eunoia
JUNIOR COLLEGE

2023 JC1 H2 CHEMISTRY (9729)
CORE IDEA 3: TRANSFORMATION
TOPIC 6: REACTION KINETICS

Name: ____ Civics Group: _________

Students should be able to:

- **(a)** explain and use the terms: *rate of reaction; rate equation; order of reaction; rate constant; half-life of a reaction; rate-determining step; activation energy; catalysis*
- **(b)** construct and use rate equations of the form rate = $k[A]^m[B]^n$ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including:
  - (i) deducing the order of a reaction by the initial rates method
  - (ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs
  - (iii) verifying that a suggested reaction mechanism is consistent with the observed kinetics
  - (iv) predicting the order that would result from a given reaction mechanism
  - (v) calculating an initial rate using concentration data [integrated forms of rate equations are not required]
- **(c)** (i) show understanding that the half-life of a first-order reaction is independent of concentration
  - (ii) use the half-life of a first-order reaction in calculations
- **(d)** calculate a rate constant using the initial rates method
- **(e)** devise a suitable experimental technique for studying the rate of a reaction, from given information
- **(f)** explain qualitatively, in terms of frequency of collisions, the effect of concentration changes on the rate of a reaction
- **(g)** show understanding, including reference to the Boltzmann distribution, of what is meant by the term *activation energy*
- **(h)** explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction
- **(i)** (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, *i.e.* one of lower activation energy, giving a larger rate constant
  - (ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution
- **(j)** outline the different modes of action of homogeneous and heterogeneous catalysis, including:
  - (i) the Haber process
  - (ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines
  - (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide
  - (iv) catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction
- **(k)** describe enzymes as biological catalysts which may have specific activity
- **(l)** explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical system

REFERENCES

1 **Chemistry for Advanced Level,** by Peter Cann & Peter Hughes, John Murray (Publishers) Ltd, 2002
2 **Chemistry,** Chris Conoley & Phil Hills, Harper Collins Publishers Ltd, 2002
3 **Chemistry, the Molecular Nature of Matter & Change,** Martin S. Silberberg, McGraw-Hill, 2003
4 **Chemistry the Central Science,** Brown, LeMay & Bursten, Prentice-Hall, 2006

LECTURE CONTENT

1 Introduction

Reaction kinetics is the study of the rate of chemical reactions. Some aspects that we study include the factors which affect rate of reactions (*e.g.* concentration, temperature, *etc*.) and how the reactions occur (*e.g.* if the reaction involves only one step or multiple steps, what bonds are broken or formed during the reaction, the molecularity of each of the steps (i.e. whether the reaction is unimolecular or bimolecular), the activation energy barrier *etc*.).

LO **(a)** explain and use the terms: *rate of reaction*

1.1 Rate of Reaction

*The **rate of reaction** is defined as the **change in concentration of a reactant or product per unit time**.*

- $\text{rate of reaction} = \dfrac{\text{change in concentration of a reactant or product}}{\text{time}}$
- units: mol dm^{-3} s^{-1} (*or* mol dm^{-3} min^{-1} *or* mol dm^{-3} h^{-1})
- By convention, rate is a **positive quantity**.
- Consider the reaction: $a\mathbf{A} + b\mathbf{B} \rightarrow c\mathbf{C}$ where *a*, *b* and *c* are stoichiometric coefficients of the balance chemical equation. The rate of reaction is given by:

$$\text{rate} = -\frac{1}{a}\frac{d[\mathbf{A}]}{dt} = -\frac{1}{b}\frac{d[\mathbf{B}]}{dt} = \frac{1}{c}\frac{d[\mathbf{C}]}{dt}$$

i.e. $\dfrac{\mathbf{1}}{\boldsymbol{a}} \times \text{rate of consumption of } \mathbf{A} = \dfrac{\mathbf{1}}{\boldsymbol{b}} \times \text{rate of consumption of } \mathbf{B} = \dfrac{\mathbf{1}}{\boldsymbol{c}} \times \text{rate of formation of } \mathbf{C}$.

It is necessary to divide the rate of reaction with respect to the reactants or products by the respective coefficient *i.e. a*, *b* and *c* in the balanced equation to ensure that **the numerical value of reaction rate is the same** regardless of the choice of species used as reference.

The negative sign is included before the reactant concentrations to convert the negative change in reactant concentration to a positive value for the rate (since the change in reactant concentration is always negative as the reaction proceeds).

Example 1

When dilute aqueous solution of peroxodisulfate(VI) and iodide ions are mixed, the following reaction occurs:

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

Suppose the rate of reaction was found to be 0.100 mol dm^{-3} s^{-1}, determine the following:

(a) rate of formation of I_2(aq)
(b) rate of consumption of $S_2O_8^{2-}$(aq)
(c) rate of formation of SO_4^{2-}(aq)

$$\boxed{\text{Rate} = -\frac{1}{2}\frac{d[I^-]}{dt} = -\frac{d[S_2O_8^{2-}]}{dt} = \frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[SO_4^{2-}]}{dt}}$$

(a) rate of formation of $I_2 = \frac{d[I_2]}{dt} =$

(b) rate of consumption of $S_2O_8^{2-} = -\frac{d[S_2O_8^{2-}]}{dt} = \frac{d[I_2]}{dt} =$

(c) rate of formation of $SO_4^{2-} = \frac{d[SO_4^{2-}]}{dt} =$

1.2 Expressing Rate of Reaction

Based on the definition, we should be able to determine the rate of reaction from a graph of concentration-versus-time.

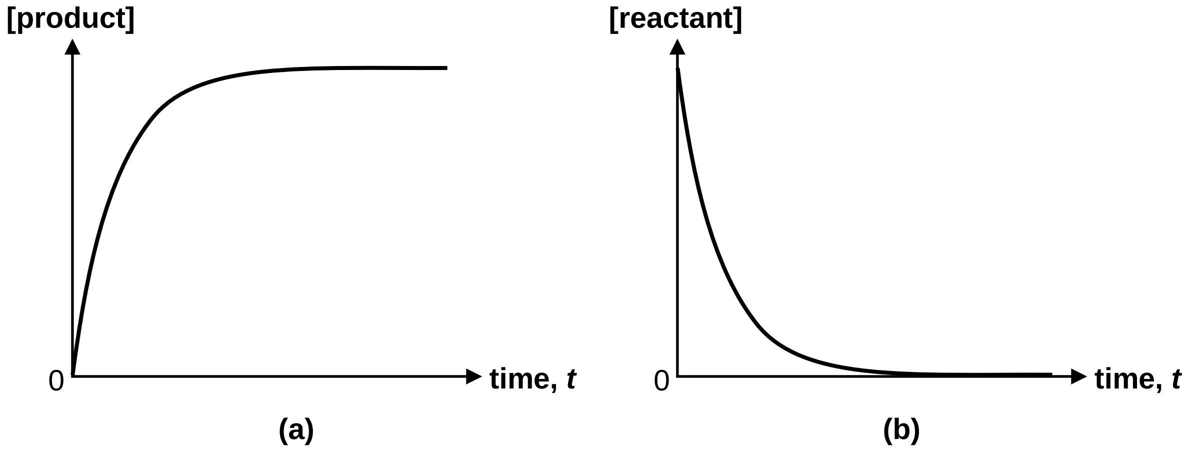
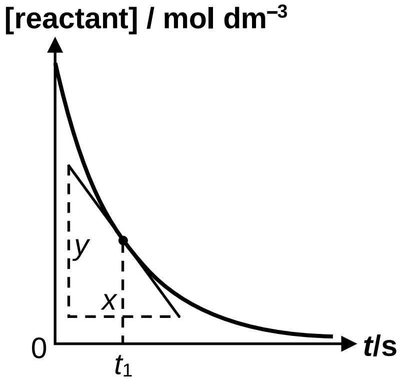
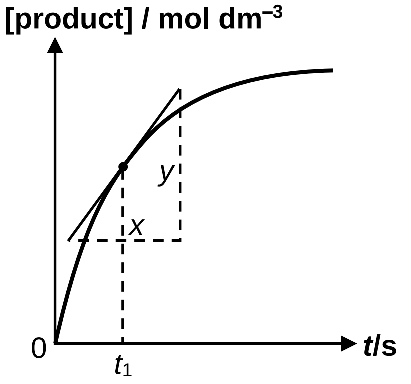


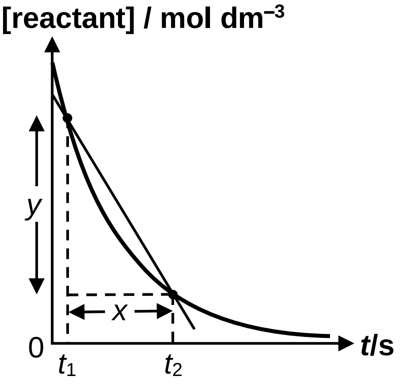
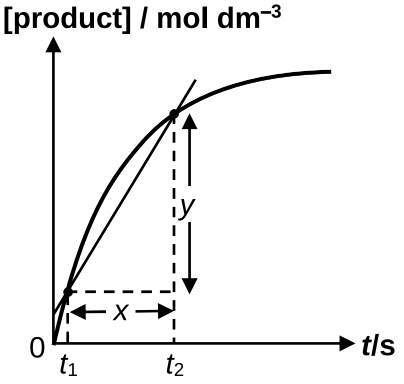
Fig. 1. **(a)** is the [product]-time graph and **(b)** is the corresponding [reactant]-time graph for the same reaction

(a) Instantaneous rate

<table>
<tr><td colspan="3">⌛ The instantaneous rate is the rate at a particular time <i>i.e.</i> the rate at a particular instant during the reaction.</td></tr>
<tr><td>
</td><td>
</td><td rowspan="3">The instantaneous rate at time <i>t</i> is obtained by measuring the gradient of the tangent drawn to the curve at time t.
The steeper the gradient is, the faster is the reaction.
The gradient of the graph decreases with time. Hence the rate of the reaction decreases with time.
When the gradient is zero, the rate of the reaction is zero.</td></tr>
<tr><td>rate at t_1
$= -\frac{d[\text{reactant}]}{dt}$
$=$ –gradient of tangent to the curve at t_1
$= -\left(-\frac{y}{x}\right) = \frac{y}{x}$</td><td>rate at t_1
$= \frac{d[\text{product}]}{dt}$
$=$ gradient of tangent to the curve at t_1
$= \frac{y}{x}$</td></tr>
<tr><td colspan="2">Note:
⌛ Rate is a positive quantity.
⌛ For the reactant-time graph, $y_2 – y_1$ is negative while $x_2 – x_1$ is positive, so the gradient of the graph as given by $\frac{d[\text{reactant}]}{dt}$ is negative as [reactant] decreases with time. The negative sign ensures that the rate determined from the change in [reactant] is positive.</td></tr>
</table>

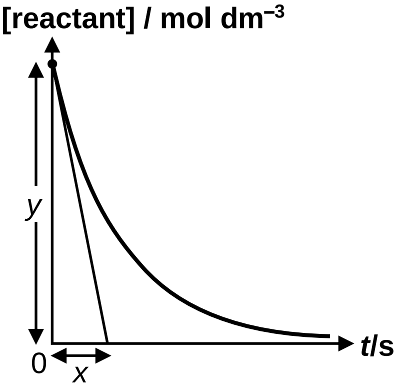
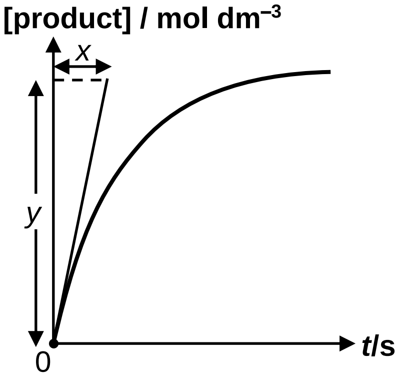
(b) Average rate

- The **average rate** of a reaction during a specified time interval is the change in concentration of a reactant or a product over that time interval.

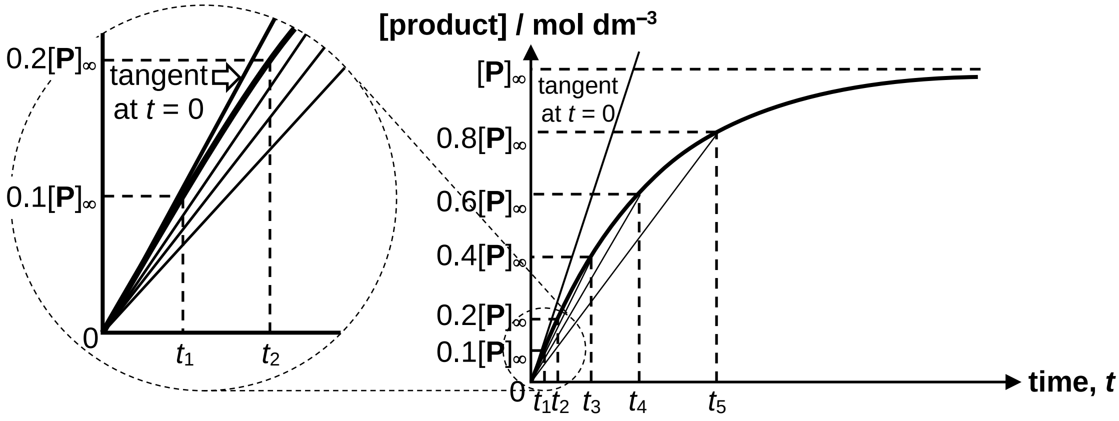
		In this case, the average rate during the time interval t_1 (which may be 0) to t_2 seconds is obtained by measuring the gradient of the line drawn between two points on the curve that are related to the time interval concerned.
average rate between t_1 and t_2 $= -\frac{\Delta[\text{reactant}]}{\Delta t}$ = –gradient of straight line joining points at t_1 and t_2 $= \frac{y}{x}$	average rate between t_1 and t_2 $= \frac{\Delta[\text{product}]}{\Delta t}$ = gradient of straight line joining points at t_1 and t_2 $= \frac{y}{x}$	

(c) Initial rate

- The **initial rate** of a reaction is the instantaneous rate at time t = 0.
- It is the instantaneous rate **at the start of the reaction**, when an infinitesimally small amount of the reactant has been used up.

		The initial rate is obtained by measuring the gradient of the tangent drawn to the curve at time $t = 0$.
initial rate = –gradient of tangent to the curve at $t = 0$ $= \frac{y}{x}$	initial rate = gradient of tangent to the curve at $t = 0$ $= \frac{y}{x}$	

- In practice, the **initial rate can be approximated by the average rate** provided
  1) the time interval is small enough, such that at most
     - 10% of the reactants had reacted, *or*
     - 10% of the eventual products had been formed.
  2) the time interval starts from $t = 0$ (since this is initial rate).
- Example:

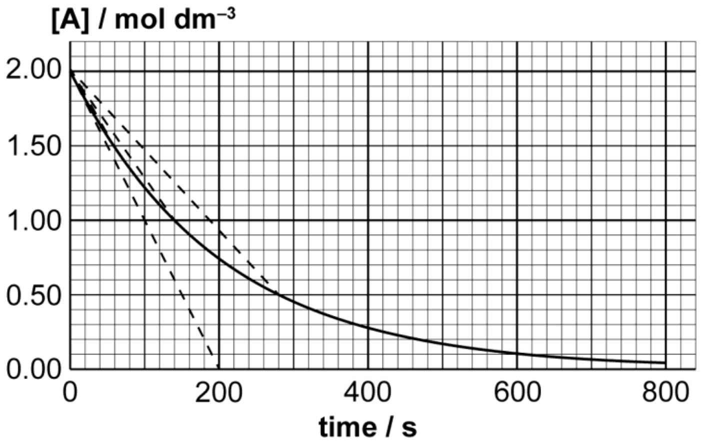


- The initial rate is given by the gradient of the tangent to the curve at $t = 0$.
- The *average rate* between 0 and t_1, where the reaction is 10% completed, approximates the *initial rate*, *i.e.*

$$\text{average rate between 0 and } t_1 = \frac{\Delta[\text{product}]}{\Delta t} = \frac{0.1[\mathbf{P}]_\infty}{t_1}$$

$$\approx \frac{d[\text{product}]}{dt}(\text{at } t = 0) = \text{initial rate}$$

- The average rate between 0 and t_2, where the reaction is 20% completed, can be seen to already *deviate significantly* from the initial rate.
- As the reaction proceeds, with increasing time intervals (*e.g.* 0 to t_3, 0 to t_4 and 0 to t_5), the larger the average rate deviates from the initial rate.



$$\textbf{initial rate} = -\frac{d[\mathbf{A}]}{dt} \text{ at } t = 0 \text{ s}$$

$$= -\frac{2.00 - 0.00}{0 - 200}$$

$$= \mathbf{1.00 \times 10^{-2}\ mol\ dm^{-3}\ s^{-1}}$$

$$\textbf{average rate} \text{ btw 0 and 20 s (10\%)}$$

$$= -\frac{2.00 - 1.80}{0 - 20}$$

$$= \mathbf{1.00 \times 10^{-2}\ mol\ dm^{-3}\ s^{-1}}$$

$$\textbf{average rate} \text{ btw 0 and 60 s (25\%)}$$

$$= -\frac{2.00 - 1.50}{0 - 60}$$

$$= \mathbf{8.33 \times 10^{-3}\ mol\ dm^{-3}\ s^{-1}}$$

$$\textbf{average rate} \text{ btw 0 and 140 s (50\%)}$$

$$= -\frac{2.00 - 1.00}{0 - 140}$$

$$= \mathbf{7.14 \times 10^{-3}\ mol\ dm^{-3}\ s^{-1}}$$

$$\textbf{average rate} \text{ btw 0 and 280 s (75\%)}$$

$$= -\frac{2.00 - 0.50}{0 - 280}$$

$$= \mathbf{5.36 \times 10^{-3}\ mol\ dm^{-3}\ s^{-1}}$$

Making Thinking Visible

Q: When the question says “rate”, is it normally referring to instantaneous rate or average rate?
A: In general, it is more meaningful to talk about instantaneous rate, because we are constructing the rate equation (or *rate law*) to show the mathematical relationship between the rate and the concentration of the reactants at a particular temperature. To do so, the exact value of the concentration of the reactants and the corresponding rate (at the same point of time) must be known. It is less meaningful to discuss average rate because the “instantaneous rates” are different for the range of reactant (or product) concentrations used, and it is inaccurate to construct a rate equation based on the average rate. Instantaneous rate can be approximated by average rate is when there is very small change to the reactant concentration (within a very small time interval).

To this end, it would be meaningful to carefully evaluate the “rate” we are measuring when we visit Sections 4 and 5.

Q: Why do we want to talk about average rate? Isn’t instantaneous rate better?
A: It is always easier to measure the average rate, as you will see in the comparison of continuous and discontinuous methods used to measure rate in Section 5. When done correctly, the average rate in certain experimental setup can be approximated to the instantaneous rate (at t=0, i.e. the initial rate).

Q: What is meant by “time”? Is there a difference between the **(1)** “time” used in the horizontal axis of the graph, **(2)** “time” used in (calculating) the rate of reaction, and **(3)** “time” elapsed for a specific change to be observed (in Sections 4 and 5)?
A: We are easily confused when we understand a term literally and assume that the meaning is identical for all contexts (i.e. a word can only have one meaning, which is not true).
(1) refers to the time that has elapsed since the reaction has started, i.e. from a specific reference point in time. In this case, we are thinking about time as a “dimension” that allows for observations to be made.
(2) is slightly different from **(1)**, and refers to a generic time interval between two reference points since the reaction has started. If we are talking about instantaneous rate (d[product]/dt), then we would be talking about an “instant” which means an infinitesimally small amount of time has passed. This instantaneous rate can be approximated by the average rate, when given the correct conditions.
(3) typically refers to the time that has elapsed between the start of the experiment and the change that is to be observed, and is hence *dependent* on the observation to be made.
In a way the "time” in **(1)**, **(2)** and **(3)** all refer to an interval (or a very small interval), but the specific reference points are different.

2 The Rate Equation

LO **(a)** explain and use the terms: *rate equation; order of reaction; rate constant*

2.1 Relationship between Rate and Reactant Concentrations

- For a general reaction $a\mathbf{A} + b\mathbf{B} \rightarrow$ products, the rate of reaction can be experimentally shown to be related to the concentrations of the reactants by a rate equation of the form:

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

where [**A**] and [**B**] are concentrations of reactant **A** and **B** respectively,
m and *n* are order of reaction with respect to reactant **A** and **B** respectively,
k is the rate constant,
$m + n$ = overall order of reaction.
(Note: when the order of reaction is 1, it is normally not written out.)

(Note: it is possible to have reactions that have more than 2 reactants in a single step. However, as you would learn from Section 8, it is difficult for 3 or more reactant particles to collide with the correct geometry and have sufficient energy to overcome the activation energy barrier. Hence, this set of lecture notes uses only 2 reactant particles to illustrate the concepts for the rate equation.)

2.2 Definition of Terms Relating to the Rate Equation

rate equation	The rate equation (or rate law) is an **experimentally determined mathematical equation between the reaction rate and the concentration of reactants at a particular temperature**. ⧖ The rate of reaction is related to the concentration of each reactant raised to the appropriate power. It may not include all reactants in the chemical equation. ⧖ The rate equation can only be experimentally determined and cannot be deduced from the stoichiometric equation (*i.e.* *m* and *n* may or may not be equal to *a* and *b* respectively).
order of reaction (with respect to a reactant)	The order of reaction with respect to a particular reactant is the **power to which the concentration of that reactant is raised in the experimentally determined rate equation**. *e.g.* rate = $k[\mathbf{A}]^2[\mathbf{B}] \Rightarrow$ order of reaction w.r.t. **A** is 2 ⧖ The order of reaction can be an integer, fraction, positive or negative value. ⧖ **Overall order of reaction** is the **sum of the individual orders of reaction** *i.e.* (2 + 1) = 3 in this case.
rate constant	Rate constant, *k*, is a **proportionality constant for a given reaction at a specified temperature**. ⧖ The units of *k* depends on the rate equation. For example, if rate = k[A], units of $k = \dfrac{\text{mol dm}^{-3}\ \text{s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$ if rate = $k[\text{A}]^2$, units of $k = \dfrac{\text{mol dm}^{-3}\ \text{s}^{-1}}{(\text{mol dm}^{-3})^2} = \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$ ⧖ Value of *k* can be affected by temperature and catalyst. ⧖ The larger the value of *k*, the faster the rate of reaction.

2.3 Understanding the Rate Equation

⌛ Consider a reaction of the form $a\mathbf{A} + b\mathbf{B} \rightarrow c\mathbf{C}$.

The rate equation is: rate = $k[\mathbf{A}]^m[\mathbf{B}]^n$

m	*n*	overall order of reaction (m+n)	rate equation	deductions
0	0	zero order	rate = $k[\mathbf{A}]^0[\mathbf{B}]^0 = k$ (units of *k*: mol dm^{-3} s^{-1})	⌛ Reaction is **zero** order with respect to **A** and **zero** order with respect to **B**. ⌛ Rate of reaction is **independent** of the concentrations of **A** and **B**, *i.e.* changing [**A**] and [**B**] does not affect rate of reaction, as $[\mathbf{A}]^0=[\mathbf{B}]^0=1$. ⌛ Rate is **constant** at constant temperature.
1	0	first order	rate = $k[\mathbf{A}]$ (units of *k*: s^{-1})	⌛ Reaction is **first** order with respect to **A** and **zero** order with respect to **B** (i.e. $[\mathbf{B}]^0=1$, which is not shown in the equation). ⌛ Rate of reaction is **directly proportional** to [**A**]. ⌛ As [**A**] doubles, rate increases 2 times.
1	1	second order	rate = $k[\mathbf{A}][\mathbf{B}]$ (units of *k*: mol^{-1} dm^{3} s^{-1})	⌛ Reaction is **first** order with respect to **A** and **first** order with respect to **B**. ⌛ Rate of reaction is **directly proportional** to [**A**][**B**]. ⌛ As [**A**] doubles, rate increases 2 times. ⌛ As [**A**] doubles and [**B**] doubles, rate increases 4 times.
0	2		rate = $k[\mathbf{B}]^2$ (units of *k*: mol^{-1} dm^{3} s^{-1})	⌛ Reaction is **zero** order with respect to **A** and **second** order with respect to **B** (i.e. $[\mathbf{A}]^0=1$, which is not shown in the equation). ⌛ Rate of reaction is **directly proportional** to $[\mathbf{B}]^2$. ⌛ As [**A**] doubles, rate remains unchanged. ⌛ As [**B**] doubles, rate increases 4 times. As [**B**] triples, rate increases 9 times.

Example 2A

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

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

(a) State the order of the reaction with respect to each of the reactants and the overall order of the reaction.

Order of reaction with respect to NO =
Order of reaction with respect to H_2 =
Overall order of reaction =

(b) State the units of the rate constant *k*.

Self Check 2A

Bromine and methanoic acid react as follows:

$$Br_2\text{ (aq)} + HCO_2H\text{ (aq)} \rightarrow 2Br^-\text{ (aq)} + 2H^+\text{ (aq)} + CO_2\text{ (g)}$$

The rate of reaction is found to be first order with respect both to bromine and to methanoic acid.

Which of the following deductions can be made from this information?

1 Doubling the concentration of methanoic acid doubles the rate of evolution of gas.
2 Halving the concentration of both reactants simultaneously will halve the reaction rate.
3 The overall order of the reaction is one.

A **1**, **2** and **3** **B** **1** and **2** only **C** **2** and **3** only **D** **1** only

Checkpoints for Section 1 & 2

I know how to:

☐ Define rate of reaction and understand that rate is always a positive quantity
☐ Define instantaneous rate, average rate and initial rate and determine them from a graph
☐ Write the expression of rate, its unit, and calculate rate.
☐ Define and use of the terms: rate of reaction, rate equation, order of reaction, rate constant.
☐ Construct and use the rate equation of the form: rate = $k[A]^m[B]^n$.

3 Zero-order, First-order and Second-order Reactions

LO **(b)** construct and use rate equations of the form rate = $k[A]^m[B]^n$ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2)
(ii) justifying, for zero-order reactions, the order of reaction from concentration-time graphs

3.1 Zero-order Reactions

- Consider the zero-order reaction: $\mathbf{A} \rightarrow \mathbf{B} + \mathbf{C}$, the rate equation is:

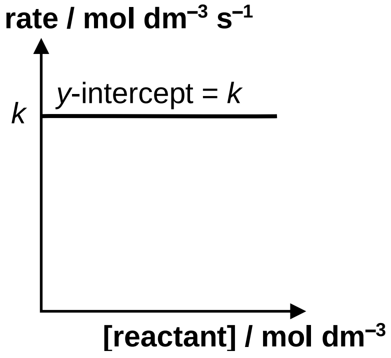
$$\text{rate} = k[\mathbf{A}]^0 = k$$

The rate is **constant** (at a particular temperature), *i.e.* rate = k (since $[\mathbf{A}]^0 = 1$)

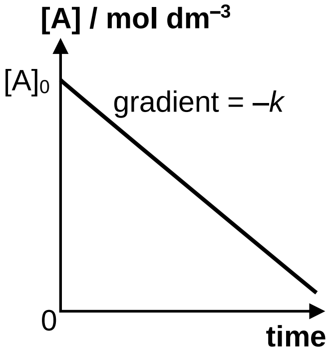
- If the order of reaction with respect to any reactant is zero, then **changing the concentration of that reactant will not affect the rate of reaction**, *i.e.* rate of a zero order reaction is **independent** of the concentration of the reactant.

- The graphs associated with zero order reactions are as shown:

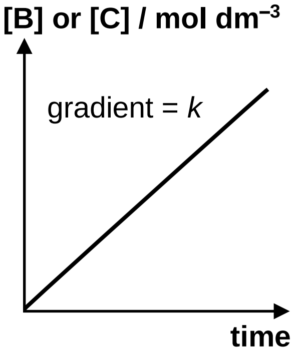
rate–[reactant] graph



[reactant]–time graph



[product]–time graph



3.2 First-order Reactions

LO **(a)** explain and use the term: *half-life of a reaction*
(b) (ii) justifying, for first-order reactions, the order of reaction from concentration-time graphs
(c) show understanding that the half-life of a first-order reaction is independent of concentration and use the half-life of a first-order reaction in calculation

- Consider the first-order reaction: $\mathbf{A} \longrightarrow \mathbf{B} + \mathbf{C}$, the rate equation is:

$$\text{rate} = k[\mathbf{A}].$$

- If the order of reaction with respect to any reactant is one, then the **rate is <u>directly proportional</u> to the concentration of that reactant**.

Half-life ($t_{½}$) *of a reaction is the* ***time taken for the concentration of a reactant to decrease to half its initial value****.*

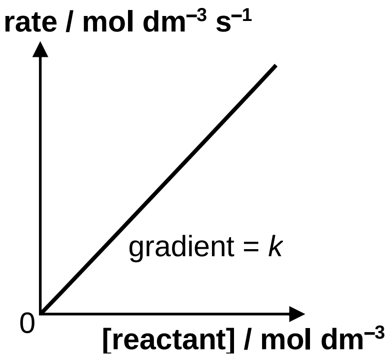
A unique feature of **<u>first-order reaction</u>** is that its **<u>half-life is constant</u>** (at a particular temperature) and the **<u>half-life is independent of the concentration of the reactant</u>**.

- For ***non-overall*** first-order reactions, the half-life is not constant. It changes throughout the experiment.
- To determine if a given reaction follows first order kinetics, plot a graph of concentration against time and check if the half-life is constant.

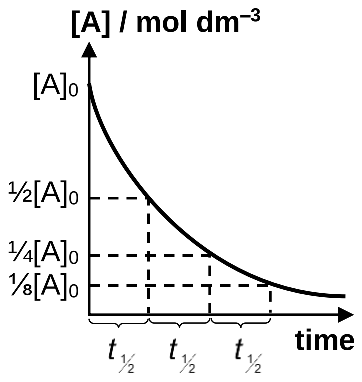
- The half-life of a first-order reaction given by: $\boxed{t_{½} = \frac{\ln 2}{k} = \frac{0.693}{k}}$

- The graphs associated with first-order reactions are as shown:

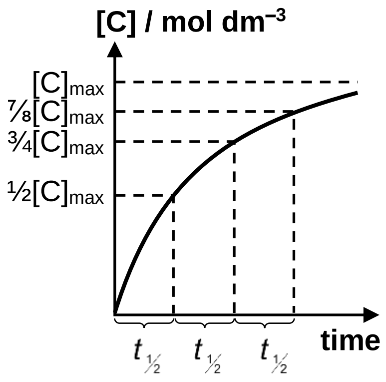
rate–[reactant] graph



[reactant]–time graph



[product]–time graph



time	[A] remaining	Total [A] reacted	Total [C] formed
1st $t_{½}$	½$[A]_0$	½$[A]_0$	½$[C]_{max}$
2nd $t_{½}$	¼$[A]_0$	¾$[A]_0$	¾$[C]_{max}$
3rd $t_{½}$	⅛$[A]_0$	⅞$[A]_0$	⅞$[C]_{max}$
∞	0	$[A]_0$	$[C]_{max}$

Example 3A

At a certain temperature, sucrose hydrolyses as follows:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \text{glucose} + \text{fructose}$$

The concentration of sucrose, [**S**], was measured at different times.

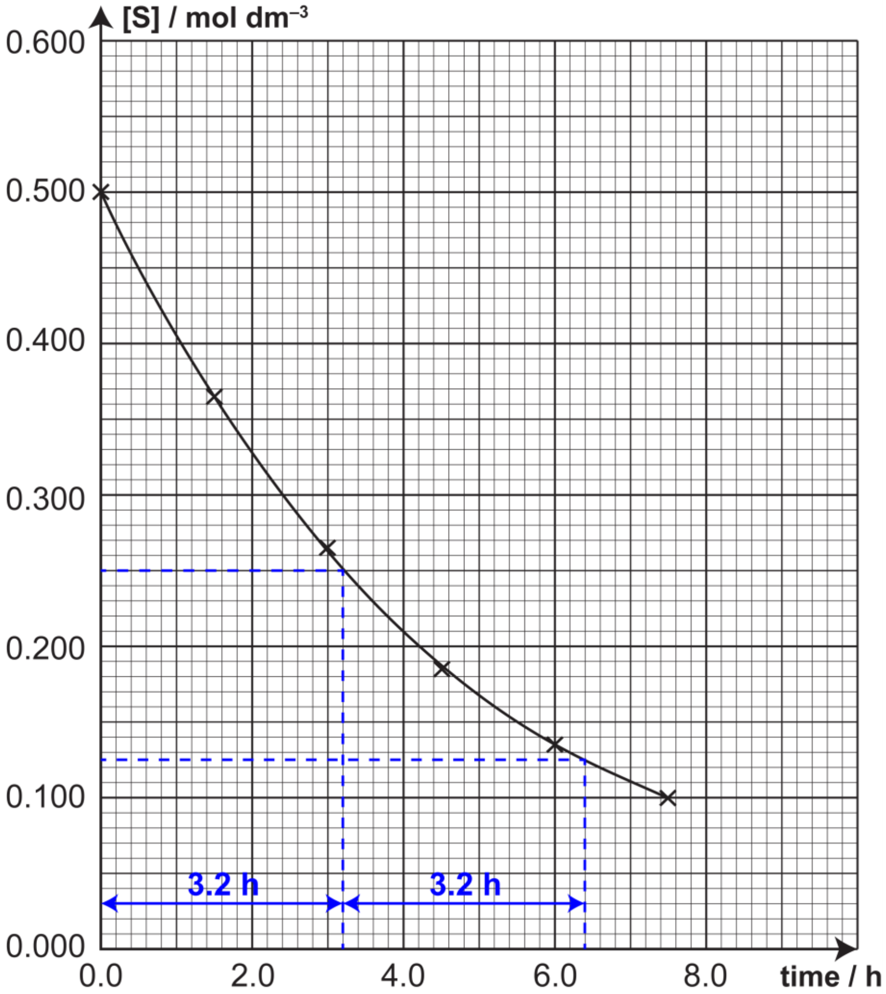
time / h	0	1.5	3.0	4.5	6.0	7.5
[S] / mol dm^{-3}	0.500	0.363	0.267	0.185	0.136	0.098

(a) Plot a suitable graph and determine the half-life of the reaction.

(b) What is the order of reaction w.r.t. sucrose?

(c) What is the rate constant of the reaction? Give the units.

(d) The experiment was repeated at the same temperature using 0.250 mol dm^{-3} sucrose solution. State the half-life of the reaction.



(a)

(b)

(c)

(d)

⌛ For a reaction that follows first-order kinetics (where half-life is constant), the following set of equations involving concentration of the reactants is applicable throughout the reaction graph:

$$\frac{c_t}{c_0} = \left(\frac{1}{2}\right)^n \qquad \text{and} \qquad t = n(t_{1/2})$$

where c_t is the concentration at time = t

c_0 is the concentration at time = 0

n is the number of half-lives

Example 3B

H_2O_2 decomposition is a 1st order reaction. If the initial concentration of H_2O_2 is 2.3 mol dm^{-3} and the half-life of this reaction is 14 minutes, how long has the decomposition occurred if the concentration is now 1.0 mol dm^{-3}?

Self Check 3A

1 Iodine-131 is a radioactive isotope with a half-life of 8 days. Following the nuclear power plant disaster at Chernobyl in 1986, it was stated that a cloud of vapour containing iodine-131 was formed which would not become safe for 80 days.

Given that radioactive decay is a first order reaction, what fraction of the isotope would remain after that time?

A $\frac{1}{20}$ **B** $\frac{1}{160}$ **C** $\frac{1}{2^8}$ **D** $\frac{1}{2^{10}}$

2 Lead is the final product formed by a series of changes in which the rate-determining step is the radioactive decay of uranium-238. This radioactive decay is a 1st order reaction with a $t_{1/2}$ of 4.5×10^9 years. What would be the age of a rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1:3?

A 1.5×10^9 years **C** 9.0×10^9 years

B 2.25×10^9 years **D** 13.5×10^9 years

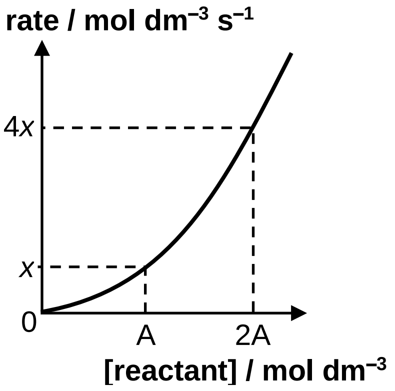
3.3 Second-order Reactions

- Consider the second-order reaction: **2A** → **B** + **C**, the rate equation is:

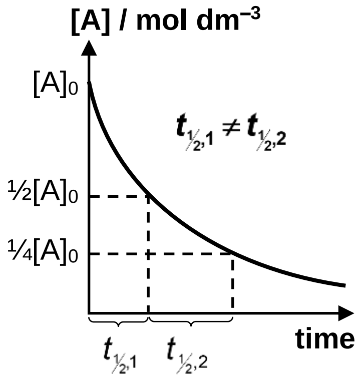
$$\text{rate} = k[\mathbf{A}]^2$$

- If the order of reaction with respect to any reactant is two, then the **rate is <u>directly proportional to the square of the concentration</u> of that reactant**.
- The graphs associated with second-order reactions are as shown:

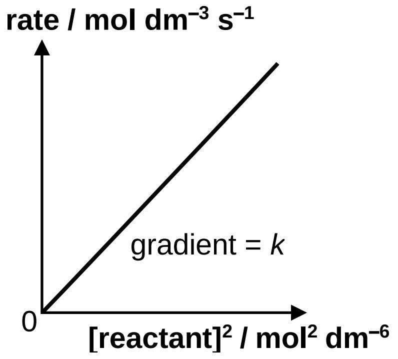
rate–[reactant] graph



[reactant]–time graph



rate–[reactant]^2 graph



3.4 Pseudo First-order Reactions

- Suppose the reaction **A + B** → **C**, where the rate equation is

$$\text{rate} = k[\mathbf{A}][\mathbf{B}].$$

- If **B is used in large excess** compared to **A**, say [**B**] is about 10 times more than [**A**], then [**B**] **is effectively constant** during the reaction and thus k[**B**] is also constant.
- The above rate equation can then be rewritten as: rate = k'[**A**] where $k' = k$[**B**]
- Now, it appears that the reaction follows **first-order kinetics** (i.e. the observed change in [**A**] follows first-order kinetics) and thus we say that the reaction follows **pseudo first-order** kinetics. The $t_{½}$ of **A** is now equal to $\frac{\ln 2}{k'}$.

$$t_{½} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[\mathbf{B}]}$$

The table below shows how the $t_{½}$ of **A** is affected when [**A**] and [**B**] are changed.

experiment	**[A] / mol dm^{-3}**	**[B] / mol dm^{-3}**	**$t_{½}$ / min**
1	0.01	1	10
2	0.02	1	10
3	0.01	2	5

(a) Presence of a large excess of a reactant

- Consider the reaction of peroxodisulfate ions and iodide ions:

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

The rate equation is found to be: **rate = $k[S_2O_8^{2-}][I^-]$**

- If **initial $[S_2O_8^{2-}] \gg$ initial $[I^-]$**, then $[S_2O_8^{2-}]$ will hardly change during a reaction relative to the change in $[I^-]$.
- In this case, $[S_2O_8^{2-}]$ may be regarded as effectively constant throughout the reaction *i.e.* at all times in the reaction mixture, **$[S_2O_8^{2-}]$ = initial $[S_2O_8^{2-}] \approx$ constant**.
- Hence the rate equation can be modified as: **rate = $k'[I^-]$** where **$k' = k[S_2O_8^{2-}]$**
- In this case, the reaction is said to exhibit **pseudo-first-order kinetics** and **k'** is a pseudo-first-order rate constant.

(b) Solvent is a reactant

- Consider the hydrolysis of ethyl ethanoate in water.

$$CH_3CO_2CH_2CH_3 + H_2O \rightarrow CH_3CO_2H + CH_3CH_2OH$$

The rate equation is: **rate = $k[CH_3CO_2CH_2CH_3][H_2O]$**

- As water is a reactant and also the **solvent** in this reaction (and hence present in a **large excess**), its concentration remains essentially constant throughout the reaction. The total amount of water reacted is negligible as compared to the total amount of water present.
- Hence the rate equation can be modified as: **rate = $k'[CH_3CO_2CH_2CH_3]$**
  where **$k' = k[H_2O]$**. We now have a **pseudo first-order** reaction for the hydrolysis of ethyl ethanoate.

(c) Presence of a catalyst

- Consider the hydrolysis of sucrose in the presence of hydrochloric acid as the catalyst.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{HCl} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

- Experimentally, the rate equation is found to be: **rate = $k[H^+]$[sucrose]**
- In this case, H^+ , which is contributed through the dissociation of hydrochloric acid, is a **catalyst**. It increases the rate of the reaction but is not consumed by the reaction. It participates in the reaction but is **regenerated**. Thus the $[H+]$ can be regarded as essentially constant during the reaction *i.e.* $[H^+] \approx$ constant.
- Hence the rate equation can be modified to: **rate = k'[sucrose]**
  where **$k' = k[H^+]$ = constant**. We now have a **pseudo first-order** reaction in this example.

Example 3C

A reaction occurs between I^- and $S_2O_8^{2-}$. The rate equation for this reaction is

$$\text{rate} = k[S_2O_8^{2-}][I^-].$$

An experiment is performed where initial concentrations of $S_2O_8^{2-}$ at 1×10^{-4} mol dm^3 and I^- at 9×10^{-1} mol dm^{-3} were used. A graph of $[S_2O_8^{2-}]$ against time was plotted and the half-life was determined to be 40 s. Determine the value and units of the rate constant, k.

The units of k is not s^{-1} as it should not be determined from pseudo rate law (i.e. $k \neq k'$).

Checkpoints for Section 3

I know how to:

☐ Appreciate and interpret graphical representations of zero-, first- and second-order reactions.

☐ Justify, for zero- and first-order reactions, the order of reaction from concentration-time graphs

☐ Define half-life, its determination, usage and calculations for first-order reactions; $t_{\frac{1}{2}} = \frac{\ln 2}{k}$;

☐ Understand that half-life is independent of concentration of the reactant in first-order reactions.

☐ Appreciate and understand pseudo-order reactions, and the conditions in which pseudo-first order reaction could be justified.

4 Determination of Orders of Reaction from Experimental Data

LO **(b)** (i) deducing the order of a reaction by the initial rates method
(v) calculating an initial rate using concentration data
(d) calculate a rate constant using the initial rates method

There are various methods to determine the orders of reaction from experimental data:

4.1 Non-graphical Methods – Using Initial Rates Data

Hydrogen peroxide reacts with acidified iodide ions, liberating iodine.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

In investigations of this reaction, the following results were obtained.

experiment	**initial concentrations of reactants / mol dm^{-3}**			**initial rate of formation of I_2 / mol dm^{-3} s^{-1}**
	[H_2O_2]	**[I^-]**	**[H^+]**	
1	0.010	0.010	0.010	2.0×10^{-6}
2	0.030	0.010	0.010	6.0×10^{-6}
3	0.030	0.020	0.010	1.2×10^{-5}
4	0.030	0.040	0.020	2.4×10^{-5}

(a) Deduce the orders of reaction with respect to H_2O_2, I^- and H^+.

Inspection method:

Comparing experiments 1 and 2, where [I^-] and [H^+] are kept constant,
When **[H_2O_2] is tripled**, **initial rate** is **tripled**.

∴ the reaction is **1st order** with respect to **H_2O_2**.

Comparing experiments 2 and 3, where [H_2O_2] and [H^+] are kept constant,
When **[I^-] is doubled**, **initial rate** is **doubled**,

∴ the reaction is **1st order** with respect to **I^-**.

Comparing experiments 3 and 4, where [H_2O_2] is kept constant,
When **[I^-] is doubled** and **[H]$^+$ is doubled**, **initial rate** is **doubled**. Since the reaction is 1st order with respect to I^-, **doubling [I^-] would double the rate**, hence **doubling [H^+] did not change the initial rate**.

∴ the reaction is **zero order** with respect to H^+.

Mathematical method:

Comparing experiments 3 and 4, $\dfrac{\text{rate}_3}{\text{rate}_4} = \dfrac{k[H_2O_2][I^-][H^+]^z}{k[H_2O_2][I^-][H^+]^z}$

$$\frac{1.2\times10^{-5}}{2.4\times10^{-5}} = \frac{k(0.030)(0.020)(0.010)^z}{k(0.030)(0.040)(0.020)^z}$$

$$\left(\frac{1}{2}\right)^z = 1 \Rightarrow z = 0$$

∴ the reaction is **<u>zero order</u>** with respect to H^+.

(b) Write the rate equation of the reaction and calculate the rate constant, *k*, stating its units.

rate = $k[H_2O_2][I^-]$

Using values from experiment 1,

$$2.0 \times 10^{-6} = k\,(0.010)\,(0.010)$$

$$k = \underline{\mathbf{2.0 \times 10^{-2}\ mol^{-1}\ dm^{3}\ s^{-1}}}$$

Example 4A

The table gives data for the reaction between **X** and **Y** at constant temperature.

experiment	initial [**X**] / mol dm^{-3}	initial [**Y**] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.3	0.2	4.0×10^{-4}
2	0.6	0.4	1.6×10^{-3}
3	0.6	0.8	6.4×10^{-3}

What is the rate equation for the reaction?

A rate = k[**X**][**Y**]^2 **B** rate = k[**X**]^2[**Y**] **C** rate = k[**X**]^2 **D** rate = k[**Y**]^2

- If the data given in the table is the volume of the reactants instead of their concentration, we can use the relationship that **<u>$V_{reactant} \propto$ [reactant]</u>**, provided that the **<u>total volume of solution is kept constant</u>** (often achieved by adding various volumes of water).

- If the data given in the table is the time taken for the reaction to be complete, we can use the relationship that **<u>rate is inversely proportional to time taken for the reaction to be complete</u>**.

Example 4B

The reaction of potassium iodate, KIO_3, with potassium sulfite, K_2SO_3, in the presence of sulfuric acid can be studied using sodium thiosulfate, $Na_2S_2O_3$. The equation of the reaction is shown.

$$5SO_3^{2-}(aq) + 2H^+(aq) + 2IO_3^-(aq) \rightarrow 5SO_4^{2-}(aq) + I_2(aq) + H_2O(l) \qquad \text{rxn } \mathbf{I}$$

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2\,I^-(aq) + 2S_4O_6^{2-}(aq) \qquad \text{rxn } \mathbf{II}$$

When a small but constant amount of $Na_2S_2O_3$ is added to a reaction mixture, the iodine slowly produced by rxn **I** will immediately react in rxn **II** until all the $Na_2S_2O_3$ has been used up. At that point, free iodine will be present in the solution, which will cause a sudden appearance of a deep blue colour if starch is present.

The stated volumes of solutions were mixed in expt 1 and the time for the blue colour to appear recorded.

expt	volume of KIO_3 / cm^3	volume of K_2SO_3 / cm^3	volume of H_2SO_4 / cm^3	volume of $Na_2S_2O_3$ / cm^3	volume of deionised water / cm^3	volume of starch / cm^3	time / s
1	20	20	20	2	0	1	30
2	*a*	*b*	10	2	*c*	1	

(a) If the purpose of experiment 2 is to determine the order of reaction with respect to sulfuric acid, suggest the volumes *a*, *b*, and *c* to use in experiment 2.

(b) If the time taken for experiment 2 is 60 s, deduce the order of reaction with respect to H_2SO_4. Explain clearly your deduction.

(a)

(b)

Self Check 4A

The kinetics of the acid – catalysed reaction of propanone with iodine

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + HI(aq)$$

can be investigated experimentally by varying the concentrations of the three substances involved and determining the time for the colour of the iodine to disappear. In this method the rate of the reaction is measured in terms of the rate at which the iodine concentration changes,

i.e. $\text{rate of reaction} \propto \dfrac{\text{volume of aqueous iodine used}}{\text{time for colour of iodine to disappear}}$

(Note: **rate is NOT directly proportional to** $\dfrac{1}{\Delta t}$ **because [I_2] and amount of I_2 is changing**)

The following results were obtained in such an experiment.

experiment	volume of propanone/ cm^3	volume of iodine/ cm^3	volume of sulfuric acid/ cm^3	volume of water/ cm^3	relative time for colour of iodine to disappear
1	8	4	8	0	1
2	8	4	4	4	2
3	4	4	8	4	2
4	8	2	8	2	0.5

(a) What is the purpose of adding water in experiments 2, 3 and 4?

(b) Determine the rate law for the reaction.

(a) Water is added to keep the total volume of the reaction mixture constant so that the concentration of a reactant is ______________ to its volume (*i.e.* ________________).

(b)

Order of reaction w.r.t H^+	Order of reaction w.r.t. CH_3COCH_3	Order of reaction w.r.t. I_2
Compare experiment 1 & 2, where [CH_3COCH_3] and [I_2] are kept constant, when [H^+] × ½, rate × ½ Reaction is **1st order** w.r.t. H^+, *or* Let order of reaction w.r.t. H^+ be x $\dfrac{rate_1}{rate_2} = \left(\dfrac{V_{H^+,1}}{V_{H^+,2}}\right)^x$ $\dfrac{4/1}{4/2} = \left(\dfrac{8}{4}\right)^x$ $\boldsymbol{x = 1}$		

Rate =

4.2 Graphical Methods – from Concentration–Time Graph

Bromoethane, C_2H_5Br, is hydrolysed by NaOH(aq) according to the following equation:

$$C_2H_5Br(aq) + OH^-(aq) \rightarrow C_2H_5OH(aq) + Br^-(aq)$$

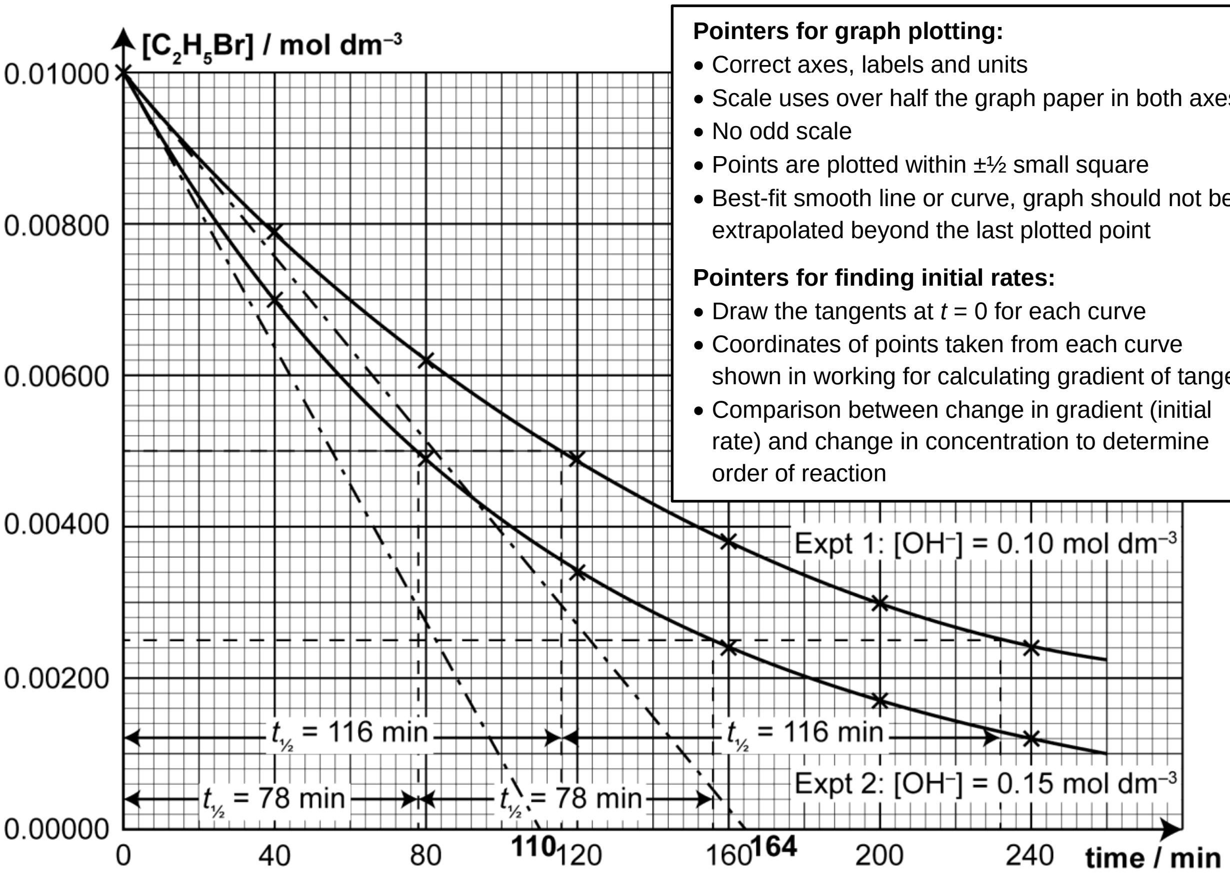
The following results were obtained from two experiments. In each experiment, the overall $[OH^-]$ remained relatively constant at the value given at the top of the column.

	experiment 1 **$[OH^-] = 0.10$ mol dm^{-3}**	**experiment 2** **$[OH^-] = 0.15$ mol dm^{-3}**
time / min	**$[C_2H_5Br]$ / mol dm^{-3}**	
0	0.0100	0.0100
40	0.0079	0.0070
80	0.0062	0.0049
120	0.0049	0.0034
160	0.0038	0.0024
200	0.0030	0.0017
240	0.0024	0.0012

(a) Plot these data on suitable axes and use your graphs to determine the following:

  (i) Use the half-life method to deduce the order of reaction with respect to C_2H_5Br.

  (ii) Use the initial rates method to deduce the order of reaction with respect to NaOH.



Pointers for graph plotting:

- Correct axes, labels and units
- Scale uses over half the graph paper in both axes
- No odd scale
- Points are plotted within ±½ small square
- Best-fit smooth line or curve, graph should not be extrapolated beyond the last plotted point

Pointers for finding initial rates:

- Draw the tangents at $t = 0$ for each curve
- Coordinates of points taken from each curve shown in working for calculating gradient of tangent
- Comparison between change in gradient (initial rate) and change in concentration to determine order of reaction

Pointers for finding half-lives:

- At least 2 half-lives shown on graph (3 half-lives if graph is obtained from practical expts)
- Values of half-life (time taken) clearly shown on graph
- Half-lives shown on graph must have **minimal overlap** with one another, i.e. take **consecutive** half-lives where possible. (To illustrate this point, note that a zero-order will have similar half-lives if you took the time lapsed for reactant concentration to drop from for e.g., 100 units to 50 units, and 96 units to 48 units.)

(i) Since **half-life is constant at 116 min for experiment 1** (or 78 min for experiment 2), the reaction is **first order** with respect to C_2H_5Br.

(ii) initial rate for experiment 1 $= -\dfrac{0.0100 - 0.0000}{0 - 164} = 6.098 \times 10^{-5}$ mol dm^{-3} min^{-1}

initial rate for experiment 2 $= -\dfrac{0.0100 - 0.0000}{0 - 110} = 9.091 \times 10^{-5}$ mol dm^{-3} min^{-1}

When **[OH⁻] increases 1.5 times**, the **initial rate also increases $\dfrac{\mathbf{9.091 \times 10^{-5}}}{\mathbf{6.098 \times 10^{-5}}} \approx$ 1.5 times**, hence the reaction is **first order** with respect to NaOH.

(b) Write the rate equation for the reaction and use it to calculate the rate constant.

rate = k[C_2H_5Br][OH^-]

From experiment 1, $6.098\times10^{-5} = k(0.0100)(0.10)$

$$k = \underline{\mathbf{0.0610\ mol^{-1}\ dm^3\ min^{-1}}}$$

Alternatively, since [OH^-] is approximately constant, rate = k'[C_2H_5Br], where $k' = k$[OH^-]

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k\left[OH^-\right]}$$

$$116 = \frac{\ln 2}{k(0.10)}$$

$$k = \underline{\mathbf{0.0598\ mol^{-1}\ dm^3\ min^{-1}}}$$

(c) Complete the following table:

	[C_2H_5Br] / mol dm^{-3}	[OH^-] / mol dm^{-3}	$t_{1/2}$ (C_2H_5Br) / min
Experiment 3	0.0200	0.10	
Experiment 4	0.0150	0.30	
Experiment 5	0.0300	0.10	

Note:

- Why was OH^- used in large excess (concentration is at least 10 times larger) as compared to C_2H_5Br?
  This is to ensure that the [OH^-] stays almost constant throughout the reaction so that the effect of changing [C_2H_5Br] on the rate of reaction can be determined. The reaction thus follows pseudo first-order kinetics.

  We can simplify the rate equation to: rate = k'[C_2H_5Br], where $k' = k$[OH^-]

  $$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[OH^-]}$$

- Recall: half-life is independent of the concentration of the reactant (C_2H_5Br) for a first-order reaction.

Checkpoints for Section 4

I know how to:

☐ Determine the orders of reaction through:

- Non-graphical method using initial rate data; by inspection or mathematical method
- Graphical method using conc-time graph; finding half-life, initial rate (gradient of tangent at $t = 0$)

☐ Calculate rate constant using initial rate method: using the orders of reaction with respect to the reactants

☐ Write the rate equation and determine rate constant, k.

** NOT IN H1 Chemistry Syllabus

5 Experimental Methods for Studying Reaction Rates

LO **(e)** devise a suitable experimental technique for studying the rate of a reaction, from given information

The rate of a chemical reaction may be studied by monitoring the change of a physical property of the reacting system. Properties which may be monitored include concentration, volume, pressure, mass, electrical conductivity, and colour intensity.

5.1 Continuous Methods

Continuous methods can be used to study the change in concentration of either the reactant or the product at a specific point of time. Some examples of continuous methods are illustrated in the next few sub-sections.

5.1.1 Sampling: Monitoring rate of reaction using titrations

This method is used for reactions in aqueous solutions. An **aliquot** (*i.e.* a fixed volume of the reaction mixture) is drawn out of the reacting system (using a pipette) at **regular time intervals**. Before analysis is done, the reaction is **quenched** to **slow down or stop the reaction** so that the **composition of the reaction mixture in each aliquot stops changing**.

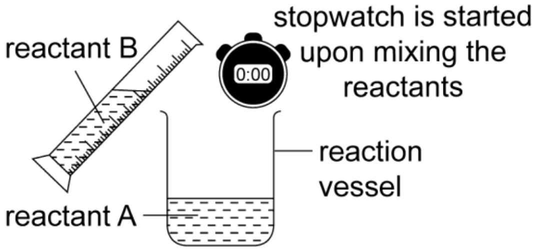
A reaction may be **quenched** by **adding** any of the following:

(i) A **large volume of cold solvent to dilute the sample** and **slow down** the reaction significantly (refer to Section 8)
(ii) A **quenching agent** which reacts with one of the reactants to **stop** the reaction.
(iii) An **inhibitor** or a negative catalyst to **slow down** the reaction.

The concentration of either the reactant remaining or the product formed can then be determined by carrying out a **titration**.

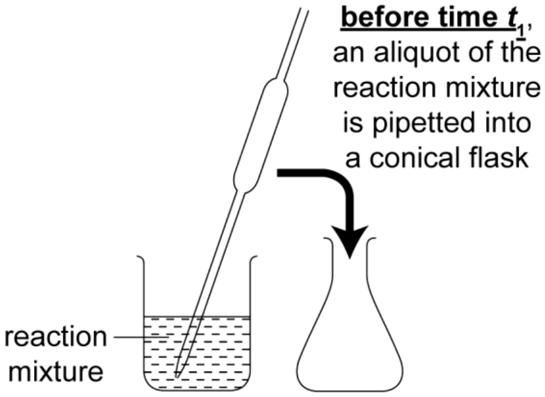
General procedure

1. Starting the reaction



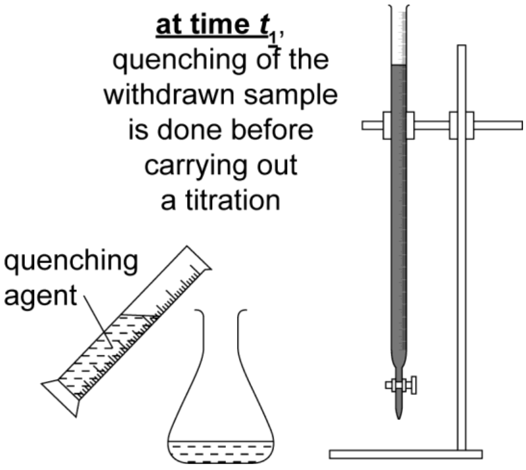
- In this method of measuring reaction rate, the reaction is started by mixing known volumes of concentration and volume of reactants, and a stopwatch started simultaneously.

2. Sampling



- Using a pipette, an aliquot portion (*i.e.* a fixed volume of the sample) is withdrawn from the reaction mixture at a suitable time into a conical flask.

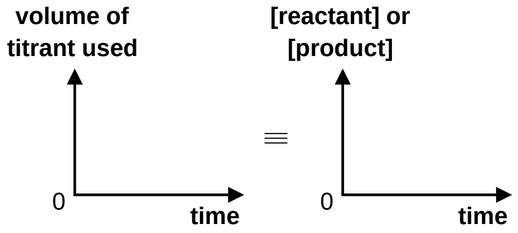
3. Quenching followed by titration



- Before a titrimetric analysis is done, the reaction in the withdrawn sample has to be halted so that the composition of the reaction mixture in the withdrawn sample does not continue to change.
- At a suitable time t_1, the reaction in the withdrawn sample is slowed down or halted effectively by
  - adding a large volume of ice-cold water (which dilutes and cools the mixture), or
  - adding an excess of a suitable **quenching agent** (which reacts immediately with one of the reactants or the catalyst).
- The concentration of either the reactant remaining (or the product formed) at the time t_1 in the reaction mixture can then be determined by carrying out a titration of the quenched sample.

4. Repeat (2) and (3) at other timings

time/min	0	t_1	t_2	t_3	t_4	t_5	t_6
volume of titrant used/cm^3	V_0	V_1	V_2	V_3	V_4	V_5	V_6



- The sampling–quenching–titration steps are repeated at suitable time intervals.
- A graph of volume of titrant used (or concentration of reactant or product) against time can be plotted.
- The graph plotted can be used to determine
  - the order of reaction with respect to the reactant under consideration, and
  - the instantaneous rate at any specified time by finding the gradient of the tangent drawn to the curve at that time (for [reactant] or [product] against time graph).

Example 1: Decomposition of Hydrogen Peroxide

Hydrogen peroxide decomposes according to the equation: $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

Procedure

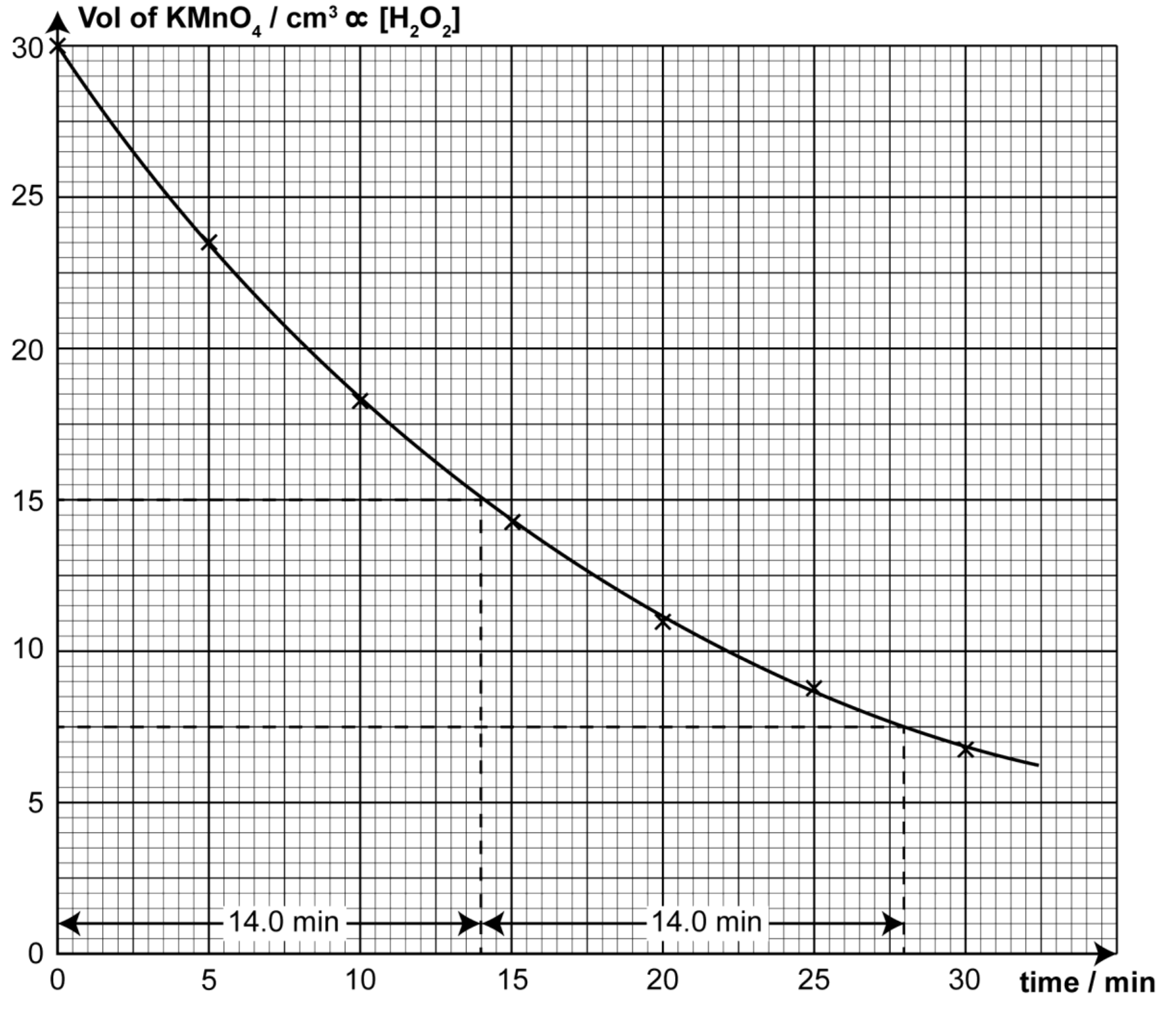
The rate of decomposition of a 3.0 mol dm^{-3} solution of H_2O_2 may be measured by pipetting out 10.0 cm^3 portions of the reaction mixture at regular time intervals of 5 minutes into a 250 cm^3 conical flask. These portions can be quenched by adding 30 cm^3 of cold water. The concentration of the unreacted H_2O_2 in the quenched samples can be found by titrating the sample with acidified 0.1 mol dm^{-3} aqueous $KMnO_4$. The results are shown below.

time / min	0.0	5.0	10.0	15.0	20.0	25.0	30.0
vol of $KMnO_4$ / cm^3	30.0	23.40	18.30	14.20	11.10	8.70	6.80

A graph of volume ($KMnO_4$) against time can be plotted.

Since the unreacted [H_2O_2] in the conical flask is proportional to the volume of $KMnO_4$ reacted, the graph of volume ($KMnO_4$) against time is equivalent to [H_2O_2] against time.

The rate of reaction at various times can be determined by drawing tangents to the curve and determining the gradients of the tangents.



Since **half-lives are constant** $\left(t_{1/2} = \mathbf{14.0\ min}\right)$, reaction is **first order with respect to H_2O_2**.

Thus, rate = $k[H_2O_2]$

Example 2: Acid-catalysed Reaction between Iodine and Propanone

In the presence of an acid, propanone reacts with iodine according to the following equation:

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + HI(aq)$$

The reaction rate may be studied by determining the amount of unreacted iodine in the reaction mixture at different times so that the relationship between rate and $[I_2]$ can be found. To investigate the order of reaction w.r.t. I_2, the concentration of propanone and H^+ used should be at least 10 times that of I_2, so that the kinetics becomes a pseudo zero order w.r.t. to both propanone and H^+.

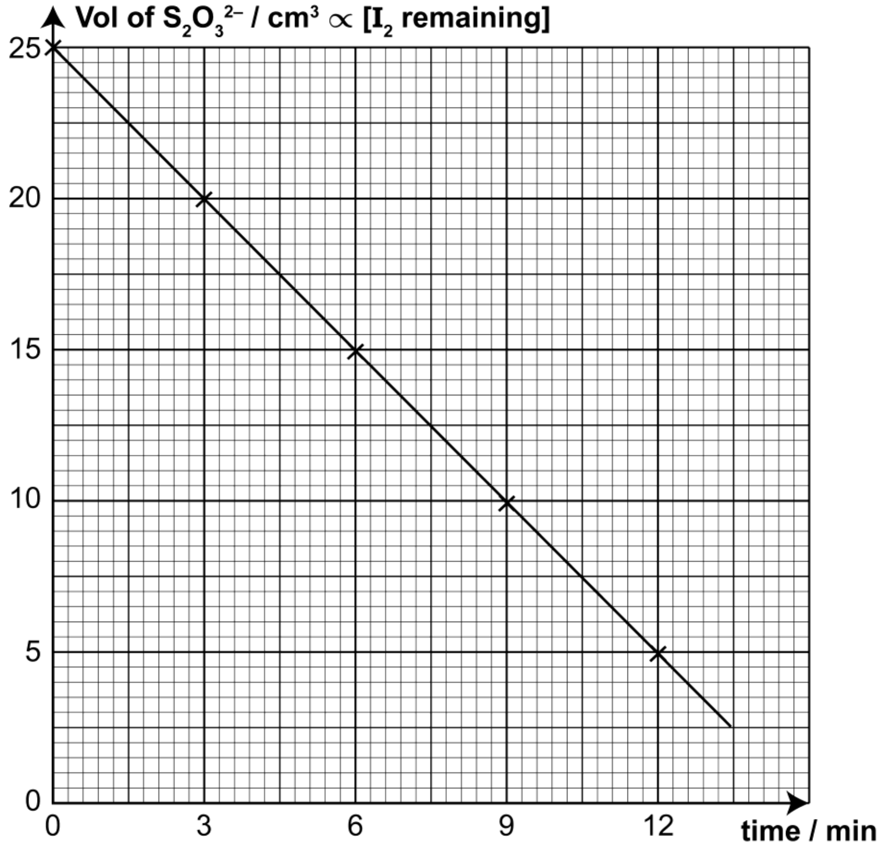
Procedure

Propanone, iodine solution and dilute sulfuric acid of known concentrations are mixed together and a stopwatch is started. At regular time intervals, samples of known volumes are pipetted out. The withdrawn sample is quenched by adding a quenching agent, sodium hydrogen carbonate, which neutralises the acid catalyst: $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$

The concentration of the unreacted iodine in the quenched sample is determined by titrating with against a standard solution of aqueous sodium thiosulfate, $Na_2S_2O_3$.

time / min	0	3	6	9	12
vol of $S_2O_3^{2-}$ / cm^3	25.00	20.00	15.00	10.00	5.00

A graph of volume of $S_2O_3^{2-}$ against time can be plotted.



A straight line graph is obtained. This implies that the rate of reaction is constant.

At time *t* = 0, the reaction has not started, hence the volume of $S_2O_3^{2-}$ used indicates the number of moles of iodine present initially. As reaction progresses, the amount of unreacted iodine present decreases, hence the volume of $S_2O_3^{2-}$ used also decreases.

Since volume of $S_2O_3^{2-}$ used is directly proportional to the [I_2 remaining], a graph of [I_2] against time would also give a straight line, indicating that the rate of reaction is independent of concentration of iodine, *i.e.* reaction is zero order with respect to I_2.

5.1.2 Monitoring rate by measuring volume of gaseous product

- In a reaction whereby a gas is produced from non-gaseous reactants, the progress of the reaction can be followed by measuring the volume of the gas evolved at suitable time intervals under the same temperature and pressure conditions.
- The rate of the reaction is given by the change in the volume of the gas produced over a specified time interval.

The examples that follow illustrates three examples of reactions which produce gaseous products. The reactions are carried out with the gaseous products formed, collected and monitored.

Example 1: Reaction between reactive metal and dilute acid

Zinc reacts with sulfuric acid according to the equation:

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

The rate of reaction may be studied by measuring the volume of $H_2(g)$ produced.

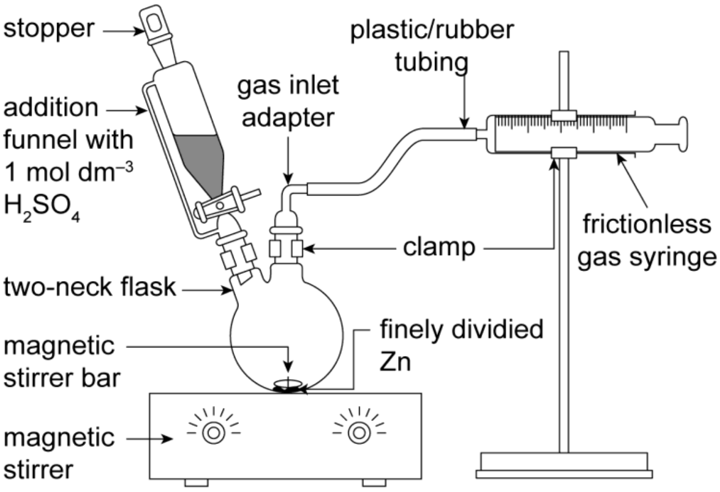
<u>Procedure</u>

Place a known mass of finely divided zinc in a two-neck round- bottomed flask and set up the apparatus as shown on the right.

Add a known amount (limiting reagent) of 1.0 mol dm^{-3} sulfuric acid into the flask *via* the pressure-equalising addition funnel.

Use a magnetic stirrer to mix the reactants.

Record the volume of $H_2(g)$, V_t, collected in the frictionless gas syringe at regular time intervals, t, until three constant readings are obtained.



Example 2: Reaction between carbonate and dilute acid

Calcium carbonate reacts with hydrochloric acid according to the equation:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

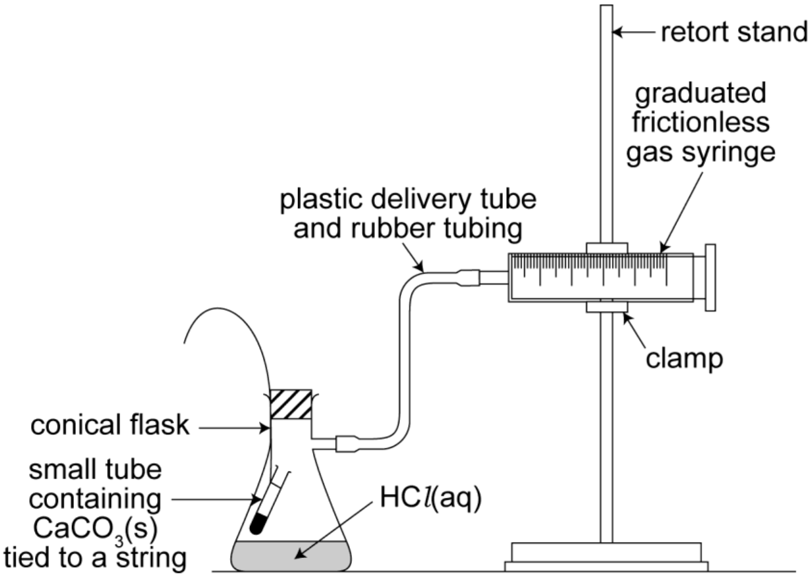
The rate of reaction may be studied by measuring the volume of $CO_2(g)$ produced.

Procedure

Set up the apparatus as shown.

Calcium carbonate is added to the hydrochloric acid by pulling the thread thus dropping the small test tube into the acid and a stopwatch is started.

Record the volume of $CO_2(g)$ collected in the frictionless gas syringe at regular time intervals, until three constant readings are obtained.



Example 3: Decomposition of hydrogen peroxide (in the presence of MnO_2 catalyst)

Hydrogen peroxide decomposes in the presence of a catalyst according to the equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The rate of this reaction can be studied by determining the volume of oxygen gas produced over time.

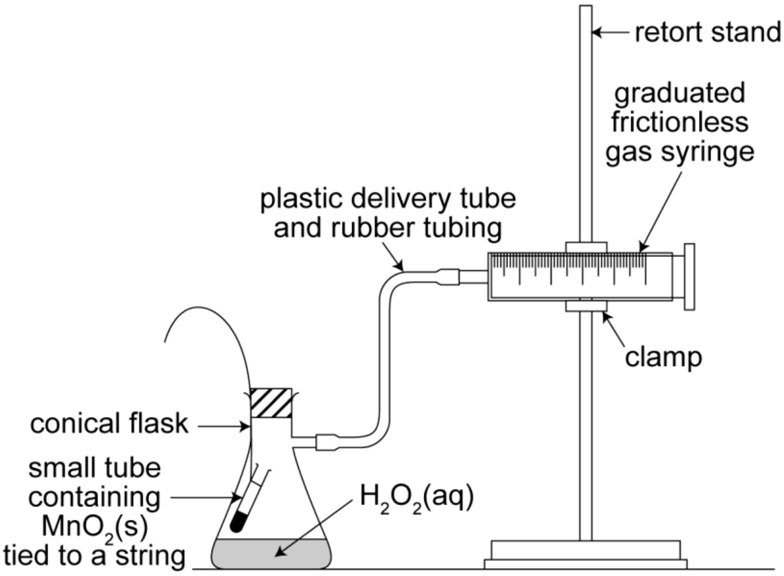
$O_2(g)$ is collected in a graduated frictionless gas syringe and its volume measured at regular time intervals during the reaction.

Procedure

Set up the apparatus as shown.

The MnO_2 catalyst is added to the hydrogen peroxide and a stopwatch is started.

Record the volume of $O_2(g)$, V_t, collected in the frictionless gas syringe at regular time intervals, t, until three constant readings are obtained.



Analysis of Results

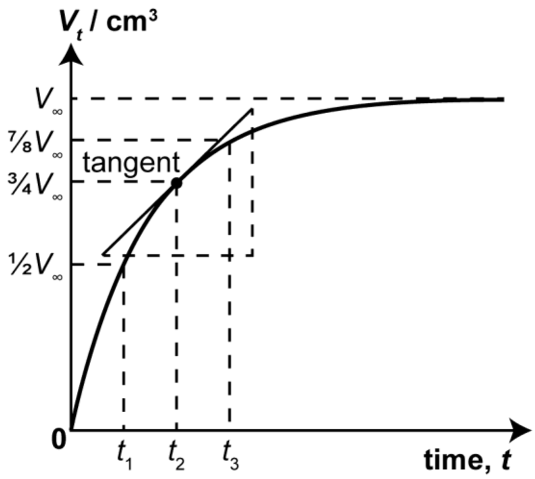
- For all three examples described, the volume of gaseous product formed is monitored at regular time intervals. Using the volumes of gaseous product, and with some manipulation, different graphs of volume of gases against time can be plotted. From these graphs, orders of reaction with respect to the reactants can be obtained.

Using the results obtained from **Example 3: Decomposition of hydrogen peroxide**,

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

(A) Graph of volume of O_2 against time

- A graph of volume of $O_2(g)$ evolved against time can be plotted. The rate of reaction at any instant, *t*, is the gradient of the tangent to the curve at that instant.
- From the graph of volume of $O_2(g)$ against time, the order of reaction with respect to H_2O_2 can be found from the shape of the graph:
  - zero order: straight line through origin with positive gradient
  - first order: concave curve with constant half-life
  - second order (and above): concave curve with non-constant (increasing) half-lives



Note:

1st $t_{½}$ = time taken for volume of O_2 to increase from 0 to $\frac{1}{2}V_\infty = t_1$

2nd $t_{½}$ = time taken for volume of O_2 to increase from $\frac{1}{2}V_\infty$ to $\frac{3}{4}V_\infty = t_2 - t_1$

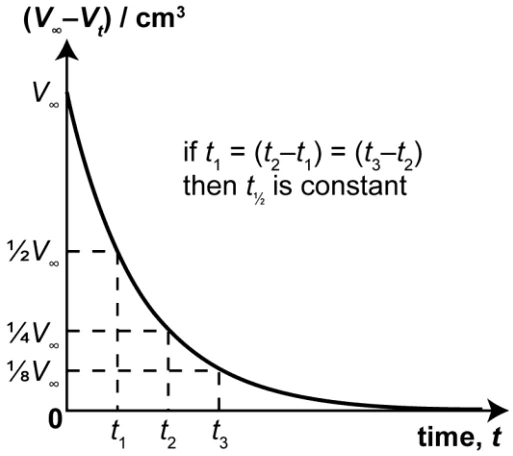
3rd $t_{½}$ = time taken for volume of O_2 to increase from $\frac{3}{4}V_\infty$ to $\frac{7}{8}V_\infty = t_3 - t_2$

(B) Graph of $(V_\infty - V_t)$ against time

- Alternatively, the values of $(V_\infty - V_t)$ can be determined and a graph of $(V_\infty - V_t)$ against time can be plotted.

Note:

V_t = volume of $O_2(g)$ evolved at time *t*
V_∞ = volume of $O_2(g)$ evolved at the end of the reaction
$(V_\infty - V_t)$ = volume of $O_2(g)$ **yet** to be evolved at time *t*
$(V_\infty - V_t) \propto [H_2O_2]$ remaining at time *t*



A graph of $(V_\infty - V_t)$ against time is equivalent to a graph of $[H_2O_2]$ against time.
From this graph, the half-life of the reaction can be determined.

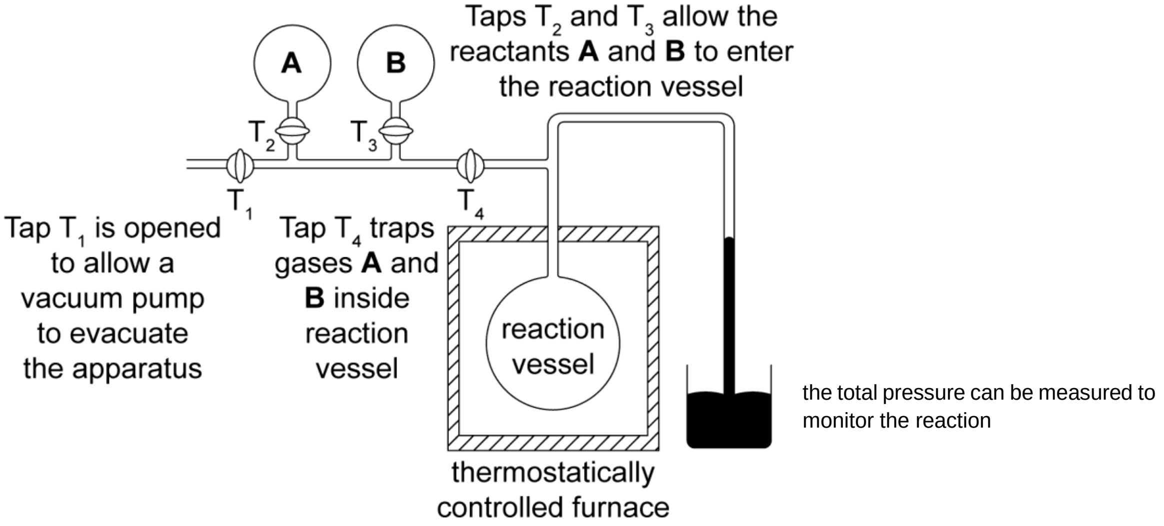
- The order of reaction with respect to H_2O_2 can be found from the shape of the graph:
  - zero order: straight line with negative gradient
  - first order: convex curve with constant half-life
  - second order (and above): convex curve with non-constant (increasing) half-lives

5.1.3 Monitoring rate by measuring changes in pressure

- If a reaction involves a change in the number of moles of gas, the total pressure of the reaction mixture can be measured at regular time intervals. The partial pressure of the reactant or product under consideration can then be calculated. The rate of the reaction can be determined from the change in partial pressure (at constant volume and temperature) of the reactant or product over time.

- For the experiments described in section 5.1.2, we can also monitor the rate of the reaction by measuring changes in pressure since there is a **change in the number of moles of gas molecules present**.

- The reaction is usually carried out in a closed metal container of a fixed volume fitted with a pressure gauge and the total pressure is measured at regular time intervals.



Some examples of reactions which involved changes in the amount of gaseous molecules and hence a change in total pressures are:

1. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
2. $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$

For these reactions, a manometer can be attached to the reaction vessel of known volume for measurement of gas pressure at various time intervals. The reaction vessel is also immersed in a constant-temperature bath. A graph of pressure against time can be plotted and the rates at various times are obtained by drawing tangents to the curve and calculating the gradients.

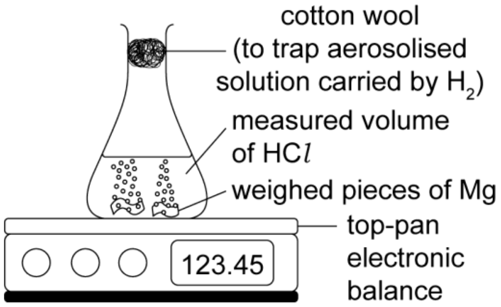
5.1.4 Monitoring rate by measuring changes in mass

In a reaction whereby a gas is produced and the gas allowed to escape, we can monitor the rate of the reaction by measuring changes in the loss in mass of the reacting system.

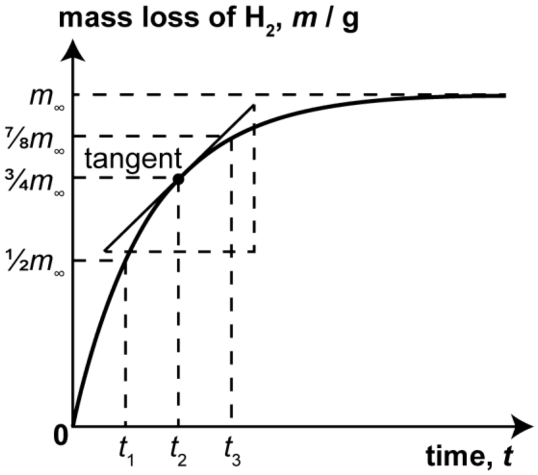
Consider the reaction: $Mg(s) + 2HC\ell(aq) \rightarrow MgC\ell_2(aq) + H_2(g)$

Procedure

Set up the apparatus as shown. Record the mass of reaction mixture at regular time intervals.



A graph of mass loss of H_2(g), m, against time can be plotted.



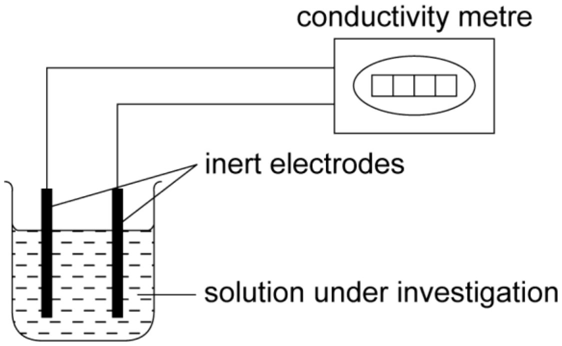
The rate of reaction at any time t is given by the gradient of the tangent drawn to the graph of m against t.

For example, by varying the concentration of HCl and measure the initial rate for each of the concentrations, one can find the order w.r.t. HCl.

Alternatively, one can also determine the half-life as shown in the graph and hence the order w.r.t. HCl (assuming the reaction is zero order w.r.t. Mg).

5.1.5 Monitoring rate by measuring changes in electrical conductivity

Aqueous solutions containing ions are able to conduct electricity when a current is passed through. The **number and types of ions** present in a solution affect its **electrical conductivity**. If a reaction involves a change in the **concentration of ions**, the rate of reaction may be studied by monitoring the change in electrical conductivity using an electrode (*i.e.* **conductometric** method).



Essentially, this method involves immersing two inert electrodes in the reaction mixture and then following the change in electrical conductivity of the solution with time.

An example of a reaction which may be studied by the conductometric method is:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The reactant ions act as **charge carriers** so the reaction mixture will conduct electricity. Electrical conductivity decreases with time as the reaction proceeds because the number of ions decrease since the products do not contain any ions.

5.1.6 Monitoring rate by measuring changes in colour intensity

This method can be used provided one of the reactants or products of the reaction is coloured.

Note: The **concentration** of a coloured substance in a reaction mixture is directly proportional to its **absorbance** (or **colour intensity**). The progress of the reaction is followed by measuring the absorbance (or colour intensity) of the reaction mixture at regular time intervals using a **colorimeter** (or a **spectrophotometer**). The rate of the reaction can be determined from the change in colour intensity over a specified time. Once the colorimeter is calibrated, it can be used to determine the unknown concentration of a particular substance.

Acid-catalysed Reaction between Iodine and Propanone

In the presence of an acid, propanone reacts with iodine according to the following equation:

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + HI(aq)$$

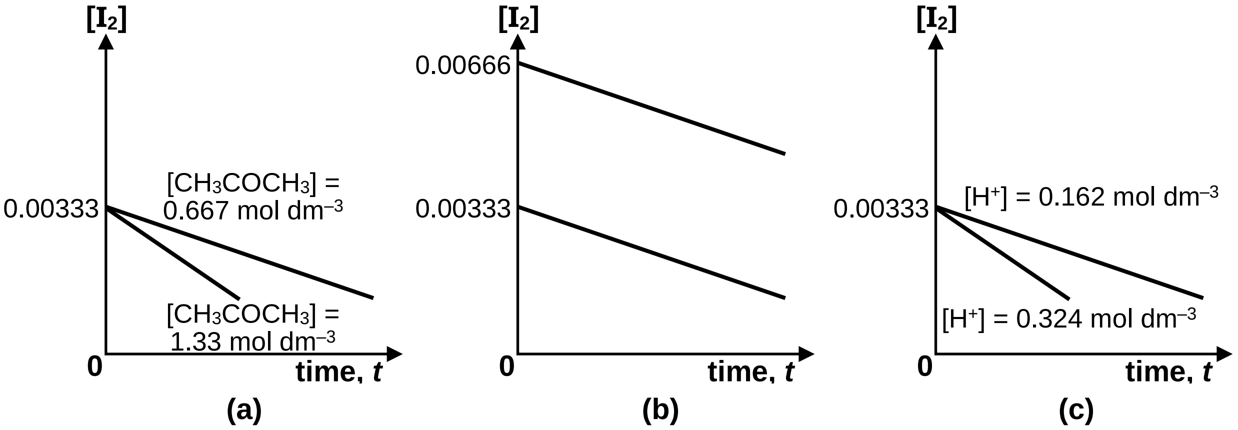
The brown colour of aqueous iodine fades as the reaction progresses. The rate of reaction may be studied by following the change in colour intensity of aqueous iodine.

Procedure

Mix iodine and acidified propanone and monitor the change in concentration using a colorimeter. Repeat the experiment by varying the concentrations of propanone, iodine and the acid one at a time as shown in the table.

experiment	$[CH_3COCH_3]$ / mol dm^{-3}	$[I_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}
1	0.667	0.00333	0.162
2	1.33	0.00333	0.162
3	0.667	0.00666	0.162
4	0.667	0.00333	0.324

Treatment of Results



Comparing experiments 1 and 2 (see **(a)**), keeping $[I_2]$ and $[H^+]$ constant,
when $[CH_3COCH_3]$ doubled, the rate doubled. Hence, reaction is **<u>1st</u>** order w.r.t. CH_3COCH_3.

Comparing experiments 1 and 3 (see **(b)**), keeping $[CH_3COCH_3]$ and $[H^+]$ constant,
when $[I_2]$ doubled, the rate remained the same. Hence, reaction is **<u>zero</u>** order w.r.t. I_2.

Comparing experiments 1 and 4 (see **(c)**), keeping $[I_2]$ and $[CH_3COCH_3]$ constant,
when $[H^+]$ doubled, the rate doubled. Hence, reaction is **<u>1st</u>** order w.r.t. H^+.

$\therefore$ **rate = $k[CH_3COCH_3][H^+]$**

Notice that $[I_2] \ll [CH_3COCH_3]$ and $[H^+]$, hence the reaction is *pseudo-zero order* w.r.t. CH_3COCH_3 and H^+. The straight line plots of $[I_2]$ against time also confirm that reaction is zero order w.r.t. I_2. What shape would you expect if the concentrations of all three reactants are comparable?

Checkpoints for Section 5.1

I know how to:

☐ Appreciate and understand the continuous methods where rate of reaction in a **single reaction mixture** is studied by monitoring the change in a physical property of the reactant or product.

☐ Understand the sampling-quenching-titration method.

☐ Describe methods to monitor the rate of reaction by measuring changes in: volume of gaseous product; pressure of gases; loss in mass of reacting system; electrical conductivity; colour intensity.

5.2 Discontinuous Methods or Method of Initial Rates or Clock Reactions

- In studying kinetics using the **method of initial rates**, the determination of the initial rate involves measuring the change in concentration of one of the reactants or products, which occurs in the first small time interval after the reagents are mixed.

- Hence in this method, the **initial rate** of the reaction is actually approximated by the **average rate** of the reaction. The approximation is a good one provided the time interval is small enough. In practice, the average rate of **reacting a fixed concentration of a reactant** or **forming a fixed concentration of product** is usually measured using the “clock” method.

- Certain reactions are accompanied by **prominent visual changes** such as the formation of a precipitate or an obvious colour change. The rate of reaction may be studied by repeating the experiment many times using **different reaction mixtures**, measuring the time taken for such a visual change to occur each time. Reactions that are studied this way are called **clock reactions**.

Example 1: Reaction between thiosulfate ions and hydrogen ions to produce sulfur

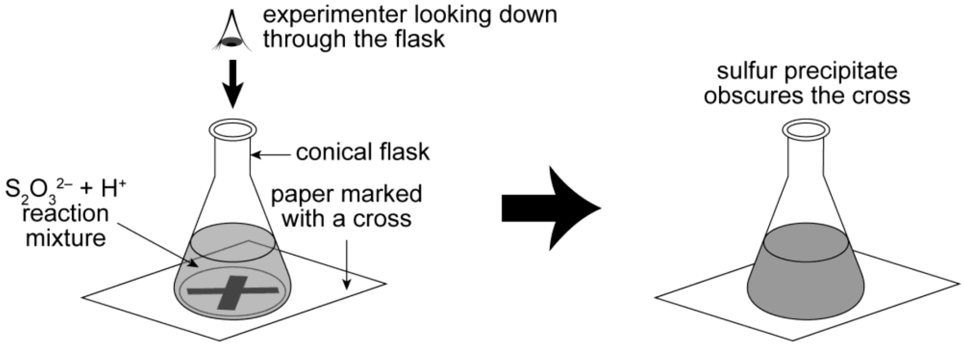
Sodium thiosulfate reacts with hydrochloric acid according to the equation:

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + SO_2(g) + \underset{\text{yellow ppt}}{S(s)}$$

The rate of reaction may be studied by measuring the time taken for a fixed amount of sulfur to form.

Procedure

- Place 20 cm^3 of $Na_2S_2O_3(aq)$ in a conical flask. Place the card, marked with a cross (“✕”), below the conical flask.
- Measure 30 cm^3 of $HCl(aq)$. Pour the acid into the conical flask containing $Na_2S_2O_3(aq)$ and start the stopwatch at the same time. Record the time taken for the cross (“✕”) on the card to be completely obscured by the sulfur produced.



- Repeat the experiments by varying the concentrations of thiosulfate and acid used as shown in the table below. Keep the total volume of the reaction mixture constant by adding distilled water.
- Calculate and record the reciprocal of time t $\left(i.e.\ \frac{1}{t}\right)$ for each of the experiment.

Experimental Data

expt	volume of 1.0 mol dm^{-3} $HCl(aq)$ used, V_1 /cm^3	volume of 0.2 mol dm^{-3} $Na_2S_2O_3(aq)$ used, V_2 /cm^3	volume of water used /cm^3	time taken for the mark “✕” to be obscured, t /s	$\frac{1}{t}\Big/s^{-1}$
1	30	40	0	16	0.06250
2	30	20	20	32	0.03123
3	40	30	0	19	0.05263
4	20	30	20	20	0.05000

Note: Since rate $\propto \frac{1}{t}$, if at least 5 experiments were conducted with different $[S_2O_3^{2-}]$ (or $[H^+]$), a graph of $\frac{1}{t}$ against $[S_2O_3^{2-}]$ (or $[H^+]$) can be plotted to find the order of reaction with respect to $S_2O_3^{2-}$ (or H^+). Alternatively, we can find the order of reaction with respect to the reactants by making a direct comparison of experimental results, as shown in the Treatment of Results at the following page.

Important questions to take note

Q1: Why is the volume of water varied in each experiment?

- The volume of water is varied in each experiment to keep the **total volume of the reaction mixture constant** for the different experiments.
- In this way, the initial concentration of each reactant in the reaction mixture is directly proportional to its volume used.

Q2: What is the relationship between the <u>initial concentration</u> of $Na_2S_2O_3$ in the reaction mixture and its volume used?

- The initial concentration of $Na_2S_2O_3(aq)$ in the reaction mixture is **directly proportional** to its volume used since the total volume of the reaction mixture is kept constant for all the different experiments.

$$\text{initial } [Na_2S_2O_3] \text{ in reaction mixture}$$

$$= \frac{\text{amount of } Na_2S_2O_3 \text{ used}}{\text{total volume of reaction mixture}}$$

$$= \frac{\begin{pmatrix}\text{volume of}\\ Na_2S_2O_3 \text{ used}\end{pmatrix}\begin{pmatrix}\text{concentration of}\\ Na_2S_2O_3 \text{ used}\end{pmatrix}}{\text{total volume of reaction mixture}}$$

kept constant for all the experiments by adding appropriate volume of water to each reaction mixture

constant for all the experiments since the same $Na_2S_2O_3$ stock solution is used

$$\text{initial } [Na_2S_2O_3] \propto \text{volume of } Na_2S_2O_3 \text{ used}$$

$$\text{initial } [Na_2S_2O_3] \propto V_2$$

Note: initial $[H^+] \propto V_1$

Q3: What is the relationship between the rate of reaction and the time *t* taken for the "cross" to be obscured?

- $\text{rate} \propto \frac{1}{t}$
- The rate of reaction is **inversely proportional** to the time *t* taken for the "cross" to be obscured by the sulfur since the amount of sulfur produced to obscure the printed material is **kept the same** for all the experiments.

- Why is $\text{rate} \propto \frac{1}{t}$?

In this experiment, the **initial rate** of formation of sulfur is **approximated** by the **average rate** of formation of sulfur since the amount of sulfur formed is small and *t* is measured from zero. For simplicity,

$$\text{initial rate} \approx \text{avg rate of formation of sulfur}$$

$$= \frac{\Delta(\text{amt. of sulfur})}{\Delta t} = \frac{x-0}{t-0} = \frac{x}{t}$$

where *x* = amount of sulfur formed to obscure the "cross"

t = time taken for the "cross" to be obscured by sulfur

In this case, ***x* is kept constant** for all the experiments (*i.e.* the same amount of sulfur is formed to obscure the "cross" for all the experiments) since the same "cross" is used.

Hence $\text{rate} \propto \frac{1}{t}$ **Note:** $\text{rate} \neq \frac{1}{t}$

Treatment of Results

Compare experiments 1 and 2.

When V_2 is doubled, $1/t$ is doubled.
$\Rightarrow 1/t \propto V_2$
$\Rightarrow \text{rate} \propto [S_2O_3^{2-}]$
$\therefore$ order of reaction w.r.t. $S_2O_3^{2-}$ is one.

The rate equation is: **$\text{rate} = k[S_2O_3^{2-}]$**

Compare experiments 3 and 4.

When the V_1 is doubled, $1/t$ remains the same.
$\Rightarrow$ rate is unchanged when [HC*l*] is doubled.
$\therefore$ order of reaction w.r.t. HC*l* is zero.

Example 2: Reaction between hydrogen peroxide and iodide ions in acidic medium

Hydrogen peroxide reacts with iodide ions in an acidic medium according to the equation:

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The initial rate of the reaction between H_2O_2 and acidified KI solution can be studied by the “clock” method, using sodium thiosulfate.

- When a small but constant amount of sodium thiosulfate is added to a reaction mixture, the iodine being slowly produced by reaction **(1)** will immediately react in reaction **(2)**.

  reaction (1): $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$

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

- Since reaction **(2)** is relatively faster than reaction **(1)**, the concentration of iodine in the reaction mixture will remain effectively zero so long as there are still some $S_2O_3^{2-}$ ions in the mixture.
- At that point when the small amount of $Na_2S_2O_3$ is completely used up, free iodine will be present in the solution, which will cause a sudden appearance of a blue-black colour characteristic of the starch–iodine complex if starch is present. (Note: since reaction **(1)** is slower, we are effectively observing the rate of reaction based on reaction **(1)** and not **(2)**, which is aligned to our aim).
- **Note:** By carrying out the reaction in the presence of a **small but fixed amount of $Na_2S_2O_3$** and the starch indicator, a ‘clock’ is introduced into the system. The ‘clock’ tells us when a given concentration of I_2 has formed. (*Recap why we use small but fixed amount of* ***$Na_2S_2O_3$*** *by reading Section 1.2(c)*)
- A series of experiments was carried out using different volumes of the five reagents, each solution being made up to the same total volume with appropriate volume of water added.
- The **volume and hence amount of $Na_2S_2O_3$ was kept constant** for each experiment to ensure that the amount of iodine produced (which reacted with the thiosulfate ions) was constant for all the experiments.

<u>Experimental Data</u>

expt	vol of 0.10 mol dm^{-3} H_2O_2 /cm^3	vol of 1.00 mol dm^{-3} KI /cm^3	vol of 1.00 mol dm^{-3} HCl /cm^3	vol of 0.050 mol dm^{-3} $Na_2S_2O_3$ /cm^3	vol of starch solution /cm^3	vol of water /cm^3	time for the appearance of deep blue colour, t / s	$\frac{1}{t}$ / s^{-1}
1	15	10	5	2	3	65	33	0.0303
2	5	10	10	2	3	70	100	0.0100
3	5	15	10	2	3	65	67	0.0149
4	10	10	10	2	3	65	50	0.0200

- **Note:** Always consider the following questions when analysing the volume and time data obtained from an initial rates experiment.
  - How was the rate measured?
  - Was the total volume kept constant?
  - What is the relationship between the initial [reactant] and its volume used?
  - What is the relationship between the initial rate and time t?

- **What is the relationship between the time taken for the blue colour to appear, *t*, and the initial rate of the reaction (1)?**

The initial rate of reaction **(1)** is *inversely proportional* to the time taken for the blue colour to appear *i.e.* initial rate $\propto \frac{1}{t}$.

initial rate of reaction = initial rate of formation of iodine = $\frac{d[\mathrm{I_2}]}{dt}(\text{at time } t=0)$

Since the amount of I_2 formed is small and t is measured from zero,

initial rate $\approx$ average rate of formation of iodine from 0 to t

$$=\frac{\Delta[\mathrm{I_2}]}{\Delta t}=\frac{x-0}{t-0}=\frac{x}{t}$$

time /s	$[I_2]$ /mol dm^{-3}
0	0
t	x

where x = $[I_2]$ formed when the solution just turned deep blue

t = time noted for the appearance of the deep blue colour
= time taken for $[I_2]$ to reach x mol dm^{-3}

Since all the reaction mixtures contains the **same amount of $Na_2S_2O_3$** (and the same amount of starch solution), each reaction mixture will turn deep blue only when it has produced the same $[I_2]$ as the others *i.e.* ***x* has been kept constant in all the experiments.**

$$\text{initial rate} \propto \frac{1}{t}$$

Treatment of Results (Determination of the rate equation)

Note:

- Since the total volume of the reaction mixture was kept constant for all the experiments,

  initial [reactant] $\propto$ volume of reactant used

- Since the same amount of $Na_2S_2O_3$ was used and hence the same $[I_2]$ was produced to form the deep blue solution for all the experiments, **initial rate $\propto \frac{1}{t}$**

Compare experiments 2 and 4.

When volume of H_2O_2 was doubled, 1/t was doubled.
$\Rightarrow$ 1/t $\propto$ volume of H_2O_2
$\Rightarrow$ rate $\propto$ $[H_2O_2]$
Order of reaction with respect to H_2O_2 = 1

Compare experiments 2 and 3.

When volume of KI was increased 1.5 times,
1/t increased 1.5 times.
$\Rightarrow$ 1/t $\propto$ volume of KI
$\Rightarrow$ rate $\propto$ $[I^-]$
Order of reaction with respect to I^- = 1

Compare experiments 1 and 4.

Note: rate = $k[H_2O_2][I^-][H^+]^n$

$$\frac{\text{rate}(1)}{\text{rate}(4)}=\frac{k(15)(10)(5)^n}{k(10)(10)(10)^n}=\frac{0.0303}{0.0200}$$

$$\left(\frac{1}{2}\right)^n=1.01$$

$$n=0$$

Order of reaction with respect to H^+ = 0

Hence the rate equation is:

rate = $k[H_2O_2][I^-]$

Checkpoints for Section 5.2

I know how to:

☐ Understand discontinuous methods or clock reactions; and appreciate the use of average rate to approximate initial rate.

☐ Appreciate the relationship between rate and the time taken for a fixed concentration of reactant to be used or that of a product to be formed.

☐ Understand the relationship between initial concentration of reactants in the reaction mixture and their volume used when the total volume of the mixture is kept constant.

6 Reaction Mechanisms

**** NOT IN H1 Chemistry Syllabus**

LO **(a)** explain and use the terms*: rate-determining step*
(b) **(iii)** verifying that a suggested reaction mechanism is consistent with the observed kinetics
(iv) predicting the order that would result from a given reaction mechanism

A **reaction mechanism** describes how a reaction occurs by showing the progression of events from reactants to products. For example, among other things, it shows us whether a reaction occurs in a single step or in a certain sequence of steps. These steps are individually called an **elementary reaction**, which describes a single molecular event that cannot be made up of simpler steps. Examples of elementary reactions are (i) one particle decomposing or (ii) two particles colliding and combining.

*The **rate determining step** is the **slowest step in a sequence of elementary reactions**.*

⌛ The **rate determining step** has the **highest activation energy** amongst all the steps involved in the mechanism.

Consider the reaction: $2\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C} + \mathbf{D}$

Suppose the experimentally determined rate equation is given by: rate = $k[\mathbf{A}][\mathbf{B}]$

The following mechanism of the reaction is proposed:

step 1: $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C} + \mathbf{X}$ (slow)

step 2: $\mathbf{A} + \mathbf{X} \rightarrow \mathbf{D}$ (fast)

overall equation: $2\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C} + \mathbf{D}$

⌛ **X** is formed in step 1 but is used up in step 2. We call **X** an **intermediate**, a species which is formed in an elementary reaction and used up in another. Hence, **intermediates do not appear either in the stoichiometric equation or the rate equation**.

⌛ In any proposed mechanism, the **equations in all the steps must sum up to give the overall balanced chemical equation of the reaction**.

- Also, the **rate equation determined from the mechanism must match the experimentally determined rate equation**. To decide what the rate equation for any mechanism is, we **look at its slow step to see what are the coefficients of the reactant species in this step**.
- The **molecularity** of an elementary reaction refers to the **number of reacting species** in that step. Since there are 2 reacting species in step 1, it is a bimolecular elementary reaction.

molecularity	**type of elementary reaction**
1	unimolecular
2	bimolecular
3	termolecular

- Here, since step 1 is the **slow** step, it is the **rate determining step** (RDS). How fast the reaction proceeds depends on how fast 1 molecule of **A** react with 1 molecule of **B**.

$1\mathbf{A} + 1\mathbf{B} \rightarrow \mathbf{C} + \mathbf{X}$ (slow)

rate = $k[\mathbf{A}]^1[\mathbf{B}]^1$ (deduced from RDS)

rate = $k[\mathbf{A}][\mathbf{B}]$ (experimentally determined rate equation)

The rate equations are the same, so the mechanism is consistent with the observed kinetics.

Example 6A

The decomposition of hydrogen peroxide can be catalysed by bromide ions:

$$2H_2O_2(aq) \xrightarrow{Br^-} 2H_2O(l) + O_2(g)$$

The rate law is given by: rate = $k[H_2O_2][Br^-]$

Which of the following mechanisms is consistent with this rate equation?

<u>Mechanism 1</u>

$H_2O_2 \rightarrow 2HO$ slow
$2HO + Br^- \rightarrow BrO^- + H_2O$ fast
$H_2O_2 + BrO^- \rightarrow H_2O + O_2 + Br^-$ fast

<u>Mechanism 2</u>

$H_2O_2 + Br^- \rightarrow H_2O + BrO^-$ slow
$BrO^- + H_2O_2 \rightarrow H_2O + O_2 + Br^-$ fast

Example 6B

The decomposition of nitrous oxide, N_2O, is believed to occur via two elementary steps:

Step 1: $N_2O \rightarrow N_2 + O$
Step 2: $N_2O + O \rightarrow N_2 + O_2$

Experimentally, the rate equation is found to be: rate = $k[N_2O]$

(a) Write the equation for the overall reaction.
(b) Identify the intermediate
(c) What can you say about the relative rates of steps 1 and 2?

Answer:
To remove the intermediates, add equations for steps 1 and 2 to give the overall reaction:
Overall equation: (This is the stoichiometric or overall equation.)

____________ is the intermediate, as it does not appear in the overall equation.

From the rate equation: rate = $k[N_2O]$, reaction is _________ order with respect to $[N_2O]$.
______________________ must be involved in the rate-determining step.
Hence, step _____ is the slow step / RDS.
Step 2 must be the ___________.

Example 6C

The overall reaction between **X** and **Y** in the presence of an acid catalyst is shown:

$$\mathbf{X} + \mathbf{Y} \xrightarrow{H^+} \mathbf{Z}$$

The proposed mechanism for the reaction is:

$\mathbf{X} + H^+ \rightleftharpoons \mathbf{X}H^+$ fast

$\mathbf{X}H^+ + \mathbf{Y} \rightarrow \mathbf{Z} + H^+$ slow

Which one of the following rate equations would be consistent with the proposed mechanism?

rate = k[**X**][**Y**]
B rate = k[**X**]

rate = k[**X**][H^+][**Y**]
D rate = k[**X**H^+][**Y**]

Looking at the second/slow step, rate =

However, **X**H^+ is an____________and it should not be in the rate equation.

Since the fast step is an equilibrium, [**X**H^+] = K[**X**][H^+], where K is the equilibrium constant, the rate equation is thus rate = , where $k' = k\,K$.

rate =

Answer:

Self Check 6A

1. Consider the reaction between nitrogen dioxide and carbon monoxide.

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

The rate law is given by: rate = $k[NO_2]^2$

Which of the following mechanisms is consistent with this rate equation?

<u>Mechanism 1</u>

Step 1: $NO_2(g) \rightarrow O(g) + NO(g)$	slow
Step 2: $CO(g) + O(g) \rightarrow CO_2(g)$	fast

<u>Mechanism 2</u>

Step 1: $2NO_2(g) \rightarrow NO_3(g) + NO(g)$	slow
Step 2: $CO(g) + NO_3(g) \rightarrow NO_2(g) + CO_2(g)$	fast

2. Nitrogen monoxide and hydrogen gas reacts to form nitrogen and steam according to the equation: $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

Deduce a rate equation that is consistent with the mechanism below.

Step 1: $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$	slow
Step 2: $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O$	fast

3. In the presence of iodide ions, hydrogen peroxide decomposes according to the equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

Deduce a rate equation and an overall order that is consistent with the mechanism below.

Step 1: $H_2O_2 + I^- \rightarrow H_2O + OI^-$	slow
Step 2: $H^+ + OI^- \rightarrow HOI$	fast
Step 3: $HOI + H^+ + I^- \rightarrow H_2O + I_2$	fast

4. In the acidic medium, bromate(V) and bromide ions react according to the equation:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

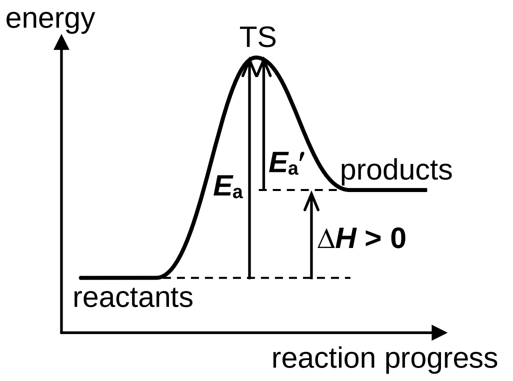
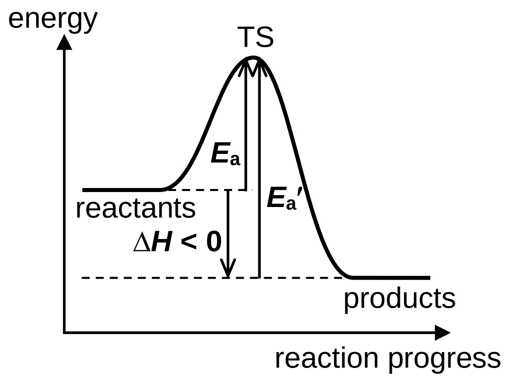
Deduce a rate equation that is consistent with the mechanism below.

Step 1: $Br^- + H^+ \rightleftharpoons HBr$	fast
Step 2: $BrO_3^- + H^+ \rightleftharpoons HBrO_3$	fast
Step 3: $HBrO_3 + HBr \rightarrow HBrO + HBrO_2$	slow
Step 4: $HBrO_2 + HBr \rightarrow 2HBrO$	fast
Step 5: $HBrO + HBr \rightarrow Br_2 + H_2O$	fast

7 Energy Profiles

Previously in Chemical Energetics, we saw the energy profiles of single-step reactions. Having discussed multi-step reactions in Section 6, we will also look at the energy profiles of multi-step reactions.

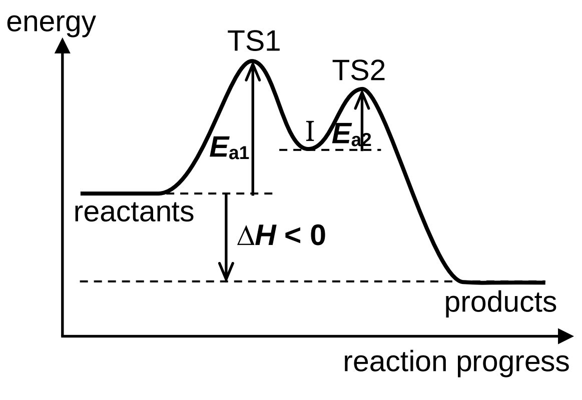
7.1 Energy Profile of a Single-Step Reaction

endothermic reaction, $\Delta H > 0$	**exothermic reaction, $\Delta H < 0$**
	

Energy profiles (or reaction pathway diagrams) for 1-step reactions

- The activation energy of the forward reaction (*i.e.* from reactants to products) is given by E_a while the activation energy of the backward reaction (*i.e.* from products to reactants) is given by E_a'.
- The profiles suggest that both reactions take place *via* a **single step** (which is also the rate determining step) because each profile only has **one transition state** (TS).

7.2 Energy Profile of a Multi-Step Reaction



Reaction pathway diagram (or energy profile) for a 2-step exothermic reaction

- There are **two transition states**, TS1 and TS2, and **one intermediate**, I.
- Applying a simplistic argument, since **$E_{a1} > E_{a2}$**, the **first step** (from reactants to intermediate) is the **rate determining step**.

Note: *Intermediate can be observed / isolated but transition state cannot be isolated. TS are usually postulated.*

Example 7A

Ozone in the stratosphere breaks down according to the reaction:

$2O_3(g) \rightarrow 3O_2(g)$ ΔH is negative

Mechanism

Step 1: $O_3(g) \rightarrow O_2(g) + O(g)$	slow
Step 2: $O(g) + O_3(g) \rightarrow 2O_2(g)$	fast

Draw the energy profile diagram given the above information and reaction mechanism.

Checkpoints for Section 6 & 7

I know how to:

☐ Explain and use the term: *rate-determining step*

☐ Appreciate and verify that a suggested reaction mechanism is consistent with observed kinetics.

☐ Predict the order that would result from a given reaction mechanism.

☐ Appreciate and interpret energy profiles of single- and multi-step reactions.

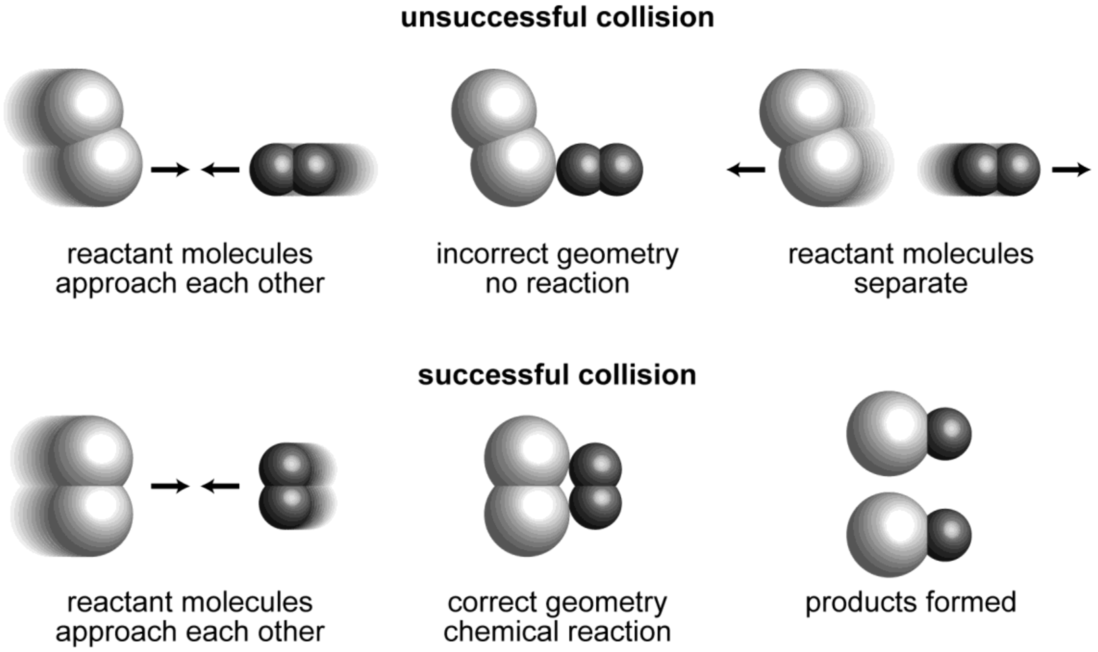
8 Factors Affecting Rate of Reaction

LO **(a)** explain and use the terms: *activation energy*
(f) explain qualitatively, in terms of frequency of collisions, the effect of concentration changes on the rate of a reaction
(h) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction

To better understand the factors affecting rate of reaction, let us take a look at the collision theory.

Collision Theory

When reactant particles collide with each other, not all collisions lead to reactions. The collision theory suggests that **only effective collisions lead to reactions** and for collisions to be effective, the **reactant particles must have a certain minimum energy known as the activation energy** and also the reactant particles must have the **correct orientation**.



Activation energy, E_a*, is the* ***minimum amount of energy that the reactant particles must have to collide effectively to form products****.*

- At the same temperature, a reaction with a lower activation energy will proceed faster.
- The **rate of any reaction will increase with the number of reactant particles that have energies greater than or equal to E_a.**
- The activation energy is required to overcome repulsion between the reactant particles, break chemical bonds and rearrange atoms, ions and/or valence electrons. If this energy barrier is not surmounted, colliding reactant particles will rebound without reacting.

Note that **reactions with overall order of 3 (or higher)** are **unusual and tend to be slow as it is difficult for 3 (or more) particles to collide in the correct orientation with the necessary amount of energy in the rate determining step**.

8.1 Surface Area of Reactants

- For a given mass of solid reactant, as **particle size decreases, surface area per unit volume increases**.
- Hence, the **frequency of effective collisions increases** and the reaction **rate increases**.

E.g. $CaCO_3$ (marble chips) + $2HC\ell(aq) \rightarrow CaC\ell_2(aq) + H_2O(\ell) + CO_2(g)$ slower

$CaCO_3$ (powder) + $2HC\ell(aq) \rightarrow CaC\ell_2(aq) + H_2O(\ell) + CO_2(g)$ faster

8.2 Concentration of Reactants

- As the **concentration** of a reactant **increases,** the **reactant particles are closer together** as the **number of molecules per unit volume increases**.
- Hence, the **frequency of effective collisions increases** and the reaction **rate increases**.

8.3 Pressure of Gaseous Reactants

Note:
$pV = nRT$

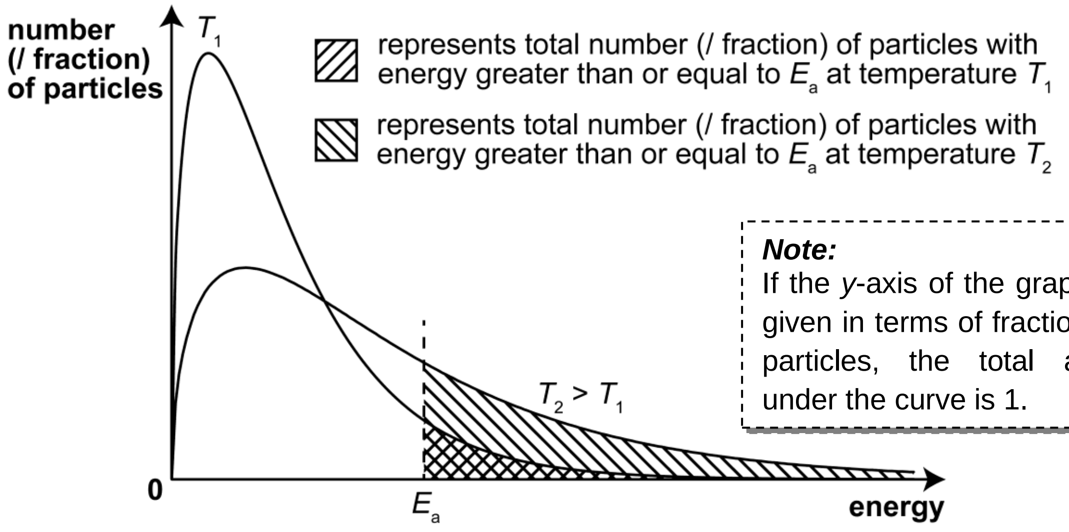
$$\Rightarrow p = \frac{n}{V}RT = cRT$$

$\Rightarrow p \propto c$ (at constant T)

- Pressure changes in a **gaseous** system will affect the rate of reaction as the **partial pressure of a gas is directly proportional to its concentration** at a particular temperature.
- An **increase in the partial pressure of a gaseous reactant** leads to an **increase in the concentration** of the reactant.
- Hence, the **frequency of effective collisions increases** and the reaction **rate increases**.

8.4 Temperature

A Maxwell-Boltzmann distribution curve shows how energy is distributed amongst the reactant particles in the system for a particular temperature.



Note:
If the *y*-axis of the graph is given in terms of fraction of particles, the total area under the curve is 1.

From the curve, at a given temperature,

- The **total area** under the Maxwell-Boltzmann distribution curve is proportional to the **total number of reactant particles** present. The particles do not all have the same **kinetic energy or speed**.
- Only a **small proportion** of reactant particles possesses **energy greater than or equal to the activation energy, E_a.**
- Hence, only a small fraction of colliding reactant particles is able to lead to reaction.

- As temperature increases, the **curve broadens and flattens** out as the distribution of energies become more spread out. Since the total area under the curve must remain constant (as the total no. of particles remains constant), the **peak shifts to the right and is lower than before**.

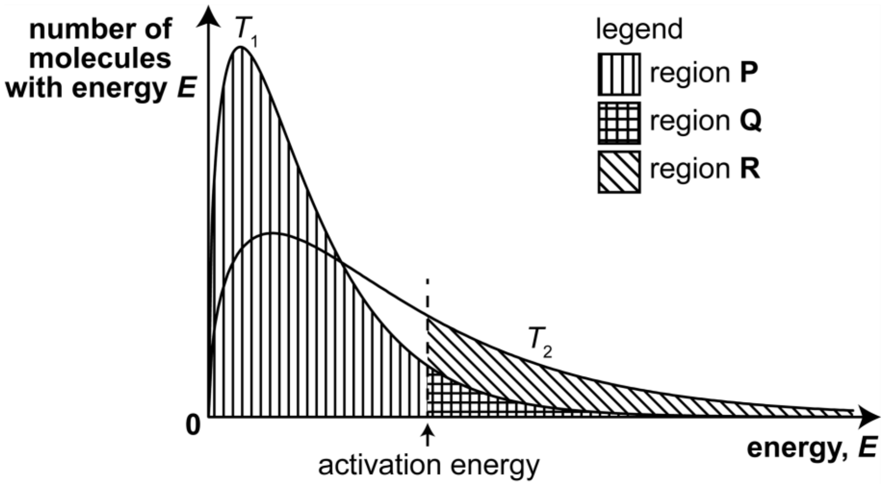
When temperature is increased, the

1. average speed and hence **average kinetic energy of the reacting particles increases, increasing the frequency of collisions**;
2. **number of reactant particles with energy greater than or equal to the activation energy, E_a, increases** (as shown by the larger shaded region).

Hence, the **frequency of effective collisions increases** and the rate constant increases, hence the reaction **rate increases**.

Example 8A

The distribution of the number of molecules with energy *E* is given in the sketch for two temperatures, T_1 and a higher temperature T_2. The letters **P**, **Q**, **R** refer to the separate and differently shaded areas. The activation energy is marked on the energy axis.



Which expression gives the fraction of the molecules present which have at least the activation energy at the higher temperature T_2?

A $\dfrac{\mathbf{Q}}{\mathbf{P}}$

B $\dfrac{\mathbf{Q}+\mathbf{R}}{\mathbf{P}}$

C $\dfrac{\mathbf{Q}+\mathbf{R}}{\mathbf{P}+\mathbf{Q}}$

D $\dfrac{\mathbf{Q}+\mathbf{R}}{\mathbf{P}+\mathbf{Q}+\mathbf{R}}$

8.4.1 Rate constant and the Arrhenius equation

The Arrhenius equation relates the rate constant, k, to the activation energy, E_a, and the absolute temperature, T (in Kelvin).

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

where A is the Arrhenius constant and R is the molar gas constant.

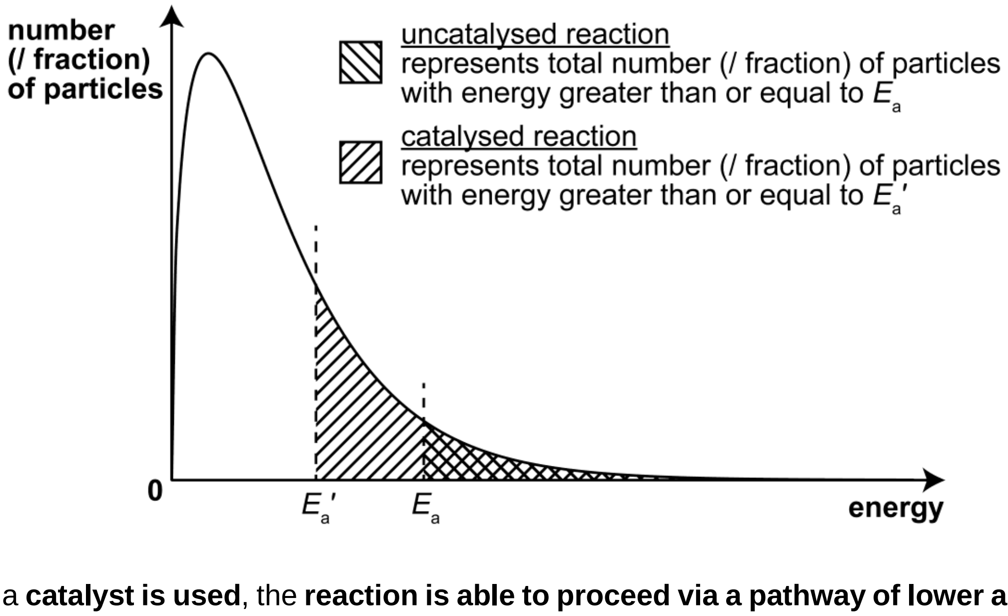
- When **temperature increases**, the **rate constant and hence the rate of reaction increases** (generally, rate is roughly **doubled** for every 10 K rise in temperature).
- When a **catalyst is used**, the reaction takes place via an **alternative reaction pathway of lower activation energy**. The **rate constant and hence the rate of reaction increases**.

8.5 Catalyst

LO **(a)** explain and use the terms: *catalysis*
(i) (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, *i.e.* one of lower activation energy, giving a larger rate constant
(ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution

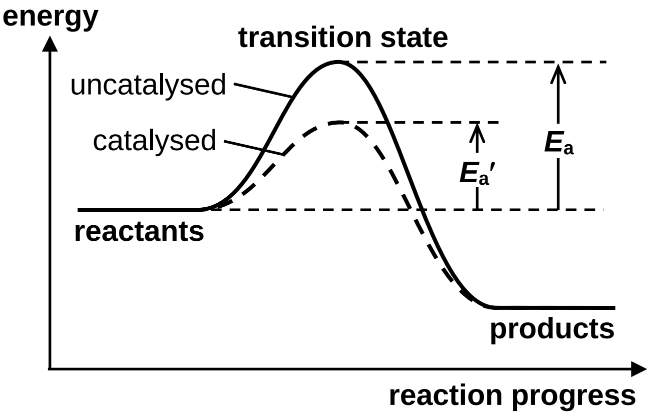
A ***catalyst*** *is a substance which* ***increases the rate of a chemical reaction*** *by* ***providing an alternative reaction pathway with lower activation energy*** and **remains chemically unchanged at the end of the reaction**.

A **catalyst does not affect the yield of the reaction** and is **regenerated at the end of the reaction**.



- When a **catalyst is used**, the **reaction is able to proceed via a pathway of lower activation energy, E_a'**. The **fraction of reacting particles having energy greater than or equal to the activation energy increases**.
- The **frequency of effective collisions increases** and the rate constant increases, and hence the reaction **rate increases**.

The energy profile below compares the difference in activation energies between a catalysed reaction (E_a') and an uncatalysed reaction (E_a).



There are four types of catalysis reactions: **(1) heterogeneous** catalysis **(2) homogeneous** catalysis **(3) autocatalysis (4) enzymatic** catalysis.

LO **(j)** outline the different modes of action of heterogeneous catalysis, including:
(i) the Haber process
(ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines (see also Section 11.3)

8.5.1 Heterogeneous catalysis

- The catalyst and reactants are in **<u>different physical phases</u>**.
  - The catalyst is usually in the solid phase while the reactants are usually liquids or gases.
- For heterogeneous catalysis to occur, the reactant molecules need to be readily **adsorbed** onto the catalyst surface. The heterogeneous catalyst provides sites (termed as **active sites**) on its surface at which there can be **formation of weak bonds between the reactant molecules and the surface catalyst atoms**.

Note: Adsorption is the **adhesion** of a substance to the surface of another substance

- Adsorption **weakens the covalent bonds** within the reactant molecules, thereby **reducing the activation energy** for the reaction.
- Adsorption **increases the concentration of the reactant molecules at the catalyst surface** and allows the reactant molecules to come into close contact and align in the **correct orientation** for successful reaction.

The table below shows some examples of heterogeneous catalysts.

reactions	heterogeneous catalyst
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Fe or Fe_2O_3
$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$	Rh, Pd & Pt
$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$	Pd, Pt or Ni
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	V_2O_5
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$	MnO_2

8.5.1.1 Haber Process

The reaction between nitrogen and hydrogen to form ammonia is a reversible reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

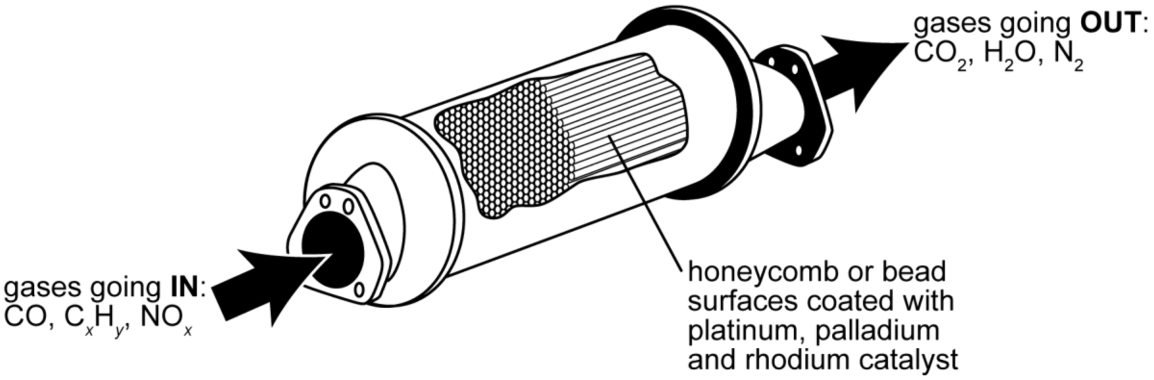
In order to speed up the reaction and favour the formation of ammonia, the Haber process is carried out industrially at 450 °C and at a pressure of 250 atm.

Finely divided **iron**, together with a promoter *e.g.* Al_2O_3, is used as a **heterogeneous catalyst** to further increase the rate of reaction by **weakening the triple bond in N_2**.

8.5.1.2 Catalytic removal of oxides of nitrogen in exhaust gases from car engines

To reduce air pollution, cars are fitted with **catalytic converters** to **remove three main pollutants (carbon monoxide, oxides of nitrogen and unburnt hydrocarbons) from exhaust fumes**.

A typical catalytic converter consists of a ceramic honeycomb structure coated with the precious metals **platinum (Pt), palladium (Pd) and rhodium (Rh)**, which acts as catalysts. A honeycomb structure helps to maximise the surface area on which heterogeneously catalysed reactions take place.



The three catalysts are selective in the reactions they promote. As the gases enter, the **oxides of nitrogen (NO_x) are reduced to N_2 by the excess CO present**, with **rhodium** acting as the **catalyst**.

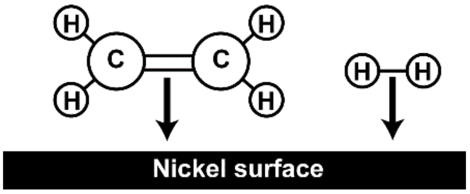
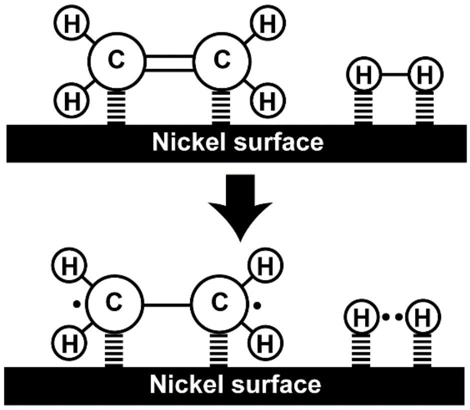
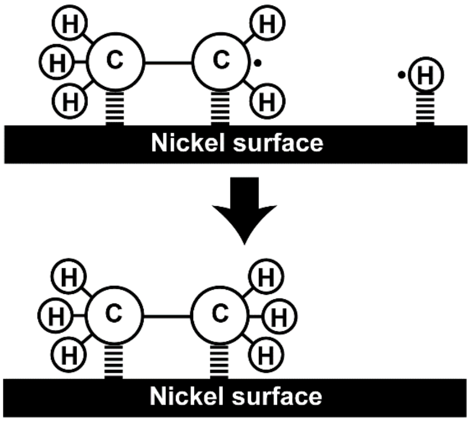
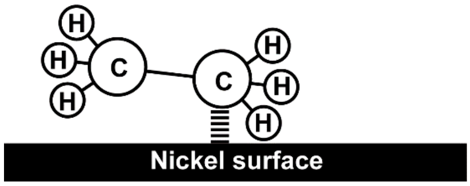
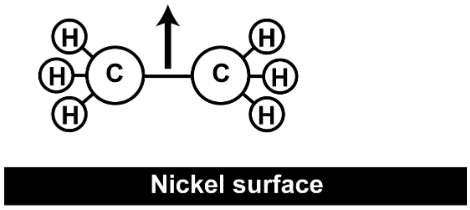
$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$ (Rh(s) as catalyst)

The **unburnt hydrocarbons and CO are oxidised to CO_2 and H_2O** with **platinum and palladium as the catalysts**. Catalytic converters are de-activated (or poisoned) by lead; *i.e.* the lead is preferentially adsorbed on the catalyst surface thereby occupying their actives sites. Hence, cars fitted with catalytic converters must be run on unleaded petrol.

$$\left.\begin{aligned} &\mathbf{2CO(g) + O_2(g) \rightarrow 2CO_2(g)} \\ &\mathbf{C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(g)} \end{aligned}\right\} \text{(Pt/Pd as catalyst)}$$

8.5.1.3 Catalytic Hydrogenation of Alkenes

Consider the reaction $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

	**Step 1: Diffusion** Reactant molecules diffuse towards the solid catalyst surface.
	**Step 2: Adsorption** These molecules **<u>physically adsorb onto the active sites</u>** of the solid catalyst surface by intermolecular forces of attraction. This **<u>increases the local concentration of reactants</u>**. Chemical bonds are formed between molecules on the active sites, thereby **<u>weakening the covalent bonds in the adsorbed reactant molecules</u>**.
	**Step 3: Chemical Reaction** Adjacent reactant molecules react to form products. This reaction has **<u>lower E_a</u>** than the uncatalysed reaction.
	**Step 4: Desorption** This is the reverse of adsorption. After the reaction, the **<u>adsorbed product molecules breaks free from the catalyst surface and leave the nickel surface</u>**.
	**Step 5: Diffusion** The product molecules diffuse away from the surface. The vacant active sites are now available for adsorbing other reactant molecules.

Note:
The use of a heterogeneous catalyst increases the rate of reaction. However, there is a **limited number of active sites on the surface of the catalyst**. Hence, the rate will not increase any further when all the active sites are occupied.

LO **(j)** outline the different modes of action of homogeneous catalysis, including:
(iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide
(iv) catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

8.5.2 Homogeneous catalysis

- The catalyst and reactants are in the **same physical phase**, either liquid or gaseous
- A **homogeneous** catalyst provides an alternative pathway with **lower activation energy** by forming an **intermediate** which is later consumed in the reaction. The product is formed with the regeneration of the catalyst.
- The catalytic activity of a homogeneous catalyst depends on its ability to exist in **variable oxidation states**.

The table below shows some examples of homogeneous catalysts.

reactions	homogeneous catalyst
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	$NO(g)$ or $NO_2(g)$
$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$	$Fe^{2+}(aq)$ or $Fe^{3+}(aq)$
$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + HI(aq)$	$H^+(aq)$

8.5.2.1 Reaction of iodide and peroxodisulfate ions

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

Due to **repulsion** between the negatively charged $S_2O_8^{2-}$ and I^- ions, the reaction has **high activation energy**, hence this reaction is slow. Ions such as $Fe^{2+}(aq)$ act as **homogeneous catalysts** by providing an alternative reaction pathway of lower activation energy.

Mechanism

Step 1: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

Step 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Since both steps involve the reaction between oppositely charged ions, the absence of electrostatic repulsion here (unlike in the uncatalysed reaction) results in a **lower** activation energy and increases the frequency of effective collisions and hence, increases the rate of reaction.

Note:
Only a small amount of $Fe^{2+}(aq)$ is required since it is regenerated by the reaction. $Fe^{3+}(aq)$, an intermediate in the reaction, may also catalyse the reaction (i.e. step 2 will take place before step 1).

8.5.2.2 Oxidation of atmospheric sulfur dioxide by atmospheric oxides of nitrogen

Atmospheric sulfur dioxide (from volcanic eruptions and burning of fossil fuels) can be oxidised to sulfur trioxide, but the reaction is slow in the absence of a catalyst.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Due to the high temperature involved in the combustion of fossil fuels and during lightning discharges, the *endothermic* oxidation of nitrogen in the air occurs.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Note: Most combustion reactions are exothermic, with the rare exception of nitrogen, due to its exceptionally strong N≡N triple bond.

In the atmosphere, further oxidation readily occurs.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Nitrogen dioxide formed can catalyse the oxidation of sulfur dioxide.

Mechanism

Step 1: $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$

Step 2: $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$

Sulfur trioxide is a secondary pollutant which dissolves in water vapour (in the air) to form sulfuric acid.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4\,(l)$$

This results in acid rain and amplifies the pollution problem caused by atmospheric sulfur dioxide. To reduce the emission of sulfur dioxide, many industrial countries enforce flue gas desulfurisation, *i.e.* removing sulfur dioxide from waste gases by reacting it with limestone, $CaCO_3$.

8.5.3 Autocatalysis

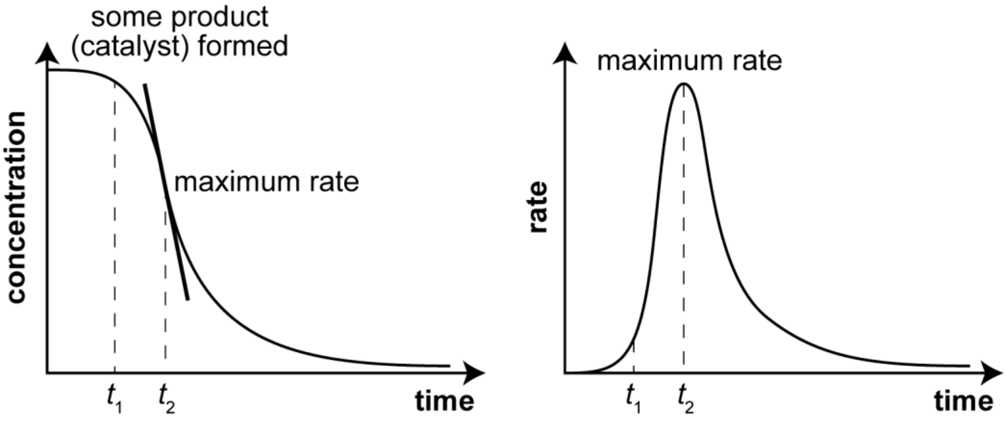
**** NOT IN H1 Chemistry Syllabus**

Catalysis *is a process in which a substance increases the rate of a chemical reaction without itself undergoing any permanent chemical change.*

Autocatalysis *is a process in which a product of a chemical reaction increases the rate of that reaction. This particular product is called an* ***autocatalyst****.*

Characteristics of an autocatalysed reaction:

- Reaction is **initially slow** due to **lack of catalyst**.
- Upon the **formation of the product/autocatalyst**, the rate **begins to increase** more and more rapidly.
- The rate will reach a maximum as more of the product/autocatalyst is formed. After this point, the **rate slows down due to the decrease in concentration of reactants**.



8.5.3.1 Reaction of manganate(VII) and ethanedioate ions in acidic medium

The reaction between MnO_4^- and $C_2O_4^{2-}$ in acid solution is catalysed by the Mn^{2+} formed during the reaction.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Initially, the reaction is slow. As the reaction proceeds, the purple MnO_4^- rapidly decolourises due to the formation of Mn^{2+} which act as the catalyst. Rate of reaction starts to increase when greater amount of the catalyst starts to form. The rate of reaction will eventually decrease despite the increasing concentration of the Mn^{2+} catalyst because the concentration of reactants decrease to very low levels.

LO **(k)** describe enzymes as biological catalysts which may have specific activity
(l) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

Making Thinking Visible

Q: Does the original reaction stop once the catalysis begins in an autocatalytic reaction? What determines the rate of reaction at any one point of time?

A: The original reaction does not stop, although it remains to be a slow reaction (and goes even slower as the concentration of reactants decrease to lower levels. The observed rate of decrease in reactant concentration is a consequence of two reactions, i.e. the original uncatalysed reaction and the catalysed reaction, albeit the catalysed reaction tends to be much faster.

Q: More Mn^{2+} is produced as the reaction proceeds, and there is an increasing rate of reaction at the start due to that. Does it mean that $[Mn^{2+}]$ affects the reaction and is in the rate equation even though Mn^{2+} is only a catalyst?

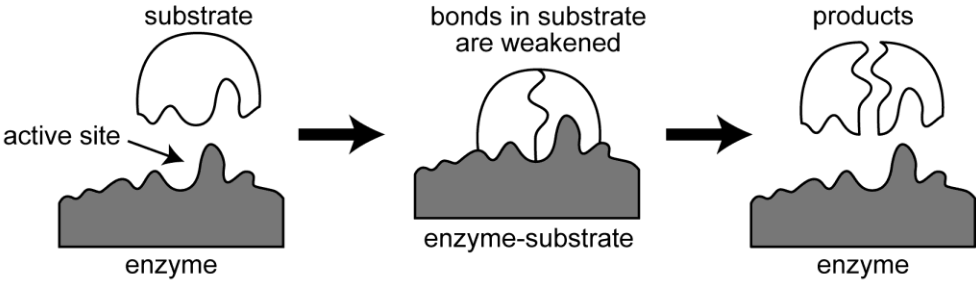
A: Catalysts can be part of the rate equation (see page 17)! In catalysed reactions, the concentration of the catalyst does not change over time, and hence the reaction tends to slow down with time. In auto-catalytic reactions, the concentration of the catalyst increases with time as it is the product of the reaction, and as such, there is an increasing rate of reaction at the start. The rate of the auto-catalysed reaction is a function of both the concentration of the catalyst (which is increasing) and the concentration of the reactants (which is decreasing), which explains the shape of the graph.

8.5.4 Enzymes

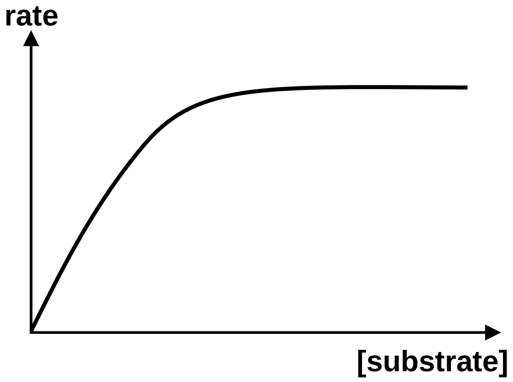
Enzymes are proteins which act as **biological catalysts** as they catalyse chemical reactions in living organisms. They are **highly specific** in that they catalyse particular reactions and react with specific reactants (referred to as substrates). A theory which accounts for this specificity is the **lock and key model**.

According to it, the substrate and the enzyme molecules have complementary shapes so that they fit together like a lock and its key. Each enzyme has an **active site** (specific region of the enzyme) into which **only one type of substrate** (reactant) can fit.

The substrate molecule moves into the active site on the enzyme and is bound by attractive forces. An enzyme-substrate complex is formed and this weakens the intramolecular bonding within the substrate, thus providing an alternative reaction pathway of lower activation energy.
The enzyme-substrate complex then breaks apart to release the products as the products formed are no longer of the right shape to remain in the active site. Now the enzyme is free to bind to another substrate molecule.



For a fixed amount of enzymes, there is a limited number of **active sites**. When substrate is in excess, the rate of reaction is **directly proportional** to [enzyme], *i.e.* reaction is **first order** with respect to the enzyme.



At low [substrate]

- There are **available active sites for the substrate molecules to bind to**.
- **Rate of reaction is directly proportional to [substrate]** *i.e.* reaction is **first order** with respect to the substrate.

As **[substrate] increases**, there are **fewer active sites available** for catalysis. Thus, the **increase in rate of reaction becomes smaller** and reaction is **no longer first order with respect to the substrate**.

At high [substrate]

- **Substrate molecules occupy all the active sites** and the **enzyme is saturated**.
- **Rate of reaction will be independent of [substrate]** *i.e.* reaction is **zero order** with respect to the substrate. The rate remains the same even though the substrate concentration increases.

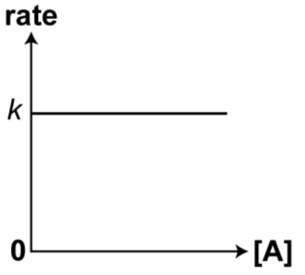
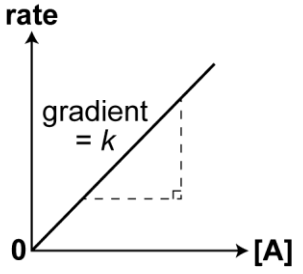
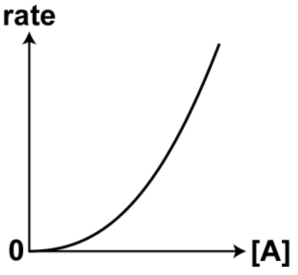
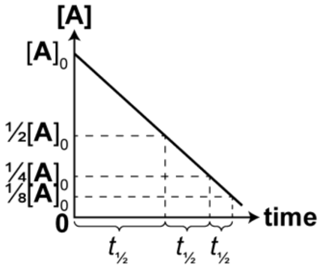
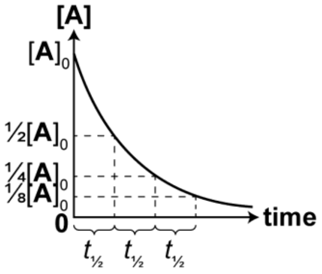
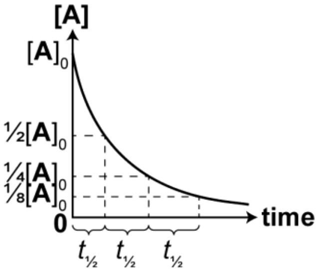
Checkpoints for Section 8

I know how to:

☐ Understand factors affecting rate of reaction in terms of collision theory and activation energy.
☐ Interpret, draw and explain, using Maxwell-Boltzmann distribution curve, the effect of temperature and catalyst on the rate of reaction, with reference to activation energy, collision frequency.
☐ Understand how temperature affects rate constant (in Arrhenius equation) and hence rate of reaction.
☐ Understand how catalyst (including enzymes) affects rate of reaction.
☐ Appreciate and understand some examples of homogeneous, heterogeneous and autocatalysis.

9 Summary

Types of Order of Reaction

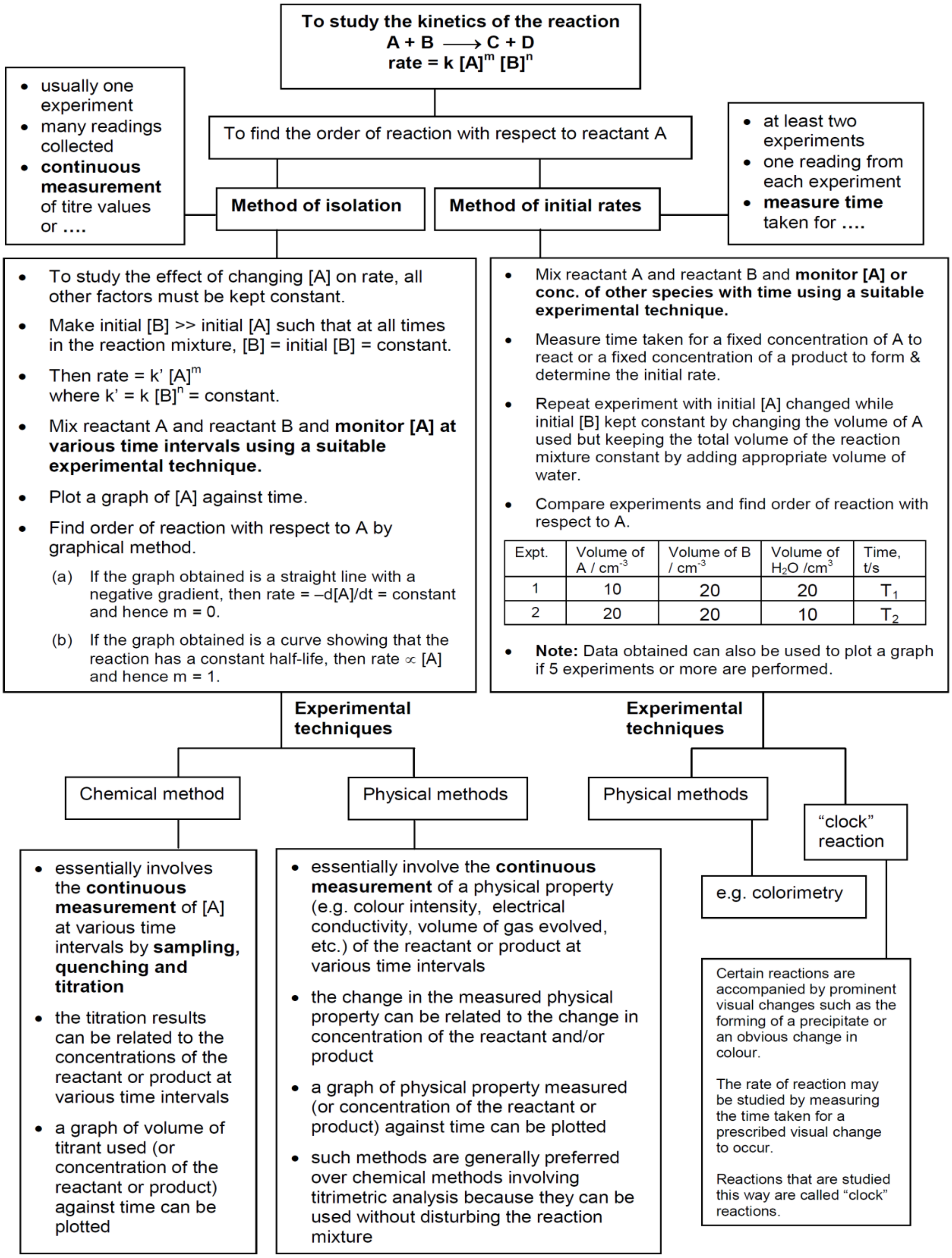
	zero order	first order	second order
rate eqn	rate = $k[A]^0$	rate = $k[A]^1$	rate = $k[A]^2$
units of *k*	mol dm^{-3} s^{-1}	s^{-1}	mol^{-1} dm^3 s^{-1}
graph: **rate of rxn against [reactant]**			
graph: **[A] against time**			
to determine the order of reaction:	1. Plot **[A]** against **time** graph. 2. A **straight-line** graph (with –ve gradient) should be obtained.	1. Plot **[A]** against **time** graph and check that successive **half-lives are constant**. 2. Plot **rate** against **[A]** graph and a **straight line** passing through origin should be obtained.	1. Plot **rate** against **$[A]^2$** graph 2. A **straight line** that passes through origin should be obtained.
half-lives	half-life decreases with decreasing **[A]**	constant; $t_{1/2} = \frac{\ln 2}{k}$	half-life increases with decreasing **[A]**

Factors Affecting Rate of Reaction

change	effect on rate of reaction	effect on rate constant, *k*	effect on activation energy, E_a
increase in concentration	increased (if the reaction is not a zero order reaction)	no effect	no effect
increase in pressure (gaseous system)	Increased (if the reaction is not a zero order reaction)	no effect	no effect
increase in temperature	increased	increased	no effect
addition of a catalyst	increased	increased	decreased

Studying Kinetics – Experimental Methods for Studying Reaction Rate

- To study the kinetics of a reaction (*i.e.* to measure the reaction rate and subsequently to determine the rate equation), we need to be able to monitor the concentration of a reactant or product of that reaction at various times as the reaction proceeds.
- The choice of which reactant or product to monitor depends on which species in the reaction can be easily, yet accurately analysed.



To study the kinetics of the reaction
$A + B \longrightarrow C + D$
rate = k $[A]^m$ $[B]^n$

To find the order of reaction with respect to reactant A

Method of isolation

- usually one experiment
- many readings collected
- **continuous measurement** of titre values or ….

- To study the effect of changing [A] on rate, all other factors must be kept constant.
- Make initial [B] >> initial [A] such that at all times in the reaction mixture, [B] = initial [B] = constant.
- Then rate = k' $[A]^m$ where k' = k $[B]^n$ = constant.
- Mix reactant A and reactant B and **monitor [A] at various time intervals using a suitable experimental technique.**
- Plot a graph of [A] against time.
- Find order of reaction with respect to A by graphical method.
  - (a) If the graph obtained is a straight line with a negative gradient, then rate = –d[A]/dt = constant and hence m = 0.
  - (b) If the graph obtained is a curve showing that the reaction has a constant half-life, then rate ∝ [A] and hence m = 1.

Method of initial rates

- at least two experiments
- one reading from each experiment
- **measure time** taken for ….

- Mix reactant A and reactant B and **monitor [A] or conc. of other species with time using a suitable experimental technique.**
- Measure time taken for a fixed concentration of A to react or a fixed concentration of a product to form & determine the initial rate.
- Repeat experiment with initial [A] changed while initial [B] kept constant by changing the volume of A used but keeping the total volume of the reaction mixture constant by adding appropriate volume of water.
- Compare experiments and find order of reaction with respect to A.

Expt.	Volume of A / cm^{-3}	Volume of B / cm^{-3}	Volume of H_2O /cm^3	Time, t/s
1	10	20	20	T_1
2	20	20	10	T_2

- **Note:** Data obtained can also be used to plot a graph if 5 experiments or more are performed.

Experimental techniques

Chemical method

- essentially involves the **continuous measurement** of [A] at various time intervals by **sampling, quenching and titration**
- the titration results can be related to the concentrations of the reactant or product at various time intervals
- a graph of volume of titrant used (or concentration of the reactant or product) against time can be plotted

Physical methods

- essentially involve the **continuous measurement** of a physical property (e.g. colour intensity, electrical conductivity, volume of gas evolved, etc.) of the reactant or product at various time intervals
- the change in the measured physical property can be related to the change in concentration of the reactant and/or product
- a graph of physical property measured (or concentration of the reactant or product) against time can be plotted
- such methods are generally preferred over chemical methods involving titrimetric analysis because they can be used without disturbing the reaction mixture

Experimental techniques

Physical methods

e.g. colorimetry

"clock" reaction

Certain reactions are accompanied by prominent visual changes such as the forming of a precipitate or an obvious change in colour.

The rate of reaction may be studied by measuring the time taken for a prescribed visual change to occur.

Reactions that are studied this way are called "clock" reactions.

10 Self-Check Answers

2A

D

Let rate = r, $[Br_2]$ be a, and $[HCO_2H]$ be b. Hence, rate = $k[Br_2][HCO_2H] \Rightarrow$ Thus $r = kab$

If $[HCO_2H] \times 2$ $r' = ka(2 \times b) = 2kab = 2r$ $\Rightarrow$ rate × 2	If $[HCO_2H] \times \frac{1}{2}$, $[Br_2] \times \frac{1}{2}$ $r' = k(\frac{1}{2}a)(\frac{1}{2}b) = \frac{1}{4}kab = \frac{1}{4}r$ $\Rightarrow$ rate × ¼	Overall order = 1 + 1 = 2

3A

1 $\boldsymbol{c_t = c_0 (\frac{1}{2})^n}$

$n = \frac{80}{8} = 10$ half-lives. Hence, fraction of isotope remaining = $(\frac{1}{2})^{10} = \frac{1}{2^{10}}$ **(D)**

2

Time	**Uranium**	**Lead**
0	x	0
1st $t_{½}$	$\frac{1}{2}x$	$\frac{1}{2}x$
2nd $t_{½}$	$\frac{1}{4}x$	$\frac{3}{4}x$

After 2 half-lives, the mole ratio of U to Pb is 1 : 3.

Time taken = $2 \times 4.5 \times 10^9 = 9.0 \times 10^9$ years Ans: **C**

4A

(a) Water is added to keep the total volume of the reaction mixture constant so that the concentration of a reactant is **directly proportional** to its volume (*i.e.* volume of reactant used ∝ [reactant]).

(b)

Experiment	Relative rate of reaction $\propto \frac{\text{volume of aqueous iodine used}}{\text{time for colour of iodine to disappear}}$
1	4
2	2
3	2
4	4

To determine the order of reaction w.r.t H^+	To determine the order of reaction w.r.t. CH_3COCH_3	To determine the order of reaction w.r.t. I_2
Compare experiment 1 & 2, where $[CH_3COCH_3]$ and $[I_2]$ are kept constant, when $[H^+] \times \frac{1}{2}$, rate × ½ Reaction is **1st order** w.r.t. H^+ OR Let order of reaction w.r.t. H^+ be x $\frac{\text{rate}_1}{\text{rate}_2} = \left(\frac{V_{H^+,1}}{V_{H^+,2}}\right)^x$ $\frac{4/1}{4/2} = \left(\frac{8}{4}\right)^x$ $\boldsymbol{x = 1}$	Compare experiment 1 & 3, where $[H^+]$ and $[I_2]$ are kept constant, when $[CH_3COCH_3] \times \frac{1}{2}$, rate × ½. Reaction is **1st order** w.r.t. CH_3COCH_3 OR Let order of reaction w.r.t. CH_3COCH_3 be y $\frac{\text{rate}_1}{\text{rate}_3} = \left(\frac{V_{CH_3COCH_3,1}}{V_{CH_3COCH_3,3}}\right)^y$ $\frac{4/1}{4/2} = \left(\frac{8}{4}\right)^y$ $\boldsymbol{y = 1}$	Compare experiment 1 & 4, where $[H^+]$ and $[CH_3COCH_3]$ are kept constant, when $[I_2] \times \frac{1}{2}$, rate **remains unchanged**. Reaction is **zero order** w.r.t. I_2 OR Let order of reaction w.r.t. I_2 be z $\frac{\text{rate}_1}{\text{rate}_4} = \left(\frac{V_{I_2,1}}{V_{I_2,4}}\right)^z$ $\frac{4/1}{2/0.5} = \left(\frac{4}{2}\right)^z$ $\boldsymbol{z = 0}$

	Rate = k[H^+][CH_3COCH_3]
6A	**1** Mechanism 2 **2** Rate = $k[NO]^2[H_2]$ **3** Rate = $k[H_2O_2][I^-]$, Overall order = **2** **4** The rate of reaction depends on the [HBr] and [$HBrO_3$]. In turn, the rate of formation of HBr depends on the concentrations of [H^+] and [Br^-] while the rate of formation of $HBrO_3$ depends on the concentrations of [H^+] and [BrO_3^-]. Therefore, **rate = $k[BrO_3^-][Br^-][H^+]^2$**