🧪 Cambridge (CIE) A Level Chemistry

## Simple Rate Equations, Orders of Reaction & Rate Constants

Contents

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 mol dm^{-3} 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:

$$P\,(aq) + Q\,(aq) \rightarrow R\,(aq) + S\,(g)$$
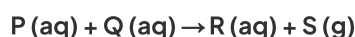
- The rate equation will include:

  - 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

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

- 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

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

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

Rate of reactions table

| Get more and ace your exams at savemyexams.com |

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

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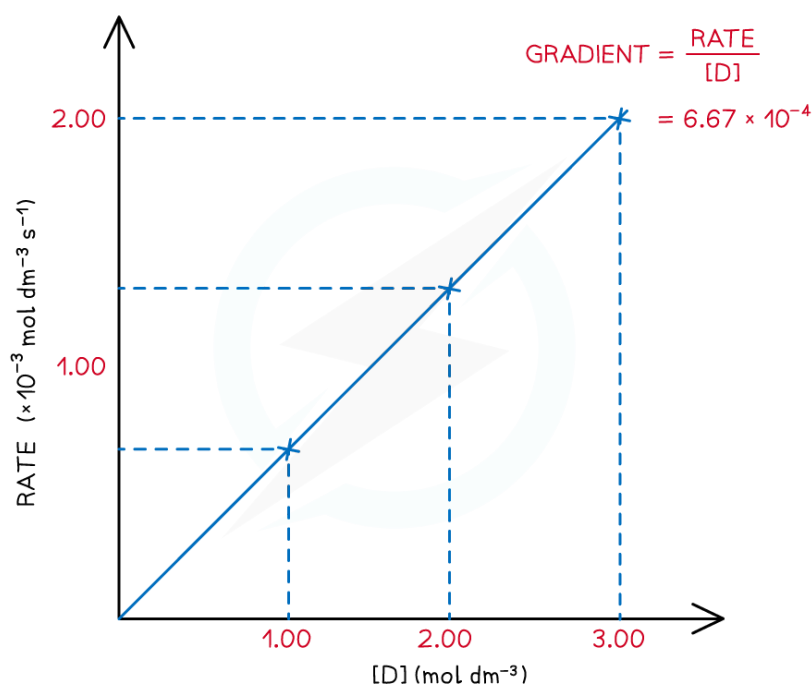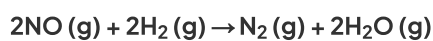

Rate of reaction over various concentrations of D

- For the above reaction, the rate equation is:

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

- 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 is 6.67 x 10^{-4} s^{-1}

Nitric oxide and hydrogen

- The reaction between nitric oxide and hydrogen is:

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

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

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

- By keeping the concentration of one reactant constant, the rate equation can show the effect of each reactants

- Keeping $[H_2]$ constant:

  - This means that the effect of $[H_2]$ is fixed

  - Any change in the rate of reaction is caused by $[NO]$

  - The change in the rate of reaction is **proportional to the square** of $[NO]$:

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

- Keeping $[NO]$ constant:

  - This means that effect of $[NO]$ is fixed

  - Any change in the rate of reaction is caused by $[H_2]$

  - The change in the rate of reaction is **proportional** to $[H_2]$:

$$\text{Rate} = k_2 \, [H_2]$$

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

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

- Notice that the $[H_2]$ 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

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

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

- 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:

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

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:

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 $[N_2O_5]$:

   - 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 or results requires calculation

- Take the reactants one at a time and find the order with respect to each reactant individually

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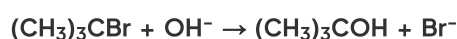
$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

Table to show the experimental data of the above reaction

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

Answer:

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

- Using experiments 1 and 2:

  - The [OH-] has remained constant
  - The $[(CH_3)_3CBr]$ has doubled
  - 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 $[OH^-]$:

- Using experiments 1 and 3:

  - The $[(CH_3)_3CBr]$ has remained constant
  - The $[OH^-]$ 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 $[OH^-]$ is 2 (second order)

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:

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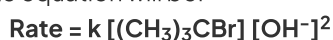
Half-life

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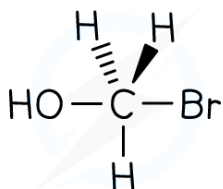
Rate-determining step & intermediates

- 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 [CH_3Br] [OH^-]

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$
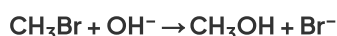
- This suggests that **both** CH_3Br and OH^- take part in the **slow rate-determining step**

- 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

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

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

- 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)

$$\text{Rate} = k\,[NO_2]\,[Cl_2]$$

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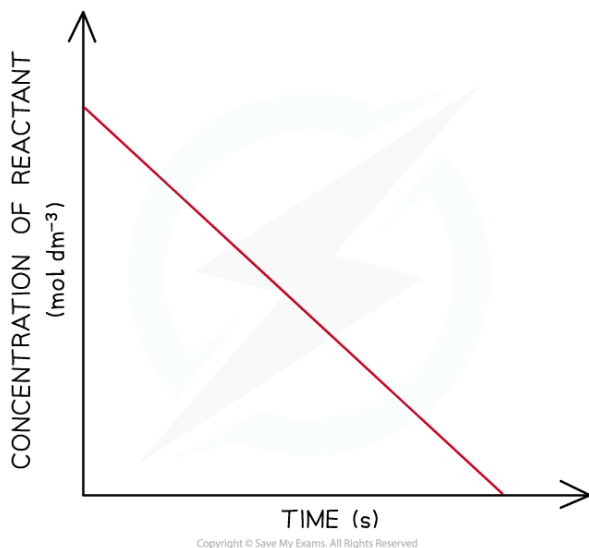
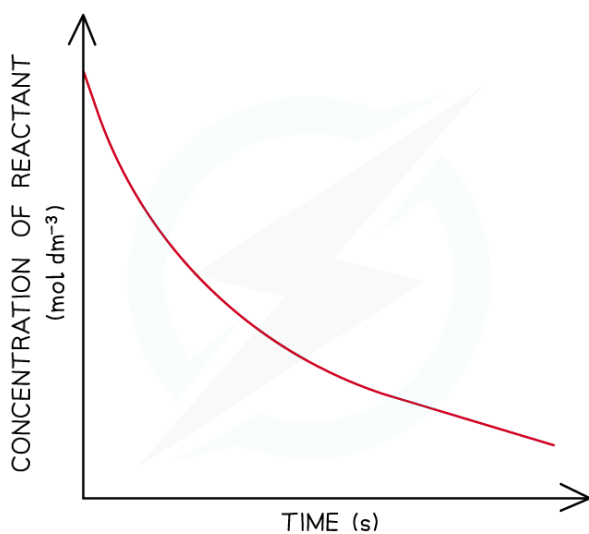*A zero-order concentration-time graph is a straight line*

- 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

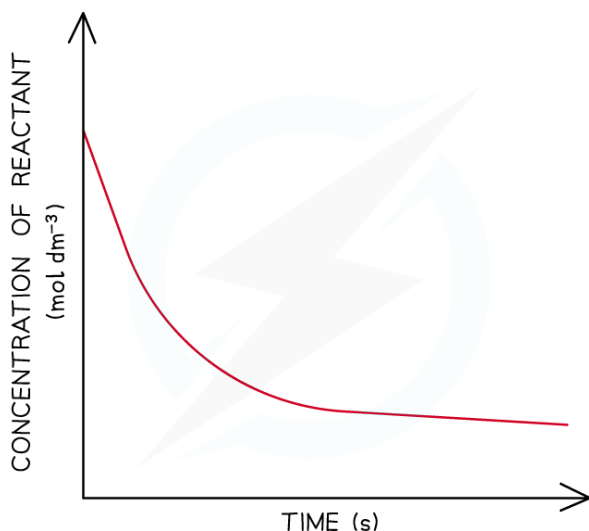*A first-order concentration-time graph is a smooth curve*

- 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

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

# Order of reaction from initial rate

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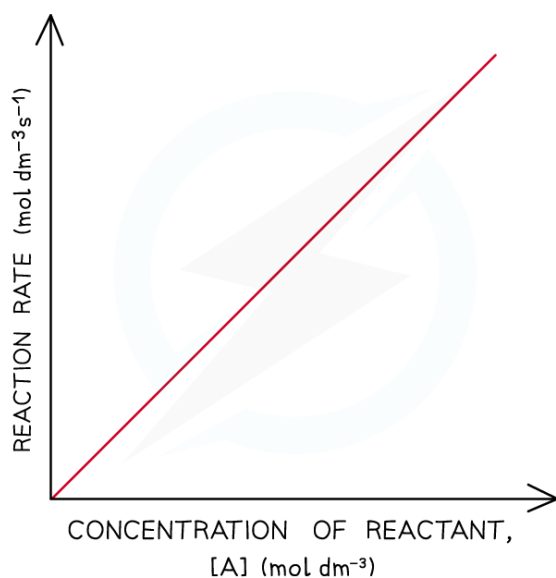
A zero-order rate-time graph
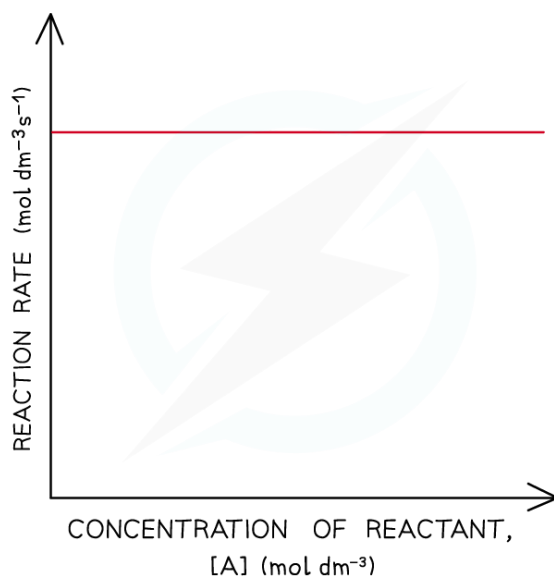
A zero-order rate-time graph is a flat line

- 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

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
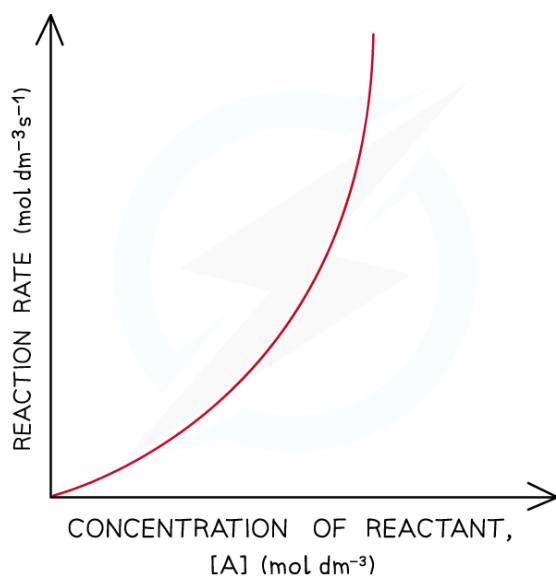

A second-order rate-time graph is a smooth curve

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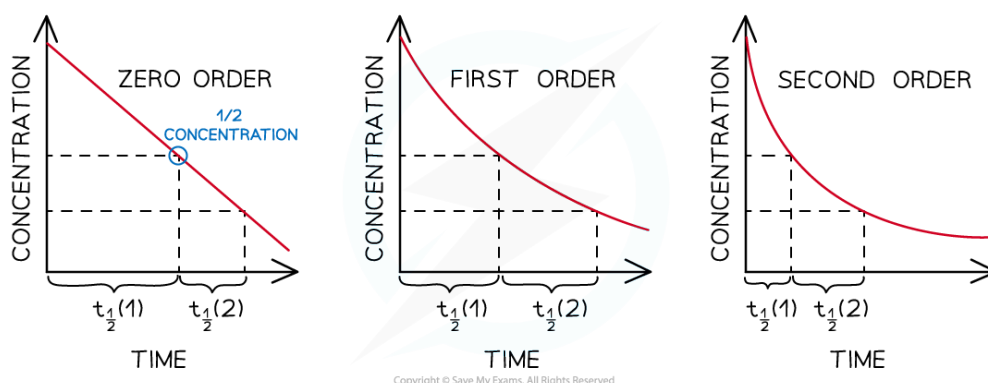
Zero-order reactions have a decreasing half-life, first-order reactions have a constant half-life and second-order reactions have an increasing half-life

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):

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$
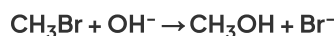
- The rate **equation** is:

$$\text{Rate} = k\,[CH_3Br]\,[OH^-]$$

- Where $k = 1.75 \times 10^{-2}\ dm^{-2}\ mol^{-1}\ s^{-1}$

- If the **initial concentrations** of CH_3Br and OH^- are 0.0200 and 0.0100 mol dm^{-3} respectively, the **initial rate** of reaction is:

    - $\text{Rate} = k\,[CH_3Br]\,[OH^-]$

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

- Initial rate = 3.50×10^{-6} mol dm^{-3} 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:

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

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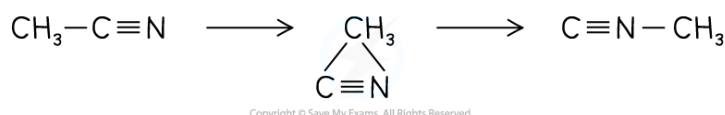
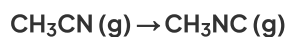$$= \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$$

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 [CH₃CN]**

Rearrangement of the CH₃ group in CH₃CN

$$CH_3-C\equiv N \longrightarrow \begin{array}{c} CH_3 \\ \diagup \backslash \\ C\equiv N \end{array} \longrightarrow C\equiv N - CH_3$$

Copyright © Save My Exams. All Rights Reserved

$$CH_3CN\,(g) \rightarrow CH_3NC\,(g)$$

- 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
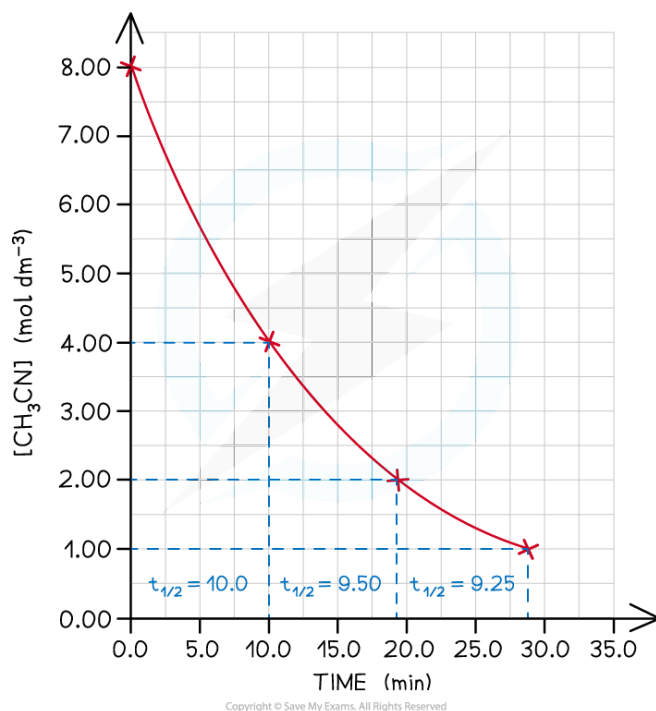
Half-life table

Change in [CH₃CN] (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 [CH₃CN] over time

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:

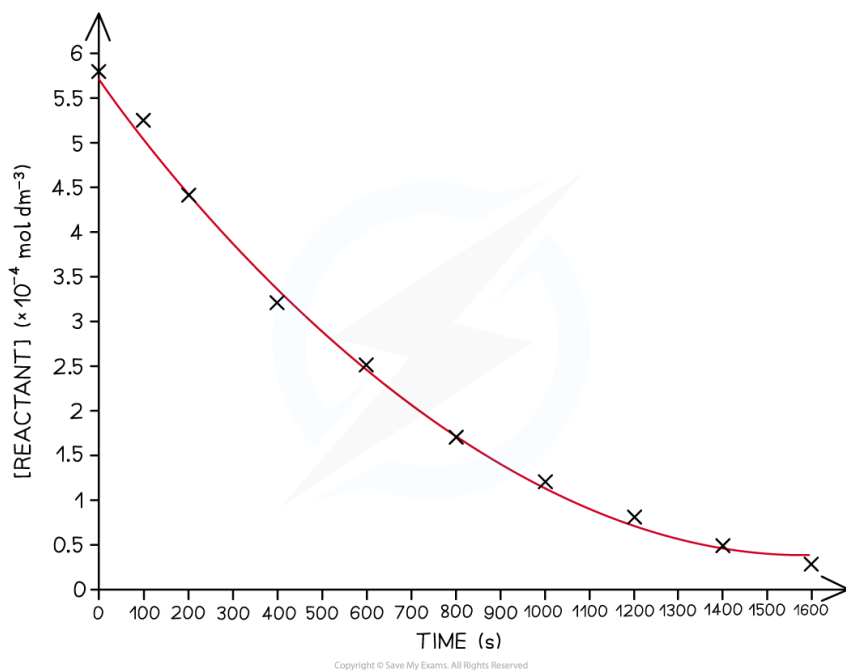| Time (s)	0	200	400	600	800	1000	1200	1400	1600
[reactant] x10^{-4} (mol dm^{-3})	5.8	4.4	3.2	2.5	1.7	1.2	0.8	0.5	0.3

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.

Copyright © Save My Exams. All Rights Reserved

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] (x10^{-4} 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:

$$CaCO_3 \text{ (s)} + 2Cl^- \text{ (aq)} + 2H^+ \text{ (aq)} \rightarrow CaCl_2 \text{ (aq)} + CO_2 \text{ (g)} + H_2O \text{ (l)}$$
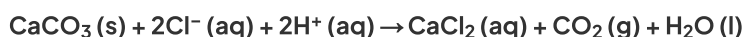
$$\text{Rate} = k \, [CaCO_3] \, [Cl^-]$$

- 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

	[CaCO$_3$] (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):
    - Rearrange the rate equation to find k:
    - $\text{Rate} = k \, [CaCO_3] \, [Cl^-] \rightarrow k = \dfrac{\text{rate}}{\left[CaCO_3 \right] \left[Cl^- \right]}$

- Substitute the values of one of the experiments to find k:
    - For example, using the measurements from experiment 1
    - $k = \dfrac{4.38 \times 10^{-6}}{[0.0250][0.0125]}$
    - $k = 1.40 \times 10^{-2} \, dm^3 \, mol^{-1} \, s^{-1}$

- The measurements from experiments 2 or 3 could also have been used to find k

  - They would also give the same result of 1.40×10^{-2} dm^3 mol^{-1} s^{-1}
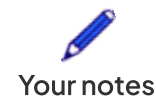
Calculating the rate constant from the half-life

- 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:

  - $k = \dfrac{0.693}{10.0 \times 60} = 1.16 \times 10^{-3}$ dm^3 mol^{-1} 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:

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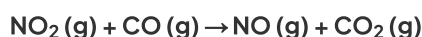
- The rate equation is:

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

- From the rate equation, it can be concluded that the reaction is **zero order** with respect to CO (g) and **second order** with respect to NO_2 (g)

- This means that there are **two molecules** of NO_2 (g) involved in the **rate-determining step**

- A possible reaction mechanism could therefore be:

  - **Step 1:**

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

  - **Step 2:**

    - $NO_3 \text{ (g)} + CO \text{ (g)} \rightarrow NO_2 \text{ (g)} + CO_2 \text{ (g)}$ **fast**

  - **Overall:**

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

    - Which simplifies to $NO_2 \text{ (g)} + CO \text{ (g)} \rightarrow NO \text{ (g)} + CO_2 \text{ (g)}$

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 given that the rate-determining step is known

- For example, the reaction of nitrogen oxide (NO) with hydrogen (H_2) to form nitrogen (N_2) and water

$$2NO \text{ (g)} + 2H_2 \text{ (g)} \rightarrow N_2 \text{ (g)} + 2H_2O \text{ (l)}$$
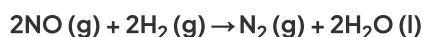
- The reaction mechanism for this reaction is:

  - **Step 1:**

    - $NO \text{ (g)} + NO \text{ (g)} \rightarrow N_2O_2 \text{ (g)}$ **fast**

  - **Step 2:**

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

  - **Step 3:**

    - $N_2O \text{ (g)} + H_2 \text{ (g)} \rightarrow N_2 \text{ (g)} + H_2O \text{ (l)}$ **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**
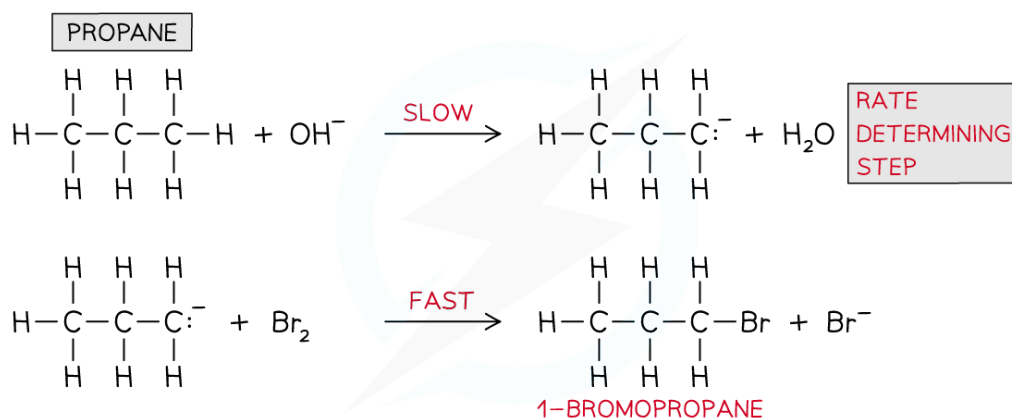
Identifying the rate-determining step

- 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:

$$CH_3CH_2CH_3 + Br_2 + OH^- \rightarrow CH_3CH_2CH_2Br + H_2O + Br^-$$
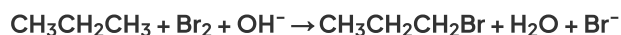
- The reaction mechanism is:

PROPANE

Reaction mechanism of the bromination of propane under alkaline conditions

- The rate equation is:

$$Rate = k\,[CH_3CH_2CH_3]\,[OH^-]$$

- 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
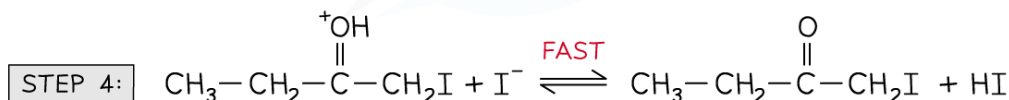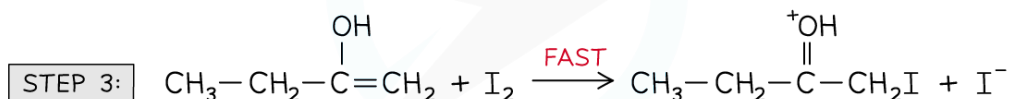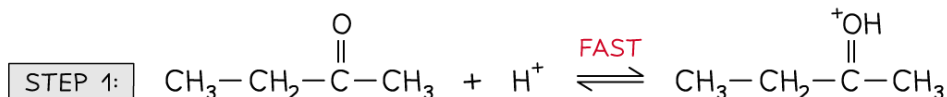
Identifying intermediates & catalyst

- 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:
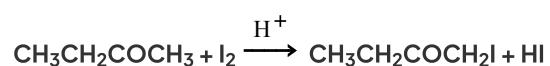
$$CH_3CH_2COCH_3 + I_2 \xrightarrow{\ H^+\ } CH_3CH_2COCH_2I + HI$$

- The reaction mechanism is:

STEP 1: $CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \; + \; H^+ \; \rightleftharpoons \; CH_3-CH_2-\overset{\overset{\displaystyle +OH}{\|}}{C}-CH_3$ **FAST**

STEP 2: $CH_3-CH_2-\overset{\overset{\displaystyle +OH}{\|}}{C}-CH_3 \; \xrightarrow{\text{SLOW}} \; CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 \; + \; H^+$

STEP 3: $CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 \; + \; I_2 \; \xrightarrow{\text{FAST}} \; CH_3-CH_2-\overset{\overset{\displaystyle +OH}{\|}}{C}-CH_2I \; + \; I^-$

STEP 4: $CH_3-CH_2-\overset{\overset{\displaystyle +OH}{\|}}{C}-CH_2I \; + \; I^- \; \rightleftharpoons \; CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2I \; + \; HI$ **FAST**

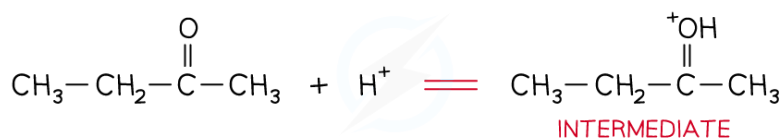*Reaction mechanism of the halogenation of butanone under acidic conditions*

The rate equation is:

Rate = k [CH$_3$CH$_2$COCH$_3$] [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 $CH_3CH_2COCH_3$ and H$^+$ must be involved in the rate-determining (slowest) step

- The $CH_3CH_2COCH_3$ 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 CH$_3$CH$_2$COCH$_3$ and H$_+$

$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \; + \; H^+ \; =\!\!=\!\!= \; CH_3-CH_2-\overset{\overset{\displaystyle +OH}{\|}}{C}-CH_3$

INTERMEDIATE

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 J K^{-1} 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

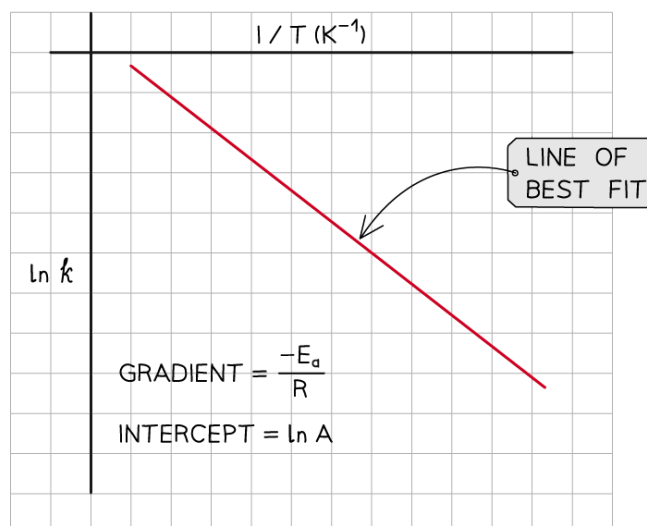$$\ln\ k = \frac{-E_a}{R}\ \frac{1}{T} + \ln\ A$$

- Where:

  - y = ln k

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

  - m = $\frac{-E_a}{R}$ (the gradient)

- - 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 –Ea/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.