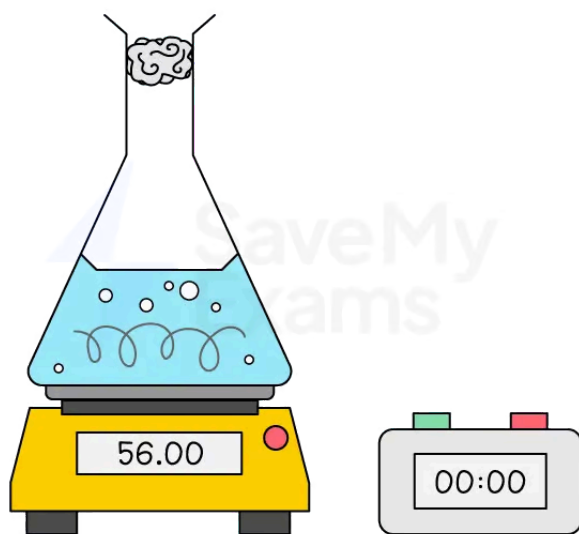
Measuring changes in mass using a balance. The cotton wool in the neck of the flask allows the gas to escape whilst preventing the other reactants and products from leaving the container

- 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

A graph to show the change in mass with time
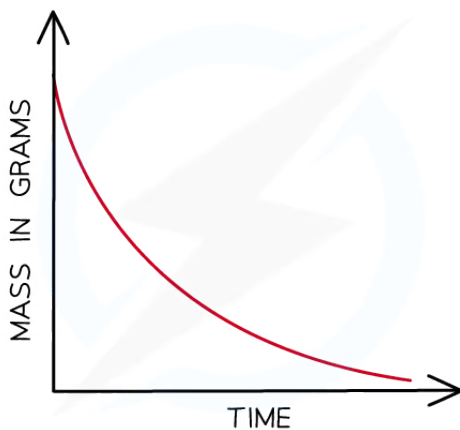
Mass loss of a product against time

- 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 decimal place balance
  - So, carbon dioxide would be suitable (M_r = 44) but hydrogen would not (M_r = 2)

Measuring rate using changes in volume 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

Measuring rate of reaction using a gas syringe
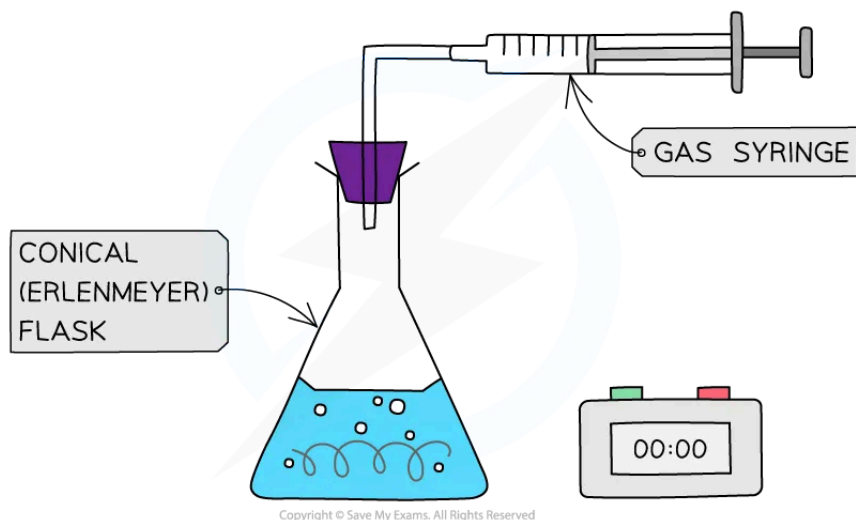
Collecting gases experimental set up

- An alternative gas collection set up involves collecting a gas through water by displacement using an inverted measuring cylinder or burette
- This method can only be used if the gas produced has a low water solubility
- Hydrogen gas can be collected using this method

Measuring the rate of reaction using an inverted measuring cylinder
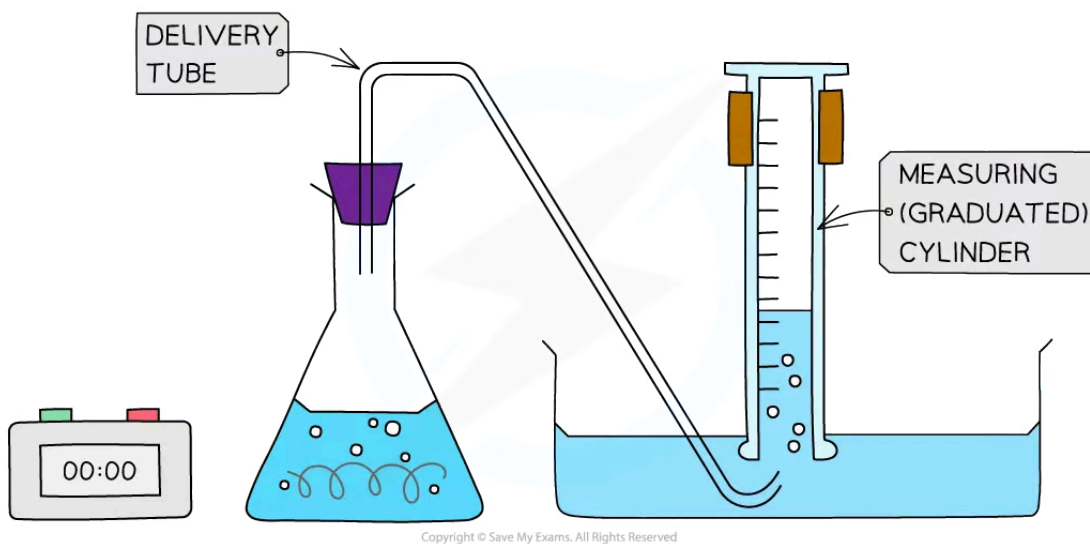
Alternative gas collection set up

- 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 the amount of product against time

Graph of gas volume evolved against time

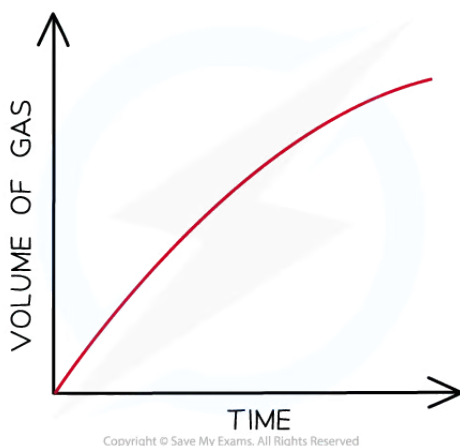Copyright © Save My Exams. All Rights Reserved

The volume of gas increases with time. The reaction has stopped when the volume of gas plateaus

Measuring concentration changes using titrations

- The concentration of a sample can be measured by performing a titration
- However, the act of taking a sample and analysing it by **titration** can affect the rate of reaction and it cannot be done continuously
- To overcome this, samples of the reaction mixture are taken at regular intervals during the course of the reaction
- The reaction in each of the samples is deliberately stopped – this is called **quenching**
  - Quenching 'freezes' the reaction at a specific point in time to allow the concentration to be determined by titration
- Based on the collected data, the rate of reaction can be calculated by determining the change in concentration with time

Measuring the rate of reaction using conductivity

- **Conductivity** can be used to measure the rate of a reaction by monitoring changes in the electrical conductivity of the reaction mixture over time
- As the reaction proceeds, the concentration of **ions** in the solution may change, affecting its conductivity
- By measuring the conductivity at different time intervals, the rate of the reaction can be determined based on how quickly the conductivity changes
- For example, in the reaction:

$$HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)$$
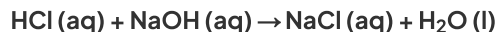
- During this reaction, HCl and NaOH dissociate into ions, increasing the conductivity of the solution
- As the reaction progresses, the concentration of ions changes which affects the conductivity

Measuring the rate of reaction using a 'clock reaction'

- Often it is more convenient to 'stop the clock' when a specific (visible) point in the reaction is reached instead of continuously monitoring the change in rate
- '**Clock reactions**' are **non-continuous** methods in which the time taken to reach a fixed point is measured
  - 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 reaction of sodium thiosulfate and hydrochloric acid
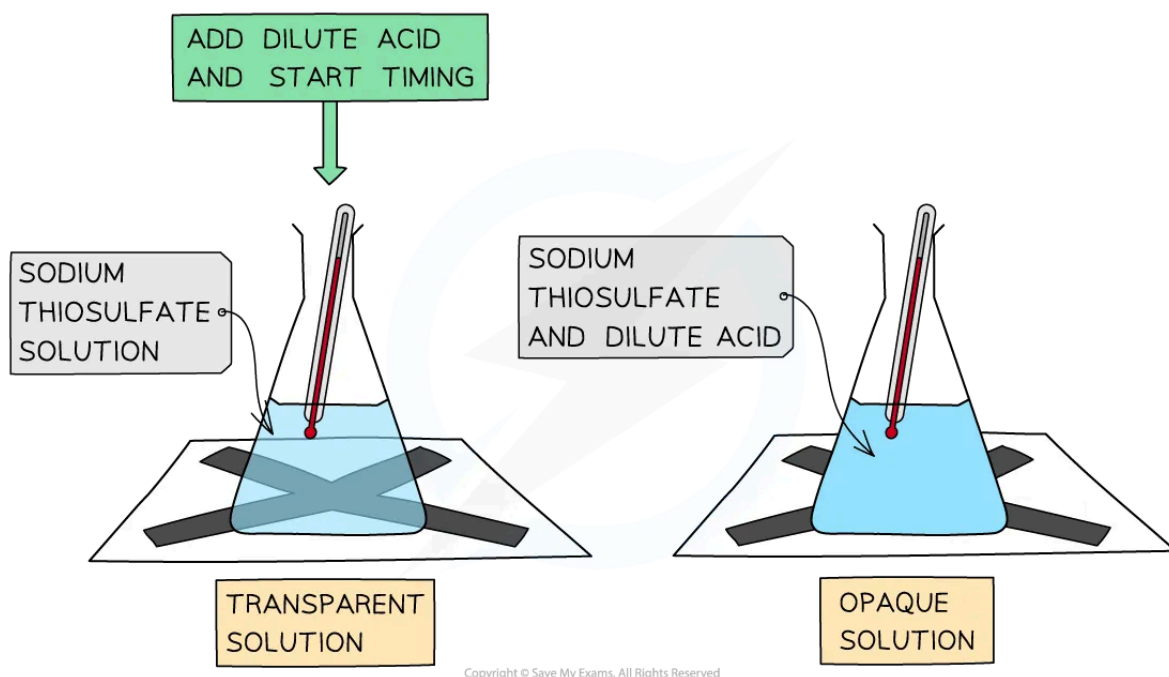
The disappearing cross experiment

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

✏️

Your notes

> 💡 **Examiner Tip**
>
> - 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
>   - For information about drawing tangents on graphs, see our revision note on Graphing in Chemistry

Collision Theory

Collision Theory

Kinetic energy and temperature

- The **kinetic theory** developed in the 18th century out of a need to explain how it is that gases exert pressure inside a container
- Theories about gas particles and movement were extended to include all states of matter
- The **kinetic theory** of matter accounts for the properties of solids, liquids and gases in terms of the interactions of particles and their relative energies

For more information on kinetic theory, see our revision note on The Kinetic Molecular Theory

- **Kinetic energy** refers to the energy associated with movement or motion. It is determined by the mass, m, and velocity, v, of the substance according to the kinetic energy formula:

$$KE = \tfrac{1}{2}mv^2$$

- As the **kinetic energy** of the particles at the same temperature is equal, this means there is an inverse relationship between mass and velocity
  - This is why substances with a lower mass diffuse more quickly than those with greater mass at the same temperature
- Particles in a substance have a range of kinetic energies due to their random motion
- The distribution of kinetic energy is shown in the **Maxwell–Boltzmann energy distribution curve**

Maxwell–Boltzmann distribution curve
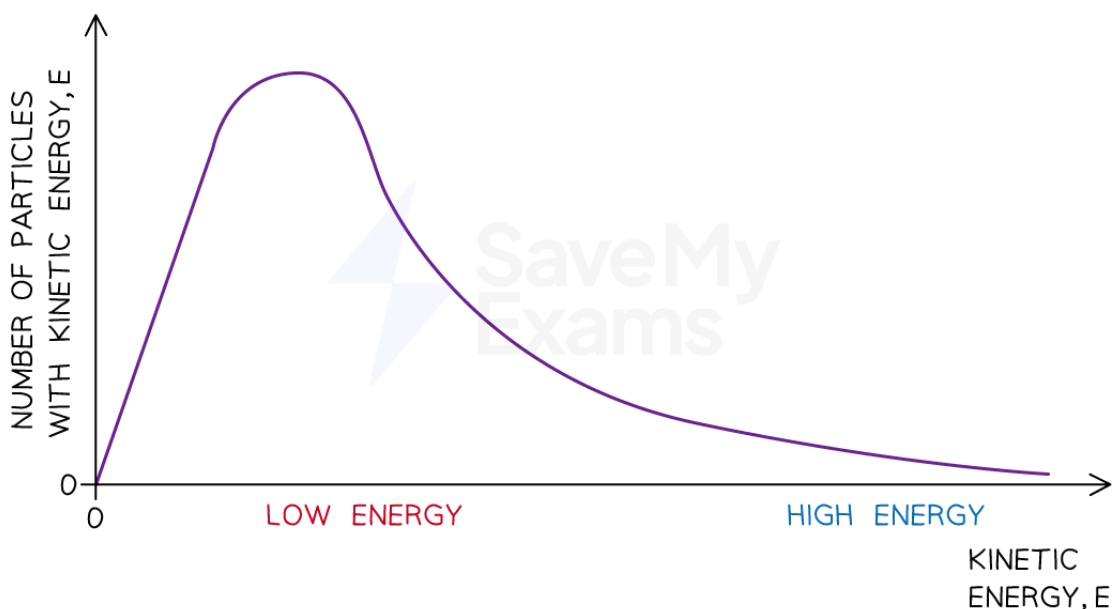
Your notes

The Maxwell-Boltzmann energy distribution curve shows the distribution of kinetic energy of particles in a sample

- The area under the curve gives the total number of particles
- The **average kinetic energy** of the particles is **directly proportional** to the temperature of the system in **Kelvin**

What is collision theory?

- **Collision theory** explains how chemical reactions occur
- 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 how often a reaction from a collision occurs, this is influenced by the following four factors:
  - **Collision frequency**
  - **Collision energy**
  - **Activation energy**
  - **Collision geometry**

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 th**e collision frequency**
- The **collision frequency** of a given system can be altered by:
  - **Changing the concentration** of the reactants
  - Changing the total **pressure**
  - Changing the **temperature**
  - Changing the **surface area** of the reacting particles

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**
  - The combined energy of the colliding particles is known as the **collision energy**

Collision energy

Collision energy is the combined energy of two colliding particles

Activation Energy

- The minimum energy the colliding particles need in order to react is known as the **activation energy**
- If the **collision energy** of the colliding particles is less than the activation energy, the collision will be unsuccessful
- If the **collision energy** is equal to or greater than the activation energy, the collision will be successful, and a reaction will take place
- The **activation energy** can be changed by the addition of a **catalyst**

Collision Geometry

- Particles have to have the right **orientation** when they collide for the reaction to be **successful**
  - This is particularly the case with large molecules with complex shapes

Collision geometry
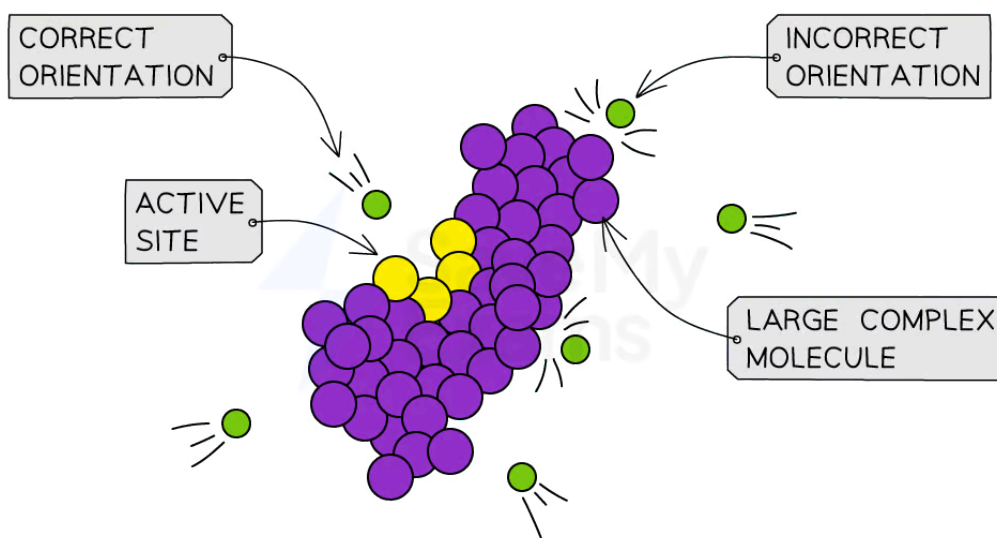
Orientation becomes increasingly important in large complex biomolecules such as proteins and carbohydrates where active sites (reactive part of the molecule) can only be accessed in one orientation

- Most collisions do not result in a reaction because **they do not reach the activation energy** rather than not having the correct collision geometry

- Ultimately, the rate of reaction depends on the number of successful collisions that happen per unit time
  - A **successful collision** is where the particles collide in the correct orientation **and** with sufficient energy for a chemical reaction to occur
- An **unsuccessful 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

Successful and unsuccessful collisions
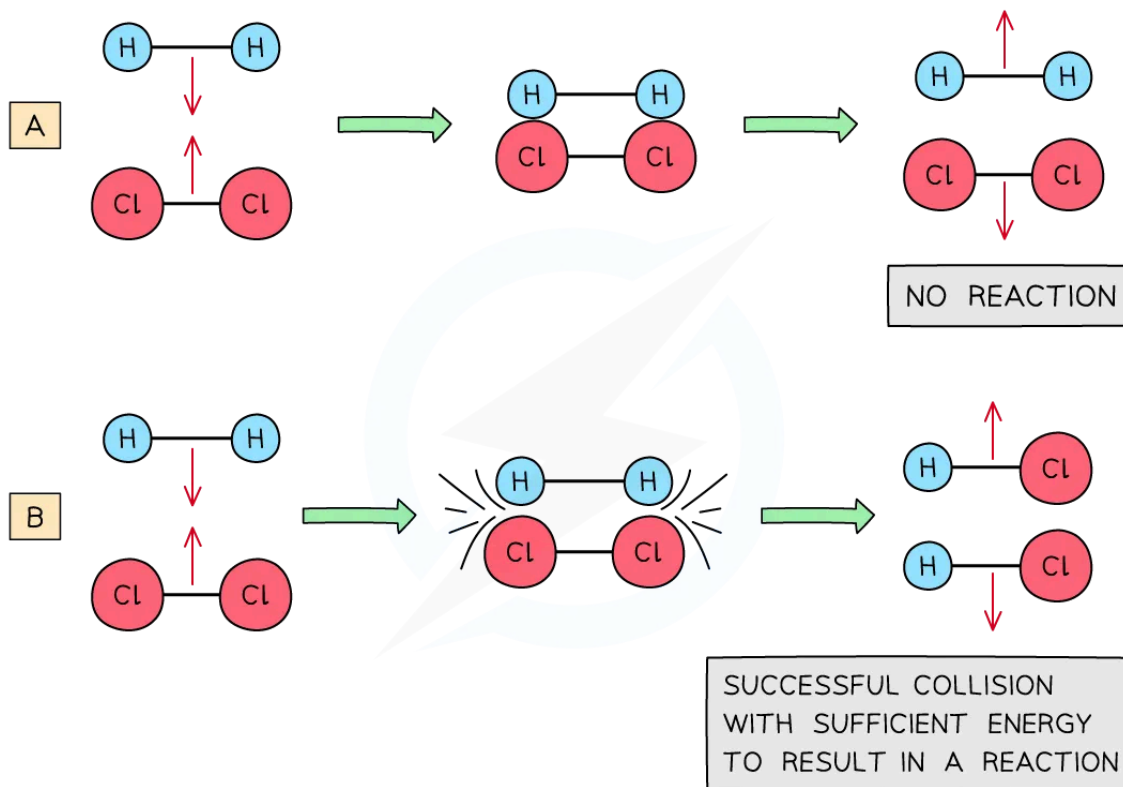
Diagram (A) shows an ineffective collision due to the particles not having enough energy whereas (B) shows an effective collision where the particles have the correct orientation and enough energy for a chemical reaction to take place

Factors Affecting Rates of Reaction

Factors Affecting Rates of Reaction

What are the factors affecting rate of reaction?

- The rate of reaction is dependent on any factor that changes the number of successful collisions
- Five such factors are:
  - **Concentration**
  - **Pressure**
  - **Temperature**
  - **Surface area**
  - The use of **catalysts**

Concentration

- The more **concentrated** a solution is, the **greater** the number of **particles** in a given volume of solvent
- An increase in **concentration** causes an increased **collision frequency** and therefore the frequency of **successful** collisions increases
- This leads to an increased **rate of reaction**

Effect of concentration on rate of reaction
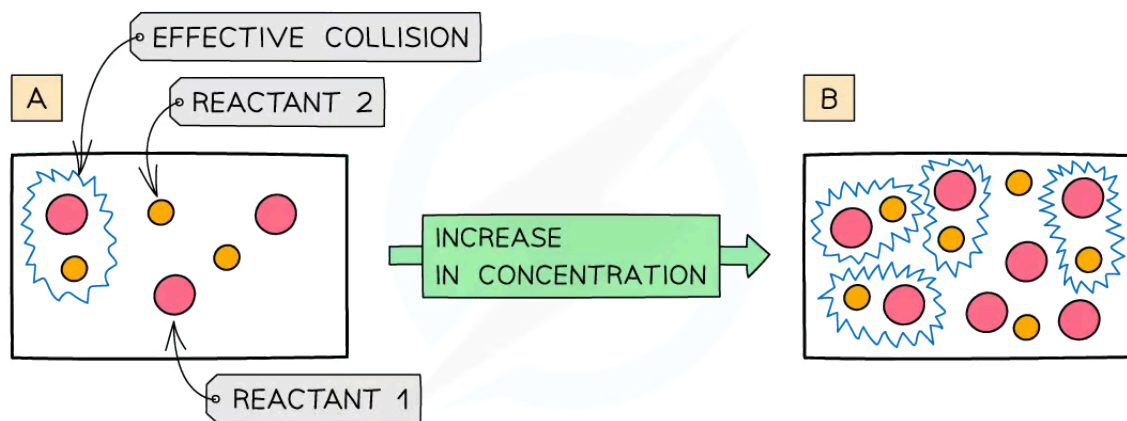
The diagram shows a higher concentration of particles in (b) which means that there are more particles present in the same volume than (a) so the chances and frequency of collisions between reacting particles are increased causing an increased rate of reaction

Pressure

- An increase in pressure in reactions that involve gases has the same effect as an increased concentration of solutions
- When the **pressure** is increased, the particles have less space in which they can move
- This means that the number of **successful collisions** increases due to an increased **collision frequency**

- An increase in pressure, therefore, increases the **rate of reaction**

Effect of pressure on rate of reaction
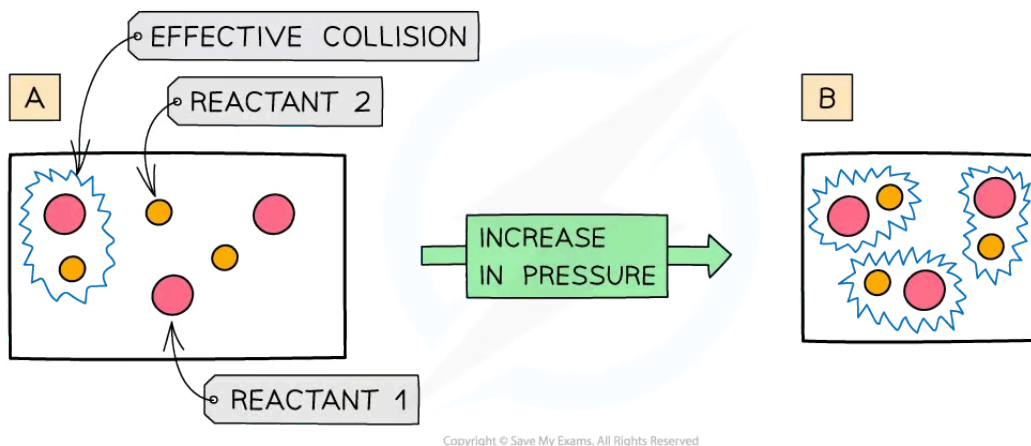
The diagram shows a higher pressure in (b) which means that the same number of particles occupy a smaller volume, resulting in an increased collision frequency and therefore increased rate of reaction

Temperature

- Increasing the temperature of the reaction mixture increases the **rate of reaction** in the following two ways:
  - At higher temperatures, the particles are moving faster, so collide more frequently
    - A higher number of collisions in total mean a higher **number** of **successful** collisions
  - At higher temperatures, a higher proportion of the particles have the activation energy or more
    - This means that a higher **proportion** of collisions are **successful**

Effect of temperature on rate of reaction
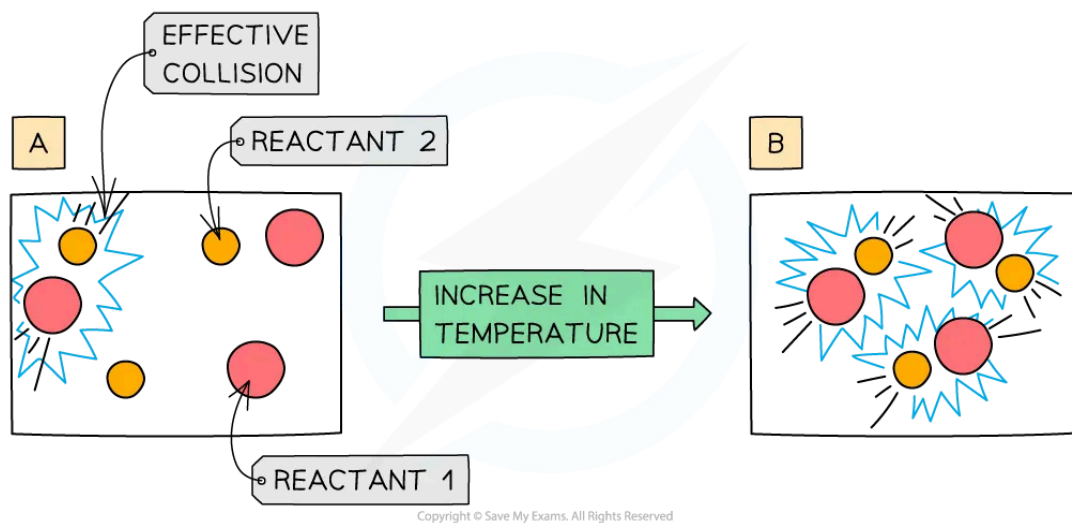
An increase in temperature causes an increase in the kinetic energy of the particles. The number of collisions increases and the proportion of successful collisions increases

- For more information about how to explain the effect of temperature on the rate of reaction, see our revision note on Maxwell–Boltzmann Distribution Curves

Surface area

- Only the particles on the surface of a solid will collide with particles of the other reactant
- If the surface area is increased, more particles will be on the surface and able to collide with particles of the other reactant
  - This means that there will be more collisions in total and therefore more **successful** collisions.
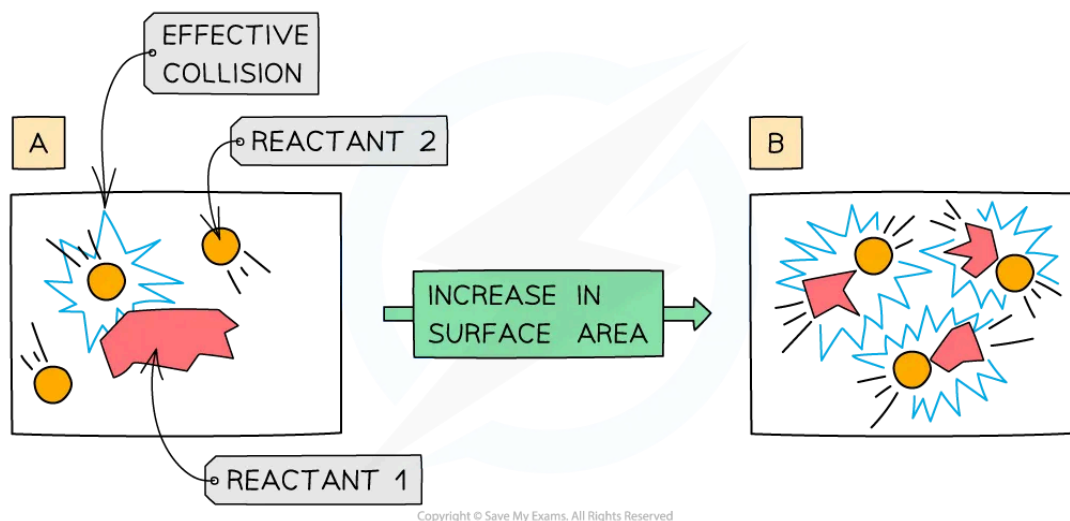- **Surface area** can be increased by **decreasing the size** of the reactant, e.g. from large pieces to a fine powder
  - Large pieces have a much smaller surface area than powders, which have a very large **surface area**

Effect of surface area on rate of reaction

An increase in surface area of a solid reactant allows more particles to come into contact with each other

Catalysts

- A catalyst provides the reactants with an **alternative reaction pathway** which is **lower in activation energy** than the uncatalysed reaction
  - This means that more **collisions** will be **successful**
  - The **rate** of reaction therefore **increases**
- A catalyst does not itself undergo permanent chemical change i.e. it is chemically unchanged at the end of the reaction
- For more information on catalysts, see our revision notes on Energy Profiles With & Without Catalysts

Your notes

✏️ Worked example

Which of the following factors can result in the rate of a chemical reaction increasing?

      I. Increasing the total pressure in reactions involving gases

      II. Raising the temperature in reactions involving gases

      III. Increasing the particle size of a solid in a reaction

    A. I and II only

    B. I and III only

    C. II and III only

    D. I, II and III

Answer:

The correct option is **A**.

- Increasing pressure and raising temperature increases the number of successful collisions
- Increasing the particle size decreases the surface area and reduces the number of collisions

Your notes

Activation Energy

Activation Energy

What is 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
- In **endothermic reactions,** the reactants are lower in energy than the products

Energy profile of an exothermic reaction, showing E_a
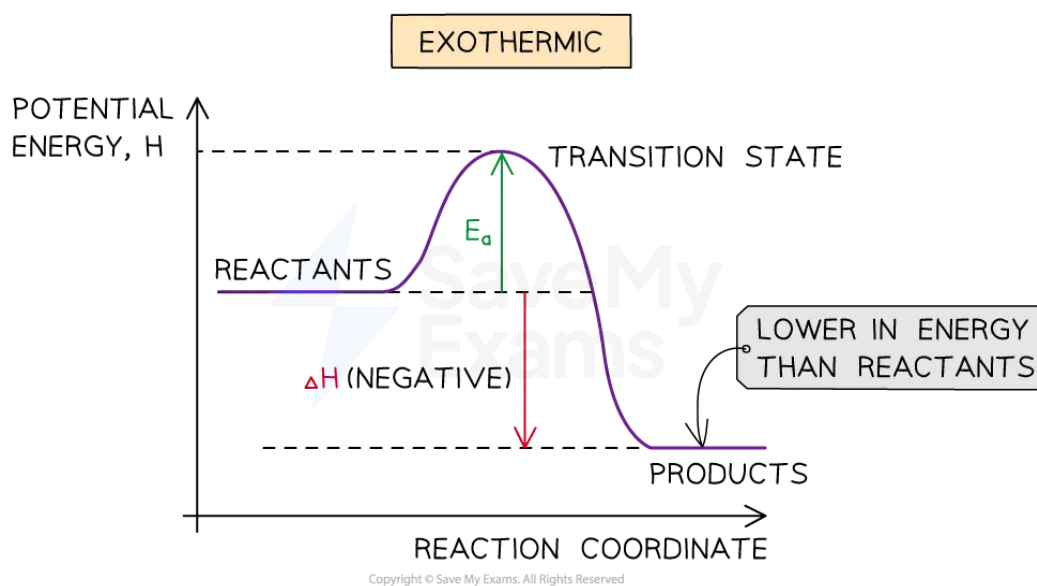
The diagram shows that the reactants are higher in energy than the products in the exothermic reaction

Energy profile of an endothermic reaction, showing E_a
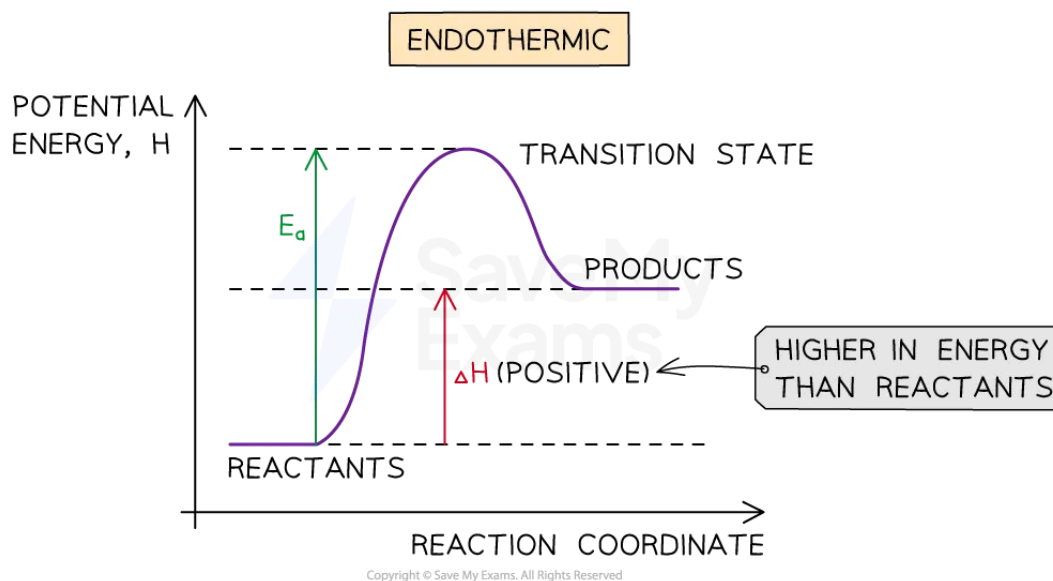
The diagram shows that the reactants are lower in energy than the products in the endothermic reaction

- 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 **successful** the reactant particles must collide in the correct orientation **AND** possess a minimum energy equal to the E_a of that reaction

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💡 Examiner Tip

How to find the activation energy of a reverse reaction

- You may be required to show or calculate the activation energy for a reverse reaction using a labelled energy profile like those above. The activation energy for the reverse reaction is found by:

    For an exothermic reaction = $\Delta H + E_a$ (forward)

    For an endothermic reaction = E_a (forward) – ΔH

- Calculations of the value of the activation energy from experimental data are not required at Standard Level but are required in Higher Level Chemistry
- For more information on how to calculate activation energy, see our revision notes on Determining Activation Energy & the Arrhenius Factor

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Energy Profiles With & Without Catalysts

Energy Profiles With & Without Catalysts

How do catalysts increase the rate of reaction?

- 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
- The catalyst remains **chemically unaltered** by the end of the reaction

How a catalyst increases the rate of reaction

Your notes

THIS SUBSTRATE MOLECULE NEEDS TO DISSOCIATE INTO TWO MOLECULES HOWEVER THIS COSTS A LOT OF ENERGY AND HAS A LOW RATE. THEREFORE, A CATALYST IS USED TO INCREASE THE RATE OF REACTION

THE SUBSTRATE MOLECULE BINDS TO THE CATALYST

CATALYST

CATALYST

THE CATALYST HAS INCREASED THE RATE OF DISSOCIATION OF THE SUBSTRATE MOLECULE

THE SUBSTRATE MOLECULE IS RELEASED. NOTE THAT THE CATALYST HAS RETURNED TO ITS ORIGINAL SHAPE AND HAS NOT BEEN USED UP IN THE REACTION!
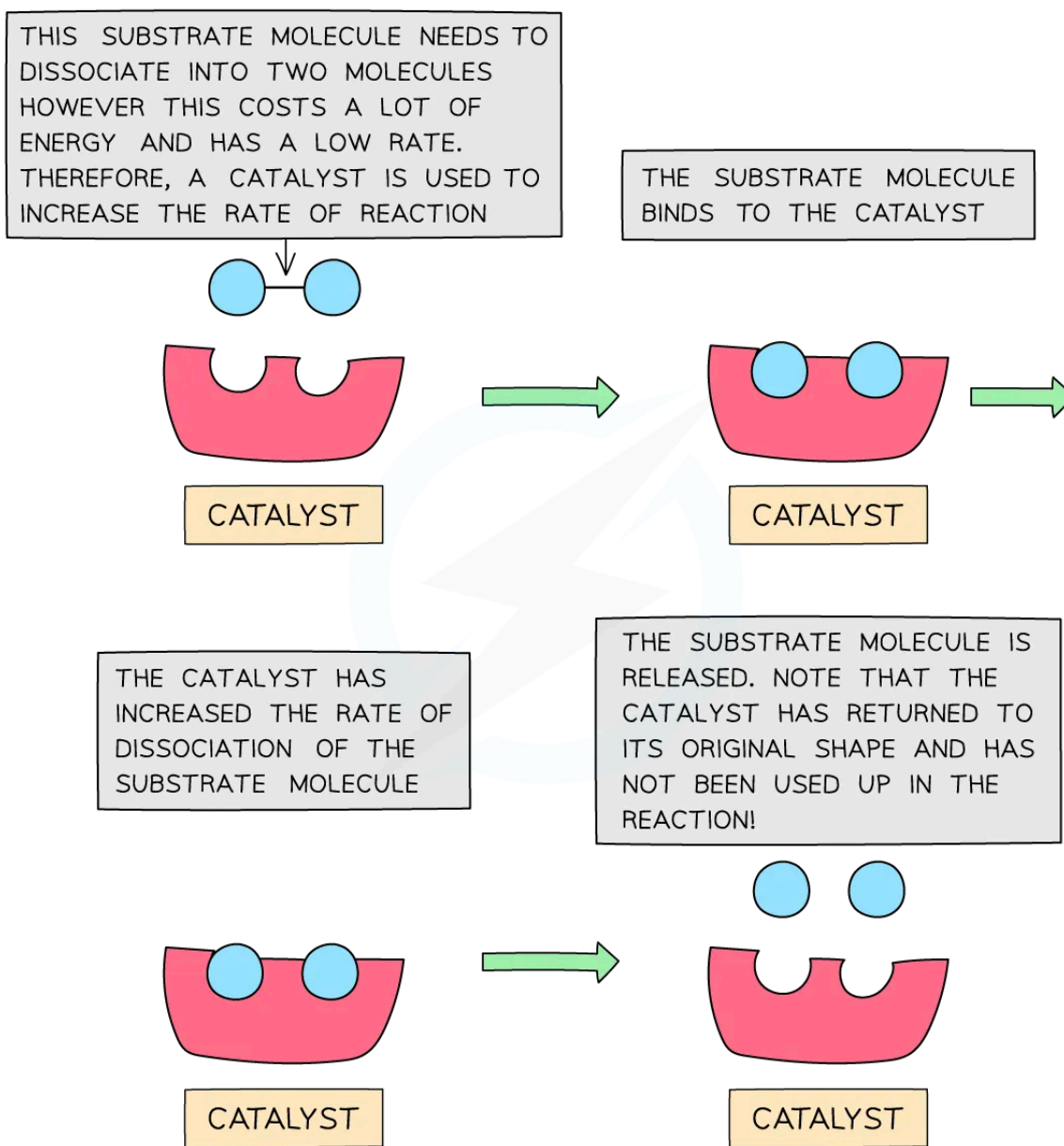
CATALYST

CATALYST

The diagram shows that the catalyst speeds up a reaction that would normally be slow due to the high activation energy. The catalyst is not used up in the chemical reaction and is not taking part in the chemical reaction

- Catalysts are important in reducing the **environmental impact** of industrial processes by:
  - Reducing the **energy requirements** of processes as they enable reactions to occur at lower temperatures and pressures

Your notes

- Reducing **waste products** as they can be reused and are only used in small quantities, increasing atom economy
- Increasing the **selectivity of processes**, promoting specific reactions and suppressing undesired side reactions

- 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 liquids
- **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

Energy profiles of reactions with catalysts

- The lower activation energy of the alternative pathway used by a catalyst can be shown on an energy profile

Energy profile with and without a catalyst
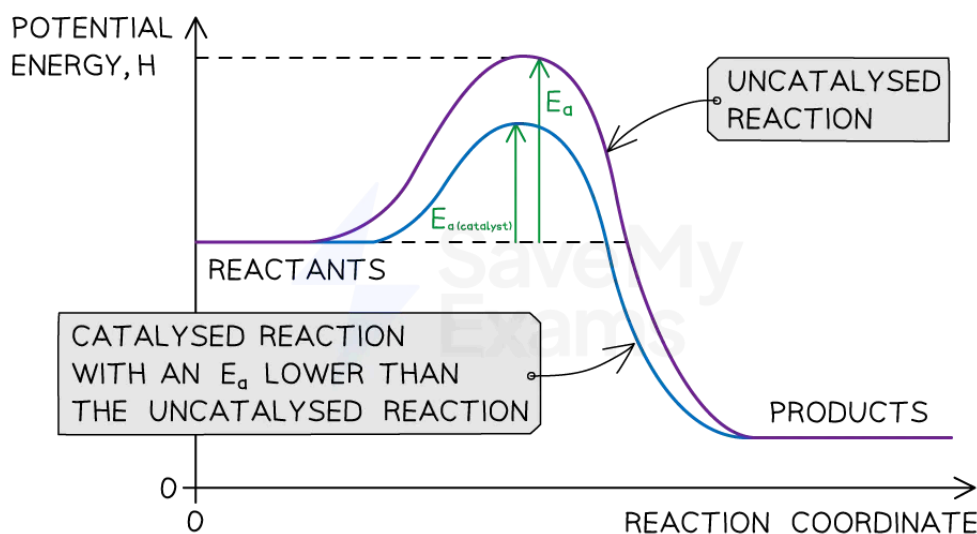
The diagram shows that the catalyst allows the reaction to take place through a different mechanism, which has a lower activation energy than the original reaction

Examples of catalysts

- **Enzymes** are **biological** catalysts
  - Enzymes act as catalysts in biological systems, controlling many biochemical reactions within cells

- As well as being important for controlling reactions in cells, they are also important in **industry**
- Enzymes allow industrial reactions to happen at **lower temperatures and pressures** than usually needed, saving money and energy
- **Transition metals** are often used as catalysts due to their ability to form more than one stable oxidation state
- For more information about the uses of transition metals as catalysts required in Higher Level Chemistry, see our revision note on the Characteristic Properties of Transition Elements

Your notes

✏️ **Worked example**

The energy profile below shows the energy changes for a reaction with and without a catalyst.
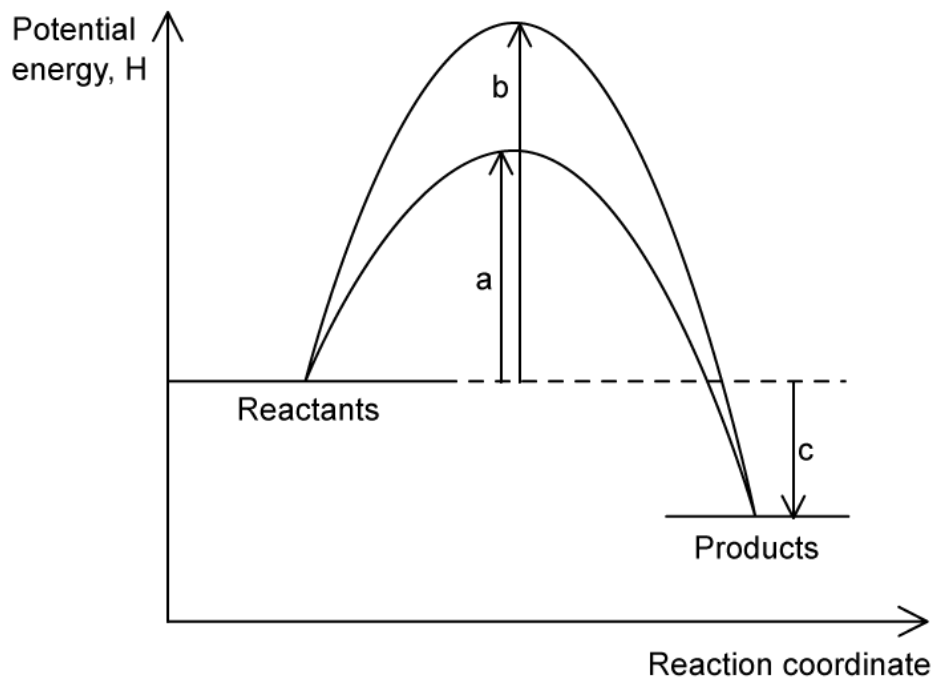
Which symbols represent the enthalpy change, ΔH, and the activation energy, E_a, for the reaction using a catalyst?

	ΔH	E_a (with catalyst)
A.	a	c
B.	b	c
C.	c	a
D.	b – a	c

Answer:

- The correct option is **C**.

- By definition, the enthalpy change is the difference in energy content between reactants and products, in this case, arrow **c**
- The catalyst lowers the activation energy, which corresponds to arrow **a**

Your notes

Maxwell-Boltzmann Distribution Curves

Maxwell-Boltzmann Distribution Curves

What is a 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 substance:
  - A few particles will have very low energy
  - A few particles will have very high energy
  - Many particles will have energy in between

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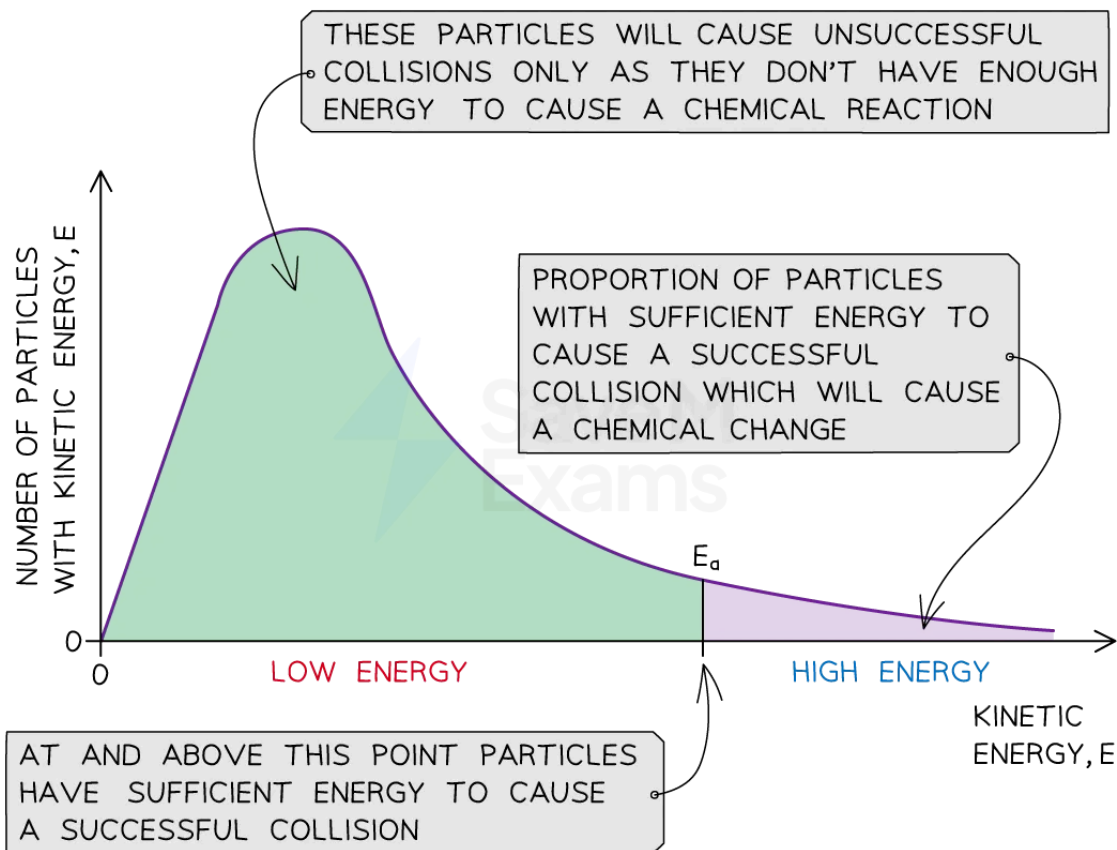
The Maxwell-Boltzmann distribution curve shows the distribution of energies and the activation energy

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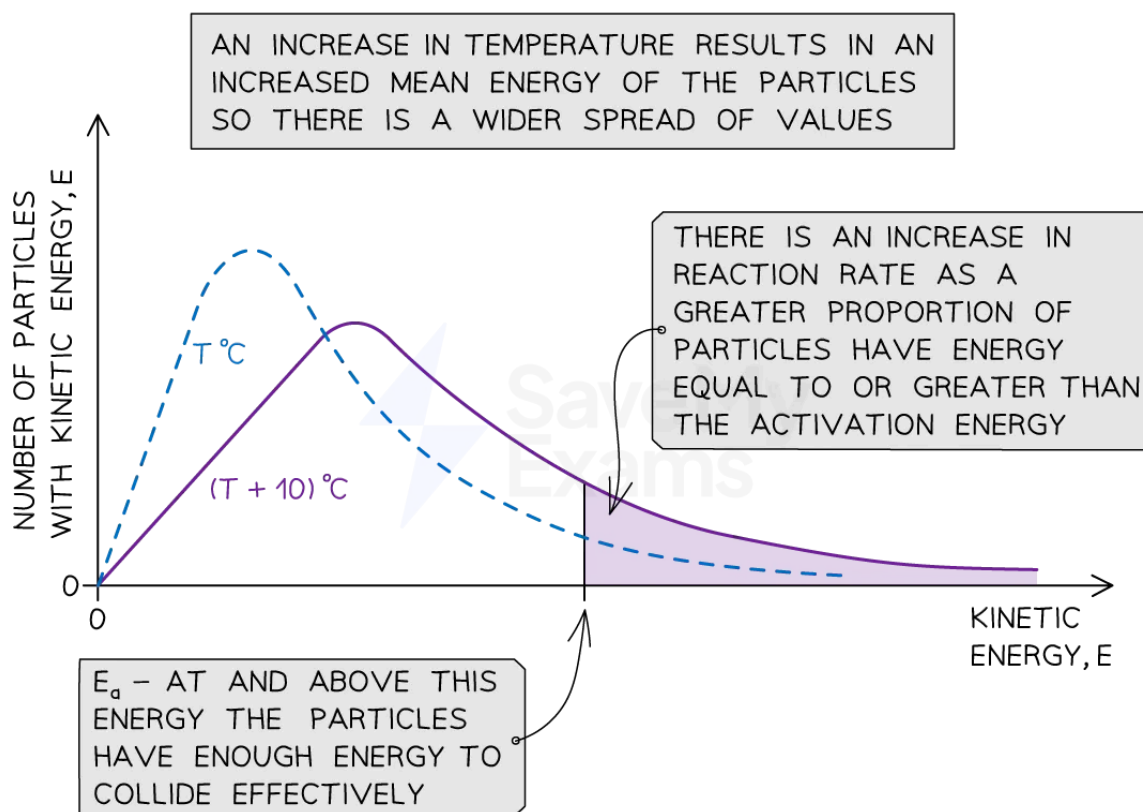
Your notes

- The **most probable** energy of a particle is represented by the **highest** point on the curve's peak
  - This is sometimes written as E_{MP}

Effect of changes in temperature on the Maxwell–Boltzmann distribution curve

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

Graph of the effect of temperature on the Maxwell–Boltzmann distribution curve

AN INCREASE IN TEMPERATURE RESULTS IN AN INCREASED MEAN ENERGY OF THE PARTICLES SO THERE IS A WIDER SPREAD OF VALUES

THERE IS AN INCREASE IN REACTION RATE AS A GREATER PROPORTION OF PARTICLES HAVE ENERGY EQUAL TO OR GREATER THAN THE ACTIVATION ENERGY

E_a – AT AND ABOVE THIS ENERGY THE PARTICLES HAVE ENOUGH ENERGY TO COLLIDE EFFECTIVELY

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**

> ### 💡 Examiner Tip
>
> - When drawing Maxwell-Boltzmann distribution curves at different temperatures, make sure that:
>   - The peak of the curve of the **higher** temperature is **lower** and to the **right** of the peak of the curve of the lower temperature
>   - The two curves should only cross each other **once**
>   - The tail of the curve of the higher temperature should be **higher** than that of the lower temperature
> - **Careful:** Examiners currently prefer to ask about the effect of reducing the temperature of a reaction, rather than increasing the temperature
>   - The underlying theory is still the same but you need to apply it in the opposite direction

Effect of a catalyst on the Maxwell-Boltzmann distribution curve

- A **catalyst** provides the reactants with another reaction pathway which has a lower activation energy
- By lowering E_a, a **greater proportion** of molecules in the reaction mixture will have sufficient energy for a **successful collision**
- As a result of this, the rate of the catalysed reaction is increased compared to the uncatalysed reaction

Maxwell-Boltzmann distribution curve with a catalyst
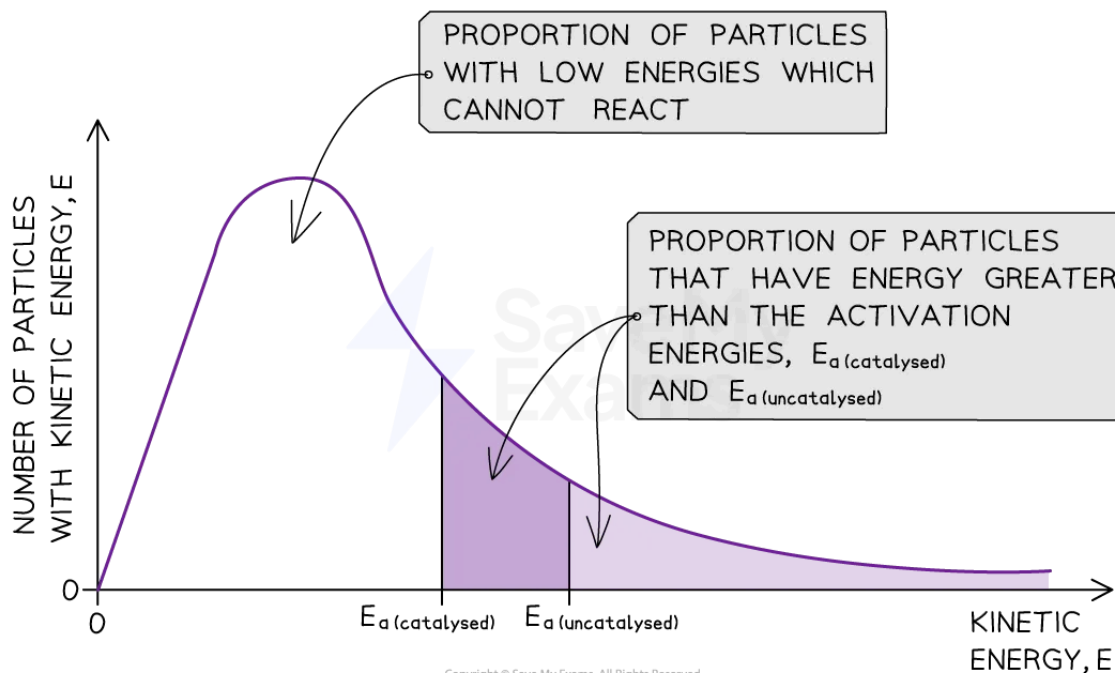
The total shaded area (both dark and light shading) under the curve shows the number of particles with energy greater than the E_a when a catalyst is present. This area is much larger than the dark shaded area

which shows the number of particles with energy greater than the E_a without a catalyst. The light–shaded area shows the extra particles which have enough energy to react with a catalyst.

> 💡 **Examiner Tip**
>
> - Make sure you know how to sketch and label the axes in Maxwell-Boltzmann distribution curves
>   - The curve must start at the origin and it approaches, but **never** touches the x-axis.
> - If you are asked to show the area that represents the particles with an energy greater than the activation energy with a catalyst, make sure you highlight the **total** shaded area, not just the light-shaded area.

Your notes

Rate Equation (HL)

Rate Equation

- The **rate of reaction** can be found by:
    - Measuring the decrease in the concentration of a reactant over time
    - Measuring the increase in the concentration of a product over time
- The units for rate of reaction are mol dm^{-3} s^{-1}

Rate of Reaction

- The following general reaction will be used as an example to study the rate of reaction

$$D \text{ (aq)} \rightarrow E \text{ (aq)} + F \text{ (g)}$$

- The rate of reaction at different concentrations of **D** is measured and tabulated and a graph of rate against [D] is drawn

- The gradient at each concentration is calculated by $\dfrac{\text{rate}}{[\text{D}]}$

Rate of reactions table

[D] (mol dm^{-3})	Rate (mol dm^{-3} s^{-1})	gradient = $\dfrac{\text{rate}}{[\text{D}]}$ (s^{-1})
3.00	2.000 x 10^{-3}	6.67 x 10^{-4}
2.00	1.334 x 10^{-3}	6.67 x 10^{-4}
1.00	6.670 x 10^{-4}	6.67 x 10^{-4}

- A **directly proportional** relationship between the **rate** of reaction and **concentration of D** is observed when the results are plotted on the graph
- The value of the gradient is constant as it is a straight line

Graph to show rate against [D]

$$\text{GRADIENT} = \frac{\text{RATE}}{[D]}$$

$$= 6.67 \times 10^{-4}$$
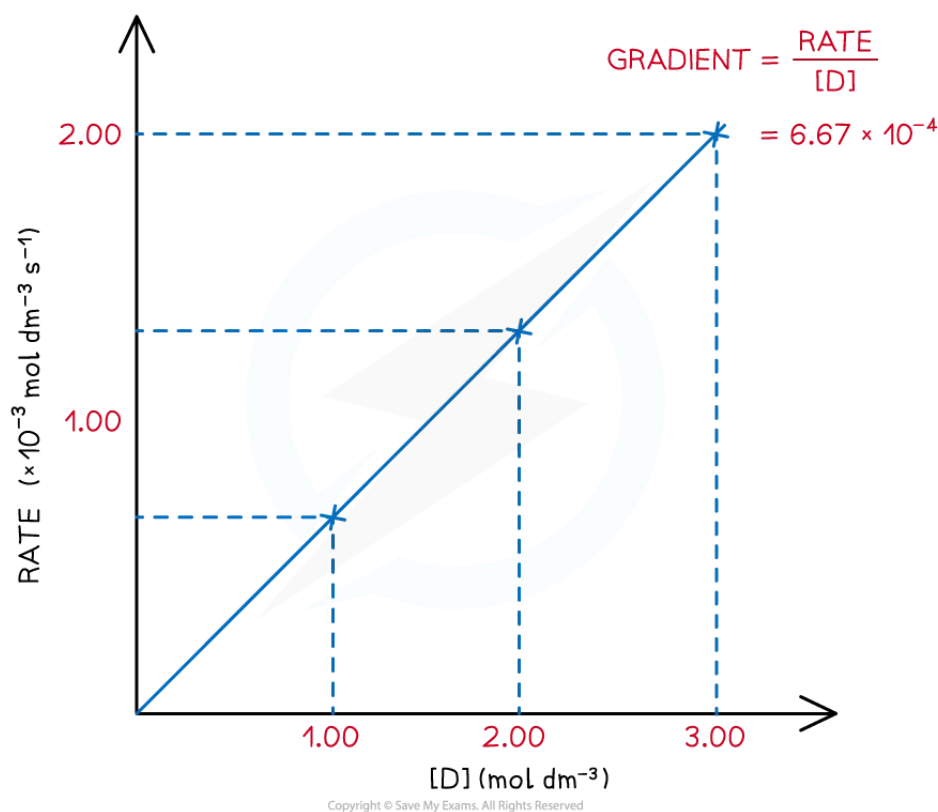
*Rate of reaction over various concentrations of D*

- This leads to a very common rate expression:

$$\text{Rate} \propto [D] \quad \text{or} \quad \text{Rate} = k[D]$$

- This rate expression means that if the concentration of **D** is doubled, then the rate doubles
  - Equally, if the concentration of **D** halves, then the rate halves
- However, the rate of a reaction does not always show this directly proportional relationship with the concentration of a reactant and we can use the **rate equation** and **orders of reaction** to explain this

What is the rate equation?

- The following reaction will be used to discuss rate equations:

$$\text{A (aq) + B (aq)} \rightarrow \text{C (aq) + D (g)}$$
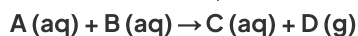
- The rate equation for this reaction is:

$$\text{Rate of reaction} = k\,[A]^m\,[B]^n$$

- Rate equations depend on the mechanism of the reaction and can only be determined experimentally, they cannot be found from the stoichiometric equations
- In the above rate equation:
  - [**A**] and [**B**] are the concentrations of the reactants

Your notes

- m and n are orders with respect to each reactant involved in the reaction
- Products and catalysts may feature in rate equations
- Intermediates do not feature in rate equations

What is the order of reaction?

- The **order** of a reactant shows how the concentration of a chemical, typically a reactant, affects the rate of reaction
- It is the power to which the concentration of that reactant is raised in the rate equation
- The order can be a positive, negative or fractional value
  - Orders that are a fraction suggest that the reaction involves multiple steps

Zero order

- When the order of reaction with respect to a chemical is **0**
  - Changing the concentration of the chemical has **no effect** on the rate of the reaction
  - Therefore, it is not included in the rate equation

First order

- When the order of reaction with respect to a chemical is **1**
  - The concentration of the chemical is **directly proportional** to the rate of reaction, e.g. doubling the concentration of the chemical doubles the rate of reaction
  - The chemical is included in the rate equation

Second order

- When the order of reaction with respect to a chemical is **2**
  - The rate is **directly proportional to the square** of the concentration of that chemical, e.g. doubling the concentration of the chemical increases the rate of reaction by a factor of four
  - The chemical is included in the rate equation (appearing as a squared term)

Overall order

- The **overall order of reaction** is the sum of the powers of the reactants in a rate equation ($m + n$)

💡 Examiner Tip

- In an exam, you may be presented with information about a reaction that uses orders that are fractions
- Examples include:
  - The decomposition of ethanal: Rate = $k[CH_3CHO]^{3/2}$
  - The reaction of hydrogen and bromine: Rate = $k[H_2][Br_2]^{1/2}$
  - The reaction between carbon monoxide and chlorine: Rate = $k[CO]^2[Cl_2]^{1/2}$
- However, for calculations only values of 0, 1 or 2 need to be considered

---

✏️ **Worked example**

The chemical equation for the thermal decomposition of dinitrogen pentoxide is:

$$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$$

The rate equation for this reaction is:

$$Rate = k[N_2O_5\,(g)]$$

1. State the order of the reaction with respect to dinitrogen pentoxide
2. Deduce the effect on the rate of reaction if the concentration of dinitrogen pentoxide is tripled

Answer 1:

- Dinitrogen pentoxide features in the rate equation, therefore, it cannot be order zero / 0
- The dinitrogen pentoxide is not raised to a power, which means that it cannot be order 2 / second order
- Therefore, the order with respect to dinitrogen pentoxide must be **order 1 / first order**

Answer 2:

- Since the reaction is first order, the concentration of dinitrogen pentoxide is directly proportional to the rate
- This means that if the concentration of the dinitrogen pentoxide is tripled, then the rate of reaction will also **triple**

✏️ Your notes

Your notes

Worked example

The following equation represents the oxidation of bromide ions in acidic solution

$$BrO_3^- (aq) + 5Br^- (aq) + 6H^+ (aq) \rightarrow 3Br_2 (l) + 3H_2O (l)$$
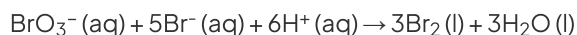
The rate equation for this reaction is:

$$Rate = k[BrO_3^- (aq)][Br^- (aq)][H^+ (aq)]$$

1. State the overall order of the reaction
2. Deduce the effect on the rate of reaction if the concentration of bromate ions is doubled and the concentration of bromide ions is halved

Answer 1:

- All three reactants feature in the rate equation but they are not raised to a power, this means that the order with respect to each reactant is order 1 / first order
- The overall order of the reaction is 1 + 1 + 1 = **3** or **third order**

Answer 2:

- Since each reactant is first order, the concentration of each reactant is directly proportional to the effect that it has on rate
- If the concentration of the bromate ion is doubled, then the rate of reaction will also double
- If the concentration of the bromide ion is halved then the rate will also halve
- Therefore, there is **no overall effect** on the rate of reaction – one change doubles the rate and the other change halves it

How can the rate equation be deduced from experimental data?

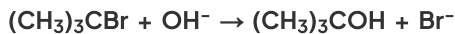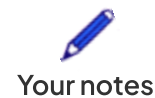- The following reaction will be used to deduce the rate equation, using experimental data

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

Table to show the experimental data of the above reaction

Experiment	Initial [$(CH_3)_3CBr$] / mol dm^{-3}	Initial [OH^-] / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
2	2.0×10^{-3}	2.0×10^{-3}	6.0×10^{-3}
3	1.0×10^{-3}	4.0×10^{-3}	1.2×10^{-2}

Your notes

4	1.5×10^{-3}	4.0×10^{-3}	4.5×10^{-3}

- To derive the rate equation for a reaction, you must first determine all of the orders with respect to each of the reactants
- This can be done using the tabulated data provided
- Take the reactants one at a time and find the order with respect to each reactant individually:
  1. Identify two experiments where the concentration of one reactant changes, but the concentrations of all other reactants are constant
  2. Calculate what happens to the concentration
  3. Calculate what happens to the rate of reaction
  4. Deduce the order of reaction with respect to that chemical
  5. Repeat this for all of the reactants, one at a time, until you have determined the order with respect to all reactants

Order with respect to $[(CH_3)_3CBr]$

1. In experiments 1 and 2, the concentration of $(CH_3)_3CBr$ changes while the concentration of OH^- remains constant
2. The $[(CH_3)_3CBr]$ has doubled
3. The rate of the reaction has also doubled
4. Therefore, the order with respect to $[(CH_3)_3CBr]$ is 1 (first order)
   - $[\text{Change in concentration}]^{\text{order}}$ = change in rate
   - $[2]^{\text{order}} = 2$
   - $[2]^1 = 2$

Order with respect to $[OH^-]$

1. In experiments 1 and 3, the concentration of OH^- changes while the concentration of $(CH_3)_3CBr$ remains constant
2. The $[OH^-]$ has doubled
3. The rate of the reaction has increased by a factor of 4
4. Therefore, the order with respect to $[OH^-]$ is 2 / second order
   - $[\text{Change in concentration}]^{\text{order}}$ = change in rate
   - $[2]^{\text{order}} = 4$
   - $[2]^2 = 2$

Building the rate equation

- Once the order with respect to all of the reactants is known the rate equation can be constructed
  - Zero order reactants are not included in the rate equation
  - First order reactants are included in the rate equation – they do not require a power
  - Second order reactants are included in the rate equation – they are raised to the power of 2
- So, for this reaction the rate equation will be:

$$\text{Rate} = k \, [(CH_3)_3CBr] \, [OH^-]^2$$

Your notes

> **💡 Examiner Tip**
>
> - Examiners will often give concentration and rate data in standard form to test your mathematical skills!
> - Take your time because it is easy to make a mistake
>   - The most common mistake is failing to notice a factor of ten, e.g. one rate value is $\times 10^{-4}$ while the rest are $\times 10^{-3}$

Your notes

## Reaction Orders (HL)

Reaction Orders

How to determine reaction orders from graphs

- Reaction orders can be determined by using graphical representations of experimental data
- Two different types of graphs can be used:
  - Concentration-time graphs
  - Rate-concentration graphs
- Rate-concentration graphs show the distinction between zero, first and second order more clearly than concentration-time graphs, as shown below

Reaction Order Using Concentration-Time Graphs

- In a **zero-order** reaction, the concentration of the reactant is inversely proportional to time
  - This means that the reactant concentration decreases as time increases
  - The graph is a straight line going down as shown:

Concentration-time graph of a zero-order reaction
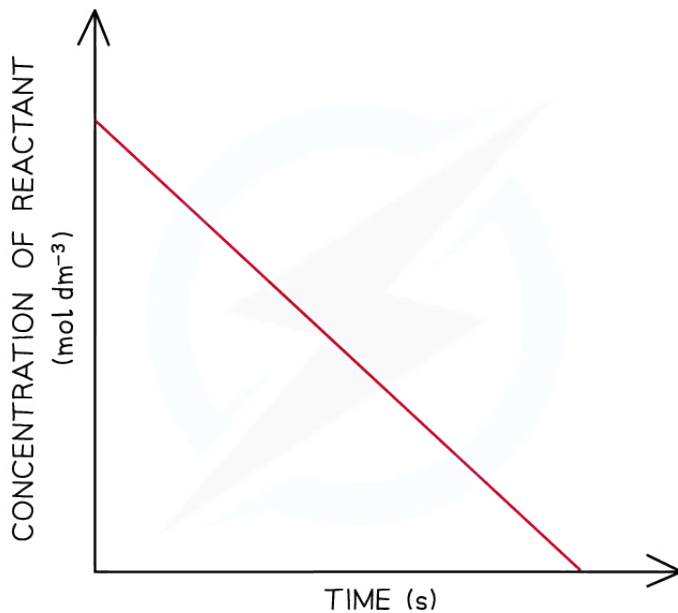
A concentration-time graph of a zero-order reaction shows that concentration is inversely proportional to time

- The gradient of the line is the rate of reaction

Your notes

- Calculating the gradient at different points on the graph, will give a constant value for the rate of reaction
- When the order with respect to a reactant is 0, a change in the concentration of the reactant has no effect on the rate of the reaction
- Therefore:

Rate = k

- This equation means that the gradient of the graph is the rate of reaction as well as the rate constant, k

- In a **first-order** reaction, the concentration of the reactant decreases with time
  - The graph is a curve going downwards and eventually plateaus:

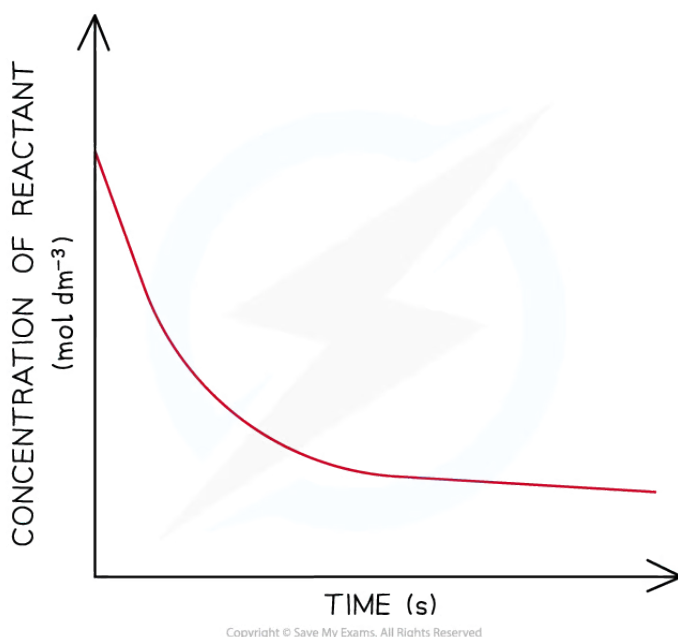### Concentration-time graph of a first-order reaction
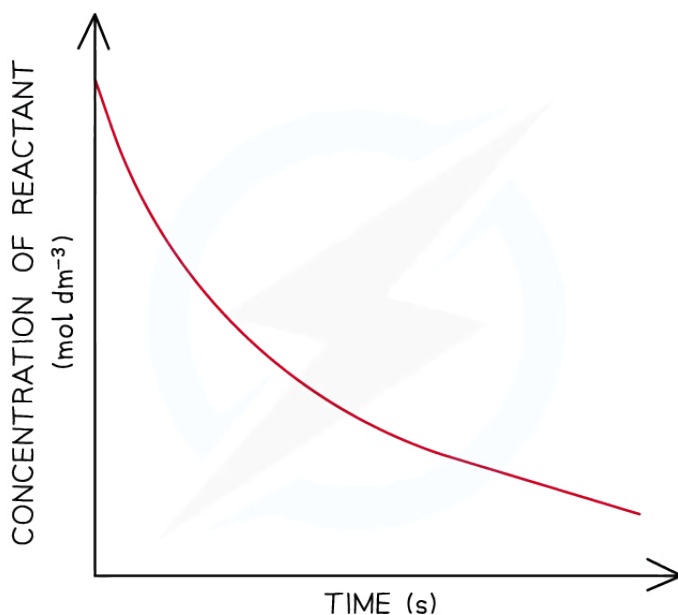
A concentration-time graph of a first-order reaction curves downwards

- In a **second-order** reaction, the concentration of the reactant decreases more steeply with time
  - The concentration of reactant decreases **more** with increasing time compared to a first-order reaction
  - The graph is a steeper curve going downwards:

Concentration-time graph of a second-order reaction

A concentration-time graph of a second-order reaction shows a downward curve with a steeper gradient than the curve for a first-order reaction

> 💡 **Examiner Tip**
>
> - Make sure that you know the correct shapes for the concentration-time graphs
> - It can be easy to confuse some concentration-time graphs with the following rate-concentration graphs, particularly:
>   - The straight line of a zero-order concentration-time graph with the straight line of a first-order rate-concentration graph.
>   - The curve of a first-order concentration-time graph with the curve of a second-order rate-concentration graph.
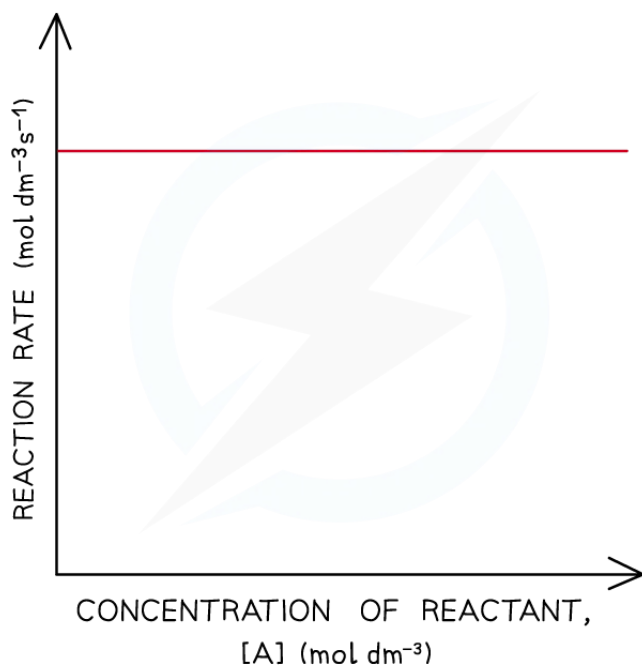
Reaction order using rate-concentration graphs

- In a **zero-order** reaction, the rate does not depend on the concentration of the reactant
  - The rate of the reaction, therefore, remains constant throughout the reaction
  - The graph is a horizontal line
  - The rate equation is **rate = k**

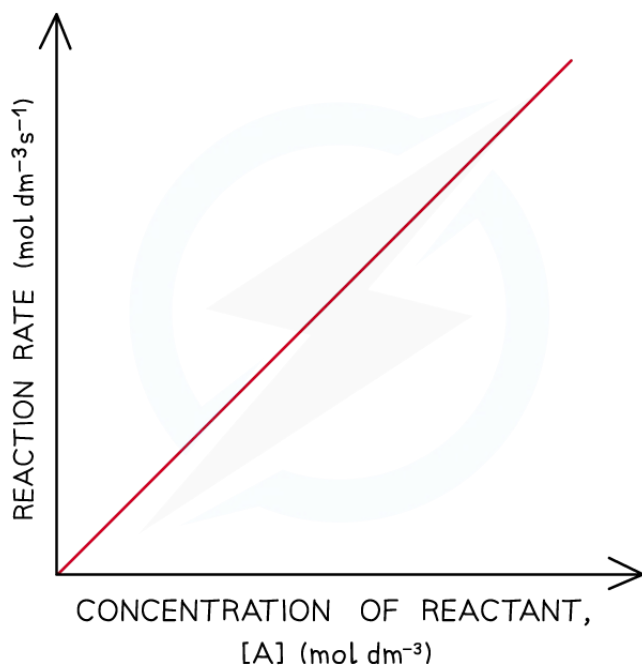### Rate-concentration graph of a zero-order reaction

A rate-concentration graph of a zero-order reaction shows a horizontal line

- In a **first-order** reaction, the rate is directly proportional to the concentration of a reactant
  - The rate of the reaction increases as the concentration of the reactant increases
  - This means that the rate of the reaction decreases as the concentration of the reactant decreases when it gets used up during the reaction
  - The graph is a straight line
  - The rate equation is **rate = *k*[A]**

Rate-concentration graph of a first-order reaction

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A rate-concentration graph of a first-order reaction shows a directly proportional relationship

- In a **second-order** reaction, the rate is directly proportional to the square of concentration of a reactant
  - The rate of the reaction increases more as the concentration of the reactant increases
  - This means that the rate of the reaction decreases more as the concentration of the reactant decreases when it gets used up during the reaction
  - The graph is a curved line
  - The rate equation is **rate = $k[A]^2$**
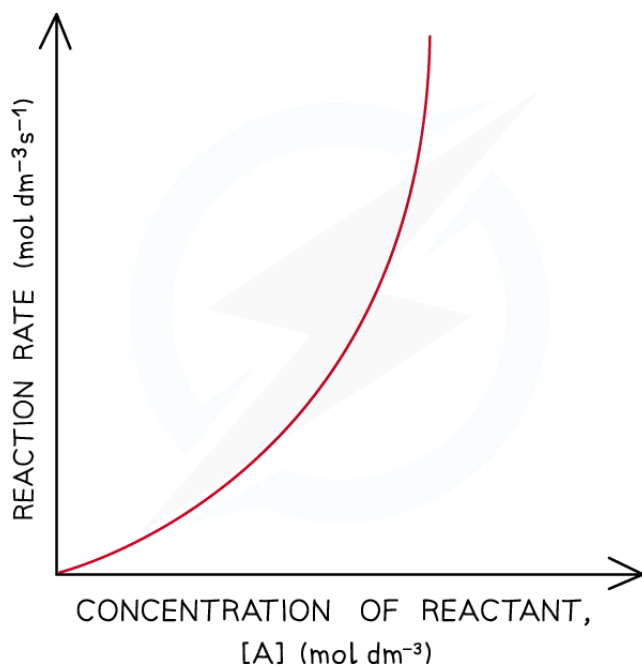
Rate-concentration graph of a second-order reaction

A rate-concentration graph of a second-order reaction shows an upward curve

---

💡 Examiner Tip

- **Careful:** Sometimes when asked to complete calculations for the rate constant, *k*, the exam question will give you a graph as well as tabulated data
  - Do not ignore the graph as this demonstrates the order of one of the reactants, while the tabulated data allows you to determine the order for the other reactants.

The Rate Constant (HL)

The Rate Constant

How to calculate the rate constant

- The rate constant, k, of a reaction can be calculated using the **initial rate** and the **rate equation**
- The reaction of sodium carbonate with chloride ions (from hydrochloric acid) to form sodium chloride will be used as an example to calculate the rate constant from the **initial rate** and **initial concentrations**
- The reaction and rate equation are as follows:

$$Na_2CO_3 \text{ (aq)} + 2Cl^- \text{ (aq)} + 2H^+ \text{ (aq)} \rightarrow 2NaCl \text{ (aq)} + CO_2 \text{ (g)} + H_2O \text{ (l)}$$
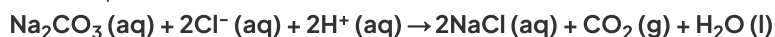
$$rate = k[Na_2CO_3][Cl^-]$$

- The rate equation rearranges to give:

$$k = \frac{rate}{[Na_2CO_3][Cl^-]}$$

- The progress of the reaction can be followed by measuring the initial rates of the reaction using various initial concentrations of each reactant

Experimental results of concentrations & initial rates table

Measurement	[Na$_2$CO$_3$] / mol dm^{-3}	[Cl$^-$] / mol dm^{-3}	[H$^+$] / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.0250	0.0125	0.0125	4.38 x 10^{-6}
2	0.0375	0.0125	0.0125	6.63 x 10^{-6}
3	0.00625	0.0250	0.0250	2.19 x 10^{-6}

- To find the rate constant, k:
  - Substitute the values of one of the experiments to find k (for example, **measurement 1**)

$$k = \frac{4.38 \times 10^{-6}}{0.0250 \times 0.0125}$$

$$k = 1.40 \times 10^{-2}$$

- The values of **measurement 2** or **3** could also have been used to find k
- They all give the same result of 1.40 x 10^{-2}

Calculating rate constant units

- When you are asked to calculate the rate constant, k, for a reaction you must also be able to deduce the units
- This is done by replacing the values in the rearranged rate equation with the units of that value
- The units can then be combined or cancelled as required
- For example, to calculate the units for the above reaction:

$$\text{Units of } k = \frac{(\cancel{\text{mol dm}^{-3}} \text{ s}^{-1})}{(\cancel{\text{mol dm}^{-3}})(\text{mol dm}^{-3})}$$

$$= \frac{\text{s}^{-1}}{\text{mol dm}^{-3}}$$

$$= \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

- The units of the rate constant, k, are dependent on the overall order of the reaction
- When the rate is measured per second:
  - Rate constant units of a **zero order** reaction are **mol dm^{-3} s^{-1}**
  - Rate constant units of a **first order** reaction are **s^{-1}**
  - Rate constant units of a **second order** reaction are **mol^{-1} dm^3 s^{-1}**
  - Rate constant units of a **third order** reaction are **mol^{-2} dm^6 s^{-1}**

How does temperature affect the rate constant, k?

- Consider the following reaction:

$$A + B \rightarrow C + D$$
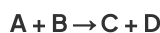
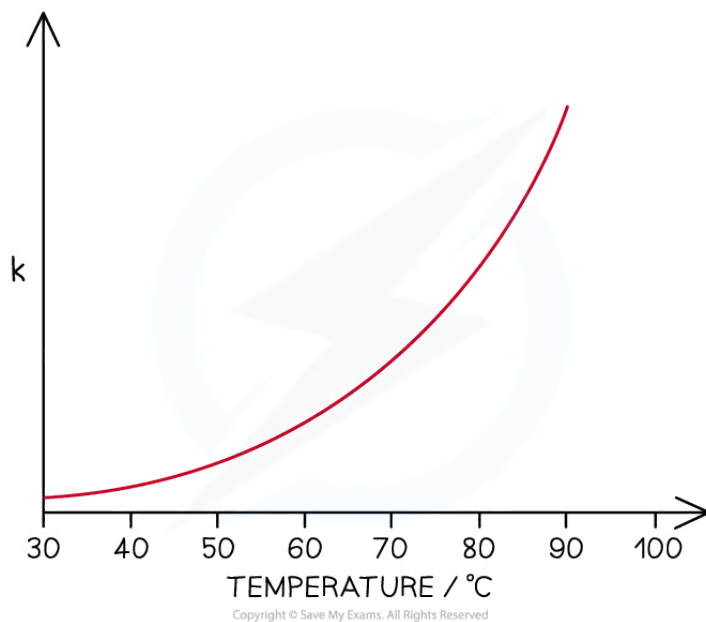**Rate of reaction = k[A][B]**

- The rate equation shows that the rate of reaction depends on the rate constant, k, and the concentration of the reactants, **A** and **B**
  - As the rate of reaction increases, the rate constant will increase
- Increasing the temperature of a reaction increases the rate of a chemical reaction
  - **Remember:** This does not necessarily increase the yield of a chemical reaction
  - The yield depends on whether a reaction is endothermic or exothermic according to Le Châtelier's principle
- Therefore, increasing the temperature also increases the value of the rate constant, k, assuming that the concentration of the reactants remains unchanged

- An exponential relationship between the rate of reaction and temperature is observed when seen on a graph

A graph to show the rate constant against temperature

Your notes

Relationship between temperature and rate constant, k

- This general relationship does not apply to all reactions
  - The graph shows that the rate of reaction roughly doubles with an increase of 10 °C
    - It is not necessarily every 10 °C, the rate may double every 9 °C or 11 °C
 - The number of degrees needed to double the rate also changes gradually as temperature increases

Reaction Mechanisms (HL)

Reaction Mechanisms

What is a reaction mechanism?

- Most reactions do not occur in one step but in a series of simple steps
- Each step is called an **elementary step** and involves a small number of particles
- Some of the products of an elementary step exist as **intermediates** and react in subsequent steps
- The sequence of elementary steps is called the **reaction mechanism**
- The **sum** of the elementary steps must equal the **overall** reaction equation
  - Intermediates that are produced in one elementary step and react in another step cancel out
- Chemical kinetics can only **suggest** a reaction mechanism, they cannot prove it
  - However, they can be used to disprove a proposed mechanism
- Elementary steps are the steps involved in a reaction mechanism
  - For example, in the following general reaction:

$$A + B \rightarrow C + D$$
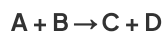
  - The elementary steps could involve the formation of an intermediate:

Elementary step 1: $A \rightarrow R + D$

Elementary step 2: $R + B \rightarrow C$

- It is important that the elementary steps for a proposed mechanism agree with the overall stoichiometric equation
  - For example, combining the 2 elementary steps above gives the overall stoichiometric equation

$$A + R + B \rightarrow R + C + D$$

$$A + B \rightarrow C + D$$

Your notes
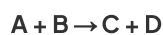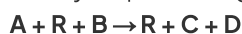
✏️ **Worked example**

Sulfur dioxide reacts with oxygen to form sulfur trioxide

1. Propose a one-step mechanism for the above reaction
2. The above reaction is catalysed by the formation of nitrogen dioxide from nitrogen monoxide. Propose a two-step mechanism for this reaction.

Answer 1:

- A one-step reaction mechanism is simply the overall stoichiometric equation
- Therefore, the correct answer is $2SO_2 + O_2 \rightarrow 2SO_3$

Answer 2:

- One of the two elementary steps for this two-step mechanism can be taken from the question:
  - **Elementary step 1: $2NO + O_2 \rightarrow 2NO_2$**
- The second elementary step must involve the reaction of the nitrogen dioxide formed with sulfur dioxide:
  - **Elementary step 2: $NO_2 + SO_2 \rightarrow NO + SO_3$ (or $2NO_2 + 2SO_2 \rightarrow 2NO + 2SO_3$)**

💡 **Examiner Tip**

- It is important that you check the equations you are proposing for a reaction mechanism
- They **must** add up to the overall stoichiometric equation, otherwise the proposed mechanism is wrong.

What is the rate-determining step?

- A chemical reaction can only go as fast as the slowest part of the reaction
  - So, the **rate-determining step** is the slowest step in the reaction

What does the rate equation tell us about the rate-determining step?

- If a reactant appears in the rate-determining step, then the concentration of that reactant will also appear in the **rate equation**
- The **order** with respect to a reactant describes the **number of particles** of that reactant that take part in the **rate-determining step**

Predicting the reaction mechanism

- The overall reaction equation and rate equation can be used to predict a possible reaction mechanism of a reaction
- For example, nitrogen dioxide (NO_2) and carbon monoxide (CO) react to form nitrogen monoxide (NO) and carbon dioxide (CO_2)
  - The overall reaction equation is:

$$NO_2 \text{ (g)} + CO \text{ (g)} \rightarrow NO \text{ (g)} + CO_2 \text{ (g)}$$
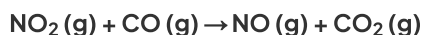
- The rate equation is:

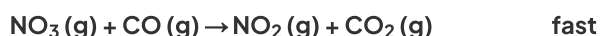$$\text{Rate} = k \, [NO_2]^2$$

- From the rate equation, it can be concluded that the reaction is zero-order with respect to CO (g) and second-order with respect to NO_2 (g)
- This means that there are two molecules of NO_2 (g) involved in the rate-determining step and zero molecules of CO (g)
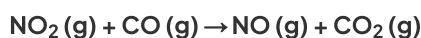- A possible reaction mechanism could therefore be:

Step 1:

$$2NO_2 \text{ (g)} \rightarrow NO \text{ (g)} + NO_3 \text{ (g)} \qquad \textbf{slow} \text{ (rate-determining step)}$$

Step 2:

$$NO_3 \text{ (g)} + CO \text{ (g)} \rightarrow NO_2 \text{ (g)} + CO_2 \text{ (g)} \qquad \textbf{fast}$$

Overall:

$$2NO_2 \text{ (g)} + NO_3 \text{ (g)} + CO \text{ (g)} \rightarrow NO \text{ (g)} + NO_3 \text{ (g)} + NO_2 \text{ (g)} + CO_2 \text{ (g)}$$

Simplify (remove species on both sides of the equation)**:**

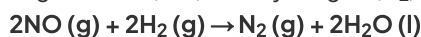$$NO_2 \text{ (g)} + CO \text{ (g)} \rightarrow NO \text{ (g)} + CO_2 \text{ (g)}$$

> ### 💡 Examiner Tip
>
> - It is important that the elementary steps for a proposed mechanism also agree with the experimentally determined rate equation
>   - The rate equation and the overall reaction must be related, i.e. the correct chemical species involved
> - **Remember:** There is no direct link between the orders in the rate equation and the stoichiometry of the overall equation
>   - However, the rate equation can be derived directly from the rate-determining step and its stoichiometry

Predicting the reaction order & deducing the rate equation

- The **order** of a reactant and thus the rate equation can be deduced from a reaction mechanism if the rate-determining step is known
- For example, the reaction of nitrogen oxide (NO) with hydrogen (H_2) to form nitrogen (N_2) and water

$$2NO \text{ (g)} + 2H_2 \text{ (g)} \rightarrow N_2 \text{ (g)} + 2H_2O \text{ (l)}$$

- The reaction mechanism for this reaction is:
  Step 1:

$$NO \text{ (g)} + NO \text{ (g)} \rightarrow N_2O_2 \text{ (g)} \qquad \textbf{fast}$$

Step 2:

$$N_2O_2 \text{ (g)} + H_2 \text{ (g)} \rightarrow H_2O \text{ (l)} + N_2O \text{ (g)} \qquad \textbf{slow} \text{ (rate-determining step)}$$

Step 3:

$$N_2O \text{ (g)} + H_2 \text{ (g)} \rightarrow N_2 \text{ (g)} + H_2O \text{ (l)} \qquad \textbf{fast}$$
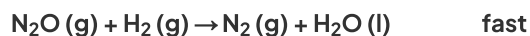
- The second step in this reaction mechanism is the **rate-determining step**
- The rate-determining step consists of:
  - N_2O_2 which is formed from the reaction of **two NO molecules**
  - **One H_2 molecule**
- The reaction is, therefore, **second order** with respect to NO and **first order** with respect to H_2
- So, the **rate equation** becomes:

$$\text{Rate} = k \, [NO]^2 \, [H_2]$$

- The reaction is, therefore, **third order overall**

> 💡 **Examiner Tip**
>
> - Intermediates in the mechanism **cannot** appear as substances in the rate equation
> - Instead, the chemicals required to make the intermediate feature in the rate equation
> - This is why you substitute the N_2O_2 in the above example
>   - Step 1 shows that 2NO molecules are required to form the necessary N_2O_2

Energy Profiles in Multistep Reactions

Single-step reactions

- When any reacting molecules collide with bond breaking and bond formation occurring, the interacting molecules will be in an unstable, high-energy state temporarily
  - This **transition state** will be of a higher energy than either the reactants or products and corresponds to the activation energy
- The exothermic reaction of hydrogen and iodine to form hydrogen iodide will be used to discuss how energy level diagrams relate to the rate-determining step

**Energy profile of an exothermic reaction, showing the transition state**
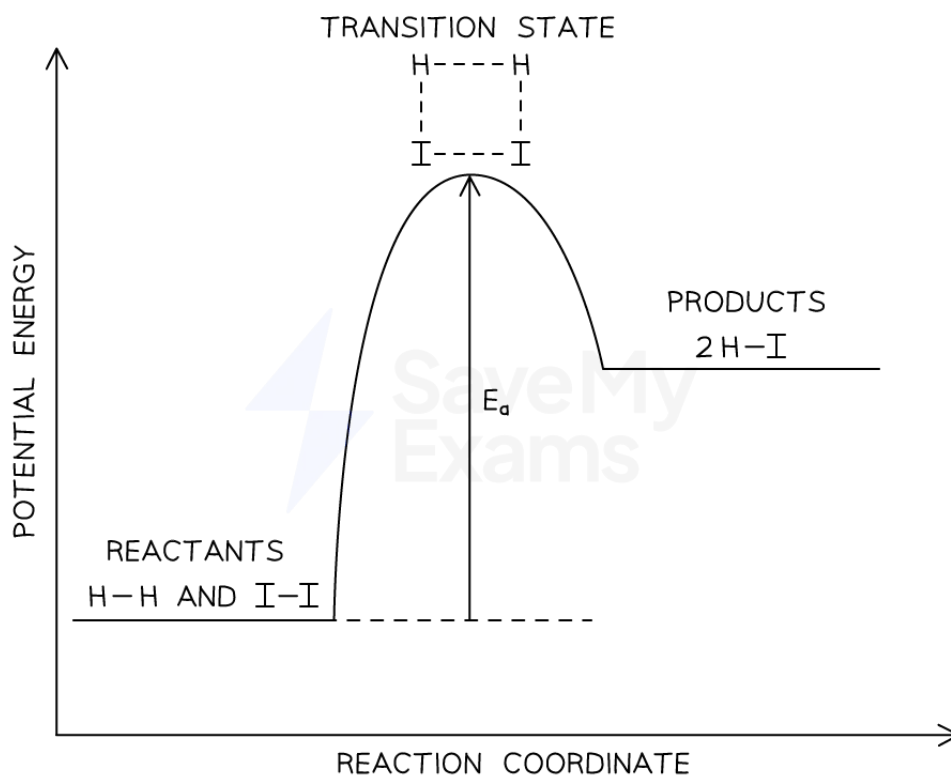
The energy profile for the exothermic reaction of hydrogen and iodine

- As the reaction proceeds, covalent bonds start to form between the hydrogen and iodine atoms from the hydrogen and iodine molecules
- At the same time, the covalent bonds within the hydrogen and iodine molecules grow longer and become weaker
- This results in the transition state complex shown

Transition state
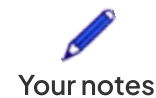
The transition state complex for the reaction of hydrogen and iodine

- From this transition state, the bonds between the hydrogen and iodine atoms can continue to grow shorter and stronger resulting in the formation of hydrogen iodide
- Alternatively, the bonds within the hydrogen and iodine molecules can grow shorter and stronger which would result in the formation of the reactants
- Hydrogen iodide will **only** form if the hydrogen and iodine molecules collide with kinetic energy greater than or equal to the activation energy
  - The molecules will also need to collide in the correct orientations
- The reaction, or elementary, step with the greatest activation energy will be the rate-determining step and can be used to determine the rate equation

Multi-step reactions

- The exothermic reaction of nitrogen dioxide and fluorine to form nitryl fluoride (NO_2F) will be used to relate rate equations and rate-determining steps to the energy level diagram of a multi-step reaction:

$$2NO_2 \text{ (g)} + F_2 \text{ (g)} \rightarrow 2NO_2F \text{ (g)}$$

- This reaction is unlikely to occur in a single step as that would require three molecules to collide in the correct orientation and with sufficient kinetic energy
  - This is even less likely to occur as all three molecules are gaseous
- Experimental data shows that the rate equation for this reaction is:

$$\text{Rate} = k[NO_2][F_2]$$

- One proposed reaction mechanism for this reaction involves the following elementary steps:
  - **Step 1: $NO_2 + F_2 \rightarrow NO_2F + F$**
  - **Step 2: $NO_2 + F \rightarrow NO_2F$**
- Step 1 must be the rate-determining step as it is the only step that has reactants matching the rate equation
  - Therefore, on an energy profile, the activation energy for step 1 will be greater than the activation energy for step 2
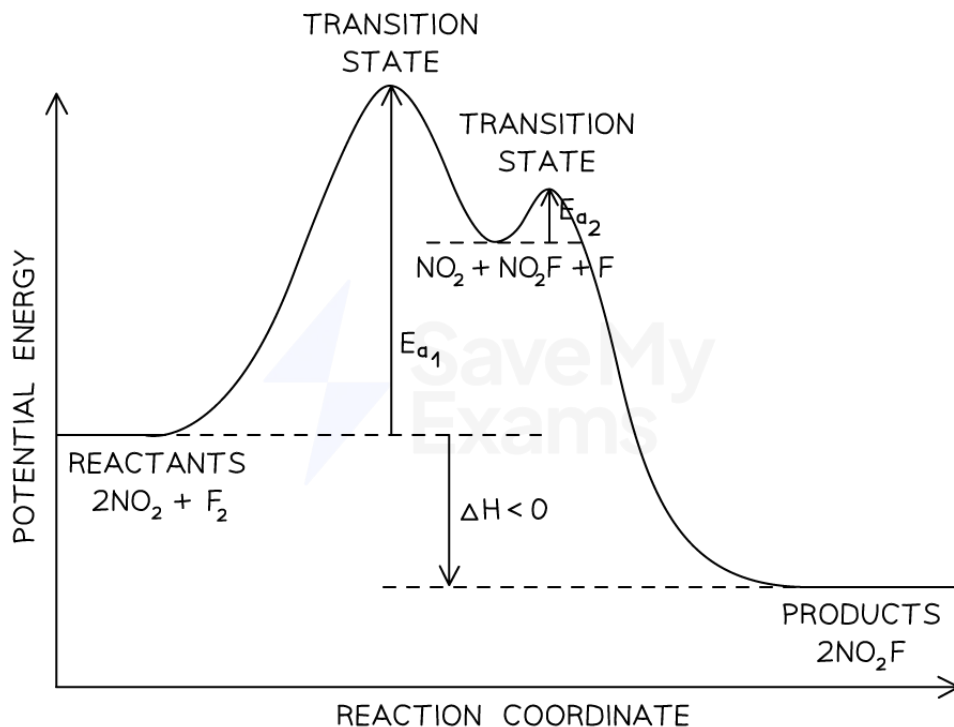- The species present after the first step must be:

$$NO_2 + NO_2F + F$$

- This can be deduced using the equation for elementary step 1 and the overall equation
  - The overall equation states that two NO_2 react with one F_2
  - Elementary step 1 uses one NO_2 to form the intermediates, $NO_2F + F$
  - This leaves one NO_2 along with $NO_2F + F$

- This leads to the following energy profile:

Your notes

Your notes

Energy profile of a multistep reaction

TRANSITION
STATE

TRANSITION
STATE

E_{a_2}

$NO_2 + NO_2F + F$

E_{a_1}

REACTANTS
$2NO_2 + F_2$

$\Delta H < 0$

PRODUCTS
$2NO_2F$

POTENTIAL ENERGY

REACTION COORDINATE

Energy profile for the formation of nitryl fluoride

- Key points from the energy profile are:
  - The overall reaction is exothermic, as stated
  - The rate-determining step is the step that has the greatest activation energy
  - There is a labelled energy level for the species present after the first step which include the intermediates and unreacted reactant

> 🔋 **Examiner Tip**
>
> - Multi-step reactions where the first elementary step is not the rate-determining step prove more challenging in terms of energy profiles
> - **Remember:** The rate-determining step **must** have the greatest activation energy
>   - Do not confuse the greatest with the highest!
>   - When people talk about the highest they are normally referring to where the activation energy peak is, not the actual value it represents

Molecularity (HL)

Your notes

Molecularity

What is meant by the term molecularity?

- The **molecularity** of an elementary step is the number of reacting particles taking part in that step.
- Reactions can be classified as unimolecular, bimolecular or termolecular depending on how many reactant particles are involved:
  - **Unimolecular**: one reactant particle is involved in the elementary step
  - **Bimolecular**: two reactant particles are involved in the elementary step
  - **Termolecular**: three reactants particles are involved in the elementary step
- For example, consider the reaction below:
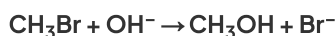
$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

- It has been shown that the reaction mechanism involves two elementary steps:

$$\text{Step 1: } CH_3Br + OH^- \rightarrow CH_3OHBr^-$$

$$\text{Step 2: } CH_3OHBr^- \rightarrow CH_3OH + Br^-$$

- CH_3OHBr^- is an **intermediate** produced in **step 1** that subsequently reacts in **step 2**
- **Step 1** involves two reactant particles so is a **bimolecular** reaction
- **Step 2** involves one reactant particle so is a **unimolecular** reaction

---

💡 Examiner Tip

- The chances of three reacting particles colliding are very small
  - Therefore, termolecular reactions in reaction mechanisms are avoided
- Instead, more steps are proposed giving a more probable reaction mechanism.

Your notes

The Arrhenius Equation

- The rate equation shows how each of the reactants in a reaction affects the rate of the reaction and it includes the rate constant, *k*
- However, *k* only remains constant if the concentration of the reactants is the only factor which is changed
  - If the temperature is changed or a catalyst is used or changed, then the rate constant, *k*, changes
- At higher temperatures, a greater proportion of molecules have energy greater than the activation energy
- Since the **rate constant** and **rate of reaction** are **directly proportional** to the fraction of molecules with energy equal or greater than the activation energy, then at higher temperatures:
  - The **rate of reaction** increases
  - The **rate constant** increases

What is the Arrhenius equation?

- The relationship between the rate constant, the temperature and also the activation energy is given by the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

- Where:
  - *k* = Rate constant
  - *A* = **Arrhenius factor** (also known as the **frequency factor** or **pre-exponential factor**) which is a constant that takes into account the frequency of collisions with proper orientations
  - E_a = Activation energy (J mol^{-1})
  - *R* = Gas constant (8.31 J K^{-1} mol^{-1})
  - *T* = Temperature (Kelvin, K)
  - e = Mathematical constant (can be found on your calculator – it has the approximate value of 2.718)
- E_a and *A* are constants that are characteristic of a specific reaction
  - *A* does vary slightly with temperature but it can still be considered a constant
- *R* is a fundamental physical constant for all reactions
- *k* and *T* are the only variables in the Arrhenius equation
- The Arrhenius equation is used to describe reactions that involve gases, reactions occurring in solution or reactions that occur on the surface of a catalyst

Using the Arrhenius Equation

- The Arrhenius equation is easier to use if you take natural logarithms of each side of the equation, which results in the following equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Your notes

- The **Arrhenius equation** can be used to show the effect that a change in temperature has on the rate constant, k, and thus on the overall rate of the reaction
  - An increase in temperature (higher value of T) gives a greater value of $\ln k$ and therefore a higher value of k
  - Since the rate of the reaction depends on the rate constant, k, an increase in k also means an increased rate of reaction
- The equation can also be used to show the effect of increasing the activation energy on the value of the rate constant, k
  - An increase in the activation energy, E_a, means that the proportion of molecules which possess at least the activation energy is less
  - This means that the rate of the reaction, and therefore the value of k, will decrease
- The values of k and T for a reaction can be determined experimentally
  - These values of k and T can then be used to calculate the activation energy for a reaction
  - This is the most common type of calculation you will be asked to do on this topic

> 💡 **Examiner Tip**
>
> - In the exam, you could be asked to calculate any part of the Arrhenius equation
>   - Using the equation in its natural logarithm form makes this easier.

Your notes

✎ Worked example

Calculate the activation energy of a reaction which takes place at 400 K, where the rate constant of the reaction is 6.25×10^{-4} s^{-1}.

$A = 4.6 \times 10^{13}$ and R = 8.31 J K^{-1} mol^{-1}.

Answer:

- Rearrange the Arrhenius equation for E_a:

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\frac{E_a}{RT} + \ln k = \ln A$$

$$\frac{E_a}{RT} = \ln A - \ln k$$

$$E_a = (\ln A - \ln k) \times RT$$

- Insert values from the question:

$$E_a = \left[(\ln 4.6 \times 10^{13}) - (\ln 6.25 \times 10^{-4})\right] \times (8.31 \times 400)$$

$$= \left[(31.4597) - (-7.3778)\right] \times 3324$$

$$= 129{,}095.85 \text{ J}$$

- Convert E_a to kJ:

$$E_a = 129{,}095.85 \div 1000$$

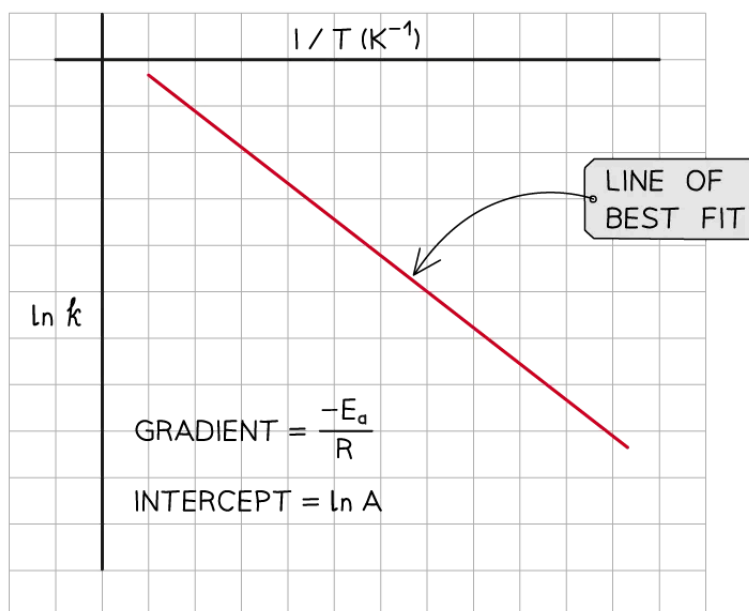$$= \mathbf{129 \ \ kJ}$$

Graphing the Arrhenius Equation

Finding the activation energy and Arrhenius factor

- A graph of experimental data can be used to determine the activation energy and the Arrhenius factor

Arrhenius equation graph

- A graph of $\ln k$ against $1/T$ can be plotted, and then used to calculate E_a
  - This gives a line which follows the form $y = mx + c$

Graph of ln k against 1/T

The graph of ln k against 1/T is a straight line with gradient $-E_a/R$

- From the graph, the equation is in the form of $y = mx + c$ is as follows:

$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A$$

$$y = m\, x + c$$

- Where:
  - $y = \ln k$
  - $x = \dfrac{1}{T}$
  - $m = \dfrac{-E_a}{R}$ (the gradient)

Your notes

- $c = \ln A$ (the y-intercept)
- E_a can be calculated by:
  - $E_a = -$ gradient x R
- As the slope has a negative gradient, the minus signs cancel giving E_a as a positive value
- The Arrhenius factor, A, can be calculated by:
  - $A = e^{\text{y-intercept}}$

💡 Examiner Tip

- If the x-axis does not start at the origin, you **cannot** use the y-intercept to find A
- Instead, take a point from the graph and substitute the values of $\ln k$, $1/T$ and the gradient into the logarithmic Arrhenius equation to find $\ln A$, and use this to calculate A.

Determining Activation Energy & the Arrhenius Factor (HL)

Determining Activation Energy & the Arrhenius Factor

How to use the Arrhenius equation graph

- Once the rate constant at different temperatures for a reaction has been determined experimentally, the results can be used to determine the activation energy, E_a, and the Arrhenius factor, A
- This is best shown through a worked example

Worked example
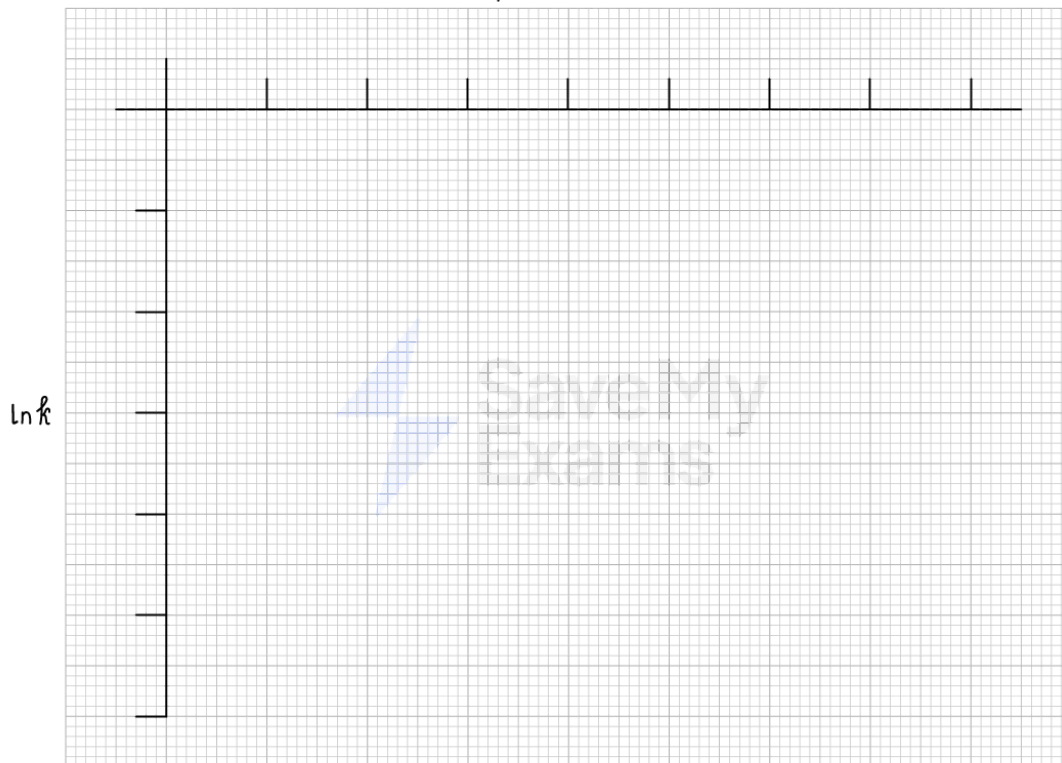
The data in the table below was collected for a reaction.

Temperature / K	$\dfrac{1}{T}$ / K^{-1}	Time, t / s	Rate constant, k / s^{-1}	ln k
310	3.23×10^{-3}	57		−9.2
335		31	3.01×10^{-4}	−8.1
360	2.78×10^{-3}	19	5.37×10^{-4}	−7.5
385	2.60×10^{-3}	7	9.12×10^{-4}	

1. Complete the table
2. Plot a graph of ln k against $1/T$ on the graph below
3. Use this to calculate:
   a. the activation energy, E_a, in kJ mol^{-1}
   b. the Arrhenius factor, A, of the reaction

$$\frac{1}{T} \times 10^{-3}(K^{-1})$$

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Answer 1:

Temperature / K	$\frac{1}{T}$ / K^{-1}	Time, t / s	Rate constant, k / s^{-1}	ln k
310	3.23×10^{-3}	57	1.01×10^{-4}	–9.2
335	2.99×10^{-3}	31	3.01×10^{-4}	–8.1
360	2.78×10^{-3}	19	5.37×10^{-4}	–7.5
385	2.60×10^{-3}	7	9.12×10^{-4}	–7.0

Answer 2:

- Choose a suitable scale for the axes

- The scale does not need to start from (0,0)
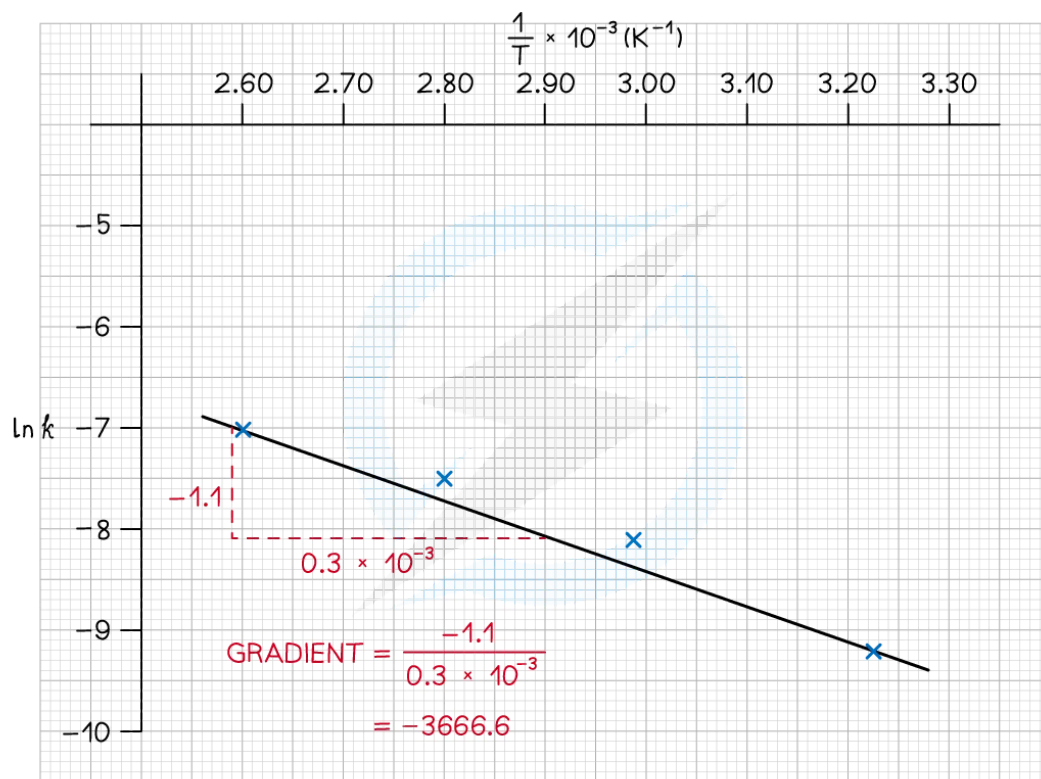- The plotted points should fill as much of the graph provided as possible
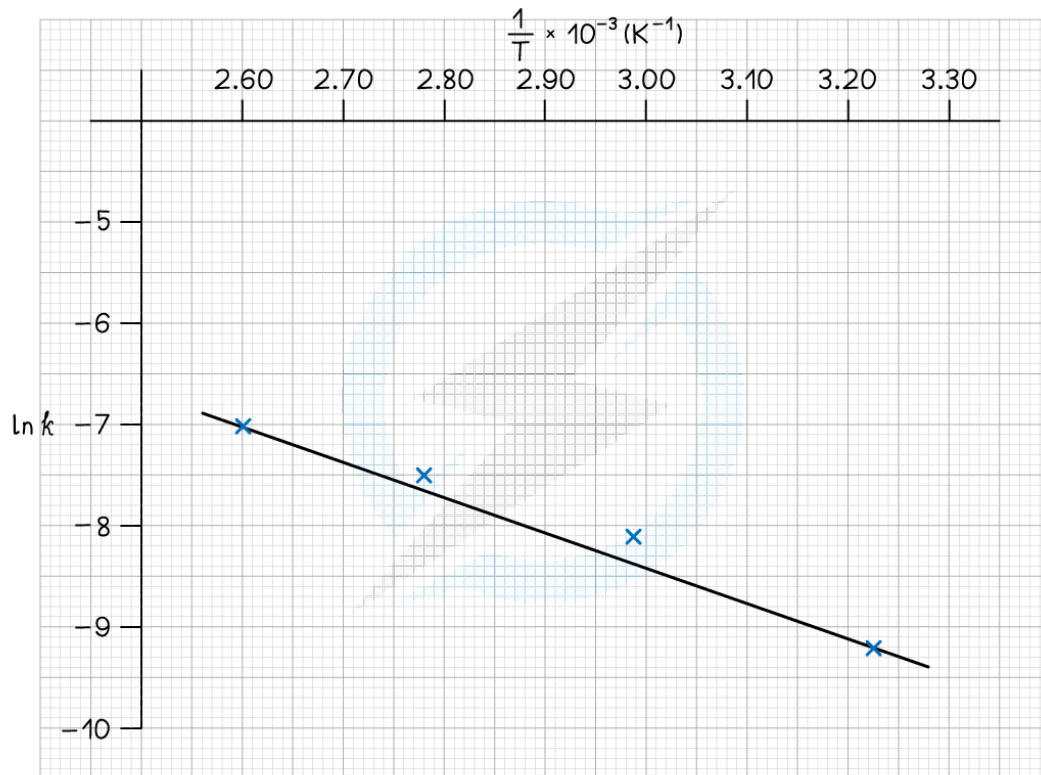
Answer 3a:

Your notes

CALCULATE THE ACTIVATION ENERGY:

- To calculate E_a:
  - Gradient = $\dfrac{-E_a}{R}$ = –3666.6
  - E_a = –(–3666.6 x 8.31) = 30,469 J mol⁻¹
- Convert to kJ mol⁻¹:
  - E_a = 30.5 kJ mol⁻¹

Answer 3b:

CALCULATE A:

Your notes
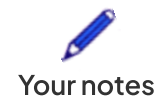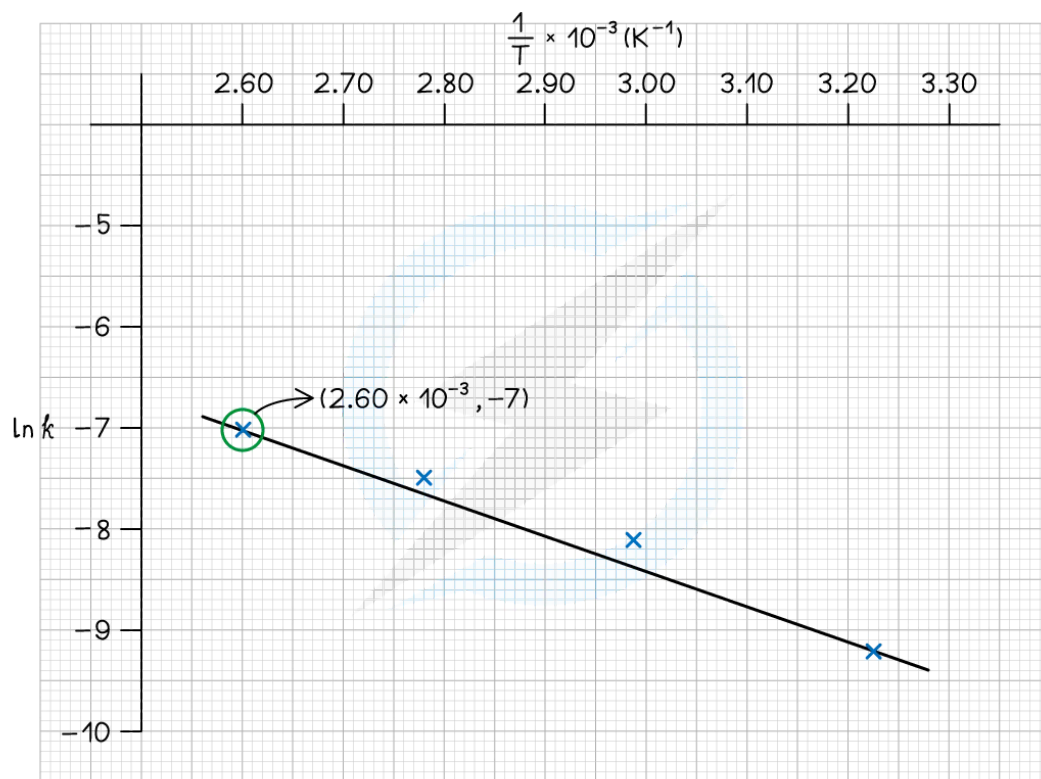
- Choose a point on the graph:
  - $(2.60 \times 10^{-3}, -7)$
- Use the logarithmic form of the Arrhenius equation

$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$$

$$y = m\,x + c$$

- From the point chosen from the graph:
  - $\ln k = -7.0$
  - $\frac{1}{T} = 2.60 \times 10^{-3}$
  - $\frac{-E_a}{R} = \frac{-1.1}{0.3 \times 10^{-3}} = -3666.6$
- Substituting these values:
  - $-7.0 = (-3666.6 \times 2.60 \times 10^{-3}) + \ln A$
  - $-7.0 = -9.53 + \ln A$
- Rearranging gives:
  - $\ln A = -7.0 + 9.53 = 2.53$

Your notes

- $A = e^{2.53}$
- **A = 12.55**

💡 Examiner Tip

- You are not required to learn these equations as they are given in the Data Booklet
- However, you do need to be able to rearrange them, and knowing them is helpful in understanding the effects of temperature on the rate constant.