

REACTION KINETICS

Content

- Simple rate equations; orders of reaction; rate constants
- Concept of activation energy
- Effect of concentration, temperature, and catalysts on reaction rate
- Homogeneous and heterogeneous catalysis
- Enzymes as biological catalysts

Learning Outcomes

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

(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 SO_2
- (iv) catalytic role of Fe^{2+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction

(k) describe enzymes as a protein molecules that act as biological catalysts with high specificity (in the reactions that they catalyse and in their choice of substrates as exemplified by the lock-and-key model), temperature

1 DEVELOPMENT OF CHEMICAL KINETICS

The concept of Chemical Kinetics started since 1700s and was developed by numerous experts of various nationalities in the field of Science and Mathematics to reach the understanding which we have today. The conceptual development started first with the focus on the finding of general laws for chemical reactions and relating kinetics to thermodynamics, followed by understanding of reactions through mechanism and transition states to describe multi-step chemical reaction. Below is a quick look at the progress in the development of Chemical Kinetics (or during those time, *Chemical Dynamics*).

Period of Chemical Affinity Understanding Chemical Bonding	17th Century Dominated by the investigation in a concept that chemical force, called "<i>affinity</i>", causes dissimilar substances are held together to form a chemical compound.  French Chemist, Antoine-Laurent de Lavoisier (1743-1794) proposed quantitative methods to justify the explanations rather than make merely qualitative description.
The Beginnings Initial exploration to better understand Chemical Dynamics (Kinetics)	1770s German Chemist, Carl Friedrich Wenzel (1740-1793) - measured rates of solution of metals in acid - found the rate of reaction to be proportional to acid concentration 1818  French Chemist, Louis Jacques Thenard (1777-1857) - did an experimental study of the rate of decomposition of H_2O_2 but did no quantitative explanation. 1850s  German Physicist, Ludwig Ferdinand Wilhelm (1812-1864) - Investigated the effect of various acid concentration on acid-catalysed hydrolysis of sucrose by polarimeter First to quantitatively describe instantaneous rate of change of sugar concentration being proportionate to sugar and acid concentration. - Also examined the influence of temperature on rate of reaction and again proposed equation to justify results. Their research focus was on discovering new compounds rather than interpreting behaviour in concepts or theory. Hence, did not went at length to derive equations to justify the observation His work caught little attention despite being the first of such work. This could be due to it being in the less popular physical-chemical area, polarimetry being a new and less used technique and also his lack of fame that led to his work going unnoticed until 1884 when the more famous Ostwald draw attention to his work.

The Beginnings
Initial exploration to better understand Chemical Dynamics
(Kinetics)

1860s



French Chemists,

Pierre Eugene Marcelin Berthelot (1827-1907) **picture on left*
Leon Pean De Saint Gilles (1832-1863)

- Found as a side result that rate is proportionate to the product of the reactant concentration.
- Studied the kinetics of reversible reactions.

Norwegian Chemist, **Peter Waage** (1833-1900)Norwegian Mathematician, **Cato M. Guldberg** (1836-1902)

- Waage involved Guldberg as he was limited in mathematics, as were other scientists back then.
- Built on Berthelot's work and developed the Law of Mass action, stating that rate of reaction is directly proportional to the **product of the masses** of the reactants
- Tried deriving the rate equation, but incorrectly assumed that rate equation can be deduced from stoichiometric equations. Also, lack the instruments to justify and interpret the equation correctly.

Finding the Law that Governs it all
Deriving General Law using Mathematical Equations

1880s



Dutch Chemist,

Jacobus Henricus Van 't Hoff (1852-1911)

- One of the founders of Physical Chemistry
- Discovered the relationship between rate constant and equilibrium constant. Later, related the rate constant to temperature. All these, he justified using mathematical equations.
- Classified chemical reactions at microscopic level as mono, bi or poly molecular (order of reaction).
- These conclusions were later used by Arrhenius for his studies
- He laid down many equations which was picked up by other researchers, furthering the studies in this field.



Swedish Chemist-Physicist,

Svante August Arrhenius (1859-1927)

- Re-studied the classical case of acid-catalysed hydrolysis of sugar (as done by Wilhelmy)
- Introduced the concept of activation energy.
- Using the equations proposed by Van 't Hoff, came up with the *Arrhenius Equation*, relating activation energy to rates of reaction, and related temperature to the rate constant.



Russian-German Chemist,

Friedrich Wilhelm Ostward (1853-1932)

- Was studying Catalysis when he found kinetics an intricate part which needs to look deeper into.
- Developed the idea of method of isolation (pseudo first order), half-life, autocatalysis and classification of catalysis.
- He brought to spotlight many of the other studies on kinetics which had not been noticed and even translated a few into German, the language of science back then.

Towards Modern Chemical Kinetics
Kinetics and its application in understanding reaction

1900s and beyond



German Physical Chemist,
Max Bodenstein (1871-1942)

- Developed the concept of **Transition State Theory**
- Clarified mechanisms of Catalysed Reaction
- Proposed a mechanism for Chain Reaction



English Physical Chemist,
Cyril Norman Hinshelwood (1897 –1967)

- Studied Molecular Kinetics which was then used to quantitatively explain the phenomenon of Chain Reaction



Russian Physicist and Chemist,
Nikolay Nikolayevich Semyonov (1896 – 1986)

- Also independently explain quantitatively the kinetics involved in Chain Reaction.
- Awarded Nobel Prize with Hinshelwood for their works in seeking mechanism for Chain Reaction.

What can we learn from these events leading up to the modern concept of Kinetics?

Science is a pursuit to explain the natural phenomenon happening around us.

Scientific knowledge and ideas are generated through observation of nature either through experiment or simply by daily encounters.

Science is built upon evidences.

Scientists built the general laws and concepts through gathering and evaluating of evidences. Scientists cannot just give a statement and call it a scientific knowledge. Evidences need to be sought through thorough studies in order to formulate a durable idea.

Science is a complex social construct, is durable yet tentative.

Science is not made by one man alone. As we can see from the development of the concept of Kinetics, scientists of different nationalities, different research interest and different abilities collectively contribute to the pool of knowledge over a long period of time, testing and building on each other's hypothesis/proposal in order to derive general laws which accurately describe the natural state. Hence, what we have today is credible and is as close as we can know with our technology (durable). However, as new discoveries and advances are made, new evidences may appear which require us to re-evaluate what we have and adjust our knowledge accordingly (tentative).

2 INTRODUCTION

Chemical reactions are processes where starting materials are converted into specific products. For a chemical reaction to occur, three important questions should be asked:

Chemical Reaction		
Can a particular reaction <u>occur</u> under defined conditions?	How much of the starting material can be converted to products?	If a reaction can occur, <u>how fast</u> will it proceed?
Feasibility	Yield	Speed
These two questions can be easily answered by THERMODYNAMICS concept through the consideration of the <i>energy</i> and <i>entropy</i> changes associated with a reaction.		The investigations of rates of reactions are the domain of KINETICS. The effects of concentrations of reactants, catalyst and the temperature on the rate of reaction provides insight into the mechanism of a reaction (how particles react with each other).

In this chapter, we will focus on learning about the concept of kinetics and its use in understanding chemical reactions.

This will be done through studying kinetics qualitatively and quantitatively at two levels:

- (1) **MACROSCOPIC LEVEL**: addresses rates of reactions: what reaction rate means, how to determine a reaction rate and the rate equation experimentally, and how factors such as temperature, reactant concentration and the use of a catalyst influence rate.
- (2) **PARTICULATE LEVEL**: addresses the mechanism of the reaction, the detailed pathway taken by atoms and/or **particles** as a reaction proceeds. We need to learn at a particulate level, how does the distribution of energy before, during and after reaction affect the (i) **energetic** feasibility and (ii) **kinetic** feasibility (rate) of a chemical reaction?

3 BASIC CONCEPT IN KINETICS

3.1 COLLISION THEORY

(Understanding reaction at particulate level)

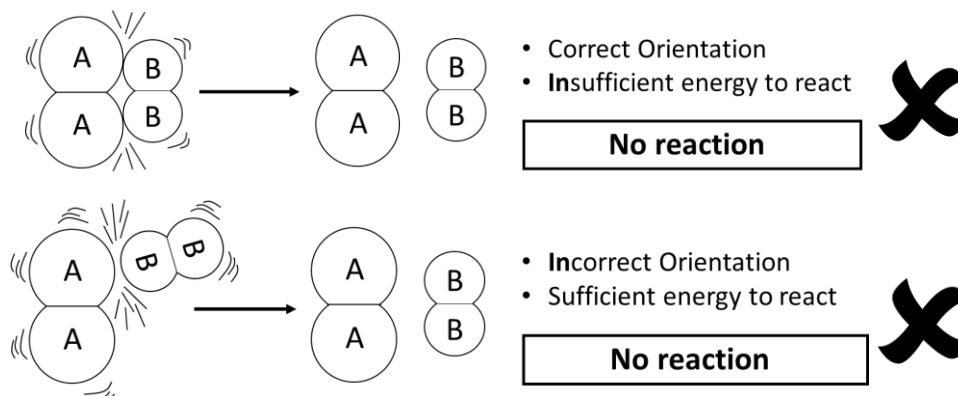
For a reaction between two particles to occur two conditions must be met:

- 1) The particles must collide in the **correct orientation**.
- 2) The particles must collide with **sufficient minimum energy (known as the activation energy)** to bring about the necessary re-organisation of the bonds in the colliding particles.

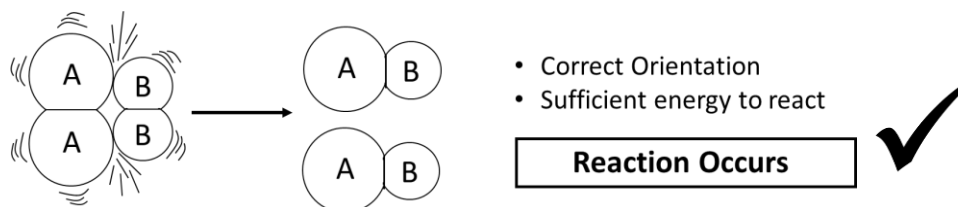
Assuming product to be A-B ,

Note:

The greater the number of particles involved in a single step, the more difficult it is to have all of them to collide at the correct orientation to affect a reaction. Hence usually, only a maximum of two particles will collide in a particular step of a reaction.



When particles **collide at the correct orientation and sufficient energy**, this collision is known as **effective collision** which will bring about a chemical reaction.



The greater the frequency of effective collisions, the greater the rate of reaction.

Hence, we can easily deduce that the experimental conditions required for increasing the number of effective collisions to increase reaction rate are:

- Increase in temperature of the reacting particles
- Increase concentration of particles/ increasing surface area of solid particles
- Use of catalyst

3.2 FACTORS AFFECTING RATE OF REACTION

3.2.1 Concentration of Aqueous or Gaseous Reactants

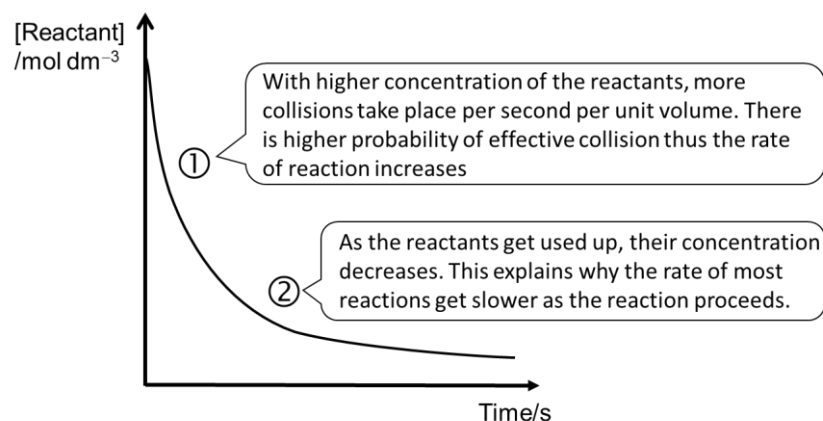
Success criteria:

- I can explain how changes to the concentration or pressure affects the rate of a reaction.

Rate of reaction **increases** as the concentration of reactants is increased.

Increasing the concentration or pressure (for gases) is equivalent to increasing the amount of reactants particles per unit volume. This will increase the frequency of effective collisions between **particles** and this increases the rate of reaction.

The rate of a typical reaction is fastest at the beginning, where concentration of reactants is at their highest and gradually decreases as the reactants are used up and their concentration decreases.

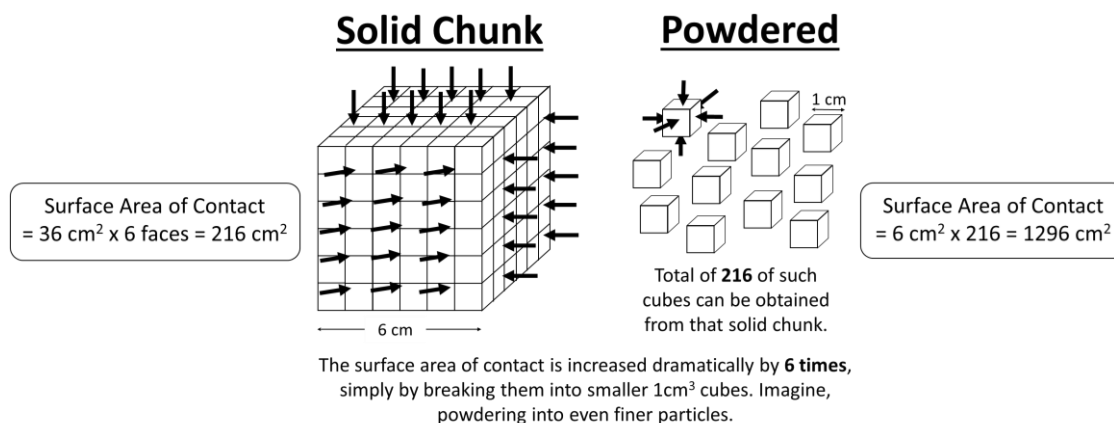


3.2.2 Surface Area of Solid Reactant

Success criteria:

- I can explain how changes to the particle size of a solid reactant/surface area of contact affects the rate of reaction.

In a solid substance, only the particles on the surface can come into contact with a surrounding reactant. If the solid is in powdered form, then the surface area of contact increases dramatically, frequency of effective collision increases. Hence, rate increases correspondingly.



BOLTZMANN DISTRIBUTION CURVE

Success criteria:

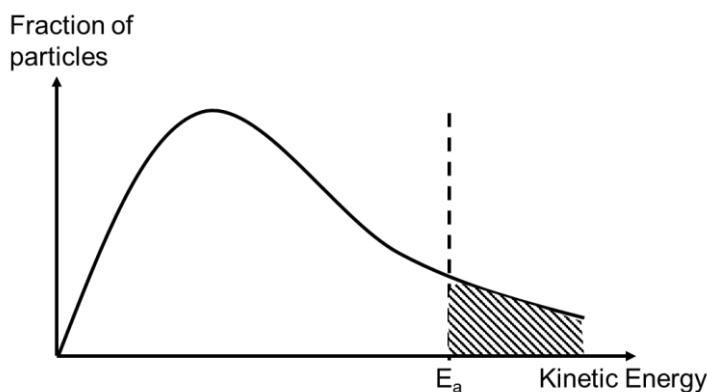
- I can draw the Boltzmann distribution curve and use it to explain the change in rate of a reaction by relating to the fraction of particles having kinetic energy greater or equal to the activation energy.

Note for drawing Boltzmann distribution curve:

- Graph must start from origin as there are no particles with zero energy.
- Graph should taper off.
- Shade the appropriate area under the curve to show proportion of particles with K.E. $\geq E_a$.

Boltzmann Distribution Curve shows energy distribution of reactant particles before reaction. Particles in a system have a range of kinetic energies. This energy distribution of particles can be represented using the Boltzmann distribution curve. In practice, only a certain fraction of the reactant particles has sufficient energy ($\text{K.E.} \geq E_a$) that result in reaction upon collision, as shown by the shaded area in the Boltzmann distribution curve.

The greater the number of particles having kinetic energy $\geq E_a$, the greater the frequency of effective collision, the faster the rate of reaction



3.2.3 Temperature

Success criteria:

- I can draw the Boltzmann distribution curve at two different temperatures and use it to explain how a change in temperature affects the rate of the reaction.

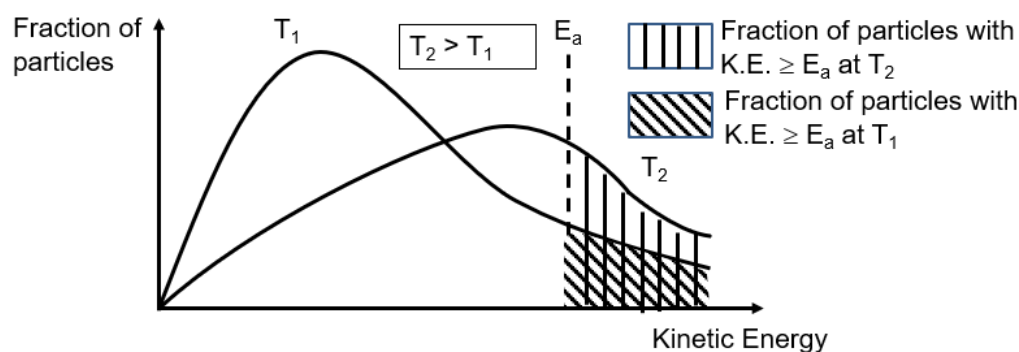
Increasing temperature of the reaction causes an increase in the rate of reaction. Rate approximately doubles for every 10 °C increase in temperature.

Worked example 1

$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ undergoes a substitution reaction to form $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ as shown in the reaction below.



With the aid of Boltzmann distribution curve, predict and explain the effect on the rate of this reaction when the reaction temperature is increased.



When temperature of the reaction increases, average kinetic energy of the reacting **particles** increases. The fraction of **particles** with $\text{K.E.} \geq E_a$ increases as shown in the Boltzmann distribution. The frequency of effective collisions increases hence rate of reaction increases.

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3.2.4 Catalyst

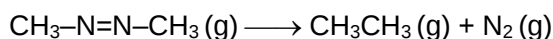
Success criteria:

- I can draw the Boltzmann distribution and use it to explain how the catalyst increases the rate of a chemical reaction.

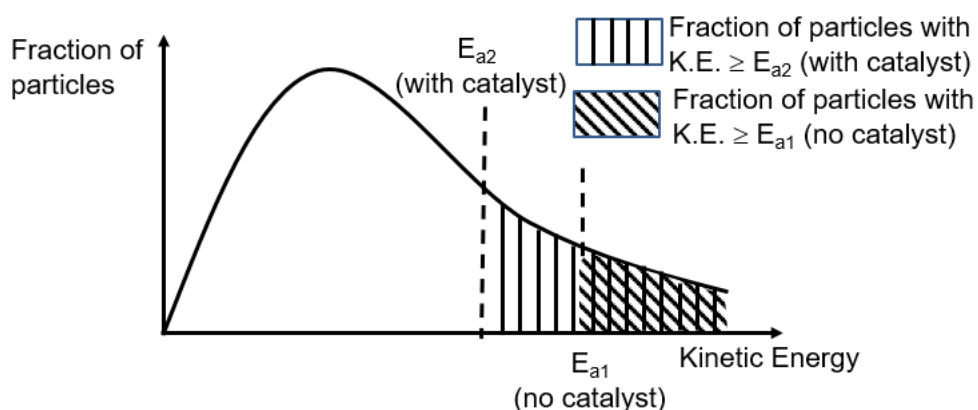
A catalyst speeds up the rate of a chemical reaction by **providing an alternative pathway with lower activation energy**. It does not undergo any permanent chemical change (not used up at the end of reaction). It exerts **no effect on the enthalpy change** of the reaction.

Worked example 2

Azomethane, $\text{CH}_3\text{--N=N--CH}_3$, is a common compound used in cancer research. It decomposes according to the following equation:



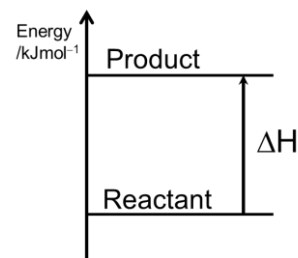
With the aid of the Boltzmann distribution, explain why the addition of a catalyst increases the rate of a reaction.



A catalyst provides an alternative reaction pathway with lower activation energy (E_{a2}). The fraction of **particles** with K.E. $\geq E_a$ increases as shown in the Boltzmann distribution. The frequency of effective collisions increases hence rate of reaction increases.

ENERGY PROFILE DIAGRAM

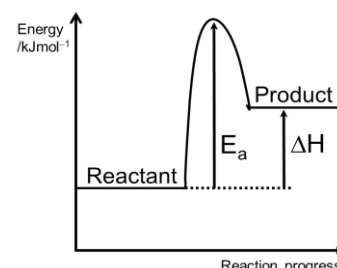
In Energetics, we have learnt to draw **energy level diagram** which shows the stability of product relative to reactant. The energy level diagram (on the left) shows that in an endothermic reaction, product is less stable than reactant. The reaction is thus not energetically favorable.



Note:

From the energy profile diagram, the energy changes during a reaction are shown. The **activation energy (E_a)**, which is the minimum amount of energy required to initiate a chemical reaction, influences the rate of reaction. A similar reaction which follows a different reaction pathway will have a different activation energy.

To address both energetic feasibility and kinetic feasibility (rate) of a reaction, an **energy profile diagram** should be drawn. It shows energy changes of particles *throughout a reaction*.



From the energy profile diagram, the following can be inferred:

- relative stability of reactants/ products
- number of steps
- magnitude of activation energy in the reaction.

From the magnitude of the activation energy (E_a), the rate of reaction can be inferred. A higher E_a indicates a slower reaction.



How to make sense of an energy profile diagram?
Watch <https://go.gov.sg/njc-kinetics-1> to find out.



Below are examples of energy profile diagram for reactions with a single and double step.

Case 1: Single Step Reaction

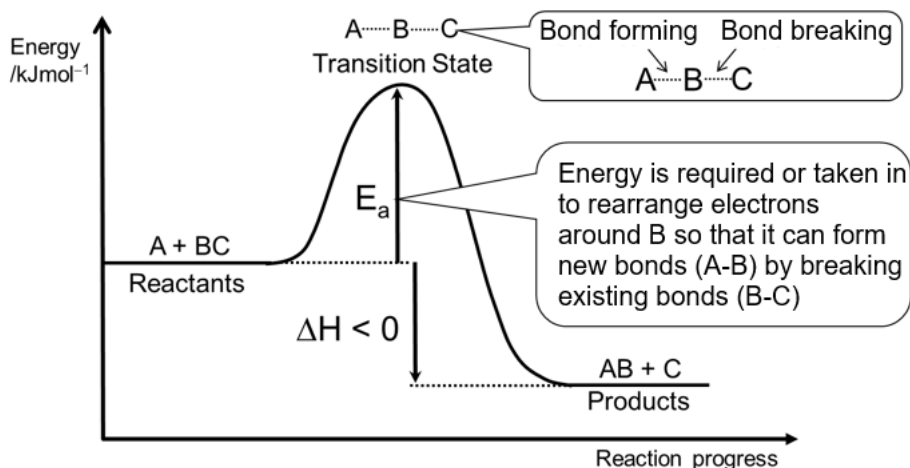
Consider $A + BC \longrightarrow AB + C$ (taking place in one single step)

Note:

A **transition state** is a hypothetical stage that resulted from the collision of reactants at the correct orientation and with sufficient energy.

At this stage, it is equally likely to form the reactants and the products. It is the **most unstable** state therefore appears at the maximum energy.

There will be only a **single transition state (hump)**, indicating simultaneous bond breaking and bond forming.



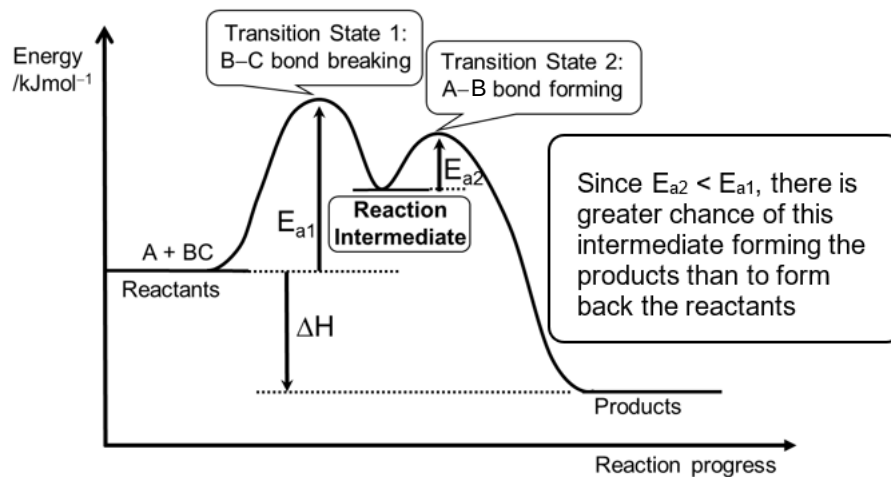
Case 2: Two Steps Reaction

Consider $A + B-C \longrightarrow AB + C$ (taking place in 2 steps)

In such cases, there will be **two transition states (humps)**, since **two elementary steps** are needed to reach the final product.

Note:

In this example, the first elementary step of this reaction has higher E_a , therefore overall rate of this reaction depends on the first elementary step which is also known as **slow step (rate determining step)**.



A **reaction intermediate** is a **short-lived species** formed in one of the steps in a multi-step reaction and is consumed in a subsequent step. It is neither a reactant nor an ultimate product of the overall reaction but is **stable** enough to be isolated for a short period of time.

3.3 TYPES OF CATALYST

Success criteria:

- I can distinguish between homogeneous and heterogeneous catalyst.
- I can provide examples, (i) the Haber process and (ii) the catalytic removal of oxides of nitrogen in car engine exhaust gases, to illustrate the modes of action of heterogeneous catalysis.
- I can provide examples, (i) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric SO_2 , and (ii) the catalytic role of Fe^{2+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction, to illustrate the modes of action of homogeneous catalysis.
- I can identify an autocatalyst given a concentration-time graph and explain the shape of the graph.
- I can describe enzymes as biological catalysts with specific activity.
- I can explain how changes to the substrate concentration affect the rate of an enzyme-catalysed reaction in terms of the availability of the active sites.

3.3.1 Heterogeneous Catalyst

Catalyst and the Reactants are in different phases.

WATCH
and
learn

How does catalytic hydrogenation reaction work?
Watch <https://go.gov.sg/njc-kinetics-2> to find out.



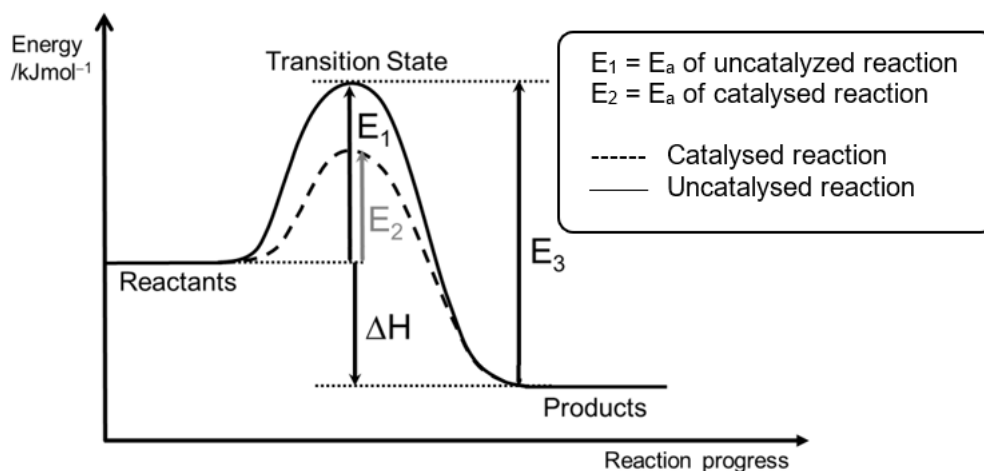
- Usually involves a solid catalyst that catalyses the reaction between gaseous reactants.
- It catalyses the reaction by bringing ALL reactant particles closer to each other and weakens the existing bonds in ALL reactant particles thereby providing an alternative pathway of lower activation energy for reaction to take place at a faster rate.
- It is usually a **ONE STEP** reaction.

The **energy profile diagram** of the reaction with and without catalyst is as shown:

Question to consider:

E_1 is the E_a of uncatalysed forward reaction.

- What does E_3 measure?
- How is it related to E_1 ?

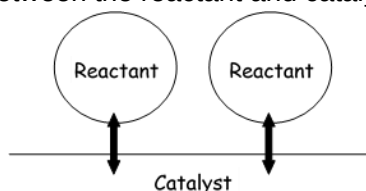


Mode of action in heterogeneous catalysis:**Note:**

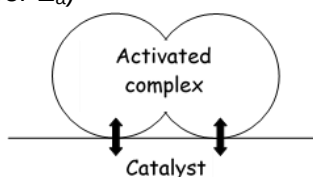
Adsorption is the adhesion of particles to a surface.

This is different from "absorption" where particles are drawn into the material.

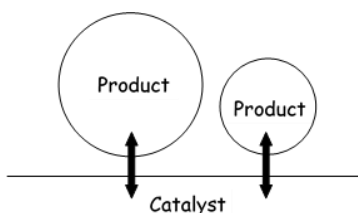
Step 1: **Adsorption** of reactant particles onto the surface of the catalyst. Weak interactions form between the reactant and catalyst.



Step 2: **Reaction** at the surface occurs at a faster rate as reactant particles are brought closer together and existing interactions in the reactant particles are weakened. (lower E_a)



Step 3: **Desorption** of products from the catalyst surface. Catalyst is regenerated.



Catalysis at the solid metal surface involves the adsorption of reactant particles on the surface catalyst atoms. This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reactant particles, i.e. activation energy is lowered.

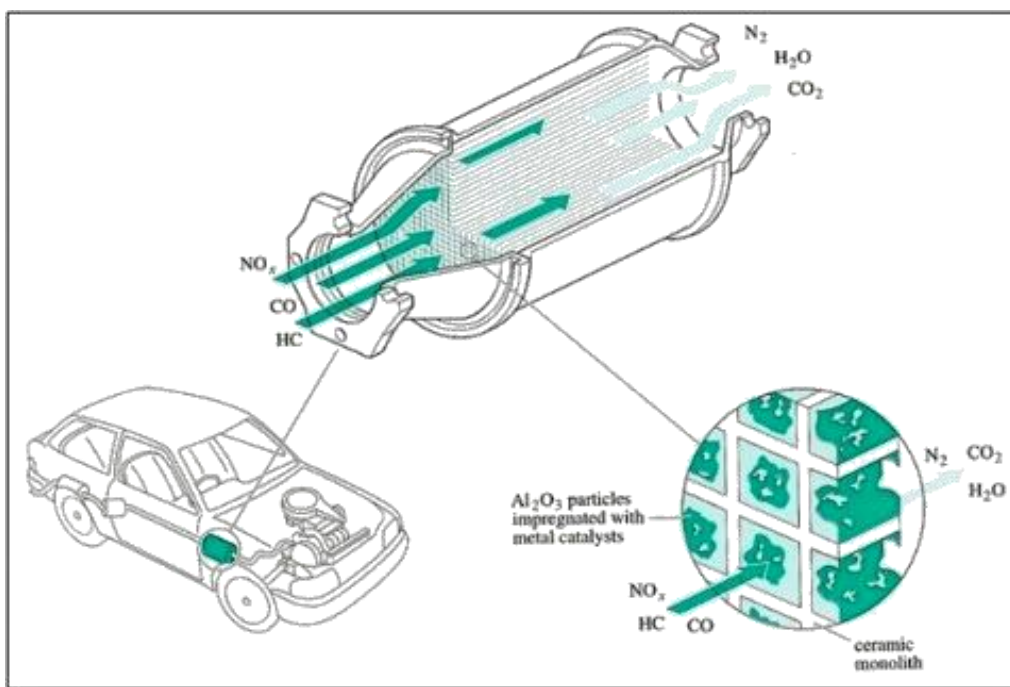
Examples of heterogeneous catalyst

solid catalyst	Reaction catalysed (usually involves gaseous reactants)
Fe or Fe_2O_3	Haber process: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
V_2O_5	Contact process: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
Ni	Hardening of vegetable oils to manufacture margarine $\text{RCH}=\text{CH}_2 + \text{H}_2 \longrightarrow \text{RCH}_2\text{CH}_3$
Pt, Pd or Rh	Removal of polluting substance from the car exhaust (catalytic converter) $2\text{CO}(\text{g}) + 2\text{NO}(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + \text{N}_2(\text{g})$

Note:

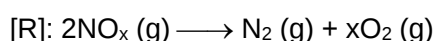
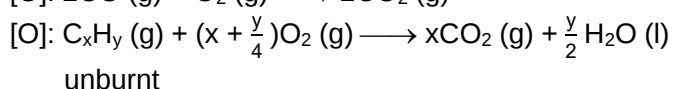
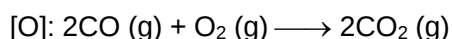
Transition metals are particularly effective as heterogeneous catalysts since they have partially filled d-orbitals which can be utilized in bonding.

Catalytic removal of oxides of nitrogen in the exhaust gases



Oxides of nitrogen are formed in the car exhaust due to the high temperature. (Under normal conditions, nitrogen is very unreactive). NO can be easily oxidized to NO_2 which contributes to acid rain by reacting with water to form nitrous and nitric acid.

Vehicles can be fitted with catalytic converters containing platinum, palladium and rhodium as catalysts to convert the harmful emissions to harmless products. In Singapore, all new cars must be fitted with catalytic converter. Harmful gases such as CO , NO and unburnt hydrocarbon undergoes **catalysed redox** reactions to give harmless products such as CO_2 , N_2 and H_2O .



3.3.2 Homogeneous Catalyst

Catalyst and the reactants are in the same phase.

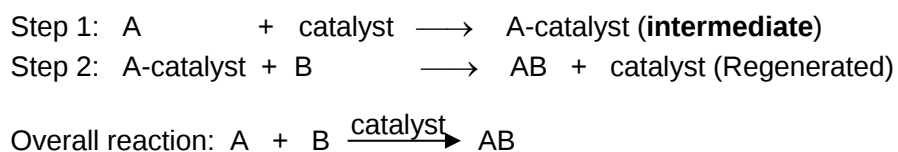
WATCH
and
learn

What are the different types of catalyst?
How does a homogeneous catalyst affect the reaction pathway of a reaction?

Watch <https://go.gov.sg/njc-kinetics-3> to find out.

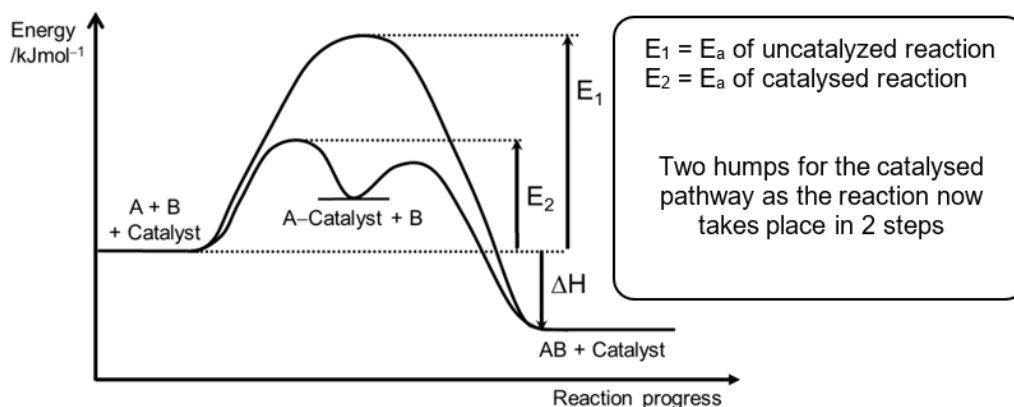


A homogeneous catalyst functions by reacting with **ONE of the reactants** to form a reactive **intermediate** (Step 1). The reactive **intermediate** will then react with remaining reactant in later stage to complete the reaction (Step 2).



Due to the involvement of the homogenous catalyst, the **alternative pathway** will **require one additional step to complete the reaction**. This is because there can only be a maximum of two colliding particles in a particular step as probability of effective collision between 3 or more particles are unlikely.

The **energy profile** diagram with and without the catalyst is as shown:



Worked example 3

Explain how $\text{Fe}^{2+}(\text{aq})$ ions can be used as a catalyst for the reaction of $\text{I}^{-}(\text{aq})$ ions with $\text{S}_2\text{O}_8^{2-}(\text{aq})$ ions as shown below.

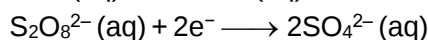
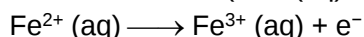


The reaction has a high activation energy and it involves the collision of two anions. $\text{Fe}^{2+}(\text{aq})$ catalysed the reaction by providing an alternative reaction pathway of lower activation energy as it enables the reaction between oppositely charged ions in both steps.

Note:

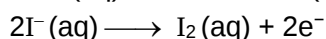
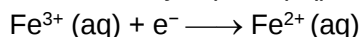
Fe^{2+} can act as catalyst since it changes its oxidation state to +3 in the intermediate and then back to +2 (regenerated).

Step 1: Formation of intermediate ($\text{Fe}^{2+}(\text{aq})$ colliding with $\text{S}_2\text{O}_8^{2-}(\text{aq})$)



Step 1 overall: $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$

Step 2: Regeneration of catalyst ($\text{Fe}^{3+}(\text{aq})$ colliding with $\text{I}^{-}(\text{aq})$)



Step 2 overall: $2\text{I}^{-}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq}) \longrightarrow \text{I}_2(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$

Examples of Homogeneous Catalysts

Homogeneous Catalyst	Reaction catalysed
Concentrated $\text{H}_2\text{SO}_4(\text{l})$	Ester formation $\text{HCOOH}(\text{l}) + \text{CH}_3\text{OH}(\text{l}) \longrightarrow \text{HCOOCH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$
$\text{NO}_2(\text{g})$ (a pollutant gas produced in car exhaust)	Oxidation of $\text{SO}_2(\text{g})$ to $\text{SO}_3(\text{g})$ in the atmosphere $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g})$ Burning of sulfur in fossil fuels produce large quantities of sulfur dioxide which can be readily oxidized to sulfur trioxide if $\text{NO}_2(\text{g})$ is present in the atmosphere. $\text{NO}_2(\text{g})$ can catalyse the oxidation of $\text{SO}_2(\text{g})$ to $\text{SO}_3(\text{g})$. Step 1: $\text{NO}_2(\text{g}) + \text{SO}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g}) + \text{NO}(\text{g})$ Step 2: $\text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{NO}_2(\text{g})$ (regenerated) The SO_3 produced can readily react with water in the atmosphere to form acid rain (H_2SO_4). $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$

3.3.3 Autocatalyst

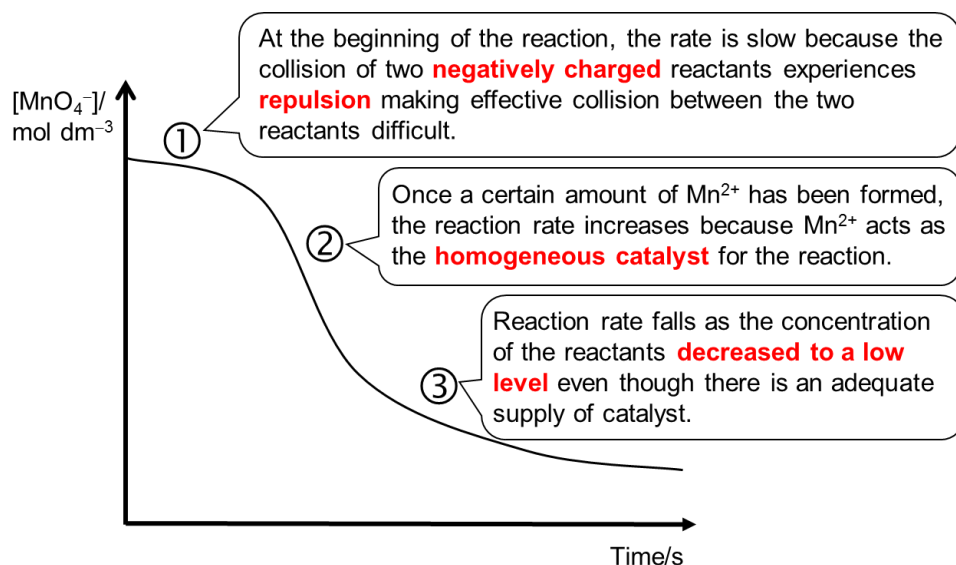
Autocatalysis is the **catalysis** of a reaction **by one of its products**. An autocatalysed reaction is slow at first and then becomes more rapid as the catalyst is produced in the reaction.

WATCH and learn

How does autocatalysis of the above redox reaction affect its rate during the course of reaction?
 Watch <https://go.gov.sg/njc-kinetics-4> to find out.
(Focus on from 4th min onwards)

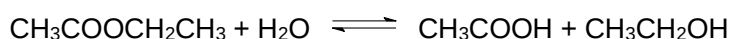


Example 1: Redox reaction between manganate(VII) and ethanedioate ions



Example 2: Hydrolysis of ester

The rate of the reaction below gradually increases at first, but then decreases.



The reaction yields CH_3COOH as one of the products at first. It is a weak acid which partially ionizes in water to produce H^+ (aq).

The reaction rate gradually increases because it is auto-catalysed by H^+ .

The reaction rate decreases after some time because the concentration of the reactant ethyl ethanoate decreases as rate is directly proportional to $[\text{CH}_3\text{COOCH}_2\text{CH}_3]$.

3.3.4 Biological catalyst (Enzymes)

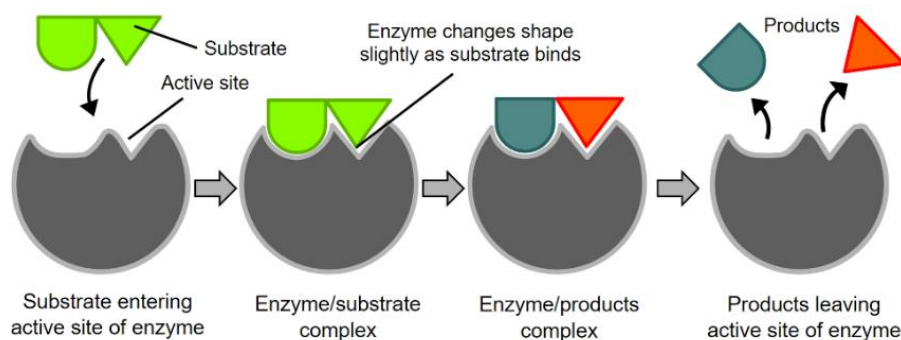
Enzymes are complex **globular proteins** that function as **biological catalysts**, accelerating biochemical reactions without being consumed.

Each enzyme has a uniquely shaped **active site**, into which a **specific reactant molecule** (known as the **substrate**) fits exactly — much like a **key fits into a lock**. This analogy is known as the **lock-and-key model**.

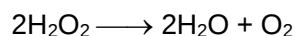
The shape and size of the substrate must match precisely with the active site of the enzyme. This **high specificity** ensures that enzymes catalyse only one particular reaction or act on a narrow group of substrates.

When the substrate binds to the enzyme's active site, **temporary attractive forces** (e.g. hydrogen bonds, van der Waals forces) form between them. This interaction **stabilises the transition state** and **weakens bonds within the substrate**, effectively **lowering the activation energy** required for the reaction to proceed. As a result, the rate of reaction increases significantly.

After the reaction, the **products are released**, and the enzyme remains unchanged, ready to catalyse another reaction.



Enzymes are more effective and efficient catalysts as illustrated by the following example. Consider the decomposition (disproportionation) of hydrogen peroxide.



Catalyst	Activation energy, E_a / kJ mol^{-1}
Iodide ion (inorganic catalyst)	56.5
Catalase (enzyme)	8

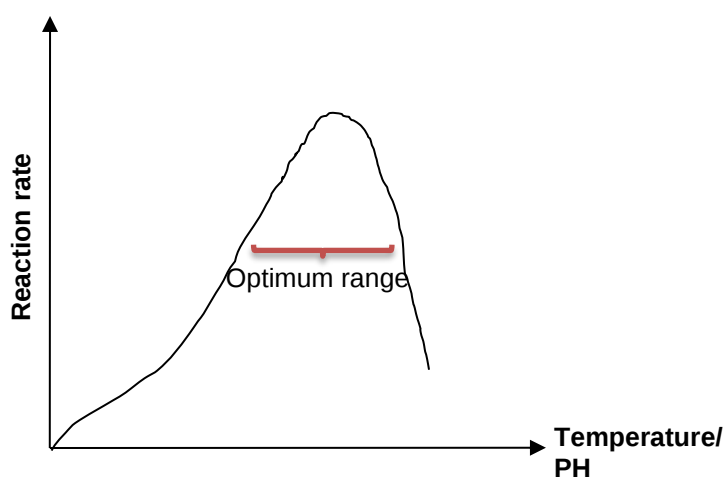
A. Effect of high temperatures and pH on enzyme activity

Enzymes are denatured by high temperature and extremes of pH. The 3-dimensional structure of enzymes is altered and its catalytic activity is destroyed.

Enzymes only work well over a narrow pH range (about 5 – 8) and over a narrow temperature range (about 20 - 50°C)

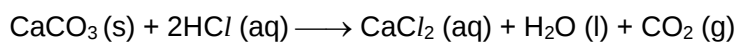
The rate of an enzyme-catalysed reaction increases at first and then decreases as temperature increases (because the enzyme starts to denature).

Denaturation destroys an enzyme.



Checkpoint 1

The following graphs are obtained when the volume of product of the following reaction is being monitored over time. HCl is used in excess.

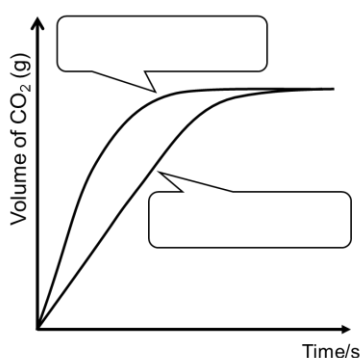


(a) For each factor, indicate, in the box provided, the condition that resulted in the difference in rate.

Temperature

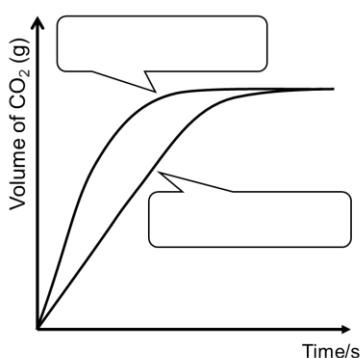
Reaction at:

- 1) 300 K
- 2) 350 K

**Surface Area of Contact**

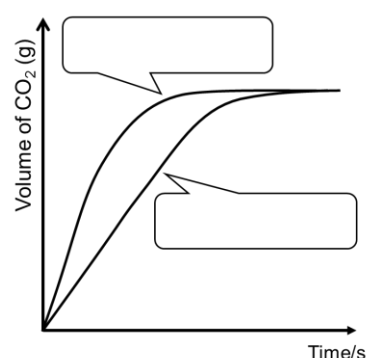
Reaction with:

- 1) Large Chunk of CaCO_3
- 2) Powdered CaCO_3

**Concentration of HCl**

Reaction with:

- 1) $1 \text{ mol dm}^{-3} \text{HCl}$
- 2) $2 \text{ mol dm}^{-3} \text{HCl}$



Note: When the above reaction allows CO_2 to escape into a collecting flask, the reaction goes to completion. Therefore, the temperature will only affect the rate of reaction but **not the experimental yield**.

(b) Suggest the reason why the total volume of CO_2 at the end of the reaction is the same for all the above experiments.

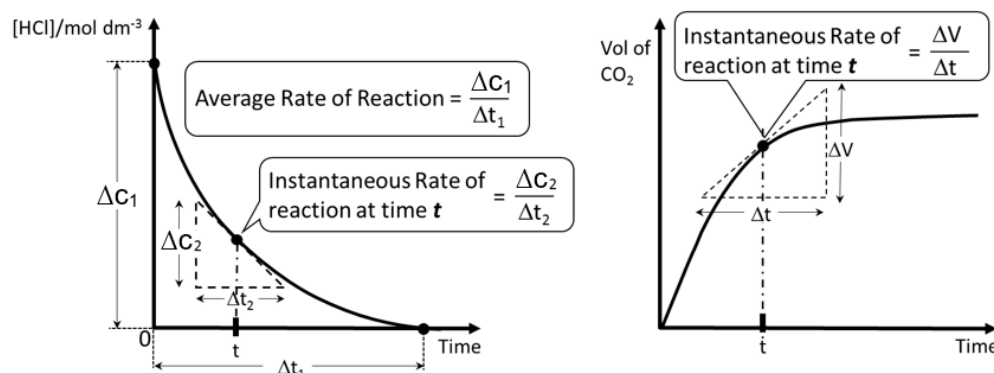
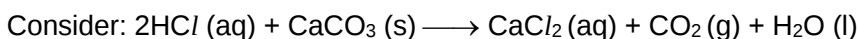
4 QUANTITATIVE KINETICS

In the following sections, we will study the ways to quantify kinetic observation to draw predictions on reaction pathways and mechanisms.

4.1 DIFFERENCE BETWEEN AVERAGE RATES, INSTANTANEOUS RATE, INITIAL RATE

Success criteria:

- I can define the rate of reaction correctly in terms of the rate of change of concentration of (i) reactant or (ii) product over time.



Note:

The rate of reaction is a positive quantity.

The negative sign

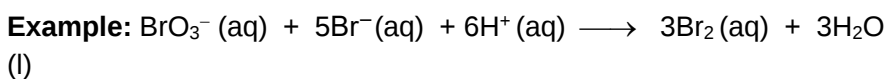
(i.e. $-\frac{d[\text{reactant}]}{dt}$)

indicates that [reactant] decreases with increasing time.

- Average rate** of reaction is the overall rate of reaction with no consideration of the rate variation during the reaction process itself.

Rate of a chemical reaction can be defined either as:

the increase in concentration of products per unit time, rate = $\frac{d[\text{product}]}{dt}$	the decrease in concentration of reactants per unit time, rate = $-\frac{d[\text{reactant}]}{dt}$
---	--



$$-\frac{d[\text{BrO}_3^-]}{dt} = -\frac{1}{5} \frac{d[\text{Br}^-]}{dt}, \quad \text{similarly, } -\frac{d[\text{BrO}_3^-]}{dt} = \frac{1}{3} \frac{d[\text{Br}_2]}{dt}$$

$$\text{AVERAGE Rate of Reaction} = -\frac{d[\text{BrO}_3^-]}{dt} = -\frac{1}{5} \frac{d[\text{Br}^-]}{dt} = \frac{1}{3} \frac{d[\text{Br}_2]}{dt}$$

Based on the mole ratio of the reaction, on average

The rate of consumption of Br^- would be $5 \times$ consumption rate of BrO_3^- .

The rate of production of Br_2 would be $3 \times$ consumption rate of BrO_3^- .

- Instantaneous rate** of reaction is the rate at a particular point of time, it can be determined by finding the gradient of the tangent at any one point of the concentration-time graph.

Note:

The RATE of appearance of PRODUCT is **not necessarily equal** to the RATE of disappearance of REACTANT. However, these rates can be related via **molar quantities** in a balanced chemical equation.

- **Initial rate** of reaction is the reaction rate measured at the very start of the reaction ($t=0$), when no significant amount of reactants has been consumed. It corresponds to the slope of the tangent when $t=0$. At the initial rate, the reaction rate is highest because the concentration of reactants is at its maximum.

4.2 THE RATE EQUATION

Success criteria:

- I can define the rate equation, rate constant and order of reaction correctly.
- I can write the rate equation based on the order of reaction determined experimentally.
- I can interpret the meaning of zero, first and second order of reactions.

As a reaction may not adopt a fix rate throughout the reaction, a different approach from average rate is needed to understand the kinetics of a reaction. This can be achieved through the rate equation. The rate equation can give the kinetic profile of a reaction, providing information on the instantaneous rate and verify mechanism of a reaction.

The rate equation is stipulated as follows:

$$\text{Rate} = k[\text{reactant}]^x$$

Note:

Slow step (rate determining step) is the step with the highest activation energy. It contains the reactants that affects the overall rate of reaction.

Rate Constant (k) (Section 4.2.2)

- Proportionality constant to show dependence of rate of reaction on activation energy and temperature.
- The value of k must be experimentally determined.
- Defined by Arrhenius Equation:

$$k = Ae^{-\frac{E_a}{RT}} \quad (*\text{Not in syllabus}*)$$

Order of Reaction (Section 4.2.1)

- Shows no. of reactants in **slow step (rate determining step)** or no. of reactants that form the reactive intermediate involved in slow step.
- **Can only be determined experimentally.**

- By **monitoring how rate** of a particular reaction **varies with changing concentration** of each reactant, rate equation can be **deduced**.
- Rate equation **identifies the reactants** involved in the **rate determining step** of a multi-step reaction.

4.2.1 Order of Reaction

Order of reaction with respect to a reactant is the **power** of the concentration of that reactant in the **experimentally determined** rate equation.

Overall order of reaction is the **sum** of the orders of reaction with respect to the reactants which are the **powers** of the concentrations of the reactants in the **experimentally determined** rate equation.

$$\text{Rate Equation: } \text{Rate} = k[A]^x[B]^y$$

(where x and y are the order of reaction with respect to A and B respectively.)

The **overall order** of the reaction = $x + y$.

	What is meant by 1 st and 2 nd order of reaction with respect to certain reactants in each elementary step? Watch https://go.gov.sg/njc-kinetics-10 to find out.	
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In H2 Chemistry, we will need to know zero, first and second order of reaction.

Order of reaction is always with respect to a reactant. It will describe the effect of the concentration change of that reactant on the rate of reaction.

Order	Effect on Rate of Reaction
Zero Order	Rate of reaction is not affected by this reactant. (e.g. rate of reaction remains the same despite concentration is doubled)
First Order	Rate of reaction is directly proportionate to the concentration of the reactant (linear relationship). (e.g. rate of reaction doubles when concentration is doubled)
Second Order	Rate of reaction is directly proportionate to square of concentration of reactant. (e.g. rate of reaction quadruples when concentration is doubled)

4.2.2 Rate constant, k

Success criteria:

- I can state the effect on the rate constant with the change in condition.
- I can state the units for rate constant based on the overall order of reaction.

a. Factors affecting rate constant, k

	What are the factors affecting rate constant k ? How do these factors affect the rate constant? Watch https://go.gov.sg/njc-kinetics-9 to find out.	
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Note:

The effect of the changed conditions on rate of reaction can be explained by the collision theory with the aid of Boltzmann distribution curve. (Refer to section 3.2)

Changed condition	Effect on rate of reaction	Effect on value of rate constant, k
Increase concentration of a reactant	Increases (if the order is NOT zero with respect to the reactant)	No change
*Increase temperature	Increases	Increases

*Addition of a catalyst	Increases	Increases
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- The units of rate constant, **k**, depend on the **overall order** of the reaction.
- rate = $\frac{d[\text{ }]}{dt}$, hence, **units for rate is always mol dm⁻³ t⁻¹**.
- Time (t) can be seconds, hour, day etc. depending on what is suitable for a particular reaction. For a reaction that is very slow, there is only a significant change in the concentration after a few hours, therefore it is only sensible to define its rate as change in concentration per unit hour or per day. **Refer to question for specific units of t.**

Overall reaction order	Units for rate constant, k
Zero order rate = $k[A]^0$	units for k = units of rate = mol dm ⁻³ t ⁻¹
First order rate = $k[A]^1$	units for k = $\frac{\text{units of rate}}{\text{units of } [A]^1} = \frac{\text{mol dm}^{-3} \text{ t}^{-1}}{\text{mol dm}^{-3}} = \text{t}^{-1}$
Second order rate = $k[A]^2$ or rate = $k[A][B]$	units for k = $\frac{\text{units of rate}}{\text{units of } [A]^2} = \frac{\text{mol dm}^{-3} \text{ t}^{-1}}{(\text{mol dm}^{-3})^2} = \text{mol}^{-1} \text{ dm}^3 \text{ t}^{-1}$
Third order rate = $k[A]^2[B]$	units for k = $\frac{\text{units of rate}}{\text{units of } [A]^2[B]} = \frac{\text{mol dm}^{-3} \text{ t}^{-1}}{(\text{mol dm}^{-3})^3} = \text{mol}^{-2} \text{ dm}^6 \text{ t}^{-1}$

Checkpoint 2

The rate of reaction between propanone, CH₃COCH₃, and iodine catalysed by H⁺ to give iodopropanone, CH₃COCH₂I, is found experimentally to be independent of iodine concentration but directly proportional to each concentration of H⁺ and propanone.

(i) Construct the balanced stoichiometric equation for the overall

(ii) Write the rate equation for this reaction, state the overall order and the units of the rate constant.

Rate equation :

Overall order :

Units of rate constant :

4.3 REACTION MECHANISM AND RATE EQUATION

Success criteria:

- I can derive the rate equation (i.e. $\text{rate} = k[\text{A}]^m[\text{B}]^n$, where m and n could be 0, 1 or 2) from the rate determining step (i.e. slow step) of the reaction mechanism and vice versa.
- I can verify the reaction mechanism by matching with the rate equation; and predict the order of reaction that would result from a given reaction mechanism.

4.3.1 What is Mechanism?

For reaction involving 3 or more reacting particles, it is unlikely to combine all reactants in one step. Such reactions are likely to take place in multiple steps with maximum of 2 reacting particles per elementary step.

The breakdown and details of how and what reacts at each elementary step of a multi-step reaction is known as the **reaction mechanism**.

Each elementary step in a mechanism proceeds at its own rate. The elementary step which determines the rate of reaction is known as the slow step or the rate determining step. The slow step will provide the rate equation for the mechanism.

Mechanisms are usually suggested and require multiple investigation to confirm.

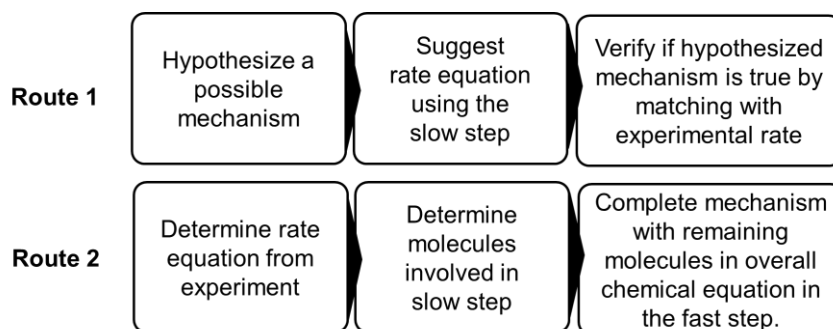
WATCH and learn	What is meant by (i) multi-step reaction (ii) each elementary step proceeding at their own rate Watch https://go.gov.sg/njc-kinetics-11 to find out.	
WATCH and learn	What about 'rate determining step'? What is it? Watch https://go.gov.sg/njc-kinetics-12 to find out.	

4.3.2 Deducing and Verifying Reaction Mechanism

Mechanism can be deduced and verified in 2 ways:

Note:

- Each elementary step involves a single or at most 2 reacting particles
- The elementary steps do not occur at the same rate and must add up to give the overall chemical equation.



The rate of the reaction is determined by the rate determining step as no elementary steps can be slower than the slow step. Hence, the rate equation will help us verify which suggested mechanism is true.

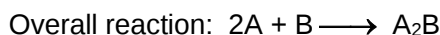
The rate equation for the suggested mechanism is derived from the stoichiometric coefficient of the reactants in the rate determining step.

4.3.2.1 Route 1: Verify Suggested Mechanism Using Experimental Rate Equation

Consider the following example:

Note:

- AB and A₂ are called intermediates, substances that are formed and used up during the overall reaction. They do not appear in the overall balanced equation but are absolutely necessary for the reaction to occur
- Intermediates are not included in the rate equation.



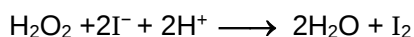
Given the rate equation for this reaction is experimentally determined as $\text{rate} = k[A]^2$, deduce which of the following suggested mechanism is the mechanism for this reaction.

Mechanism 1	Mechanism 2
$A + A \longrightarrow A_2$ slow	$A + B \longrightarrow AB$ slow
$A_2 + B \longrightarrow A_2B$	$AB + A \longrightarrow A_2B$
Rate = $k[A]^2$	Rate = $k[A][B]$

Since the rate equation matches that for **mechanism 1**, this reaction should undergo the reaction according to **mechanism 1**.

Checkpoint 3

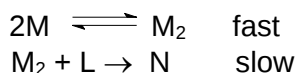
1) Two different mechanisms have been proposed for this reaction.



Given the rate equation of the above reaction is experimentally determined to be $\text{Rate} = k[H_2O_2][I^-]$, suggest with reasons which of the two mechanisms, A or B, fits the kinetic data.

Mechanism A:	Mechanism B:
$H_2O_2 + I^- \longrightarrow H_2O + OI^-$ (slow)	$H_2O_2 + I^- + H^+ \longrightarrow H_2O + HIO$ (slow)
$OI^- + H^+ \longrightarrow HOI$ (fast)	$HIO + I^- \longrightarrow I_2 + OH^-$ (fast)
$HOI + H^+ + I^- \longrightarrow I_2 + H_2O$ (fast)	$OH^- + H^+ \longrightarrow H_2O$ (fast)

2) The reaction between **M** and **L** to form **N** is believed to adopt the following mechanism.



Given that the equilibrium constant, K_c for the 1st step in the following mechanism is defined as,

$$K_c = \frac{[M_2]}{[M]^2}$$

Determine the rate equation for the reaction between **M** and **L**.

4.3.2.2 Route 2: Use Experimental Rate Equation to Construct Mechanism

- (i) Decide which **particles (species)** are involved in the rate-determining step from the experimentally determined rate equation.
- (ii) Suggest possible products from the reactants you have chosen. (These products may include species which do not appear as products in the stoichiometric equation)
- (iii) Compare the rate-determining step with the stoichiometric equation to see how many **particles (species)** are still to be accounted for.
- (iv) Add up the reaction steps and this must coincide with the overall stoichiometric equation.

Worked Example 4

Consider the reaction between $\text{CH}_3\text{CH}_2\text{Br}$ and NaOH and propose a possible mechanism.

Overall equation: $\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \longrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}$

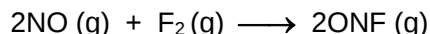
Rate equation: $\text{rate} = k[\text{CH}_3\text{CH}_2\text{Br}][\text{NaOH}]$ *Determined experimentally*

Both reactants in the overall equation appear in the rate equation with the order of reaction stated according to its stoichiometric ratio. This indicates both reactants are in the rate determining step and reaction proceeds in a single step.

Mechanism: $\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \longrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}$
(same as balanced equation)

Worked Example 5

The compound nitrosyl fluoride, ONF, can be produced from nitrogen monoxide and fluorine.



The rate equation for this reaction is $\text{rate} = k[\text{NO}][\text{F}_2]$. The mechanism has two steps. One of these steps produces ONF and the free radical $\text{F}\bullet$ in equimolar amounts.

Suggest equations for the two steps of the mechanism, stating which one is the slower step.

Step 1: Decide which particles (species) are involved in the rate-determining step.	NO, F ₂
Step 2: Suggest possible products from the reactants you have chosen. (These products may include species which do not appear as products in the stoichiometric equation)	ONF, F•
Step 3: Compare the rate-determining step with the stoichiometric equation to see how many particles (species) are yet to be accounted for.	rate equation (1 mol of NO and 1 mol of F₂ in the <i>slow</i> step) Chemical equation and rate equation are not the same therefore reaction cannot occur in 1 step. (there is 2 mol of NO and 1 mol of F₂ in the overall reaction) Hence there are 2 steps in this mechanism with F• as the intermediate and also to introduce the 2nd mole of NO to react with F•
Step 4: Add up the reaction steps and this must coincide with the overall stoichiometric equation.	1st step: (slow) $\text{NO (g)} + \text{F}_2\text{(g)} \longrightarrow \text{F}\bullet\text{(g)} + \text{ONF (g)}$ 2nd step: $\text{F}\bullet\text{(g)} + \text{NO (g)} \longrightarrow \text{ONF (g)}$ Overall: $2\text{NO (g)} + \text{F}_2\text{(g)} \longrightarrow 2\text{ONF (g)}$

4.4 DEDUCING THE RATE EQUATION

We have seen from previous section how rate equation gives us not only information about the rate of a reaction but also the mechanism by which a reaction takes place.

Recall that $\text{rate} = \frac{d[\text{ }]}{dt}$, hence rate of reaction can be tracked using the **changes in the concentration** of the reactant (or product as its production rate depends on the reactant consumption rate) and the **time taken**.

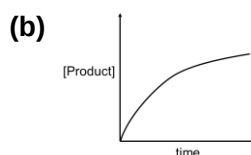
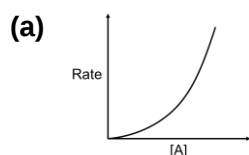
The **order of reaction** can then be deduced from two different methods (continuous and initial rate) and used to construct the rate equation. The two methods can also be combined to deduced the rate equation.

	CONTINUOUS METHOD	INITIAL RATE METHOD
No. of Experiments involved	<u>A single</u> experiment. The concentration of reactant or product is tracked <u>over a period of time</u> .	<u>Multiple</u> experiments. Compare the change in reaction rate (measured by time taken) when concentration of a reactant is systematically changed between the experiments.
Data to collect from experiment	Concentration remaining in the reaction needs to be obtained through experiment.	Time taken in each experiment needs to be taken to determine the reaction rate for comparison.
Data Processing method	A concentration-time graph is plotted for analysis. Half-life of graph can be used to deduce if reaction is first order.	Order of reaction can be deduced by: (a) Rate-Concentration Graph (b) Comparing how the degree of rate change due to change in concentration

Checkpoint 4

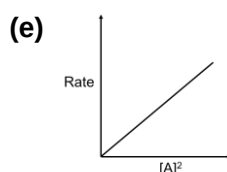
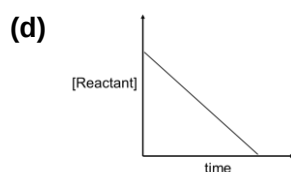


Referring to the following data, suggest whether they are obtained from continuous or initial rate method.



(c)

Time/min	[A]
0	1.0
1	0.9
2	0.7
3	0.5



(f)

Exp	[A]	[B]	Time/min
1	0.1	0.2	2
2	0.1	0.1	4
3	0.2	0.2	2

4.4.1 Experiments to Determine Rate Equation

Success criteria:

- I can devise a suitable experimental technique for studying the rate of a reaction, using continuous method or initial rate method from given information.

In this segment, we will look at various experimental techniques to obtain data for the rate analysis.

To monitor rate of reaction, several experimental approaches can be used:

(a) Making Physical Measurement (**For Continuous or Initial Rate Method**)

Following are some examples of physical measurements that can be taken to monitor reaction rate:

- Volume of Gases (Gas Collection)
- Mass Loss (Gravimetric method)
- pH changes
- Electrical conductivity
- Intensity of colour
- Pressure

(b) Titrimetric Method (**For Continuous Method**)

- Monitoring concentration of reactant left using a series of titration

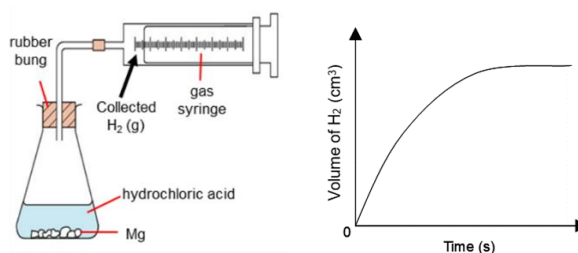
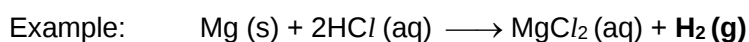
(c) Clock reaction (**For Initial Rate Method**)

- Monitoring time taken for a sample to be reacted indicated by appearance or disappearance of colour

4.4.1.1 Examples of Physical Measurements

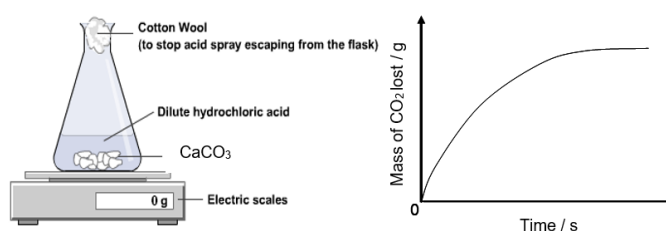
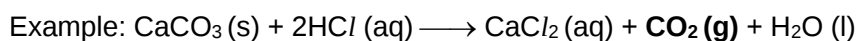
(a) Gas Collection Method

- measure the increase in volume at regular time interval under constant pressure.



(b) Gravimetric Method

- measure the decrease in mass over time
- measuring loss of mass and hence applicable for a reaction involving a gaseous product.



(c) Monitor change in pH using Data Logger/ pH Meter

- measure the change in pH of a reaction over time
- measurement with the use of a pH probe

Example: $\text{CH}_3\text{Br} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{NaBr}$
 (the pH of the solution decreases with time as NaOH is being consumed)

**(d) Monitor change in electrical conductivity using Data Logger/ Conductivity meter**

- measure change in electrical conductivity of a reaction over time due to a change in the number of ions in solution

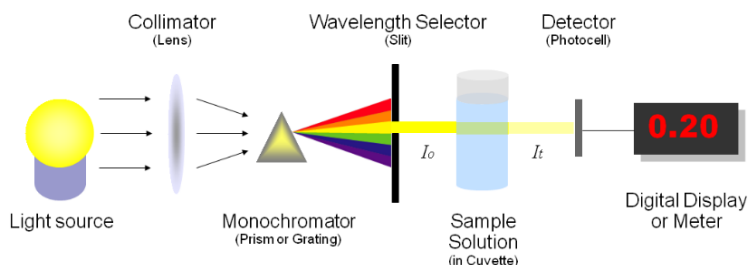
Example:

$\text{BrO}_3^- (\text{aq}) + 5\text{Br}^- (\text{aq}) + 6\text{H}^+ (\text{aq}) \longrightarrow 3\text{Br}_2 (\text{aq}) + 3\text{H}_2\text{O} (\text{l})$
 (decrease in number of ions present and thus conductivity of the solution falls as reaction proceeds, and hence electrical conductivity decreases with time.)

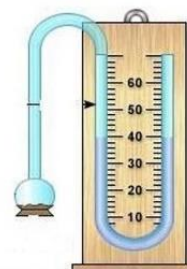
(e) Colorimetry Method

- measure the change in colour intensity over time
- intensity of colour is proportional to the concentration of the coloured substance

Example: $\text{CH}_3\text{COCH}_3 (\text{aq}) + \text{I}_2 (\text{aq}) \longrightarrow \text{CH}_2\text{ICOCH}_3 (\text{aq}) + \text{HI} (\text{aq})$
 (colour intensity decreases with time as brown $\text{I}_2(\text{aq})$ is being consumed)

**(f) Changes in pressure**

- measure change in pressure over time while volume of reaction vessel is kept constant.
- pressure change is due to number of moles of gaseous reactants being different from the number of moles of gaseous products.



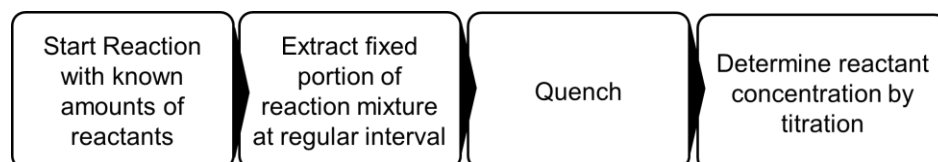
Example: $\text{N}_2\text{O}_4 (\text{g}) \rightarrow 2\text{NO}_2 (\text{g})$

(reaction is accompanied by an increase in number of moles of gas, and hence pressure increases with time at constant volume)

4.4.1.2 Titrimetric method (Continuous Method)

Reactions may not always have colour or other means by which physical measurement can be taken directly to track reaction progress. In such, titration with the use of an indicator/coloured titrant is useful to determine the concentration of reactant left at regular time interval. A graph is then plotted which could be used to determine the order of reaction, rate or rate constant.

Reaction with coloured reactants can also use this method of monitoring if continuous method is the choice of analysis.



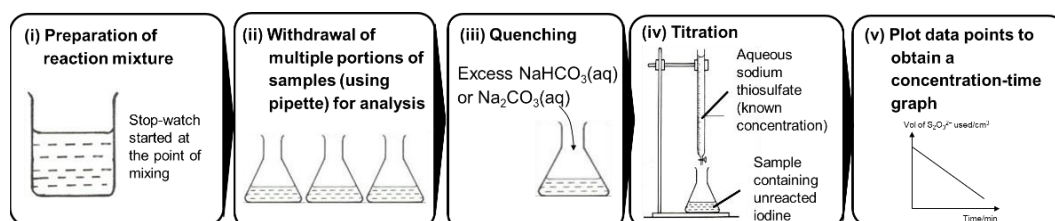
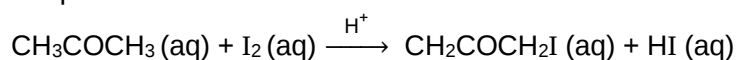
The withdrawn portions are then “**quenched**”.

Quenching is the **slowing of the reaction abruptly at a measured time** from the start of the reaction. This is to **allow analysis of the content in the reaction mixture at that point of time** so that the concentration of products or reactants can be monitored with time.

Quenching usually can be achieved by:

- (i) rapid cooling in ice bath (lower temp of reaction mixture),
- (ii) removing the catalyst,
- (iii) by adding large volume of cold water which lowers the reaction temperature and dilutes the reactants.

Example of titrimetric method: Consider the reaction



Titrimetric study of the reaction of propanone with iodine
Watch <https://go.gov.sg/njc-kinetics-6> to find out.



4.4.1.3 Clock reactions (Initial Rate Method)

Note:

Initial rate method is the determination of the rate of reaction by **measuring the time taken for a prescribed visual change to occur** (such as the formation of a precipitate or an obvious change in colour).

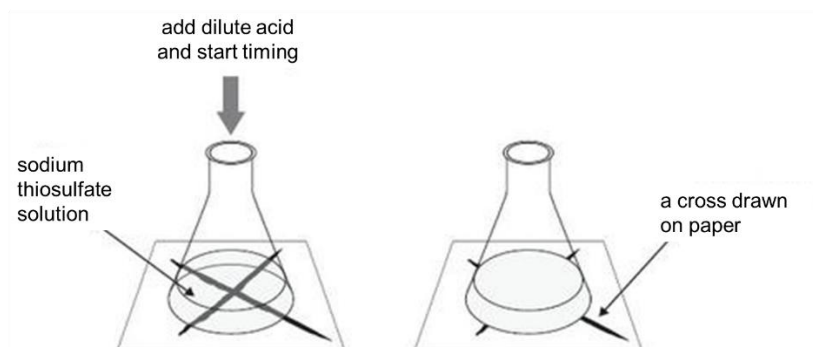
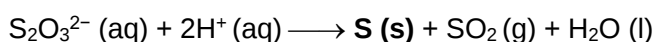
For reactions that are accompanied by **prominent visual changes**, the rate of reaction may be studied by “clock reaction”, which **measures the time taken for a sudden observable change to occur**. The time taken to reach the easily seen stage should be inversely proportional to the reaction rate.

$$\text{Rate of reaction} = \frac{\text{change in concentration of reactants/products}}{\text{time taken for sudden observable change}}$$

To compare average rates of reaction with initial reactant concentrations, the **concentration of one of the reactants could be varied in a series of experiments**. Different mixtures would have different starting concentration of one reactant (say, reactant **A**) while all other factors (i.e. concentration of remaining reactants, temperature, etc) remain constant to determine the order of reaction with respect to reactant **A**.

Some examples of this experimental approaches are as follows:

Example 1: Production of Solid



The average rate of reaction for the reaction mixture can be measured by noting the **time taken for sufficient sulfur to be produced** such that the **“X” mark on the white paper is no longer visible**.

Since the same “X” on the white paper is obscured for all experiments, we are measuring the **time taken for a fixed amount of sulfur to be formed**.

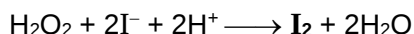
Hence, **rate of reaction** $\propto \frac{1}{\text{time taken}}$.



Sulfur clock reaction

Watch <https://go.gov.sg/njc-kinetics-7> to find out.



Example 2: Appearance of Colour

For reactions involving for appearance of colour, e.g. colourless to dark blue colouration with starch indicator.

By adding a known, small amount of $\text{Na}_2\text{S}_2\text{O}_3$, the appearance of dark blue colouration indicates a **fixed amount of I_2 formed**. Iodine liberated from the reaction between H_2O_2 and I^- will immediately react with the sodium thiosulfate.



When all $\text{S}_2\text{O}_3^{2-}$ are removed, an excess of I_2 forms and the solution give a deep blue colouration in the presence of starch indicators.

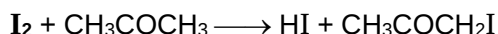
Since amount of $\text{S}_2\text{O}_3^{2-}$ is fixed for all experiments, we are measuring the **time taken for a fixed amount of I_2 to be formed**.

Hence, **rate of reaction** $\propto \frac{1}{\text{time taken}}$.

WATCH
and
Learn

Iodine clock reaction.

Watch <https://go.gov.sg/njc-kinetics-8> to find out.

**Example 3: Disappearance of Colour**

For reactions involving for disappearance of colour, e.g. brown to colourless. The rate of reaction may be studied by measuring the time taken for the colour of iodine of varying concentration to disappear.

As the amount of I_2 can vary between experiments,

$$\text{rate of reaction} = \frac{\text{change in concentration of iodine}}{\text{time taken for iodine to disappear}}$$

How to identify when to simplify the rate of rxn for initial rate method?

Rate can in certain situation be simplified to: $\text{rate} \propto \frac{1}{\text{time taken}}$.

- Appearance of colour (**Example 1 & 2**)

We measure the time taken for a **fixed amount** of coloured product to be produced for all experiments.

$$\text{rate} = \frac{\text{change in fixed amount of coloured products}}{\text{time taken for sudden observable change}}$$

It **CAN** be simplified as $\text{rate} \propto \frac{1}{\text{time taken}}$

- Disappearance of colour (**Example 3**)

As the amount of coloured reactant **can vary between experiments**,

$$\text{rate} = \frac{\text{change in concentration of coloured reactant}}{\text{time taken for coloured reactant to disappear}}$$

It **CANNOT** be simplified.

4.4.2 Data Processing Methods to Deduce Rate Equation

With the data obtained from the experiment, the data can be processed in one or more of these methods to deduce the rate equation.

- (i) **Inspection/Mathematical Method** – For Initial Rate Only
- (ii) **Graphical Methods** – For both Continuous and Initial Rate

In each of these methods, we will allow only the concentration of one reactant to change, while keeping the other concentrations to stay constant. The concentrations which were kept constant may have impact on the rate of reaction but cannot be observed due to it being kept constant across the experiments.

Comparing the change in the rate of reaction with the changing concentration of reactant (or product), we can deduce the **order of reaction**. This can be used to construct the rate equation.

4.4.2.1 Inspection/Mathematical Method

When given a series of data obtained from multiple experiments, especially in table form,

- (i) **Inspection method:** compare concentration vs rate between suitable pair of experiments.
- (ii) **Mathematical method:** use rate equation to compare suitable pair of experiments

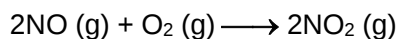
Success criteria:

I can use initial rate method to

- (i) determine the order of reaction via inspection or mathematical method or shape of the rate-time graph
- (ii) calculate the rate constant

Worked Example 6 (Reaction of NO with O₂)

The reaction kinetics of reaction between NO and O₂ was monitored using the initial rate method.



Experiment	[NO] / mol dm ⁻³	[O ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ h ⁻¹
1	0.001	0.001	7×10^{-6}
2	0.001	0.002	14×10^{-6}
3	0.001	0.003	21×10^{-6}
4	0.002	0.003	84×10^{-6}

- (a) Determine the order of reaction with respect to NO and O₂.

Method 1 : Inspection method

Compare expt 1 and 2 where [NO] is the same.

When [O₂]_{expt2} is twice of [O₂]_{expt1}, rate (2) is twice of rate (1), therefore the order w.r.t O₂ must be one.

Compare expt 3 and 4 where [O₂] is the same.

When [NO]_{expt4} is twice of [NO]_{expt3}, rate (4) is 4 times of rate (3), therefore the order w.r.t NO must be two.

Method 2 : Mathematical method

Let the rate equation be: rate = k [NO]^x[O₂]^y

Using expt 1 and 2, where [NO] is a constant,

$$\frac{\text{rate (2)}}{\text{rate (1)}} = \frac{k(0.001)^x(0.002)^y}{k(0.001)^x(0.001)^y}$$

$$\frac{14 \times 10^{-6}}{7 \times 10^{-6}} = \frac{(0.002)^y}{(0.001)^y}$$

$$2 = (2)^y$$

therefore y = 1.

order w.r.t O₂ must be 1

Using expt 3 and 4, where [O₂] is a constant,

$$\frac{\text{rate (4)}}{\text{rate (3)}} = \frac{k(0.002)^x(0.003)^y}{k(0.001)^x(0.003)^y}$$

$$\frac{84 \times 10^{-6}}{21 \times 10^{-6}} = \frac{(0.002)^x}{(0.001)^x}$$

$$4 = (2)^x$$

therefore x = 2.

order w.r.t. NO must be 2

Note:

To find the order of reaction, choose expt such that the conc of the species varies while the other species are kept CONSTANT.

- (b) Deduce the rate equation and calculate the rate constant, giving its units.

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

Using data from expt 1,

$$7 \times 10^{-6} = k [0.001]^2 [0.001]$$

$$k = 7000 \text{ mol}^{-2} \text{ dm}^6 \text{ h}^{-1}$$

Checkpoint 5

- (a) The dehydration reaction of butan-2-ol to form butene is catalysed by an acid. Three experiments were carried out to find the relationship between rate of reaction and the initial concentrations of butan-2-ol and the acid catalyst.

Experiment	[butan-2-ol] _{initial} / mol dm ⁻³	[H ⁺] _{initial} / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.25	0.25	1.4×10^{-7}
2	0.50	0.25	2.8×10^{-7}
3	0.50	0.50	2.8×10^{-7}

- (i) Deduce the order of reaction with respect to:

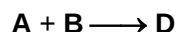
- butan-2-ol,
- H⁺.

- (ii) Hence, calculate the rate constant for this reaction, stating its units.

- (b) Explain how an increase in temperature will affect the rate of this reaction.

Worked Example 7 (Appearance of colour)

Using a colourimeter, the following reaction is studied by **finding the time taken for a coloured product D of concentration 0.01 mol dm^{-3} is formed.**



The following results were obtained.

Experiment	Vol of A added / cm^3	Vol of B added / cm^3	Vol of H_2O added / cm^3	Time taken for 0.01 mol dm^{-3} of D formed / s	Relative rate
1	10	20	30	20	0.05
2	10	10	40	40	0.025
3	20	40	0	5	0.2

Note:

Relative reaction rates between experiments are determined by **comparing time taken for a certain amount of coloured product to be formed – pre-setting a point in the reaction.**

- (a) Explain why rate of reaction is inversely proportional to time taken for 0.01 mol dm^{-3} of D to be formed.

$$\text{Rate} = \frac{d[\text{D}]}{dt}$$

Since change in [D] is the same for expts 1–3, therefore rate can be taken to be **inversely proportional** to time taken for fixed amt or conc of D to be formed.

- (b) Why different volumes of water is added in each experiment?

Water is added to maintain a constant total volume of solution for each experiment. This is such that the volume of reagents used would be directly proportional to its concentration in the final reaction mixture.

$$[\text{A}]_{\text{mixture}} = \frac{\text{vol of A used} \times [\text{A}]_{\text{original}}}{\text{total vol of mixture}}$$

Constant for all expts since it is the solution provided

$$[\text{A}]_{\text{mixture}} \propto \text{vol of A used}$$

Kept constant for all expts

- (c) Using the reaction rates given in the table above, determine the rate equation.

1) Inspection method for expt 1 and 2

Compare expt 1 and 2 where [A] the same.

When $[\text{B}]_{\text{expt1}}$ is **doubled** of $[\text{B}]_{\text{expt2}}$ (volume of B added is doubled), the rate (1) is **doubled of rate (2)**, therefore the reaction is **first order** w.r.t B.

2) Mathematical method for expt 1 and 3 OR 2 and 3

Compare expt 1 and 3;

Let the rate equation: $\text{rate} = k[\text{A}]^x[\text{B}]^1$ where volume is proportional to its concentration in the mixture.

$$\frac{\text{rate (3)}}{\text{rate (1)}} = \frac{k(20)^x(40)^1}{k(10)^x(20)^1}$$

$$\frac{0.2}{0.05} = \frac{(20)^x}{(10)^x} \times 2$$

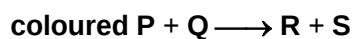
$$2 = 2^x$$

therefore $x = 1$.

Rate equation: **Rate = $k[\text{A}]^1[\text{B}]^1$**

Worked Example 8 (Disappearance of colour)

The reaction kinetics of the following reaction is being investigated.



The following results were obtained.

Note:

Varying volume of H₂O was added to the reaction mixture to keep the total volume of the reaction mixture constant.

For disappearance of colour,

$$\text{rate} = \frac{d[\text{coloured rxt}]}{dt}$$

Expt	Vol of P added / cm ³	Vol of Q added / cm ³	Vol of H ₂ O added / cm ³	Time taken for P to decolourize / s	Relative rate
1	10	20	10	20	$\frac{10}{20} = 0.5$
2	10	10	20	40	$\frac{10}{40} = 0.25$
3	5	20	15	10	$\frac{5}{10} = 0.5$

Determine the rate equation for the reaction between **Q** and **P**.

Due to constant total volume, $[\text{reactant}]_{\text{mixture}} \propto V_{\text{reactant}}$.

Compare expt 1 and 2 where **[P]** are the same;

When **[Q]_{expt1}** is **double** of **[Q]_{expt2}** (volume of **Q** added is doubled), rate (1) is **double** of rate (2), therefore the reaction is **first** order w.r.t **Q**.

Compare expt 1 and 3 where **[Q]** are the same;

When **[P]_{expt1}** is **double** of **[P]_{expt3}** (volume of **P** added is doubled), rate (1) is **same as** rate (3), therefore the reaction is **zero** order w.r.t **P**.

Hence, rate equation is $\text{rate} = k [\text{Q}]$

Checkpoint 6

Ethene reacts with bromine in tetrachloromethane (solvent) to form 1,2-dibromoethane as shown by the equation:



To find out the orders of reaction with respect to ethene and bromine, ethene and bromine were first dissolved separately in tetrachloromethane. Various volumes of these solutions and tetrachloromethane were mixed and the time taken for the colour of bromine to disappear was recorded. The results are shown in the table below:

Experiment	Volume of $\text{CH}_2=\text{CH}_2$ in CCl_4 / cm^3	Volume of $\text{Br}_2(l)$ / cm^3	Volume of CCl_4 / cm^3	Time taken for colour of Br_2 to disappear/ s
1	20	20	0	15
2	12	20	8	25
3	20	10	10	15
4	40	20	20	t_4

(i) Explain why varying volumes of tetrachloromethane were used.

(ii) State the relationship between the rate of reaction and

- time taken for the colour of bromine to disappear
- volume of bromine used

Checkpoint 6 (continued)

(iii) Deduce the order of reaction with respect to ethene and show that the order of reaction with respect to bromine is 1.

(iv) Suggest a value for t_4 , time taken for the colour of bromine to disappear in experiment 4.

4.4.2.2 Graphical Method

Success criteria:

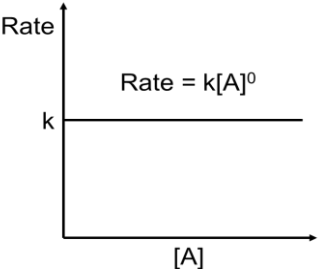
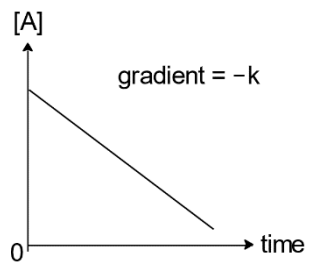
- I can deduce zero, first and second order of reaction from the shape of the rate-conc graph.
- I can deduce zero order of reaction from a straight line conc-time graph
- I can deduce first order of reaction from a conc-time graph with constant half-life.
- I can sketch both rate-conc graph and conc-time graph for zero, first and second order of reaction.
- I can use the formula, $t_{1/2} = \frac{\ln 2}{k}$, to calculate half-life and rate constant, k , for first order reaction.

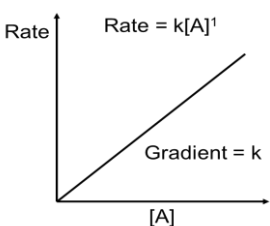
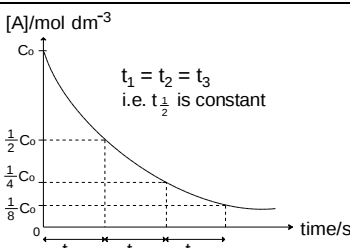
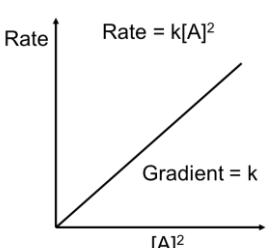
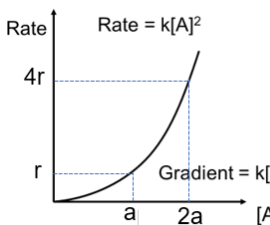
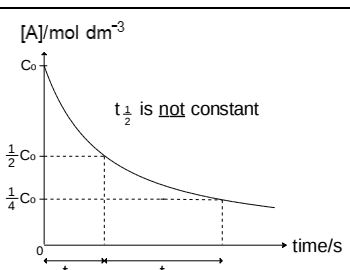
Graphical method used to determine **order of reaction**

Method	Initial Rate method	Continuous method
Graph	A rate-concentration graph is usually plotted.	A concentration-time graph is usually plotted.
Dependent variable (Y-axis)	Rate	Concentration of reactants (or any measurement $\propto$ conc)
Independent variable (X-axis)	Concentration of reactant in repeated experiments	Time at which the reaction mixture is analysed.
Order of Reaction deduced from	Shape	Shape and Gradient

(a) Rate-Concentration Graph (Initial Rate Method)

Concentration and rate of reaction obtained from multiple experiments can be plotted into a rate-concentration graph for deducing the order of reaction.

	Rate-conc graph	Conc-time graph
Zero Order	 Since the rate is independent of the concentration of reagent, rate is constant (rate = k) when reagent concentration changes.	 Gradient of conc-time graph represents the rate of reaction. For zero order reaction, the conc-time graph is a straight line with constant gradient (i.e. rate is constant).

	Rate-conc graph	Conc-time graph
First Order	 Increase in $[A]$ results in increase in rate in the <u>same extent</u>. $[A]$ decreases <u>exponentially with time</u>. (As compared to zero order reactions).	 Constant $t_{1/2}$ for first-order reaction.
Second Order	 	 No constant $t_{1/2}$ for second order reaction.

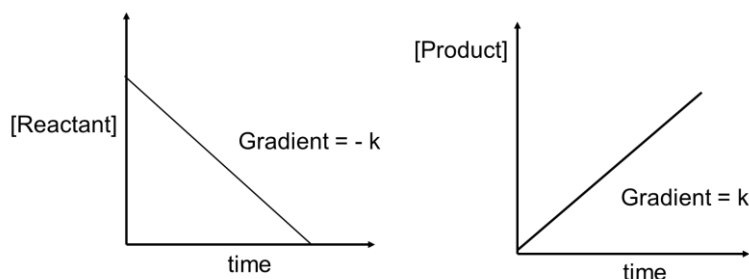
(b) Concentration-Time Graph (Continuous Method)

Concentration of reactant or product can be used to track the reaction progress.

To deduce Order of Reaction from Concentration-Time graph, check the following in sequence

i. Shape of graph

- **LINEAR:** Zero Order



As reaction proceeds, **[A] decreases**. It is observed that the **rate of reaction (gradient of conc-time graph) remains unchanged**.

→ It is zero order reaction w.r.t. A.

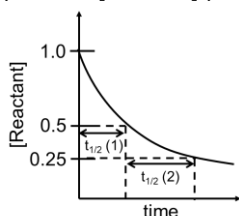
- **CURVE:** First or Second Order
 - Check the half-life to confirm if the order of reaction is 1st order.

ii. Half-Life

Half-life ($t_{1/2}$) is defined to be the time taken for the concentration of the reactant to fall to half of its initial concentration.

Note:

For 2nd Order reactions, as the **[reactant] decreases**, the rate decrease sharply as the decrease is squared (Rate = $k[\text{reactant}]^2$).



Subsequent half-life is also lengthened due to much slower rate of reaction.

- **Half-Life of First Order Reaction**

If the reaction has a **constant** half-life, the reaction is **first order** with respect to the investigated reactant.

This is due to rate of reaction decreasing linearly with the **change** in concentration.

This half-life can be used to determine the value of rate constant, k , using the equation below.

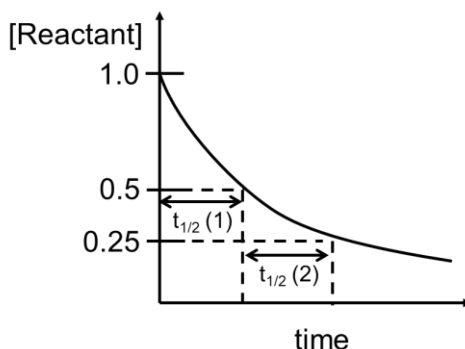
$$t_{1/2} = \frac{\ln 2}{k}$$

where k is the rate constant

• Determining Half-life from Graph

○ [Reactant]-time graph

Assuming the initial [reactant] to be 1.0 mol dm^{-3} ,



- first half-life ($t_{1/2}(1)$) is the time for the concentration to fall from 1.0 mol dm^{-3} to 0.5 mol dm^{-3} .
- second half-life ($t_{1/2}(2)$) is the time for the concentration to fall from 0.5 mol dm^{-3} to 0.25 mol dm^{-3} .

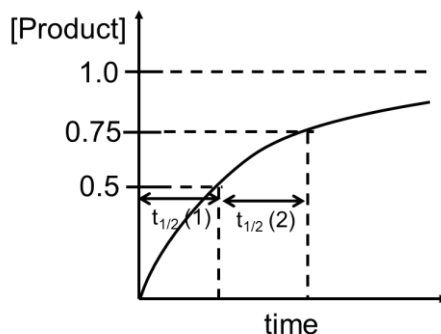
○ [Product]-time graph

Half-life can also be determined from [product]-time graph. Firstly, the 100% yield of the product has to be determined from the mole stoichiometry. The time taken for 50% of the product to be formed is taken as the first $t_{1/2}$.

Time	0	1 st $t_{1/2}$	2 nd $t_{1/2}$	3 rd $t_{1/2}$
[reactant]	100%	50%	25%	12.5%
[product]	0%	50%	75%	87.5%

Assuming initial [reactant] to be 1.0 mol dm^{-3} , and mole ratio of reactant to product is 1:1,

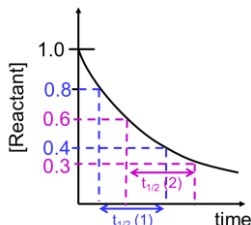
Time	0	1 st $t_{1/2}$	2 nd $t_{1/2}$
[reactant] / mol dm^{-3}	1.0	0.5	0.25
[product] / mol dm^{-3}	0.0	0.5	0.75



Note:

To determine if $t_{1/2}$ is constant, any concentration on the y-axis can be the "initial concentration", not only concentration at $t = 0$.

1st and 2nd $t_{1/2}$ also need not necessarily be taken in a consecutive manner as long as the "initial concentration" of 2nd $t_{1/2}$ is different from 1st $t_{1/2}$.

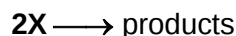


For example,

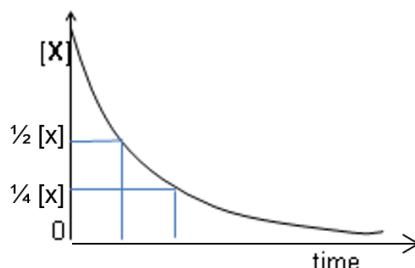
- 1st $t_{1/2}$ is obtained by taking the "initial concentration" to be 0.8 mol dm^{-3} , "final concentration" to be 0.4 mol dm^{-3} .
- 2nd $t_{1/2}$ is obtained by taking the "initial concentration" to be 0.6 mol dm^{-3} , "final concentration" to be 0.3 mol dm^{-3} .

Checkpoint 7

- 1) The following reaction was believed to be first order.

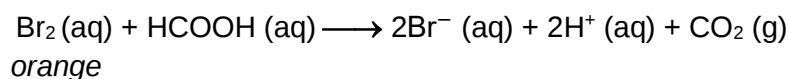


In an experiment, concentration of **X** is plotted against time as shown in the following graph.



Which of the following key information that can be obtained from the graph?

- 1 Rate of the reaction at any given instant can be calculated from the gradient of the tangent drawn at any point of the curve.
 - 2 To verify that the rate equation is: $\text{Rate} = k[X]$.
 - 3 Rate constant k can be determined using the equation, $k = \frac{\ln 2}{t_{1/2}}$.
- 2) The rate of reaction between bromine and methanoic acid is first order with respect to bromine and methanoic acid respectively.



The reaction kinetics of above reaction is investigated by using 0.10 mol dm^{-3} each of bromine and methanoic acid. Which of the following can be deduced from this information?

- 1 A linear graph is obtained when rate is plotted against $[\text{Br}_2][\text{HCOOH}]$ while a curve is obtained if rate is plotted against $[\text{Br}_2]$.
- 2 Rate of disappearance of Br_2 is twice rate of appearance of Br^- .
- 3 Doubling the concentration of methanoic acid and doubling concentration of bromine doubles the rate of evolution of gas.

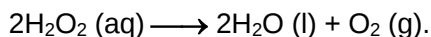
Success criteria:

I can use continuous method to

- (i) determine the order of reaction via shape of concentration-time graph and half-life
- (ii) use the half-life of a first order reaction to calculate the rate constant

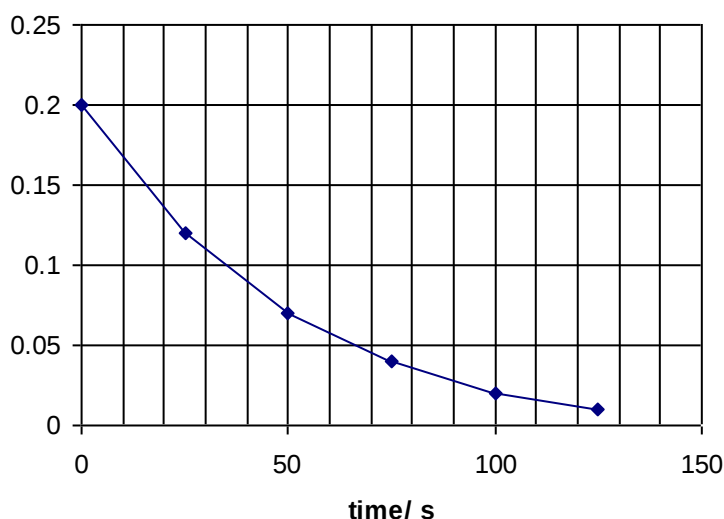
Worked Example 9 (Decomposition of H₂O₂)

Hydrogen peroxide undergoes catalysed decomposition.



The following results are obtained in an experiment and the results are plotted on the graph shown below:

Time / s	0	25	50	75	100	125
[H ₂ O ₂] / mol dm ⁻³	0.20	0.12	0.07	0.04	0.02	0.01

**Note:**

Graph must be plotted to determine the half-life pattern. You will be penalized if the half-life pattern is deduced from the numerical data without graph plotting

- (a) Deduce the order of reaction with respect to hydrogen peroxide.

As reaction proceeds, [H₂O₂] decreases. It is observed that the rate of reaction (gradient of conc vs time graph) decreases with a constant half-life of 33s.

→ It is first order reaction w.r.t. H₂O₂

- (b) Write a rate equation for the reaction.

$$\text{Rate} = k [\text{H}_2\text{O}_2]$$

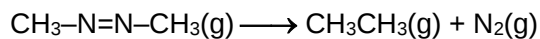
- (c) Calculate the rate constant, giving its units.

$$\text{For first order reaction: } t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{33} = 0.0210 \text{ s}^{-1}$$

Checkpoint 8

Azomethane, $\text{CH}_3\text{--N=N--CH}_3$, is a common compound used in cancer research. It decomposes according to the following equation:

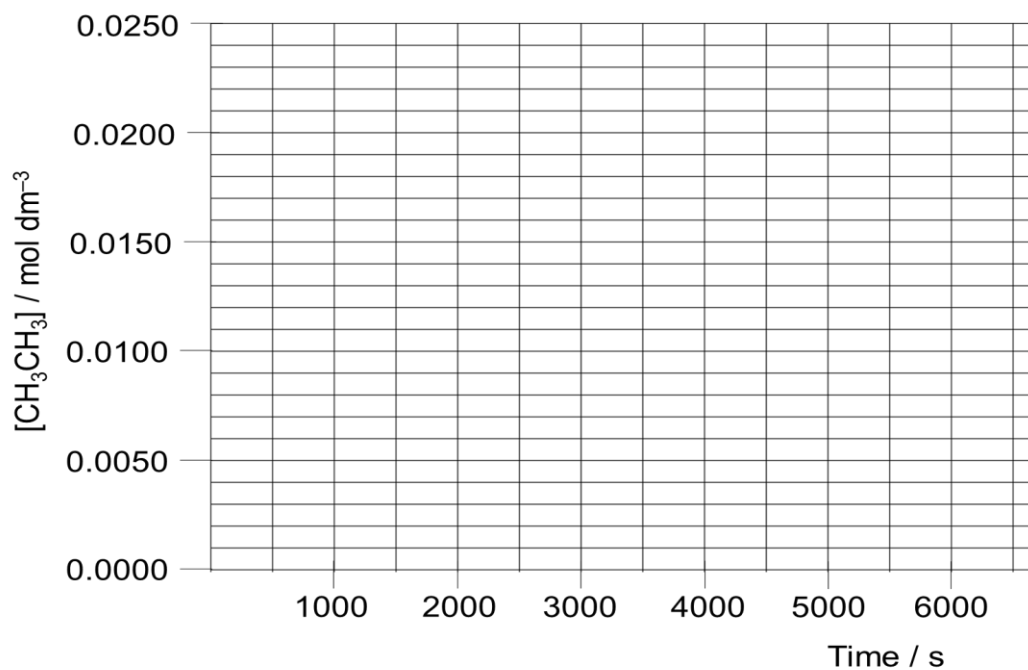


- (i) Suggest a variable that can be monitored experimentally to study the rate of the reaction. Explain your answer.

- (ii) $0.0220 \text{ mol dm}^{-3}$ of $\text{CH}_3\text{--N=N--CH}_3$ was decomposed in a reaction. The concentration of ethane, $[\text{CH}_3\text{CH}_3]$, was determined at different times in a particular experiment and is shown below:

t / s	$[\text{CH}_3\text{CH}_3] / \text{mol dm}^{-3}$
0	0.0000
1000	0.0121
2000	0.0176
3000	0.0200
4000	0.0211
5000	0.0216

Using the given data, plot a suitable graph to determine the order of the reaction with respect to azomethane.



(iii) Calculate the rate constant for this reaction and state its units.

(c) Combination of Initial Rate and Continuous Methods

When the reaction involves two types of reactants, the **overall rate** of reaction could **depend on either one or both types of the reactants**.

To construct the rate equation, we will need to find the order of reaction with respect to each reactant. This can be done through a combination of continuous and initial rate methods.

Using the following reaction as example,



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

Reactant B is used in large excess (≥ 10 times the conc of reactant A).

Note:

- The word 'pseudo' means "not the actual one".

The use of pseudo rate equation arises in situation that involved pseudo order reaction when the concentration of one reactant remains essentially constant in the reaction due to
(a) a reactant that is present in large excess (at least 10 times greater than the rest)

(b) a reactant acts as a solvent (present in large excess) in the reaction

(c) a reactant acts as a catalyst (remains chemical unchanged) in the reaction.

Step 1: Continuous Method (Find order of reaction w.r.t A)

- Keep [B] constant by using large excess of B. Due to large excess, a very small amount of B will be consumed and hence the concentration of B is relatively constant. Any change in the rate of reaction would then not be due to B. The rate equation could be re-written below as pseudo rate equation:

$$\text{Rate} = k' [A]^m, \text{ where } k' = k[B]^n \text{ (a constant)}$$

- Use the pseudo rate equation: $\text{Rate} = k' [A]^m$ to find the order of reaction with respect to the changing reactant concentration, [A].

Observe the shape and use half-life data to determine the order of reaction with respect to A.

Step 2: Initial Rate Method (Find order of reaction w.r.t B)

Repeat the same experiment in step 1

- Keep [A] constant
- Change [B], but still keeping B in large excess.

Compare time taken for both reactions to reach the same [A] left. Use inspection method to deduce the order of reaction.

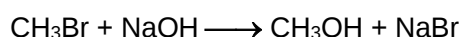
Success criteria:

For pseudo order reactions, I can use both

- (i) continuous method to determine the order of reaction w.r.t reactant that is not in excess and
- (ii) initial rate method via inspection method to determine the order of reaction w.r.t reactant that is present in excess.

Worked Example 10

The kinetics of reaction between bromomethane, CH_3Br and NaOH is being investigated. The balanced chemical equation is as follows:

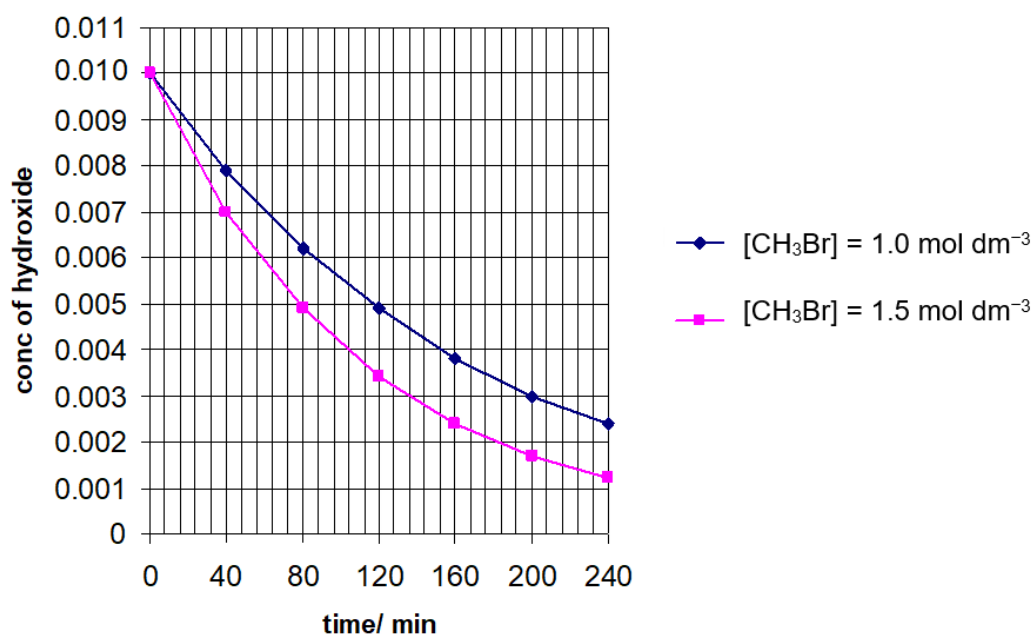


In order to determine the order with respect to each type of reactant, two experiments can be carried out. $[\text{CH}_3\text{Br}]$ used is at least 10 times of the $[\text{NaOH}]$.

The following results were obtained from two experiments.

Time/ min	Expt 1 [OH ⁻]/ mol dm ⁻³ when [CH ₃ Br] = 1.0 mol dm ⁻³	Expt 2 [OH ⁻]/ mol dm ⁻³ when [CH ₃ Br] = 1.5 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

The results are then plotted on the same axis for ease of comparison.



(a) Determine the order of reaction with respect to OH^- .

Either experiment 1 **or** experiment 2 (since OH^- is the low concentration reactant in both experiments)

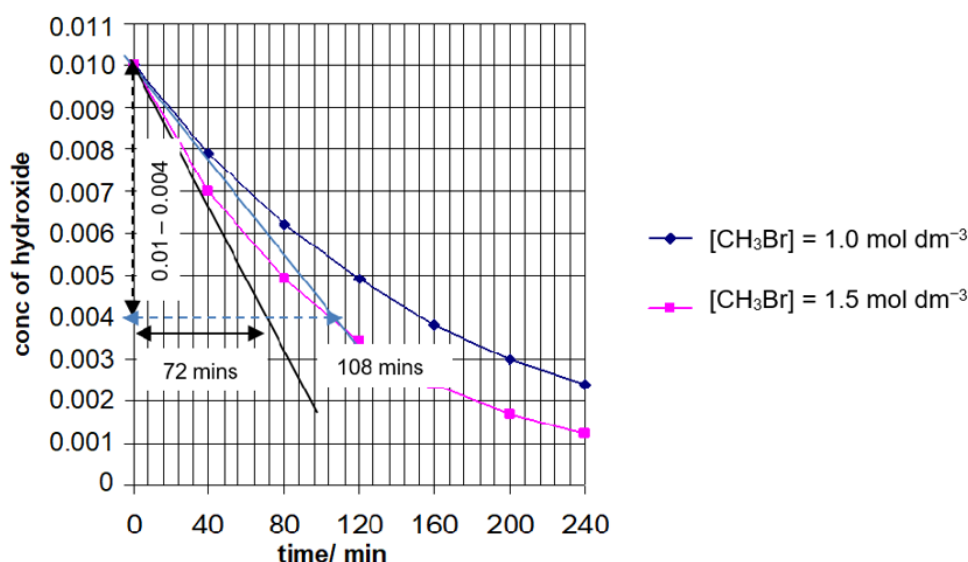
Suppose we look at experiment 1, where $[\text{CH}_3\text{Br}] = 1.0 \text{ mol dm}^{-3}$ and $[\text{OH}^-]_{\text{initial}} = 0.01 \text{ mol dm}^{-3}$

As reaction proceeds, $[\text{OH}^-]$ decreases significantly while $[\text{CH}_3\text{Br}]$ remains approximately constant. It is observed that the rate of reaction decreases with a constant half-life of 120mins.

→ It is first order reaction w.r.t. OH^- .

(b) Determine the order of reaction with respect to CH_3Br .

To determine the order of reaction with respect to CH_3Br (the reactant in high concentration), compare the initial rate of the two experiments.



$$\text{Initial rate for expt 1} = -\frac{d[\text{OH}^-]}{dt} = \frac{0.01 - 0.004}{108} = 5.56 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$\text{Initial rate for expt 2} = -\frac{d[\text{OH}^-]}{dt} = \frac{0.01 - 0.004}{72} = 8.33 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$$

Expt	$[\text{OH}^-]$	$[\text{CH}_3\text{Br}]$	Rate
1	0.01	1.0	5.56×10^{-5}
2	0.01	1.5	8.33×10^{-5}

Compare expt 1 and 2 where $[\text{OH}^-]$ is the same.

When $[\text{CH}_3\text{Br}]_{\text{expt2}}$ is 1.5 times of $[\text{CH}_3\text{Br}]_{\text{expt1}}$, rate (2) is 1.5 times of rate (1),

$$\text{OR} \quad \text{When } \frac{[\text{CH}_3\text{Br}]_{\text{expt2}}}{[\text{CH}_3\text{Br}]_{\text{expt1}}} = 1.5, \quad \frac{\text{rate}_{\text{expt2}}}{\text{rate}_{\text{expt1}}} = 1.5$$

therefore the reaction is first order w.r.t CH_3Br .

Note:

When CH_3Br is used in large excess, $[\text{CH}_3\text{Br}]$ remains relatively constant.

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

(1st order)

$$\text{where } k' = k[\text{CH}_3\text{Br}]$$

$$t_{1/2} = \frac{\ln 2}{k'}, \text{ hence}$$

$$k[\text{CH}_3\text{Br}] = \frac{\ln 2}{t_{1/2}}$$

Using $t_{1/2}$ of expt 2 (80mins),

$$\begin{aligned} k &= \frac{\ln 2}{80 \times 1.5} \\ &= 5.78 \times 10^{-3} \\ &\quad \text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1} \end{aligned}$$

(c) Calculate the rate constant for this reaction and state its units.

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

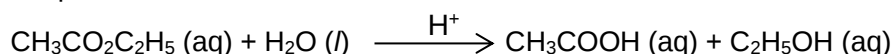
By using the initial rate of expt 2:

$$8.33 \times 10^{-5} = k (1.5)(0.01)$$

$$k = 5.55 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1} \text{ (3sf)}$$

Worked Example 11

The kinetics of acid catalysed hydrolysis of ester is being investigated. The balanced chemical equation is as follows:



The following results were obtained from two experiments.

Time/ min	Expt 1	Expt 2
	$[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] / \text{mol dm}^{-3}$ when $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$	$[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] / \text{mol dm}^{-3}$ when $[\text{HCl}] = 0.2 \text{ mol dm}^{-3}$
0	0.200	0.200
25	0.152	0.115
50	0.115	0.067
75	0.088	0.038
100	0.067	0.022
125	0.051	0.013

Note:

We can also compare the initial rates by drawing the tangent at $t = 0$ and finding the gradient of the tangent.

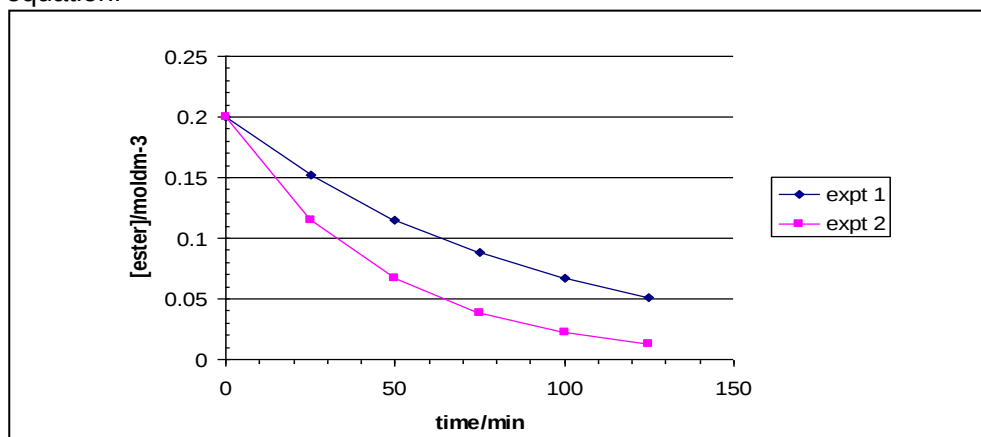
- (a) Identify the role of HCl and hence deduce whether its concentration changes during reaction in a particular experiment.

HCl (H^+) is a catalyst in the above reaction. (appears above arrow in balanced equation) Since catalyst is reacted and regenerated during reaction, its concentration is effectively constant within one experiment.

- (b) Explain why analysis of one graph (one experiment) gives the order with respect to ester only.

Within one expt, $[\text{H}^+]$ and $[\text{water}]$ do not change as their concentrations remain relatively constant, hence will not affect rate. (i.e. $\text{rate} = k'[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5]^x$ where $k' = k[\text{H}^+]^y [\text{H}_2\text{O}]^z$). The change in rate during the course of reaction or half-life pattern can only be due to decrease in concentration of ester.

- (c) Plot these data on suitable axes and use your graphs to determine the order of reaction with respect to $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ (ester) and HCl and hence the rate equation.



Suppose we look at experiment 2, where $[\text{ester}] = 0.2 \text{ mol dm}^{-3}$ and $[\text{H}^+]_{\text{initial}} = 0.2 \text{ mol dm}^{-3}$

As reaction proceeds, [ester] decreases significantly while $[\text{H}^+]$ remains approximately constant. It is observed that the rate of reaction decreases with a constant half-life of 34 mins.

→ It is first order reaction w.r.t. ester.

Comparing expt 1 and 2, $[\text{ester}]$ is kept constant while $[\text{H}^+]$ is doubled.

Half-life for ester in expt 1 = 66 mins

Half-life for ester in expt 2 = 34 mins

For the *same amount or conc* of ester reacted, expt 2 takes half the time compared to expt 1. ∴ **Average rate** of expt 2 must be twice of **average rate** of expt 1. Since the concentration of HCl in expt 2 is twice of expt 1, the reaction is first order w.r.t HCl .

Rate equation: rate = $k'[\text{ester}][\text{H}^+]$ where $k' = k[\text{H}_2\text{O}]^2$

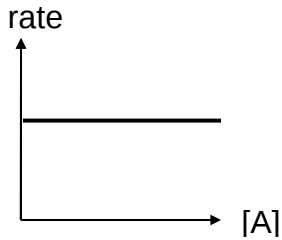
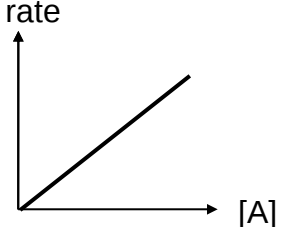
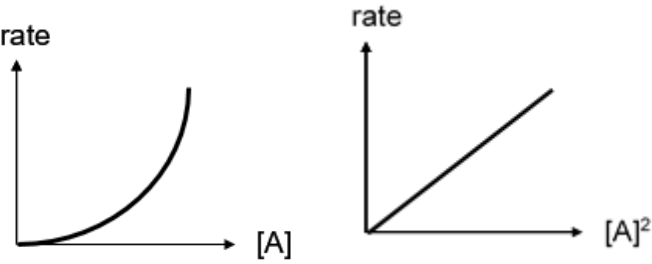
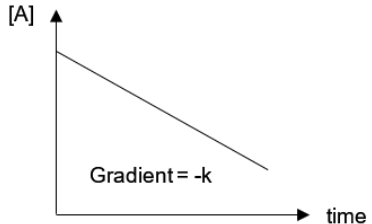
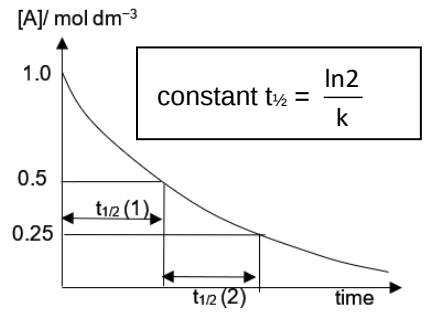
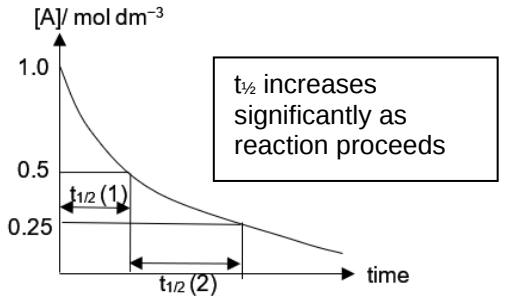
- (d) Discuss why it is not possible to determine the order of reaction with respect to water.

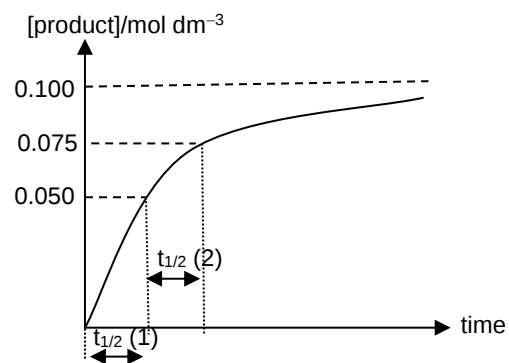
This is because water is present in large excess as it assumes the role of a solvent in aqueous solutions of HCl and ester. The conc of water is large and remains relatively constant, it is therefore impossible to determine the order with respect to water.

Learning points:

- When aqueous catalyst is involved in the slow step, its concentration matters (as opposed to solid catalyst). The more aqueous catalyst used, the higher the rate of reaction.
- In order to obtain the order of reaction for a single species in the rate equation, there is a need to ensure all other reactants (including catalysts) do not affect the rate. However, as long as a reactant is an aqueous species, it has the potential to impact the rate. Hence, **to ensure a particular reactant seemingly exert no effect on rate**, it has to be
 - present in relatively much larger concentration (large excess such that consumption is negligible from start to end of experiment) or,
 - kept the same between experiments.
- Hence, when the reactant is a solvent, the order w.r.t this reactant cannot be determined as its concentration cannot be varied. Being a solvent, it will be present in large excess.

Summary of Reaction Rate and Concentration

Order of reaction	0	1	2
Example	$A \longrightarrow \text{products}$	$A \longrightarrow \text{products}$	$2A \longrightarrow \text{products}$
Rate equation	Rate = $k [A]^0$ = k	Rate = $k [A]$	Rate = $k [A]^2$
Units of k	$\text{mol dm}^{-3} \text{ t}^{-1}$	t^{-1}	$\text{mol}^{-1} \text{ dm}^3 \text{ t}^{-1}$
Graph of rate vs $[A]$			
Graph of $[A]$ vs time Gradient = rate of reaction			
Notes	Rate of reaction is unaffected by concentration of reactants. Gradient of conc vs time graph is constant.	Rate of reaction decreases as [reactants] decreases. Gradient of conc vs time graph decreases with time. Half-life is constant, $t_{1/2} = \frac{\ln 2}{k}$	Rate of reaction decreases sharply as concentration of reactants decreases. Gradient of conc vs time graph decreases sharply with time. Half-life increases significantly as the reaction proceeds.

[Product]-time graph for first order reaction:

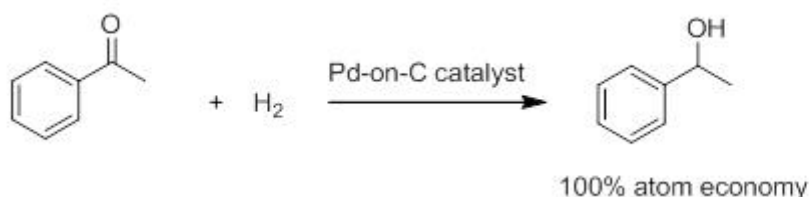
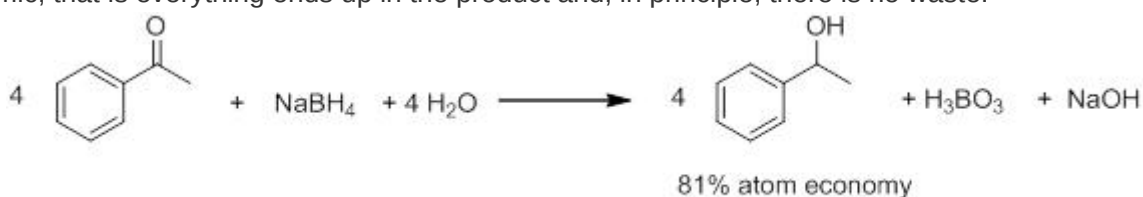
When [product] vs time graph is being analysed, do note that first half-life, $t_{1/2}$ (1) corresponds to time needed to attain **50% yield** while $t_{1/2}$ (2) is time taken to increase the product yield from **50% to 75%**

Time	[Reactant]	[Product]
0	100%	0%
1 st $t_{1/2}$	50%	50%
2 nd $t_{1/2}$	25%	75%
3 rd $t_{1/2}$	12.5%	87.5%

Chemistry Application...(for your interest)

Taken from "Green Chemistry Principle #9 Catalysis" by Roger A. Sheldon, PhD, Emeritus Professor of Biocatalysis and Organic Chemistry, Delft University of Technology and CEO of CLEA Technologies B.V.
Web Source: <https://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/principles/green-chemistry-principle--9.html>

A primary goal of green chemistry is the minimization or preferably the elimination of waste in the manufacture of chemicals and allied products: *"prevention is better than cure"*. This necessitates a paradigm shift in the concept of efficiency in organic synthesis, from one that is focused on chemical yield to one that assigns value to minimization of waste. What is the cause of waste? The key lies in the concept of atom economy: *"synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product"*. In the reaction scheme we compare, for example, the reduction of a ketone to the corresponding secondary alcohol using sodium borohydride or molecular hydrogen as the reductant. Reduction with the former has an atom economy of 81% while reduction with the latter are 100% atom economic, that is everything ends up in the product and, in principle, there is no waste.



Unfortunately, hydrogen does not react with ketones to any extent under normal conditions. For this we need a **catalyst such as palladium-on-charcoal**. A catalyst is defined as **"a substance that changes the velocity of a reaction without itself being changed in the process"**. It lowers the activation energy of the reaction but in so doing it is not consumed. This means that, in principle at least, it can be used in **small amounts and be recycled indefinitely**, that is it doesn't generate any waste. Moreover, molecular hydrogen is also the least expensive reductant and, for this reason, catalytic hydrogenations are widely applied in the petrochemical industry, where the use of other reductants is generally not economically viable. It is only in the last two decades, however, following the emergence of green chemistry, that catalysis has been widely applied in the pharmaceutical and fine chemical industries, with the goal of minimizing the enormous amounts of waste generated by the use of stoichiometric inorganic reagents. This involves the use of the full breadth of catalysis: heterogeneous, homogeneous, organocatalysts and, more recently, Nature's own exquisite catalysts: enzymes. The latter are particularly effective at catalyzing highly selective processes with complex substrates under mild conditions and, hence, are finding broad applications in the pharmaceutical and allied industries. Moreover, they are expected to play an important role in the transition from a chemical industry based on non-renewable fossil resources to a more sustainable bio-based economy utilizing renewable biomass as the raw material, yet another noble goal of green chemistry.

BASIC CONCEPTS IN KINETICS		
Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
1. I can explain how changes to (i) the concentration or pressure (ii) the particle size of a solid reactants/surface area of contact affects the rate of a reaction.	A1: Q1(i)	
2. I can draw the Boltzmann distribution curve and use it to explain: (i) the change in rate of a reaction by relating to the fraction of particles having kinetic energy greater or equal to the activation energy (ii) how a change in temperature affects the rate of reaction (iii) how the catalyst increases the rate of a chemical reaction.	A1: Q1(ii), Q2 A1: Q1(iii)	
3. I can distinguish between homogeneous and heterogeneous catalyst.		
4. I can provide examples: (i) the Haber process (ii) the catalytic removal of oxides of nitrogen in car engine exhaust gases to illustrate the modes of action of heterogeneous catalysis.	A2: Q4	
5. I can provide examples: (i) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric SO ₂ (ii) the catalytic role of Fe ²⁺ in the I ⁻ /S ₂ O ₈ ²⁻ reaction to illustrate the modes of action of homogeneous catalysis.	A2: Q3	
6. I can identify an autocatalyst given a concentration-time graph and explain the shape of the graph.	A2: Q5	
7. (a) I can describe enzymes as biological catalysts with specific activity. (b) I can explain how pH and temperature affect the structure of the enzyme and its catalytic activity.	A2: Q6	

QUANTATITIVE KINETICS		
Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
1. I can define the rate of reaction correctly in terms of the rate of change of concentration of (i) reactant or (ii) product over time.	B1: Q7(b) B3: Q15(a)	
2. (a) I can define the rate equation, rate constant and order of reaction correctly. (b) I can write the rate equation based on the order of reactions determined experimentally. (c) I can interpret the meaning of zero, first and second order of reactions.	B1: Q7(a) B1: Q8(a)(i)-(iv)	
(b) (a) I can state the effect on the rate constant with the change in condition (temperature or catalyst). (b) I can state the units for rate constant based on the overall order of reaction.	B1: Q8(a)(v)-(vi)	
(c) (a) I can derive the rate equation (i.e. $\text{rate} = k[A]^m[B]^n$, where m and n could be 0, 1 or 2) from the rate determining step (i.e. slow step) of the reaction mechanism and vice versa. (b) I can verify the reaction mechanism by matching with the rate equation; and predict the order of reaction that would result from a given reaction mechanism.	B2: Q9, Q10 B2: Q11, Q12 B3: Q15(e)	
(d) I can devise a suitable experimental technique for studying the rate of a reaction, using continuous or initial rate method from given information.	B4.2: Q18(d)	
(e) (a) I can deduce zero, first and second order of a reaction from the shape of the rate-conc graph. (b) I can deduce zero order of reaction from a straight line conc-time graph (c) I can deduce first order of reaction from a conc-time graph with constant half-life. (d) I can sketch both rate-conc graph and conc-time graph for zero, first and second order of reaction. (e) I can use the formula, $t_{1/2} = \frac{\ln 2}{k}$, to calculate half-life and rate constant, k , for first order reaction.	B4.1: Q16 C: Q23	

Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
(f) I can use initial rate method to (i) determine the order of reaction via inspection or mathematical method or shape of the rate-time graph (ii) calculate the rate constant	B3: Q13, Q14, Q15(b) B3: Q15(c)	
(g) I can use continuous method to (i) determine the order of reaction via shape of concentration-time graph and half-life (ii) use the half-life of a first order reaction to calculate the rate constant	B4.2: Q17, Q18, Q19 B4.2: Q17(c)	
(h) For pseudo order reactions, I can use (i) continuous method via half-life to determine the order of reaction w.r.t reactant that is not in excess and (ii) initial rate method via inspection method to determine the order of reaction w.r.t reactant that is present in excess.	B4.3: Q20	
(i) Predict the time taken of a first order reaction to reach a particular state from the given information and half-time.	C: Q21, Q22	

REACTION KINETICS TUTORIAL**A. BASIC CONCEPTS (QUALITATIVE KINETICS)****Section A1: Boltzmann distribution**

- 1** Explain, using collision theory, how the following changes can affect the initial reaction rate of a gaseous system.

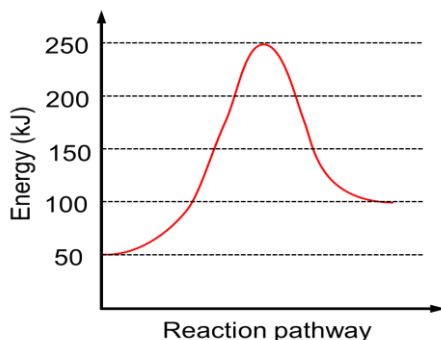
Illustrate your answer with the Boltzmann distribution curve for parts **(ii)** and **(iii)**.

- (i)** increasing the pressure
 - (ii)** decreasing the temperature
 - (iii)** addition of a catalyst
- 2** Which statement best explains why a small increase in temperature leads to a significant increase in the rate of a gaseous reaction?
- A** The frequency of collisions between the molecules is greater at a higher temperature.
 - B** The activation energy of the reaction is lower when the gases are at a higher temperature.
 - C** The average kinetic energy of the molecules is greater at a higher temperature.
 - D** The frequency of effective collisions between molecules with kinetic energy greater than the activation energy is greater at a higher temperature

Section A2: Catalysis

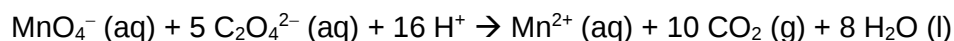
- 3** Which is a correct statement about the effect of a homogeneous catalyst?
- A** It does not appear in the rate equation for the reaction.
 - B** It causes the reaction to proceed via a different mechanism.
 - C** It increases the rate constant of the forward reaction but not that of the backward reaction.
 - D** It increases the kinetic energy of the reactant particles and therefore the frequency of effective collision.

4 Answer the following questions based on the energy profile diagram shown below:

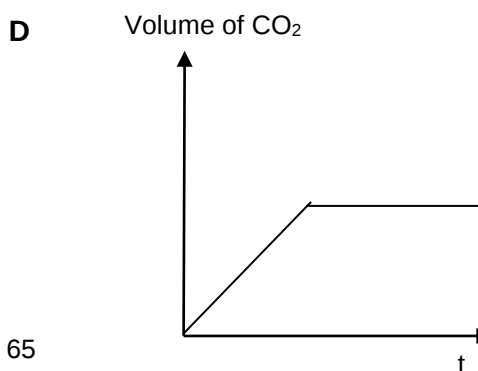
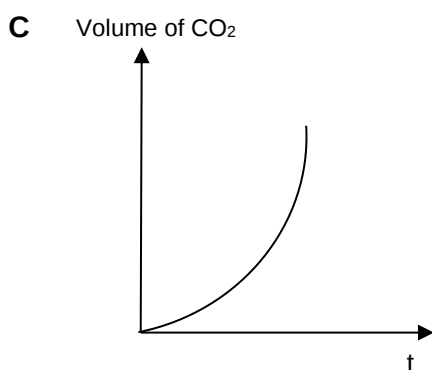
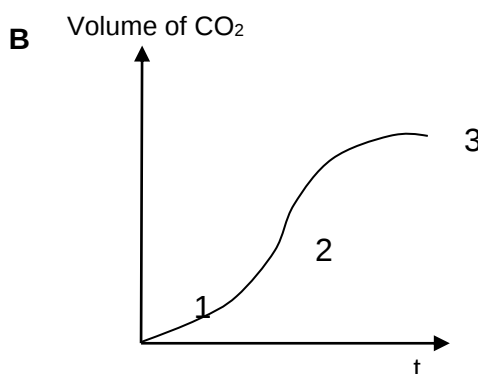
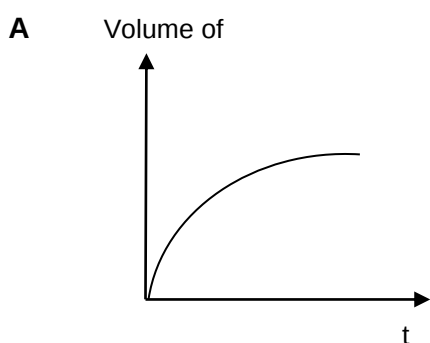


- (a) Does the graph represent an endothermic or exothermic reaction?
- (b) Label the position of the reactants, products, and transition state.
- (c) Determine the heat of reaction, ΔH , (enthalpy change) for this reaction.
- (d) Determine the activation energy, E_a (f) for forward reaction.
- (e) Determine the activation energy, E_a (b) for backward reaction. Hence explain why this reaction could be reversible.
- (f) Sketch how the energy profile will change, if any, if a homogeneous catalyst is added to the reaction system.
- (g) Describe how a heterogeneous catalyst can increase effective collision between gaseous reactants by referring to the collision theory.

5 The reaction represented by the following equation was carried out.



Which graph best shows the relationship between volume of CO_2 collected over time from mixing of the reactants?

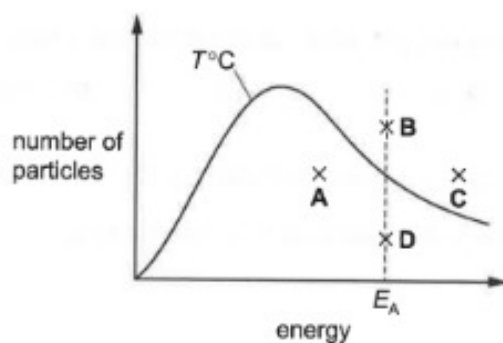


- 6 A Boltzmann distribution for a sample of a reaction gas at a constant temperature, $T^{\circ}\text{C}$, is shown.

The activation energy, E_A , for the reaction is marked.

The temperature of the sample of gas is decreased to $(T-50)^{\circ}\text{C}$.

Which point could show the intercept of the new Boltzmann distribution curve with the value of the activation energy of the reaction at $(T-50)^{\circ}\text{C}$.



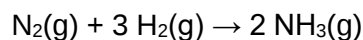
B. QUANTITATIVE KINETICS**Section B1: The Rate Equation**

7 (a) Define the following terms with the help of a rate equation.

(i) Order of reaction and overall order of reaction

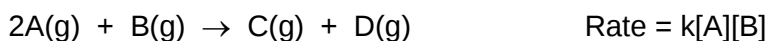
(ii) Rate constant

(b) Consider the following reaction:



If the rate of loss of hydrogen gas is $0.03 \text{ mol dm}^{-3} \text{ s}^{-1}$, calculate the rate of production of ammonia.

8 (a) Given the following equation and rate equation,



Predict how would the rate change when the following changes are made.

(i) Partial pressures of both A and B are doubled

(ii) Partial pressure of A doubles but that of B remains constant

(iii) Volume of the reaction vessel is doubled

(iv) Addition of an inert gas causing a doubling of the overall pressure

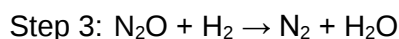
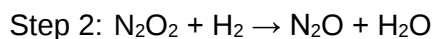
(v) Temperature of the reaction system is raised

(vi) A catalyst is added.

Section B2: Mechanisms

9 Nitrogen monoxide reacts with hydrogen gas to produce nitrogen gas and water vapour.

The mechanism is believed to be:



(a) Write the overall balanced equation.

(b) Identify any reaction intermediates.

10 The proposed mechanisms of two reactions are as shown below.

In each case, determine the:

(a) Rate equation

(b) order of reaction with respect to each reactant

(c) units for the rate constant

(i) $A + B \rightarrow C$ single step

(ii) $S + R \rightarrow P$

$S + H^+ \rightleftharpoons SH^+$ fast

$SH^+ + R \rightarrow P + H^+$ slow

11 The mechanism for a given reaction is shown below.

Step 1 : $2A \rightleftharpoons C$ fast

Step 2 : $C + B \rightarrow D$ slow

Step 3 : $D + B \rightarrow A_2B_2$ fast

What conclusion(s) can be drawn from the information given above?

1 rate = $k[A]^2[B]$

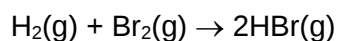
2 The overall equation is $2A + 2B \rightarrow A_2B_2$.

3 The rate of formation of A_2B_2 is proportional to the initial concentration of **B**.

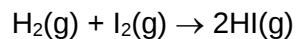
A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

12 [N2021/1/13]

Hydrogen reacts with gaseous bromine to form hydrogen bromide:



It also reacts with gaseous iodine to form hydrogen iodide:



For the first reaction, the rate equation is

$$\text{rate} = \frac{k_1 [\text{H}_2][\text{Br}_2]^{1.5}}{[\text{Br}_2] + k_2 [\text{HBr}]}$$

For the second reaction, the rate equation is

$$\text{rate} = k[\text{H}_2][\text{I}_2]$$

k_1 , k_2 and k represent rate constants.

What can be deduced based on this information only?

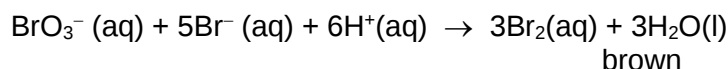
- 1** For the hydrogen / bromine reaction, the formation of HBr slows down the rate of the forward reaction.
- 2** Only the hydrogen and iodine reaction could be a single-step reaction.
- 3** Doubling the concentration of the halogen in each reaction doubles each rate of reaction.

- A** 1, 2 and 3
B 1 and 2 only

- C** 2 and 3 only
D 1 only

Section B3: Inspection Method (Initial Rate Method)

- 13** In acid medium, bromate ions, BrO_3^- , oxidize bromide ions to bromine:

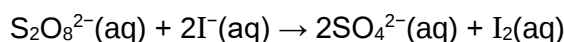


A series of experiments were conducted, involving different volumes of each of the reagents, $1 \text{ mol dm}^{-3} \text{BrO}_3^-$, $1 \text{ mol dm}^{-3} \text{Br}^-$ and $1 \text{ mol dm}^{-3} \text{H}^+$. The time taken for the first appearance of Br_2 was determined.

Mixture	Volume of reagent / cm^3				Total volume / cm^3	Time taken for brown Br_2 to appear / s
	BrO_3^-	Br^-	H^+	Water		
1	100	500	600	800	2000	305
1'	50	250	300	400	1000	305
2	50	250	600	100	1000	77
3	100	250	600	50	1000	38
4	50	125	600	225	1000	149

- (a) Data for mixture 1' is derived from mixture 1.
- Explain the purpose of halving every volume of the reagent used for mixture 1.
 - Explain why the time taken for brown Br_2 to appear is not halved.
- (b) Using the above data, determine how the initial rate depends on the concentration of BrO_3^- , Br^- and H^+ . Hence determine the rate equation.
- (c) Explain why water is added.

- 14** An experiment was carried out to investigate the initial rate of reaction between ammonium peroxodisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, an oxidizing agent, and potassium iodide, KI.



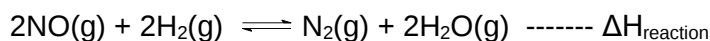
The initial concentrations of the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and KI solutions in the mixture, together with the time taken for the mixture to darken for the various experimental runs are given below:

Experiment	Initial concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ / mol dm^{-3}	Initial concentration of KI / mol dm^{-3}	Time taken to darken/ s
1	0.10	0.20	35
2	0.05	0.20	70
3	0.10	0.067	105
4	0.02	0.75	?

Which statements about the reaction is/are true?

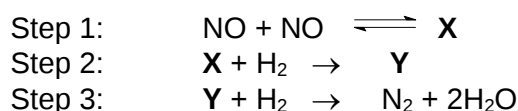
- The reaction involves the formation of an intermediate.
 - The time taken for the mixture to darken in Experiment 4 is 47s.
 - The slow step involves the reaction between 1 mole of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 1 mole of KI.
- A** 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

- 15** The following data was collected for the gas-phase reaction between nitrogen monoxide and hydrogen at 700°C.



Expt No.	[NO] _{initial} / mol dm ⁻³	[H ₂] _{initial} / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ s ⁻¹
1	0.002	0.012	0.0033
2	0.004	0.012	0.0132
3	0.008	0.012	0.0528
4	0.010	0.012	0.0825
5	0.012	0.012	0.119
6	0.012	0.0020	0.0198
7	0.029	To be calculated	1.33

- (a) How is the rate of appearance of N₂ related to the rate of disappearance of hydrogen?
- (b) (i) Determine the order of reaction with respect to H₂ by making use of suitable pairs of data from the table above.
- (ii) Determine the order of reaction with respect to NO by plotting a suitable graph by making use of the data from experiments 1 to 5.
- (iii) Hence derive the rate law or otherwise known as the rate equation.
- (c) Calculate the value of the rate constant and state its units.
- (d) Calculate the initial concentration of H₂ for experiment 7.
- (e) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. **X** and **Y** are intermediate species.



Suggest which one of the three steps is the rate-determining step.

Explain your answer.

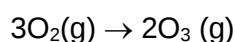
- (f) Given that the bond energy of NO is 420 kJ mol⁻¹, Determine the enthalpy change of this reaction, $\Delta H_{\text{reaction}}$ by making use of suitable data from the Data Booklet.

Section B4.1: Graphical Method – Initial Rate vs Continuous

- 16 (a)** A reaction is found to be first order with respect to reactant **A**.
- (i) Give the rate equation of this reaction, assuming that **A** is the only reactant.
- (ii) Given that half-life of reactant **A** is 10 mins, sketch the following graphs:
- concentration of **A** vs time graph (continuous method) and
 - rate vs concentration of **A** (initial rate method)
- (b)** If reaction is second order with respect to **A**,
- (i) Give the rate equation of this reaction, assuming that **A** is the only reactant.
- (ii) Sketch the following graph
- concentration of **A** vs time graph (continuous method) and
 - rate vs concentration of **A** (initial rate method)
- (iii) How would you modify the axis of the rate vs concentration graph to obtain a linear graph?
- (c)** If reaction is zero order with respect to **A**
- (i) Give the rate equation of this reaction, assuming that **A** is the only reactant.
- (ii) Sketch the following graph
- concentration of **A** vs time graph (continuous method) and
 - rate vs concentration of **A** (initial rate method)

Section B4.2: Graphical Method – Continuous Method

- 17** The following reaction is monitored by measuring the changes in total pressure during the reaction, with initial pressure of O_2 at 300 kPa.

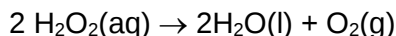


Time /s	15	30	45	60	75	90	∞
P_{total} / kPa	278	267	257	250	240	238	

- (a)** Work out the total pressure at time infinity.
- (b)** Given that $P_{O_2} = 3P_{\text{total}} - 600\text{kPa}$, determine the order of reaction with respect to oxygen with the aid of a suitable graph.
- (c)** Determine the value of rate constant, stating its units.

- 18** Hydrogen peroxide of original concentration 3.0 mol dm^{-3} was placed in a contaminated bottle some time ago. The student was then asked to determine how long the hydrogen peroxide had been stored in the bottle. In order for the student to find out how long the H_2O_2 is stored in the bottle, the kinetics of decomposition of H_2O_2 must be followed to determine its half-life.

The rate of decomposition of hydrogen peroxide was investigated by monitoring remaining H_2O_2 with time.



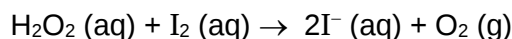
The remaining H_2O_2 can be determined by withdrawing 10 cm^3 portions of H_2O_2 solution at regular time intervals and titrating it with acidified $0.1 \text{ mol dm}^{-3} \text{KMnO}_4(\text{aq})$. This is known as the **titrimetric method**.

The following results were obtained:

Time / min	Volume of $0.1 \text{ mol dm}^{-3} \text{KMnO}_4(\text{aq})$ / cm^3
0	30.0
5	23.4
10	18.3
15	14.2
20	11.1
25	8.7
30	6.8

- Identify the type of reaction H_2O_2 has undergone when it decomposes to form O_2 and H_2O . Illustrate type of reaction by making specific reference to H_2O_2 .
- The remaining H_2O_2 is titrated against KMnO_4 , construct a balanced equation between the two reactants. Identify the oxidizing and reducing agent in this reaction.
- By drawing a suitable graph on the graph paper, determine the order of reaction with respect to H_2O_2 . Write the rate equation (rate law) for the decomposition of H_2O_2 and calculate the rate constant and half-life.
- Suggest other ways this reaction can be monitored continuously to determine order of reaction with respect to H_2O_2 .
- Calculate the concentration of the hydrogen peroxide at time $t = 0$. Hence estimate how long the solution had been in the contaminated bottle before it was analyzed by making use of the half-life determined in part (c).

- 19** The following reaction is monitored by measuring the increase in pressure with time as O_2 is collected into a vessel of 0.05 dm^3 using 100 cm^3 each of H_2O_2 and I_2 solution for reaction.



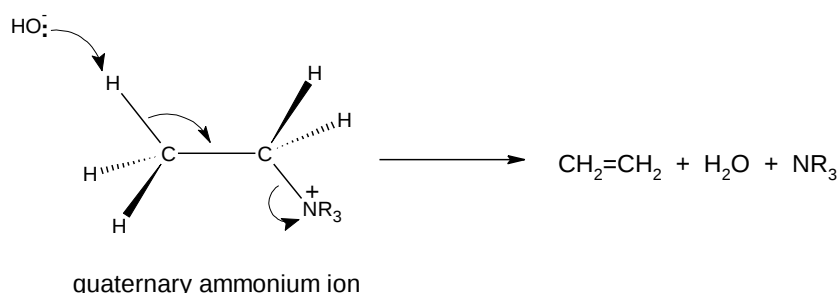
The starting concentration of H_2O_2 and I_2 are 1.0 mol dm^{-3} and $0.005 \text{ mol dm}^{-3}$ respectively.

Time / s	0	30	60	90	120	150	180
$[\text{O}_2] / \text{mol dm}^{-3}$	0	0.003	0.006	0.0075	0.0084	0.0089	0.0094

- (a) Determine the concentration of oxygen produced at time infinity.
- (b) With the aid of a suitable graph, determine the order with respect to iodine.
- (c) Suggest how the above experiment can be modified so that the order with respect to H_2O_2 can be determined. Your answer should also include details of how the order with respect to H_2O_2 can be deduced from the data collected.

Section B4.3: Graphical Method – Combined Method

- 20** Quaternary ammonium ions can undergo Hofmann elimination in a single step mechanism as shown.



The following concentrations of OH^- and $\text{CH}_3\text{CH}_2\text{NR}_3^+$ were used in *Experiment 1* and the half-life was found to be 10 s.

$$[\text{OH}^-] = 0.001 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{CH}_2\text{NR}_3^+] = 0.100 \text{ mol dm}^{-3}$$

What will be the half-life when the experiment is repeated with the following changes in concentrations?

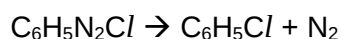
	Half-life for <i>Experiment 2</i> when $[\text{OH}^-]$ is doubled	Half-life for <i>Experiment 3</i> when $[\text{CH}_3\text{CH}_2\text{NR}_3^+]$ is doubled
A	10 s	10 s
B	10 s	5 s
C	5 s	10 s
D	5 s	5 s

Section C: First order reaction- Half life of reaction

- 21** Lead is the final product formed by a series of changes in which the rate-determining stage is the radioactive decay of uranium-238. This radioactive decay is a first order reaction with a half-life of 4.5×10^9 years.

What would be the age of the rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1:7?

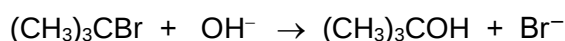
- 22** The decomposition of benzene diazonium chloride is a first order reaction which proceeds according to the equation:



A solution gave 80 cm^3 of N_2 on complete decomposition and it took 40 minutes for 40 cm^3 of N_2 to be evolved. How long would it take for 70 cm^3 of N_2 to be evolved?

- A** 20 min **B** 60 min **C** 80 min **D** 120 min

- 23** 2.0 mol dm^{-3} of 2-bromo-2-methylpropane was reacted with an excess of hot aqueous sodium hydroxide. The following results were obtained.



Time/min	0	15	40	80	∞
$[(\text{CH}_3)_3\text{COH}] / \text{mol dm}^{-3}$	0	0.5	1.0	1.5	2.0

What is the value of the rate constant?

- A** 8.66×10^{-3} **B** 1.73×10^{-2} **C** 2.77×10^{-2} **D** 4.62×10^{-2}