RAFFLES INSTITUTION
YEAR 5 H2 CHEMISTRY 2022
Lecture Notes 6: 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 rate = $k[A]^m[B]^n$ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including:

- **(i)** deducing the order of a reaction by the initial rates method
- **(ii)** justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs
- **(iii)** verifying that a suggested reaction mechanism is consistent with the observed kinetics
- **(iv)** predicting the order that would result from a given reaction mechanism
- **(v)** calculating an initial rate using concentration data

[Integrated forms of rate equations are **not** required]

(c) **(i)** show understanding that the half-life of a first-order reaction is independent of concentration
- **(ii)** use the half-life of a first-order reaction in calculations

(d) calculate a rate constant using the initial rates method

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

(f) explain qualitatively, in terms of frequency of collisions, the effect of concentration changes on the rate of a reaction

(g) show understanding, including reference to the Boltzmann distribution, of what is meant by the term *activation energy*

(h) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction

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

(j) outline the different modes of action of homogeneous and heterogeneous catalysis including:

- **(i)** the Haber process
- **(ii)** the catalytic removal of oxides of nitrogen in the exhaust gases from car engines
- **(iii)** the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide
- **(iv)** catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

(k) describe enzymes as biological catalysts which may have specific activity

(l) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

Lecture Outline

1 Introduction
2 Experimental techniques
3 Factors affecting the rate of a reaction
4 The rate equation and its components
5 More on rate equations
6 Finding the order of reaction
7 Reaction mechanism
8 Explanations of reaction rate
9 Catalysis
10 Enzymes

References

- http://www.chemguide.co.uk/
- A-Level Chemistry (Ramsden)
- A-Level Study Guide Chemistry (CS Toh)
- Chemistry in Context (Hill & Holman)
- Chemistry: The Molecular Nature of Matter and Change (Silberberg)

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Introduction

1.1 Reaction Kinetics

- From lecture 5, we learnt that ΔH provides information with regards to the amount of energy absorbed or released by the reaction system. It does not indicate how fast a reaction takes place. The rate of a chemical reaction can only be obtained by experiment. This area of study is known as **Reaction Kinetics**.
- **Reaction kinetics** is the study of the rates of chemical reactions, which include the factors that affect them. Knowing the effect of reactant concentrations on the reaction rate allows us to write a rate equation, from which we can obtain information about the mechanism of the reaction.
- There are five overarching questions that need to be answered in order to guide your understanding:
  1. What is the definition of *rate of reaction*?
  2. How is the rate of a reaction determined experimentally?
  3. What are the factors affecting the rate of a reaction?
  4. What is the relationship between rate and these factors?
  5. How does knowledge of this relationship provide information about how the reaction proceeds?

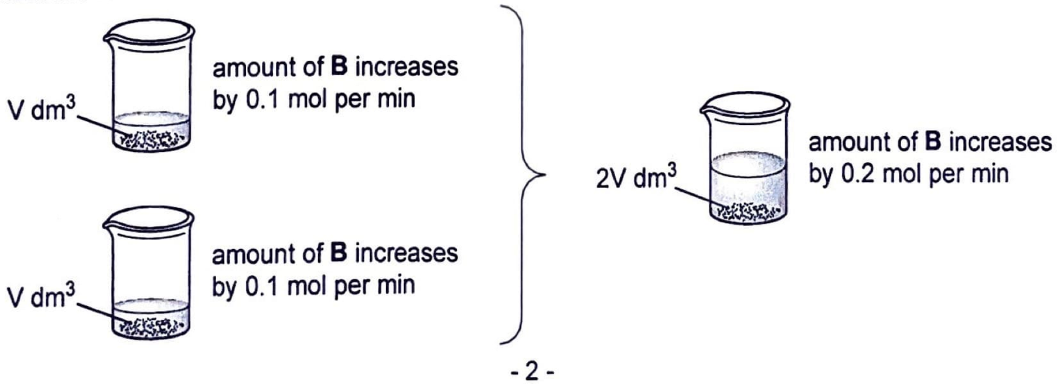
1.2 Understanding "Rate"

- When we talk about "rate", what comes to mind? We intuitively understand it as the speed at which something is happening. We observe *how a quantity changes with time.* If the change is large over a short period of time, we say it is "fast", and vice versa. The table on the right shows some examples of rates that we see in our daily lives.

type of rate	quantity that changes with time
speed of a car	distance moved
flowrate of a tap	volume of water
typing speed	number of characters typed

- The rate of a reaction must thus be quantified by observing some physical quantity that changes with time.
- Let us think about a reaction (**A** ⟶ **B**) that is happening in an aqueous solution of fixed volume of V dm^3. As the reaction proceeds, the amount of **A** decreases while the amount of **B** increases. Thus, it might seem like a good idea to observe how amount of **A** or **B** changes with time to obtain the rate of reaction.

  Let us now consider the same reaction but using twice the quantities. This can be thought of as having two of the initial reaction setup but with both carried out simultaneously. It is clear that now the change in amount of **B** is doubled. However, the rate of reaction should remain the same because all conditions remained the same. Therefore, observing **how the amount of a reactant/product changes with time does not truly reflect the rate of reaction.**



1.3 Rate of Reaction

> Overarching Question 1
>
> What is the definition of *rate of reaction*?

- The **rate of reaction** can be defined as the change in concentration of a particular reactant or product per unit time, i.e.

rate of reaction = $\dfrac{\text{change in concentration of a reactant or product}}{\text{time taken}}$	
common units: **mol dm^{-3} s^{-1}**	Other possible units: mol dm^{-3} min^{-1} or mol dm^{-3} h^{-1}

- Consider a reaction: **A** $\longrightarrow$ **B**

  The rate of reaction is a positive quantity that expresses

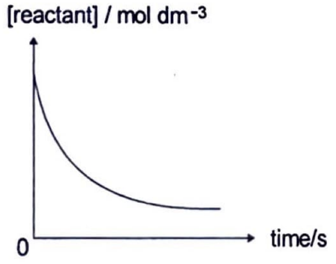
  - how the concentration of the reactant A decreases with time, or
  - how the concentration of the product B increases with time.

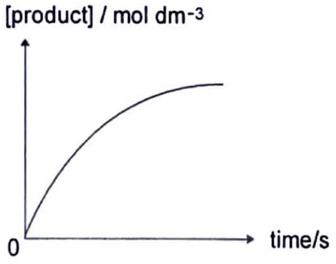
- As seen in the figure in Section 1.2, the change in amount of **B** over time is not the same but the change in concentration of **B** is the same. Hence, rate of reaction is defined using concentration, and not amount.

- **Note:** By convention, rate is a positive quantity.

1.4 Expressing Reaction Rates

- Reaction rates can be obtained from concentration-time graphs, which are obtained by monitoring [reactant] or [product] over time.





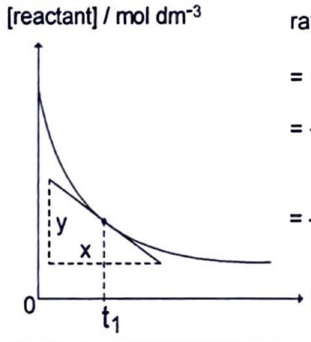
Note:

[X] = concentration of X

- The square brackets denote concentration which is expressed in mol dm^{-3}.

(a) Instantaneous rate

- The **instantaneous rate** is the rate at a particular time i.e. the rate at a particular instant during the reaction.

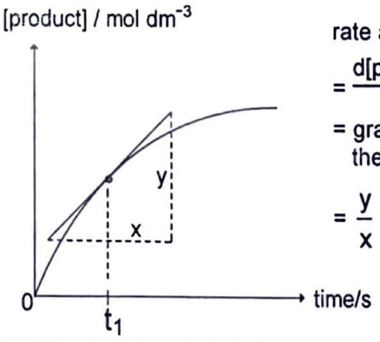


rate at time t_1

$= -\dfrac{d[\text{reactant}]}{dt}$

$=$ – gradient of tangent to the curve at *time t_1*

$= -\dfrac{y}{x}$



rate at time t_1

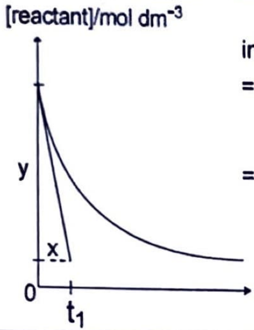
$= \dfrac{d[\text{product}]}{dt}$

$=$ gradient of tangent to the curve at *time t_1*

$= \dfrac{y}{x}$

(b) Initial rate

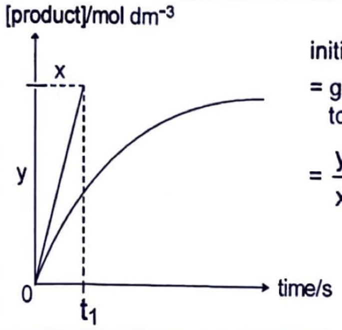
- The initial rate of a reaction is the <u>instantaneous rate at time t = 0</u>.
- It is the instantaneous rate at the start of the reaction, when an infinitesimally small amount of the reactant has been used up.



initial rate

= – gradient of tangent to the curve at *time 0 s*

$= -\frac{y}{x}$



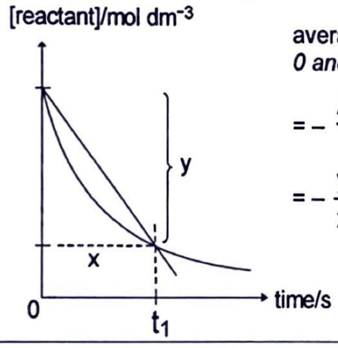
initial rate

= gradient of tangent to the curve at *time 0 s*

$= \frac{y}{x}$

(c) Average rate

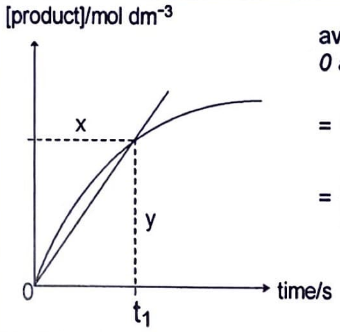
- The average rate of a reaction during a specified time interval is the change in concentration of a reactant or a product over that <u>time interval</u>.



average rate *between 0 and t$_1$ s*

$= -\frac{\Delta[\text{reactant}]}{\Delta t}$

$= -\frac{y}{x}$



average rate *between 0 and t$_1$ s*

$= \frac{\Delta[\text{product}]}{\Delta t}$

$= \frac{y}{x}$

- In practice, the initial rate can be approximated by the average rate provided

  1. the time interval (Δt) is small enough; and
  2. the time interval starts from t = 0.

- The smaller the time interval (Δt), the closer is the value of the average rate to the initial rate.

1.5 Relationship between the different rates of a reaction

- In general, for the following reaction: **aA + bB ⟶ cC + dD**

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

$$\text{rate of formation of D} = \frac{d[D]}{dt} = \left(\frac{d}{c}\right)\left(\frac{d[C]}{dt}\right)$$

- **Note:** The coefficients are to ensure that when we discuss the rate of a reaction, we get the same value for the rate of reaction regardless of which reactant's (or product's) concentration we are following.
  For example, for a reaction 2**A** ⟶ **B**, if **[A]** is decreasing at 0.2 mol dm^{-3} s^{-1}, then **[B]** is increasing at 0.1 mol dm^{-3} s^{-1}. Someone observing **[A]** would report a different value from another observing **[B]**. So for standardisation purposes, the coefficient is introduced to ensure the same value for the rate of reaction is obtained.

■■ Worked Example 1 ■■

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

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

The iodine produced can be detected by adding a little starch solution to the reaction mixture, since a blue colouration is obtained when the iodine concentration reaches 1.0 x 10^{-5} mol dm^{-3}. Suppose the time taken for the blue colouration to be observed is 80 s at 25 °C, calculate the following:

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

$$-\frac{1}{2}\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[SO_4^{2-}]}{\Delta t}$$

Solution

(a) rate of formation of $I_2(aq) = \frac{\Delta[I_2]}{\Delta t} = \frac{1.0\times10^{5}-0}{80-0}$ $= \underline{1.25 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}}$

(b) rate of consumption of $S_2O_8^{2-}(aq) = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$ $= \underline{1.25 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}}$

(c) rate of formation of $SO_4^{2-}(aq) = \frac{\Delta[SO_4^{2-}]}{\Delta t} = 2\frac{\Delta[I_2]}{\Delta t}$ $= \underline{2.50 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}}$

2 Experimental Techniques to Measure Reaction Rates

Overarching Question 2

How is the rate of a reaction determined experimentally?

- To determine the reaction rate, we need to be able to monitor the concentration of a reactant or product at various times as the reaction proceeds. There are many physical quantities we can monitor that will give us an indication of the concentration of a reactant or product in the reaction mixture. Some examples are listed in the table below.

For a reaction that involves...	**monitor...**
a reactant / product that is acidic/basic or oxidising/reducing	amount of reactant / product (Section 2.1.1) (most reactions take place in a fixed volume, so amount ∝ conc.) e.g., redox titration using $KMnO_4$ to monitor the amount of H_2O_2 left in reaction mixture
gas as product	volume of gas evolved (vol. of gas ∝ amount of gas) (Section 2.1.4) **OR** mass loss = mass of gas evolved (mass of gas ∝ amount of gas) (Section 2.1.5) **Note:** If we assume that the gas never escaped the solution, then the amount of gas ∝ "conc. of gas in solution".
coloured reactant / product	intensity of colour using colorimetry (colour intensity ∝ conc.) (Section 2.1.2)
change in total number of ions	electrical conductivity (electrical conductivity ∝ conc. of ions) (Section 2.1.3)
change in the number of moles of gas	change in pressure of gaseous system (Section 2.1.6)

- The choice of which reactant or product to monitor depends on which species in the reaction can be easily, yet accurately analysed.
- Generally, reaction rates can be determined either by using the Continuous method or the 'Clock' reaction.

	Continuous method	'Clock' reaction
Features	Monitor the concentration of a reactant or product species **continuously over time.** Concentration can be monitored by different methods, including: 1. Sampling and titration (Section 2.1.1) 2. Colorimetry (Section 2.1.2) 3. Electrical conductivity (Section 2.1.3)	Involve measuring the time taken for a stated change to occur. The species responsible for the stated change is the 'clock'.
Examples	1. Monitor how concentration of iodine produced changes with time using colorimetry 2. Monitor how [H_2O_2] changes with time using sampling and titration	Sulfur clock reaction (Section 2.2.1) • Time taken for "X" to be obscured by solid sulfur produced. Iodine clock reaction (Section 2.2.2) • Time taken for first appearance of blue-black starch-iodine complex
Things to note	The procedure for a typical sampling and titration consists of the following: 1. Start reaction. 2. Draw sample from reaction mixture. 3. Quench sample at appropriate time. 4. Use titration to determine concentration of species in quenched sample. For colorimetry and electrical conductivity, the measurements of colour intensity or electrical conductivity are monitored using instrumentation.	1. Identify the "clock" 2. If the clock is a reactant, then rate is proportional to $\frac{V_{clock}}{t}$; if the clock is a product, then rate is proportional to $\frac{1}{t}$. 3. Total volume of every experiment is the same. This allows $V_{reactant}$ to be directly proportional to [reactant]. This can be done by varying the $V_{reactant}$ while keeping the other volumes constant. Water is added to the reaction mixture to keep the total volume constant.

2.1 Continuous Method

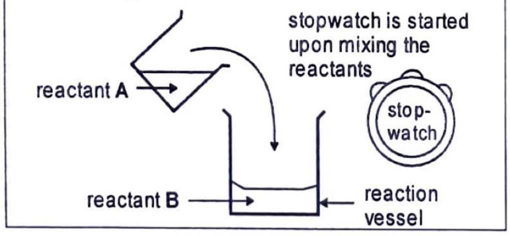
2.1.1 Sampling and Titration

1. Examples:

1. catalytic decomposition of $H_2O_2(aq)$ $\mathbf{H_2O_2(aq)} \longrightarrow H_2O(l) + ½O_2(g)$	• Titrate H_2O_2 left against a standard solution of acidified $KMnO_4$
2. acidic hydrolysis of an ester $RCOOR'(l) + H_2O(l) \xrightarrow[H^+]{} \mathbf{RCOOH(aq)} + R'OH(aq)$	• titrate RCOOH in reaction mixture against a standard solution of NaOH(aq)
3. acid-catalysed reaction of propanone with iodine $CH_3COCH_3(aq) + \mathbf{I_2(aq)} \xrightarrow[H^+]{} CH_3COCH_2I(aq) + HI(aq)$	• titrate I_2 left against a standard solution of $Na_2S_2O_3(aq)$

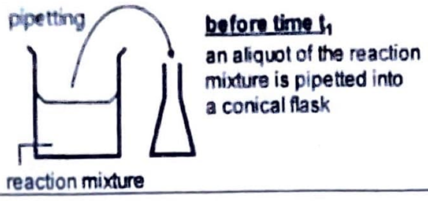
- General procedure

1. Starting the reaction

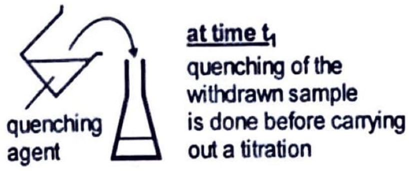


1. Mix the reactants and start a stopwatch simultaneously.

2. Sampling



3. Quenching

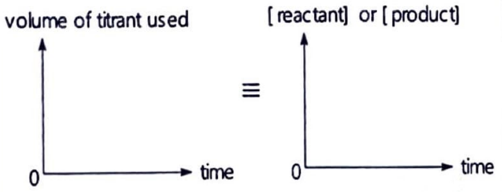


Then

4. Titration

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

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



2. **Sampling**
At a suitable time (e.g. before t_1), withdraw an aliquot portion (i.e. a fixed volume of the sample) from the reaction mixture into a conical flask by using a pipette.

3. **Quenching**
At time t_1, stop the reaction mixture in the withdrawn sample by either:
   - adding a large volume of ice-cold water (which dilutes and cools the mixture); or
   - adding an excess of a suitable quenching agent (which reacts immediately with one of the reactants or the catalyst).

   This ensures that the composition of the reaction mixture does not continue to change

4. **Titration**
Titrate the quenched sample to determine the concentration of either the reactant remaining (or the product formed) at the time t_1.

5. Repeat the sampling-quenching-titration steps at suitable time intervals.

6. Plot a graph of volume of titrant used (or [reactant] or [product]) against time.

7. Determine the instantaneous rate at any specified time by finding the gradient of the tangent drawn to the curve at that time (for [reactant] or [product] against time graph).

2.1.2 Measuring the colour intensity at regular time intervals

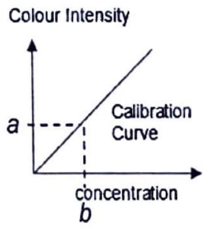
If one of the reactants or products of the reaction is coloured, this method can be used.
Note: The concentration of a coloured substance in a reaction mixture is directly proportional to its colour intensity.

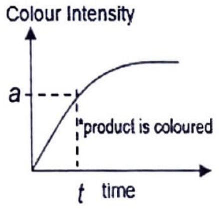
1. Prepare a calibration curve of colour intensity against known concentration of the coloured species. This can be done by preparing at least five solutions containing the coloured species, each with a different but known concentration. Then the colour intensity of these five solutions are measured with a colorimeter. The data is then be plotted to form a calibration curve.

2. Measure the colour intensity (or absorbance) of the reaction mixture at regular time intervals using a colorimeter (or a spectrophotometer).

3. The rate of the reaction can be determined from the change in colour intensity over a specified time.

4. Use the calibration curve to determine the concentrations of the coloured species in the reaction mixture at various time intervals (e.g. colour intensity *a* means concentration *b* at time *t*)

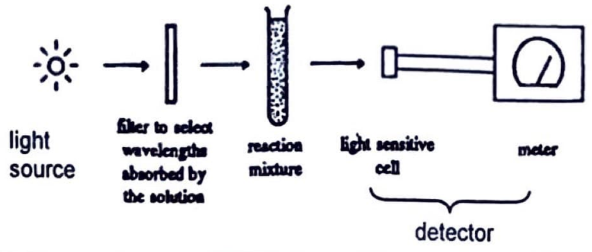




Examples of reaction in which the rate can be studied by colorimetric analysis:

1. oxidation of methanoic acid by aqueous bromine	$HCOOH(aq) + \underset{\text{orange}}{Br_2(aq)} \longrightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$
2. acid-catalysed reaction of propanone with iodine	$CH_3COCH_3(aq) + \underset{\text{brown}}{I_2(aq)} \xrightarrow{H^+} CH_3COCH_2I(aq) + HI(aq)$
3. oxidation of iodide ions by hydrogen peroxide in acidic medium	$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow 2H_2O(l) + \underset{\text{brown}}{I_2(aq)}$

Main components of a colorimeter

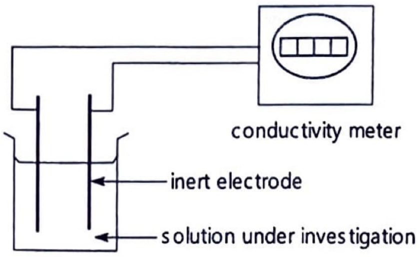


2.1.3 Measuring the electrical conductivity at regular time intervals

- A solution containing ions conducts electricity. The number and types of ions present in a solution affect its electrical conductivity.

- Many reactions in aqueous solution involve changes in the ions present as the reaction proceeds. Consequently, the electrical conductivity of the solution will change during the reaction. This can be used to determine the changing concentrations of reactants and products with time.

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



- A graph of electrical conductivity against time can be plotted.

Examples:

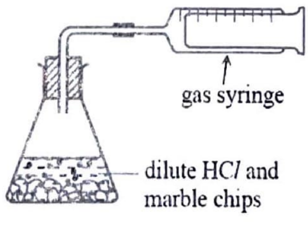
1. $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$
2. $CH_3CH_2COOCH_2CH_3(aq) + OH^-(aq) \longrightarrow CH_3CH_2COO^-(aq) + CH_3CH_2OH(aq)$

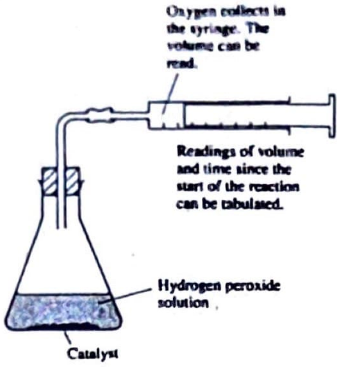
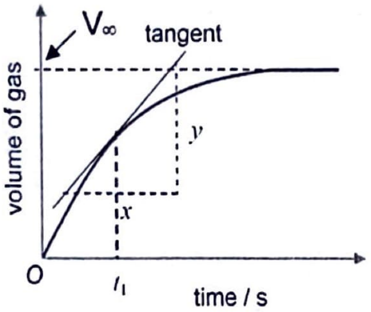
2.1.4 Measuring the volume of gas produced at regular time intervals

- In a reaction whereby a gas is produced, the progress of the reaction can be followed by measuring the volume of the gas evolved at suitable time intervals.

- The rate of the reaction is given by the change in the volume of the gas produced over a specified time interval.

Examples:

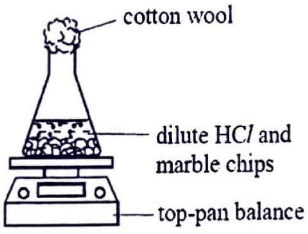
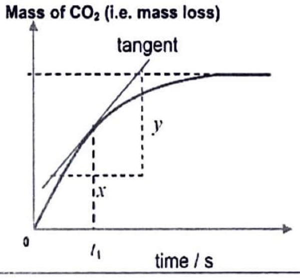
1. Reaction of $CaCO_3$ with hydrochloric acid	$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ 

2. Reaction of Mg with hydrochloric acid	$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$
3. Decomposition of hydrogen peroxide (in the presence of MnO_2 catalyst)   	$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$ $O_2(g)$ is collected in a graduated gas syringe and its volume measured at regular time intervals during the reaction. Graph of volume of O_2 against time Plot a graph of volume of $O_2(g)$ evolved against time. The rate of reaction at any instant is proportional to the gradient of the tangent to the curve at that instant. Graph of $(V_\infty - V_t)$ against time Alternatively, determine the values of $(V_\infty - V_t)$ and plot a graph of $(V_\infty - V_t)$ against time. Note: V_t = volume of $O_2(g)$ evolved at time t V_∞ = volume of $O_2(g)$ evolved at the end of the reaction $(V_\infty - V_t)$ = volume of $O_2(g)$ yet to be evolved at time t $(V_\infty - V_t) \propto [H_2O_2]$ remaining at time t A graph of $(V_\infty - V_t)$ against time is equivalent to a graph of $[H_2O_2]$ against time.

2.1.5 Measuring the mass of the reaction mixture at regular time intervals

In a reaction whereby a gas is produced and allowed to escape, the rate of the reaction can be followed by measuring the mass of the reaction mixture at regular time intervals.

Example:

Reaction of $CaCO_3$ with hydrochloric acid  A piece of cotton wool is placed at the mouth of the conical flask to prevent the loss of any reactant due to acid spray. The $CO_2(g)$ produced can still escape out of the conical flask. **Note:** This method cannot be used if the electronic balance cannot detect small changes in mass accurately.	$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ • The rate of this reaction can be studied by determining the mass of $CO_2(g)$ produced (i.e. mass loss) over time. • The initial mass of the conical flask and its contents, m_o, is determined and noted. • As the reaction progresses, the mass of the conical flask and its contents at various time intervals, m_t, is measured. • The mass loss i.e. $(m_o - m_t)$ at various time intervals can be determined and a graph of mass loss against time can be plotted. • The rate of reaction at any instant is proportional to the gradient of the tangent to the curve at that instant. 

2.1.6 Measuring the pressure at regular time intervals

- If a reaction involves a change in the number of moles of gas, the total pressure of the reaction mixture can be measured at regular time intervals.

- The partial pressure of the reactant or product under consideration at a specified time can then be calculated. The rate of the reaction can be determined from the change in partial pressure (at constant volume and temperature) of the reactant or product over time.

- Example: $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

2.2 'Clock' reaction (also known as Method of Initial Rates)

- Certain reactions are accompanied by prominent visual changes such as the forming of a precipitate or an obvious change in colour.
- The rate of reaction may be studied by measuring the time taken for a prescribed visual change to occur.
- Reactions that are studied this way are called 'clock' reactions. The species responsible for the stated change is the 'clock'.
- The determination of the initial rate involves measuring the change in concentration of one of the reactants or products over a short time interval after the reagents are mixed.

2.2.1 Reaction between thiosulfate ions and hydrogen ions

Reaction: $Na_2S_2O_3(aq) + 2HCl(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l) + 2NaCl(aq)$

or

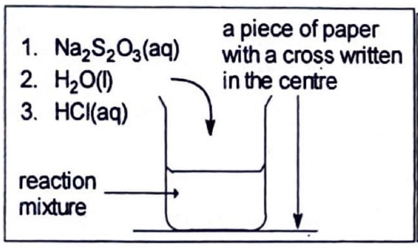
$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$

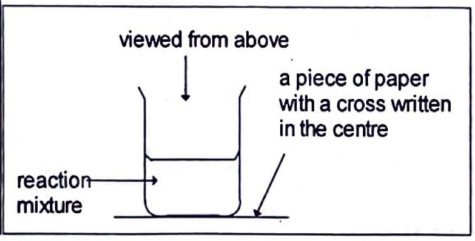
- When sodium thiosulfate reacts with an acid, a yellow precipitate of sulfur is formed to produce a colloidal suspension.

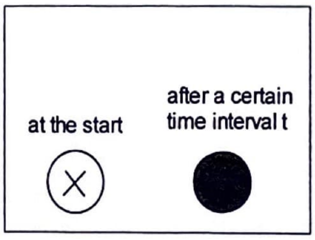
- The rate of the above reaction can be studied by a 'clock' reaction (or method of initial rates). In this case, the initial rate of the reaction is *approximated* by the average rate of the reaction.

- Procedure

  1. Add known volumes of $Na_2S_2O_3(aq)$ and $HCl(aq)$ into a beaker.
  2. Start the stopwatch simultaneously.
  3. Measure the time taken for a fixed amount of sulfur to form. This happens when a sufficient amount of sulfur is produced to obscure a "cross" drawn on a piece of white paper.
  4. Repeat steps 1 to 3 by using different volumes of the two solutions, making sure that the total volume of the reaction mixture is constant. This is done by adding water to the reaction mixture. The beaker used must also be the same.







- A hypothetical set of results is shown below.

Expt. No.	Volume of 1.00 mol dm^{-3} HCl(aq) used, V_1 / cm^3	Volume of 0.20 mol dm^{-3} $Na_2S_2O_3(aq)$ used, V_2 / cm^3	Volume of water used/cm^3	Time taken for the mark "X" to be obscured, t / s	Rate $\propto \frac{1}{t}$ / s^{-1}
1	30.0	40.0	0.0	16.0	0.0625
2	30.0	20.0	20.0	32.0	0.0313
3	40.0	30.0	0.0	20.0	0.0500
4	20.0	30.0	20.0	20.0	0.0500

- **Important questions to take note of**

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

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

Q2: If the total volume of the reaction mixture is constant, what is the relationship between the initial concentration of $Na_2S_2O_3$ in the reaction mixture and its volume used?

$$\text{initial } [Na_2S_2O_3] \text{ in the reaction mixture} = \frac{\text{amount of } Na_2S_2O_3 \text{ used}}{\text{total volume of the reaction mixture}}$$

$$= \frac{\left(\text{volume of } Na_2S_2O_3 \text{ used}\right)\left(\text{concentration of } Na_2S_2O_3 \text{ solution}\right)}{\text{total volume of the reaction mixture}}$$

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

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

initial $[Na_2S_2O_3] \propto$ volume of $Na_2S_2O_3$ used

initial $[S_2O_3^{2-}] \propto V_2$

Similarly, initial $[H^+] \propto V_1$

In general, the initial concentration of a reactant A in the reaction mixture is directly proportional to its volume used (i.e. $[A] \propto V_A$) if the total volume of the reaction mixture is kept constant for the different experiments.

Q3: Why must the same beaker be used in each experiment?

The same beaker (and also the same total volume) is used to ensure that the depth of the reaction mixture remains the same. This will ensure that the same amount of sulfur needs to be precipitated before the cross is obscured.

Q4: What is the relationship between the initial rate of reaction and the time t taken for the "cross" to be obscured?

In this experiment, the initial rate of formation of sulfur is approximated by the average rate of formation of sulfur since the time interval t is small and is measured from zero.

initial rate of formation of sulfur ≈ average rate of formation of sulfur (i.e. $\Delta[S]/\Delta t$)

Since total volume of reaction mixture is a constant, $\Delta[S] \propto \Delta(\text{amount of sulfur})$

$$\text{Therefore, initial rate of reaction} \propto \frac{\Delta(\text{amount of sulfur})}{\Delta t} = \frac{x-0}{t-0} = \frac{x}{t}$$

where
x = amount of sulfur formed to obscure the "cross"
t = time taken for the "cross" to be obscured by sulfur

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

- same "cross" is used
- same beaker and same total volume (and hence same depth of solution) is used

$$\text{Hence initial rate of reaction} \propto \frac{1}{t} \quad \text{BUT initial rate of reaction} \neq \frac{1}{t}$$

2.2.2 Reaction between hydrogen peroxide and iodide ions in acidic medium

Reaction: $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$

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

  Reaction (1): $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow \underline{I_2(aq)} + 2H_2O(l)$

  Reaction (2): $2S_2O_3^{2-}(aq) + \underline{I_2(aq)} \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

- Since reaction (2) is relatively faster than reaction (1), the concentration of iodine in the reaction mixture will remain effectively zero so long as there are still some $S_2O_3^{2-}$ ions in the mixture.

- At the point when the small amount of $Na_2S_2O_3$ is completely used up, reaction (2) stops but reaction (1) continues. The free iodine produced from reaction (1) will be present in the solution. This will cause a sudden appearance of a blue-black colour characteristic of the starch-iodine complex if starch is present.

- The volume and hence amount of $Na_2S_2O_3$ was kept constant for each experiment to ensure that the amount of iodine produced before the appearance of the blue-black colour (i.e. the amount of iodine which had reacted with the thiosulfate ions) was constant for all the experiments.

- Procedure
  1. Add a small fixed amount of $Na_2S_2O_3$ and known volumes of H_2O_2, I^- and H^+ into a beaker.
  2. Start the stopwatch simultaneously.
  3. Measure the time taken for the blue-black colour to appear. This happens when the $Na_2S_2O_3$ is completely used up and the I_2 produced in reaction (1) is present in the reaction mixture.
  4. Repeat steps 1 to 3 by using the same small fixed amount of $Na_2S_2O_3$ but different volumes of H_2O_2, I^- and H^+, making sure that the total volume of the reaction mixture is constant. This is done by adding water to the reaction mixture.

- A set of results is shown here

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

Try answering the following questions using information from Section 2.2.1.

- How was the rate measured?
- Why should the total volume be kept constant?
- What is the relationship between the initial [reactant] and its volume used?
- What is the relationship between the initial rate and time t?
- What is the order of adding the solutions that make up the reaction mixture?

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

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

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

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

Since t is small and measured from zero,
initial rate ≈ average rate of formation of iodine from 0 to t

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

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

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

$$\text{initial rate} = \frac{x}{t}$$

Since x was kept constant, initial rate $\propto \frac{1}{t}$

3 Factors Affecting the Rate of a Reaction

<u>Overarching Question 3:</u>
What are the factors affecting the rate of a reaction?

Studies have indicated several factors which can influence the rate of a reaction. These factors include:

1 physical state of the reactants
2 concentration of the reactants
3 temperature
4 catalyst

3.1 Physical states of the reactants

- Reactant particles must mix in order to collide and react. Thus, the frequency of collisions between reactant particles also depends on the physical states of the reactants.

(a) Are the reactants in solution or in solid form?

(1) $NaCl(s) + AgNO_3(s) \longrightarrow$ *no reaction*

(2) $NaCl(aq) + AgNO_3(aq) \longrightarrow NaNO_3(aq) + AgCl(s)$ *immediate reaction*

(b) Are the reactants in solution molecules or ions?

(1) $CH_3CH_2Cl(aq) + NaOH(aq) \longrightarrow CH_3CH_2OH(aq) + NaCl(aq)$ *slow, requires heating*

(2) $HCl(aq) + NaOH(aq) \longrightarrow H_2O(l) + NaCl(aq)$ *immediate reaction*

The activation energy of reaction (1) is high as it involves cleavage of the C–C*l* bond. Hence, heating is required to increase the temperature of the reaction mixture so that more reactant particles can have energy greater than or equal to the activation energy of the reaction to increase the rate of reaction. Refer to Section 8.3(c).	The activation energy of reaction (2) is low as no covalent bonds are broken. NaOH is a strong base while HC*l* is a strong acid. Both NaOH(aq) and HC*l*(aq) dissociate completely to give OH^- and H^+ ions in aqueous solution. These oppositely charged ions would have a natural tendency to attract each other to form H_2O. Hence, the reaction occurs readily at room temperature.

(c) Are the reactants in solid form of a finely divided state?

(1) $CaCO_3$ (marble chips) + $2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ *slower*

(2) $CaCO_3$ (powder) + $2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ *faster*

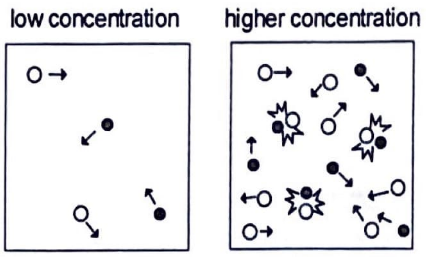
- The rate of a reaction involving a solid is affected by the available surface area of the solid.
- Reactions involving a solid take place faster when the solid is in a finely divided state.
- The more finely divided a solid reactant, the greater its surface area per unit volume, the more contact it makes with the other reactant, and the faster the reaction occurs.

3.2 Concentration of the reactants

In general, the rate of a reaction increases as the concentration of a reactant is increased (except for reactions which are *zero order with respect to the reactant* → refer to Section 5.4)

(a) Concentration and the Collision Theory

- Based on the collision theory (Section 8.1), the reactant particles must collide to react.
- As the concentration of a reactant increases, the reactant particles come closer together.
- Hence the frequency of collisions increases.
- As frequency of collisions increases, the probability of a collision having the correct collision geometry and sufficient energy for a reaction to occur must also increase.
- Hence the frequency of effective collisions increases leading to an increase in reaction rate.



When particles are closer together, they have a greater chance of reacting.

(b) Partial pressures of gaseous reactants

- Since pressure has a negligible effect on the volumes of solids and liquids, it affects only those reactions in which gases are involved.
- The partial pressure of a gas is a measure of its concentration. An increase of pressure on a gaseous system is equivalent to an increase in the concentration of the reactants.
- It follows that the rate of a reaction is greater at higher pressures because the reactant particles come closer together leading to higher frequency of effective collisions.

Note:

$pV = nRT$

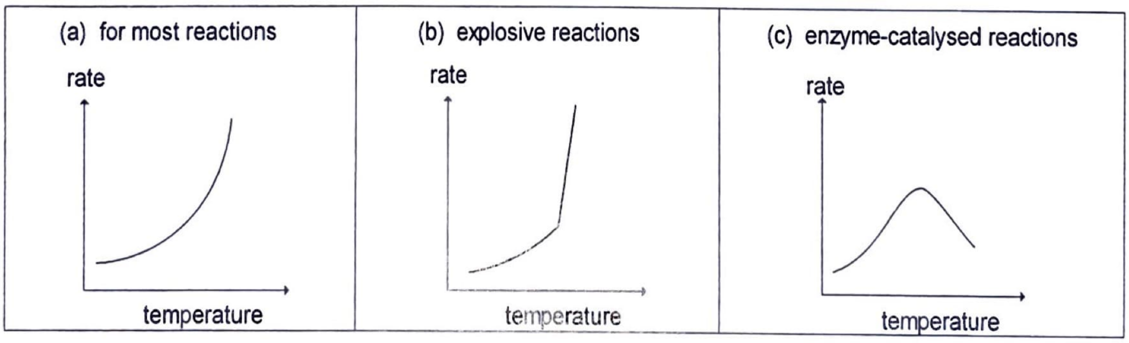
$\Rightarrow p = \frac{n}{V}RT = cRT$

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

where c = concentration $= \frac{n}{V}$

3.3 Temperature

(a) Graphs of reaction rate against temperature for different types of reactions



(b) Effect of temperature on reaction rate

- In general, increasing the temperature increases the rate of a reaction significantly.
- For many reactions, the rate is approximately doubled (i.e. increases by 100%) for every 10 K rise in temperature. Refer to Section 8.3(c) for an explanation.

3.4 Catalyst

A catalyst is a substance which increases the rate of a reaction by providing an *alternative reaction pathway with lower activation energy*, without itself undergoing any permanent chemical change. Refer to Section 8.3(c) for an explanation. (Note: It is **incorrect** to say that "a catalyst lowers the activation energy of a reaction".)

4 The Rate Equation and its Components

Overarching Question 4:

What is the relationship between rate and these factors, e.g. reactant concentrations?

Now that you have learnt how to determine the rate of a reaction experimentally and the factors that affect rate, it is timely to explore further the relationship between rate and reactant concentrations. This relationship can be expressed in the form of an experimentally determined rate equation.

4.1 Relating Rate and Reactant Concentrations

- Consider a reaction represented by the following equation: $aA + bB \longrightarrow$ products
- Experimentally, it can be shown that the rate of the reaction can be related to the concentrations of individual reactants by an equation of the form:

$$\boxed{\textbf{rate} = k\,[A]^m\,[B]^n}$$

[A] = concentration of reactant A in mol dm^{-3}
[B] = concentration of reactant B in mol dm^{-3}
k = rate constant
m = order of reaction with respect to reactant A
n = order of reaction with respect to reactant B
m + n = overall order of reaction

- The above expression is known as the rate equation (or rate law).

4.2 Definitions of the basic terms in the rate equation

rate equation	• The rate equation for a reaction is a mathematical expression that relates the rate of reaction to the concentration of each reactant raised to the appropriate power. It shows the exact dependence of the reaction rate on the concentrations of all the reactants. • The rate equation - can only be obtained by experiment, - cannot be deduced either theoretically or from the stoichiometric equation, - may not include all of the reactants written in the chemical equation.
rate constant	• The rate constant of a reaction is the constant of proportionality in the rate equation of the reaction. Example: rate $\propto [A]^m$ rate $= k\,[A]^m$ • The symbol for the rate constant is k. • Its units depend on the overall order of the reaction. • The larger the rate constant, the faster the reaction. • k is constant for a given reaction at a particular temperature. k increases with increasing temperature or in the presence of a catalyst, as shown by the Arrhenius equation.

	Arrhenius equation: $k = A\,e^{-\frac{E_a}{RT}}$ where A = Arrhenius constant or pre-exponential factor E_a = activation energy R = molar gas constant T = temperature in K Note: When temperature (T) increases and/or activation energy (E_a) decreases, rate constant, k increases.
order of reaction with respect to a reactant	• The <u>order of reaction with respect to a given reactant</u> is the power to which the concentration of that reactant is raised in the rate equation. Example: rate = k $[B]^2$ ⇒ Order of reaction with respect to reactant B = 2 • It shows the exact dependence of rate on the concentration of a given reactant. • It must be found experimentally. • It can be a whole number or a fraction; positive or negative.
overall order of a reaction	• The <u>overall order of a reaction</u> is the sum of the powers of the concentration terms in the rate equation. Example: rate = k [P] $[Q]^2$ Overall order of reaction = 1 + 2 = 3

4.3 Interpretation of the Rate Equation

Consider the following reaction: **A + B ⟶ C + D**, in which

The rate equation is given by: rate = k $[A]^m [B]^n$ and the units of rate are mol dm^{-3} s^{-1}.

m	n	Rate equation	Units of k	Remarks
0	0	rate = k	mol dm^{-3} s^{-1}	• The reaction is a <u>zero-order reaction</u>. • Order of reaction with respect to A = 0 • Order of reaction with respect to B = 0 • The reaction rate is independent of [A] and [B], i.e. changing [A] and/or [B] does not affect the reaction rate.
1	0	rate = k [A]	s^{-1}	• The reaction is a <u>first-order reaction</u>. • The reaction is first order with respect to A and zero order with respect to B. • Note: rate ∝ [A]. If [A] is doubled, rate is doubled.
1	1	rate = k [A] [B]	mol^{-1} dm^3 s^{-1}	• The reaction is a <u>second-order reaction</u>. • The reaction is first order with respect to A and first order with respect to B. • Note: rate ∝ [A] [B] If [A] is doubled, rate is doubled. If [B] is doubled, rate is doubled. If both [A] and [B] are doubled, rate is quadrupled.
0	2	rate = k $[B]^2$	mol^{-1} dm^3 s^{-1}	• The reaction is a <u>second-order reaction</u>. • The reaction is zero order with respect to A and second order with respect to B. • Note: rate ∝ $[B]^2$ If [B] is doubled, rate is quadrupled.

■■ Worked Example 2 ■■

The rate equation for the reaction, $S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$ is

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

Which of the following conclusions can be drawn from this information?

A The units of k are $mol^{-2}\,dm^6\,s^{-1}$.
B The reaction is second order overall.
C The value of k depends on the concentrations of $S_2O_8^{2-}$ and I^- ions.
D The reaction is second order with respect to I^- ion.

B

■■ Worked Example 3 ■■

The reaction between bromine and methanoic acid is first order with respect both to bromine and to methanoic acid.

$$Br_2(aq) + HCOOH(aq) \longrightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

Which of the following can be correctly deduced from this information?

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

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

D

5 More on Rate Equations

Repeating overarching Question 4:

What is the relationship between rate and these factors, e.g. reactant concentrations?

From Section 4.3, we learnt that rate depends on the order with respect to the various reactants. Given experimental results, how then do we determine the order with respect to each reactant?

5.1 Half-life of a reaction

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

5.2 First-order reactions

- Consider the following first-order reaction: $A \longrightarrow \text{product}$
- rate $\propto$ [A]

The rate equation is: $\boxed{\textbf{rate} = \textbf{k [A]}}$ where k is the rate constant

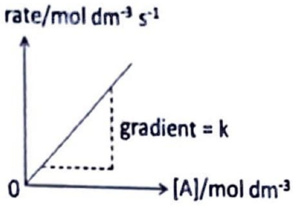
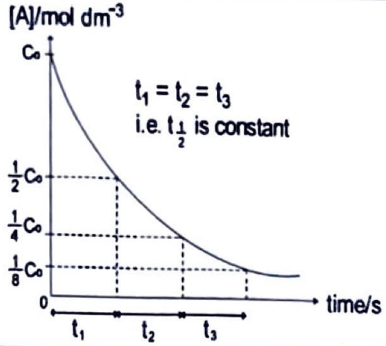
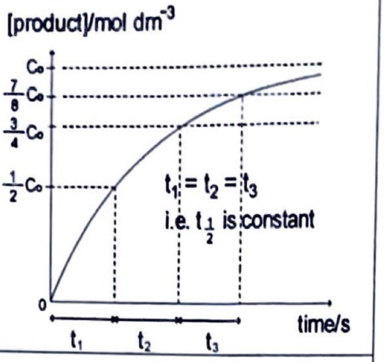
- Units of k: **s^{-1}** (or min^{-1} or h^{-1})

- For a first-order reaction, the half-life is given by:

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

- For a first-order reaction,
  - **$t_{1/2}$** is <u>constant</u> at constant temperature
  - **$t_{1/2}$** is independent of the initial concentration of the reactant.
- For all other orders of reaction, the half-life is <u>not</u> constant. It changes throughout the reaction.

- The graphs associated with the first-order reaction are shown below.

rate against [reactant]	**[reactant] against time**	**[product] against time**
		
• The graph obtained is a straight line which passes through the origin and has a positive gradient (equal to the rate constant, k) $\Rightarrow$ **rate $\propto$ [A]** • Hence the reaction is first order with respect A.	From the graph, 1st $t_{1/2}$ = time taken for [reactant] to decrease from **<u>C_o to ½C_o</u>** = t_1 2nd $t_{1/2}$ = time taken for [reactant] to decrease from **<u>½C_o to ¼C_o</u>** = t_2 • Since $t_1 = t_2$, **$t_{1/2}$ is constant.** • Hence, the reaction is first order with respect to A.	From the graph, 1st $t_{1/2}$ = time taken for [product] to increase from **<u>0 to ½C_o</u>** = t_1 2nd $t_{1/2}$ = time taken for [product] to Increase from **<u>½C_o to ¾C_o</u>** = t_2 • Since $t_1 = t_2$, **$t_{1/2}$ is constant.** • Hence, the reaction is first order with respect to A. Note: C_o is the theoretical maximum [product] for the reaction, based on stoichiometry.

■■ Worked Example 4 ■■

The decay of radioactive isotopes follows first-order kinetics. If the rate of decay of a radioactive isotope decreases from 200 counts per minute to 25 counts per minute after 24 hours, calculate

(a) its half-life
(b) the rate constant and state its units.

<u>Solution</u>

$$200 \xrightarrow{1^{st}\ t_{1/2}} 100 \xrightarrow{2^{nd}\ t_{1/2}} 50 \xrightarrow{3^{rd}\ t_{1/2}} 25$$

(a) $24h = 3t_{\frac{1}{2}}$

$t_{\frac{1}{2}} = 8h$

(b) $t_{\frac{1}{2}} = \frac{\ln 2}{k}$

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

$k = \frac{\ln 2}{8}$

$= 0.0866\ h^{-1}$

■■ Worked Example 5 ■■

A radioactive element has two isotopes, **P** and **Q**, with half-lives of 5 min and 15 min respectively. An experiment starts with 4 times as many atoms of **P** as of **Q**.

Radioactive decay is a first-order reaction. How long will it be before the number of atoms of **P** left equals the number of atoms of **Q**?

<u>Solution</u>

P $4x \xrightarrow{5min} 2x \xrightarrow{5min} x \xrightarrow{5min} \frac{1}{2}x$

<u>15 minutes</u>

Q $x \xrightarrow{15min} \frac{1}{2}x$

■■ Worked Example 6 ■■

> Consider the following first-order reaction: $X \longrightarrow Y$
> The half-life of the reaction is 30 minutes.
>
> (a) Calculate the time taken for the initial concentration of X to decrease to 1/8 of its value.
> (b) Calculate the fraction of X which remains after 100 min.

Note

Let C_o = initial [X] and C = [X] at time t

$$C_o \xrightarrow{t_{1/2}} \tfrac{1}{2} C_o \xrightarrow{t_{1/2}} \tfrac{1}{4} C_o \xrightarrow{t_{1/2}} 1/8\ C_o \dashrightarrow\dashrightarrow (\tfrac{1}{2})^n C_o$$

$$C_o \longrightarrow \tfrac{1}{2} C_o \longrightarrow (\tfrac{1}{2})^2 C_o \longrightarrow (\tfrac{1}{2})^3 C_o \dashrightarrow\dashrightarrow (\tfrac{1}{2})^n C_o$$

time taken, $t = 3\ t_{1/2}$	$C = (\tfrac{1}{2})^3 C_o$	$\frac{C}{C_o} = (\tfrac{1}{2})^3$

time taken, $t = n\ t_{1/2}$	**$C = (\tfrac{1}{2})^n C_o$**	$\frac{C}{C_o} = (\tfrac{1}{2})^n$

where **$n = t / t_{1/2}$ = number of $t_{1/2}$**

Solution

(a) $(\tfrac{1}{2})^n = 1/8 = (\tfrac{1}{2})^3$

$n = 3$

$\therefore$ time taken = (3)(30) = **90 min**

(b) $n = t/t_{1/2} = 100/30 = 10/3$

$$\frac{C}{C_o} = (\tfrac{1}{2})^n = (\tfrac{1}{2})^{10/3} = 0.0992$$

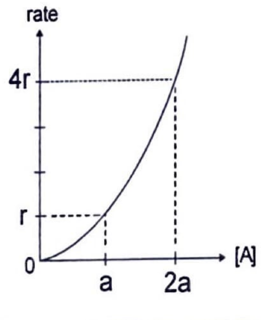
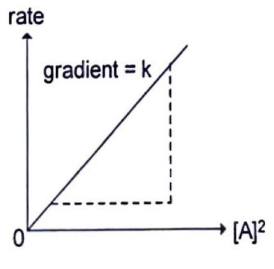
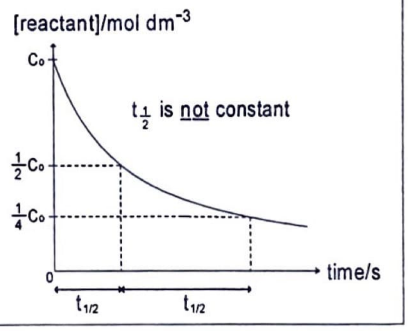
$\therefore$ fraction of X = **0.0992**

5.3 Second-order reactions

- Consider the following second-order reaction: $2A \longrightarrow$ products
- rate $\propto [A]^2$

The rate equation is: $\boxed{\textbf{rate} = k\,[A]^2}$ where k is the rate constant

- Units of k: **$mol^{-1}\ dm^3\ s^{-1}$** (or $mol^{-1}\ dm^3\ min^{-1}$ or $mol^{-1}\ dm^3\ h^{-1}$)
- The graphs associated with such a second-order reaction are shown below.

rate against [reactant]	**rate against [reactant]²**	**[reactant] against time**
		

- For a second-order reaction, the half-life of the reaction is not constant.

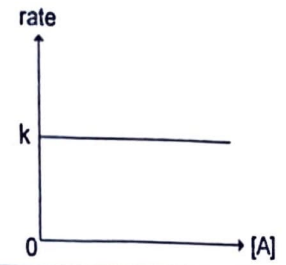
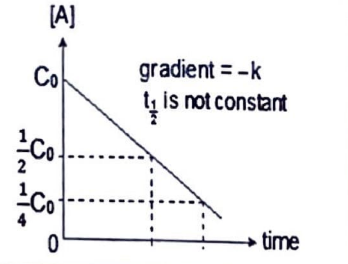
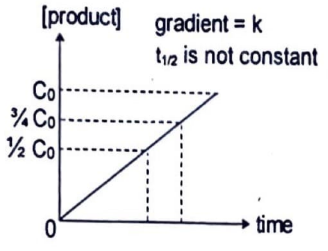
5.4 Zero-order reactions

- Consider a zero-order reaction: A $\longrightarrow$ products
- The reaction rate is independent of the concentration of the reactant, i.e. the rate is unaffected by changes in the concentration of the reactant.

The rate equation is: $\boxed{\textbf{rate = k}}$ where k is the rate constant

- Units of k: **mol dm^{-3} s^{-1}** (or mol dm^{-3} min^{-1} or mol dm^{-3} h^{-1})

- The graphs associated with a zero-order reaction are shown below.

rate against [reactant]	**[reactant] against time**	**[product] against time**
		

5.5 Pseudo-order Reactions

- There are three situations to consider.

(a) Presence of a large excess of a reactant

- Consider the following reaction: $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$

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

- Consider a reaction: aA + bB $\longrightarrow$ cC + dD

  The rate equation is: rate = $k[A]^m[B]^n$,
- If B is present in large excess i.e. initial [B] >> initial [A], then rate = $k'[A]^m$, where $k' = k[B]^n$.
- The reaction actually has an overall order of m+n but appears to have an order of m in this case. The reaction is said to be a pseudo-mth-order reaction in this case.

(b) Reactant is also the solvent

Consider the hydrolysis of ethyl ethanoate in water.

$CH_3COOCH_2CH_3 + H_2O \longrightarrow CH_3COOH + CH_3CH_2OH$

The rate equation is: rate = k [$CH_3COOCH_2CH_3$] [H_2O]

- As water is used as the solvent in this reaction (and hence present in a large excess), its concentration remains essentially constant throughout the reaction.
- Hence the rate equation can be modified as: rate = k' [$CH_3COOCH_2CH_3$] where k' = k [H_2O]

(c) Presence of a catalyst

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

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

- Experimentally, the rate equation is found to be: rate = k [HCl] [sucrose]
- In this case, HCl is a catalyst. It increases the rate of the reaction but is not consumed by the reaction. It participates in the reaction but is regenerated. Consequently the [HCl] can be regarded as essentially constant during the reaction i.e. [HCl] = constant.
- Hence the rate equation can be modified as: rate = k' [sucrose] where k' = k [HCl] = constant

6 Finding the Order of a Reaction

6.1 Finding order of reaction from initial rates data

- The order of a reaction with respect to a reactant can be found by comparing the initial rates of the reaction at different known initial concentrations.
- There are two approaches to comparing initial rates: (1) by inspection method and (2) by calculation.

■■ Worked Example 7 ■■ **(By Inspection Method)**

For the reaction X + Y ⟶ Z, the following experimental results were obtained:

Experiment	Initial [X] / mol dm^{-3}	Initial [Y] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.01	0.01	1.0×10^{-4}
2	0.01	0.02	2.0×10^{-4}
3	0.02	0.02	8.0×10^{-4}

(a) Determine the order of reaction with respect to each reactant.

(b) Write down the rate equation for the reaction and state the overall order of reaction.

(c) Using data from experiment 1, calculate the value of the rate constant, k, and determine its units.

■■ Worked Example 8 ■■ **(By Calculation)**

For the reaction P + Q ⟶ R, the following experimental results were obtained:

Experiment	Initial [P] / mol dm^{-3}	Initial [Q] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.01	0.01	0.01
2	0.02	0.02	0.04
3	0.04	0.08	0.32

Find the order of reaction with respect to each reactant and hence write down the rate equation.

Solution

(a) Compare experiments 1 and 2.
When initial [X] is the same and initial [Y] x 2, initial rate x 2.
$\Rightarrow$ rate $\propto$ [Y]
$\therefore$ order of reaction with respect to Y is 1.

Compare experiments 2 and 3.
When initial [Y] is the same and initial [X] x2, initial rate x4
$\Rightarrow$ rate $\propto [X]^2$
$\therefore$ order of reaction with respect to X is 2.

(b) The rate equation is: rate = k[X^2][Y]

where k is the rate constant

Overall order of reaction = 1+2 = 3

(c) $k = \dfrac{\text{rate}}{[X]^2\,[Y]}$

Using the data from experiment 1,

$k = \dfrac{1.0\times10^{-4}}{(0.01)^2\,(0.01)}$ = **$100\ \text{mol}^{-2}\ \text{dm}^{6}\ \text{s}^{-1}$**

Solution

Let the rate equation be: rate = k $[P]^m\,[Q]^n$ where k is the rate constant.

$$\frac{\text{rate of expt. 2}}{\text{rate of expt. 1}} = \frac{k(0.02)^m(0.02)^n}{k(0.01)^m(0.01)^n} = \frac{0.04}{0.01}$$

$\Rightarrow \quad (2)^{m+n} = 4 = 2^2$

$\Rightarrow \quad m + n = 2$ .... (1)

$$\frac{\text{rate of expt. 3}}{\text{rate of expt. 1}} = \boxed{\frac{k(0.04)^m(0.08)^n}{k(0.01)^m(0.08)^n} = \frac{0.32}{0.01}}$$

$\Rightarrow \quad (2)^{2m+3n} = 2^5$

$\Rightarrow \quad 2m + 3n = 5$ .... (2)

(1) x 2 $\Rightarrow$ 2m + 2n = 4 ...... (3)
(2) – (3) $\Rightarrow$ n = 1
From (1), m = 2 – 1 = 1

Order of reaction with respect to P = 1
Order of reaction with respect to Q = 1
The rate equation is: rate = k[P][Q]
where k is the rate constant.

6.2 Finding the order of reaction from concentration–time graphs

■■ Worked Example 9 ■■

A substance A undergoes decomposition in aqueous solution as represented by the following equation:

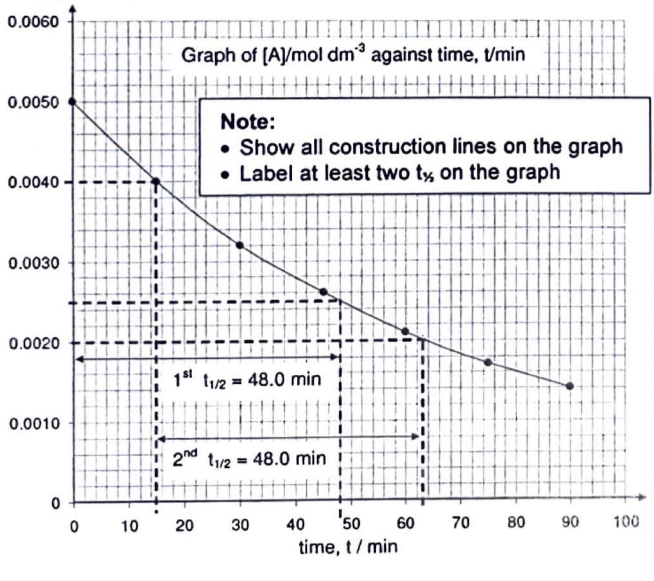
$$A(aq) \longrightarrow B(aq) + C(aq)$$

The kinetics of the above reaction was studied by measuring the concentration of the A at various time intervals and the results obtained are shown below.

Time/min	0	15	30	45	60	75	90
[A]/mol dm^{-3}	0.0050	0.0040	0.0032	0.0026	0.0021	0.0017	0.0014

(a) With the aid of a suitable graph, determine the order of reaction with respect to A.
(b) Write the rate equation for the reaction.
(c) Calculate a value for the rate constant and state its units.

Solution



Note:
- Show all construction lines on the graph
- Label at least two $t_{1/2}$ on the graph

(a) From the graph,

1st $t_{1/2}$ = time taken for [A] to drop from 0.0050 to 0.0025 mol dm^{-3} = 48.0 min

2nd $t_{1/2}$ = time taken for [A] to drop from 0.0040 to 0.0020 mol dm^{-3} = 63.0 – 15.0 = 48.0 min

Since $t_{\frac{1}{2}}$ is constant,

the reaction is first order with respect to A.

Hence order of reaction with respect to A is 1.

(b) The rate equation is: rate = k [A]

(c) For a first order reaction, $k = \dfrac{\ln 2}{t_{1/2}} = \dfrac{\ln 2}{48.0} =$

$0.0144\ \text{min}^{-1}$

■■ Worked Example 10 ■■

The following reaction takes place in aqueous medium:

$$P + Q \longrightarrow R + S$$

The kinetics of the above reaction was studied. The following results were obtained from two experiments (I) and (II). In each experiment, the concentration of Q can be regarded as effectively constant at the value given at the top of the column in the table.

time/min	**Experiment (I)** [P]/mol dm^{-3} when [Q] = 0.10 mol dm^{-3}	**Experiment (II)** [P]/mol dm^{-3} when [Q] = 0.15 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

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

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

(b) Use the initial rates method to deduce the order of reaction with respect to Q.

(c) Construct a rate equation for the reaction and use it to calculate a value for the rate constant.

(a)
Consider the graph of Experiment (I).

1st $t_{1/2}$ = time taken for [P] to drop from 0.0100 to 0.0050 mol dm^{-3}
= 116 min

2nd $t_{1/2}$ = time taken for [P] to drop from 0.0050 to 0.0025 mol dm^{-3}
= 232 – 116
= 116 min

Since $t_{1/2}$ (i.e. half-life) is constant, the reaction is first order with respect to P.
Hence order of reaction with respect to P = 1.

Note:

- Show relevant dotted lines and labels on the graph plotted.
- Can also determine $t_{1/2}$ values from the graph of Experiment (II) and use them to find the order of reaction with respect to P.
- Why was Q used in large excess?
This is to ensure that the [Q] stayed effectively constant throughout the reaction so that the effect of changing [P] on the rate of the reaction can be studied.

(b)
Note: Draw the tangent at time 0 min for each graph, and find the gradient of each tangent.

Consider the graph of Experiment (I).
Initial rate for Experiment (I)

$= -$ gradient of tangent to the curve at t=0 min

$= -\frac{(0.0050 - 0.0100)}{84}$

$= 5.95 \times 10^{-5}$ mol dm^{-3} min^{-1}

Consider the graph of Experiment (II).
Initial rate for Experiment (II)

$= -$ gradient of tangent to the curve at t=0 min

$= -\frac{(0.0050 - 0.0100)}{56}$

$= 8.93 \times 10^{-5}$ mol dm^{-3} min^{-1}

Compare Experiments (I) & (II).
When initial [Q] x 1.5,

initial rate x $\frac{8.93 \times 10^{-5}}{5.95 \times 10^{-5}}$ i.e. initial rate x 1.5

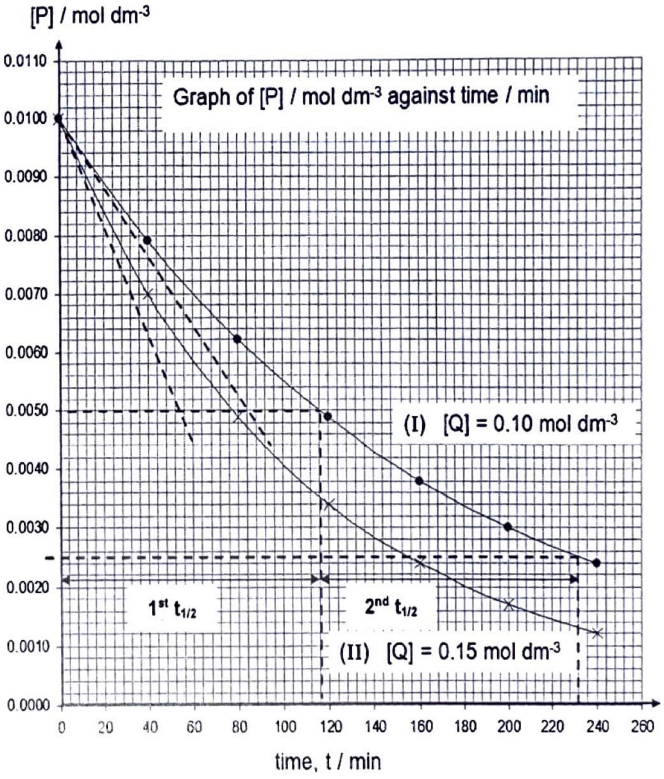
$\Rightarrow$ rate $\propto$ [Q]
Hence order of reaction with respect to Q is 1.

(c)
rate = k [P] [Q]
initial rate = k (initial [P]) (initial [Q])

$$k = \frac{\text{initial rate}}{(\text{initial}[P])(\text{initial}[Q])}$$

Using data from Experiment (I),

$$k = \frac{5.95 \times 10^{-5}}{(0.01)(0.10)} = 0.0595 \text{ mol}^{-1}\text{ dm}^{3}\text{ min}^{-1}$$



■■ Worked Example 11 ■■

Referring to the reaction between H_2O_2 and I^- in an acidic medium in Section 2.2.2,

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

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

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

Note:

- Since the total volume of the reaction mixture was kept constant for all the experiments,
  initial [reactant] ∝ volume of reactant used

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

Compare experiments 2 and 4.
When only volume of $H_2O_2 \times 2$, $1/t \times 2$.
$\Rightarrow 1/t \propto$ volume of H_2O_2
$\Rightarrow$ rate $\propto [H_2O_2]$
Order of reaction with respect to H_2O_2 = 1

Compare experiments 2 and 3.
When volume of KI × 1.5, $1/t \times 1.5$.
$\Rightarrow 1/t \propto$ volume of KI
$\Rightarrow$ rate $\propto [I^-]$
Order of reaction with respect to I^- = 1

Compare experiments 1 and 4.
Note: rate = k $[H_2O_2]\,[I^-]\,[H^+]^n$

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

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

$$n = 0$$

Order of reaction with respect to H^+ = 0

Hence the rate equation is:
rate = k $[H_2O_2]\,[I^-]$

Alternative presentation to obtain order of reaction with respect to H^+

Compare experiments 1 and 4.

When volume of H_2O_2 **x 1.5** and volume of HC*l* x 0.5, **1/t x 1.5**.

Since order of reaction with respect to H_2O_2 = 1, changing volume of HC*l* has no effect on rate.

Hence, order of reaction with respect to H^+ is 0.

7 Reaction Mechanism

Overarching Question 5:

How does knowledge of the rate equation provide information about how the reaction proceeds? In other words, how does the rate equation inform us about the reaction mechanism?

- One of the most important reasons to study reaction rates is the fact that rate equations help us to understand reaction mechanisms, the sequence of bond-making and bond-breaking steps that occurs during the conversion of reactants to products.

- The kinetics data allow us to interpret reactions at a molecular level.

- Some terms and definitions:

<table>
<tr><td>reaction mechanism</td><td>The reaction mechanism of a reaction is a collection of elementary steps in the proper sequence showing how reactant particles are converted into products. It is the explanation of how a reaction takes place.</td></tr>
<tr><td>elementary step</td><td>An elementary step is a distinct step in a reaction mechanism which describes a <u>single molecular event</u> that involves breaking and/or making bonds, such as one reactant particle decomposing or two reactant particles colliding and combining.
Note:
An elementary step cannot be broken down into simpler steps.</td></tr>
<tr><td>molecularity of an elementary step</td><td>The molecularity of an elementary step in a reaction mechanism is the number of reactant particles (e.g. atoms, molecules or ions) taking part in that step.
<table>
<tr><th>Molecularity</th><th>Example</th></tr>
<tr><td>A unimolecular step involves one reactant particle in that step.</td><td>$A \longrightarrow 2B$</td></tr>
<tr><td>A bimolecular step involves two reactant particles in that step.</td><td>$A + B \longrightarrow AB$</td></tr>
<tr><td>A termolecular step involves three reactant particles in that step.</td><td>$A + 2B \rightarrow AB_2$</td></tr>
</table>
Some termolecular elementary steps occur, but they are extremely rare. This is because the probability of three particles colliding simultaneously with the required activation energy and the correct orientation is very small.</td></tr>
<tr><td>intermediate</td><td>An intermediate is a species that is formed in one step of a reaction mechanism and consumed in a subsequent step.
Note: An intermediate
is not represented in the stoichiometric equation;
does not appear in the rate equation for the overall reaction;
may be isolated for a very short duration during the course of the reaction.</td></tr>
</table>

7.1 Single–step reactions

- A <u>single-step reaction</u> is one that takes place in a single step and is termed an <u>elementary reaction</u>.
- Example of a single-step reaction: $CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$

Reaction mechanism	$CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$
Rate equation	rate = k $[CH_3CH_2Br]\,[OH^-]$

- For a single–step reaction,
  - the reaction mechanism consists of one elementary step,
  - the reaction mechanism is identical to the stoichiometric equation for the reaction,
  - the rate equation can be deduced directly from the stoichiometric equation.

Elementary reaction	Reaction mechanism	Molecularity	Rate equation
$A \longrightarrow 2R$	$A \longrightarrow 2R$	unimolecular reaction	rate = k [A]
$2A \longrightarrow P_2$	$2A \longrightarrow P_2$	bimolecular reaction	rate = k $[A]^2$
$A + B \longrightarrow C + D$	$A + B \longrightarrow C + D$	bimolecular reaction	rate = k [A] [B]
$2A + B \longrightarrow C + D$	$2A + B \longrightarrow C + D$	termolecular reaction	rate = k $[A]^2$ [B]

7.2 Multi-step reactions

- A multi-step reaction takes place by two or more steps. For such a reaction, the different steps are likely to proceed at different rates.

- The rate of the overall reaction depends on the rate of the rate-determining step.

- The rate-determining step is the slowest step in the reaction mechanism of a multi-step reaction and it determines the overall reaction rate. It is the step with the highest activation energy.

- In a proposed reaction mechanism for a multi-step reaction, the rate-determining step is stated as the slow step while all other steps are referred to as fast steps.

- Example: $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

Rate equation	rate = k $[NO_2]^2$	**Note:** • Step 1 is the rate-determining step. • NO_3 is an intermediate.
Reaction mechanism	Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ (slow) Step 2: $NO_3 + CO \longrightarrow CO_2 + NO_2$ (fast)	
Overall equation	$NO_2 + CO \longrightarrow NO + CO_2$	

7.3 Deducing the rate equation from a given reaction mechanism

- Given a rate equation, a reaction mechanism can be proposed. A proposed reaction mechanism must meet the following criteria:

1. It must agree with the stoichiometric equation.
   - The elementary steps in the proposed reaction mechanism must sum to give the overall equation.
   - Intermediates do not appear in the overall equation.
2. It must be consistent with the observed kinetics i.e. it must agree with the rate equation obtained.
3. It must include intermediates that are detected during the reaction.

- Given a reaction mechanism, the rate equation can be deduced. There are 2 situations to consider.
  - reaction mechanism with step 1 as the slow step
  - reaction mechanism with step 1 not as the slow step

(a) Reaction mechanism with step 1 as the slow step

Reaction	$2N_2O \longrightarrow 2N_2 + O_2$	
Reaction mechanism	Step 1: $N_2O \longrightarrow N_2 + O$ slow Step 2: $N_2O + O \longrightarrow N_2 + O_2$ fast	From the slow step, rate $\propto [N_2O]$ rate equation is: rate = k $[N_2O]$
Overall equation	$2N_2O \longrightarrow 2N_2 + O_2$	

- How to deduce the rate equation from the given mechanism?

  The rate equation for the overall reaction can be deduced starting from the slow step.

Note:

The reactants that participate in the slow step are those reactants that appear in the rate equation.	• N_2O is the reactant that appears in the slow step. $\Rightarrow$ N_2O must appear in the rate equation.
The order of reaction with respect to a reactant X is the number of X particles that participates in the slow step.	• There is only one N_2O molecule reacting in the slow step. $\Rightarrow$ Order of reaction with respect to N_2O = 1
• Another N_2O molecule participates in the fast step after the slow step and hence does not appear in the rate equation i.e. rate $\neq [N_2O]^2$. • O is an intermediate and does not appear in the overall equation nor the rate equation.	

(b) Reaction mechanism in which step 1 is not the slow step

Reaction	$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$	
Reaction mechanism	Step 1: $NO + Cl_2 \rightleftharpoons NOCl_2$ Step 2: $NO + NOCl_2 \longrightarrow 2NOCl$	fast slow
Overall equation	$2NO + Cl_2 \longrightarrow 2NOCl$	

- The rate equation for the overall reaction can be deduced by considering the slow step and all the fast steps before the slow step

Solution

From the slow step, rate $\propto$ [NO] [$NOCl_2$]

From step 1, the rate of formation of $NOCl_2$ depends on [NO] and [Cl_2]

$\Rightarrow$ [$NOCl_2$] $\propto$ [NO] [Cl_2]
rate $\propto$ [NO] [$NOCl_2$]
rate $\propto$ [NO] [NO] [Cl_2]

Hence the rate equation is: rate = k $[NO]^2$ [Cl_2]

Note:

- $NOCl_2$ is an intermediate and should not appear in the rate equation.
- The reactants that appear in the rate equation are
  - the reactants that participate in the slow step

    and
  - the reactants that participate in any fast step before the slow step.

■■ Worked Example 12 ■■

For each of the following, deduce the rate equation based on the given reaction mechanism.

(a)

Reaction	$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$	
Reaction mechanism	Step 1: $H_2O_2 + I^- \longrightarrow H_2O + OI^-$ Step 2: $OI^- + H^+ \longrightarrow HOI$ Step 3: $HOI + H^+ + I^- \longrightarrow I_2 + H_2O$	slow fast fast
Rate equation	rate $= k [H_2O_2][I^-]$	

(b)

Reaction	$5Br(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$
Reaction mechanism	Step 1: $H^+ + Br \longrightarrow HBr$ fast Step 2: $H^+ + BrO_3^- \longrightarrow HBrO_3$ fast Step 3: $HBr + HBrO_3 \longrightarrow HBrO + HBrO_2$ slow Step 4: $HBrO_2 + HBr \longrightarrow 2HBrO$ fast Step 5: $HBrO + HBr \longrightarrow H_2O + Br_2$ fast
Rate equation	From the slow step, rate $\propto$ [HBr][$HBrO_3$] But HBr and $HBrO_3$ are intermediates. From Step 1: [HBr] $\propto$ [H^+] [Br^-]; From Step 2: [$HBrO_3$] $\propto$ [H^+] [BrO_3^-] Hence, rate $\propto$ [H^+] [Br^-] [H^+] [BrO_3^-] $\Rightarrow$ rate = k [H^+]^2 [Br^-] [BrO_3^-]

8 Explanation of Reaction Rate

In this section, we make use of the collision theory and transition state theory to interpret experimental reaction rates. These theories are formulated based on the particulate nature of matter.

8.1 The Collision Theory

The theory is based on three major postulates:

1 Reactant particles must collide in order to react.

- Not all collisions result in reaction.
- Only a small fraction of the collisions that occur actually leads to reaction. These are said to be effective collisions.

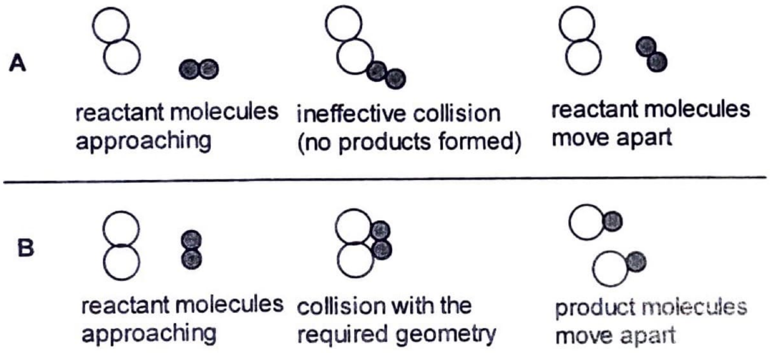
2 Reactant particles must collide in a favourable orientation in order to react.

- In order for the reaction to occur, specific bonds must be broken, and the colliding particles must be oriented favourably with respect to each other (i.e. with the correct collision geometry) so that new bonds can be formed.

3 Reactant particles must collide with a certain minimum amount of energy (i.e. activation energy, E_a) in order to react.

- Not every collision results in a reaction: there must be a certain minimum energy (i.e. activation energy, E_a) in the collision to bring about the necessary re-organisation of the bonds in the colliding particles.
- The activation energy (E_a) of a reaction is the minimum amount of energy that the reactant particles must possess before their collisions can result in a reaction.

Reactant molecules must collide with the correct collision geometry if products are to be formed.



The activation energy of a reaction can be thought of as a sort 'energy barrier'.

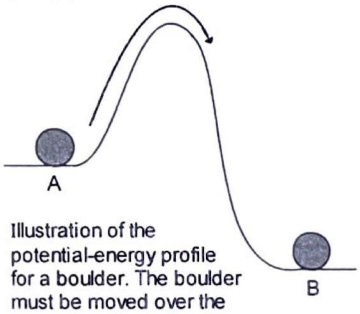


Illustration of the potential-energy profile for a boulder. The boulder must be moved over the energy barrier before it can come to rest in the lower-energy location, B.

8.2 Transition State Theory

- The transition state theory is concerned with what actually happens during a collision. The theory pictures the kinetic energy of the particles changing to potential energy during a collision.

- Given a sufficiently energetic collision and a correct molecular orientation, the reactant species become an unstable transition state (or activated complex) that exists at a potential energy maximum.

partial breaking of old bond — partial formation of new bond

$$\underset{\text{reactants}}{A{-}B + X} = \underset{\textbf{transition state}}{[A\text{---}B\text{---}X]^{\ddagger}} \longrightarrow \underset{\text{products}}{A + B{-}X}$$

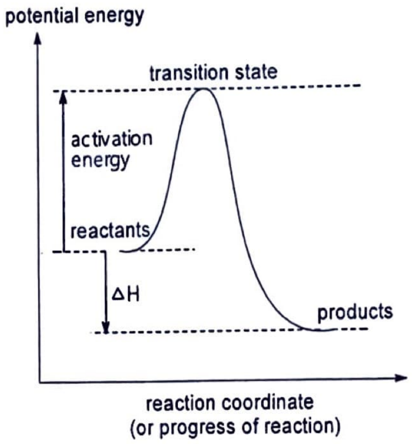
- Unlike a reactive intermediate, a transition state cannot be isolated. Once formed, the transition state can transform into the products; it can also transform back into the reactants.

- Energy profile diagrams depict the changing energy of the chemical system as it progresses from reactants through transition state(s) to products:

Energy profile diagram for a one-step reaction

Mechanism:
reactants ⟶ products

Note: There is only one transition state.

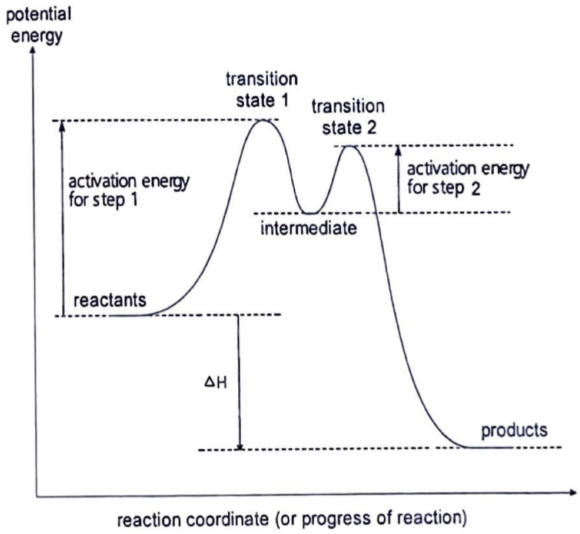


Energy profile diagram for a two-step reaction

Mechanism:
Step 1: reactants ⟶ intermediate (slow)
Step 2: intermediate ⟶ products (fast)

Note:

- There are two transition states, one for each step.
- In this case, the activation energy for step 1 is greater than the activation energy for step 2 since the first step is the slow step/rate-determining step.



8.3 Kinetic stability versus Thermodynamic stability

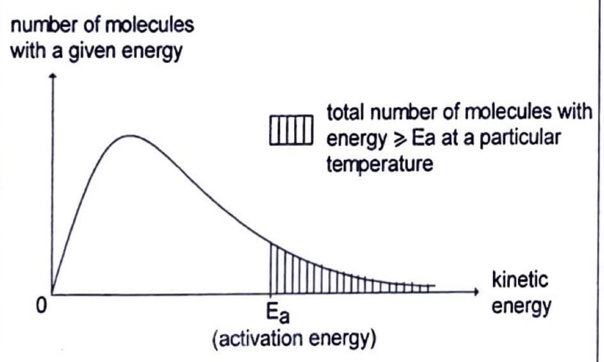
- Recall from *Lecture Notes 5b*:
  - $\Delta G^\ominus$ indicates the thermodynamic feasibility (spontaneity) of a reaction i.e. whether it can occur. It gives no information about the kinetic feasibility (whether the reaction proceeds at an observable rate).
  - The kinetic feasibility of a reaction depends on the activation energy.
- A thermodynamically spontaneous reaction will take place very slowly if the activation energy of the reaction is too high.
- An example of such a reaction is the conversion of diamond to graphite.
  - The reaction is thermodynamically feasible (negative $\Delta G^\ominus$) but occurs too slowly to be observed due to the high activation energy involved.
  - Hence diamond is said to be kinetically stable.
- Another example is the combustion of petrol.
  - Although the combustion reaction is expected to be thermodynamically spontaneous, petrol is kinetically stable until the change is triggered by a spark or a flame.
  - This is due to the high activation energy of the combustion reaction.

8.4 Maxwell-Boltzmann Distribution Curve

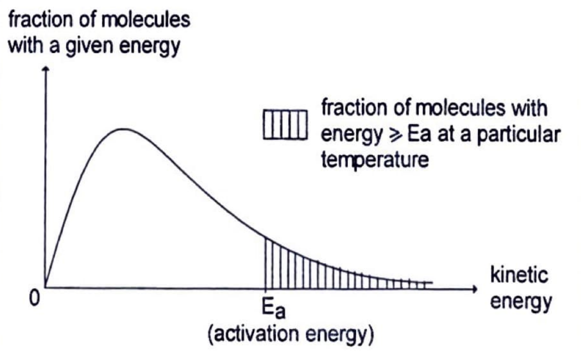
The Maxwell-Boltzmann distribution curve shows the distribution of kinetic energies of the molecules at a particular temperature.

(a) Maxwell-Boltzmann Distribution of Kinetic Energies

- In the context of the kinetic theory of gases, a gas contains a large number of particles in rapid motions. Each particle has a different speed, and each collision between particles changes the speeds of the particles.
- Therefore, the kinetic energy of any particular molecule in a gas system is always changing. This is due to collisions and the resultant change in speed and hence energy.
- At any given instant, the distribution of kinetic energies is always constant under the same conditions. This is because of the large number of molecules involved.
- At a particular temperature, the distribution of kinetic energies follows the Maxwell-Boltzmann distribution curve shown below.

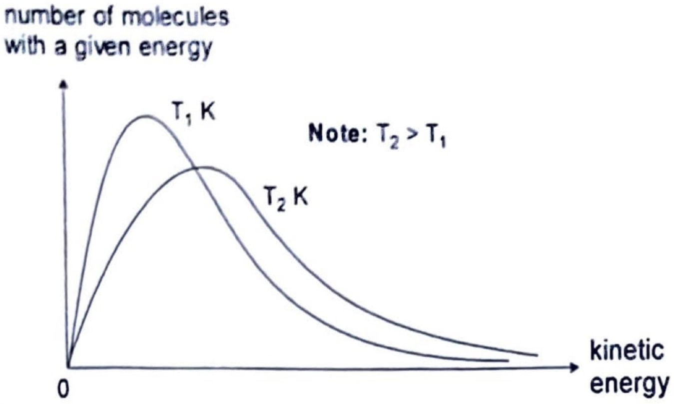


- The area beneath the curve is proportional to the total number of particles present.



- If the vertical axis is given in terms of fraction, then the total area beneath the curve is 1.

- The diagram below shows the Maxwell-Boltzmann distribution of kinetic energies at two different temperatures, T_1 and T_2 K.



Note:

The area under the curve at T_1 K is the same as that at T_2 K since the total number of particles in the system remains the same.

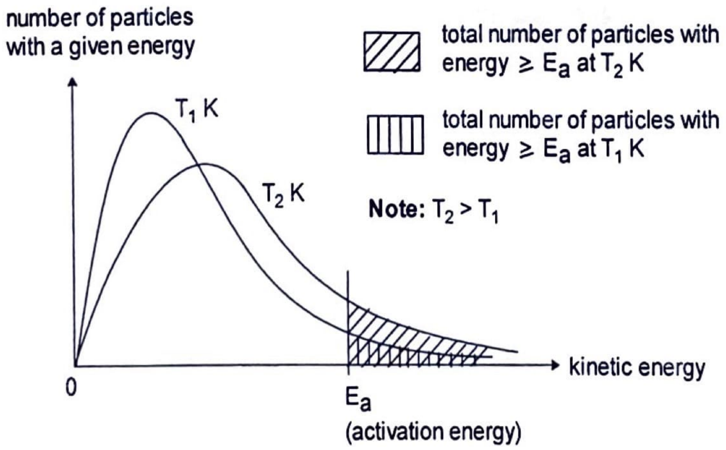
- As temperature increases from T_1 K to T_2 K,
  1. the maximum of the curve is displaced to the right and takes on a smaller value.
  2. there is a greater spread of kinetic energies i.e. the distribution curve broadens.

(b) Application of Maxwell-Boltzmann Distribution Curve

- We can make use of the Maxwell-Botlzmann Distribution curve to explain why a reaction rate increases significantly when temperature increases.

Effect of temperature on reaction rate

Maxwell-Boltzmann distribution of kinetic energies at two different temperatures.

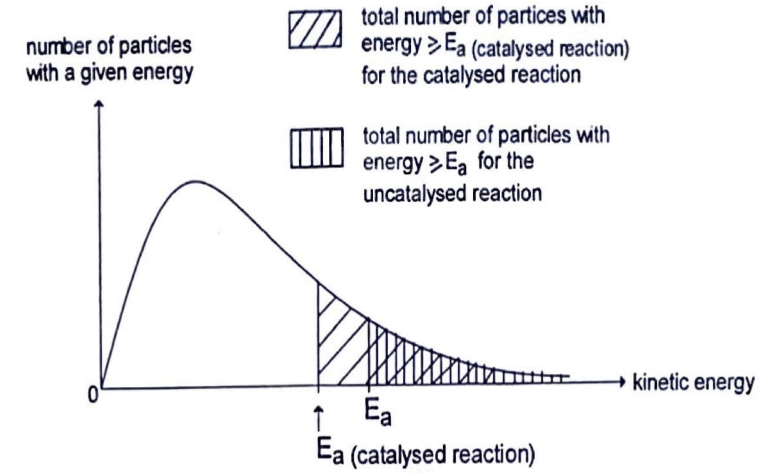


- When temperature is increased from T_1 to T_2 K, the average kinetic energy of the reactant particles increases.
- As such, significantly more reactant particles have energy greater than or equal to the activation energy of the reaction. This is as shown by the larger shaded area at a higher temperature in the above diagram.
- This results in an increase in effective collision frequency and hence an increase in the rate of the reaction.
- In addition, a higher temperature also results in a larger rate constant k and hence an increase in reaction rate.

- Similarly, we can make use of the Maxwell-Boltzmann Distribution curve to explain how a catalyst increases the rate of a reaction.

Effect of a catalyst on reaction rate

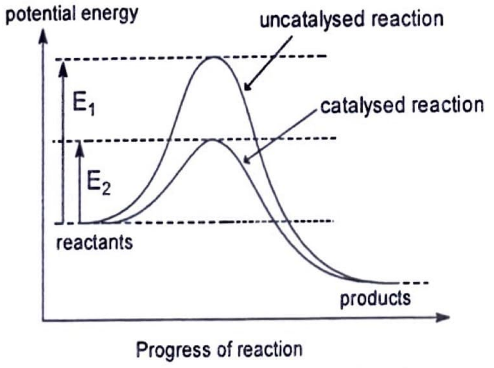
Maxwell-Boltzmann distribution of kinetic energies at a temperature T K.



- A catalyst increases the rate of a reaction by providing an alternative reaction pathway, one of lower activation energy ($E_{a\ (catalysed\ reaction)}$) than the uncatalysed reaction.
- As such, significantly more reactant molecules have energy greater than or equal to the activation energy for the catalysed reaction. This is as shown by the larger shaded area for the catalysed reaction in the above diagram.
- This results in an increase in effective collision frequency and hence an increase in the rate of the reaction.
- An alternative reaction pathway of lower activation energy also results in a larger rate constant k and hence an increase in the reaction rate.

- Energy profile diagrams of an uncatalyzed reaction and a catalyzed reaction

Energy Profiles for a Catalysed and Uncatalysed Reaction



E_1 = activation energy of uncatalysed reaction
E_2 = activation energy of catalysed reaction

9 Catalysis

- Some related terms:

catalyst	• A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change.
inhibitor	• An inhibitor is a substance which decreases the rate of a chemical reaction. • Example: presence of dilute acids or glycerine retards the decomposition of H_2O_2.

- What are the two types of catalysis?

1. Homogeneous catalysis – the catalyst and the reactants are in the same phase
2. Heterogeneous catalysis – the catalyst and the reactants are in different phases

- Examples of catalysts and the reactions they catalysed:

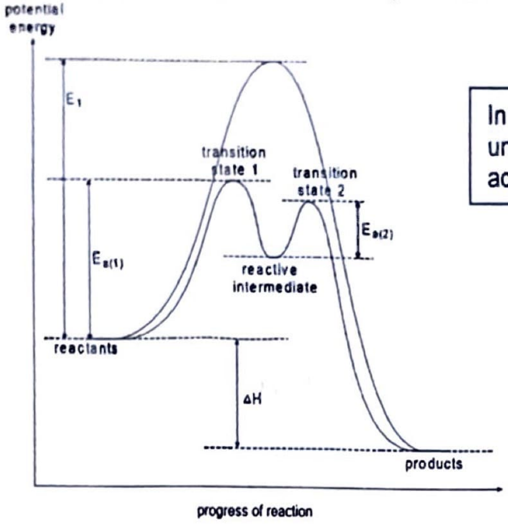
Type of catalysis	Catalyst	Reaction catalysed
Homogeneous	Fe^{2+} or Fe^{3+}	Reaction between peroxodisulfate ions and iodide ions $S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$
	NO_2	Catalytic oxidation of atmospheric sulfur dioxide $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$
	Mn^{2+}	An example of autocatalytic reaction $2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$
Heterogeneous	Ni	Catalytic reduction/hydrogenation of alkenes to form alkanes $RCH{=}CH_2(g) + H_2(g) \longrightarrow RCH_2CH_3(g)$
	Fe	Haber process $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
	V_2O_5	Contact process $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

9.1 Homogeneous Catalysis

- In homogeneous catalysis, the catalyst and the reactants are in the same phase, either liquid or gaseous.
- Consider a reaction $A + B \longrightarrow D + E$, catalysed by Ct

Uncatalysed reaction	$A + B \longrightarrow D + E$	Typical features of homogeneous catalysis
Catalysed reaction	Step 1: $A + Ct \longrightarrow D + Ct'$ Step 2: $Ct' + B \longrightarrow E + Ct$ -------------------------------- Overall reaction: $A + B \longrightarrow D + E$	1. The catalyst (Ct) takes a definite part in the reaction by being converted into an intermediate Ct'. 2. The intermediate Ct' subsequently undergoes reaction to yield the product(s) and the catalyst is regenerated.

- Energy profile diagrams for a catalysed reaction and an uncatalysed reaction



In this case, the larger activation energy for the uncatalysed reaction is replaced by two smaller activation energies for the catalysed reaction.

E_1 = activation energy of uncatalysed reaction
$E_{a(1)}$ = activation energy of first step of catalysed reaction
$E_{a(2)}$ = activation energy of second step of catalysed reaction

- Example 1: Reaction between peroxodisulfate ions and iodide ions catalysed by Fe^{2+} or Fe^{3+}.

Uncatalysed reaction	$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$ Type of reaction: Redox Reaction • In the uncatalysed reaction, there is a direct reaction between two anions. • The electrostatic repulsion between the two anions partly causes the reaction to have a **high activation energy** and hence to proceed slowly. • In this case, Fe^{2+} or Fe^{3+} serves as a possible catalyst to speed up the reaction.
Reaction catalysed by Fe^{2+}	• The catalysed reaction proceeds via a 2-step mechanism. • Each step involves a reaction between **oppositely charged ions** which have a natural tendency to attract each other. This lowers the activation energy and enhances the reaction rate. Step 1: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$ Step 2: $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$ overall reaction: $S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$ **Note:** Each step is a redox reaction, i.e. oxidation and reduction occur simultaneously.
Reaction catalysed by Fe^{3+}	Step 1: $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$ Step 2: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$ overall reaction: $S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$

- Example 2: Catalytic oxidation of atmospheric sulfur dioxide by atmospheric oxides of nitrogen

Uncatalysed reaction	$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$ • Atmospheric SO_2 can be oxidised to SO_3 by O_2 but the reaction is very slow in the absence of a catalyst.
Reaction catalysed by NO_2 (from car exhaust fumes)	• In the presence of NO_2, the rate of oxidation of SO_2 is increased. The catalysed reaction occurs in two steps. Step 1: $SO_2(g) + NO_2(g) \longrightarrow SO_3(g) + NO(g)$ Step 2: $NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$ overall reaction: $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$ • In step 1, NO_2 (from car exhaust fumes) oxidises atmospheric SO_2 (from the burning of fossil fuels) to SO_3. • In step 2, the catalyst NO_2 is regenerated.
Remarks	• The SO_3 (a secondary pollutant) formed then reacts with rain water to form sulfuric acid. $SO_2(g) \xrightarrow{\text{oxidation}} SO_3(g) \xrightarrow{H_2O(l)} H_2SO_4(aq)$ • This results in acid rain and thus, amplifies the problem of atmospheric SO_2 as a pollutant.

9.2 Heterogeneous Catalysis

- In heterogeneous catalysis, the catalyst and the reactants are in different phases. The catalyst is usually in the solid phase while the reactants are usually liquids or gases.

- For heterogeneous catalysis to occur, the reactant molecules need to be readily adsorbed onto the active sites of the catalyst surface. This involves the formation of weak bonds between the reactant molecules and the catalyst surface.

- The adsorption of the reactant molecules at the catalyst surface (i.e. the formation of weak bonds between the catalyst surface and the reactant molecules) increases the reaction rate because:

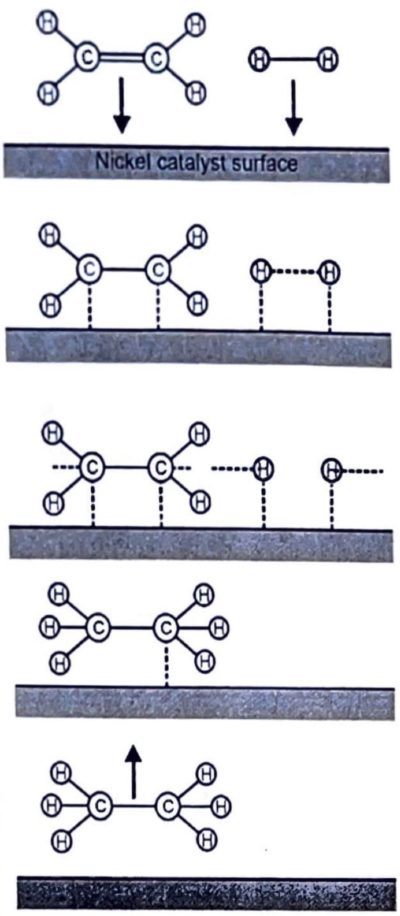
1. the adsorption weakens the covalent bonds within the reactant molecules, thereby lowering the activation energy for the reaction.

2. the adsorption increases the concentration of reactant molecules at the catalyst surface and allows the reactant molecules to come into close contact with proper orientation for reaction.

- Example 1: Addition of H_2 to alkenes catalysed by nickel metal
  (e.g. the conversion of vegetable oil into margarine)

$$R\text{–}CH\text{=}CH_2(g) + H_2(g) \xrightarrow{\text{Ni, heat}} R\text{–}CH_2\text{–}CH_3(g)$$

Reaction: Catalytic reduction/hydrogenation of ethene



1. Diffusion

   Reactant molecules diffuse towards the catalyst surface.

2. Adsorption

   Reactant molecules become adsorbed onto the active sites of the catalyst surface. This increases the concentration of reactants at the catalyst surface and also weakens the covalent bonds in the molecules.

3. Reaction

   Adjacent reactant molecules react to form products. This reaction has lower activation energy (E_a) than the uncatalysed reaction.

4. Desorption

   This is the reverse of adsorption. The product molecule eventually breaks free from the catalyst surface.

5. Diffusion

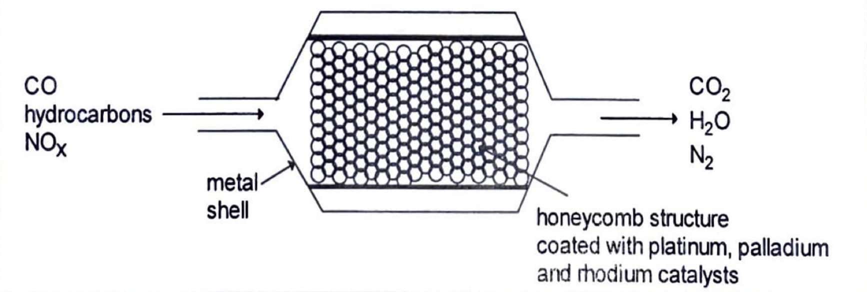
   The product molecules diffuse away from the surface. The vacant active sites are now available for adsorbing other reactant molecules.

- Example 2: Haber Process using Fe as catalyst

$$N_2(g) + 3H_2(g) \xrightleftharpoons[Fe(s)]{250\text{ atm, }450°C} 2NH_3(g)$$

- Example 3: Catalytic removal of oxides of nitrogen in the exhaust gases from car engines

The catalytic converter



- Cars are fitted with catalytic converters to remove three main pollutants (CO, NO_x and unburnt hydrocarbons) from exhaust gases. The harmful gases are converted into CO_2, N_2 and H_2O.

- A "three-way" catalytic converter consists of a ceramic honeycomb structure coated with platinum (Pt), palladium (Pd) and rhodium (Rh) which act as catalysts. A honeycomb structure is used so as to maximise the surface area on which heterogeneously catalysed reactions take place.

- The three catalysts are selective in the reactions they catalyse:

1	$2NO(g) + 2CO(g) \xrightarrow{Rh} 2CO_2(g) + N_2(g)$ $NO_2(g) + 2CO(g) \xrightarrow{Rh} 2CO_2(g) + \frac{1}{2}N_2(g)$ • The oxides of nitrogen (NO and NO_2) are reduced to N_2 by the excess CO present, with Rh acting as the catalyst.
2	$2CO(g) + O_2(g) \xrightarrow{Pt/Pd} 2CO_2(g)$ • CO is also oxidised to CO_2 with Pt and Pd as the catalysts.
3	$C_xH_y(g) + (x + \frac{y}{4}) O_2(g) \xrightarrow{Pt/Pd} xCO_2(g) + \frac{y}{2}H_2O(g)$ • The unburnt hydrocarbons are oxidised to CO_2 and H_2O with Pt and Pd as the catalysts.

- The catalysts in the catalytic converters can be de-activated (or poisoned) by lead as lead is preferentially adsorbed on the catalyst surface thereby occupying the active sites. Hence, cars fitted with catalytic converters must be run on unleaded petrol.

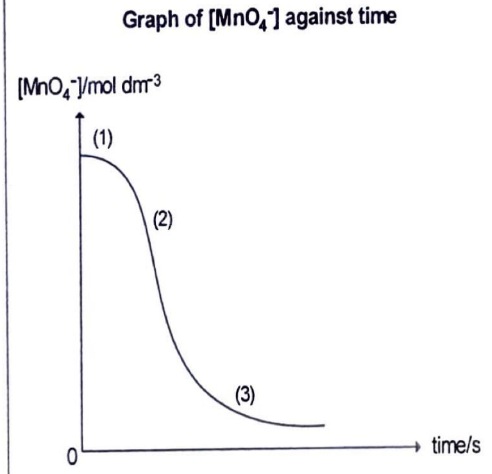
9.3 Autocatalysis

- Autocatalysis is a type of catalytic action whereby the product of a reaction acts as a catalyst for the reaction. A reaction in which a product acts as a catalyst is said to be autocatalytic.

- Example 1

Reaction	$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow \underset{\textbf{autocatalyst}}{2Mn^{2+}(aq)} + 10CO_2(g) + 8H_2O(l)$ In the oxidation of ethanedioate ions by manganate(VII) ions, the reaction is accelerated by the Mn^{2+} ions produced during the reaction.

- Graph of [reactant] against time for an autocatalytic reaction



The graph on the left represents how the concentration of manganate(VII) ions changes with time in the reaction between manganate(VII) ions and ethanedioate ions.

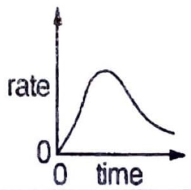
[Recall: For a [reactant] against time graph, the instantaneous rate at time t = – gradient of tangent to the curve at time t]

(1) Initially, the reaction is slow since it is not catalysed.

(2) As the Mn^{2+} ions are produced, they increase the rate of the reaction by acting as an autocatalyst.

(3) Towards the end of the reaction, the concentration of the reactants has fallen to a low level and so the rate of the reaction decreases, even though there is an adequate supply of catalyst.

- Graph of rate against time for an autocatalytic reaction



- Example 2

Reaction	$2AsH_3(g) \longrightarrow 2As(s) + 3H_2(g)$ The decomposition of arsine (AsH_3) by heat is catalysed by the metallic arsenic formed.

- Note: A test for an autocatalyst is to add the autocatalyst at the start of the reaction. The reaction should then be very rapid at the start.

10 Enzymes

- Enzymes are proteins which catalyse chemical reactions in living systems. They are often called biological catalysts or biocatalysts. Without them, most biochemical reactions would be too slow to sustain life.

- Examples of enzymes: amylase (hydrolyses starch)
  trypsin (hydrolyses proteins)
  lipase (hydrolyses fats/lipids)

10.1 Properties of enzymes

1. Nature and size

- Enzymes are globular proteins with active sites contained in their three-dimensional structure. They have relative molecular masses which range from 10^5 to 10^7.

2. Efficiency

- Enzymes are required in very small amounts – they are very effective catalysts. This is because the enzyme molecules are regenerated during their catalytic activity. A typical enzyme molecule may be regenerated a million times in one minute.

- An example is the enzyme catalase. In one second, one molecule of this enzyme decomposes some 50000 molecules of hydrogen peroxide at 0°C: $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(l)$.

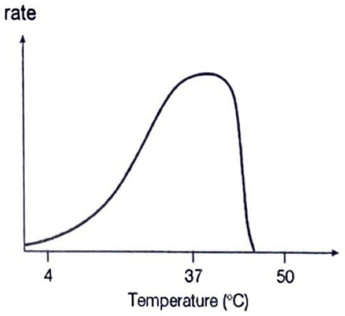
3. Specificity

- In general, enzymes are very specific to a particular reaction or type of reaction due to the three-dimensional conformation of the active site.

4. Temperature

- Enzymes operate most effectively at body temperature, that is, about 37°C.

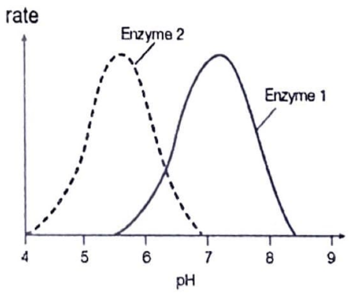
- When the temperature rises about 50 to 60°C, this can result in a change in the three-dimensional conformation of the active site, which then causes the enzyme to become denatured and inactive.



5. Sensitivity to pH

- Enzymes only work well over a narrow pH range.

- Enzyme activity is affected by pH – different enzymes have differing optimum pH levels.



10.2 Enzymatic Action

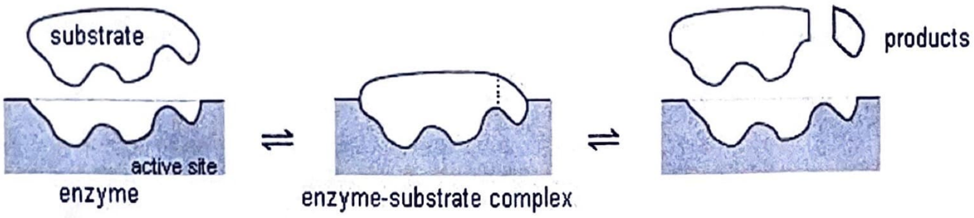
- Enzymes catalyse reactions by providing an alternative reaction pathway with lower activation energy. To bring this about, the enzyme forms a complex with the substrate (i.e. reactant) of the reaction. Thus, a simple picture of the enzyme action is:

substrate + enzyme ⟶ enzyme/substrate complex ⟶ enzyme + products

- In general, enzymes are very specific in their catalytic activity, catalyzing only one particular type of reaction. They are also highly specific with respect to the substrates they act on and the products that they form.

- Two models have been proposed to explain how an enzyme binds its substrate (reactant).

(a) lock and key model



- In the lock and key model proposed by Emil Fisher in 1894, the substrate and the enzyme molecules are thought to have complementary shapes so that they fit together like a key into its lock. The specific shape of the enzyme gives the enzyme its specificity as only substrate of a specific shape can interact with it.

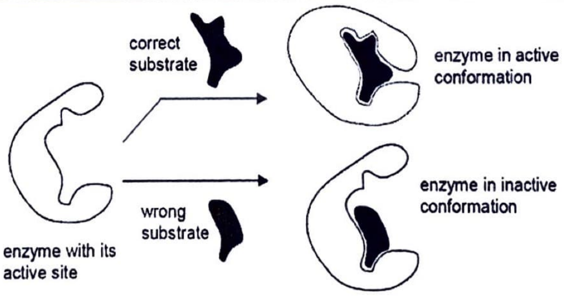
- When brought together in the right alignment, the substrate (reactant) fits the active site on the enzyme (catalyst) in the same way that a key fits a lock, and is bound by attractive forces at the active site.

- An enzyme-substrate complex is formed and this weakens the bonding within the substrate. Thus the substrate is enable to react via an alternative reaction pathway of lower activation energy.

- Once the catalysed reaction has occurred, the enzyme-substrate complex breaks apart as the product formed is no longer of the right shape to remain in the active site. Now the enzyme is free to bind to another substrate molecule.

(b) induced-fit model

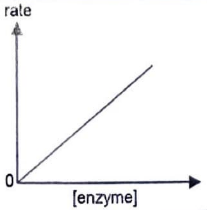
- In the induced-fit model proposed in 1958, the binding of the correct substrate induces a conformational change in the active site of the enzyme and brings catalytic groups into exactly the right position to facilitate the reaction.



10.3 Factors affecting the rate of an enzyme-catalysed reaction

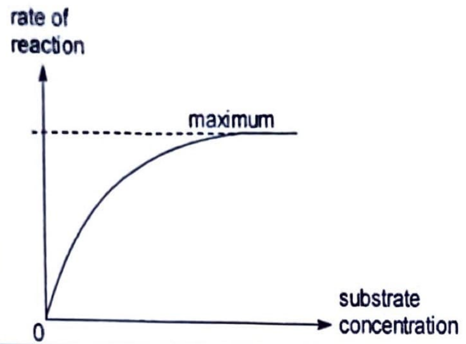
(a) Temperature
(b) pH
(c) Concentration of enzyme

In an enzyme-catalysed reaction,
- [enzyme] is very small compared to [substrate]
- rate of reaction is directly proportional to [enzyme]



(d) Concentration of substrate

- The graph below shows the effect of substrate concentration on an enzyme-catalysed reaction.



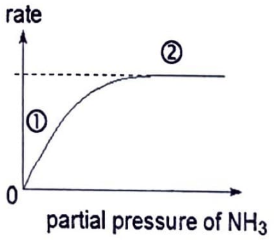
- At a constant concentration of the enzyme, the rate of the reaction increases with increasing substrate concentration until a maximum is reached.
- At this point where the substrate concentration is high, the active sites of the enzyme become saturated with substrate. Further increase in the concentration of the substrate will not have any effect on the reaction rate.

- For a fixed amount/concentration of enzyme, there is a finite number of active sites in the enzyme.

1	At low [substrate], not all of the active sites are occupied.	• In this case, rate $\propto$ [substrate]. • The reaction is first order with respect to the substrate.
2	At high [substrate], all the active sites are occupied i.e. the active sites of the enzyme become saturated with substrate.	• In this case, any increase in [substrate] will not have any effect on the reaction rate. • The reaction is zero order with respect to the substrate.

- Note: A similar rate against [reactant] graph is observed for reaction involving a gaseous reactant catalysed by a heterogeneous catalyst.

Example: Decomposition of NH_3 into N_2 and H_2 on a hot tungsten wire

Partial pressure of NH_3	Order of reaction with respect to NH_3	Explanation	
① Low	First	• At low pressures, the active sites on the catalyst surface are not saturated with NH_3 molecules. • Hence, rate of decomposition of NH_3 only depends on the partial pressure of NH_3.	
② Moderate or high	Zero	• At moderate or high pressures, most, if not all, of the active sites present on the tungsten surface are taken up by NH_3 molecules. • Consequently, any increase in the partial pressure of NH_3 has no effect on the rate of decomposition.	

RAFFLES INSTITUTION
YEAR 5 H2 CHEMISTRY 2022
Tutorial 6: Reaction Kinetics

Self-Check

1 Outline how the rate of each of the following reactions may be followed experimentally.
*[**Note:** Use a different experimental technique for each reaction.]*

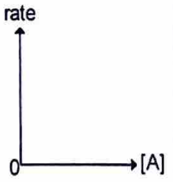
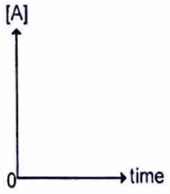
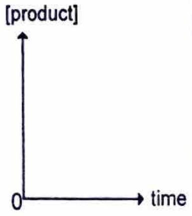
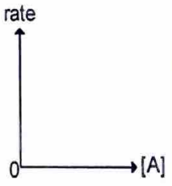
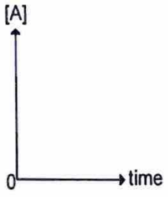
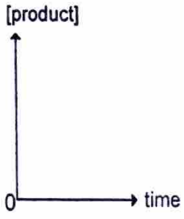
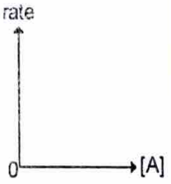
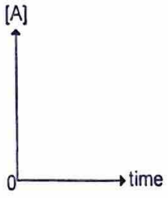
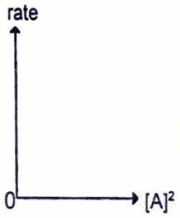
(a) $5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

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

General Strategy

1. Identify what can be monitored over time, then identify the method to use:
   - change in [reactant] or [product] with time can be monitored by different methods, e.g. colorimetry.
2. Perform the experiment and collect data over time.
3. Plot a graph of data against time.
4. Instantaneous rate may be found by drawing a tangent to the curve at that particular time and finding its gradient, g_1.
   - Rate = – g_1 if data ∝ [reactant] while rate = g_1 if data ∝ [product]

2 Fill in the blanks and sketch the graphs in the table below.

Overall order of reaction	Rate equation	Common units of k	Half-life	Rate-[reactant] Graph	[reactant]-Time Graph	Other Graphs
zero	rate = k		$t_{1/2}$ is ______			
one	rate = k [A]		$t_{1/2}$ = ______ $t_{1/2}$ is ______			
two	rate = k $[A]^2$		$t_{1/2}$ is ______			

3 **[N14/P1/Q11]**

The hydrolysis of ethyl ethanoate in aqueous solution can be catalysed by hydrogen ions from sulfuric acid. To determine the order of this reaction with respect to hydrogen ions, which method should be used?

A Measure the change in pH during the reaction.

B Measure the rate of the reaction several times, but with a different concentration of ethyl ethanoate each time.

C Measure the rate of the reaction several times, but with a different concentration of sulfuric acid each time.

D Remove samples at various time intervals and titrate against a standard solution of aqueous sodium hydroxide.

4 **[RI 2014 Promotion Exam Section A Q9]**

The decomposition of compound XY_2 follows first-order kinetics with a half-life of 45 min.

$$XY_2 \longrightarrow X + 2Y$$

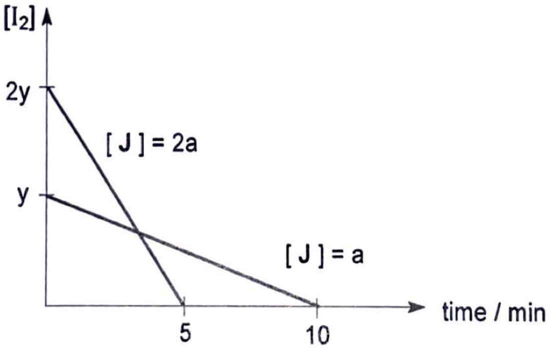
What is the total time taken for the mole ratio of XY_2 : Y to reach 1 : 6?

A	45 min	**C**	135 min
B	90 min	**D**	180 min

5 The rate equation for the reaction $3A(g) + B(g) \longrightarrow C(g) + D(g)$ is given by: rate = $k[A]^2[B]$. If rate = ***R*** for certain pressures of A and B (at constant temperature), write down in terms of ***R***, the rate of reaction when

(a) partial pressures of both A and B are doubled,
(b) partial pressure of A doubles, but that of B remains constant,
(c) the volume of the reacting vessel is doubled,
(d) the total pressure is doubled by addition of an inert gas into the system at constant volume.

6 The kinetics of the reaction between iodine and compound **J** is investigated. Deduce the order of reaction with respect to each of the reactants.



7 **[RI 2013 Promotion Exam Section A Q9]**

The reaction of hydrogen peroxide with acidified aqueous potassium iodide can be monitored by an initial rate method.

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

initial concentration of reactants / mol dm^{-3}			initial rate of formation of iodine / mol dm^{-3} min^{-1}
[H_2O_2]	[I^-]	[H^+]	
0.020	0.005	0.20	1.0 x 10^{-6}
0.040	0.005	0.20	2.0 x 10^{-6}
0.030	0.010	0.20	3.0 x 10^{-6}
0.060	0.010	0.40	6.0 x 10^{-6}

Which of the following can be correctly deduced from the results obtained above?

A The rate constant of this reaction is 0.01 mol^{-2} dm^6 min^{-1}.

B H^+ provides an alternative pathway of lower activation energy in this reaction.

C The magnitude of the rate constant increases with the concentration of H_2O_2 and I^- ions.

D Increasing [H_2O_2], [I^-] and [H^+] each by a factor of 3 at constant temperature causes a nine-fold increase in the initial rate of formation of iodine.

8 **[N18/P1/11]**

For the following reaction, the rate equation is rate = $k[NO_2]^2$.

$$CO + NO_2 \longrightarrow CO_2 + NO$$

What could be a two-step mechanism for this reaction?

A
$NO_2 \longrightarrow NO + O$ (slow)
$CO + O \longrightarrow CO_2$ (fast)

B
$NO_2 + NO_2 \longrightarrow N_2O_3 + O$ (slow)
$N_2O_3 + CO \longrightarrow CO_2 + 2NO$ (fast)

C
$NO_2 + NO_2 \longrightarrow NO + NO_3$ (slow)
$NO_3 + CO \longrightarrow CO_2 + NO_2$ (fast)

D
$NO_2 + CO \longrightarrow NCO_3$ (slow)
$NCO_3 \longrightarrow CO_2 + NO$ (fast)

Practice Questions

9 Sucrose has been used as a feedstock in the production of alcohol for use as a motor fuel. The initial reaction is its hydrolysis: $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

sucrose **glucose** **fructose**

This reaction can be catalysed by dilute acid or the enzyme, sucrase, which is found in yeast. The following results were obtained using hydrochloric acid as the catalyst.

experiment	initial [HC*l*] / mol dm^{-3}	initial [sucrose] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
I	0.10	0.10	0.024
II	0.10	0.15	0.036
III	0.20	0.10	0.048
IV	0.25	y	0.048

(a) Define the following terms:
(I) order of reaction
(II) rate constant
(III) half-life

(b) Deduce the order of reaction with respect to both HC*l* and sucrose. Hence, calculate the rate constant for the reaction, stating the units.

(c) Calculate the value of y.

(d) The half-life of sucrose in experiment I was 3.0 s. Predict the half-life of sucrose in experiment II and in experiment III, giving your reasoning.

10 **[RI 2018 Prelim/1/10 modified]**
The reaction between NO_2 and SO_2 is a key stage in the formation of acid rain.

$$NO_2(g) + SO_2(g) \longrightarrow NO(g) + SO_3(g)$$

A series of experiments was conducted with various concentrations of NO_2 and SO_2 in the absence of air.

experiment	[NO$_2$] / mol dm^{-3}	[SO$_2$] / mol dm^{-3}	relative rate
1	0.010	0.20	1
2	0.020	0.20	2
3	0.040	0.40	8

The half-life of NO_2 in experiment 1 was 48 seconds. What is the half-life of NO_2 in experiments 2 and 3?

11 **[N12/P1/13]**

The decomposition of hydrogen peroxide in aqueous solution is a first order process.

If 10 % of the hydrogen peroxide in a solution of concentration 0.1 mol dm^{-3} decomposes in 5 minutes at a certain temperature, what percentage of the hydrogen peroxide in a solution of concentration 0.2 mol dm^{-3} would decompose in 5 minutes at the same temperature?

A 5 % **B** 10 % **C** 19 % **D** 20%

12 The rate of reaction between propanone, CH_3COCH_3, and acidified iodine to give iodopropanone, CH_3COCH_2I, is found to be independent of $[I_2]$, but directly proportional to $[H^+]$ and directly proportional to $[CH_3COCH_3]$.

(a) Define the following terms:
(I) rate equation
(II) rate-determining step

(b) Write the rate equation for this reaction and state the overall order.

(c) Suggest, with reasons, which of the following two possible mechanisms, **A** or **B**, fits the observed kinetic data. (X and Y are intermediates)

A: $CH_3COCH_3 + H^+ \longrightarrow X$ slow
$X + I_2 \longrightarrow$ products fast

B: $CH_3COCH_3 + I_2 \longrightarrow Y$ slow
$Y + H^+ \longrightarrow$ products fast

(d) The reaction between propanone and bromine to give bromopropanone proceeds by a similar mechanism. Explain how the rate of the reaction between propanone and bromine would compare with that of the reaction between propanone and iodine.

13 **[N09/P3/Q3(d) (Modified)]**

The initial rate of the slow reaction between H_2O_2 and acidified potassium iodide solution can be studied by the 'clock' method, using sodium thiosulfate. The equations for the reactions are:

$H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$ (slow) reaction **I**
$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ (fast) reaction **II**

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

A series of experiments was carried out using different volumes of the five reagents, each solution being made up to the same total volume with water. The following results were obtained:

Experiment Number	Volume of 0.10 mol dm^{-3} H_2O_2/ cm^3	Volume of 1.00 mol dm^{-3} KI/ cm^3	Volume of 1.00 mol dm^{-3} HC*l* / cm^3	Volume of 0.050 mol dm^{-3} $Na_2S_2O_3$/ cm^3	Volume of starch solution/ cm^3	Volume of water/ cm^3	Time for the appearance of deep blue colour/ s
1	15	10	5	2	3	65	33
2	5	10	10	2	3	70	100
3	5	15	10	2	3	65	67
4	10	10	10	2	3	65	50

(a) Calculate the amount of iodine produced before the appearance of the deep blue colour.

(b) Hence calculate the initial rate for each of these four experiments.
Use the results to deduce the order of reaction with respect to each of the three reactants in reaction **I**. Explain your reasoning.

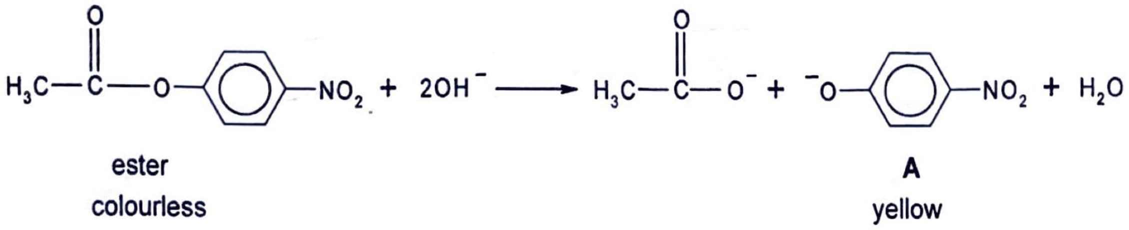
(c) Hence, write an overall rate equation for reaction **I**, stating the units of the rate constant.

In a fifth experiment, the following volumes were used.

Experiment Number	Volume of 0.10 mol dm^{-3} H_2O_2/ cm^3	Volume of 1.00 mol dm^{-3} KI/ cm^3	Volume of 1.00 mol dm^{-3} HC*l* / cm^3	Volume of 0.050 mol dm^{-3} $Na_2S_2O_3$/ cm^3	Volume of starch solution/ cm^3	Volume of water/ cm^3	Time for the appearance of deep blue colour/ s
5	30	20	10	4	6	130	y

(d) State the value of y.

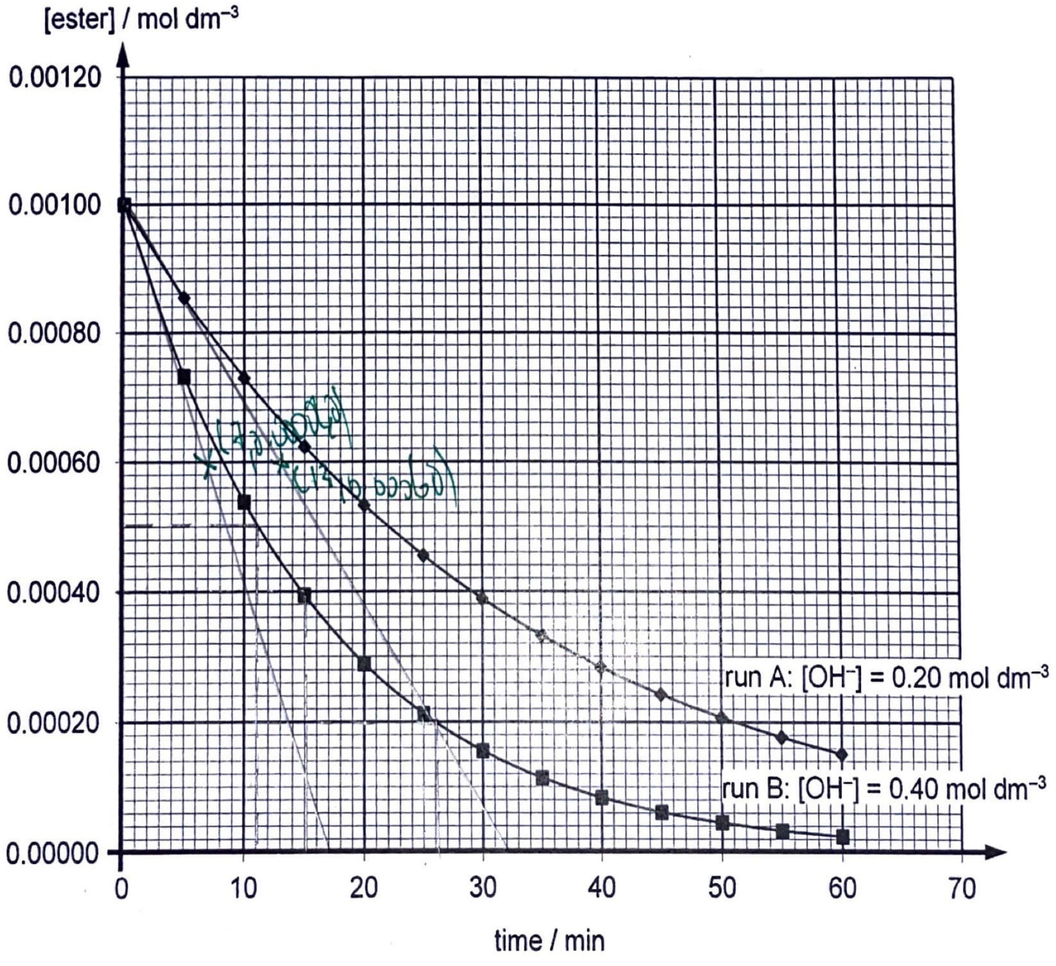
14 The hydrolysis of an ester in alkaline solution is shown below.



(a) Suggest, and briefly describe, a suitable technique for studying the rate of this reaction.

(b) The reaction rate was studied using two solutions of different hydroxide ion concentrations.

The following graphs show how the concentration of the ester varies over time in runs A and B.



(i) Using the graphs, determine the initial rates of reaction during the two runs, showing your working clearly. State the units of the initial rates.

(ii) Using your results to **(i)**, deduce the order of reaction with respect to OH^-.

(iii) Using the graph of run B, determine the order of reaction with respect to ester. Show clearly all working and construction lines on the graph.

(iv) Write the rate equation for this reaction.

(v) Using your answers to **(i)** and **(iv)**, calculate a value for the rate constant, stating the units.

(vi) Use a method different from the one you have used in **(v)** to calculate another value for the rate constant.

15 [RI 2015 Promotion Exam Section B Q2(a) – (c) Modified]

(a) The kinetics of the reaction between A and B is studied.

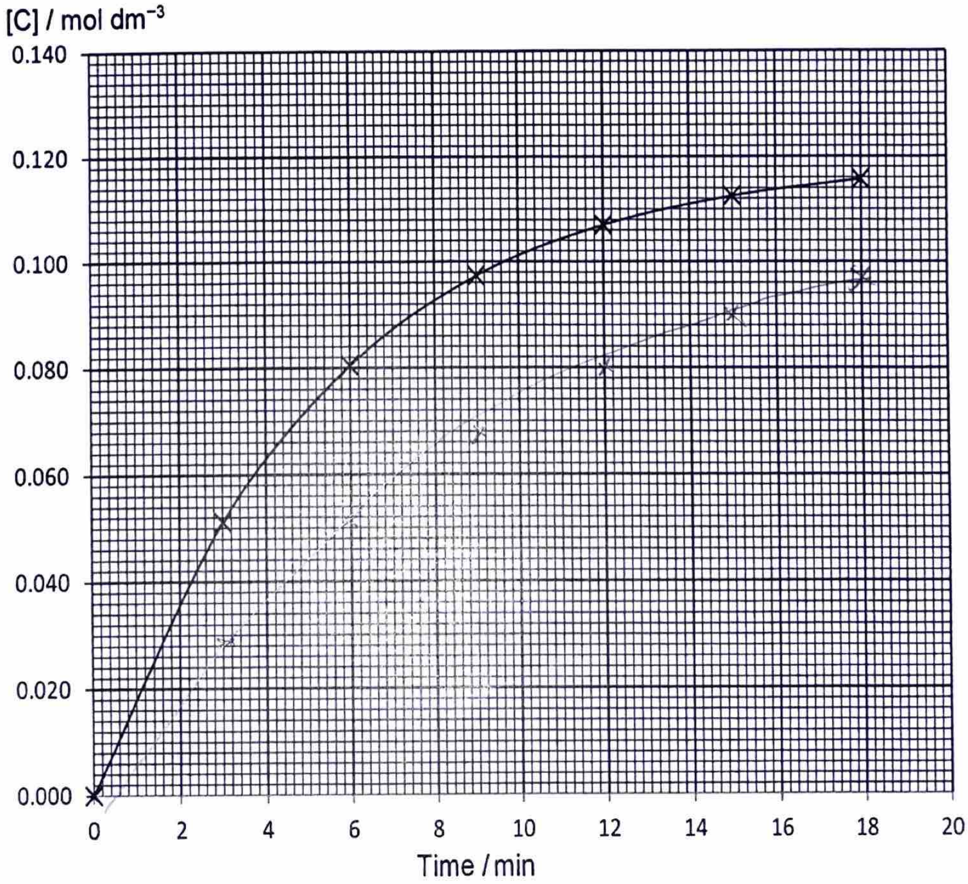
$$A(g) + B(g) \longrightarrow C(g)$$

To determine the rate equation for this reaction, two separate experiments were carried out in a vessel of fixed volume with initial concentrations of A and B as shown below:

Experiment	1	2
Initial [A(g)] / mol dm^{-3}	0.12	0.12
Initial [B(g)] / mol dm^{-3}	2.00	1.00

For each experiment, the concentration of C was determined at regular time intervals as the reaction progressed.

The graph below shows the results of Experiment 1.



(i) Why was B used in large excess?

(ii) What is the final concentration of C if the reaction were to go to completion? Hence or otherwise, determine the order of reaction with respect to A.

(b) The results of Experiment 2 with [B(g)] = 1.00 mol dm^{-3} are shown below.

Time/ min	0	3	6	9	12	15	18
[C(g)]/ mol dm^{-3}	0.000	0.029	0.051	0.068	0.080	0.090	0.097

(i) Plot the graph for Experiment 2 on the same axes as that of Experiment 1.

(ii) Using the graphs, determine the order of reaction with respect to B, showing your working clearly.

(iii) Hence, write the rate equation for the reaction between A and B.

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

(c) The reaction between A and B may be sped up by using a suitable catalyst. With the help of a Boltzmann distribution curve, explain how

(i) the use of a catalyst can speed up the rate of reaction.

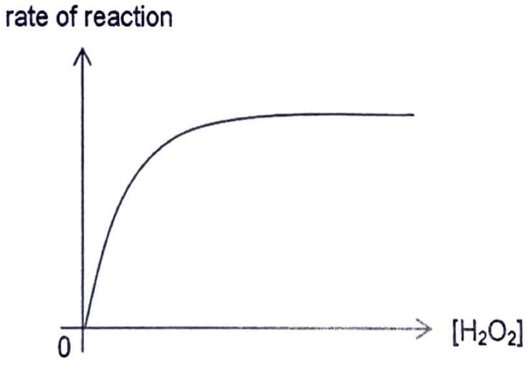
(ii) a relatively small increase in temperature can cause a large increase in the rate of reaction.

16 **[RI 2015 Promotion Exam Section B Q2(d)]**

Enzymes are biological catalysts which speed up the rate of a reaction greatly. One such enzyme is catalase, which catalyses the decomposition of aqueous hydrogen peroxide:

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

To study the effect of different concentrations of hydrogen peroxide on the rate of decomposition of H_2O_2 catalysed by catalase, 0.1 g of catalase was added to separate portions of 50 cm^3 aqueous hydrogen peroxide of different concentrations. The following graph was obtained:



Account for the shape of the graph obtained.

17 Ethyl ethanoate, $CH_3CO_2CH_2CH_3$, reacts with H_2O to form ethanoic acid, CH_3CO_2H, and ethanol, CH_3CH_2OH. The rate of this reaction was slow at first, then it gradually increased before it decreased.

Explain these observations and sketch the graph of concentration of $CH_3CO_2CH_2CH_3$ against time.
[Note: The hydrolysis of an ester can be catalysed by acid.]