

Anglo-Chinese School (Independent)





TOPIC 6 CHEMICAL KINETICS

(IBDP syllabus Topic 6)

- 6.1 Collision theory and rates of reaction
 - Essential Idea: the greater the probability that molecules will collide with sufficient energy and proper orientation, the higher the rate of reaction.

(IBDP syllabus Topic 16)

16.1 Rate expression and reaction mechanism

- Essential Idea: rate expressions can only be determined empirically and these limit possible reaction mechanisms. In particular cases, such as a liner chain of elementary reactions, no equilibria and only one significant activation barrier, the rate equation is equivalent to the slowest step of the reaction.

16.2 Activation energy

- Essential Idea: the activation energy of a reaction can be determined from the effect of temperature on reaction rate.

6.1 Collision theory and rates of reaction

Solution Nature of science:

The principle of Occam's razor (also known as Law of ecnonmy) is used as a guide to developing a theory – although we cannot directly see reactions taking place at the molecular level, we can theorise based on the current atomic models. Collision theory is a good example of this principle (2.7) It states that Pluralitas non est ponenda sine necessitate, "Plurality should not be posited without necessity." (Encyclopedia Britannica). Newer theories need to remain as simple as possible while maximizing explanatory power.

Understandings:

- Species react as a result of collisions of sufficient energy and proper orientation.
- The rate of reaction is expressed as the change in concentration of a particular reactant or product per unit time.
- Concentration changes in a reaction can be followed indirectly by monitoring changes in mass, volume and colour.
- Activation energy (E_a) is the minimum energy that colliding particles need in order to have successful collision leading to a reaction.
- By decreasing E_a, a catalyst increases the rate of a chemical reaction, without itself being permanently chemically changed.

Applications and skills:

- Description of the kinetic theory in terms of the movement of particles whose average kinetic energy is proportional to temperature in Kelvin.
- Analysis of graphical and numerical data from rate experiments.
- Explanation of the effects of temperature, pressure/ concentration and particle size on rate of reaction.
- Construction of Maxwell–Boltzmann energy distribution curves to account for the probability of successful collisions and factors affecting these, including the effect of a catalyst.
- Investigation of rates of reaction experimentally and evaluation of the results.
- Sketching and explanation of energy profiles with and without catalysts.

Guidance:

- Calculation of reaction rates from tangents of graphs of concentration, volume or mass vs time.
- Familiarisation with the interpretation of graphs of changes in concentration, volume or mass vs time.

16.1 Rate expression and reaction mechanism

Solution Nature of science:

The principle of Occam's razor (also known as Law of ecnonmy) is used as a guide to developing a theory – although we cannot directly see reactions taking place at the molecular level, we can theorise based on the current atomic models. Collision theory is a good example of this principle (2.7) It states that Pluralitas non est ponenda sine necessitate, "Plurality should not be posited without necessity." (Encyclopedia Britannica). Newer theories need to remain as simple as possible while maximizing explanatory power.

Understandings:

- Reaction may occur by more than one step and the slowest step determines the rate of reaction (rate-determining step/ RDS)
- The molecularity of an elementary step is the number of reactant particles taking part in that step.
- The order of reaction can be either integral or fractional in nature. The order of a reaction can describe, with respect to a reactant, the number of particles taking part in the rate-determining step.
- Rate equations can only be determined experimentally.
- The value of the rate constant (k) is affected by temperature and its units are determined from the overall order of the reaction.
- Catalysts alter a reaction mechanism, introducing a step with a lower Ea.

Applications and skills:

- Deduction of the rate expression for an equation from the experimental data and solving problems involving the rate expression.
- Sketching, identifying and analysing graphical representations for zero, first and second order reactions.
- Evaluation of proposed reaction mechanisms to be consistent with kinetic and stoichiometric data.

Guidance:

- Calculation of order of reactions with whole number values.
- Interpretation of concentration-time and rate-concentration graphs.
- Using potential energy level profiles to show multi-step reactions; identifying the ratedetermining step as the one with the highest E_a.
- Catalysts are involved in the rate-determining step.
- Reactions where the rate-determining step is not the first step should be considered.
- Any experiment which allows students to vary concentrations to see the effect upon the rate and hence determine a rate equation is appropriate.

16.2 Activation energy

Solution Nature of science:

Theories can be supported or falsified and replaced by new theories – changing the temperature of a reaction has a much greater effect on the rate of reaction than can be explained by its effect on collision rates. This resulted in the development of the Arrhenius equation which proposes a quantitative model to explain the effect of temperature change on reaction rate. (2.5)

Understandings:

- The Arrhenius equation uses the temperature dependence of the rate constant to determine the $\mathsf{E}_{\mathsf{a}}.$
- A graph of $\ln k v s \frac{1}{T}$ is linear plot with gradient $\frac{-E_a}{RT}$ and the y-intercept $\ln A$.
- The frequency factor (or pre-exponential factor), A, takes into account the frequencies of collisions with proper orientations.

Applications and skills:

- Analysing graphical representation of the Arrhenius equation in its linear form, $\ln k = \frac{-E_a}{PT} + \ln A$
- Using the Arrhenius equation, $k = Ae^{\frac{-E_a}{RT}}$.
- Describing the relationships between temperature and rate constant; frequency factor and complexity of molecules colliding.
- Determining and evaluating values of activation energy and frequency factors from data.

Guidance:

• Using energy level diagrams to illustrate multi-step reactions showing the rate-determining step in the diagram.

• Consider various data sources in using the linear expression $\ln k = \frac{-E_a}{RT} + \ln A$. The expression

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$
 is given in the data booklet.

6.1 Rates of Reaction

Overview

- Reaction kinetics is concerned with measuring the rate of a reaction and the sequence of step(s) by which it occurs.
- The study of reaction kinetics would allow us to:
 - o determine how fast a reaction would take place,
 - o determine conditions required for optimum reaction rates,
 - o propose a reaction mechanism by which the reaction takes place.

6.1.1 Definition of the Term Rate of Reaction

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

• Mathematically, rate = $-\frac{d[reactant]}{dt} = \frac{d[product]}{dt}$

The negative sign is placed in front of the differential expression for the reactants because their concentrations decrease as the reaction progresses, resulting in a decrease in their various concentrations.

- The units of the rate of reaction is usually expressed as mol dm⁻³ s⁻¹ or mol dm⁻³ min⁻¹.
- For example, consider the reaction:

 N_2O_4 (g) $\rightarrow 2NO_2$ (g)

where two moles of $2NO_2$ (g) are produced from one mole of N_2O_4 (g).

Rate of formation of NO₂ (g) = 2 x rate of disappearance of N₂O₄ (g) rate = $-\frac{d[N_2O_4]}{dt} = \frac{1}{2} \frac{d[NO_2]}{dt}$

• In general, consider the general chemical equation,

 $aA + bB \rightarrow cC + dD$

the rate of reaction can be expressed in a generalised differential form given below, where *a*, *b*, *c*, *d* are the stoichiometric coefficients.

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

• A common way to determine the rate of a reaction is from calculating the gradient of the tangent of a concentration (**either** reactant **or** product)–time graph.



- There are three types of rates of reaction which can be deduced from a concentrationtime graphs.
 - o Initial rate
 - The rate at the start of the reaction when an infinitesimally small amount of reactant has been used up.
 - It is the gradient of the tangent at t = 0 as shown in the [reactant]-time or graph [product]-time below.



 For most reactions, initial rate is usually the greatest as rate decreases as reaction proceeds. This is due to the highest initial concentration of reactants, which results in highest frequency of effective collisions.

o Instantaneous rate

- The rate of reaction at a particular instant in time.
- It is given by calculating the gradient of the tangent at a particular time, t, of a [reactant]-time **or** graph [product]-time graph.



• Average rate

The rate of a reaction calculated from the change in concentration of a reactant or product over a particular period of time.



Exercise 1

1. Express the rate of reaction in terms of the change in concentration of the reactants and products for the following reaction:

$$BrO_{3^{-}}(aq) + 5Br^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_{2}(aq) + 3H_{2}O(l)$$

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

2. 500 cm³ of aqueous nitric acid (0.500 mol dm⁻³) is added to some marble chips and the gas evolved is collected in a gas syringe; 1200 cm³ of gas is collected in 5.0 min. The chemical equation for the reaction is shown below.

 $CaCO_3 (aq) + 2HNO_3 (aq) \rightarrow Ca(NO_3)_2 (aq) + CO_2 (g) + H_2O (l)$

Calculate the average rate of this reaction. Suggest another property that can be monitored to determine the rate of this reaction. (Assume all gases are measured at SATP.)





6.1.2 Describe Suitable Experimental Procedures for Measuring Rates of Reactions

- Reaction rates are experimentally determined through the measurement of the change in concentration of either the reactant or product during a reaction.
- Experiments performed to find the order of reaction involve either:
 - **Discontinuous measurement** where the rate–concentration relationship is established, or
 - **Continuous measurement** where the concentration-time relationship is established.
- The common properties that are monitored during a reaction to determine the change in concentrations are,
 - o the concentrations of the reactants or products;
 - the pH of the reacting mixture;
 - o the volume of gases evolved;
 - the change in mass of the reacting mixture;
 - o colour of the reacting mixture;
 - electrical conductivity of the reacting mixture.
- Some common methods that are practised in the laboratories are described as follow.

(i) Chemical methods of analysis - titration method (Continuous measurement)

- In this method, reactants of known concentrations and measured volumes are mixed and a stop–watch is started at the point of mixing. Samples of the reaction mixture are withdrawn at regular time intervals.
- When the sample volume is withdrawn, the reaction in the sample has to be significantly slowed down or stopped. This process of significantly slowing down or stopping a reaction is called **quenching.** Quenching is necessary so that the concentration of a particular reactant in the remaining standard solution can be determined.
- The sample volume can be quenched by
 - ✓ adding a *large volume of cold solvent*, which slows a reaction down by diluting considerably the reactants and reducing the temperature;
 - ✓ adding a "quenching reagent" which would react immediately with one of the reactants and hence, stop the reaction;
 - ✓ adding an inhibitor or negative catalyst to slow down the reaction.
- Each quenched sample is titrated with suitable reagent to determine the concentration of the remaining reactant or product formed at a particular time, as illustrated in Figure 6.3.



Figure 6.1: Titration method





Figure 6.2: Titration method

The rate of reaction may be studied by determining the amount of unreacted iodine in the reaction mixture at different times.

Portions of the reaction mixture are pipetted at regular time intervals into aqueous $Na(HCO_3)_2$ or Na_2CO_3 solution which quenches the reaction by neutralizing the acid catalyst. The quenched mixture is then titrated against a standard solution of sodium thiosulfate to determine the amount of unreacted iodine. The equation for the reaction of sodium thiosulfate and iodine is shown below.

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

The volume of thiosulfate solution would indicate directly the concentration / amount of iodine left in the reacting mixture. Hence the rate of the reaction can be determined.

The order of reaction with respect to iodine may also be found by plotting a graph of volume of $S_2O_3^{2-}$ (aq) against time.

A straight line graph is obtained which shows that the rate of reaction is constant even as the amount of iodine in the reaction flask decreases with time. We can hence conclude that the reaction is zero order with respect to iodine.





Figure 6.3: Graph of volume of thiosulfate used in titration against time

Example 2: Base catalysed decomposition of hydrogen peroxide

$$\begin{array}{c} \text{base} \\ 2\text{H}_2\text{O}_2 \text{ (aq)} & \rightarrow & 2\text{H}_2\text{O} \text{ (l)} + \text{O}_2 \text{ (g)} \end{array} \end{array}$$

The rate of reaction may be studied by determining the amount of unreacted H_2O_2 (aq) in the reaction mixture at different times. At various time intervals after the start of the reaction, portions of the reaction mixture are pipetted into dilute H_2SO_4 that stops the reaction by neutralising the base catalyst.

The quenched mixture is then analysed by titrating against acidified KMnO₄, where the unreacted H_2O_2 will be oxidised by KMnO₄. The rate of reaction may be found by plotting volume of MnO₄⁻ against time (since volume of MnO₄⁻ is proportional to the concentration of H_2O_2 remaining).



Figure 6.4: Graph of volume of manganate(VII) used in titration against time

The graph obtained is a curve with a constant half–life showing that the reaction is first order with respect to H_2O_2 .

(ii) Physical methods of analysis

(a) Measuring changes in gas volume (Continuous measurement)

• For reactions that involve formation of gaseous product, the rate of reaction may be studied by determining the volume of gas produced per unit time (where the gas is collected in a syringe) or by determining the loss in mass per unit time (where the gas is allowed to escape).

Example 3: Reaction of calcium carbonate with dilute hydrochloric acid

For the reaction below:

 $CaCO_3$ (s) + 2HCl (aq) \rightarrow CaCl₂ (aq) + CO₂ (g) + H₂O (l)

- The rate of reaction may be studied by determining the volume of CO₂ (g) produced at different times. Carbon dioxide gas is first collected in a gas syringe and its volume is measured at regular time intervals during the reaction.
- The rate of reaction may be found by plotting volume of carbon dioxide gas against time. At any given time, *t*, the rate of reaction is given by the *gradient* of the tangent of the graph at time t (Figure 6.5).



Figure 6.5: Experimental setup for measuring rate of reaction via volume of gas evolved

The order of reaction with respect to the acid may be found by plotting rate against $(V_n - V_t)$ or by plotting $(V_n - V_t)$ against time, where,

 V_t : volume of CO₂ after time t; proportional to the amount of reactant that has reacted

 V_n : volume of CO₂ evolved at the end of the reaction; proportional to the total amount of reactant

 $V_n - V_t$ is proportional to the amount of reactant remaining unreacted at time t.

(b) Measuring changes in colour intensity (colourimetry) (Continuous measurement)



Figure 6.6: Internal Setup of a Colorimeter

• The colour intensity of a reaction mixture may change during the course of a reaction if one of the reactants or products has a colour.

- By Beer–Lambert Law, the colour intensity of a compound is proportional to its concentration. The higher the intensity, the greater will be the absorbance value.
- In short, Beer–Lambert Law is defined as,

Abs =
$$\epsilon l c$$
,

where,
Abs: absorbance of the solution
ε : molar absorptivity or extinction coefficient *l* : path length
c : concentration of the coloured species being studied.

• The change in concentrations of a reactant/ product may be monitored by following the change in colour intensity thus the rate of reaction can be determined.

Example 4: Acid catalysed reaction of propanone with iodine

 $CH_3COCH_3 (aq) + I_2 (aq) \xrightarrow{H^+} CH_2ICOCH_3 (aq) + HI (aq)$ red-brown

- In Example 4, the amount of iodine remaining in the reacting mixture is determined by titration with sodium thiosulfate at regular time intervals.
- However, as the iodine molecules are the only coloured substance in this reaction, the concentration of the iodine molecules can also be monitored by measuring the intensity / absorbance of the brown coloration due to iodine molecules.
- The decrease in the intensity of its reddish–brown colour as measured in a colorimeter correlates to the decreasing concentration of iodine in the reacting mixture.
- The experiment is repeated by varying the initial concentration of each of the reactants (propanone, iodine and acid) in turn, keeping the other two constant.
- The order of reaction may be found by plotting $[I_2]$ against time (since colour intensity $\propto [I_2]$).



• From the graphs, it can be deduced that the reaction is first order with respect to CH₃COCH₃, zero order with respect to I₂ and first order with respect to H⁺.

(c) Measuring changes in electrical conductivity (Continuous measurement)



Figure 6.8: Measuring the resistance of a solution with a conductance bridge

• In some chemical reactions, the resistance of the solution will change during the course of the reaction if the total number of ions or the conducting mobility of the ions at the beginning is different from that at the end of the reaction.

Example 5: NaOH (aq) + CH₃COOH (aq) \rightarrow CH₃COO⁻Na⁺ (aq) + H₂O (l)

• As the OH⁻ ions have much higher conducting mobility than the CH₃COO⁻ ions, a change in conductivity of the reaction mixture will occur, when the OH⁻ ions are being replaced by the CH₃COO⁻ ions.

(iii) Stop clock methods of analysis (Discontinuous measurement)

- Measuring the time taken for the appearance / disappearance of a particular colour (clock reaction)
- In some chemical reactions there may be some observable changes after the reaction has been progressing for some time. If the reaction is fast, the time to reach such a stage will be short. Conversely, if the reaction is slow, this time will be long. The time interval to reach this particular stage in the reaction is therefore inversely proportional to the average rate of reaction over that time interval.

Average rate
$$\infty \frac{1}{\text{total time}}$$

• Data collected via the stop clock methods does not allow the Concentration vs Time graph to be plotted. Thus this method will not yield the initial rate or instantaneous rate of the reaction under investigation.

Example 6: Reaction between sodium thiosulfate solution and hydrochloric acid



 The reaction produces a creamy yellow precipitate of colloidal sulfur slowly according to this equation:

$$S_2O_3^{2-}$$
 (aq) + 2H⁺ (aq) \rightarrow SO₂ (g) + S (s) + H₂O (l)

The time required for the formation of a certain amount of sulfur can be measured. A simple way to do this is to carry out the reaction in a beaker standing on a piece of white paper on which a cross has been marked. Looking vertically down into the reaction mixture in the beaker, the cross will gradually become faint as the precipitate forms. It will be completely obscured when a certain concentration of sulfur is present, as shown in Figure 6.9.



Figure 6.9: Measuring rate of reaction by timing how long sulfur takes to form

• Therefore,

Average rate of reaction over that particular time interval

total time taken to blot out the cross

• Or if sodium thiosulfate is the limiting reactant, then

Average rate of reaction over time interval vol. of sodium thiosulfate $\frac{1}{1}$ time taken to blot out the cross

- It should be noted for this type of experiment the precision of the results is subjective. It will vary according to the experimenter's perception of when the cross has been fully obscured. As such, whilst such a method provides a convenient and quick way of determining rate of reaction, the experimental results will not be very accurate.
- This method is only suitable for reactions in which product formation can be detected in a reasonably short time. Thus the rate can be approximated as the initial rate because the concentrations of the reactants remain very close to the initial concentrations.

6.2 The Collision Theory

Application of Occam's razor on the development of Collision Theory (Refer to Pg 166 of Chemistry Course Companion)

6.2.1 The Kinetic Theory

- Reactant particles are moving at high velocities and in random motion. The particles frequently collide with each other and the walls of the container. Their attractive and repulsive forces are negligible.
- The collisions are elastic and energy is transferred between molecules during collisions, but average kinetic energy is unchanged (as long as temperature is constant).
- A proportional rise in the temperature (K) of the particles corresponds to an increase in average kinetic energy of the particles.

6.2.2 Activation Energy, E_a

• The activation energy, E_a, is the minimum amount of energy which the reactant particles must possess for a collision to result in a reaction.



Figure 6.10: Energy profile diagram

6.2.3 The Collision Theory

- The collision theory states that for a reaction between two reactant particles to take place, three conditions must first be satisfied:
 - o the particles must **collide** with each other;
 - the particles must collide in the **correct orientation**;

For example, for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$



- the particles must collide with **sufficient kinetic energy** that minimally meets the requirement of the activation energy for the collisions.
- As a result of these three conditions, which must be fulfilled, only a small number of collisions will result in a reaction.
- Collisions that result in the formation of the products are called effective collisions.

6.2.4 Factors Affecting the Rate of Reaction

- The main factors that may affect the rate of a reaction are:
 - Particle size of solid reactants
 - Concentration / pressure of liquid / gaseous reactants
 - o Temperature
 - o Catalyst
- The collision theory can be used to explain the effects of particle size, temperature,
- concentration and pressure on the rate of a reaction.

(i) Effect of particle size of the solid reactants

- For a chemical reaction involving a solid, only the particles on its surface are available for the reaction.
- The smaller the particle size of a solid, the larger the surface area over which the other reactants can make contact. Thus decreasing the particle size of the solid will increase the fraction of particles available for collision, increasing frequency of effective collision and hence the rate of reaction (Figure 6.11).





granulated solid

powdered solid

Figure 6.11: Solid in powdered form has larger surface area than granulated form

(ii) Effect of concentration and pressure

- Increasing the concentration of a reactant (or the pressure of a gaseous reactant) will increase the number of particles in a unit volume. This will increase the frequency of effective collisions and hence the rate of reaction.
- The curve in Figure 6.12 is steeper for the more concentrated acid, indicating a higher rate of reaction. (CaCO₃ is the limiting reagent.)



Figure 6.12: Graph showing how rate varies with concentration

(iii) Effect of temperature

 The Maxwell–Boltzmann energy distribution curve (Figure 6.13) is a characteristic curve which shows the distribution of kinetic energy of reactant particles for a fixed amount of gas. It is mathematically represented by a continuous distribution and is often used to compare the relative kinetic energy of reactant particles at different temperatures.



Figure 6.13: Maxwell–Boltzmann energy distribution curve

When the temperature increases, the reactant particles gain kinetic energy. The fraction of particles possessing energy equal to or greater than the activation energy increases. This results in an increase in the frequency of effective collisions between them.



Figure 6.14: Effect of temperature on energy distribution curve

Things to note for drawing of Maxwell–Boltzmann diagram ($T_2 > T_1$)

- The graph T₂ (higher T) must be <u>broader and more flattened</u> than the T₁ (lower T) graph.
 The maximum point of T₂ graph should be to the right of the maximum point of T₁ graph.
- The last part of the graph tapers towards but **does not touch the x-axis**.
- All labelling must be accurate including the legend.

- The area under the curve is proportional to the total number of particles involved. For a fixed mass of gas, the total number of particles is the same at both temperatures, the areas under the two curves must also be the same.
- At a higher temperature, T₂, more particles possess higher kinetic energy, thus shifting the peak towards the right and the shape of the distribution 'flattened out', as fewer particles possess the new average value as the distribution has widened and the number of particles with high kinetic energy has increased.
- The shaded area indicates the increased in the number of particles possessing kinetic energy more than or equal to the activation energy, E_a, hence leading to an increase in frequency of effective collisions and rate of reaction.

(iv) Effect of catalyst on rate of reaction

- A catalyst is a substance that increases the rate of a chemical reaction without being chemically changed at the end of the reaction.
- The catalyst provides an alternative pathway with a lower activation energy, which results in a greater proportion of particles having energy greater than the activation energy (Figure 6.15). This results in an increase in the frequency of effective collisions between them.







Figure 6.16: Maxwell–Boltzmann Distribution Curve for Catalysed and Uncatalysed reaction.

Exercise 2

Data analysis

 The graph below shows the results for five experiments involving the reaction between 1 mol dm⁻³ hydrochloric acid and excess marble.



Details of the experimental conditions are given in the table below.

Experiment	1	2	3	4	5
Volume of acid / cm ³	60.0	30.0	30.0	15.0	60.0
Volume of water / cm ³	30.0	30.0	30.0	15.0	30.0
Temperature of mixture / °C	40.0	20.0	40.0	40.0	40.0
Marble (w = whole) (p = powdered)	w	w	w	w	р

(a) For each experiment (1 to 5) identify the correct graph A to E.

Experiment	1	2	3	4	5
Graph	В	D	С	E	Α

(b) Which experiment was completed in the shortest time?

Experiment 4.

- While a catalyst is chemically unchanged at the end of the reaction, it does participate in the reaction, offering an alternative pathway as mentioned above.
- This alternate pathway would include a step which the catalyst form an intermediate product with the reactant and this step would have a lower Ea.
- These intermediate products are then converted to the final product, and the catalyst is regenerated in the process.
- There are numerous different types of catalysts:
 - Homogeneous catalyst
 - Heterogeneous catalyst
 - Enzymatic catalyst
 - o Autocatalyst

Homogeneous Catalyst

• A homogeneous catalyst is a catalyst which is in the same physical state as the reactants.



• Homogeneous catalyst will appear in the rate expression.

Example 1: Homogeneous catalysis of the oxidation of iodide anions, I^- , by peroxodisulfate anions, $S_2O_8^{2^-}$, in the presence of iron(II) ions, Fe^{2+} .

• The overall chemical equation for the reaction is shown below.

 $S_2O_8^{2-}$ (aq) + 2I⁻ (aq) $\rightarrow 2SO_4^{2-}$ (aq) + I₂ (aq)

- The reaction is slow (kinetically not favourable) because it involves the reaction of two negatively charged ions which repel each other. Thus, the activation energy of the reaction is very high.
- Iron(II) ions, Fe²⁺, catalyse the reaction by providing an alternative pathway which has a lower activation energy. This alternative pathway involves 2 steps.

Step 1: $S_2O_8^{2-}$ (aq) + 2Fe²⁺ (aq) \rightarrow 2SO₄²⁻ (aq) + 2Fe³⁺ (aq)

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

- In both the steps shown, the reactions involve oppositely charged ions which attract rather than repel each other. The two activation energies for this alternative pathway are lower as compared to the original.
- The ability of the Fe²⁺ to change its oxidation state to Fe³⁺ and then back again to Fe²⁺ plays an important role in homogeneous catalysis.
- As a catalyst, Fe²⁺ is not consumed at the end of the reaction.
- A possible energy profile for this reaction is shown below.



Example 2: Catalytic destruction of the ozone layer

- CFCs are widely used in aerosols, refrigerants, solvents and plastics due to their low reactivity and low toxicity in the troposphere.
- However, when they get into the stratosphere, the higher energy UV radiation breaks them down, releasing free chlorine atoms which are also reactive free radicals.
- CFC, also known as Freon undergoes photochemical decomposition as follows: $CCl_2F_2(g) \rightarrow CClF_2\bullet(g) + Cl(g)$
- The weaker C–Cl bond breaks in preference to the C–F bond, and the chlorine radicals catalyse the decomposition of ozone.

 $\begin{array}{l} Cl \bullet (g) + O_3 (g) \rightarrow O_2 (g) + ClO \bullet (g) \\ ClO \bullet (g) + O_3 (g) \rightarrow 2O_2 (g) + Cl \bullet (g) \end{array}$

- Here, Cl• (g) has acted as the catalyst and the net reaction is: $2O_3~(g) \to 3O_2~(g)$
- The catalytic destruction of ozone stopped only when the catalyst, the chlorine radical, is "consumed" in a termination reaction.
- Thus a small amount of CFCs can have a huge impact on the amount of ozone in the upper atmosphere.

Heterogeneous Catalyst

• A heterogeneous catalyst is a catalyst which is in a different physical state as the reactants.



- Catalytic action occurs on the surface of the solid catalyst. Thus a large surface area (more active sites) is more advantageous.
- For reactions involving gases and a solid catalyst, the catalyst used is in powder form, mounted on a support medium (honeycombed frame is a commonly used structure) for the maximal adsorption of gaseous reactants.



• Heterogeneous catalysis usually involves three key steps.

Step 1:

Adsorption: Formation of temporary bonds on the surface of the catalyst using electrons within the gaseous reactants (adsorption). Adsorption weakens the bonds present in the gases making the reaction easier. It also holds the gases in the right orientation further favouring the reaction.

Step 2:

Reaction: The reaction of the adsorbed gases on the surface of the catalysts.

Step 3:

Desorption: The products are released from the surface of the catalyst.

- Heterogeneous catalyst does not appear in the rate expression.
- Many important heterogeneous catalysts used industrially are d-block transition elements or their compounds.

Examples of reactions involving heterogeneous catalysts are:

Reaction	Catalyst
Manufacture of ammonia (Haber Process) N ₂ + 3 H ₂ \rightleftharpoons 2 NH ₃	Fe (s)
Manufacture of sulfuric acid (Contact Process) 2 SO ₂ + O ₂ \rightleftharpoons 2 SO ₃	V ₂ O ₅ (s)
Hydrogenation of alkenes C_2H_4 (g) + H_2 (g) $\rightarrow C_2H_6$ (g)	Ni (s) or Pt (s)
Catalytic Converter in cars 2 CO (g) + 2 NO (g) \rightarrow 2CO ₂ (g) + N ₂	Pt / Rh
Dehydration of ethanol C ₂ H ₅ OH (g) \rightarrow C ₂ H ₄ (g) + H ₂ O (g)	Alumina

Example 1: Catalytic convert in cars



Example 2: Manufacture of ammonia via Haber process using Fe catalyst

 $N_2 + 3 H_2 \rightleftharpoons 2 NH_3$ $N \equiv N$ Н— Н $N \equiv N$ Н— Н Н— Н Н— Н $N \equiv N$ Н— Н $N \equiv N$ Н Н $N \equiv N$ Ν Ĥ Iron Iron Iron 3) 2) Bonds Break 1) N₂ and H₂ molecules are adsorbed onto catalyst surface. Н— Н $N \equiv N$ Н— Н —н - NI Н Н Ň Ν Н Iron Iron 4) Atoms re-arrange to form 5) Ammonia molecules leave the catalyst surface; new N2 ammonia. and H₂ molecules are able to be adsorbed onto catalyst





Reaction progress

surface.

Exercise 3

1. Suggest reasons why naked flame is banned in a coal mine.

Flame will provide energy to start initial combustion which releases energy to trigger subsequent reactions. The fine suspended particles enhance the subsequent combustions due to large surface area.

2. Explain why transition metals and their compounds are good catalysts in many reactions and industrial processes.

Transition metals are good heterolytic catalysts as the partially filled d–orbitals allow gases to adorp onto them readily hence weakening the bonds in the molecules.

Transition metal ions have the ability to exhibit variable oxidation states and to transit between these states easily. Thus they are efficient homogeneous catalysts.

6.3 Rate Expression

6.3.1 Distinguishing: Rate Constant, Overall Order of Reaction and Order of Reaction with respect to a Particular Reactant

- One of the goals in kinetic study is to derive an equation that can be used to predict the relationship between rate of reaction and the concentrations of reactants.
- Such an experimentally determined equation is called *a rate law or rate expression*.
- Consider a general chemical equation

$$a\mathbf{A} + b\mathbf{B} \rightarrow c\mathbf{C} + d\mathbf{D}$$

The rate expression is defined as:

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

where, k = rate constant $m = \text{order of reaction with respect to reactant } \mathbf{A}$ $n = \text{order of reaction with respect to reactant } \mathbf{B}$ (m + n) = overall order of reaction

- The square brackets in the rate expression denote concentration in mol dm⁻³.
- *m* and *n* are numbers which are experimentally determined and cannot be deduced from the stoichiometric coefficients in the chemical equation.
- *m* and *n* may be integers or fractions. However the common values are 0, 1 or 2.
- The orders of reaction will give an indication of the mechanism of reaction.
- Rate constant, *k*, is **experimentally determined**, and the greater its value, the faster is the reaction.

It is temperature and catalyst dependant and the Arrhenius equation shows the relationship between the activation energy, temperature and the rate constant.

- The **units of** *k* **vary** and depend on the overall order of the reaction.
- One method of determining the order of reaction with respect to a reactant is the initial rate method. Instantaneous rate and average rate methods are not appropriate or accurate in determining the order of reactions.

Order of reaction with respect to a given reactant is defined as the power to which the concentration of that reactant is raised to in an experimentally determined rate expression.

Overall order of reaction is the sum of the individual orders of reaction with respect to all the reactants, which are the powers of the reactants' concentration

Rate constant, *k*, is a proportionality constant in the experimentally determined rate expression.

Exercise 4

Consider the reaction: $BrO_3^{-}(aq) + 5Br^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

Kinetic studies show that the rate equation can be expressed as: Rate = $k [BrO_3^-] [Br^-] [H^+]^2$

(a) State the order of reaction with respect to

(i) BrO₃⁻ 1 (ii) Br⁻ 1 (iii) H⁺ 2

- (b) Calculate the overall order of reaction. 1 + 1 + 2 = 4
- (c) Determine the units of k for this reaction given that the units for rate is mol $dm^{-3} s^{-1}$.

$$\frac{\text{mol dm}^{-3}\text{s}^{-1}}{(\text{mol dm}^{-3})^4} = \text{mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$$

6.3.2 Orders of Reaction

(i) Zero Order Reaction

- A zero order reaction is a reaction whose rate does not depend on the concentration of a reactant. (usually involves a solid reactant or catalyst)
- For the reaction: $A \rightarrow product$

The rate expression is: **Rate** = k [**A**]⁰ = k

- From the rate expression, it can be deduced that,
 - o the rate remains unchanged during the reaction until the reaction stops.
 - o changing the concentration of A will not affect the reaction rate.
- The integrated rate law is,

$[A] = -kt + [A]_0$

where, [A] = concentration of A $[A]_0 = \text{initial concentration of A}$

• From the differential equation, it can be deduced that the concentration of the reactant decreases at a uniform rate (constant gradient) and drops to zero eventually.

• Example of zero order reaction: Haber process in the presence of Fe, $2NH_3 (g) \rightarrow N_2 (g) + 3H_2 (g)$



(ii) First Order Reaction

- A first order reaction is a reaction whose rate depends on the concentration of a single reactant raised to the first power.
- For the reaction: $A \rightarrow product$

The rate expression is: $Rate = k[A]^1 = k[A]$

- From the rate expression, it can be deduced that,
 - the initial rate of reaction is directly proportional to the concentration of the reactant
 - o as the reaction progresses, its rate decreases exponentially with time
 - o doubling the concentration of A will cause the initial rate to double
- The integrated rate law is,

$ln[A] = -kt + ln[A]_0$

- where, [A] = concentration of A $[A]_0 = \text{initial concentration of A}$
- For an overall first order reaction, the half–life, t_{1/2}, of the reactant is a constant. It is independent of the initial concentration of the reactant, and is defined mathematically as,

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

The half–life of a reaction, $t_{1/2}$, is defined as the time taken for the concentration reactant to decrease to half its original value.

• For a zero order and second order reaction, the half-life is not constant.



Graphical determination of $t_{1/2}$ for first order reactions

• Example of first order reaction: Catalytic decomposition of hydrogen peroxide $2H_2O_2$ (l) $\rightarrow 2H_2O$ (l) + O_2 (g)



(iii) Second Order Reaction

- A second order reaction is a reaction whose rate depends on the concentration of a single reactant raised to the second power.
- For the reaction: $A \rightarrow product$

The rate expression is: **Rate =** k [**A**]²

- From the rate expression, it can be deduced that,
 o doubling the concentration of A will cause the initial rate to quadruple
- The integrated rate law is,

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

where, [A] = concentration of A $[A]_0 = \text{initial concentration of A}$



(iv) Overall Order of Reaction and Rate Constant

Consider a reaction,

A + 2B + 2C
$$\rightarrow$$
 products

where the rate expression is, rate = $k [B]^1 [C]^2$

- It can be deduced that the rate is zero order with respect to A, first order with respect to B and second order with respect to C.
- The overall order of the reaction is 3 (third order). The overall all order is the sum of the respective orders of the reaction.
- The units of the rate constant, k, is derived by applying simple dimensional analysis. The units of the rate constant are not fixed and depend on the different terms in the rate expression as shown in the following table. (In deriving the unit for k, the unit of the rate of reaction is assumed to be mol dm⁻³ s⁻¹.)

Rate Expression	Order of Reaction	Units of Rate Constant
Rate = $k [A]^0$	Zero	mol dm ⁻³ s ⁻¹
Rate = $k [A]^1$	First	S ^{−1}
Rate = k [A] ² Or Rate = k [A] ¹ [B] ¹	Second	mol⁻¹ dm³ s⁻¹
Rate = $k [A]^3$ Or Rate = $k [A]^1 [B]^2$ Or Rate = $k [A]^1 [B]^1 [C]^1$	Third	mol ^{−2} dm ⁶ s ^{−1}

6.3.3 Determining the Rate Expression for a Reaction from Experimental Data

• There are two ways to determine the rate expression given experimental data – a graphical method or a non–graphical method (mathematical).

(i) Method 1 – from experiments on Initial rates (non–graphical)

- In this first method, experiments are carried out in which the initial rate of a reaction is measured by varying the initial concentrations of the reactant(s).
- Initial rates are used rather than rates at a later stage of the reaction as some reactions are reversible and this would add elements of uncertainty into the kinetic experiment.
- For reactions involving more than one reactant, which is quite often the case, the concentrations of all the reactants but one are fixed. The concentration of this last reactant is varied and the initial rate measured. The rate of the reaction is then recorded as a function of that reactant's concentration.
- The order of reaction (n) is then determined by using the following equation:

$$\frac{r_1}{r_2} = \left[\frac{C_1}{C_2}\right]^n$$

where r_1 and r_2 are initial reaction rates for two different experiments and C_1 and C_2 are initial reactant concentrations for these two respective experiments

• For example, the initial rate of a reaction $3X + 2Y \rightarrow 2Z$ is measured for a series of different initial concentrations of X and Y. The data obtained is as follows:

Exporimont	Initial Concentr	ations / mol dm⁻³	Initial Pate / mal dm-3 min-1
Experiment	Х	Y	
1	0.01	0.01	1.5 x 10 ^{−2}
2	0.01	0.02	3.0 x 10 ⁻²
3	0.02	0.01	6.0 x 10 ⁻²
4	0.02	0.03	1.8 x 10 ^{−1}

Overall rate expression is Rate = $k [X]^m [Y]^n$

Comparing experiments 1 and 3,

$$\frac{r_1}{r_2} = \left[\frac{C_1}{C_2}\right]^n$$

$$\frac{1.5 \times 10^{-2}}{6.0 \times 10^{-2}} = \left[\frac{0.01}{0.02}\right]^n$$

$$0.25 = (0.5)^n$$

$$n = 2$$

$$\therefore$$
 The reaction is second order with respect to X.

Comparing experiments 1 and 2,

$$\frac{r_1}{r_2} = \left[\frac{C_1}{C_2}\right]^n$$

$$\frac{1.5 \times 10^{-2}}{3.0 \times 10^{-2}} = \left[\frac{0.01}{0.02}\right]^n$$

 $0.5 = (0.5)^n$ n = 1 ∴ The reaction is **first order with respect to Y**.

Therefore, the rate expression is: Rate = $k [X]^2 [Y]$

Since rate = $k [X]^2 [Y]$

Taking the results from Experiment 1,

$$k = \frac{1.5 \times 10^{-2}}{0.01^2 \times 0.01} = 1.5 \times 10^4 \,\mathrm{dm^6 \ mol^{-2} \ min^{-1}}$$

Exercise 5

Bromate(V) ions react with bromide ions in acid solution according to the following equation:

 $BrO_{3^{-}}(aq) + 5Br^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_{2}(aq) + 3H_{2}O(l)$

A series of experiments was carried out to find the order of reaction by measuring the initial rates of formation of bromine for different concentrations of reactants. The results of the experiments are given in the following table.

Expt	[H ⁺] / mol dm ⁻³	[Br⁻] / mol dm⁻³	[BrO ₃ -] / mol dm- ³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.26	0.32	0.055	0.0138
2	0.26	0.32	0.110	0.0276
3	0.26	0.48	0.110	0.0414
4	0.52	1.44	0.220	0.994

(a) Deduce the order of reaction with respect to Br^- , BrO_3^- and H^+ , explaining your reasoning clearly.

Comparing experiments 2 and 3,

 $\frac{0.276}{0.414} = \left[\frac{0.32}{0.48}\right]^{\mathsf{n}}$

n = 1

 \therefore The reaction is <u>first order with respect to Br</u>⁻.

Comparing experiments 1 and 2,

$$\frac{0.0138}{0.0276} = \left[\frac{0.055}{0.110}\right]^{\mathsf{n}}$$

n = 1

:. The reaction is first order with respect to BrO3=.

Comparing experiments 2 and 4,

0.0276	[0.26]	n	0.32	0.110	
0.994 =	0.52		1.44	0.220	

```
n = 2

∴ The reaction is second order with respect to H<sup>+</sup>.
```

- (b) Write a rate expression for the reaction and use it to calculate the value of the rate constant, k, including the units.

Rate = k [BrO₃⁻] [Br⁻] [H⁺]²

Exercise 6

Hydrogen peroxide reacts with acidified iodide ions to liberate iodine.

 H_2O_2 (aq) + 2H⁺ (aq) + 2I⁻ (aq) \rightarrow 2H₂O (l) + I₂ (aq)

In the investigation of this reaction, various sets of the experiment were carried out. The time taken for formation of iodine is monitored. The experimental results are recorded in the table shown.

Expt	Vol of H ₂ O ₂ / cm ³	Vol of I [−] / cm³	Vol of H⁺ / cm³	Vol of H ₂ O / cm ³	Time taken for solution to turn brown / s
1	10	10	20	60	14
2	20	10	20	50	7
3	10	20	20	50	7
4	10	10	40	40	14

(a) Explain the purpose of the volume of water added in each experiment.

Volume of water is added so that the **total volume of the reaction mixture** is **kept constant at 100 cm³**. When total volume of each reaction mixture is kept constant, the following relationship can be applied: **volume of reactant** \propto [reactant]

(b) Determine the order of reaction with respect to H_2O_2 , I^- and H^+ respectively.

Since volume of reactant ∞ [reactant] (since V_{total} is constant) and rate $\infty \frac{1}{\text{time}}$,

Comparing Experiment 1 and 2,

- when [H₂O₂] increased 2 times while keeping [H⁺] and [I⁻] constant,
- Time taken for solution to turn brown is decreased 2 times;
- Thus, rate of reaction is increased 2 times.

 \therefore The reaction is **first order with respect to H**₂**O**₂.

Comparing Experiment 1 and 4,

- when [H⁺] is increased 2 times while keeping [H₂O₂] and [I⁻] constant,
- Time taken for solution to turn brown remains constant;
- Thus, **rate** of reaction is **remains constant**.

: The reaction is zero order with respect to H⁺.

Comparing Experiment 1 and 3,

- when [I⁻] is increased 2 times while keeping [H⁺] and [H₂O₂] constant
- Time taken for solution to turn brown is <u>decreased 2 times;</u>
- Thus, rate of reaction is *increased 2 times*.

: The reaction is first order with respect to $\mathbf{I}^{\text{-}}.$

(c) Write the rate equation for this reaction.

Rate = $k [I^{-}] [H_2O_2]$

(ii) Method 2 – From concentration–time graphs (graphical)

• Using the relation that the rate of a reaction can be graphically derived by calculating the gradient of the tangent to the curve at a point, the graph of the concentration of a particular reactant is plotted against time. By varying the concentrations of this particular reactant and keeping the concentration of all other reactants involved in the reaction constant, different curves will be obtained which will then aid in deriving the order of reaction with respect to this reactant. This process is then repeated for the other reactants which are involved.

Example 1

lodine and propanone react together in aqueous acidic solution according to the equation.

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

The rate of the reaction can be measured by recording the reduction of the concentration of the iodine by the decrease in the colour intensity as measured in a colorimeter.

Three initial sets of separate experiments were performed in which the initial concentration of each of the reactants, iodine, propanone and acid was varied in turn, the other two being kept constant. The results are shown below in graphical form.



- The rate of reaction can be determined from the gradient of the concentrationtime graph.
- From the graphs, it can be determined how the rate of the reaction varies with the concentration of propanone, iodine and acid. Rate $\propto [I_2]^0$ Rate $\propto [CH_3OCH_3]^1$ Rate $\propto [H^+]^1$ Hence the rate expression, Rate = $k [H^+] [CH_3OCH_3]$

Example 2

Bromomethane is hydrolysed by dilute aqueous KOH to produce methanol.

 $CH_3Br(aq) + KOH(aq) \rightarrow CH_3OH(aq) + KBr(aq)$

A series of experiments was conducted to vary the concentrations of CH₃Br and KOH in turn while keeping the concentration of the other reactant constant. Deduce the order of reaction with respect to each of the reactants from the following results.



The following should be shown clearly in answer presentation:

- Construction lines to show tangent to each graph
- Calculation of gradient of each tangent
- Construction lines showing determination of $t_{\frac{1}{2}}$ (at least 2 half–lives should be shown)
- Value of $t_{\frac{1}{2}}$ as read off from the graph

To find order of reaction with respect to KOH

Method: Determine half–life of the reaction from either graph and verify if half–life is constant (for a first order reaction)

From the graph of $[CH_3Br] = 1 \mod dm^{-3}$, t_{1/2} is constant at 4 min \therefore The reaction is first order with respect to KOH.

From the graph of $[CH_3Br] = 2 \mod dm^{-3}$, t_{1/2} is constant at 2 min \therefore The reaction is first order with respect to KOH.

To find order of reaction with respect to CH₃Br

Method: Determine and compare the initial rates of reactions from the two graphs

Initial rate of reaction = gradient of tangent at t = 0

When **[CH₃Br] is increased two times** from 1 mol dm⁻³ to 2 mol dm⁻³, keeping [KOH] constant at **1 x 10⁻³** mol dm⁻³ Initial **rate is increased two times** from 5 x 10⁻⁴ mol dm⁻³ min⁻¹ to 1 x 10⁻³ mol dm⁻³ min⁻¹

 \therefore The reaction is **first order with respect to CH₃Br.**

In summary,

Reaction: $A \rightarrow$ Products				
	Zero-order w.r.t. A	First-order w.r.t. A	Second–order w.r.t.	
Rate equation	Rate = k [A] ⁰ = k	Rate = $k [A]^1$	Rate = k [A] ²	
Units of K	moi am ° s '	S S		
Graph of rate <i>vs</i> [A]	rate k rate = k	rate gradient = k	rate	
Graph of [A] <i>vs</i> time	[A] gradient = -k	[A] $\begin{bmatrix} A \end{bmatrix}$ a^{2} a^{2} a^{2} a^{2} a^{2} a^{3} a^{4} a^{3} a^{2} a^{2} a^{4} a^{3} a^{2}	[A] a $t_1 \neq t_2 \neq t_3$ i.e. $t_{\frac{1}{2}} \neq constant$ a/2 a/4 a/8 0 $t_1 t_2$ t_3 time	
Is half–life constant?	No; $t_{1/2} = \frac{[A_0]}{2k}$	Yes; $t_{1/2} = \frac{\ln 2}{k}$	No; $t_{1/2} = \frac{1}{k[A_0]}$	
Relative rate if [A] is doubled	Rate remains constant	Rate is doubled	Rate is 4 times original rate	
Relative rate if [A] is halved	Rate remains constant	Rate is halved	Rate is $\frac{1}{4}$ times original rate	

6.4 Reaction Mechanisms

(TOK: Refer to Pg 296 of chemistry course companion.)

6.4.1 Rate Expression and Reaction Mechanism

- The chemical equation only shows the identities of the reactants and the molar ratio in which they reacted in the reaction. It does not describe how each reactant particles interacts at the molecular level.
- Some reactions are single-step reactions in which the reactant particles simply collide, react and resulting the formation of the products. Some reactions, however, occurs via a few steps before forming the products.
- A reaction mechanism describes a sequence of individual steps, known as elementary steps, that results in the formation of products from the reactants.
- A reaction mechanism satisfies both the rate expression and the stoichiometric equation. In short,
 - The sum of elementary steps must give the overall balanced stoichiometric equation for the reaction.
 - The mechanism must agree with the experimentally determined rate expression.
- The particles involved in the rate-determining step will be featured in the rate expression and the coefficients of the particles in this step will be the order of reaction with respect to the reactant. Some examples are shown below.



- All chemical reactions therefore involve minimally one elementary step.
- In a reaction the elementary step with the largest E_a would be described as the ratedetermining step or the slow step.
 - In a 1-step reaction the elementary step is the rate-determining step.
 - In a multi-step reaction the elementary step with the largest E_a is the ratedetermining step.
- An elementary step involving the collision of three particles or more is rare because the probability of the three particles colliding with the correct orientation and possessing the activation energy is statistically very low.
- The molecularity refers literally to the number of reactant particles involved in each elementary step.
- All the elementary steps in a reaction do not have the same rates of reaction. Usually, one is slower than all the others and so it limits how fast the overall rate of reaction can be.
- The slowest step in a multi-step reaction mechanism is called the rate determining step. It determines the overall rate of reaction and has the highest activation energy.
- Since the rate determining step determines the overall rate of reaction, its rate expression represents the rate expression for the overall reaction.

Case	Overall equation	Mechanism	Rate expression
1	$A \rightarrow 2B$	1-step mechanism: A \rightarrow 2B	Rate = k [A]
2	$2A \rightarrow B$	1-step mechanism: $2A \rightarrow B$	Rate = $k [A]^2$
3	$2A \rightarrow C + D$	1-step mechanism: $2A \rightarrow C + D$	Rate = $k [A]^2$
4		[@] 2–step mechanism: $A \rightarrow C + X$ (slow) $X + A \rightarrow D$	Rate = k [A]
5	$2A + B \rightarrow C + D$	[@] 2–step mechanism: A + B \rightarrow C + X(slow) X + A \rightarrow D	Rate = k [A] [B]
6		[@] 2-step mechanism: A + B \rightleftharpoons X X + A \rightarrow C + D(slow)	Rate = k [X] [A] = k [A] [B] [A] = k [A] ² [B]
7	$A + B \rightarrow C + D$	^{@#} 2–step mechanism: A + Y \rightarrow C + X(slow) X + B \rightarrow D + Y	Rate = k [A] [Y]

• Some examples of reaction and the possible mechanisms are shown in the following table.

@: X is known as the intermediate in this reaction. An intermediate is a chemical species that is produced in an elementary step and consumed in another. It will not appear in the rate expression or in the overall chemical equation.

#: Y is the catalyst in this mechanism. It is involved in the slow step of the reaction and it will appear in the rate expression but will not appear in the overall chemical equation.

6.4.2 Deduction of Reaction Mechanism from the Rate Expression

• For a multi-step reaction, the rate expression is derived directly from the stoichiometry of the rate-determining step (slow step).

Example 1 (Case 6)

Consider the reaction between nitrogen(II) oxide and chlorine:

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

The experimentally determined rate expression for the above reaction is

Rate = $k [NO]^2 [Cl_2]$

From the rate expression, the slow step of the reaction mechanism would involve the collision of 2 molecules of NO and 1 molecule of Cl_2 . However, a slow step that involves the collision of 3 particles is highly unlikely as the probability of 3 particles colliding with the right kinetic energy and the right orientation to start a reaction is highly improbable.

The reaction mechanism has been observed as such:

Step 1: NO (g) + Cl₂ (g)
$$\stackrel{\kappa_c}{=}$$
 NOCl₂ (g) (fast)
Step 2: NOCl₂ (g) + NO (g) $\stackrel{k_1}{\rightarrow}$ 2NOCl (g) (slow)

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Since Step 2 is the slow step, it is therefore the rate-determining step. Hence, assuming that all steps in the proposed mechanism are elementary steps:

Rate = k_1 [NOCl₂] [NO]

Based on the observed reaction mechanism, $NOCl_2$ appears in the rate equation. It is a reactive intermediate that is in equilibrium with NO and Cl_2 . To see how this rate equation is consistent with the observed kinetics, let us consider what happens in step 1.

From step 1,

$$K_c = \frac{[NOCl_2]}{[NO][Cl_2]}$$

Rearranging, $[NOCl_2] = K_c$ $[NO][Cl_2]$. This can then be substituted into the rate equation from the observed mechanism.

Substituting into the rate equation:

Rate =
$$k_1 K_c [NO] [Cl_2] [NO]$$

= $k [NO]^2 [Cl_2]$, where $k = k_1 K_c$

We can hence conclude that the observed mechanism is consistent with the observed kinetics.

Example 2 (Case 4)

Consider the reaction: $2O_3 \rightarrow 3O_2$

Where the reaction mechanism is as follows:

Overall: $2O_3 \rightarrow 3O_2$

From the slow step, it can be deduced that Rate = $k [O_3]$

In the first step, species O is formed. This species is then used up in the second step. This species O is known as the intermediate.

It should be noted that the activation energy for the slow step is always larger than that for the fast step, as illustrated in the energy profile for the reaction



Figure 6.17: Energy profile diagram

Exercise 7

1. Given the decomposition equation of hydrogen peroxide catalysed by iodide ions $H_2O_2 \to 2H_2O + O_2$

From the following proposed mechanism, find the rate expression of this reaction.

Step 1:	$H_2O_2 + I^- \rightarrow IO^- + H_2O$	(slow)
Step 2:	IO^- + $H_2O_2 \rightarrow H_2O$ + O_2 + I^-	(fast)

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

2. The gas-phase decomposition of dinitrogen monoxide is considered to occur in two steps.

Step 1:
$$N_2O(g) \xrightarrow{k_1} N_2(g) + O(g)$$

Step 2: $N_2O(g) + O(g) \xrightarrow{k_2} N_2(g) + O_2(g)$

The experimental rate expression for this reaction is Rate = $k [N_2 O]$.

- (a) Identify the rate-determining step. **Step 1.**
- (b) Identify the intermediate involved in the reaction. **O atom.**

6.5 Arrhenius Equation

A Quantitative explanation of effect of temperature on rate of reaction (Refer to pg 301 of chemistry course companion)

6.5.1 Describe Qualitatively the Relationship between the Rate Constant (k) and Temperature (T)

• Swedish chemist Svante Arrhenius suggested a mathematical relationship between the rate constant, *k*, and the temperature, T, for a given reaction.

$$k = Ae^{\frac{-E_a}{RT}}$$
 OR $\ln k = \frac{-E_a}{RT} + \ln A$

where,

A : Arrhenius constant; takes into account to the orientation of the reactant at the point of collision as well as the frequency of collisions of the reactants

- E_a : activation energy of the reaction; will be lowered if a catalyst is used.
- **R** : the molar gas constant (8.31 J mol⁻¹ K⁻¹)
- *T*: the absolute temperature (in Kelvin); can be manipulated experimentally.
- Rate constant, *k*, is thus affected by temperature and presence of catalyst only. It is neither affected by any changes in concentrations of reactants nor products.
- An increase in temperature (T) and the presence of catalyst will cause an increase in the rate of reaction resulting in a larger rate constant that would infer a faster rate of reaction.
- The table below summarises how the 3 variables relate to the factors that affect the rate of a reaction.

Variable	Factor	
А	Surface area	
Ea	Catalyst	
Т	Temperature	

• If we substitute the Arrhenius equation into the rate expression,

Rate = $Ae^{\frac{-E_a}{RT}}$ [A]^m [B]ⁿ,

we can account for all the factors that affects rates of reaction.

The concentration / pressure factor can be accounted for by the order of reaction, m and n while the other factors are accounted for by the Arrhenius equation or the rate constant.

6.5.2 Determining the Activation Energy Value from the Arrhenius Equation

- The logarithmic expression of the rate constant is useful in determining the values of the E_a and A of a reaction.
- The logarithmic expression is in the form of y = mx + c :

$$\ln k = \left(\frac{-\mathsf{E}_a}{\mathsf{R}}\right) \left(\frac{1}{\mathsf{T}}\right) + \ln A$$

Thus a plot of ln *k* against $\frac{1}{T}$ will yield a straight line. The gradient of the line is equal to $\frac{-E_a}{R}$, and hence the value of the activation energy for the reaction can be determined.

Extrapolating the straight line back to y-intercept will yield the value of In A, as shown in Figure 6.18.



Example 1

Consider the following graph of ln *k* against $\frac{1}{T}$ for the first order decomposition of N₂O₄ into NO₂.



Gradient = $\frac{9.2 - 8.4}{(3.53 - 3.65) \times 10^{-3}} \approx -6.7 \times 10^3$ (2 s.f.)

$$E_a = 6.7 \times 10^3 \times 8.31 = 56 \text{ kJ mol}^{-1} (2 \text{ s.f.})$$

• Activation energy can also be calculated from values of the rate constant, *k*, at only two temperatures. The formula is derived as follows:

At temperature T_1 , when the rate constant is k_1 :

$$\ln k_1 = \left(\frac{-\mathsf{E}_a}{\mathsf{R}}\right) \left(\frac{1}{\mathsf{T}_1}\right) + \ln A \qquad - \text{Equation (1)}$$

At temperature T_2 , when the rate constant is k_2 :

$$\ln k_2 = \left(\frac{-E_a}{R}\right) \left(\frac{1}{T_2}\right) + \ln A \qquad - \text{Equation (2)}$$

• By subtracting the equation (2) from equation (1), the following equation can be derived:

$$\ln \frac{k_1}{k_2} = \left(\frac{E_a}{R}\right) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Example 2

Rate constants for the reaction

 $NO_{2}\left(g\right)+CO\left(g\right)\rightarrow NO\left(g\right)+CO_{2}\left(g\right)$ are given below

At 700 K, $k = 1.3 \text{ mol dm}^{-3} \text{ s}^{-1}$

At 800 K, $k = 23.0 \text{ mol } \text{dm}^{-3} \text{ s}^{-1}$

Calculate the value of the activation energy in kJ mol⁻¹.

$$\ln \frac{k_1}{k_2} = \left(\frac{E_a}{R}\right) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\ln \frac{1.3}{23.0} = \left(\frac{E_a}{8.31}\right) \left(\frac{1}{800} - \frac{1}{700}\right)$$
$$E_a = 1.34 \times 10^5 \text{ J mol}^{-1} \approx 130 \text{ kJ mol}^{-1} (2 \text{ s.f.})$$