Edexcel International A Level (IAL) Chemistry

Your notes

Kinetics

Contents

Your notes

Kinetic Rates – Introduction

- The **rate of reaction** refers to the change in the amount or concentration of a reactant **or** product per unit time
  - The units for rate of reaction are mol dm^{-3} s^{-1}
- It can be found by measuring:
  - The mass lost over time
  - The volume of gas produced over time
  - Colour changes, including by the use of colorimetry
  - pH changes over time
  - Changes in electrical conductivity
- The rate of reaction can be calculated by:

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

Rate of Reaction

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

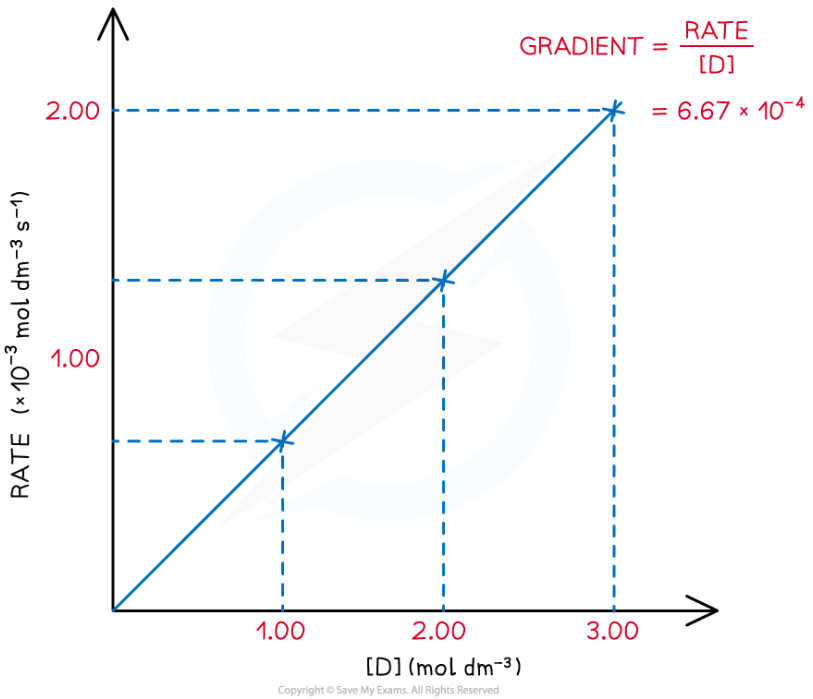
$$\mathbf{D\,(aq) \rightarrow E\,(aq) + F\,(g)}$$

- The rate of reaction at different concentrations of D is measured and tabulated

Rate of Reactions Table

[D](mol dm^{-3})	Rate (mol dm^{-3} s^{-1})	$\frac{\text{rate}}{[D]}$ (s^{-1})
3.00	2.00×10^{-3}	6.67×10^{-4}
2.00	1.33×10^{-3}	6.67×10^{-4}
1.00	6.60×10^{-4}	6.67×10^{-4}

- A **directly proportional** relationship between the **rate** of reaction and **concentration of D** is observed when the results are plotted on a graph:



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

Rate Equations

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

$$A\,(aq) + B\,(aq) \rightarrow C\,(aq) + D\,(g)$$

- The rate equation for this reaction is:

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

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

Your notes

Your notes

Rate Equations & Orders

- 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 a positive, negative or fractional value
  - Orders that are a fraction suggest that the reaction involves multiple steps
- 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
- 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
- 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)
- The **overall order of reaction** is the sum of the powers of the reactants in a rate equation

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:

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

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

Answers

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**

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:

$$\text{Rate} = k[BrO_3^-(aq)][Br^-(aq)][H^+(aq)]$$

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

Answers

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

Determining Rate Equations

- Let's take the following reaction and derive the rate equation from experimental data

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

Your notes

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}

- 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 a graph, but it doesn't have to be - you can use tabulated data provided
- Take the reactants one at a time and find the order with respect to each reactant individually
- Identify two experiments where the concentration of the reactant you are looking at first changes, but the concentrations of all other reactants remain constant
- 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 $[(CH_3)_3CBr]$

- From the above table, that is experiments 1 and 2
  - The $[(CH_3)_3CBr]$ has doubled, but the $[OH^-]$ has remained the same
  - The rate of the reaction has also doubled
  - Therefore, the order with respect to $[(CH_3)_3CBr]$ is 1 (first order)

Order with respect to $[OH^-]$

- From the above table, that is experiments 1 and 3
  - The $[OH^-]$ has doubled, but the $[(CH_3)_3CBr]$ has remained the same
  - The rate of reaction has increased by a factor of 4 (i.e. increased by 2^2)
  - Therefore, the order with respect to $[OH^-]$ is 2 (second order)

Putting the rate equation together

- Once you know the order with respect to all of the reactants, you put them together to form the rate equation
- If a reactant has an order of 0, then you do not include it in the rate equation
- If a reactant has an order of 1, then you do not need to include the number 1 as a power

Your notes

- If a reactant has an order of 2, then you raise that reactant concentration to the power of 2
- For this reaction, the rate equation will be:

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

Your notes

Examiner Tips and Tricks

Be careful when reading the values in standard form! It is easy to make a mistake.

- The **rate constant** (k) of a reaction can be calculated using the initial rates and the rate equation

Calculating the rate constant from the initial rate

- 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:

$$Na_2CO_3\,(aq) + 2Cl^-\,(aq) + 2H^+\,(aq) \rightarrow 2NaCl\,(aq) + CO_2\,(g) + H_2O\,(l)$$

$$\text{RATE} = k[Na_2CO_3][Cl^-]$$

THIS REARRANGES TO GIVE:

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

- 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	$[Na_2CO_3]$ (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	4.38×10^{-6}
2	0.0375	0.0125	0.0125	6.63×10^{-6}
3	0.00625	0.0250	0.0250	2.19×10^{-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 1.40×10^{-2}

Calculating 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:

$$\text{UNITS OF } k = \frac{(\text{mol dm}^{-3}\,\text{s}^{-1})}{(\text{mol dm}^{-3})\,(\text{mol dm}^{-3})}$$

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

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

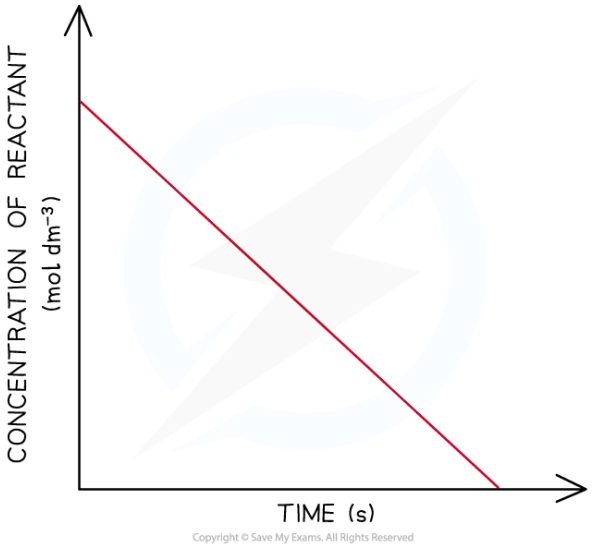
Your notes

Your notes

Reaction Orders - Graphs

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:

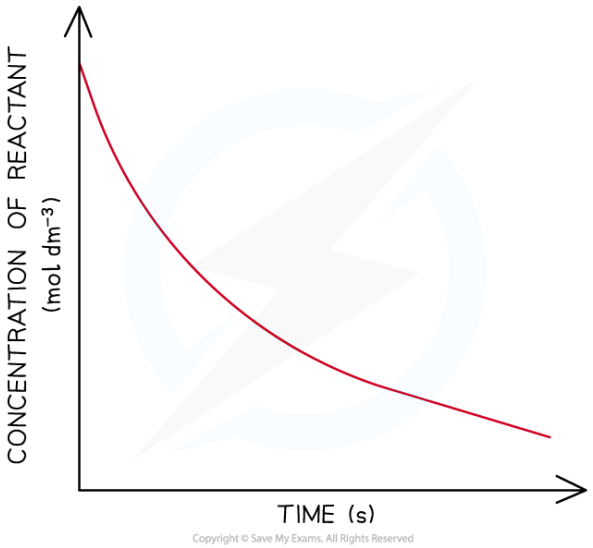


Concentration-time graph of a zero-order reaction

- The gradient of the line is the rate of reaction
  - 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:

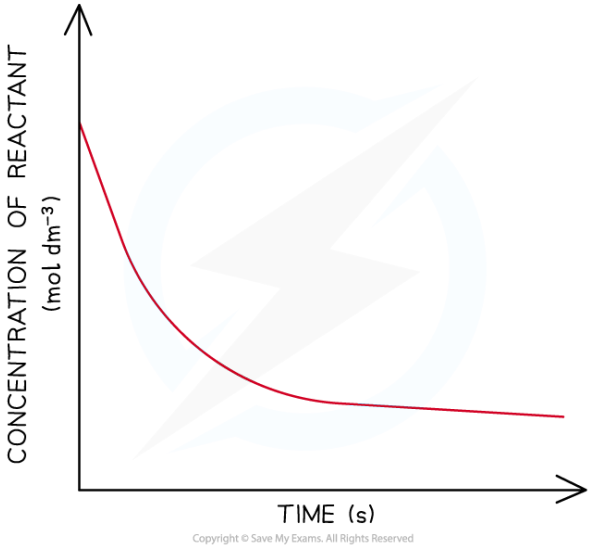
$$\text{Rate} = k$$

- 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

- 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:



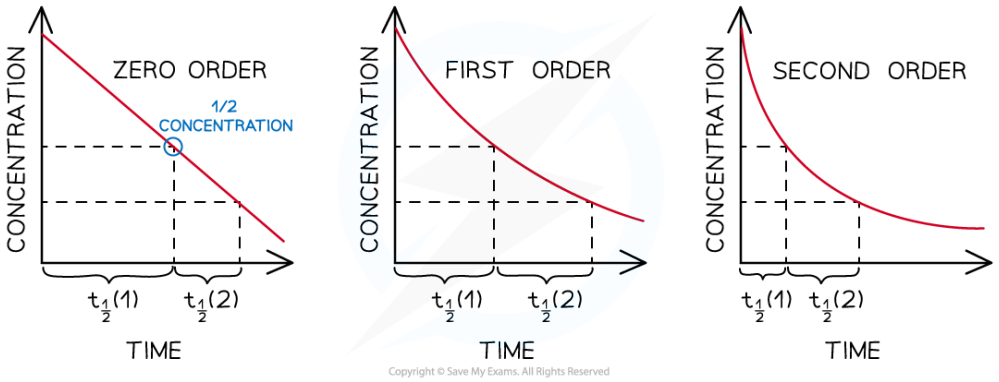
Concentration-time graph of a second-order reaction

Order of reaction from half-life

- The order of a reaction can also be deduced from its half-life **($t_{1/2}$)**
- For a zero-order reaction the successive half-lives decrease with time

- This means that it would take less time for the concentration of reactant to halve as the reaction progresses

- The half-life of a first-order reaction remains constant throughout the reaction
  - The amount of time required for the concentration of reactants to halve will be the same during the entire reaction
- For a second-order reaction, the half-life increases with time
  - This means that as the reaction is taking place, it takes more time for the concentration of reactants to halve



Half-lives of zero, first and second-order reactions

Examiner Tips and Tricks

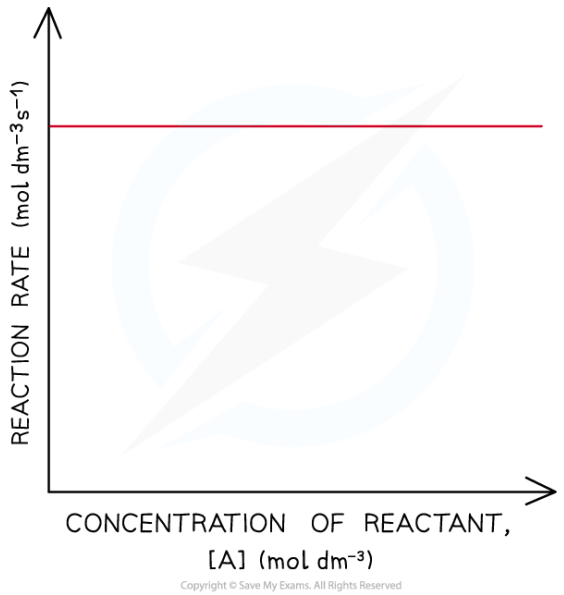
Make sure that you know the correct shapes for the concentration-time graphs. It can be easy to confuse some concentration-time graphs with the following rate-concentration graphs, particularly;

- 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

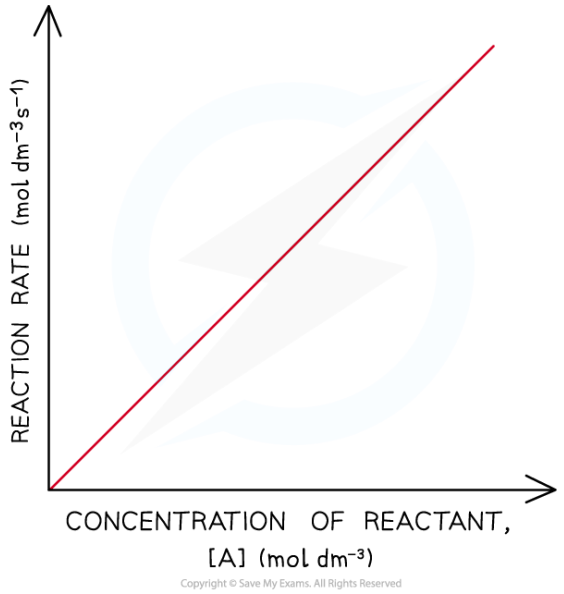
- In a **zero-order** reaction, the rate doesn't depend on the concentration of the reactant
  - The rate of the reaction therefore remains constant throughout the reaction
  - The graph is a horizontal line
  - The rate equation is **rate = *k***

Your notes



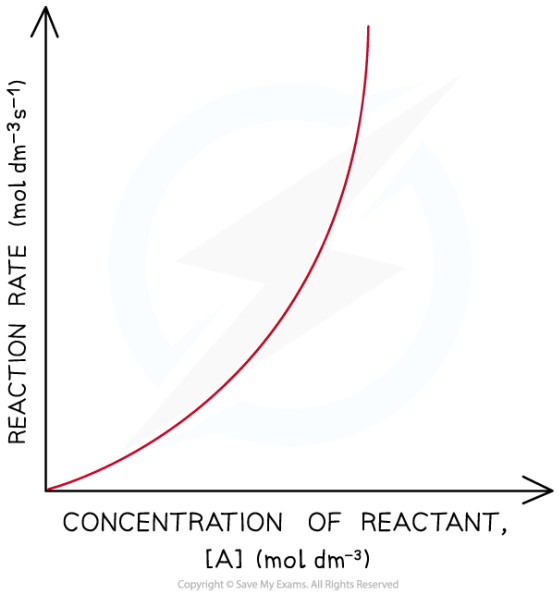
Rate-concentration graph of a zero-order reaction

- 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

- 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 graphs of a second-order reaction

Examiner Tips and Tricks

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.

Your notes

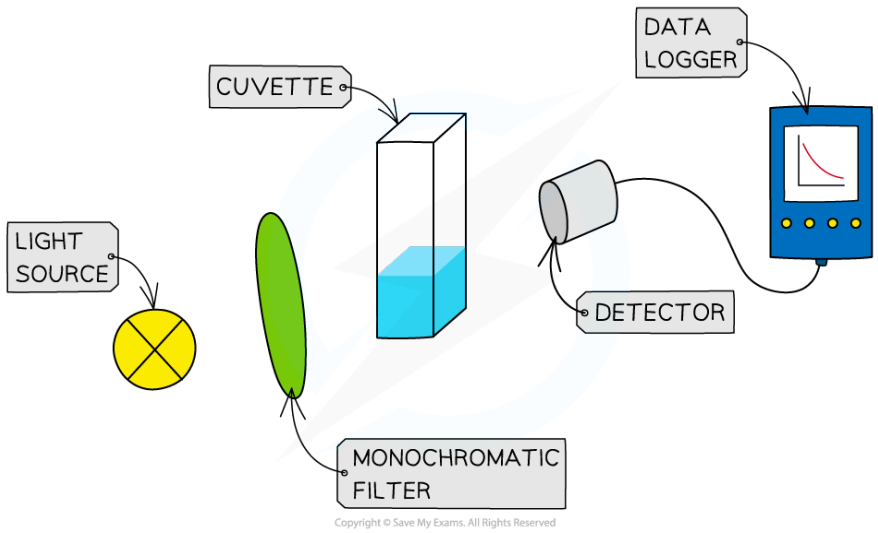
Your notes

Obtaining Rate Data

- 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
- Some commonly used techniques are:
  - **titration**
  - **colorimetry**
  - **mass loss**
  - **gas production**

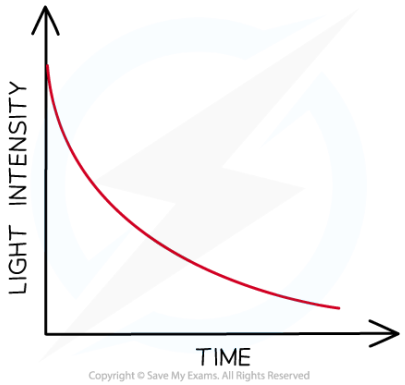
Changes in colour

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



Colorimetry Set Up

- 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

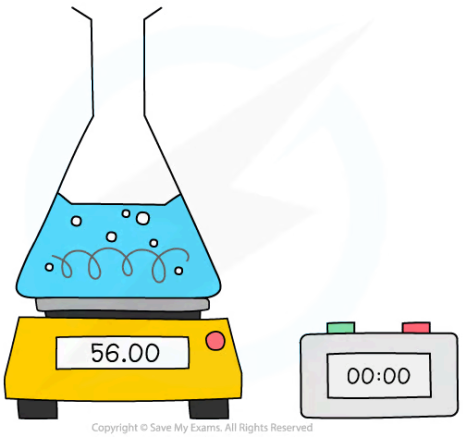


Sketch graph of colour intensity against time (the coloured species is a reactant in this case)

- 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

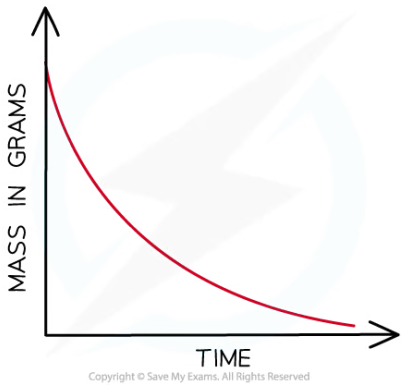
- When a gas is produced in a reaction it usually escapes from the reaction vessel, so the mass decreases
  - This can be used to measure the rate of reaction
  - For example, the reaction of calcium carbonate with hydrochloric acid produces CO_2
  - The mass is measured every few seconds and change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



Your notes

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

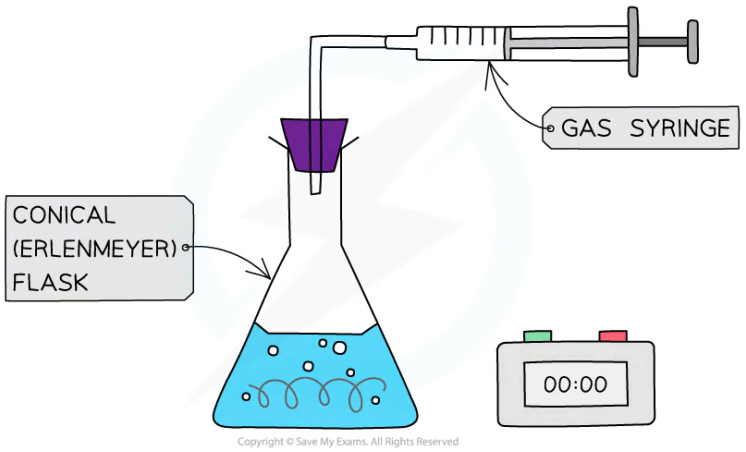


Mass loss of a product against time

- 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 (Mr = 44) but hydrogen would not (Mr = 2)

Volumes of gases

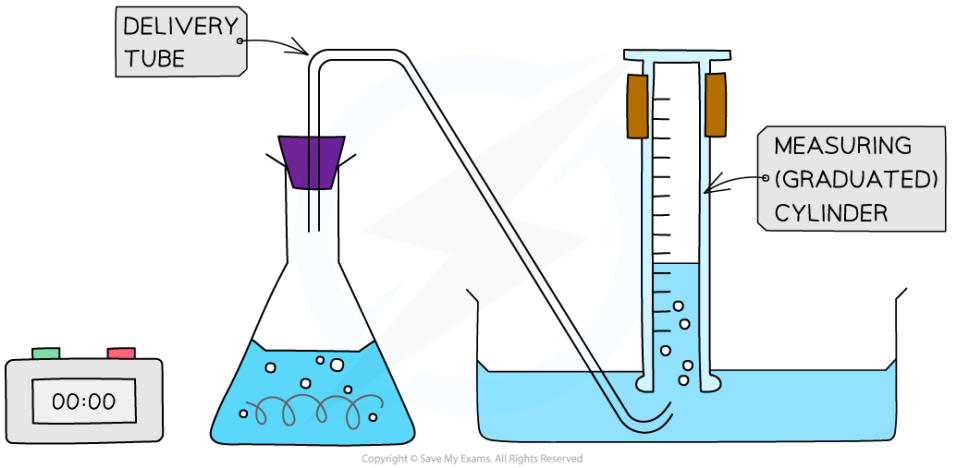
- When a gas is produced in a reaction, it can be trapped and its volume measured over time
  - This can be used to measure the rate of reaction.
  - For example, the reaction of magnesium with hydrochloric acid produces hydrogen



Collecting gases experimental set up

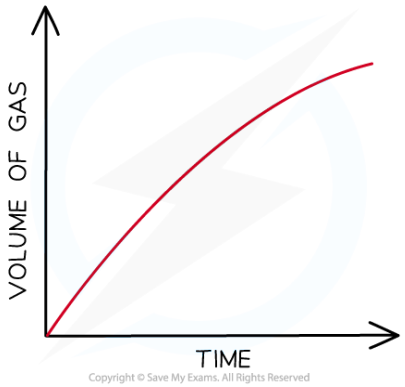
- An alternative gas collection set up involves collecting a gas through water using an inverted measuring cylinder (as long as the gas is not water soluble)

Your notes



Alternative gas collection set up

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



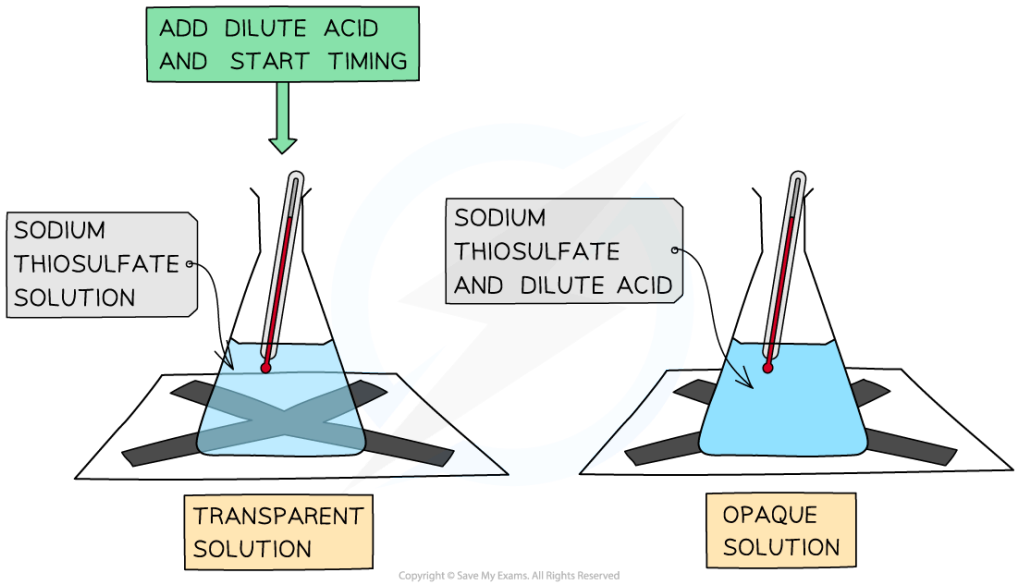
Graph of gas volume evolved against time

Measuring concentration changes

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

Your notes

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



The disappearing cross experiment

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

Examiner Tips and Tricks

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

Your notes

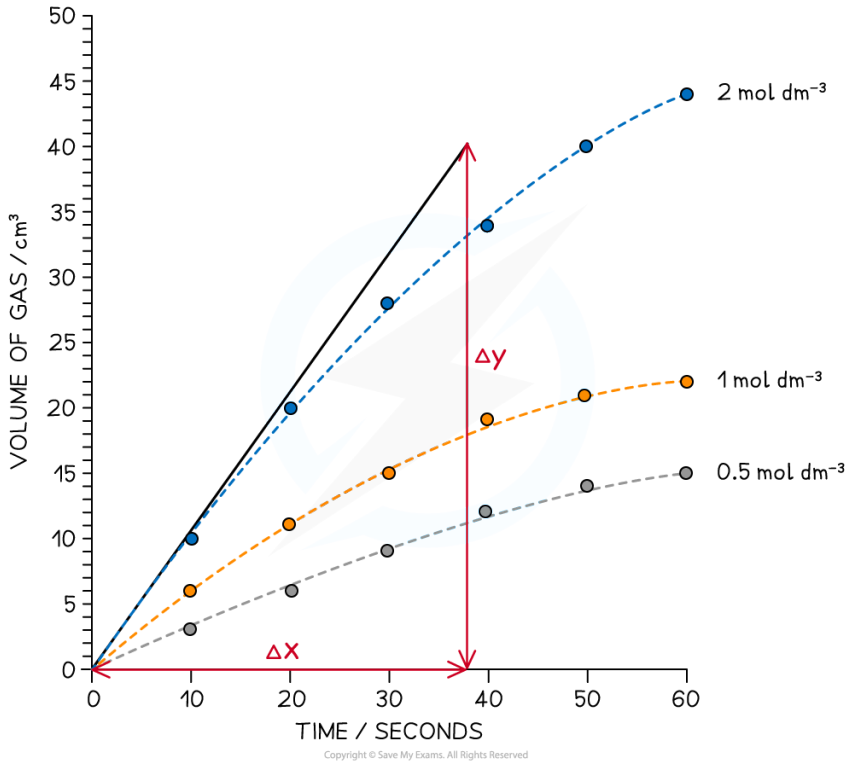
Your notes

Initial-Rate Method

- The **initial rates method** determines the rate at the very start of the reaction when $t = 0$
- The initial rate can be found by:
  - Drawing a **concentration-time graph**
  - Adding a **tangent** at $t = 0$
  - Calculating the **gradient** of the tangent
- One example of measuring the initial rate could be the reaction of calcium carbonate with hydrochloric acid
  - The volume of carbon dioxide produced with different concentrations can be measured against time
  - The results are then plotted onto a graph
  - The tangent at $t = 0$ is then added
  - The gradient of the tangent can then be calculated to give the initial rate of the reaction

Worked Example

The concentration-time graph for the reaction of calcium carbonate with three different concentrations of hydrochloric acid is shown



Calculate the initial rate of reaction for the reaction of calcium carbonate with 2.0 mol dm^{-3} hydrochloric acid

Answer

- Using the tangent drawn:
  - Gradient = $\frac{\Delta y}{\Delta x} = \frac{42}{38}$ = 1.10 mol dm^{-3} s^{-1}
  - Therefore, the initial rate of reaction is 1.10 mol dm^{-3} s^{-1}

Clock reactions

- **Clock reactions** are a more convenient way of measuring the initial rate of reaction using a **single measurement**
- The time taken, *t*, for a specific visual change in the reaction to occur is measured
  - These changes could be a colour change or formation of a precipitate
- The major assumption that clock reactions depend on is:
  - That there is no significant change in the rate of reaction between the start of the reaction and the time when the measurement is taken
- The initial rate is then proportional to $\frac{1}{t}$
- The iodine clock experiment is a common clock reaction
  - This is covered in more detail in Core Practical 9b: Investigating a Clock Reaction

Your notes

- Here is a set of typical results for the iodine clock reaction:

Your notes

Specimen Results for the Iodine Clock Reaction Table

Concentration of potassium iodide / mol dm^{-3} × 10^{-2}	Time for blue colour to appear / s	Rate, 1/t s^{-1}
1.515	40	0.025
3.030	20	0.050
4.545	13	0.075
6.060	10	0.100
7.576	8	0.120

- The initial rate is a relatively simple calculation
  - E.g. For a concentration of 0.01515 mol dm^{-3}, the rate is $\frac{1}{40}$ = 0.025 s^{-1}
- A closer look at the results shows that as the concentration doubles, the rate also doubles
  - This can be linked back to the reaction being first order
- There are limitations to the accuracy of the clock reaction
  - These are, again, based on the assumption that the rate of reaction is constant
- As the reaction progresses, the concentration of the reactants decreases - typically on a curve
  - Therefore, when the time measured for the reaction to occur is short then there is a higher chance that the initial rate calculated will be closer to the true value
  - As the time taken for the reaction to occur, the value of the initial rate will become less accurate
- The initial rate measured during a clock reaction is an estimate

Examiner Tips and Tricks

- You can be expected to work with experimental data to deduce the order of reaction with respect to specific reactants
- This is done in the same that has been previously discussed in 5.5.2 Rate Equations

Your notes

Continuous Monitoring Method

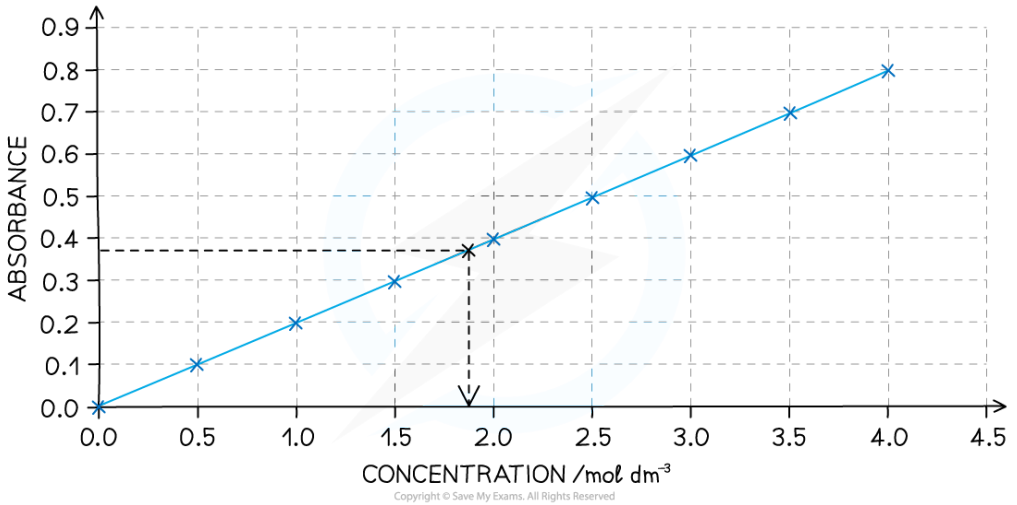
- **Continuous monitoring** involves collecting experimental data throughout the course of a reaction to plot a concentration-time graph
- Two of the most common ways to collect this data are by:
  - Measuring the volume / amount of gas evolved over time
  - Measuring the mass of reactants lost over time
- Another alternative method involves the use of colorimetry:

The iodination of propanone

- The iodination of propanone provides a suitable experiment in which the rate of reaction can be measured throughout the reaction by using a colorimeter
- The reaction is carried out using a catalyst of dilute sulfuric acid
- The iodine decolourises during the reaction as it turns into iodopropanone and hydrogen iodide:

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

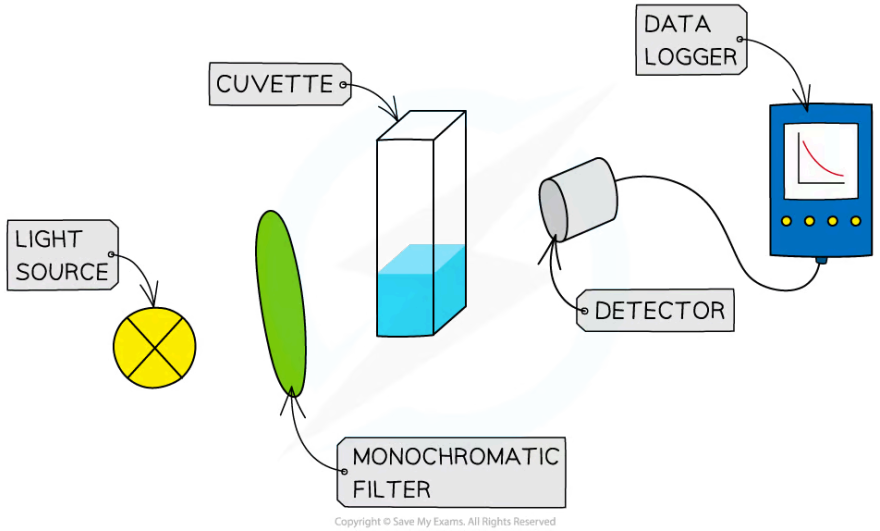
- The colorimeter measures colour absorbance which is proportional to the concentration of the coloured species
- Before the investigation begins it is necessary to measure the absorbance of a set of standard solutions of iodine and obtain a calibration curve
- For example, here is a calibration curve for a transition metal ion that allows you to convert colorimeter readings into concentrations:



A calibration curve showing the relationship between colour absorbance and concentration

Your notes

- The colorimeter uses very small volumes of solutions, so four burettes can be filled with solutions of 0.02 mol dm^{-3} iodine, 1.0 mol dm^{-3} propanone and 1.0 mol dm^{-3} sulfuric acid and distilled water
- By varying the volumes of solutions while maintaining a constant total volume with the use of distilled water, you can obtain a number of different concentrations
- The solutions are measured into a small beaker, leaving the iodine in a separate beaker - this starts the reaction, so it can be added when you start a timer or stop watch
- The iodine is added to the other liquids, the contents mixed and then quickly transferred into the cuvette (small receptacle) and the colorimeter / data logger started



The set up for using a colorimeter and data logger to continuously measure the rate of reaction

- A typical set of volume compositions could be as follows:

Volume Compositions Table

Run	Iodine / cm^3	Sulfuric acid / cm^3	Water / cm^3	Propanone / cm^3
1	4	1	4	1
2	4	1	3	2
3	4	1	2	3
4	4	1	1	4
5	4	1	0	5

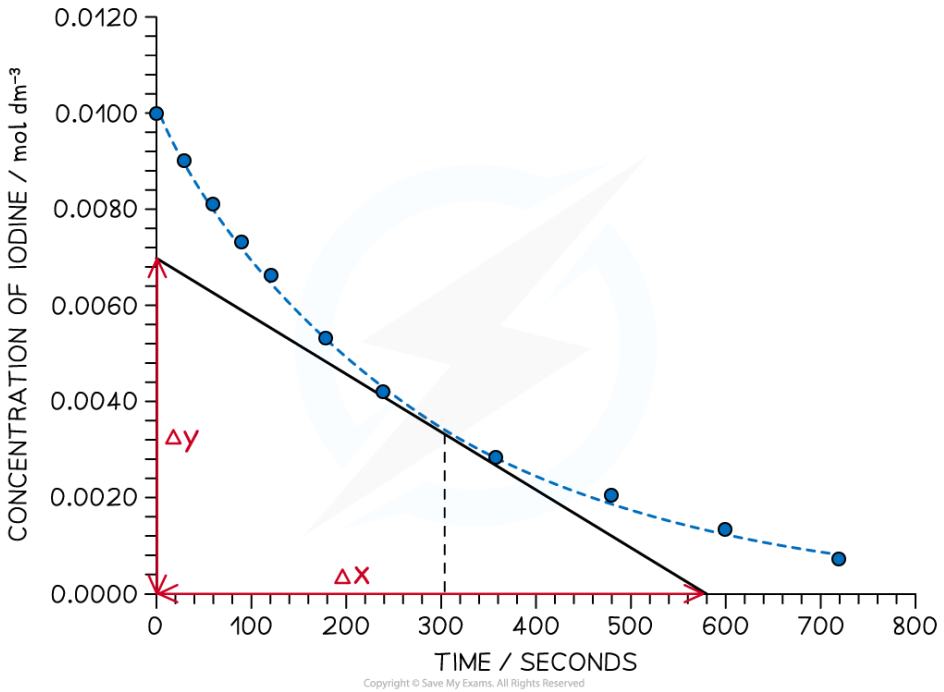
Practical tip

- Choose a filter that gives the strongest absorbance for the solution you are using - this will be the complementary colour to the colour of the solution under investigation

Your notes

Specimen Results Table for the Iodination of Propanone

Concentration of iodine / mol dm^{-3}	Time / s
0.0100	0
0.0090	30
0.0081	60
0.0073	90
0.0066	120
0.0053	180
0.0042	240
0.0028	360
0.0020	480
0.0013	600
0.0007	720



Graph showing the change in concentration of iodine during the course of the reaction

Your notes

Measuring rate

- To find the rate of reaction at any point, a tangent is drawn and the gradient is determined
- The gradient gives the rate of reaction
- For example, in the graph above, the rate of reaction at 300 seconds can be found
  - A vertical line is drawn from the 300 s mark until it meets the curve, then a tangent is drawn
  - Gradient = $\frac{\Delta y}{\Delta x} = \frac{0.0069}{590} = 1.17 \times 10^{-5}$ mol dm^{-3} s^{-1}
- The gradient is the rate of reaction at that point

Examiner Tips and Tricks

Whichever rates experiments you carry out, make sure you can

- describe the steps in the procedure
- name all the apparatus used
- draw data tables which include headings and units
- draw graphs showing labels, units and best fit lines
- determine an initial gradient or at any point in the curve

Your notes

Rate-Determining Steps from Equations

Rate-determining step & intermediates

- 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
- If a reactant appears in the **rate-determining step**, then the concentration of that reactant will also appear in the **rate equation**
- For example, the rate equation for the reaction below is rate = k [CH_3Br] [OH^-]

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

- This suggests that **both** CH_3Br and OH^- take part in the **slow 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
  - This shows the individual reaction steps which are taking place
- 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:

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

- 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:

$2NO_2\,(g) \rightarrow NO\,(g) + NO_3\,(g)$ **slow** (rate-determining step)

Step 2:

$NO_3\,(g) + CO\,(g) \rightarrow NO_2\,(g) + CO_2\,(g)$ **fast**

Overall:

~~2~~$NO_2\,(g) + $ ~~$NO_3\,(g)$~~ $+ CO\,(g) \rightarrow NO\,(g) + $ ~~$NO_3\,(g)$~~ $+$ ~~$NO_2\,(g)$~~ $+ CO_2\,(g)$

= $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

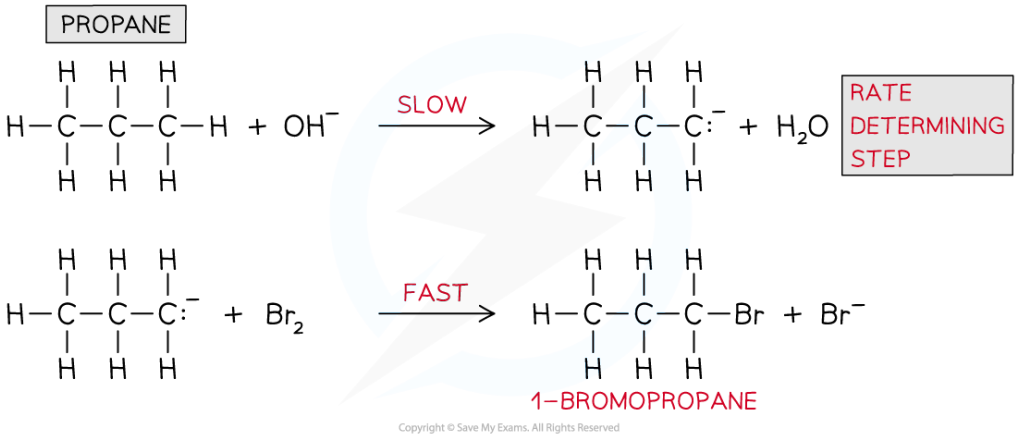
Your notes

Identifying the rate-determining step

- The rate-determining step can be identified from a rate equation given that the reaction mechanism is known
- For example, propane ($CH_3CH_2CH_3$) undergoes bromination under alkaline solutions
- The overall reaction is:

$$CH_3CH_2CH_3 + Br_2 + OH^- \rightarrow CH_3CH_2CH_2Br + H_2O + Br^-$$

- The reaction mechanism is:



Reaction mechanism for the bromination of propane under alkaline conditions

- The rate equation is:

$$\text{Rate} = k[CH_3CH_2CH_3][OH^-]$$

- From the rate equation, it can be deduced that only $CH_3CH_2CH_3$ and OH^- are involved in the **rate-determining step** and not bromine (Br_2)
- $CH_3CH_2CH_3$ and OH^- are only involved in the first step of the reaction mechanism, therefore the **rate-determining step** is:
  - $CH_3CH_2CH_3 + OH^- \rightarrow CH_3CH_2CH_2^- + H_2O$

Your notes

Reaction Mechanisms – Deduction

- 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

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

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

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.

Answers

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 $2NO_2 + 2SO_2 \rightarrow 2NO + 2SO_3$)

Your notes

Examiner Tips and Tricks

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

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

$$2NO\,(g) + 2H_2\,(g) \rightarrow N_2\,(g) + 2H_2O\,(l)$$

- The reaction mechanism for this reaction is:

Step 1:

$NO\,(g) + NO\,(g) \rightarrow N_2O_2\,(g)$ **fast**

Step 2:

$N_2O_2\,(g) + H_2\,(g) \rightarrow H_2O\,(l) + N_2O\,(g)$ **slow** (rate-determining step)

Step 3:

$N_2O\,(g) + H_2\,(g) \rightarrow N_2\,(g) + H_2O\,(l)$ **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 Tips and Tricks

Intermediates in the mechanism **cannot** appear as substances in the rate equationThis 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

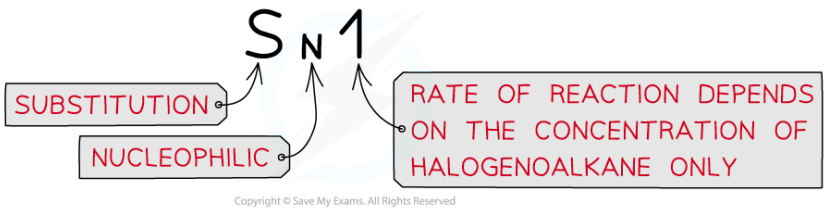
Your notes

Reaction Mechanisms – SN1 & SN2

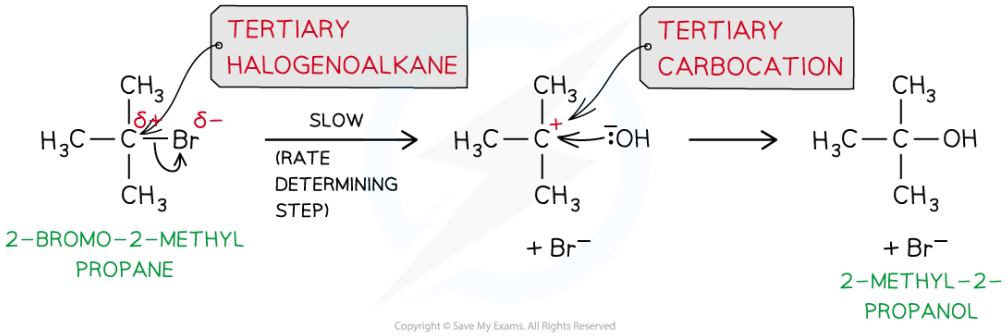
- Nucleophilic substitution reactions can occur in two different ways (known as **S_N2** and **S_N1** reactions) depending on the structure of the halogenoalkane involved

S_N1 reactions

- In **tertiary** halogenoalkanes, the carbon that is attached to the halogen is also bonded to three alkyl groups
- These halogenoalkanes undergo nucleophilic substitution by an **S_N1** mechanism
  - 'S' stands for 'substitution'
  - 'N' stands for 'nucleophilic'
  - '1' means that the rate of the reaction (which is determined by the slowest step of the reaction) depends on the concentration of only one reagent, the halogenoalkane



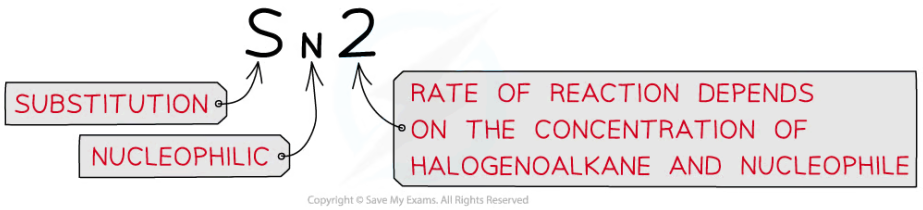
- The S_N1 mechanism is a **two-step** reaction
- In the first step, the C-X bond breaks heterolytically and the halogen leaves the halogenoalkane as an X^- ion (this is the **slow** and **rate-determining step**)
  - As the rate-determining step only depends on the concentration of the halogenoalkane, the rate equation for an S_N1 reaction is **rate = *k*[halogenoalkane]**
  - An S_N1 reaction is described as unimolecular because there is only molecule involved in the rate-determining step
  - This forms a tertiary carbocation **(which is a tertiary carbon atom with a positive charge)**
  - In the second step, the tertiary carbocation is attacked by the nucleophile
- For example, the nucleophilic substitution of 2-bromo-2-methylpropane by hydroxide ions to form 2-methyl-2-propanol



The mechanism of nucleophilic substitution in 2-bromo-2-methylpropane which is a tertiary halogenoalkane

S_N2 reactions

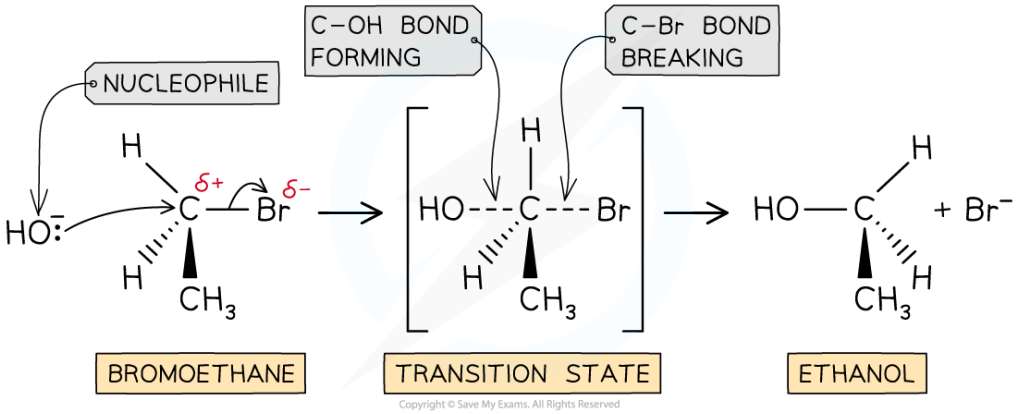
- In **primary** halogenoalkanes, the carbon that is attached to the halogen is bonded to one alkyl group
- These halogenoalkanes undergo nucleophilic substitution by an **S_N2** mechanism
  - 'S' stands for 'substitution'
  - 'N' stands for 'nucleophilic'
  - '2' means that the rate of the reaction (which is determined by the slowest step of the reaction) depends on the concentration of both the halogenoalkane and the nucleophile ions



- The S_N2 mechanism is a **one-step** reaction
  - The nucleophile donates a pair of electrons to the δ+ carbon atom of the halogenoalkane to form a new bond
    - As this is a one-step reaction, the rate-determining step depends on the concentrations of the halogenoalkane and nucleophile, the rate equation for an S_N2 reaction is **rate = *k*[halogenoalkane][nucleophile]**
    - An S_N2 reaction is bimolecular as there are two molecules involved in the rate-determining step
  - At the same time, the C-X bond is breaking and the halogen (X) takes both electrons in the bond
  - The halogen leaves the halogenoalkane as an X^- ion

Your notes

- For example, the nucleophilic substitution of bromoethane by hydroxide ions to form ethanol



The S_N2 mechanism of bromoethane with hydroxide causing an inversion of configuration

Examiner Tips and Tricks

Primary halogenoalkanes only react via with S_N2 mechanism

Secondary halogenoalkanes react via both the S_N1 and S_N2 mechanisms

Tertiary halogenoalkanes only react via with S_N1 mechanism

Your notes

Your notes

Acid-Catalysed Iodination of Propanone

- The iodination of propanone is carried out using a catalyst of dilute sulfuric acid
- The reaction between iodine in an acidic solution and propanone is

$$CH_3COCH_3\,(aq) + I_2\,(aq) \rightarrow CH_3COCH_2I\,(aq) + H^+\,(aq) + I^-\,(aq)$$

- We can follow the rate of this reaction by using a continuous monitoring method and therefore we will be able to deduce the order of reaction with respect to a substance using a concentration time graph
- We can calculate the order of reaction with respect to iodine as the propanone and acid are in a large excess so their concentration do not change during the reaction
- Once a portion of the reaction mixture has been removed, we stop the reaction by adding sodium hydrogencarbonate
- Performing a titration again sodium thiosulfate(VI) solution and using starch as an indicator is used to determine the concentration of iodine

$$2S_2O_3^{2-}\,(aq) + I_2\,(aq) \rightarrow 2I^-\,(aq) + S_4O_6^{2-}\,(aq)$$

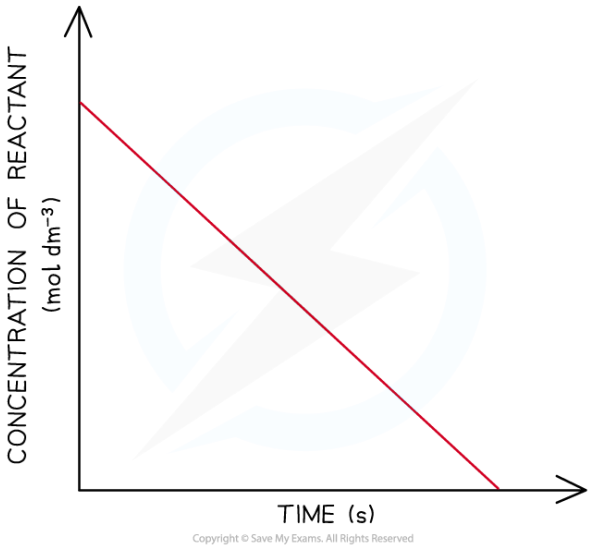
Results

Sample Data from the Reaction

Time (min)	Titre (cm^3)
2.3	39.10
8.6	35.80
14.7	33.15
21.9	26.55
38.0	22.10

- This graph is a straight line graph
  - As the gradient is constant, the rate of reaction is constant, and therefore independent of the concentration of the iodine solution
  - This means **the reaction is zero order with respect to the iodine**
  - The rate equation for the reaction is

- Rate = $k[CH_3COCH_3(aq)][H^+(aq)]$



Concentration-time graphs of a zero-order reaction

Your notes

Your notes

Activation Energy & Arrhenius

- The rate equation shows how each of the reactants in a reaction effects 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 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
- The relationship between the rate constant, the temperature and also the activation energy is given by the Arrhenius equation:

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

k = THE RATE CONSTANT

A = ARRHENIUS CONSTANT
(A CONSTANT RELATED TO THE COLLISION FREQUENCY AND ORIENTATION OF THE MOLECULES)

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 AN 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

Your notes

Finding the Activation Energy

- Very often, the Arrhenius equation is used to calculate the activation energy of a reaction
- A question will either give sufficient information for the Arrhenius equation to be used or a graph can be plotted and the calculation done from the plot

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:

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

- 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

Worked Example

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

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

Answer

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

REARRANGE THE EQUATION FOR E_a:

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

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

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

INSERT VALUES FROM THE QUESTION:

$$E_a = [(\ln 4.6 \times 10^{13}) - (\ln 6.25 \times 10^{-4})] \times (8.31 \times 400)$$
$$= [(31.4597) - (-7.3778)] \times (3324)$$
$$= 129{,}095.85 \text{ J}$$

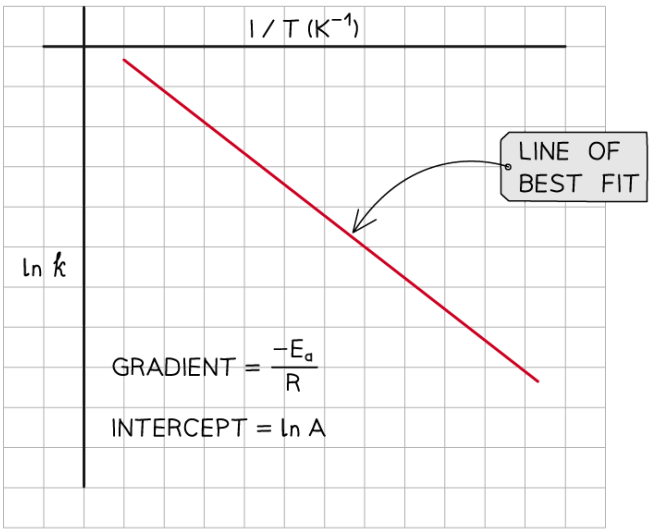
REMEMBER, E_a HAS THE UNIT kJ...

$$E_a = 129 \text{ kJ}$$

Your notes

Using an Arrhenius plot:

- 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



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

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

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

$y = \ln k$

$x = \frac{1}{T}$

$m = \frac{-E_a}{R}$ (THE GRADIENT)

$c = \ln A$ (THE y INTERCEPT)

Your notes

Worked Example

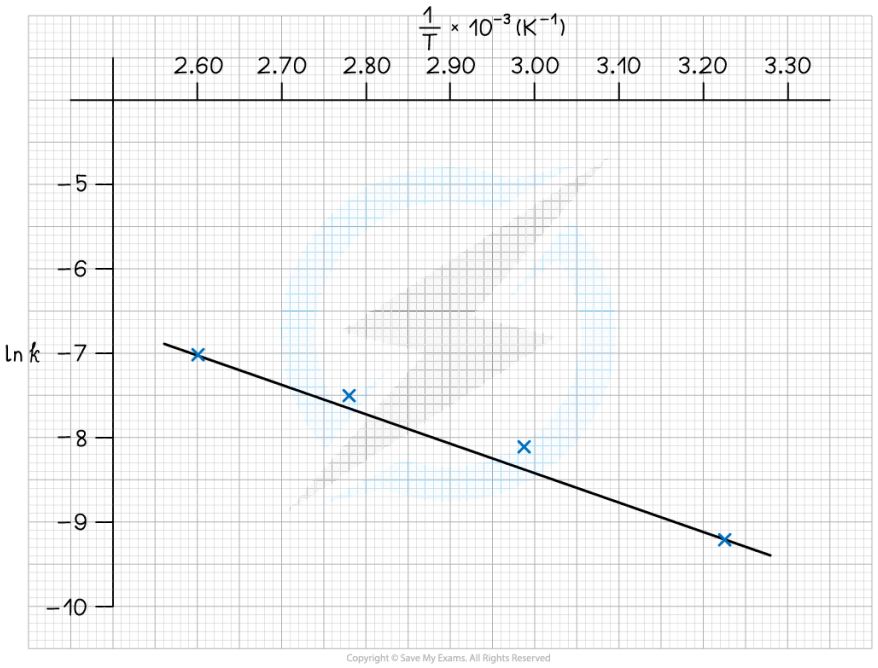
1. Complete the following table
2. Plot a graph of ln *k* against 1/*T*
3. Use this to calculate the activation energy, E_a, and the Arrhenius constant, *A*, of the reaction.

Temperature / K	$\frac{1}{T}$ / 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}	

Answer 1:

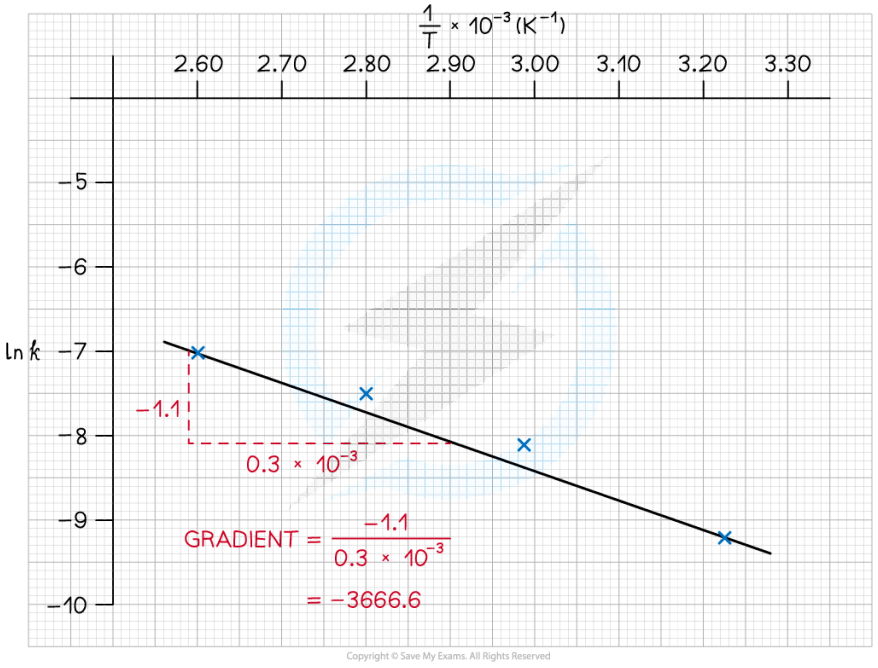
Temperature / K	$\frac{1}{T}$ / K^{-1}	Time (t) / s	Rate constant (k) / s^{-1}	ln k
310	3.23×10^{-3}	57	1.01×10^{-4}	−9.2
335	2.99×10^{-3}	31	3.01×10^{-4}	−8.1
360	2.78×10^{-3}	19	5.37×10^{-4}	−7.5
385	2.60×10^{-3}	7	9.12×10^{-4}	−7.0

Answer 2:



Answer 3:

CALCULATE THE ACTIVATION ENERGY:

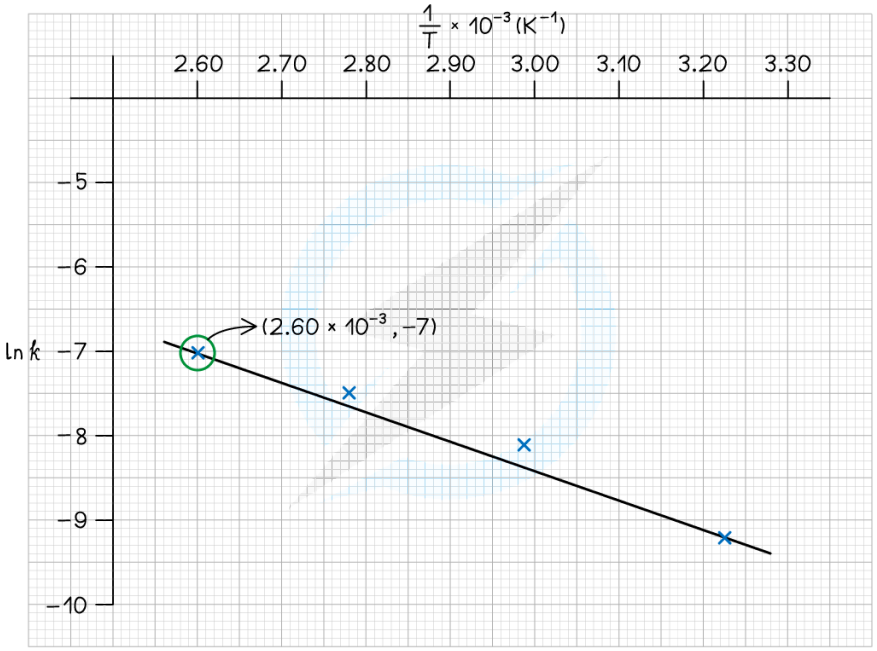


Your notes

$$\text{GRADIENT} = \frac{-E_a}{R} = -3666.6$$

$$E_a = -(-3666.6 \times 8.31)$$
$$= 30,469 \text{ J mol}^{-1}$$
$$= 30.5 \text{ kJ mol}^{-1}$$

CALCULATE A:



Your notes

CHOOSE A POINT ON THE GRAPH
$(2.60 \times 10^{-3}, -7.0)$

USE THE FOLLOWING EQUATION:

$y = m x + c$

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

$\ln k = -7.0$

$\frac{1}{T} = 2.60 \times 10^{-3}$

} FROM THE POINT CHOSEN ON THE GRAPH

$\frac{-E_a}{R} = \frac{-1.1}{0.3 \times 10^{-3}}$

$= -3666.6$

SO: $-7.0 = (-3666.6 \times 2.60 \times 10^{-3}) + \ln A$

$-7.0 = -9.53 + \ln A$

$\therefore \ln A = -7.0 + 9.53$

$= 2.53$

$A = e^{2.53}$

$A = 12.55$

Your notes