

IB Chemistry DP

16. HL Chemical Kinetics

CONTENTS

16.1 Rate Expression & Reaction Mechanism

16.1.1 Rate Equations

16.1.2 Rate Constants

16.1.3 Graphical Representations

16.1.4 Rate Determining Step

16.1.5 Mechanism Problems

16.2 Activation Energy

16.2.1 The Arrhenius Equation

16.2.2 Graphing the Arrhenius Equation

16.2.3 Activation Energy from Rate Constants

YOUR NOTES



16.1 Rate Expression & Reaction Mechanism

16.1.1 Rate Equations

Rate Equations

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

Rate of Reaction

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



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

Rate of reactions table

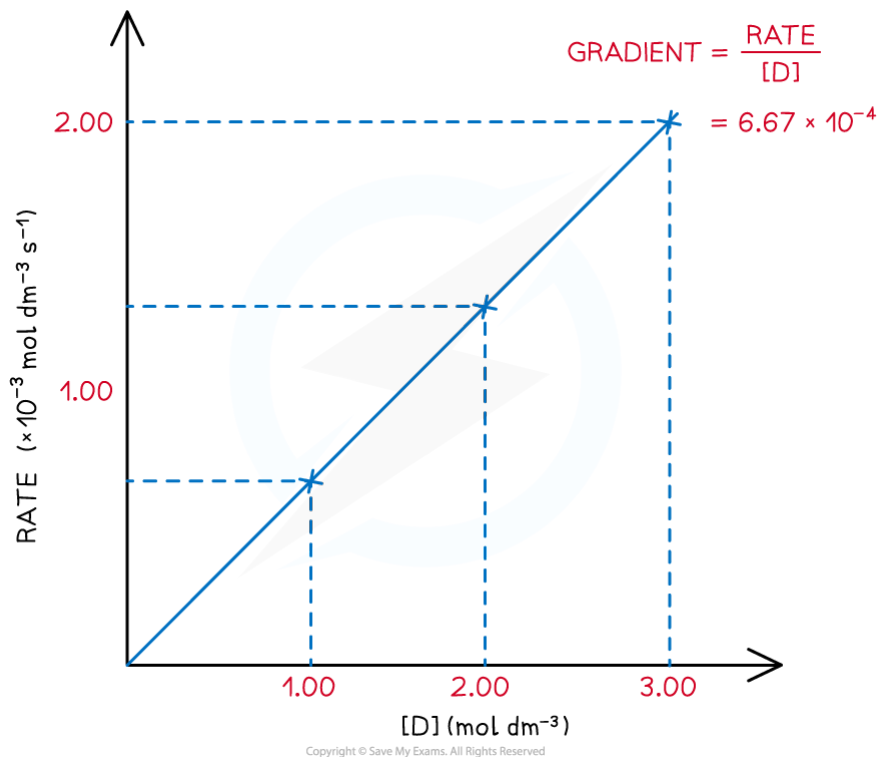
$[\text{D}] (\text{mol dm}^{-3})$	Rate ($\text{mol dm}^{-3} \text{s}^{-1}$)	$\frac{\text{rate}}{[\text{D}]} (\text{s}^{-1})$
3.00	2.00×10^{-3}	6.67×10^{-4}
2.00	1.33×10^{-3}	6.67×10^{-4}
1.00	6.60×10^{-4}	6.67×10^{-4}

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

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Rate of reaction over various concentrations of D

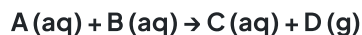
- This leads to a very common rate expression:

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

- 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:



- The rate equation for this reaction is:

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

- 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

Order of reaction

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- 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



Exam 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 = $k[\text{CH}_3\text{CHO}]^{3/2}$
 - The reaction of hydrogen and bromine - Rate = $k[\text{H}_2][\text{Br}_2]^{1/2}$
 - The reaction between carbon monoxide and chlorine - Rate = $k[\text{CO}]^2[\text{Cl}_2]^{1/2}$
- However, for calculations only values of 0, 1 or 2 need to be considered

- 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:



The rate equation for this reaction is:

$$\text{Rate} = k[\text{N}_2\text{O}_5(\text{g})]$$

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

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Answers

**Answer 1:**

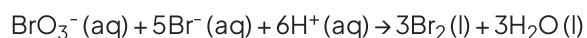
- Dinitrogen pentoxide features in the rate equation, therefore, it cannot be order zero / 0
- The dinitrogen pentoxide is not raised to a power, which means that it cannot be order 2 / second order
- Therefore, the order with respect to dinitrogen pentoxide must be **order 1 / first order**

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



The rate equation for this reaction is:

$$\text{Rate} = k[\text{BrO}_3^- (\text{aq})][\text{Br}^- (\text{aq})][\text{H}^+ (\text{aq})]$$

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

Solving Rate Equation Problems

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Deducing Rate Equations

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

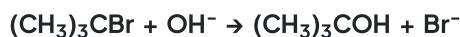


Table to show the experimental data of the above reaction

Experiment	Initial $[(\text{CH}_3)_3\text{CBr}] / \text{mol dm}^{-3}$	Initial $[\text{OH}^-] / \text{mol dm}^{-3}$	Initial rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$
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}
4	1.5×10^{-3}	4.0×10^{-3}	4.5×10^{-3}

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- 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
- Identify two experiments where the concentration of one reactant changes, but the concentrations of all other reactants are constant
 - Calculate what happens to the concentration
 - Calculate what happens to the rate of reaction
 - Deduce the order of reaction with respect to that chemical
 - 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 $[(\text{CH}_3)_3\text{CBr}]$

- In experiments 1 and 2, the concentration of $(\text{CH}_3)_3\text{CBr}$ changes while the concentration of OH^- remains constant
- The $[(\text{CH}_3)_3\text{CBr}]$ has doubled
- The rate of the reaction has also doubled
- Therefore, the order with respect to $[(\text{CH}_3)_3\text{CBr}]$ is 1 (first order)
 - $[\text{Change in concentration}]^{\text{order}} = \text{change in rate}$
 - $[2]^{\text{order}} = 2$
 - $[2]^1 = 2$

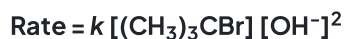
Order with respect to $[\text{OH}^-]$

- In experiments 1 and 3, the concentration of OH^- changes while the concentration of $(\text{CH}_3)_3\text{CBr}$ remains constant

2. The $[\text{OH}^-]$ has doubled
3. The rate of the reaction has increased by a factor of 4
4. Therefore, the order with respect to $[\text{OH}^-]$ is 2 / second order
 - $[\text{Change in concentration}]^{\text{order}} = \text{change in rate}$
 - $[2]^{\text{order}} = 4$
 - $[2]^2 = 2$

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:



Exam 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 one 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



16.1.2 Rate Constants

YOUR NOTES

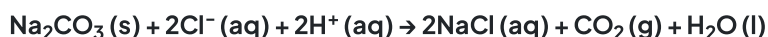


Rate Constants

- 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:



$$\text{RATE} = k[\text{Na}_2\text{CO}_3][\text{Cl}^-]$$

THIS REARRANGES TO GIVE:

$$k = \frac{\text{RATE}}{[\text{Na}_2\text{CO}_3][\text{Cl}^-]}$$

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- 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	$[\text{Na}_2\text{CO}_3]$ (mol dm^{-3})	$[\text{Cl}^-]$ (mol dm^{-3})	$[\text{H}^+]$ (mol dm^{-3})	Initial rate of reaction ($\text{mol dm}^{-3}\text{s}^{-1}$)
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}

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

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

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

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- 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:

$$\begin{aligned} \text{UNITS OF } k &= \frac{(\text{mol dm}^{-3} \text{s}^{-1})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} \\ &= \frac{\text{s}^{-1}}{\text{mol dm}^{-3}} \\ &= \text{mol}^{-1} \text{dm}^3 \text{s}^{-1} \end{aligned}$$

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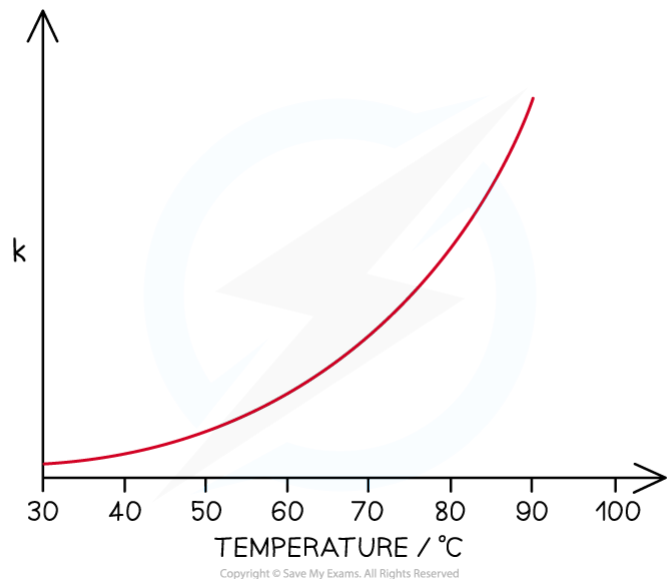
Temperature and the rate constant, k

- The following general reaction and rate equation will be used to discuss the effect of temperature on the rate constant, k :



$$\text{Rate of reaction} = k[\text{A}][\text{B}]$$

- The rate equation shows that rate of reaction depends on the rate constant, k , and the concentration of the reactants
 - 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 depending 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:



Relationship between temperature and rate constant, k

- The graph shows that the rate of reaction roughly doubles with an increase of $10\text{ }^{\circ}\text{C}$
 - This general relationship does not apply to all reactions
 - Also, it is not necessarily every $10\text{ }^{\circ}\text{C}$, the rate may double every $9\text{ }^{\circ}\text{C}$ or $11\text{ }^{\circ}\text{C}$
 - The number of degrees needed to double the rate also changes gradually as temperature increases

YOUR NOTES



16.1.3 Graphical Representations

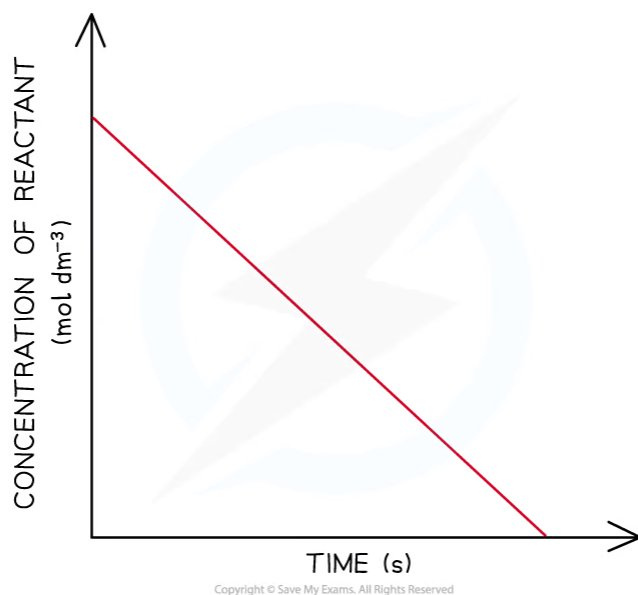
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Graphical Representations of Reaction Order

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:

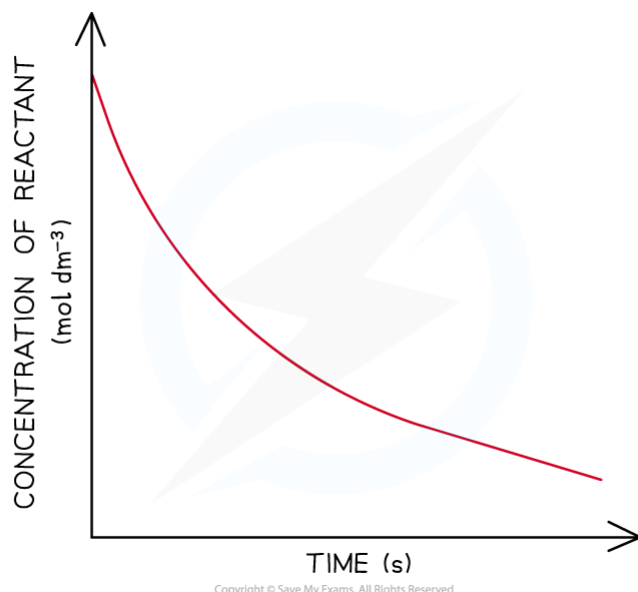


Concentration-time graph of a zero-order reaction

- 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:

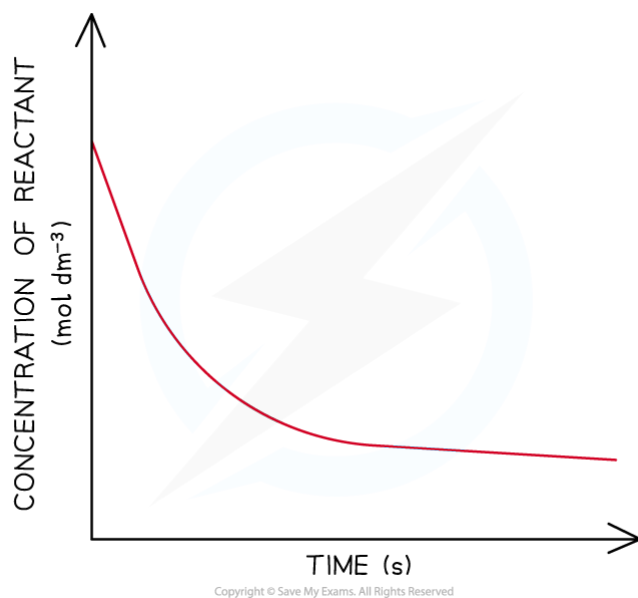
$$\text{Rate} = k$$

- 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:



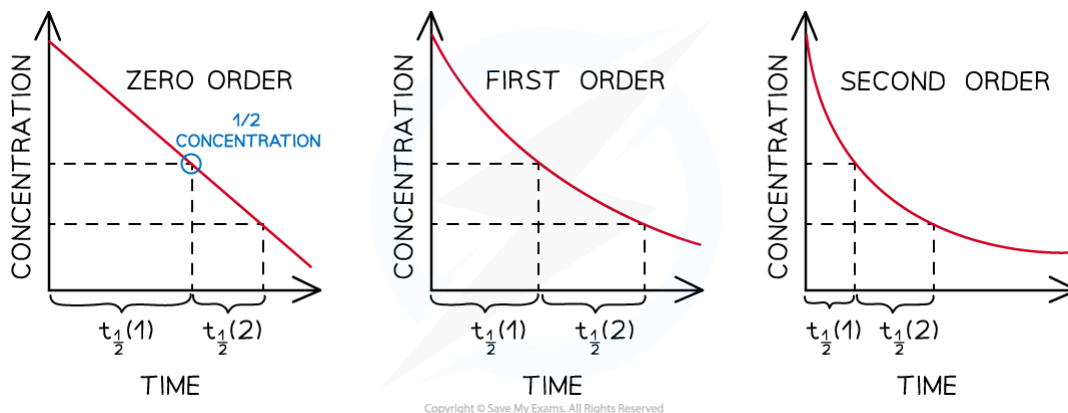
Concentration-time graph of a second-order reaction

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



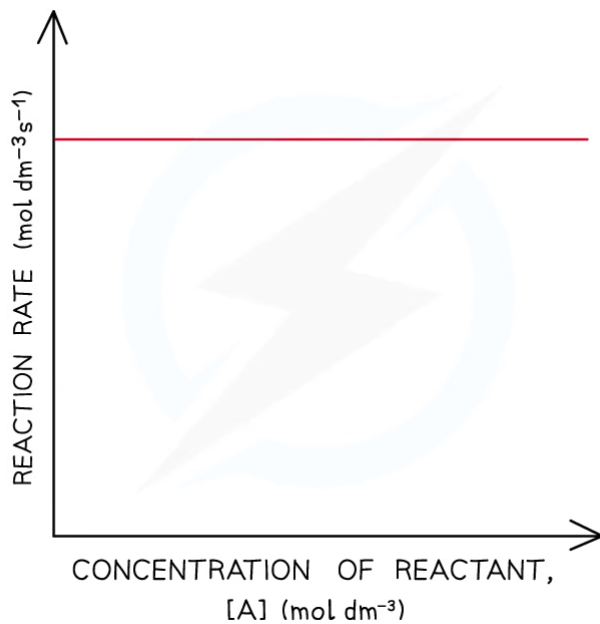
Exam Tip

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.

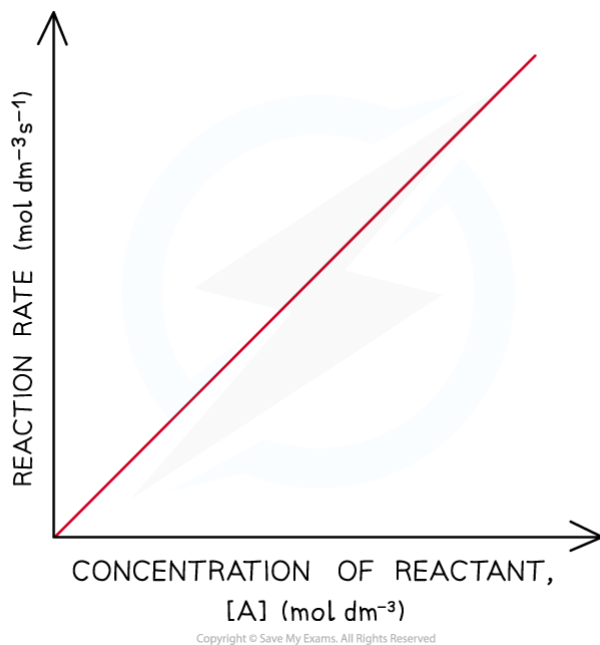
Reaction order using rate-concentration graphs

- In a **zero-order** reaction, the rate 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**



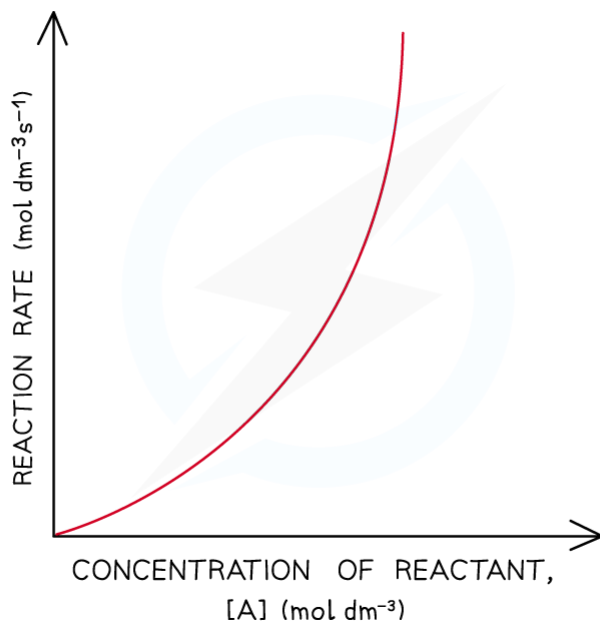
Rate-concentration graph of a zero-order reaction

- 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 = $k[A]^2$**



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Rate-concentration graphs of a second-order reaction



Exam 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.

YOUR NOTES



16.1.4 Rate Determining Step

YOUR NOTES



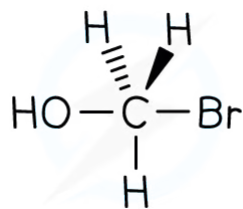
Molecularity & Rate Determining Step

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 $\text{rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$



- This suggests that both CH_3Br and OH^- take part in the slow rate-determining step
- Molecularity** is the number of reactant particles that participate in the rate-determining step
- This reaction is a **bimolecular reaction**
 - Unimolecular**: one species involved in the rate-determining step
 - Bimolecular**: two species involved in the rate-determining step
- The intermediate is derived from substances that react together to form it in the rate-determining step
 - For example, for the reaction above the intermediate would consist of CH_3Br and OH^-



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The intermediate formed from the species that are involved in the rate-determining step (and thus appear in the rate equation)

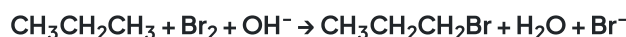


Exam Tip

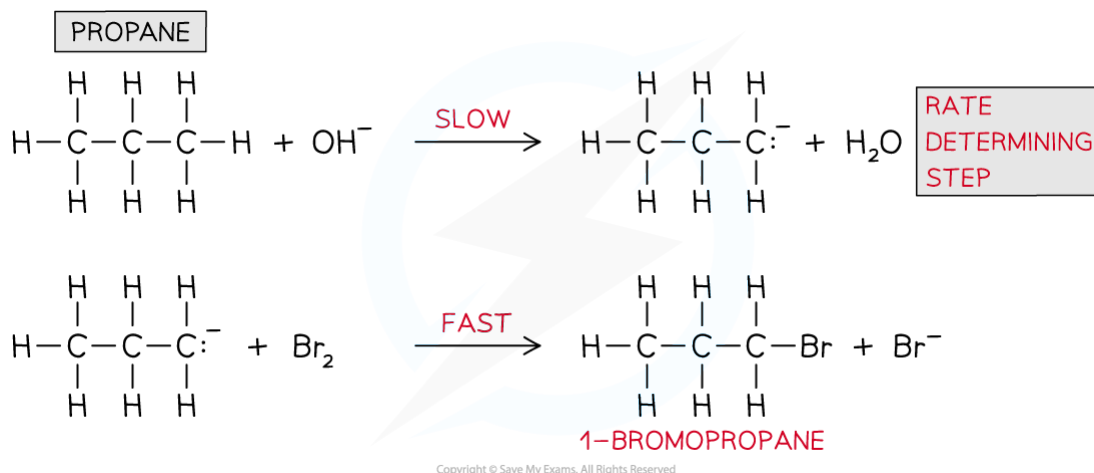
Intermediates do not feature in rate equations. Instead, the chemicals required to make the intermediate feature in the rate equation.

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 ($\text{CH}_3\text{CH}_2\text{CH}_3$) undergoes bromination under alkaline solutions
- The overall reaction is:



- The reaction mechanism is:



Reaction mechanism for the bromination of propane under alkaline conditions

- The rate equation is:

$$\text{Rate} = k[\text{CH}_3\text{CH}_2\text{CH}_3][\text{OH}^-]$$

- From the rate equation, it can be deduced that only $\text{CH}_3\text{CH}_2\text{CH}_3$ and OH^- are involved in the rate-determining step and not bromine (Br_2)
- $\text{CH}_3\text{CH}_2\text{CH}_3$ and OH^- are only involved in the first step of the reaction mechanism, therefore the rate-determining step is:
 - $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^- + \text{H}_2\text{O}$

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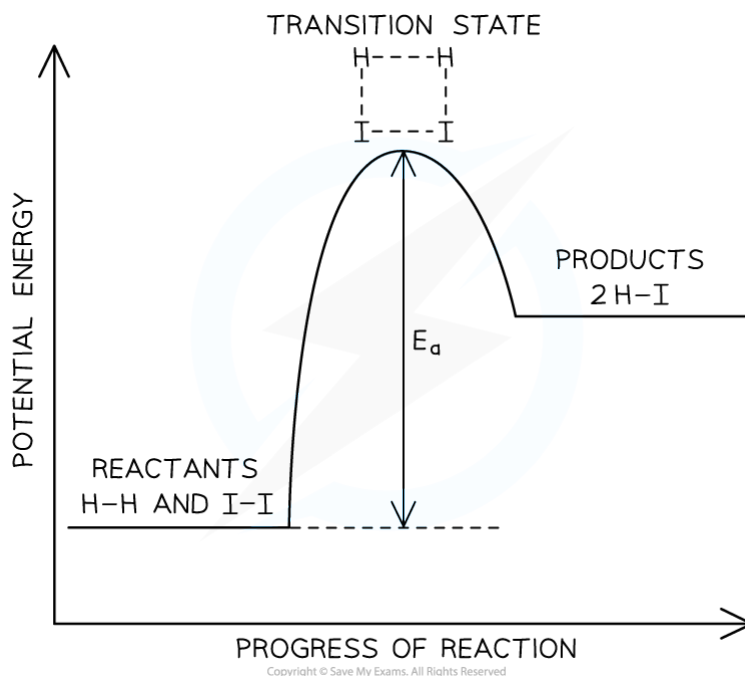
Potential Energy Level Profiles

YOUR NOTES



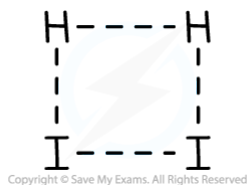
Single-step reactions

- 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



The potential energy level diagram 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



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 endothermic 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:



- 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:

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$

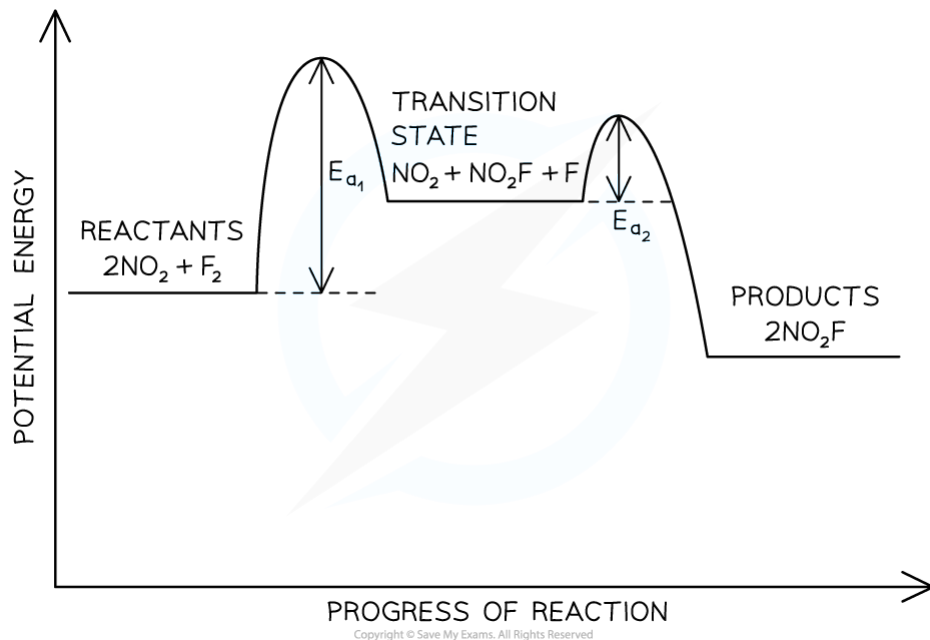
- One proposed reaction mechanism for this reaction involves the following elementary steps:
 - **Step 1:** $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$
 - **Step 2:** $\text{NO}_2 + \text{F} \rightarrow \text{NO}_2\text{F}$
- Step 1 must be the rate-determining step as it is the only step that has reactants matching the rate equation
 - Therefore, on a potential energy level diagram the activation energy for step 1 will be greater than the activation energy for step 2
- The transition state for this multi-step reaction must be:



- This can be deduced using the 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 $\text{NO}_2\text{F} + \text{F}$
 - This leaves one NO_2 along with $\text{NO}_2\text{F} + \text{F}$
- This leads to the following potential energy level diagram:

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Potential energy level diagram for the formation of nitryl fluoride

- Key points from the potential energy level diagram are:
 - The overall reaction is endothermic, as stated
 - The rate-determining step is the step that has the greatest activation energy
 - There is a labelled energy level for the transition state



Exam Tip

Multi-step reactions where the first elementary step is not the rate-determining step prove more challenging in terms of potential energy level diagrams. Remember that the rate-determining step **must** have the greatest activation energy. Do not confuse 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

YOUR NOTES



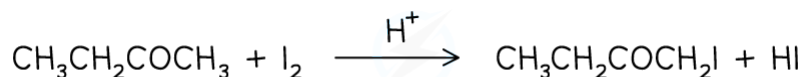
Catalysts & Mechanisms

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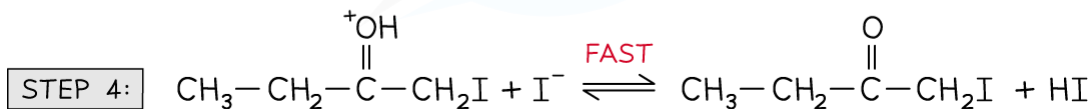
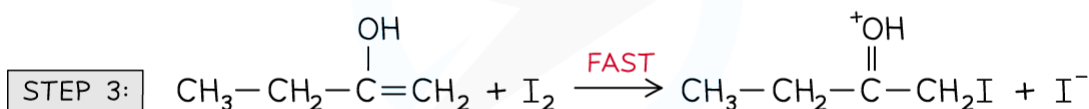
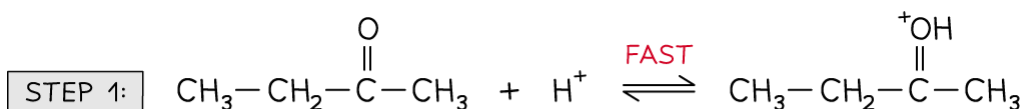
Identifying intermediates & catalyst

- When a rate equation includes a species that is not part of the chemical reaction equation then this species is a [popover id="mT5UZwSwYE9Vt6FI" label=catalyst]
- For example, the halogenation of butanone under acidic conditions
- The overall equation for this reaction is:



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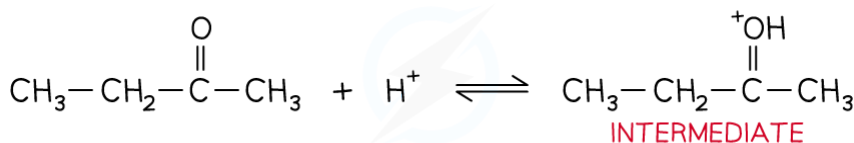
- One commonly accepted reaction mechanism is:



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Reaction mechanism for the halogenation of butanone under acidic conditions

- The rate-determining step is the slowest step, identified as step 2
- However, the $\text{CH}_3\text{CH}_2\text{C}(\text{OH}^+)\text{CH}_3$ **cannot** be used in the rate equation as it is an intermediate, not a reactant



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Reaction to form the intermediate found in the rate-determining step

- Therefore, the $\text{CH}_3\text{CH}_2\text{COCH}_3$ and H^+ that form the intermediate feature in the rate equation:

$$\text{Rate} = k[\text{CH}_3\text{CH}_2\text{COCH}_3][\text{H}^+]$$

- The H^+ is **not** a reactant in the overall chemical equation but it does appear in the rate equation
 - H^+ must, therefore, be a **catalyst**
 - This is also supported by the H^+ being used in step 1 and forming as a product in step 2

YOUR NOTES



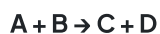
16.1.5 Mechanism Problems

YOUR NOTES



Mechanism Problems

- 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:



- The elementary steps could involve the formation of an intermediate:



- 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



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.

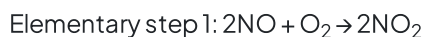
Answers

Answer 1:

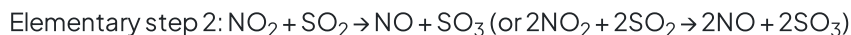
- A one step reaction mechanism is simply the overall stoichiometric equation
- Therefore, the correct answer is $2SO_2 + O_2 \rightarrow 2SO_3$

Answer 2:

- One of the two elementary steps for this two step mechanism can be taken from the question:



- The second elementary step must involve the reaction of the nitrogen dioxide formed with sulfur dioxide:





Exam Tip

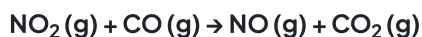
It is important that you check that the equations you are proposing for a reaction mechanism. They **must** add up to the overall stoichiometric equation, otherwise the proposed mechanism is wrong.

YOUR NOTES



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:



- The rate equation is:

$$\text{Rate} = k [\text{NO}_2]^2$$

- 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)
 - This means that in terms of [popover id="GCXR2mfBwg279t3O" label=molecularity], the rate determining step is bimolecular
- A possible reaction mechanism could therefore be:

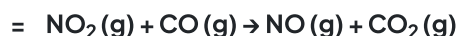
Step 1:



Step 2:



Overall:



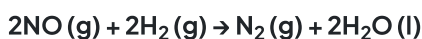


Exam Tip

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 (H₂) to form nitrogen (N₂) and water



- The reaction mechanism for this reaction is:

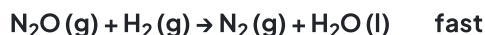
Step 1:



Step 2:



Step 3:



- The second step in this reaction mechanism is the **rate-determining step**
- The rate-determining step consists of:
 - N₂O₂ which is formed from the reaction of **two NO molecules**
 - One H₂ molecule**
- The reaction is, therefore, **second order** with respect to NO and **first order** with respect to H₂
- So, the **rate equation** becomes:

$$\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$$

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



Exam Tip

Intermediates in the mechanism **cannot** appear as substances in the rate equation. This is why you substitute the N₂O₂ in the above example. Step 1 shows that 2NO molecules are required to form the necessary N₂O₂

16.2 Activation Energy

16.2.1 The Arrhenius Equation

The Arrhenius Equation

- 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 ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)

T = TEMPERATURE (KELVIN, K)

e = MATHEMATICAL CONSTANT
(CAN BE FOUND ON YOUR CALCULATOR – IT HAS AN APPROXIMATE VALUE OF 2.718)

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- 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

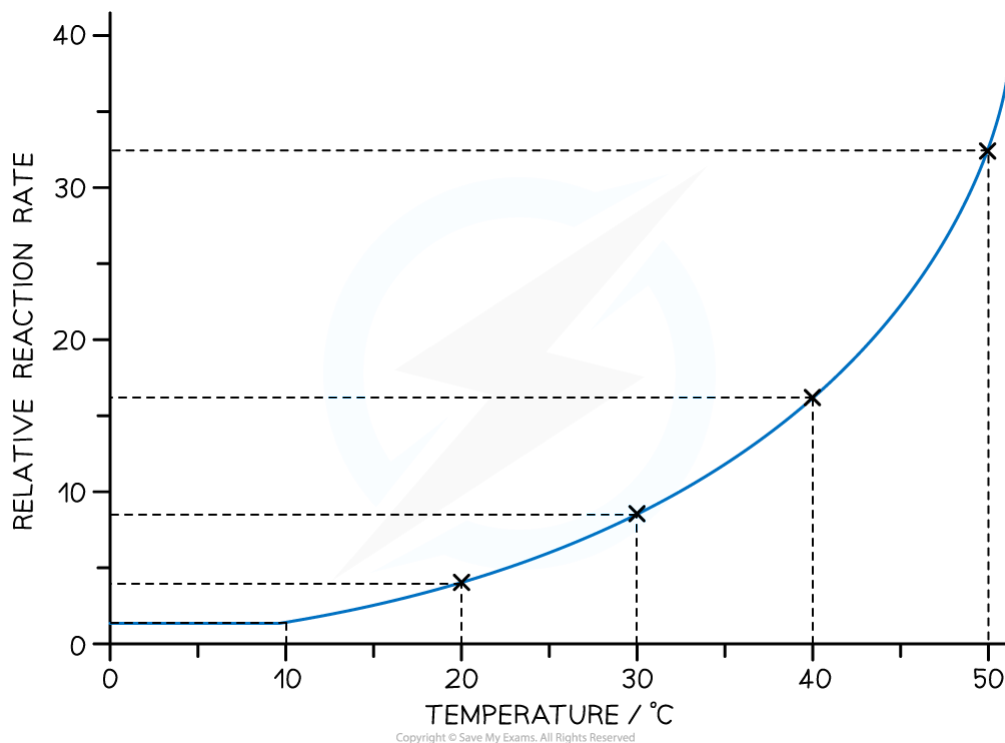
YOUR NOTES





Temperature Dependence

- The following rate-temperature graph is typical of reactions that have an activation energy, E_a , of around 50 kJ mol^{-1}



Graph showing the temperature dependence of reaction rate in the Arrhenius equation

- The graph shows a generally accepted rule that rate doubles with a temperature increase of approximately 10°C
 - This rule is not an absolute rule as values for the activation energy, E_a , of a reaction vary greatly

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:

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

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- 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



Exam 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.



Worked Example

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

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

Answer

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

REARRANGE THE EQUATION FOR E_a :

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

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

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

INSERT VALUES FROM THE QUESTION:

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

REMEMBER, E_a HAS THE UNIT kJ...

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

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16.2.2 Graphing the Arrhenius Equation

YOUR NOTES



Graphing the Arrhenius Equation

Finding the Activation Energy

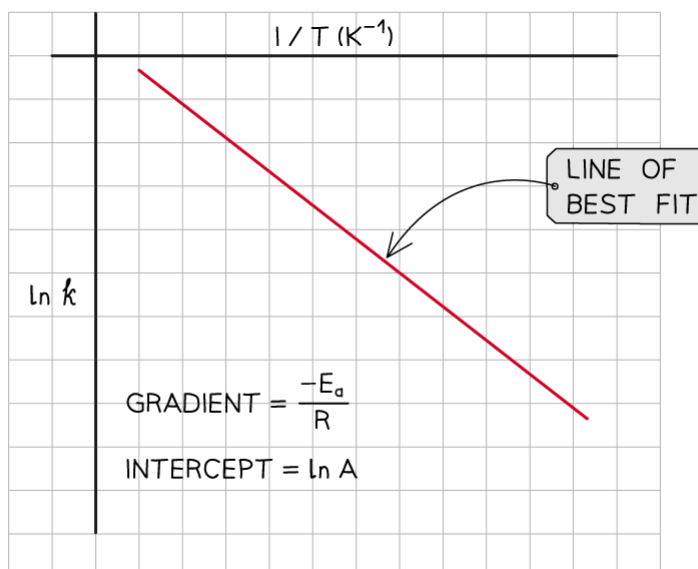
- Very often, the Arrhenius equation is used to calculate the activation energy of a reaction
- A question will either give sufficient information for the Arrhenius equation to be used or a graph can be plotted and the calculation done from the plot

Using the equation:

- Remember, it is usually easier to use the version of the Arrhenius equation after natural logs of each side have been taken

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:

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

$$y = \ln k$$

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

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

$$c = \ln A \text{ (THE } y \text{ INTERCEPT)}$$

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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}	

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Answers

Answer 1:

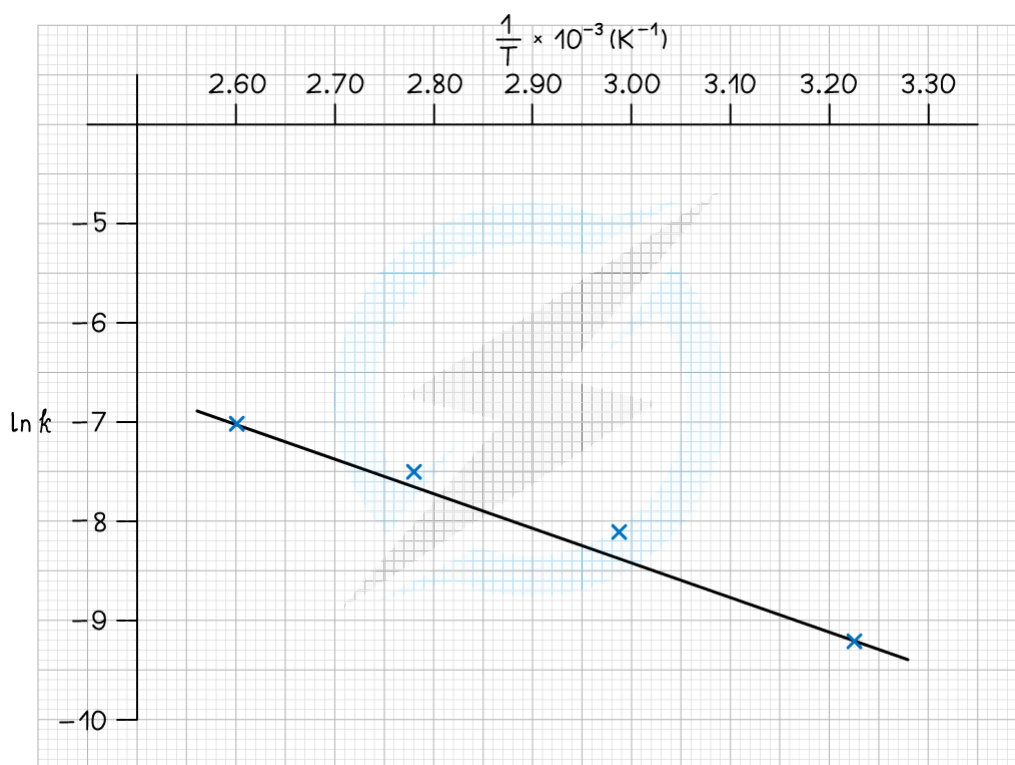
YOUR NOTES



Temperature / K	$\frac{1}{T} / \text{K}^{-1}$	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

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Answer 2:

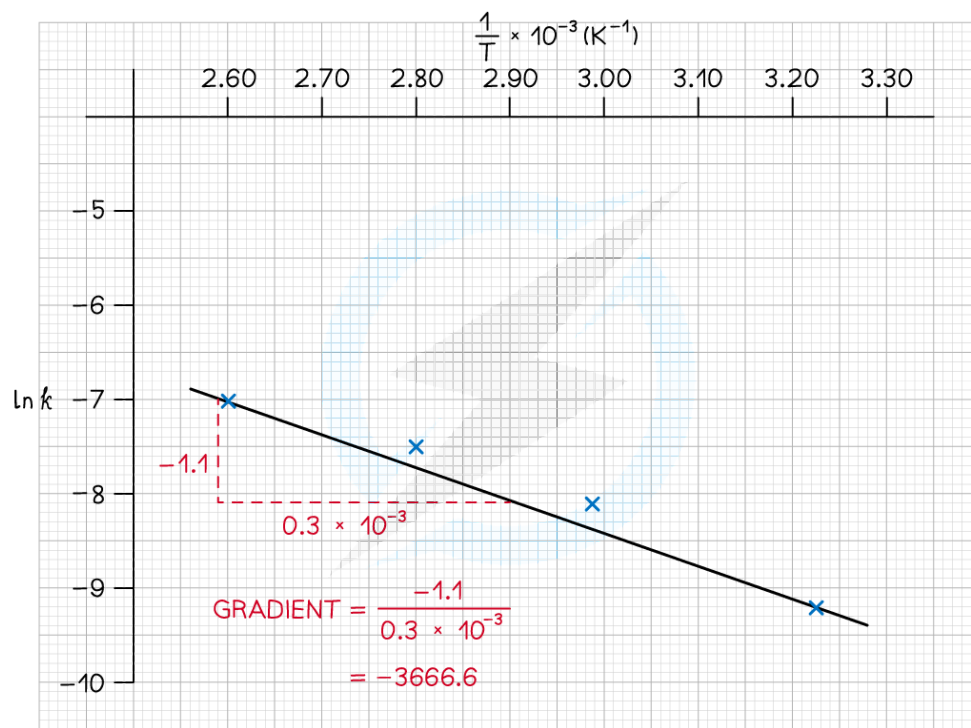


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Answer 3:

CALCULATE THE ACTIVATION ENERGY:

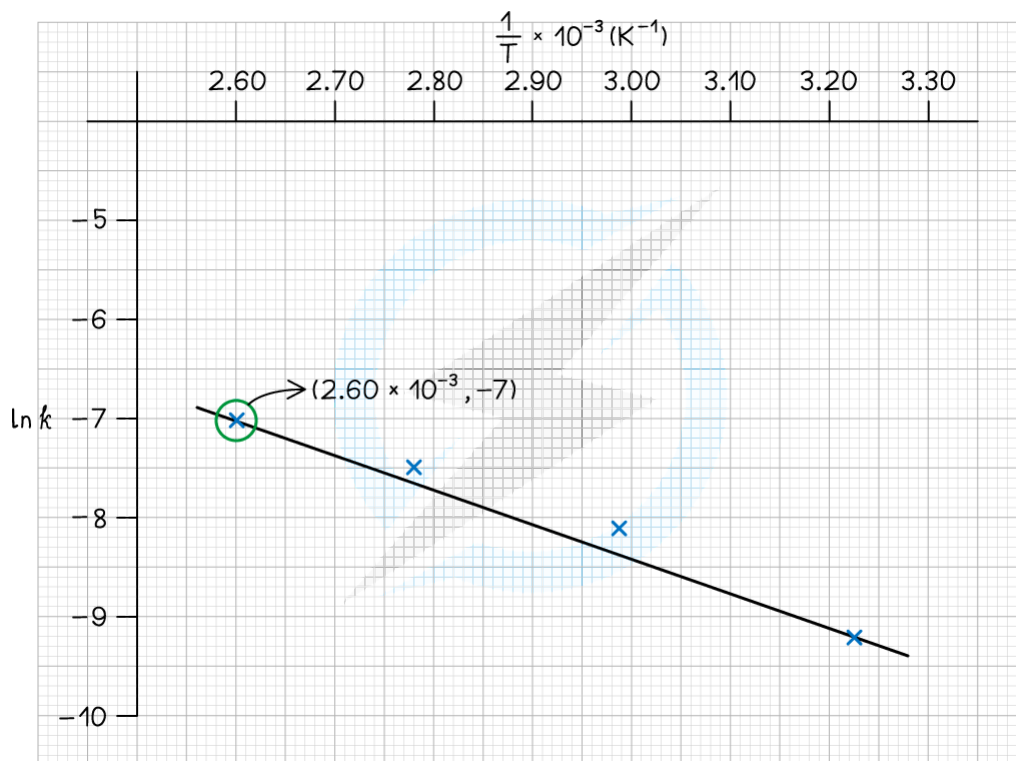


$$\text{GRADIENT} = \frac{-E_a}{R} = -3666.6$$

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

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CALCULATE A:



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CHOOSE A POINT ON THE GRAPH

 $(2.60 \times 10^{-3}, -7.0)$

USE THE FOLLOWING EQUATION:

$$y = m x + c$$

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

$$\left. \begin{array}{l} \ln k = -7.0 \\ \frac{1}{T} = 2.60 \times 10^{-3} \end{array} \right\} \begin{array}{l} \text{FROM THE POINT} \\ \text{CHOSEN ON THE GRAPH} \end{array}$$

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

$$= -3666.6$$

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

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

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

$$= 2.53$$

$$A = e^{2.53}$$

$$A = 12.55$$

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YOUR NOTES





Exam Tip

You are not required to learn these equations. 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.

YOUR NOTES



16.2.3 Activation Energy from Rate Constants

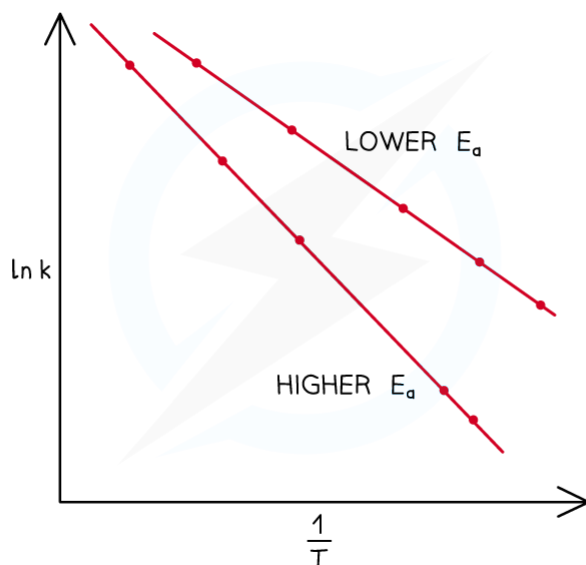
YOUR NOTES



Activation Energy from Rate Constants at Different Temperatures

Arrhenius Plots

- Arrhenius plots for two reactions with different activation energies can be drawn on the same graph



Arrhenius plots for two reactions with different activation energies

- The reaction with a steeper gradient has the higher activation energy, E_a
- This indicates that the rate constant, and therefore rate, will change quicker with temperature changes

Calculating the Activation Energy

- The activation energy, E_a , can be calculated using rate constant values, k_1 and k_2 , for two given temperatures, T_1 and T_2
- This requires the use of the following equation that is given in the data booklet:

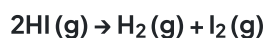
$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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Worked Example

Hydrogen iodide decomposes in the gas phase to form hydrogen and iodine



At 283 °C, the rate constant is $3.52 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ At 508 °C, the rate constant is $3.95 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$ Calculate the activation energy, E_a , for the reaction


Answer

1. Convert the temperatures from °C to K:
 - $T_1: 283 + 273 = 556 \text{ K}$
 - $T_2: 508 + 273 = 781 \text{ K}$
2. Write the appropriate Arrhenius equation from the data booklet
3. Substitute the values
4. Evaluate the equation to get the activation energy, E_a

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{3.52 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}}{3.95 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}}\right) = \frac{E_a}{8.31 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{781 \text{ K}} - \frac{1}{556 \text{ K}}\right)$$

$$-11.6281 = \frac{E_a}{8.31} \times -5.1815 \times 10^{-4}$$

$$\frac{-11.6281}{-5.1815 \times 10^{-4}} = \frac{E_a}{8.31}$$

$$\frac{-11.6281}{-5.1815 \times 10^{-4}} \times 8.31 = E_a$$

$$E_a = 1.87 \times 10^5 \text{ J mol}^{-1}$$

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