

Cambridge (CIE) A Level Chemistry



Your notes

Simple Rate Equations, Orders of Reaction & Rate Constants

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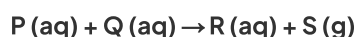
Chemical Kinetics Terminology

- The **rate of reaction** refers to the change in the amount or concentration of a reactant or product per unit time and can be found by:
- Measuring the **decrease in the concentration of a reactant** OR
- Measuring the **increase in the concentration of a product** over time
 - The units of rate of reaction are $\text{mol dm}^{-3} \text{s}^{-1}$

$$\text{Rate of reaction} = \frac{\text{change in concentration}}{\text{time}}$$

Rate equation

- Rate equations can **only** be determined **experimentally**
 - They cannot be found from the **stoichiometric equations**
- For the general reaction of P and Q reacting together to form products:



- The rate equation will include:
 - A rate / proportionality constant, k
 - This can be calculated from the gradient of the graph
 - The concentration of the reactants
 - They are shown in square brackets for concentration, e.g. [P] and [Q]
 - The order to which each reactant is raised
 - They are shown as powers, e.g. m and n
 - The order with respect to any reactant can **only** be 0, 1 or 2

$$\text{Rate of reaction} = k [\text{P}]^m [\text{Q}]^n$$

- The rate equation does not include the concentration of the products
 - This is because they do not affect the rate of reaction

Example reactions for rate equations

- 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

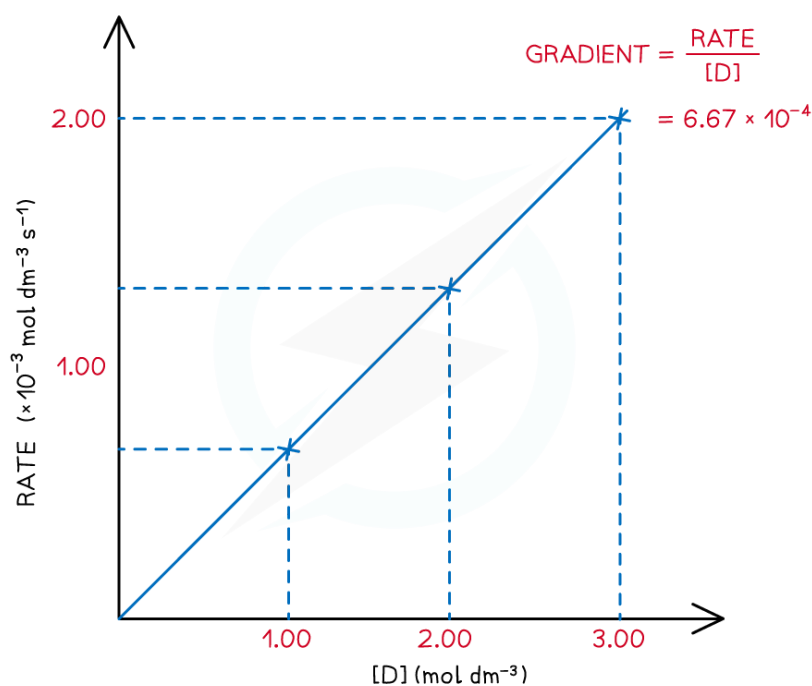
Rate of reactions table

[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}



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



Rate of reaction over various concentrations of D

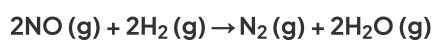
- For the above reaction, the rate equation is:

$$\text{Rate} = k [D]$$

- The value of the rate / proportionality constant, k , can be calculated from the results or from two points on the graph
 - For this example, the value is $6.67 \times 10^{-4} \text{ s}^{-1}$

Nitric oxide and hydrogen

- The reaction between nitric oxide and hydrogen is:



- The experimentally determined **rate equation** for this reaction is:

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



Your notes

- By keeping the concentration of one reactant constant, the rate equation can show the effect of each reactants
- Keeping $[\text{H}_2]$ constant:
 - This means that the effect of $[\text{H}_2]$ is fixed
 - Any change in the rate of reaction is caused by $[\text{NO}]$
 - The change in the rate of reaction is **proportional to the square** of $[\text{NO}]$:

$$\text{Rate} = k_1 [\text{NO}]^2$$

- Keeping $[\text{NO}]$ constant:
 - This means that effect of $[\text{NO}]$ is fixed
 - Any change in the rate of reaction is caused by $[\text{H}_2]$
 - The change in the rate of reaction is **proportional** to $[\text{H}_2]$:

$$\text{Rate} = k_2 [\text{H}_2]$$

- Both sets of experiments show different parts of the same **overall rate equation**:

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

- Notice that the $[\text{H}_2]$ does not have an order of 2
 - This is because the order must be determined experimentally, not from the equation

Order of reaction

- The **order** of a reactant shows how the concentration of a reactant affects the rate of reaction
- It is the power to which the concentration of that reactant is raised in the rate equation
 - The order can be 0, 1 or 2
- 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



Your notes

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

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

- For example, in the rate equation above, the reaction is:
 - Second-order with respect to NO
 - First-order with respect to H_2
 - Third-order overall (2 + 1)



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

Answers:

1. The order with respect to dinitrogen pentoxide:
 - 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**
2. The effect of tripling $[\text{N}_2\text{O}_5]$:
 - 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**

Deducing Orders

- To derive the rate equation for a reaction, you can use a graph or a table of results
 - The type and shape of the graph indicates the order with respect to a reactant
 - A table of results requires calculation
- Take the reactants one at a time and find the order with respect to each reactant individually



Your notes

■ Steps to derive a rate equation:

1. Identify two experiments where:

- The concentration of one reactant changes and the concentrations of all other reactants remain constant
- Calculate what has happened to the concentration of the reactant
- Calculate what has happened to the rate of reaction
- Determine the order with respect to that reactant

2. Repeat this for all of the reactants

- Work methodically through each reactant, one at a time
- Determine the order with respect to all reactants



Worked Example

Use the information in the table to determine the rate equation for the nucleophilic substitution of 2-bromo-2-methylpropane by hydroxide ions:

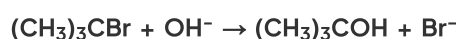


Table to show the experimental data of the above reaction

Experiment	Initial $[(\text{CH}_3)_3\text{CBr}]$ / mol dm^{-3}	Initial $[\text{OH}^-]$ / 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}

Answer:

Order with respect to $[(\text{CH}_3)_3\text{CBr}]$:

- Using experiments 1 and 2:
 - The $[\text{OH}^-]$ has remained 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)

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

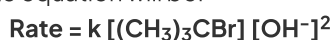
- Using experiments 1 and 3:
 - The $[(\text{CH}_3)_3\text{CBr}]$ has remained constant
 - The $[\text{OH}^-]$ has doubled
 - The rate of reaction has increased by a factor of 4 (i.e. increased by 2^2)
 - Therefore, the order with respect to $[\text{OH}^-]$ is 2 (second order)



Your notes

Building the rate equation:

- Once you know the order with respect to all of the reactants, you put them together to form the rate equation
 - If a reactant is order 0, it should not appear in the rate equation
 - If a reactant is order 1, then it features in the rate equation
 - There is no need to include the number 1 as a power
 - If a reactant is order 2, then it features in the rate equation with the number 2 as a power
- For this reaction, the rate equation will be:

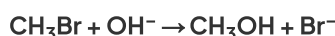


Half-life

- The **half-life** ($t_{1/2}$) is the time taken for the concentration of a **limiting reactant** to become half of its initial value

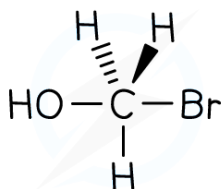
Rate-determining step & intermediates

- The **rate-determining step** is the slowest step in a 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** = $k [\text{CH}_3\text{Br}] [\text{OH}^-]$



- This suggests that **both** CH_3Br and OH^- take part in the **slow rate-determining step**
- This reaction is, therefore, 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^-

The intermediate formed during the reaction of CH_3Br and hydroxide ions



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



Chemical Kinetics Calculations

Order of reaction

- The **order of reaction** shows how the concentration of a reactant affects the rate of reaction

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

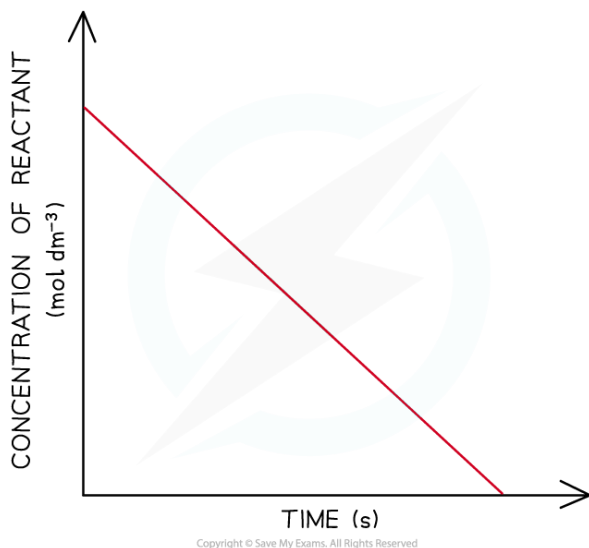
- When m or n is zero = the concentration of the reactants does not affect the rate
- When **the order of reaction** (m or n) of a reactant is 0, its concentration is ignored
- The **overall order of reaction** is the sum of the powers of the reactants in a rate equation
- For example, in the reaction below, the overall order of reaction is 2 ($1 + 1$)

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

Order of reaction from concentration–time graphs

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

A zero-order concentration–time graph



A zero-order concentration–time graph is a straight line

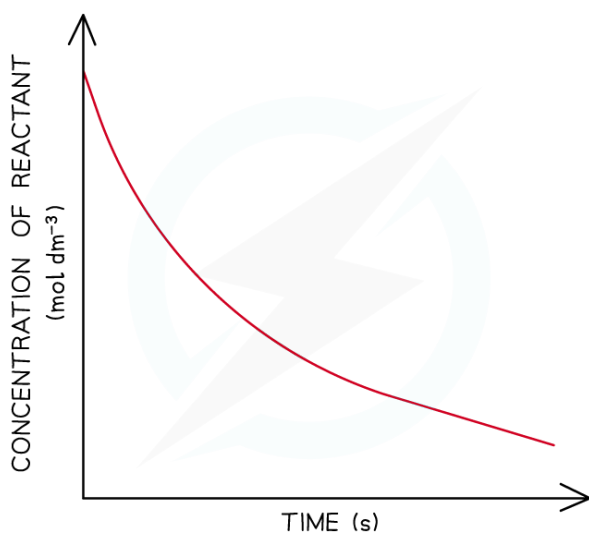
- In a **first-order** reaction, the concentration of the reactant decreases with time

- The graph is a curve going downwards and eventually plateaus

A first-order concentration-time graph



Your notes

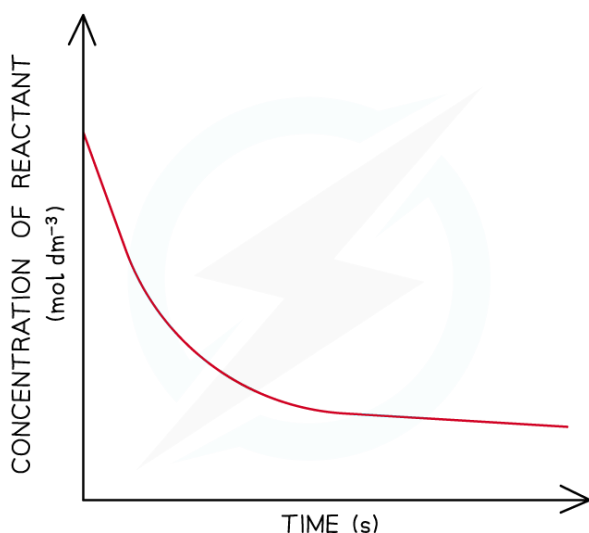


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A first-order concentration-time graph is a smooth curve

- 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 in a first-order reaction
 - The graph is a steeper curve going downwards

A second-order concentration-time graph



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A second-order concentration-time graph is a smooth and steep curve

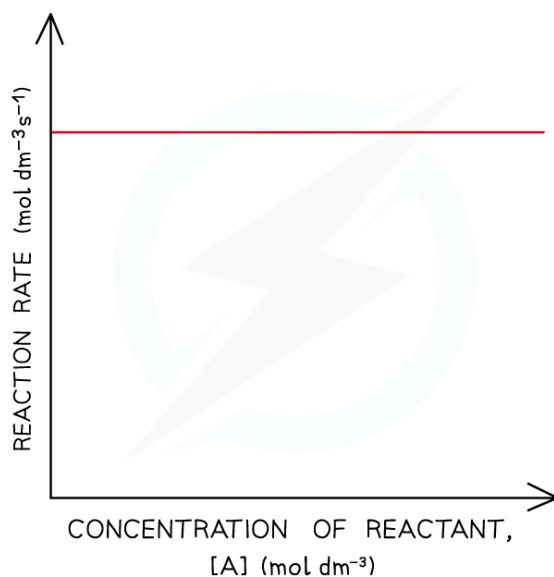
Order of reaction from initial rate



Your notes

- The **progress** of the reaction can be followed by measuring the **initial rates** of the reaction using various **initial concentrations** of each reactant
- These rates can then be plotted against time in a rate-time graph
- 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**

A zero-order rate-time graph



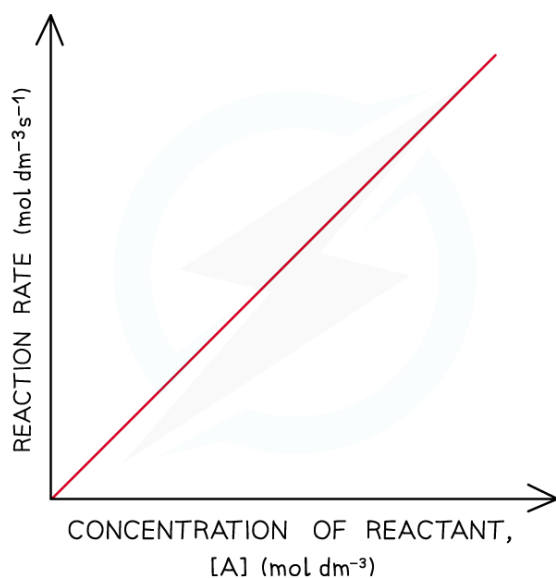
A zero-order rate-time graph is a flat line

- In a **first-order** reaction, the rate is directly proportional to the concentration of a reactant
 - 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]**

A first-order rate-time graph



Your notes

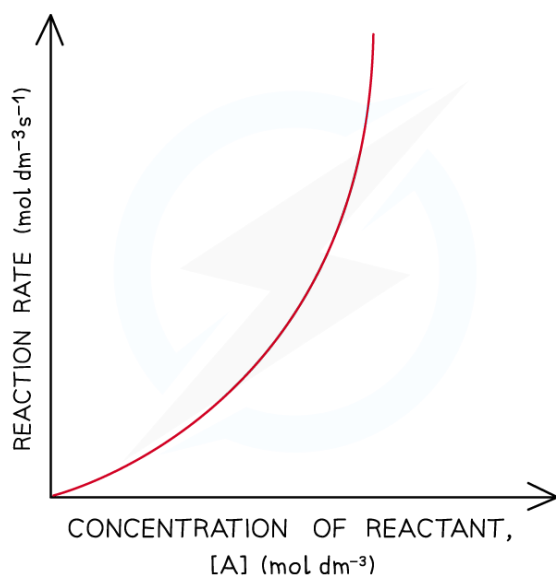


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A first-order rate-time graph is a straight line with a fixed gradient, k

- In a **second-order** reaction, the rate is directly proportional to the square of concentration of a reactant
 - 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 = $k[A]^2$**

A second-order rate-time graph



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A second-order rate-time graph is a smooth curve

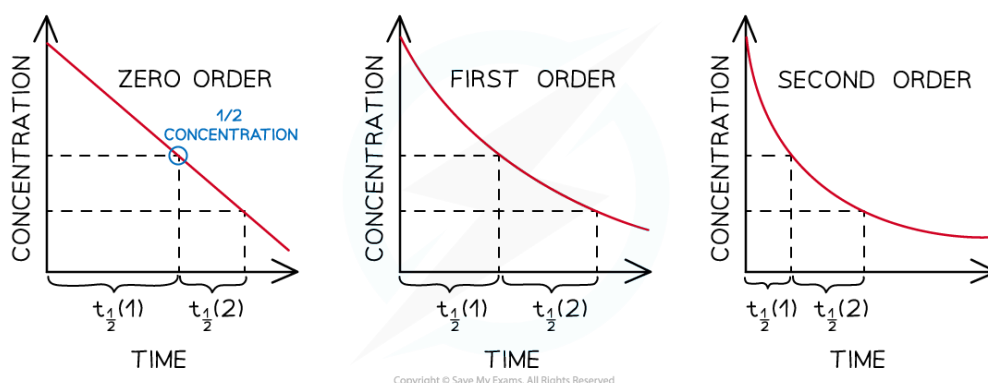
Order of reaction from half-life



Your notes

- 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

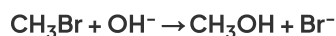
Half-lives of zero, first and second-order reactions



Zero-order reactions have a decreasing half-life, first-order reactions have a constant half-life and second-order reactions have an increasing half-life

Calculating the initial rate

- The **initial rate** can be calculated by using the **initial concentrations** of the reactants in the rate equation
- For example, in the reaction of bromomethane (CH_3Br) with hydroxide (OH^-) ions to form methanol (CH_3OH):



- The rate **equation** is:

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

- Where $k = 1.75 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
- If the **initial concentrations** of CH_3Br and OH^- are 0.0200 and $0.0100 \text{ mol dm}^{-3}$ respectively, the **initial rate** of reaction is:
 - $\text{Rate} = k [\text{CH}_3\text{Br}] [\text{OH}^-]$

- Initial rate = $1.75 \times 10^{-2} \times (0.0200) \times (0.0100)$

- Initial rate = $3.50 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

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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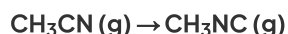
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First Order Reaction Half-life

- The **half-life** of a **first-order** reaction is **independent** of the concentration of reactants
 - This means that despite the **concentrations of the reactants decreasing** during the reaction
 - The amount of time taken for the **concentrations of the reactants to halve** will remain the same throughout the reaction
 - The concentration-time graph for a first-order reaction is a downward curve with a constant half-life.
- The **rearrangement** of the **methyl group** (CH_3) in ethanenitrile (CH_3CN) is an example of a first-order reaction with rate equation **rate = $k[\text{CH}_3\text{CN}]$**

Rearrangement of the CH_3 group in CH_3CN



- Experimental data on the changes in concentration over time suggests that the **half-life** is constant
 - Even if the half-lives are slightly different from each other, they can still be considered to remain constant
- This means that no matter what the original concentration of the CH_3CN is, the half-life will always be around 10.0 minutes

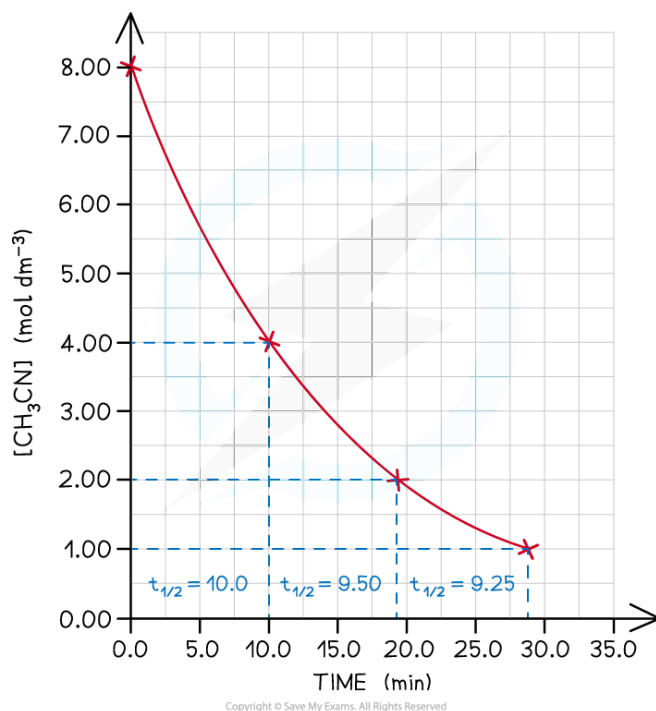
Half-life table

Change in $[\text{CH}_3\text{CN}]$ (mol dm^{-3})	Half-life (minutes)
8.00 - 4.00	10.0
4.00 - 2.00	9.50
2.00 - 1.00	9.25

Graph of $[\text{CH}_3\text{CN}]$ over time



Your notes



Since this is a first-order reaction, the time taken for the concentration to halve remains constant



Worked Example

Using the half-life of first-order reactions in calculations

The change in concentration of a reactant over time is recorded in the following table:

Time (s)	0	200	400	600	800	1000	1200	1400	1600
[reactant] $\times 10^{-4}$ (mol dm^{-3})	5.8	4.4	3.2	2.5	1.7	1.2	0.8	0.5	0.3

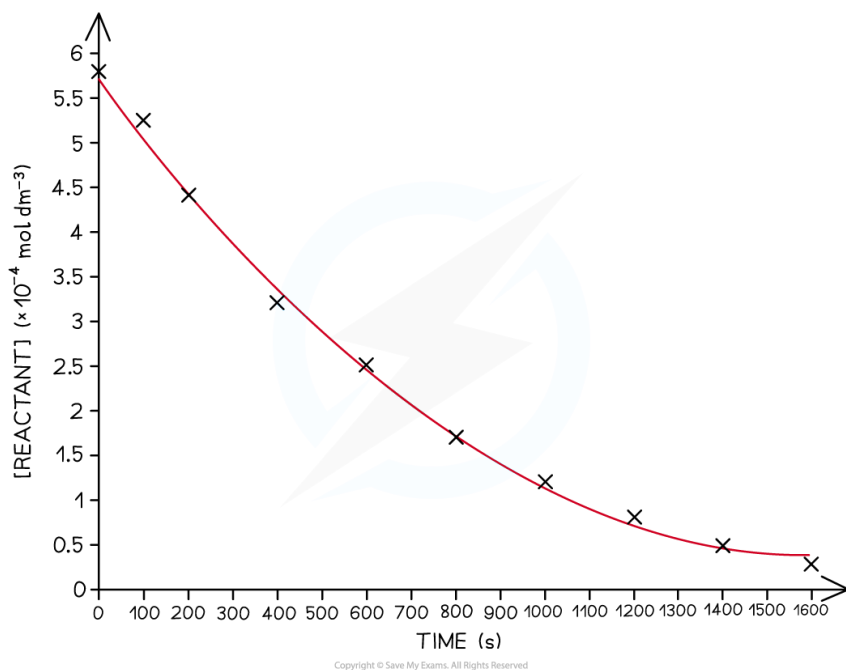
1. Draw a graph of concentration against time for these results.
2. Determine the first and second half-lives and hence determine the order of the reaction.

Answer

1. Draw a graph of concentration against time for these results.



Your notes



2. Determine the first and second half-lives and hence determine the order of the reaction.

- Find the first and second half-lives by determining when the concentrations halve using the graph:

	Change in [reactant] ($\times 10^{-4} \text{ mol dm}^{-3}$)	Half-life (s)
First half-life	5.80 - 2.90	470 - 0 = 470
Second half-life	2.90 - 1.45	920 - 470 = 450

- Determine the reaction order
 - It is a first-order reaction
 - The successive half-lives remain reasonably constant (around 450 seconds) throughout the reaction

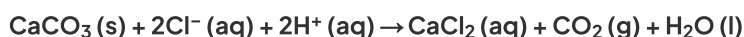


Rate Constant Calculations

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

Calculating the rate constant from the initial rate

- The reaction of calcium carbonate (CaCO_3) with chloride (Cl^-) ions to form calcium chloride (CaCl_2) 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:



$$\text{Rate} = k [\text{CaCO}_3] [\text{Cl}^-]$$

- 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

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

- To find the rate constant (k):
 - Rearrange the rate equation to find k :
 - $$\text{Rate} = k [\text{CaCO}_3] [\text{Cl}^-] \rightarrow k = \frac{\text{rate}}{[\text{CaCO}_3] [\text{Cl}^-]}$$
 - Substitute the values of one of the experiments to find k :
 - For example, using the measurements from experiment 1
 - $$k = \frac{4.38 \times 10^{-6}}{[0.0250] [0.0125]}$$
 - $$k = 1.40 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

- The measurements from experiments 2 or 3 could also have been used to find k
 - They would also give the same result of $1.40 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Calculating the rate constant from the half-life

- The rate constant (k) can also be calculated from the half-life of a reaction
- You are only expected to deduce k from the half-life of a **first-order** reaction as the calculations for **second** and **zero-order** reactions are more complicated
- For a **first-order** reaction, the **half-life** is related to the rate constant by the following expression:

$$t_{1/2} = \frac{0.693}{k}$$

- Rearranging the equation to find k gives:

$$k = \frac{0.693}{t_{1/2}}$$

- So, for a **first-order** reaction such as the **methyl** (CH_3) **rearrangement** in **ethanenitrile** (CH_3CN) with a half-life of 10.0 minutes the rate constant is:

- $k = \frac{0.693}{10.0 \times 60} = 1.16 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

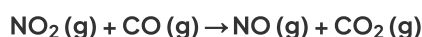


Kinetics of Multi-Step Reactions

- The **reaction mechanism** of a reaction describes how many steps are involved in the **making** and **breaking** of bonds during a chemical reaction
- It is the slowest step in a reaction and includes the reactants that have an impact on the reaction rate when their concentrations are changed
 - Therefore, all reactants that appear in the **rate equation** will also appear in the rate-determining step
 - This means that zero-order reactants and **intermediates** will not be present in the rate-determining step

Predicting the reaction mechanism

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



- The rate equation is:

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

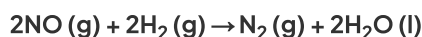
- From the rate equation, it can be concluded that the reaction is **zero order** with respect to $\text{CO}(\text{g})$ and **second order** with respect to $\text{NO}_2(\text{g})$
- This means that there are **two molecules** of $\text{NO}_2(\text{g})$ involved in the **rate-determining step**
- A possible reaction mechanism could therefore be:
 - **Step 1:**
 - $2\text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{NO}_3(\text{g})$ **slow** (rate-determining step)
 - **Step 2:**
 - $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$ **fast**
 - **Overall:**
 - $2\text{NO}_2(\text{g}) + \text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{NO}_3(\text{g}) + \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$
 - Which simplifies to $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

Predicting the reaction order & deducing the rate equation



Your notes

- The **order** of a reactant and thus the rate equation can be deduced from a reaction mechanism given that the rate-determining step is known
- For example, the reaction of nitrogen oxide (NO) with hydrogen (H₂) to form nitrogen (N₂) and water



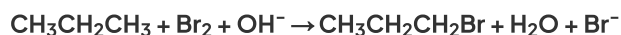
- The reaction mechanism for this reaction is:
 - **Step 1:**
 - $\text{NO (g)} + \text{NO (g)} \rightarrow \text{N}_2\text{O}_2\text{(g)}$ **fast**
 - **Step 2:**
 - $\text{N}_2\text{O}_2\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{H}_2\text{O (l)} + \text{N}_2\text{O (g)}$ **slow** (rate-determining step)
 - **Step 3:**
 - $\text{N}_2\text{O (g)} + \text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + \text{H}_2\text{O (l)}$ **fast**
- 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**

Identifying the rate-determining step

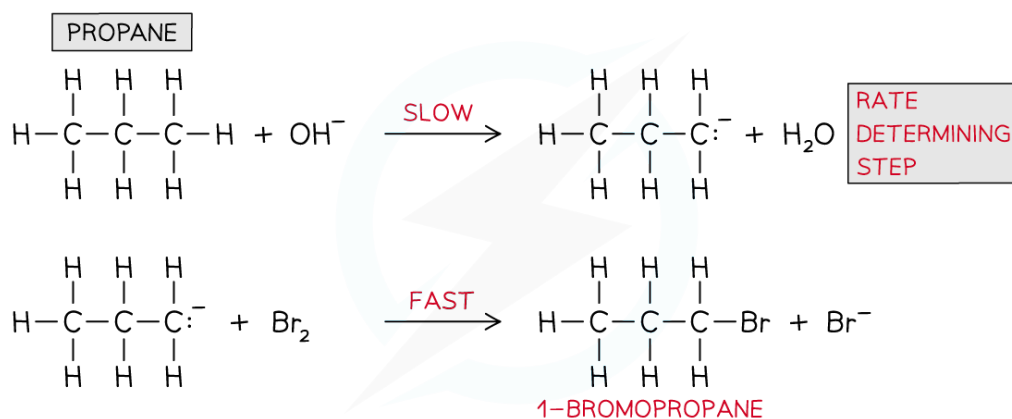
- The rate-determining step can be identified from a rate equation given that the reaction mechanism is known
- For example, propane (CH₃CH₂CH₃) undergoes bromination under alkaline solutions
- The overall reaction is:



- The reaction mechanism is:



Your notes



Reaction mechanism of the bromination of propane under alkaline conditions

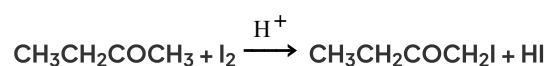
- The rate equation is:

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

- From the rate equation, it can be deduced that only CH_3COCH_3 and OH^- are involved in the **rate-determining step** and not bromine (Br_2)
- CH_3COCH_3 and OH^- are only involved in step 1
 - Therefore, the **rate-determining step** is step 1 of the reaction mechanism

Identifying intermediates & catalyst

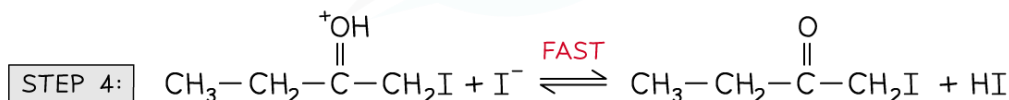
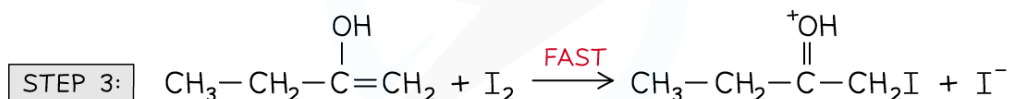
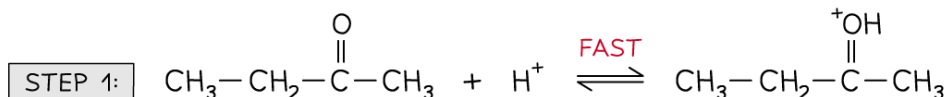
- When a rate equation includes a species that is not part of the chemical reaction equation then this species is a **catalyst**
- For example, the halogenation of butanone under acidic conditions
- The reaction mechanism is:



- The reaction mechanism is:



Your notes



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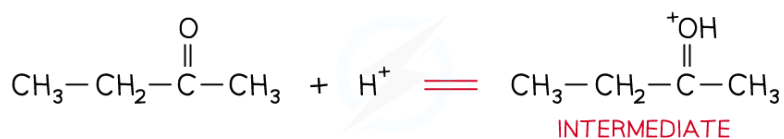
Reaction mechanism of the halogenation of butanone under acidic conditions

The rate equation is:

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

- The H^+ is not present in the **chemical reaction equation** but **does** appear in the rate equation
 - H^+ must therefore be a **catalyst**
- Furthermore, the rate equation suggests that $\text{CH}_3\text{CH}_2\text{COCH}_3$ and H^+ must be involved in the rate-determining (slowest) step
- The $\text{CH}_3\text{CH}_2\text{COCH}_3$ and H^+ appear in the rate-determining step in the form of an **intermediate** (which is a combination of the two species)

The intermediate formed in the reaction of $\text{CH}_3\text{CH}_2\text{COCH}_3$ and H^+



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This intermediate is formed in the rate-determining step



Effect of Temperature on the Rate Constant

- At higher temperatures, a greater proportion of molecules have energy greater than the activation energy
- Since the **rate constant** and **rate of reaction** are **directly proportional** to the fraction of molecules with energy equal or greater than the activation energy, then at higher temperatures:
 - The **rate constant** increases
 - The **rate of reaction** increases
- The relationship between the rate constant and the temperature is given by the following equation:

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

- Where:
 - $\ln k$ = natural logarithm of the rate constant
 - A = constant related to the collision frequency and orientation of the molecules
 - E_a = activation energy (joules, J)
 - R = gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)
 - T = temperature (kelvin, K)
- A varies only a little bit with temperature, it can be considered a constant
- E_a and R are also constants
- A graph of $\ln k$ against $\frac{1}{T}$ gives a line with an equation of the form $y = mx + c$

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

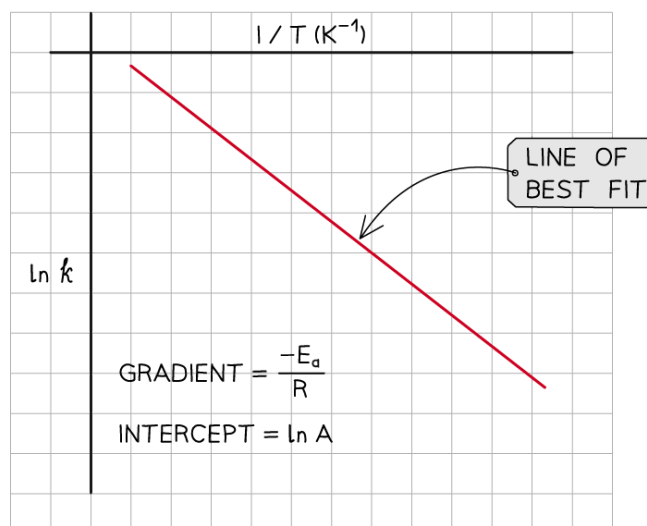
- Where:
 - $y = \ln k$
 - $x = \frac{1}{T}$
 - $m = \frac{-E_a}{R}$ (the gradient)



Your notes

- $c = \ln A$ (the y-intercept)
- The equation shows that 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

Example graph of $\ln k$ over $1/T$



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



Examiner Tips and Tricks

You are not required to learn this equation however it is helpful in understanding the effects of temperature on the rate constant.