REACTION KINETICS

Content

- Simple rate equations; orders of reaction; rate constants
- Concept of activation energy
- Effect of concentration, temperature, and catalysts on reaction rate
- 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*; *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, 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 conc-time graphs
  (iii) calculating an initial rate using concentration data

(c) show understanding that the half-life of a first-order reaction is independent of concentration

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

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

(f) 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

(g) **(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 in terms of the Boltzmann distribution

(h) outline the mode of action of heterogeneous catalysis, as exemplified by the catalytic removal of oxides of nitrogen in the exhaust gases from car engines

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

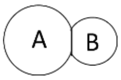
1 BASIC CONCEPT IN KINETICS

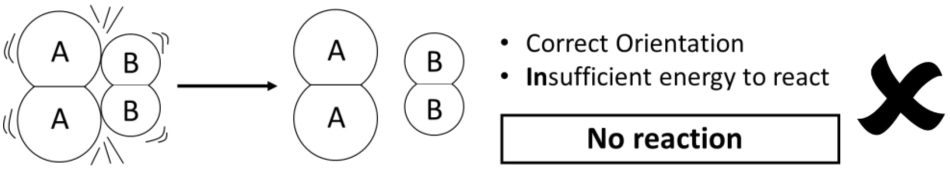
1.1 COLLISION THEORY
(Understanding reaction at particulate level)

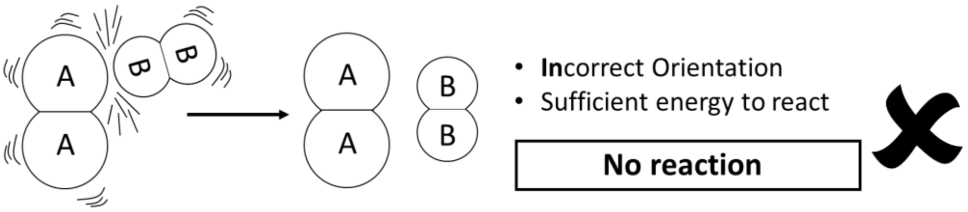
For a reaction between two particles to occur two conditions must be met:

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

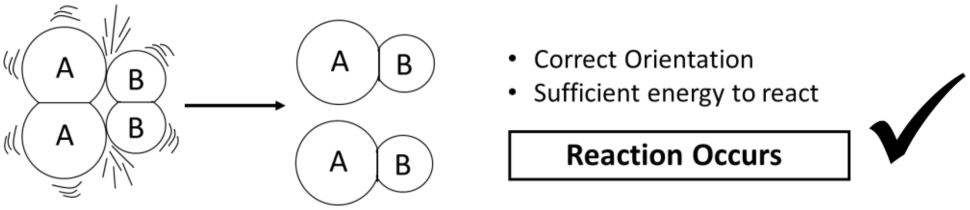
Note:
The greater the number of particles involved in a single step, the more difficult it is to have all of them to collide at the correct orientation to affect a reaction. Hence usually, only a maximum of two particles will collide in a particular step of a reaction.

Assuming product to be ,





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



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

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

(i) Increase in temperature of the reacting particles
(ii) Increase concentration of particles/ increasing surface area of solid particles
(iii) Use of catalyst

1.2 FACTORS AFFECTING RATE OF REACTION

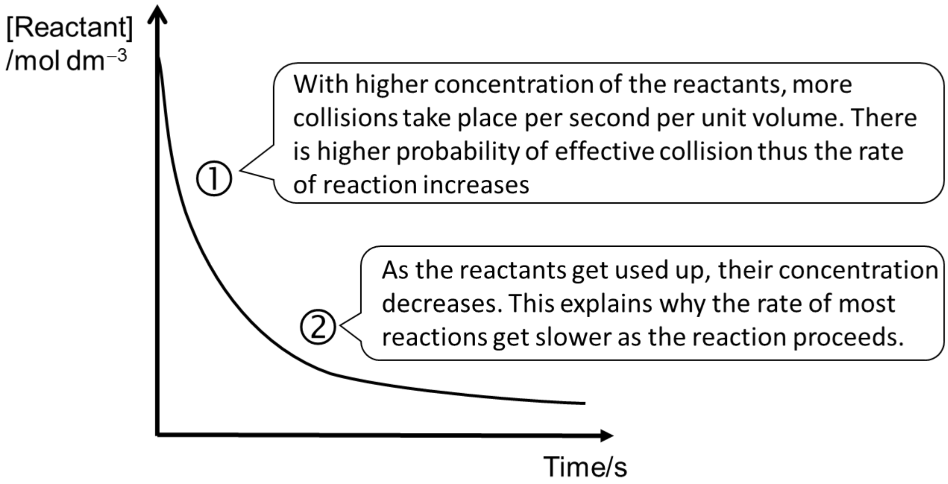
Learning Objectives:
- explain qualitatively, in terms of frequency of collisions, the effect of concentration changes on the rate of a reaction

1.2.1 Concentration of Aqueous or Gaseous Reactants

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

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

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

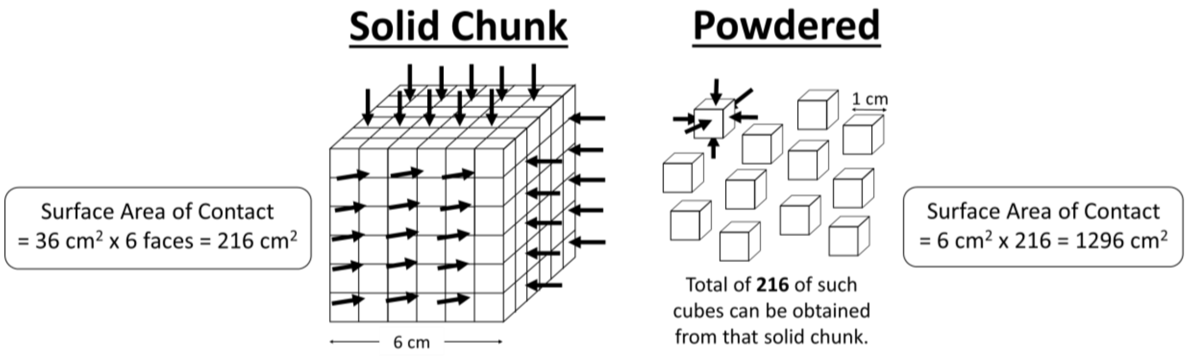


① With higher concentration of the reactants, more collisions take place per second per unit volume. There is higher probability of effective collision thus the rate of reaction increases

② As the reactants get used up, their concentration decreases. This explains why the rate of most reactions get slower as the reaction proceeds.

1.2.2 Surface Area of Solid Reactant

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



Surface Area of Contact = 36 cm^2 x 6 faces = 216 cm^2

Surface Area of Contact = 6 cm^2 x 216 = 1296 cm^2

The surface area of contact is increased dramatically by **6 times**, simply by breaking them into smaller 1cm^3 cubes. Imagine, powdering into even finer particles.

BOLTZMANN DISTRIBUTION CURVE

Learning objective:

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

Note for drawing Boltzmann distribution curve:

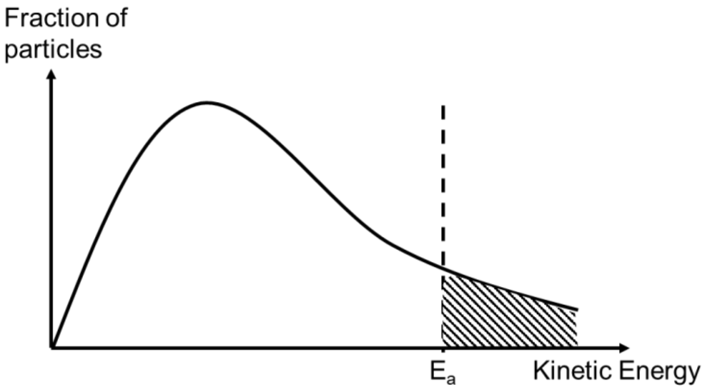
1) Graph must start from origin as there are no particles with zero energy.

2) Graph should taper off.

3) Shade the appropriate area under the curve to show proportion of particles with K.E. ≥ E_a.

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

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



1.2.3 Temperature

Learning objective:

- 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

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

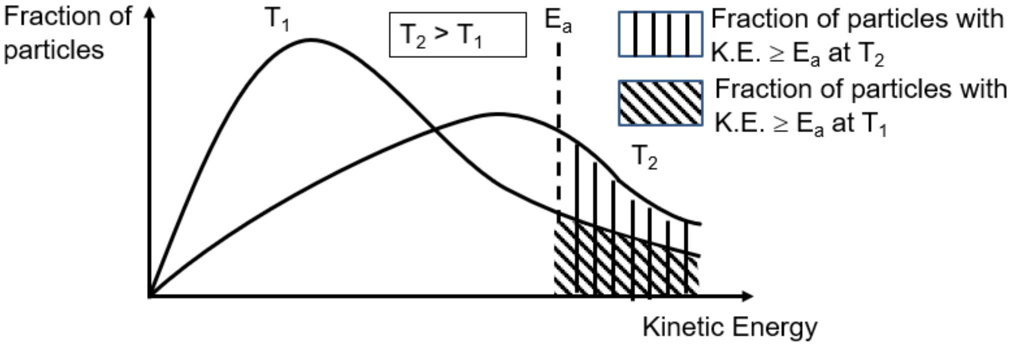
Worked example 1

$C_6H_5CH_2Cl$ undergoes a substitution reaction to form $C_6H_5CH_2CN$ as shown in the reaction below.

$$C_6H_5CH_2Cl + CN^- \longrightarrow C_6H_5CH_2CN + Cl^-$$

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

Note:
The area under the curve is a measure of the total number of particles present. This area is the same for both curves.



When temperature of the reaction decreases, average kinetic energy of the reacting molecules decreases. The fraction of molecules with K.E. ≥ E_a decreases as shown in the Boltzmann distribution. The frequency of effective collisions decreases hence rate of reaction decreases.

1.2.4 Catalyst

Learning objective:

- 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
- interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution

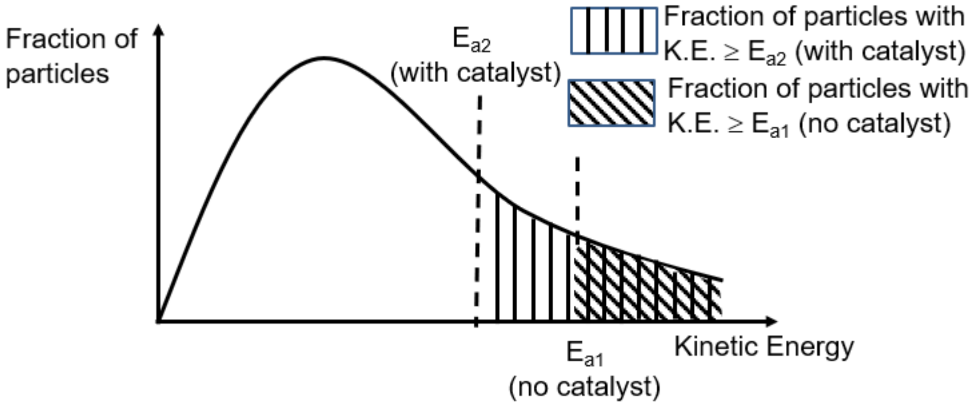
A catalyst speeds up the rate of a chemical reaction by **providing an alternative pathway with lower activation energy**. It does not undergo any permanent chemical change (not used up at the end of reaction). It exerts **no effect on the enthalpy change** of the reaction.

Worked example 2

Azomethane, $CH_3–N=N–CH_3$, is a common compound used in cancer research. It decomposes according to the following equation:

$$CH_3–N=N–CH_3\,(g) \longrightarrow CH_3CH_3\,(g) + N_2\,(g)$$

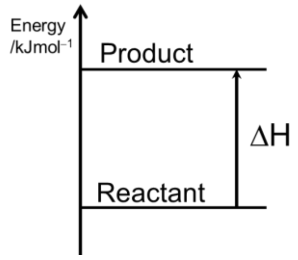
With the aid of the Boltzmann distribution, explain why the addition of a catalyst increases the rate of a reaction.



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

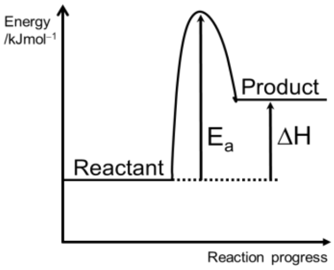
ENERGY PROFILE DIAGRAM

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



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

From the energy profile diagram, the following can be inferred:
(i) relative stability of reactants/ products
(ii) magnitude of activation energy in the reaction.



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

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

1.3 TYPES OF CATALYST

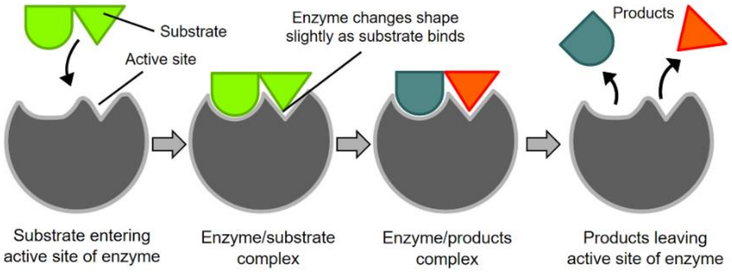
Learning objective:
- outline the mode of action of heterogeneous catalysis as exemplified by the catalytic removal of oxides of nitrogen in the exhaust gases from car engines
- describe enzymes as biological catalysts which may have specific activity

1.3.1 Biological catalyst (Enzymes)

Enzymes are complex globular proteins that catalyze biochemical reactions.

They contain an active site into which the reactant molecules of a particular shape and size will fit making them highly specific in their action.

The attractive forces between the reactant (substrate) molecule and the enzyme weakens the bonds within the substrate molecule, thereby lowering the activation energy and increasing the rate of reaction.



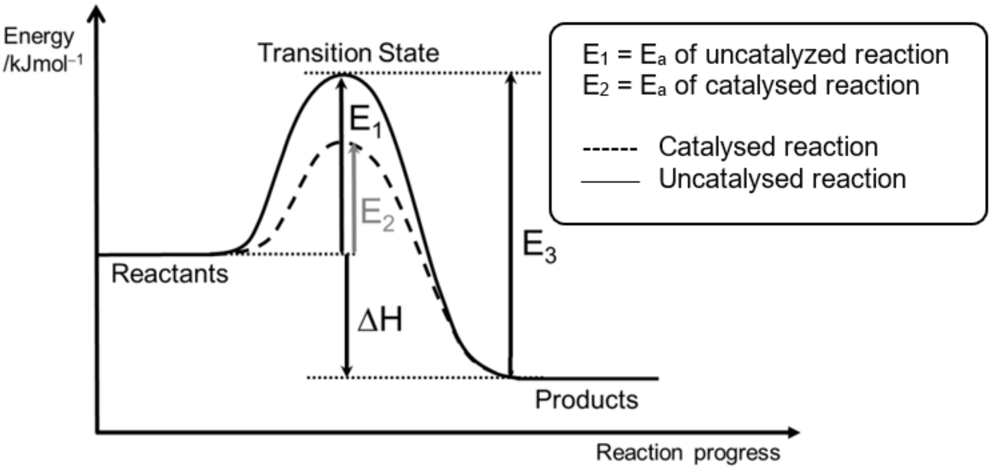
1.3.2 Heterogeneous Catalyst

Catalyst and the Reactants are in different phases.

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

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

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

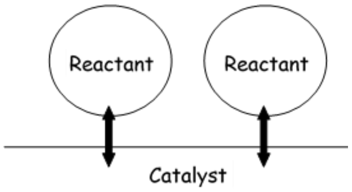


Mode of action in heterogeneous catalysis:

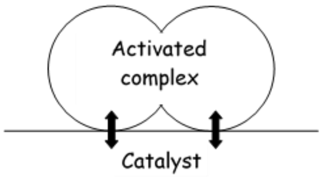
Note:
Adsorption is the adhesion of particles to a surface.

This is different from "a<u>b</u>sorption" where particles are drawn into the material.

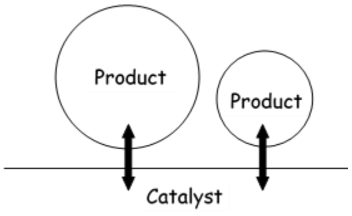
Step 1: **Adsorption** of reactant particles onto the surface of the catalyst. Weak interactions form between the reactant and catalyst.



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

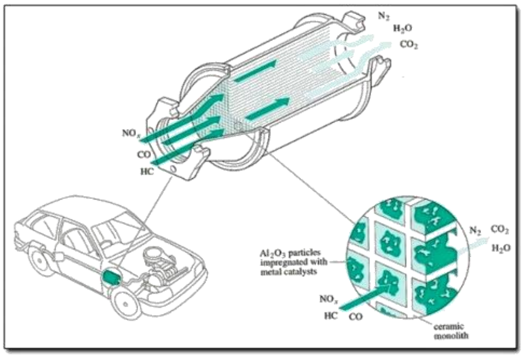


Step 3: **Desorption** of products from the catalyst surface. Catalyst is regenerated.



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

Catalytic removal of oxides of nitrogen in the exhaust gases



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

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

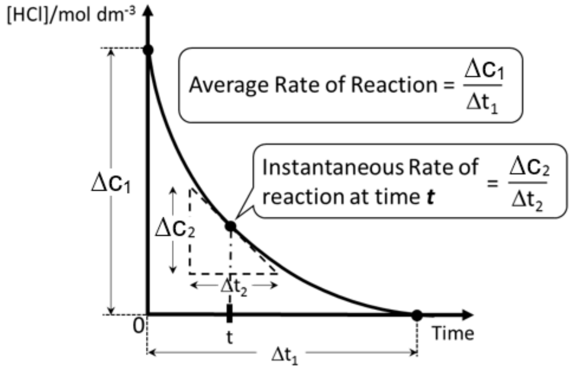
[O]: $2CO\ (g) + O_2\ (g) \longrightarrow 2CO_2\ (g)$
[O]: $C_xH_y\ (g) + (x + \frac{y}{4})O_2\ (g) \longrightarrow xCO_2\ (g) + \frac{y}{2}H_2O\ (l)$
unburnt
[R]: $2NO_x\ (g) \longrightarrow N_2\ (g) + xO_2\ (g)$

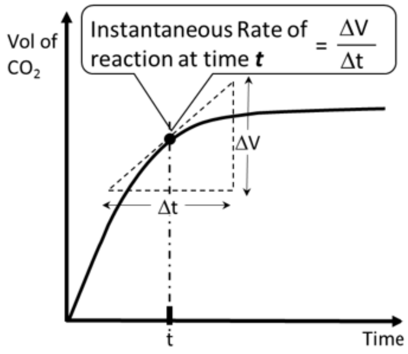
2 QUANTATITIVE KINETICS

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

2.1 DIFFERENCE BETWEEN INSTANTANEOUS RATE and INITIAL RATE

Consider: $2HCl\ (aq) + CaCO_3\ (s) \longrightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (l)$





Rate of a chemical reaction can be defined either as:

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

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

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

$$-\frac{d[BrO_3^-]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt}, \qquad \text{similarly, } -\frac{d[BrO_3^-]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt}$$

$$\text{Rate of Reaction} = -\frac{d[BrO_3^-]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt}$$

Based on the mole ratio of the reaction, on average
The rate of consumption of Br^- would be 5 × consumption rate of BrO_3^-.
The rate of production of Br_2 would be 3 × consumption rate of BrO_3^-.

- **Instantaneous rate** of reaction is the rate at a <u>particular point of time</u>, it can be determined by finding the gradient of the tangent at any one point of the concentration-time graph. This is what we are keen to know in order to understand the mechanism of a reaction.

- **Initial rate** of reaction is the reaction rate at the start of the reaction, when an extremely small amount of reactants is used up. It corresponds to the slope of the tangent when t = 0. At initial rate, the rate of reaction is the highest due to the greatest amount of reactant consumed.

2.2 THE RATE EQUATION

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

The rate equation is stipulated as follows:

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

Rate Constant (k)

- Proportionality constant to show dependence of rate of reaction on activation energy and temperature, which is consistent with collision theory.
- The value of k must be experimentally determined.
- Defined by Arrhenius Equation:

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

Not in syllabus

Order of Reaction

- **Can only be determined experimentally.**

- By **monitoring how rate** of a particular reaction **varies with changing concentration** of each reactant, rate equation can be **deduced**.

2.2.1 Order of Reaction

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

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

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

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

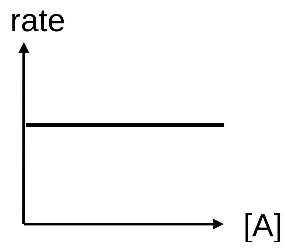
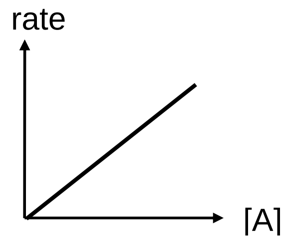
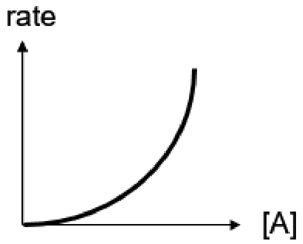
The **overall order** of the reaction = **x** + **y**.

WATCH and Learn

What is meant by 1st and 2nd order of reaction with respect to certain reactants in each elementary step? Watch https://go.gov.sg/njc-kinetics-10 to find out.

In H1 Chemistry, we will need to know zero, first and second order of reaction.

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

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

2.2.2 Rate constant, *k*

a. Factors affecting rate constant, *k*

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

Note:
The effect of the changed conditions on rate of reaction can be explained by the collision theory with the aid of Boltzmann distribution curve.

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

2.3 DEDUCING THE RATE EQUATION

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

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

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

2.3.1 Data Processing Methods to Deduce Rate Equation

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

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

In each of these methods, we will allow only 1 concentration to change and the other concentrations to stay constant. The concentrations which were kept constant may have impact on the rate of reaction but cannot be observed due to it being kept constant in that comparison / experiment.

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

2.3.1.1 Inspection/Mathematical Method

Learning Objectives:

- construct and use rate equations of the form rate = $k[A]^m[B]^n$ (limited to simple cases of single-step reactions, for which m and n are 0, 1 or 2), including:
  - deducing the order of a reaction by the initial rates method
  - calculating an initial rate using concentration data

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

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

Worked Example 3 **(Reaction of NO with O_2)**

The reaction kinetics of reaction between NO and O_2 was monitored using the initial rate method.

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

Experiment	[NO] / mol dm^{-3}	[O_2] / mol dm^{-3}	Initial rate / mol dm^{-3} h^{-1}
1	0.001	0.001	7×10^{-6}
2	0.001	0.002	14×10^{-6}
3	0.001	0.003	21×10^{-6}
4	0.002	0.003	84×10^{-6}

(a) Determine the order of reaction with respect to NO and O_2.

Method 1 : Inspection method

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

When $[O_2]_{expt2}$ is twice of $[O_2]_{expt1}$, rate (2) is twice of rate (1), therefore the order w.r.t O_2 must be one.

Compare expt 3 and 4 where [O_2] is the same.
When $[NO]_{expt4}$ is twice of $[NO]_{expt3}$, rate (4) is 4 times of rate (3), therefore the order w.r.t NO must be two.

Method 2 : Mathematical method

Let the rate equation be: rate = k $[NO]^x[O_2]^y$

Using expt 1 and 2, where [NO] is a constant,	Using expt 3 and 4, where [O_2] is a constant,
$\frac{\text{rate (2)}}{\text{rate (1)}} = \frac{\cancel{k(0.001)^x}(0.002)^y}{\cancel{k(0.001)^x}(0.001)^y}$	$\frac{\text{rate (4)}}{\text{rate (3)}} = \frac{\cancel{k}(0.002)^x\cancel{(0.003)^y}}{\cancel{k}(0.001)^x\cancel{(0.003)^y}}$
$\frac{14 \times 10^{-6}}{7 \times 10^{-6}} = \frac{(0.002)^y}{(0.001)^y}$	$\frac{84 \times 10^{-6}}{21 \times 10^{-6}} = \frac{(0.002)^x}{(0.001)^x}$
$2 = (2)^y$	$4 = (2)^x$
therefore y = 1.	therefore x = 2.
order w.r.t O_2 must be 1	order w.r.t. NO must be 2

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

(b) Deduce the rate equation.

rate = k $[NO]^2$ [O_2]

Checkpoint 1 

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

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

Deduce the order of reaction with respect to:

- butan−2−ol,
- H^+.

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

Worked Example 4 **(Appearance of colour)**

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

$$\mathbf{A + B \longrightarrow D}$$

The following results were obtained.

Experiment	Vol of **A** added / cm^3	Vol of **B** added / cm^3	Vol of H_2O added/ cm^3	Time taken for **0.01 mol dm^{-3} of D** formed / s	**rate**
1	10	20	30	20	**0.0005**
2	10	10	40	40	**0.00025**
3	20	40	0	5	**0.002**

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

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

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

Since change in [**D**] is the same for expts 1−3, therefore rate can be taken to be <u>inversely proportional</u> to time taken for certain amt or conc of **D** to be formed.

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

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

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

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

1) Inspection method for expt 1 and 2

Compare expt 1 and 2 <u>where [A] the same</u>.

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

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

Compare expt 1 and 3;

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

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

$$\frac{0.002}{0.0005} = \frac{(20)^x}{(10)^x} \times 2$$

$2 = 2^x$

therefore x = 1.

Rate equation: <u>Rate = k[A]^1[B]^1</u>

Note:
Varying volume of H_2O was added to the reaction mixture to keep the total volume of the reaction mixture constant.

For disappearance of colour,
rate = $\frac{\text{d [coloured rxt]}}{\text{dt}}$

Worked Example 5 **(Disappearance of colour)**

The reaction kinetics of the following reaction is being investigated.

$$\textbf{coloured P} + \textbf{Q} \longrightarrow \textbf{R} + \textbf{S}$$

The following results were obtained.

Expt	Vol of **P** added / cm^3	Vol of **Q** added/ cm^3	Vol of H_2O added/ cm^3	Time taken for **P** to decolourize/ s	**Relative rate**
1	10	20	10	20	$\mathbf{\frac{10}{20} = 0.5}$
2	10	10	20	40	$\mathbf{\frac{10}{40} = 0.25}$
3	5	20	15	10	$\mathbf{\frac{5}{10} = 0.5}$

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

Due to constant total volume, [reactant] ∝ $V_{reactant}$.

Compare expt 1 and 2 where [**P**] are the same;
When [**Q**]$_{expt1}$ is <u>**double**</u> of [**Q**]$_{expt2}$ (volume of **Q** added is doubled),
rate (1) is <u>**double**</u> of rate (2), therefore the reaction is <u>**first**</u> order w.r.t **Q**.

Compare expt 1 and 3 where [**Q**] are the same;
When [**P**]$_{expt1}$ is <u>**double**</u> of [**P**]$_{expt3}$ (volume of **P** added is doubled),
rate (1) is <u>**same as**</u> rate (3), therefore the reaction is <u>**zero**</u> order w.r.t **P**.

Hence, rate equation is rate = k [Q]

Checkpoint 2

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

$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

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

Experiment	Volume of $CH_2{=}CH_2$ in CCl_4 / cm^3	Volume of $Br_2(l)$ / cm^3	Volume of CCl_4 / cm^3	Time taken for colour of Br_2 to disappear/ s
1	20	20	0	15
2	12	20	8	25
3	20	10	10	15

Given that rate $\propto \frac{V_{Br_2}}{\text{time taken}}$

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

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

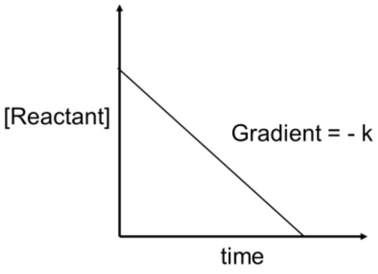
2.3.1.2 Graphical Method

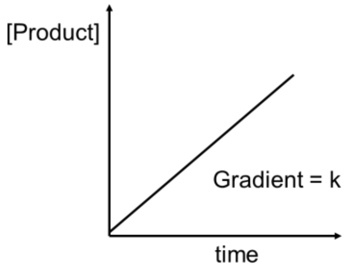
Learning Objectives:
- Justifying, for zero- and first-order reactions, the order of reaction from conc-time graphs
- show understanding that the half-life of a first-order reaction is independent of concentration

Concentration-Time Graph (Continuous Method)

To deduce Order of Reaction from Concentration-Time graph, check the **Shape of graph**

- **LINEAR**: Zero Order





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

→ It is zero order reaction w.r.t. A.

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

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

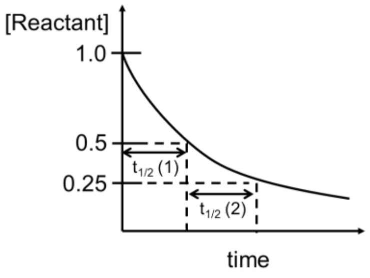
If the reaction has a **<u>constant</u>** half-life, the reaction is **<u>first order</u>** with respect to the investigated reactant.

- **Determining Half-life from Graph**

<u>[Reactant]-time graph</u>

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

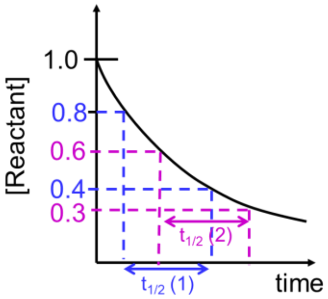
- <u>first</u> half-life ($t_{1/2}(1)$) is the time for the concentration to fall from 1.0 mol dm^{-3} to to 0.5 mol dm^{-3}.
- <u>second</u> half-life ($t_{1/2}(2)$) is the time for the concentration to fall from 0.5 mol dm^{-3} to 0.25 mol dm^{-3}.



Note:

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

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



For example,

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

Worked Example 6 **(Decomposition of H_2O_2)**

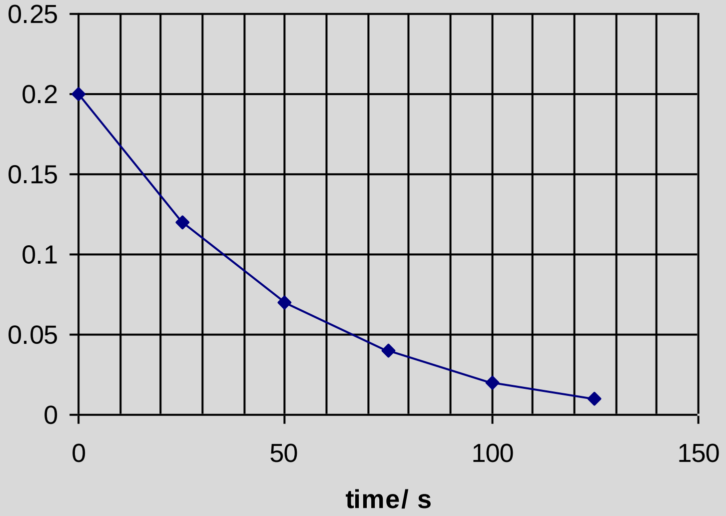
Hydrogen peroxide undergoes catalyzed decomposition.

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

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

Time / s	0	25	50	75	100	125
$[H_2O_2]$ / mol dm^{-3}	0.20	0.12	0.07	0.04	0.02	0.01

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



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

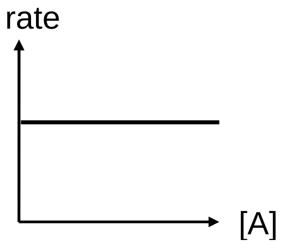
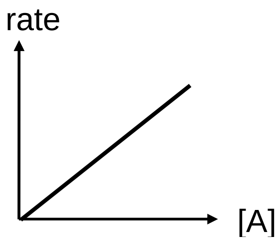
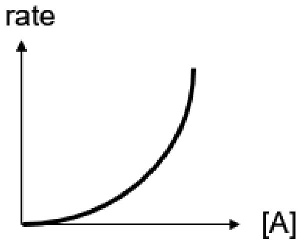
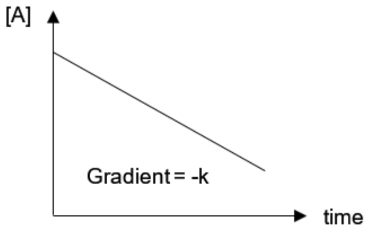
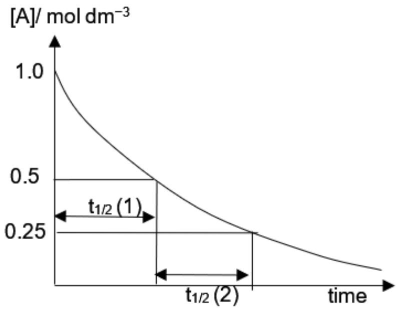
*As reaction proceeds, <u>$[H_2O_2]$ decreases</u>. It is observed that the <u>rate of reaction (gradient of conc vs time graph) decreases with a</u> <u>**constant half-life**</u> <u>of 33s</u>.*

→ It is first order reaction w.r.t. H_2O_2

(b) Write a rate equation for the reaction.

Rate = k $[H_2O_2]$

Summary of Reaction Rate and Concentration

Order of reaction	**0**	**1**	**2**
Example	**A $\longrightarrow$ products**	**A $\longrightarrow$ products**	**2A $\longrightarrow$ products**
Rate equation	Rate = k $[A]^0$	Rate = k [**A**]	Rate = k [**A**] ^{2}
Graph of rate vs [A]			
Graph of [A] vs time Gradient = rate of reaction			Not applicable for H1 chemistry
Notes	Rate of reaction is unaffected by concentration of reactants. Gradient of conc vs time graph is constant.	Rate of reaction decreases as [reactants] decreases. Gradient of conc vs time graph decreases with time. Half-life is constant	

BASIC CONCEPTS IN KINETICS		
	Success Criteria	✓
	I am able to:	
(a)	explain qualitatively, in terms of **frequency of collisions**, the effect of the following on the rate of a reaction **(i)** concentration changes **(ii)** temperature change	
(b)	explain qualitatively, with the use of a **Boltzmann distribution** curve, the effect of the following on the rate of a reaction (and rate constant) **(i)** temperature change **(ii)** addition of catalyst	
(c)	explain that, in the presence of a catalyst, a reaction has a different mechanism (pathway) with a lower activation energy, giving a larger rate constant	
(d)	outline the mode of action of **heterogeneous catalysis** as exemplified by the catalytic removal of oxides of nitrogen in the exhaust gases from car engines	
(e)	describe enzymes as biological catalysts which may have specific activity	
QUANTATITIVE KINETICS		
	Success Criteria	✓
	I am able to:	
(f)	construct and use rate equations of the form rate = $k[A]^m[B]^n$ (limited to simple cases of single-step reactions for which m and n are 0, 1 or 2), including:	
(g)	determine order of reaction using the following methods **(i)** using initial rate method • determine order of reaction via inspection or mathematical method **(ii)** using continuous method • determine order of reaction via shape of concentration-time graph and half-life	

Discussion Questions

1 The initial rate of the reaction **X** + **Z** $\longrightarrow$ **P** + **Q** was measured as a function of the concentration of each reactant. The following results were obtained:

Expt	[**X**] / mol dm^{-3}	[**Z**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.30	9.0×10^{-3}
2	0.20	0.40	12.0×10^{-3}
3	0.40	0.40	48.0×10^{-3}

(a) Determine the order of reaction with respect to **X**, **Y** and **Z**.
(b) Write the rate equation.

2 The kinetics of the reaction between iodide and peroxodisulfate can be investigated by varying the volume of the reactants used. The two reactants are mixed in the presence of a known amount of $Na_2S_2O_3$ and a little starch. The time taken for an intense blue colour to be observed is then determined.

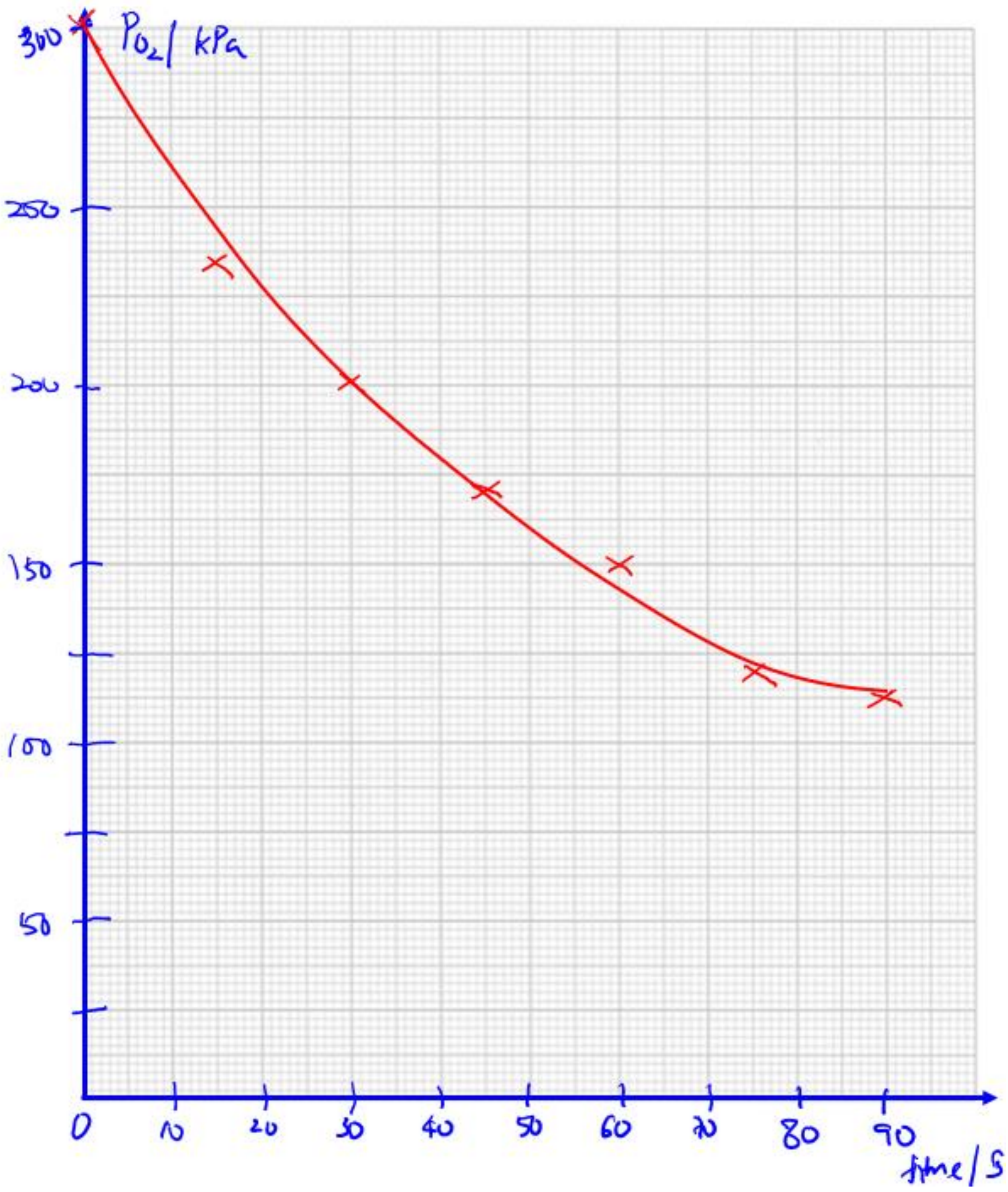
Experiment	Volume used/cm^3			t/s
	1.0 mol dm^{-3} KI	0.040 mol dm^{-3} $Na_2S_2O_8$	H_2O	
1	10.0	5.0	25.0	170
2	15.0	5.0	20.0	113
3	15.0	10.0	15.0	57
4	20.0	20.0	0.0	x

What is the value of x?

A 21 **B** 28 **C** 85 **D** 63

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

$$3O_2(g) \rightarrow 2O_3\,(g)$$



Determine the order of reaction with respect to oxygen

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

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

(i) increasing the pressure

(ii) decreasing the temperature

(iii) addition of a catalyst

5 The decomposition of hydrogen peroxide is a first order reaction.

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad \Delta H = -98 \text{ kJ mol}^{-1}$$

The uncatalysed reaction has an activation energy of 79 kJ mol^{-1}.

(a) Use the data provided to construct a reaction pathway diagram for this uncatalysed reaction.

(b) Explain what is meant by the term *activation energy*.

(c) The enzyme catalase act as catalysts, and speed up the reaction.

What effect will the presence of the catalyst have on the rate constant for this reaction? Explain your answer.

<u>Multiple Choice Questions</u>

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

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

7 The decomposition

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is first order with respect to N_2O_5.

In an experiment, 0.10 mol of pure N_2O_5 was put into an evacuated flask. It was found that there was 0.025 mol of N_2O_5 left 34 minutes later.

Which statement is true?

A It took 17 minutes for the amount of NO_2 to rise from 0 mol to 0.10 mol

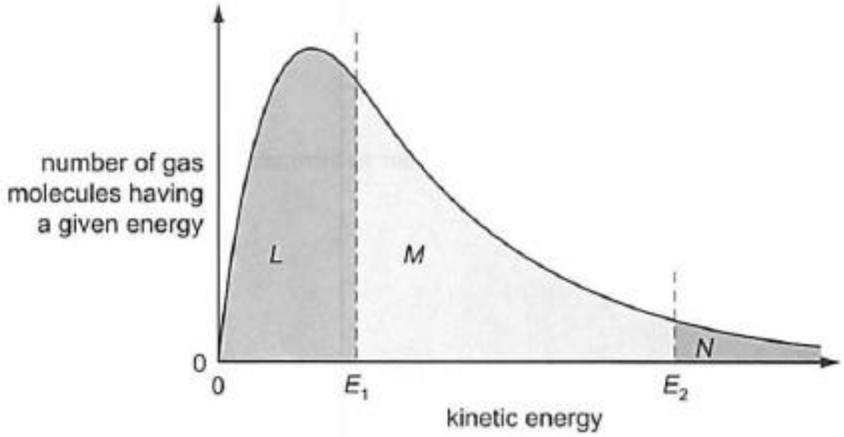
B There was 0.0625 mol of N_2O_5 left after 17 minutes.

C There was 0.0125 mol of N_2O_5 left after 68 minutes.

D The amount of NO_2 in the flask went up by four times in the first 34 minutes.

8 The Boltzmann distribution shows the number of gas molecules having a particular kinetic energy at constant temperature.

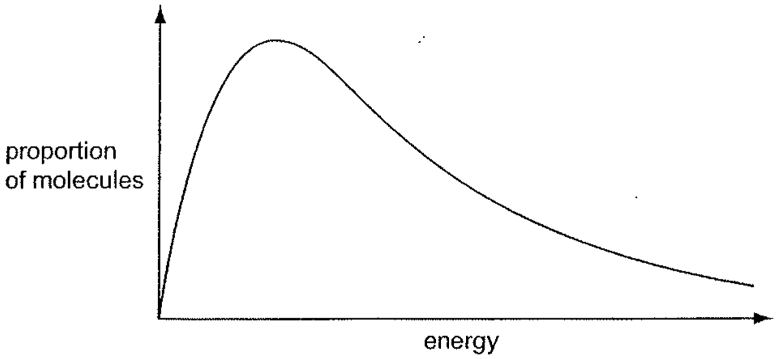
E_1 and E_2 are fixed energy values.



If the temperature is decreased, what happens to the size of the areas labelled *L*, *M* and *N*?

	L	*M*	*N*
A	decreases	decreases	decreases
B	decreases	increases	decreases
C	increases	decreases	decreases
D	increases	decreases	increases

9 The diagram represents the Boltzmann distribution of molecular energies at a given temperature.



As temperature increases, which statements are correct?

1 The maximum of the curve is displaced to the right.

2 The proportion of molecules with energies **above** any given value increases.

3 The proportion of molecules **with** any given energy increases.

A	B	C	D
1, **2** & **3** are correct	**1** & **2** only are correct	**2** & **3** only are correct	**1** only are correct