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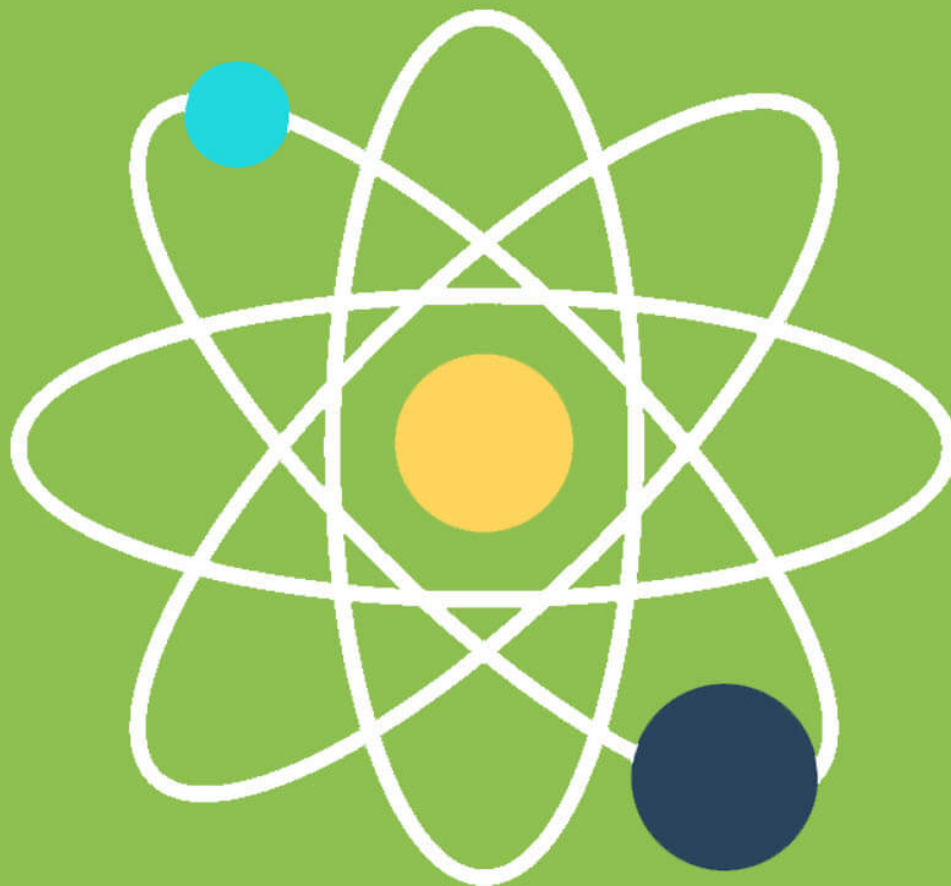
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6.1 Chemical Kinetics



IB Chemistry - Revision Notes

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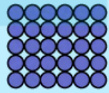
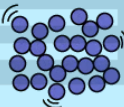
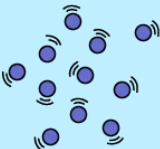


6.1.1 Collision Theory

Kinetic Theory

- 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

Summary Table of the Kinetic Theory

STATE	SOLID	LIQUID	GAS
DIAGRAM			
ARRANGEMENT OF PARTICLES	REGULAR ARRANGEMENT	RANDOMLY ARRANGED	RANDOMLY ARRANGED
MOVEMENT OF PARTICLES	VIBRATE ABOUT A FIXED POSITION	MOVE AROUND EACH OTHER	MOVE QUICKLY IN ALL DIRECTIONS
CLOSENESS OF PARTICLES	VERY CLOSE	CLOSE	FAR APART

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- The **average kinetic energy** of the particles is directly proportional to the temperature of the system in **Kelvin**
- **Kinetic energy** refers to the energy associated with movement or motion. It is determined by the mass and velocity of the substance according to the relationship:

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

- 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



Collision Theory

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 four factors:
 - **collision frequency**
 - **collision energy**
 - **activation energy**
 - **collision geometry**

Collision frequency

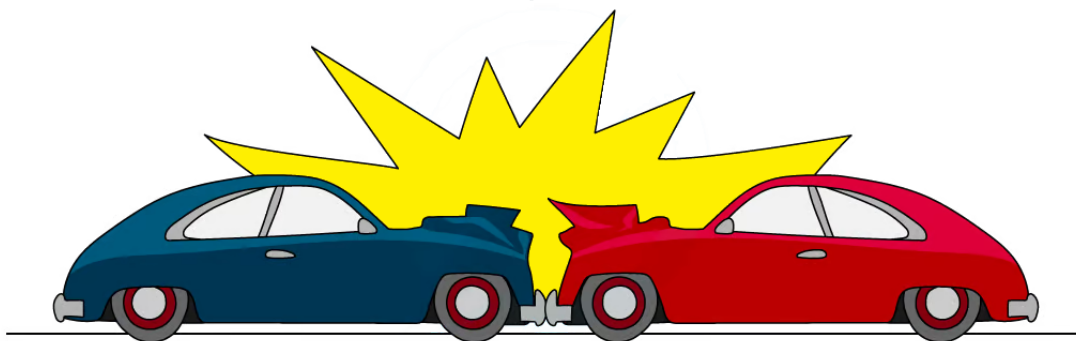
- If a chemical reaction is to take place between two particles, they must first collide
- The number of collisions between particles per unit time in a system is known as the **collision frequency**
- The **collision frequency** of a given system can be altered by **changing the concentration** of the reactants, by changing the total **pressure**, by changing the **temperature** or by changing the **size** 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**

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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**



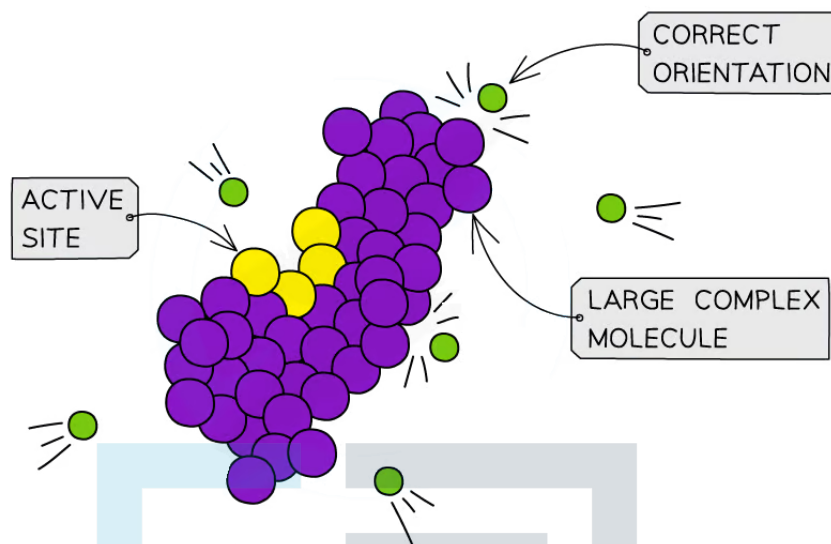
Molecules with the activation energy lead to successful collisions

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

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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 reaction because **they do not reach the activation energy** rather than not having the correct collision geometry

Summary Table of Collision Theory Factors

	Effective Collision	Ineffective Collision
Orientation	Correct orientation	Wrong orientation
Energy	Enough energy (E_d)	Not enough energy
Chemical Reaction	Yes	No

6.1.2 Rate of Reaction

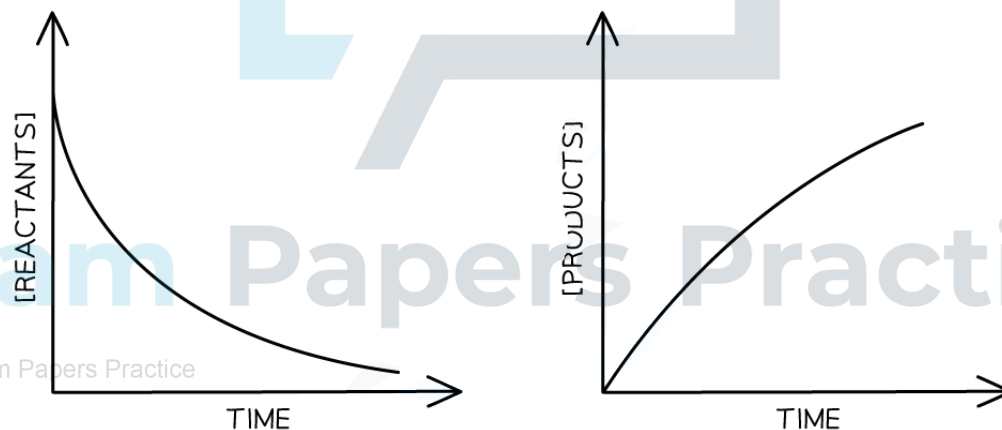
Rate of Reaction

Reaction rate

- 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:

$$\text{RATE OF A REACTION} = \frac{\text{CHANGE IN AMOUNT OF REACTANTS OR PRODUCTS (mol dm}^{-3}\text{)}}{\text{TIME (s)}}$$

- Graphically we can represent the rate of reaction as:

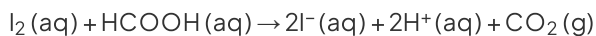


Rate of reaction graphs

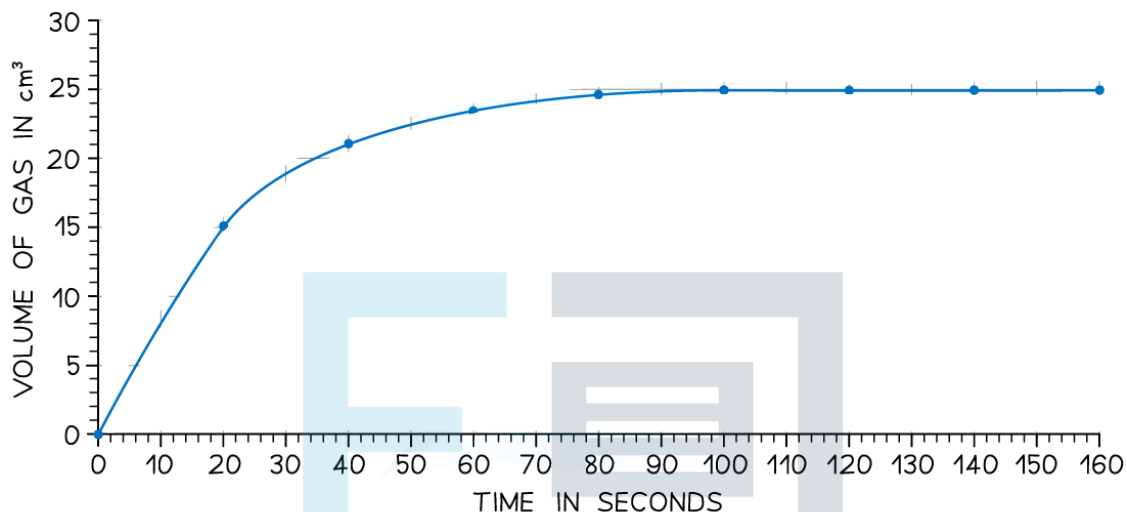


Worked example

Iodine and methanoic acid react in aqueous solution.



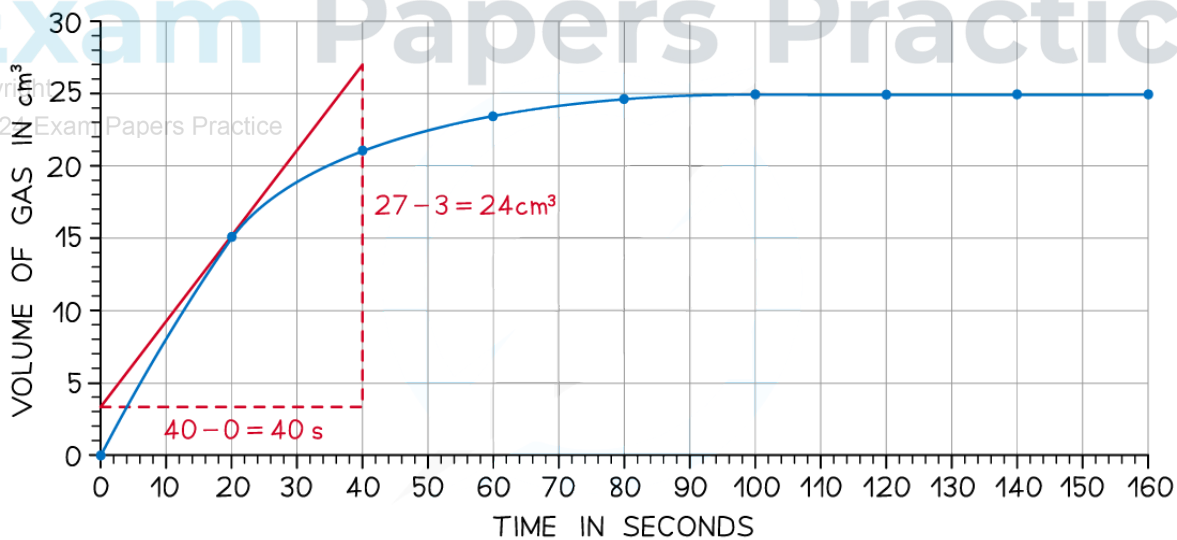
The rate of reaction can be found by measuring the volume of carbon dioxide produced per unit time and plotting a graph as shown



Calculate the rate of reaction at 20 seconds

Answer:

- Draw a tangent to the curve at 20 seconds:



- Complete the triangle and read off the values of x and y
- Determine the gradient of the line using $\Delta y / \Delta x$
- Rate of reaction = $24 \div 40 = 0.60 \text{ cm}^3 \text{ s}^{-1}$



Exam Tip

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 accidentally misread the graph values

6.1.3 Measuring Rates

Measuring Rates

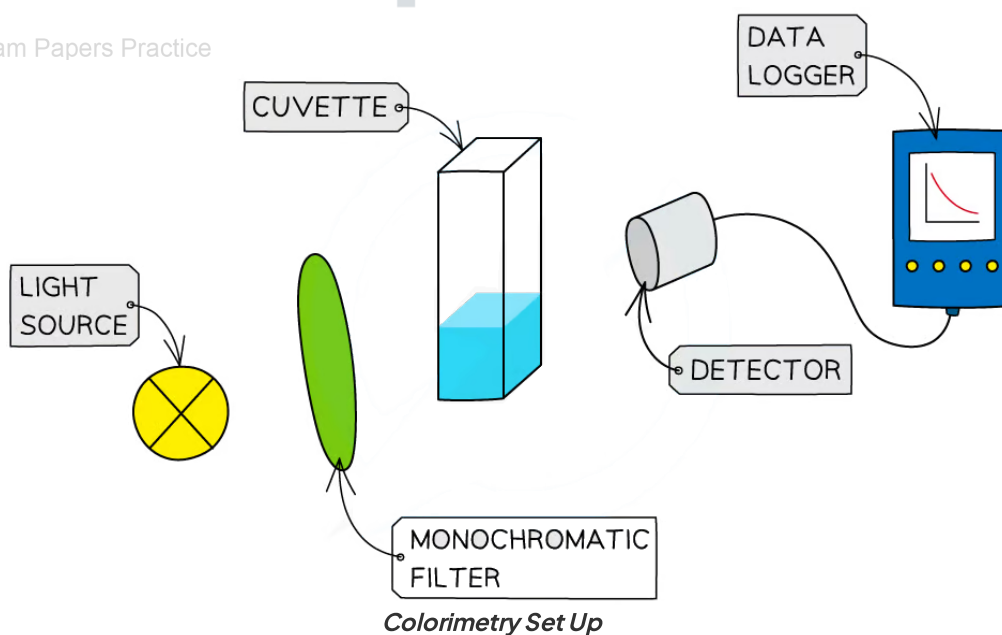
- To measure the **rate of a reaction**, we need to be able to measure either how quickly the reactants are used up or how quickly the products are formed
- The method used for measuring depends on the substances involved
- There are a number of ways to measure a reaction rate in the lab; they all depend 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**

Changes in colour

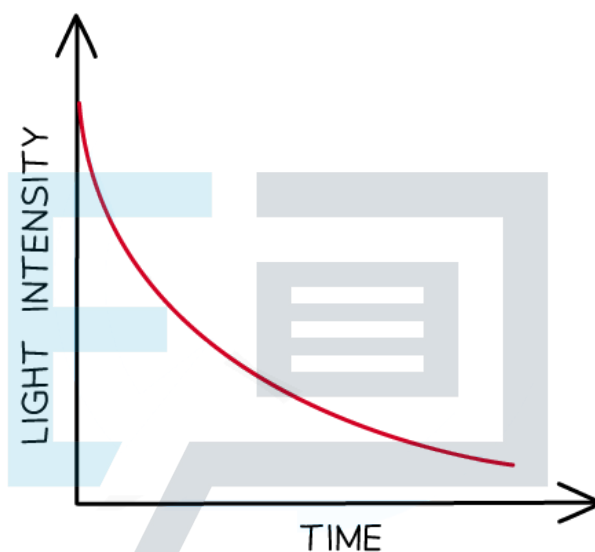
- A colorimeter measures the amount of light that passes through a solution

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- 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



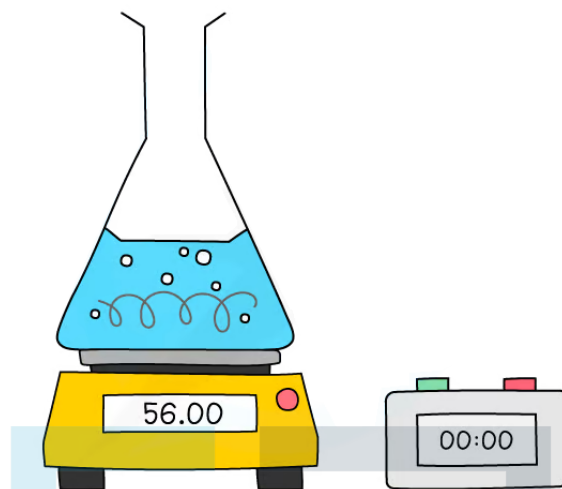
Sketch graph of colour intensity against time (the coloured species is a reactant in this case)

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

Changes in mass

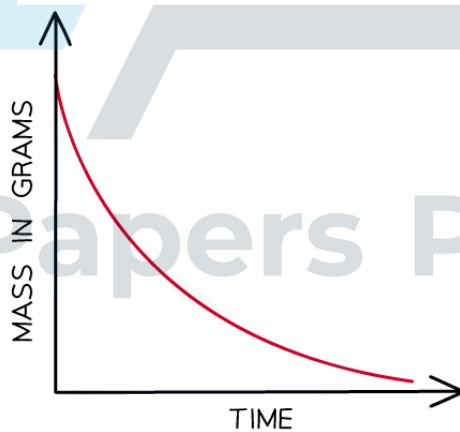
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- When a gas is produced in a reaction it usually escapes from the reaction vessel, so the mass decreases
 - This can be used to measure the rate of reaction
 - For example, the reaction of calcium carbonate with hydrochloric acid produces CO_2
 - 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



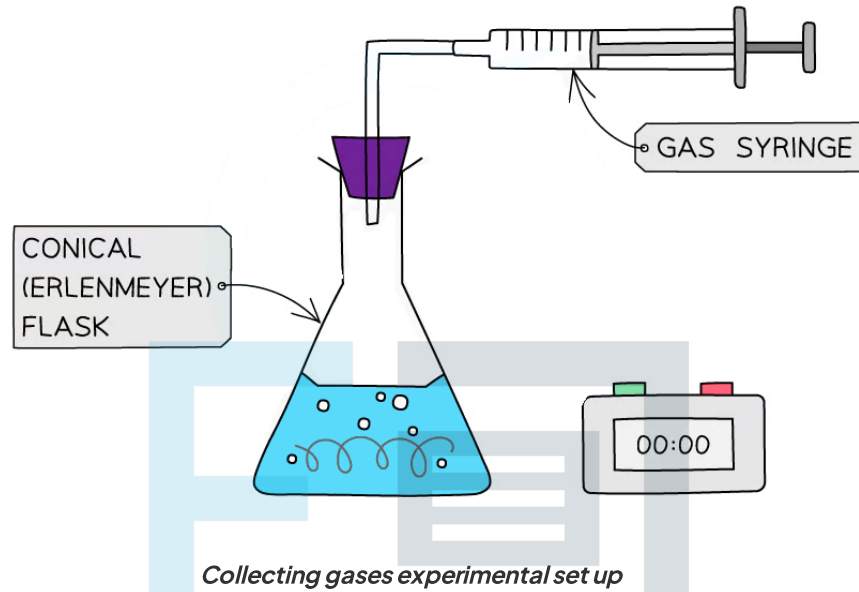
Mass loss of a product against time

- 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 dp balance
 - So carbon dioxide would be suitable ($M_r = 44$) but hydrogen would not ($M_r = 2$)

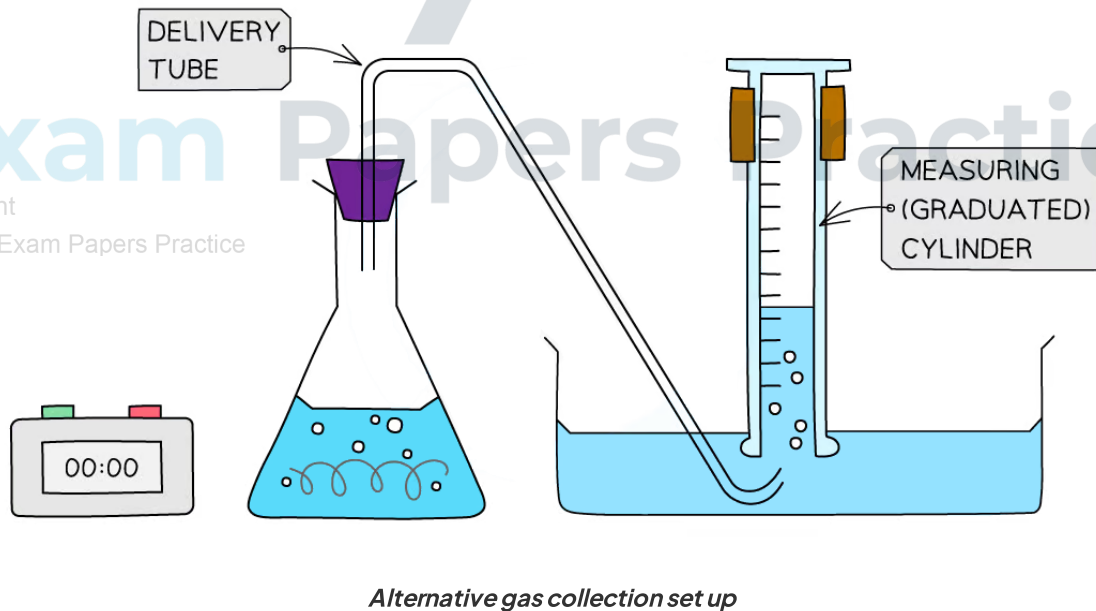
Volumes of gases

- 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



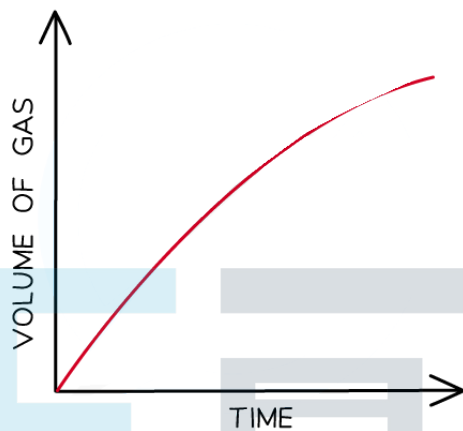
- An alternative gas collection set up involves collecting a gas through water using an inverted measuring cylinder (as long as the gas is not water soluble)



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- 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



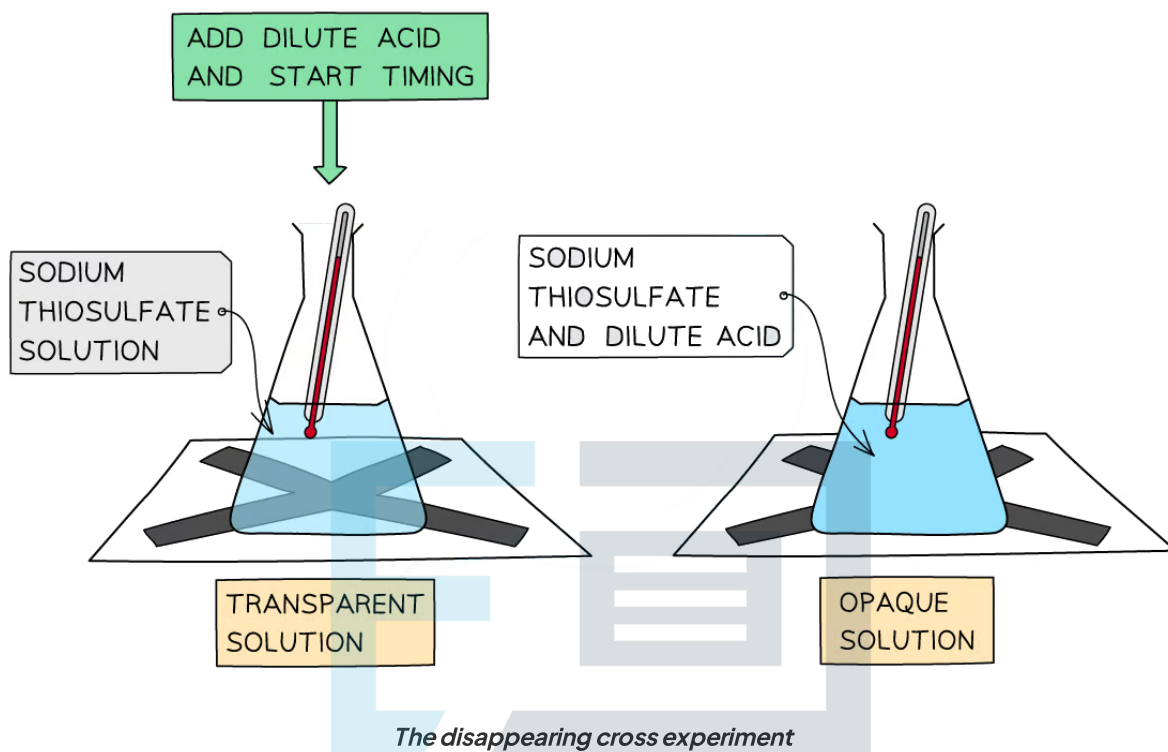
Graph of gas volume evolved against time

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

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Another common rate experiment is the reaction between sodium thio sulfate and hydrochloric acid which slowly produces a yellow precipitate of sulfur that obscures a cross when viewed through the solution:





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

Exam 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

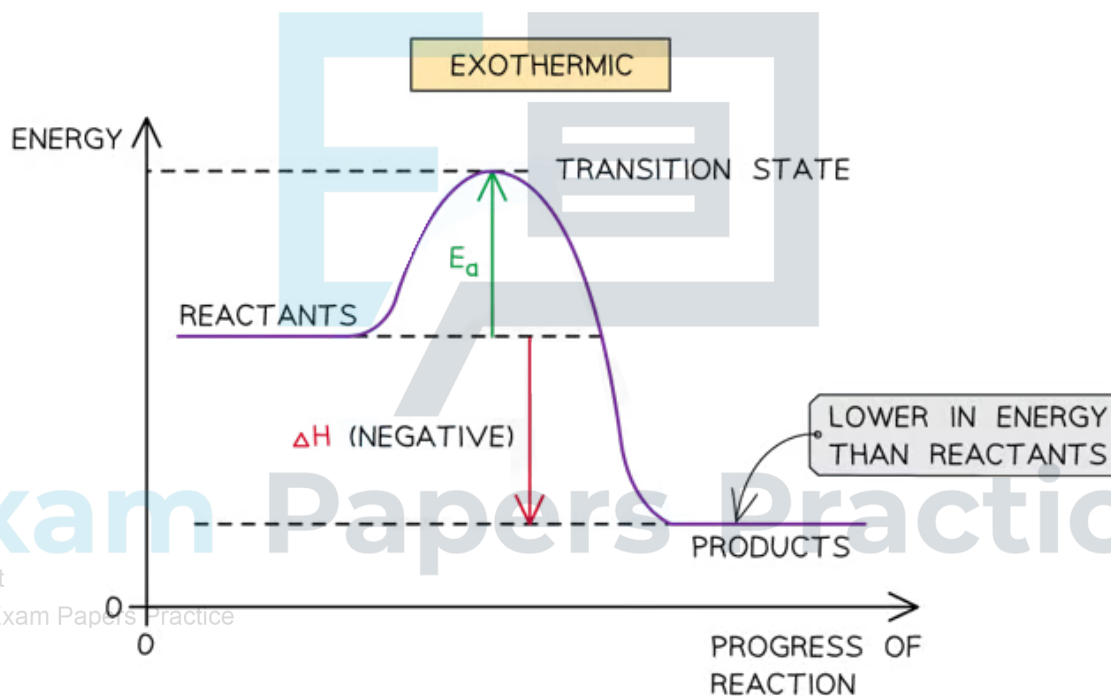
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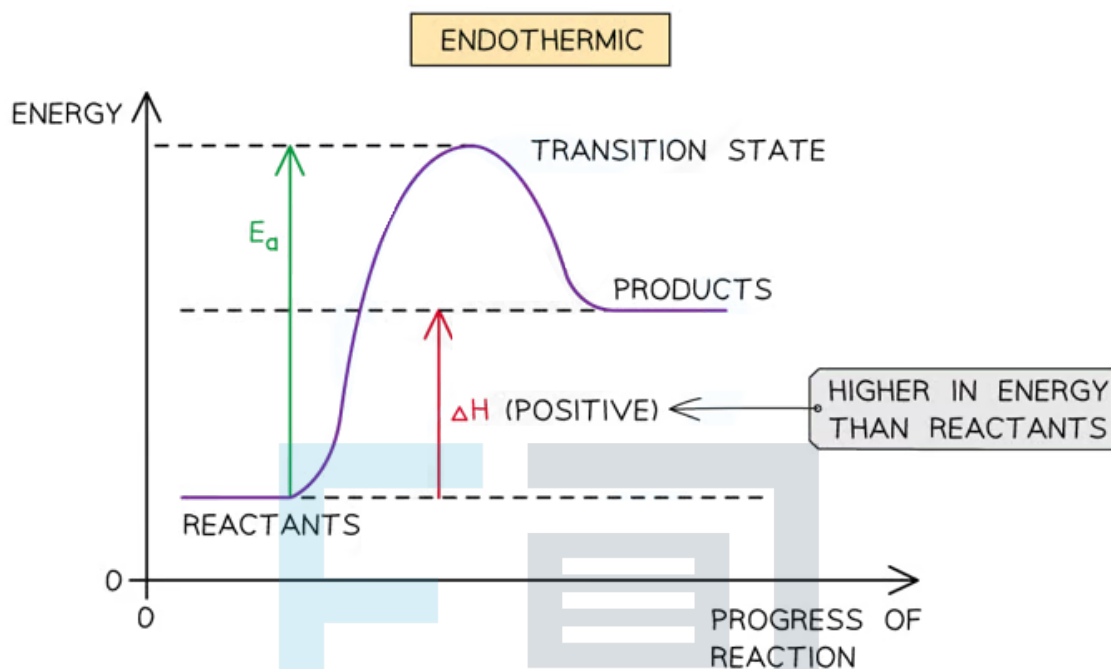
6.1.4 Activation Energy

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
- Therefore, the E_a in **endothermic reactions** is relatively larger than in exothermic reaction



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

- 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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Exam Tip

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:

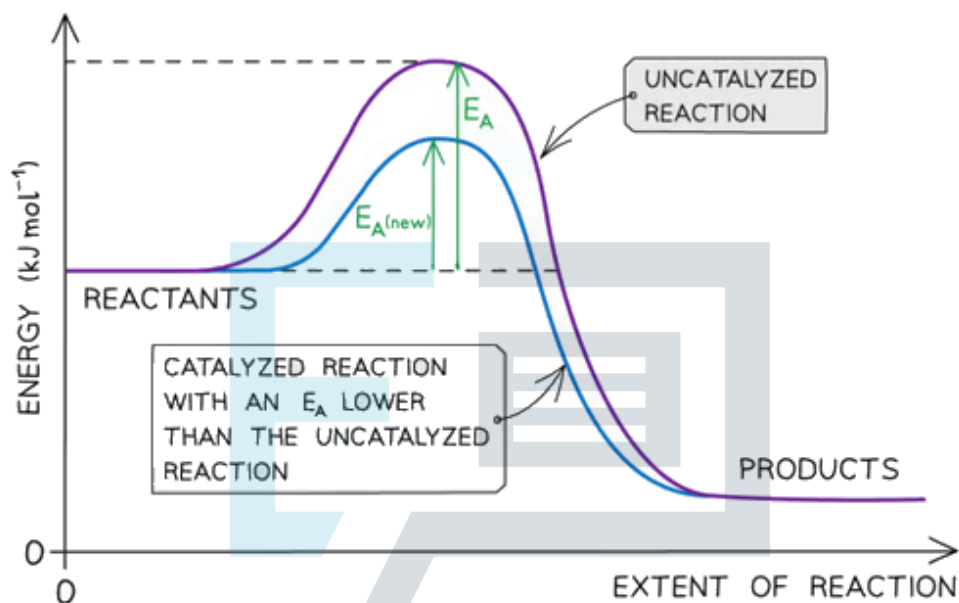
For an exothermic reaction = $\Delta H + E_a$ (forward)

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 part of Topic 16 in Higher Level Chemistry

How catalysts work

By decreasing E_a , a catalyst increases the rate of a chemical reaction, without itself being permanently chemically changed.



- More particles are able to collide with sufficient energy to react under the lower activation energy
- More frequent, successful collisions lead to a faster rate of reaction

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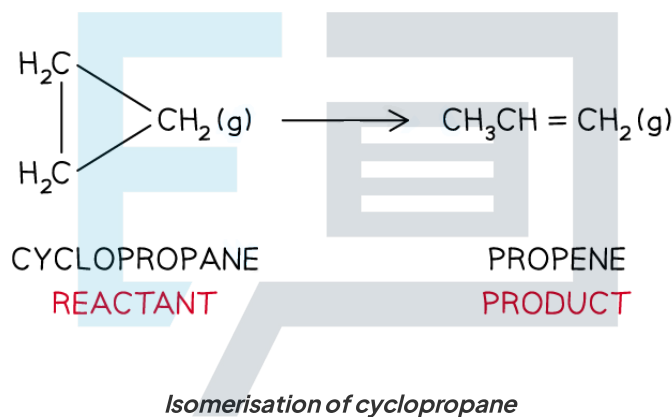
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6.1.5 Rate Experiments

Rate Experiments

- During a reaction, the **reactants** are used up and changed into the **products**
- This means that as the reaction proceeds, the concentration of the reactants is **decreasing** and the concentration of the products is **increasing**
- Because of this, the **rate of the reaction** is not the same throughout the reaction but **changes**
- The rate of reaction during the reaction can be calculated from a **concentration-time graph**.
- The **isomerisation of cyclopropane** to propene will be taken as an example:

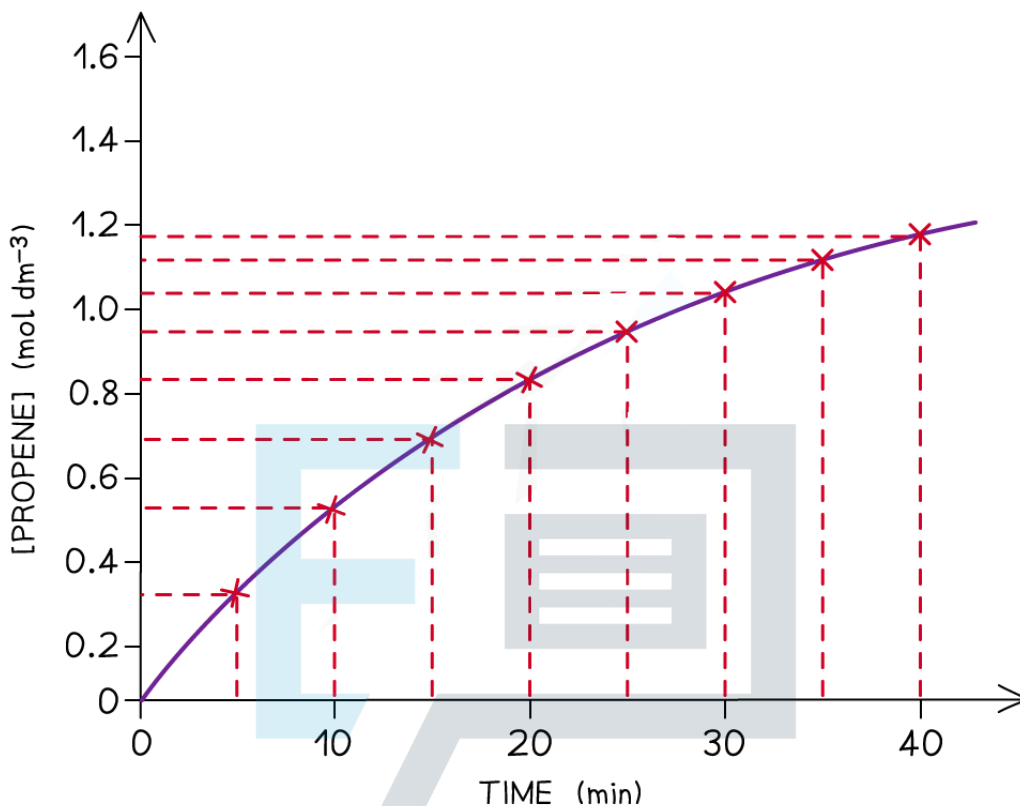


- The concentrations of reactant (cyclopropane) and product (propene) over time can be experimentally obtained

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- When taking the measurements, the **temperature** should be kept the same at all times as a **change** in temperature will change the **rate of reaction**
- A **concentration-time graph** for the **concentration of propene as well as cyclopropane** can be obtained from the above results
 - As an example, the concentration-time graph for propene is shown below:



The graph shows that the concentration of propene increases with time

Calculating the rate at the start of a reaction

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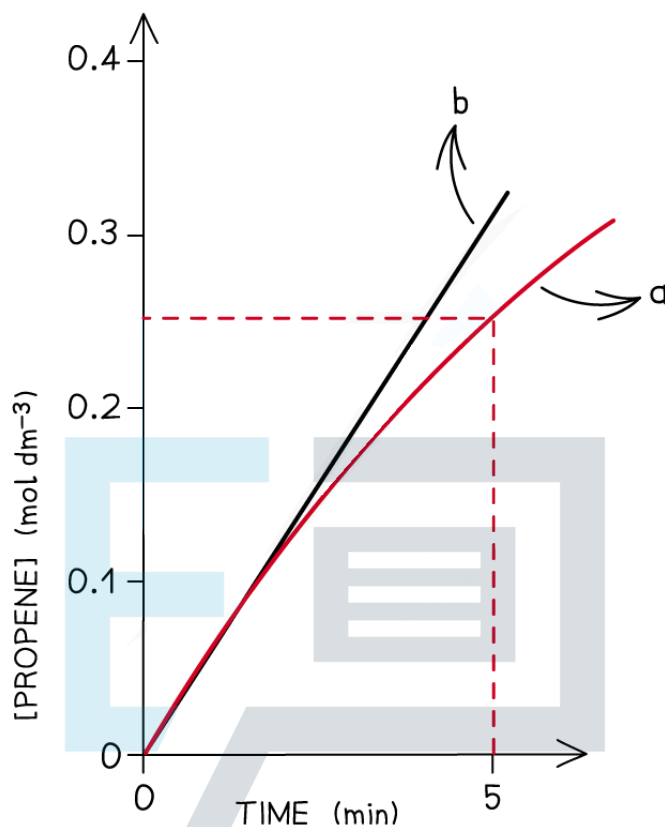
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- At the start of the reaction, the concentration-time curve looks almost linear

- The rate at this point can therefore be found by treating the curve as a linear line and by using:

$$\text{RATE OF A REACTION} = \frac{\text{CHANGE IN AMOUNT OF REACTANTS OR PRODUCTS (mol dm}^{-3}\text{)}}{\text{TIME (s)}}$$

- Using the graph, the average rate of the reaction over the first 5 minutes for propene is:



Line a shows the average rate over the first five minutes whereas line b shows the actual initial rate found by drawing a tangent at the start of the curve. The calculated rates are very similar for both methods

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$$\text{Rate} = \frac{0.27}{300}$$

$$= 0.0009 \text{ mol dm}^{-3} \text{ s}^{-1}$$

Calculating the rate as the reaction proceeds

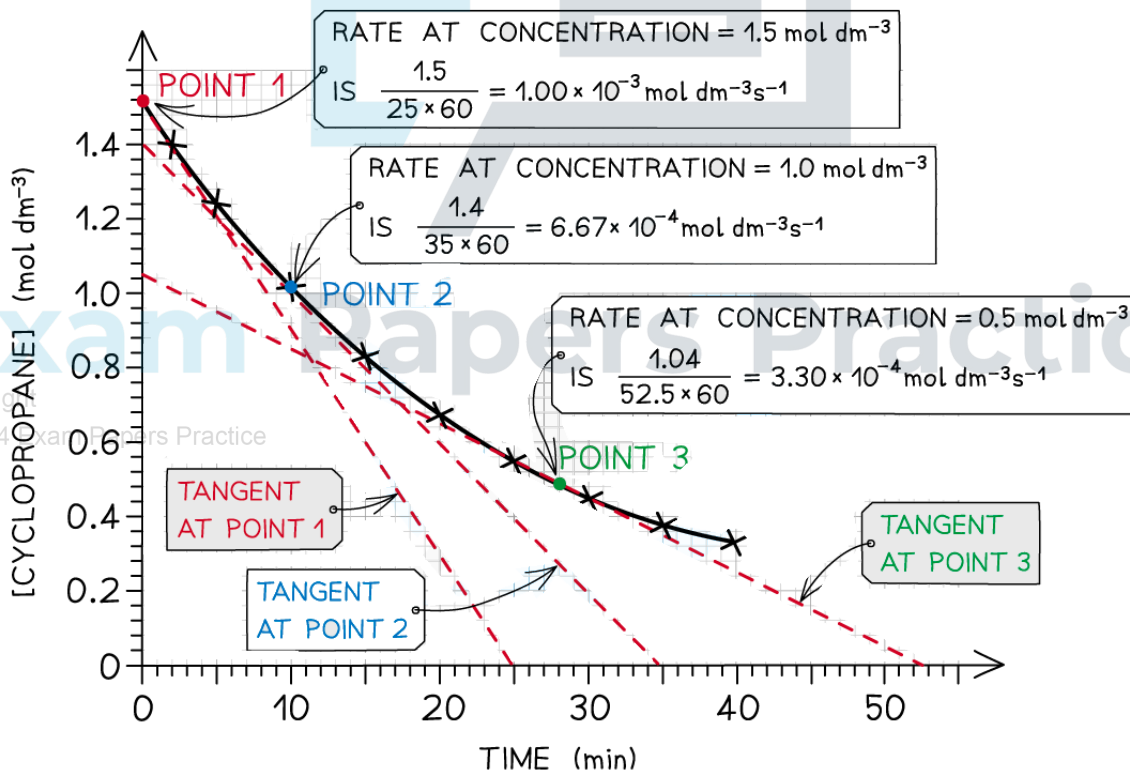
- The curve becomes shallower with time which means that the rate decreases with time
- The rate of reaction can be calculated by taking short time intervals

Eg. you can calculate the rate of reaction from 15 to 20 mins during which the concentration of propene increases from 0.68 to 0.83 mol dm⁻³:



$$\begin{aligned} \text{Rate} &= \frac{(0.83) - (0.68)}{(1200) - (900)} \\ &= \frac{0.15}{300} \\ &= 0.0005 \text{ mol dm}^{-3} \text{ s}^{-1} \end{aligned}$$

- The smaller the time intervals, the more accurate the reaction rate value is
- Even more accurate is to find the rate of reaction at **different concentrations** of reactant or product at **particular time points**
- This can be done by drawing **tangents** at several points on the graph
 - As an example, the rates of reaction at different concentrations of cyclopropane are calculated by drawing the appropriate tangents:



The rate of reaction at 3 different concentrations of cyclopropane is calculated by drawing tangents at those points in the graph



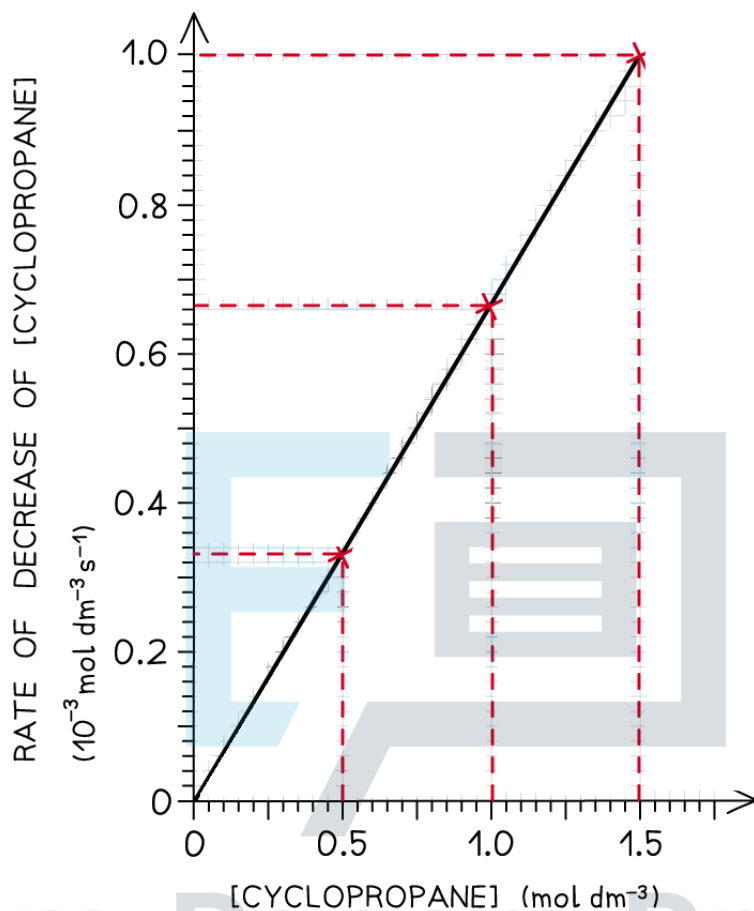
Rate-concentration graph

- The calculated rates can then be summarised in a table to show how the rate of reaction changes with changing concentration of the reactants or products

Change in Rate with Decreasing Concentration of Cyclopropane Table

[cyclopropane] (mol dm ⁻³)	Rate (10 ⁻³ mol dm ⁻³ s ⁻¹)
0.5	0.33
1.0	0.67
1.5	1.0

- This data can then be used to plot a rate-concentration graph
- The graph shows that the rate is directly proportional to the concentration of cyclopropane
 - If you double the concentration of cyclopropane the rate of reaction will double to o



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The graph shows a directly proportional correlation between the concentration of cyclopropane and the rate of reaction

Exam Tip

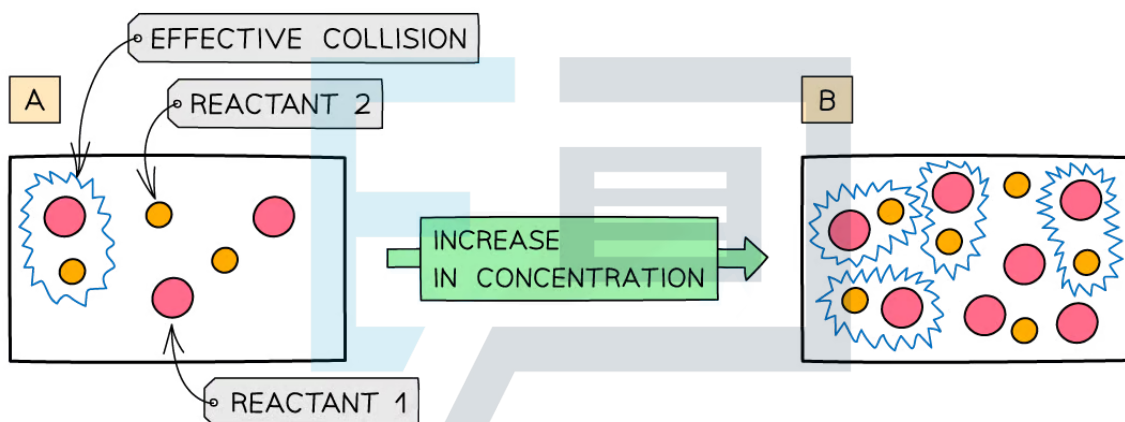
To calculate the rate of reaction you can either use the increase in concentration of products (like in the example above) or the decrease in concentration of reactants.

6.1.6 Explaining Rates

Explaining Rates

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 an increased **rate of reaction**



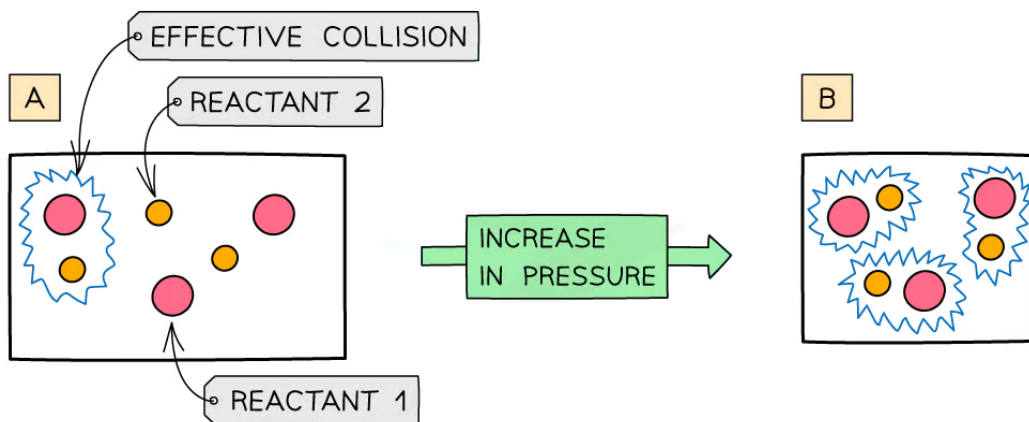
The diagram shows a higher concentration of particles in (b) which means that there are more particles present in the same volume than (a) so the chances and frequency of collisions between reacting particles is increased causing an increased rate of reaction

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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 molecules have less space in which they can move
- This means that the number of **effective collisions** increases due to an increased **collision frequency**
- An increase in pressure therefore increases the **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

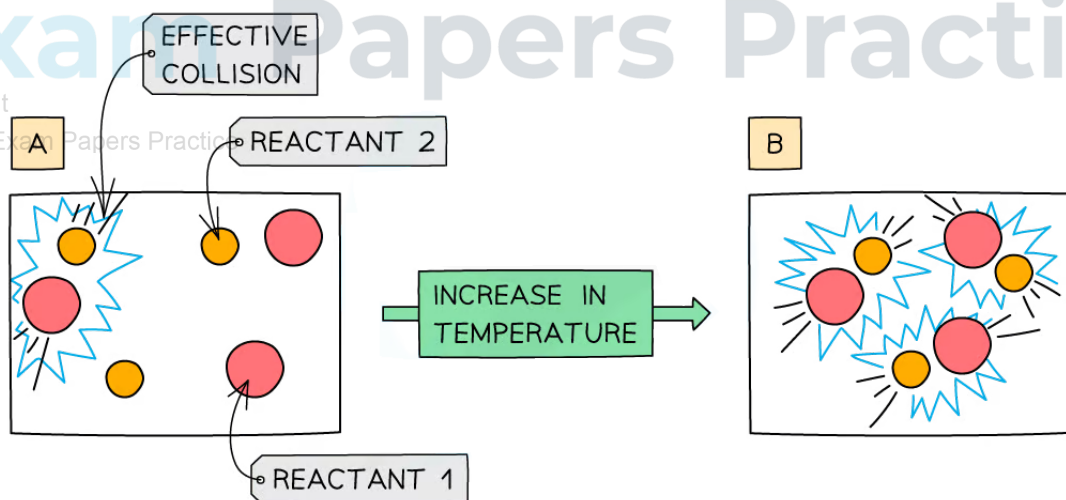
Temperature

- 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 molecules have the activation energy or more. This means that a higher **proportion** of collisions are **successful**

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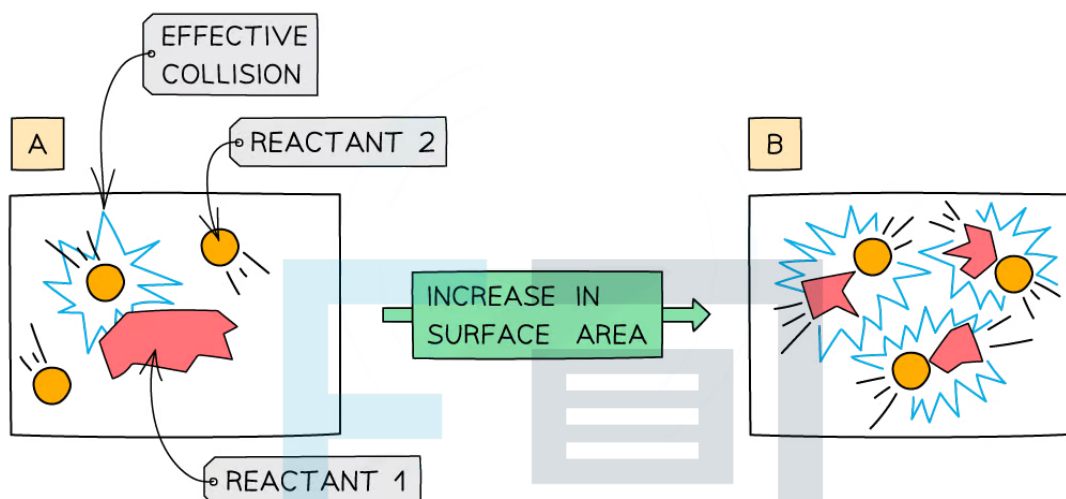
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An increase in temperature causes an increase in the kinetic energy of the particles. The number of collisions increases and the proportion of successful collisions increases

Particle Size

- 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 particles
 - For example, powders have a very large **surface area**



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

Worked example

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

- Increasing the total pressure in reactions involving gases
- Raising the temperature in reactions involving gases
- Increasing the particle size of a solid in a reaction

- I and II only
- I and III only
- II and III only
- I, II and III

Answer:

The correct option is **A**.

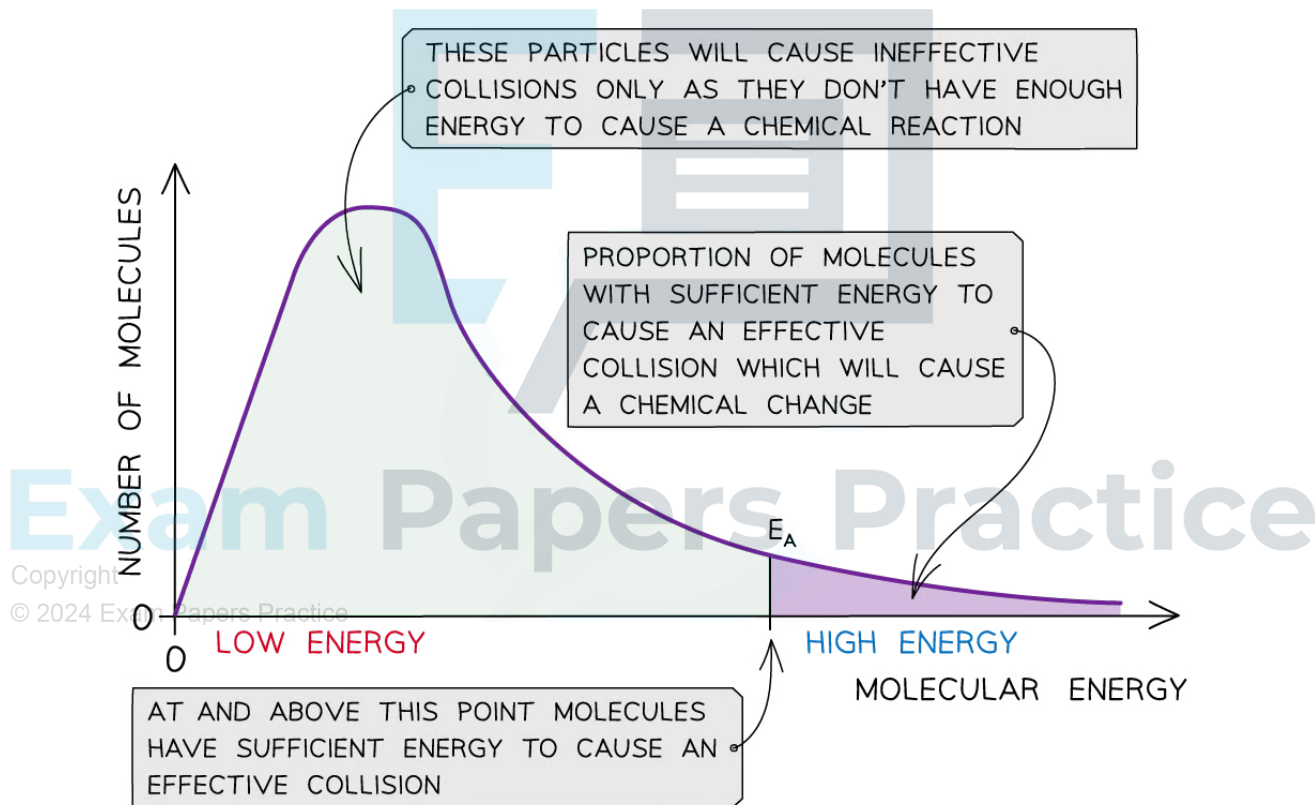
- Increasing pressure and raising temperature increases the number of successful collisions
- Increasing the particle size decreases the surface area and reduces the number of collisions

6.1.7 Maxwell-Boltzmann Curves

Maxwell-Boltzmann Curves

Boltzmann distribution curve

- The **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, and many particles will have energy in between

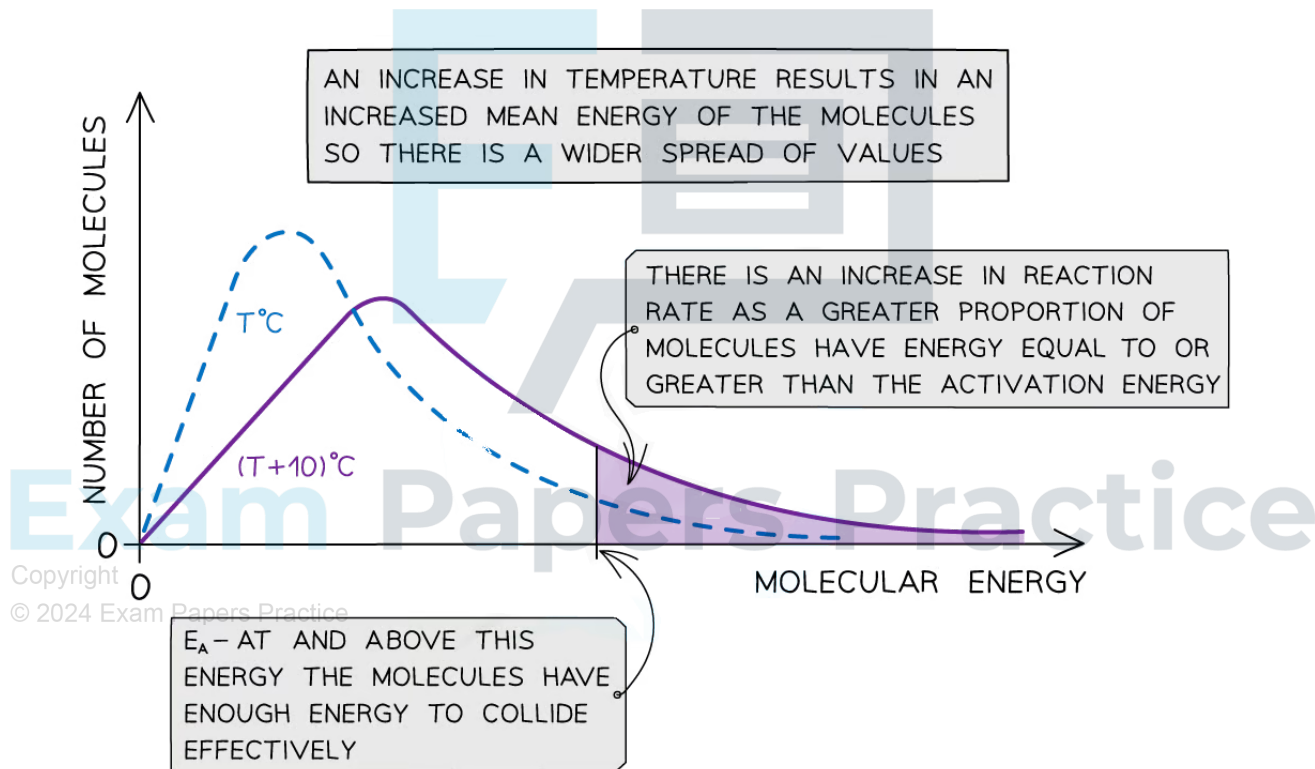


The Boltzmann distribution curve shows the distribution of the energies and the activation energy

- The graph shows that only a small proportion of molecules in the sample have enough energy for an **effective or successful 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
- With higher temperatures, the Boltzmann distribution curve **flattens** and the peak **shifts** to the right



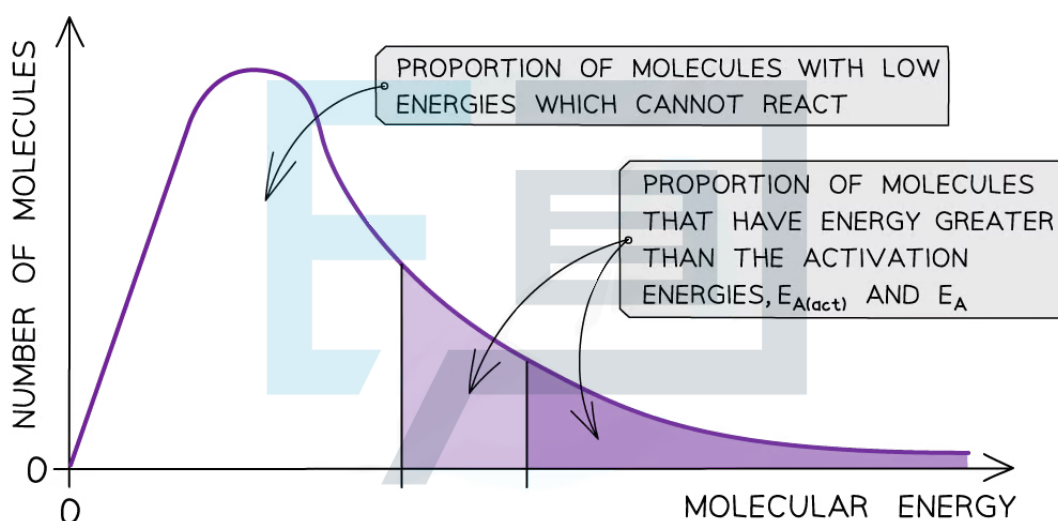
The Boltzmann distribution curve at $T^\circ\text{C}$ and when the temperature is increased by 10°C

- 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**

Effect of a catalyst on the Maxwell-Boltzmann distribution curve

- A **catalyst** provides the reactants another pathway which has a lower activation energy
- By lowering E_a , a **greater proportion** of molecules in the reaction mixture 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



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

Exam 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



6.1.8 Energy Profiles & Catalysis

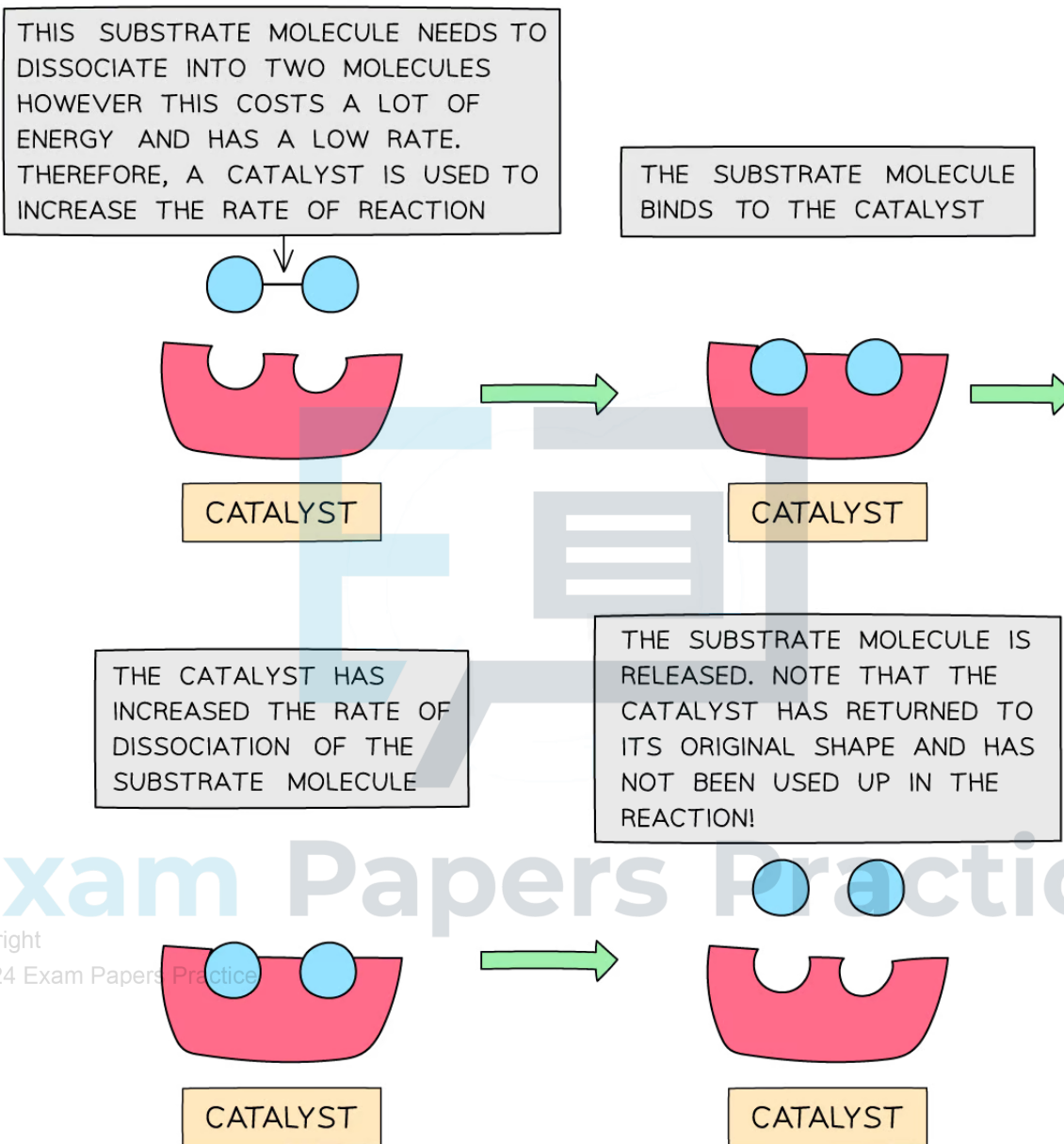
Energy Profiles & Catalysis

- **Catalysis** is the process in which the rate of a chemical reaction is increased, by adding a substance called 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
- 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

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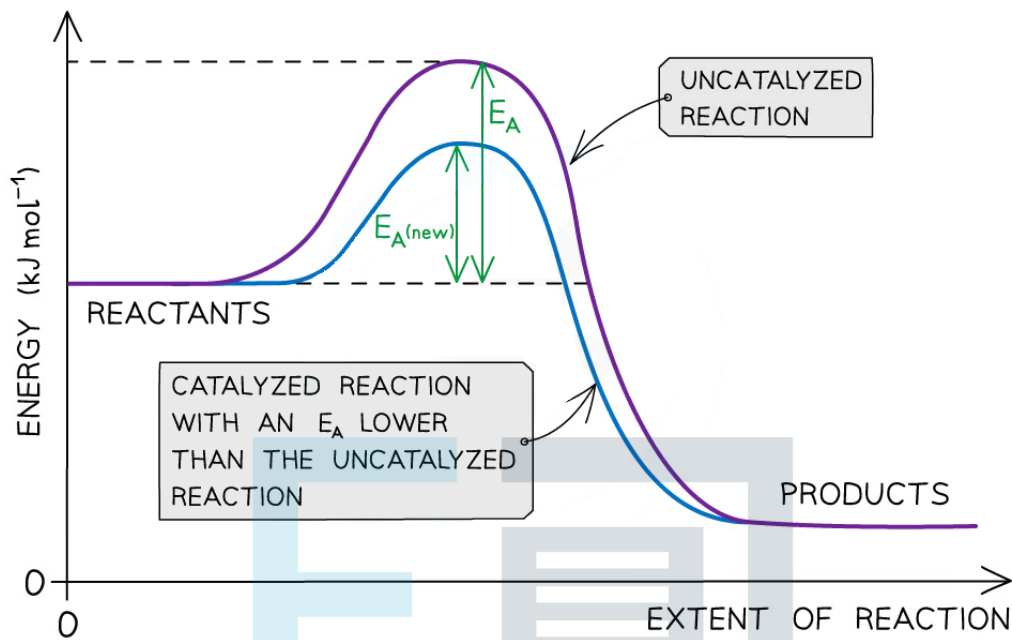


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The diagram shows that the catalyst speeds up a reaction that would normally be slow due to the high activation energy. The catalyst is not used up in the chemical reaction and is not taking part in the chemical reaction



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

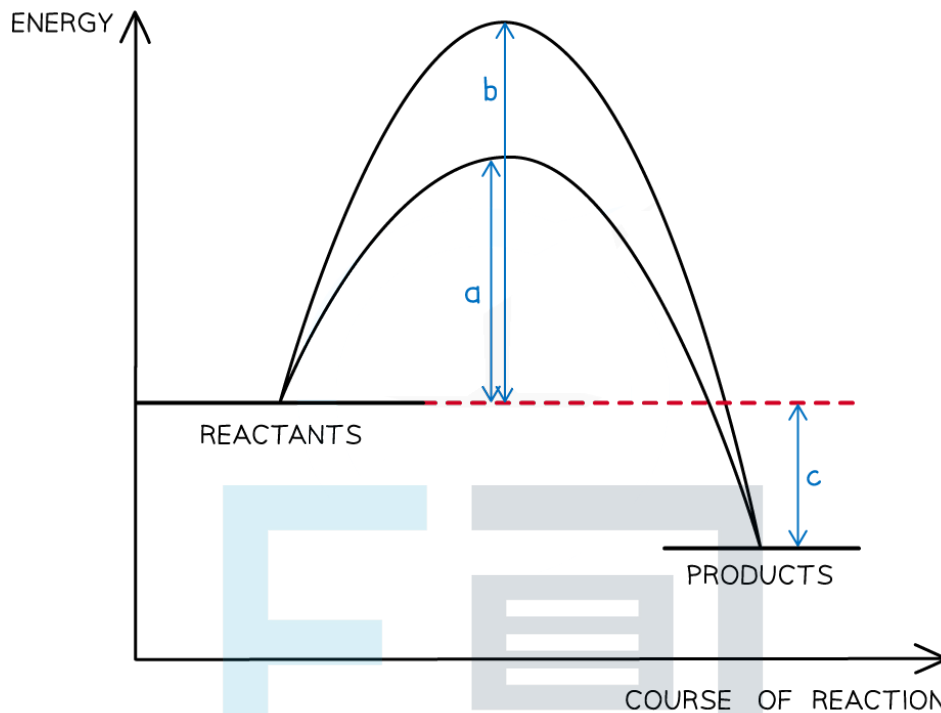
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Worked example

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, so that corresponds to arrow **a**