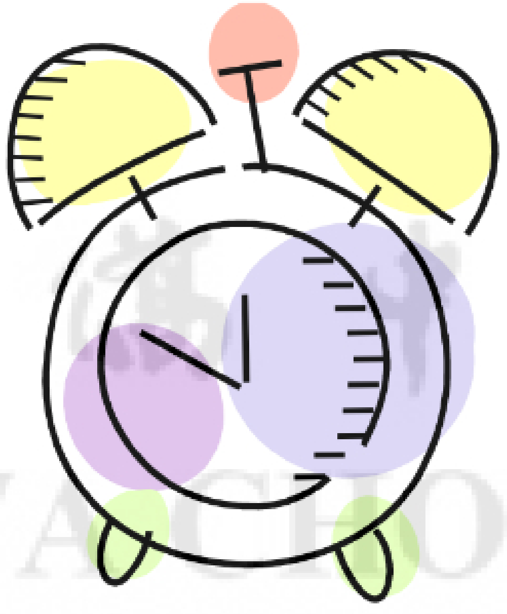
06 Reaction Kinetics



GUIDING QUESTIONS:

- What do we mean by rate of reaction? How could we measure it?
- What are the factors affecting rate? Why?
- How can we determine and express the relationship between rate and concentration mathematically? How are the other factors affecting rate featured in this equation?
- What can we infer about the mechanism of a reaction from the order of reaction? Why do many reactions not occur in a single step?
- What are the general types of catalysts? How are they similar and how do their modes of action differ?

LEARNING OUTCOMES

At the end of the topic, you should be able to:

8(a) explain and use the terms: rate of reaction; rate equation; order of reaction; rate constant; half-life of a reaction; rate-determining step; activation energy; catalysis

8(b) construct and use rate equations of the form rate = $k\,[A]^m\,[B]^n$ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including:

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

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

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

(ii) use the half-life of a first-order reaction in calculations

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

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

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

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

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

8(i) **(i)** explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant

(ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution

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

- **(i)** the Haber process
- **(ii)** the catalytic removal of oxides of nitrogen in the exhaust gases from car engines (refer to Topic 10 Alkanes under catalytic converter)

(iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide

(iv) catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

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

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

REFERENCES

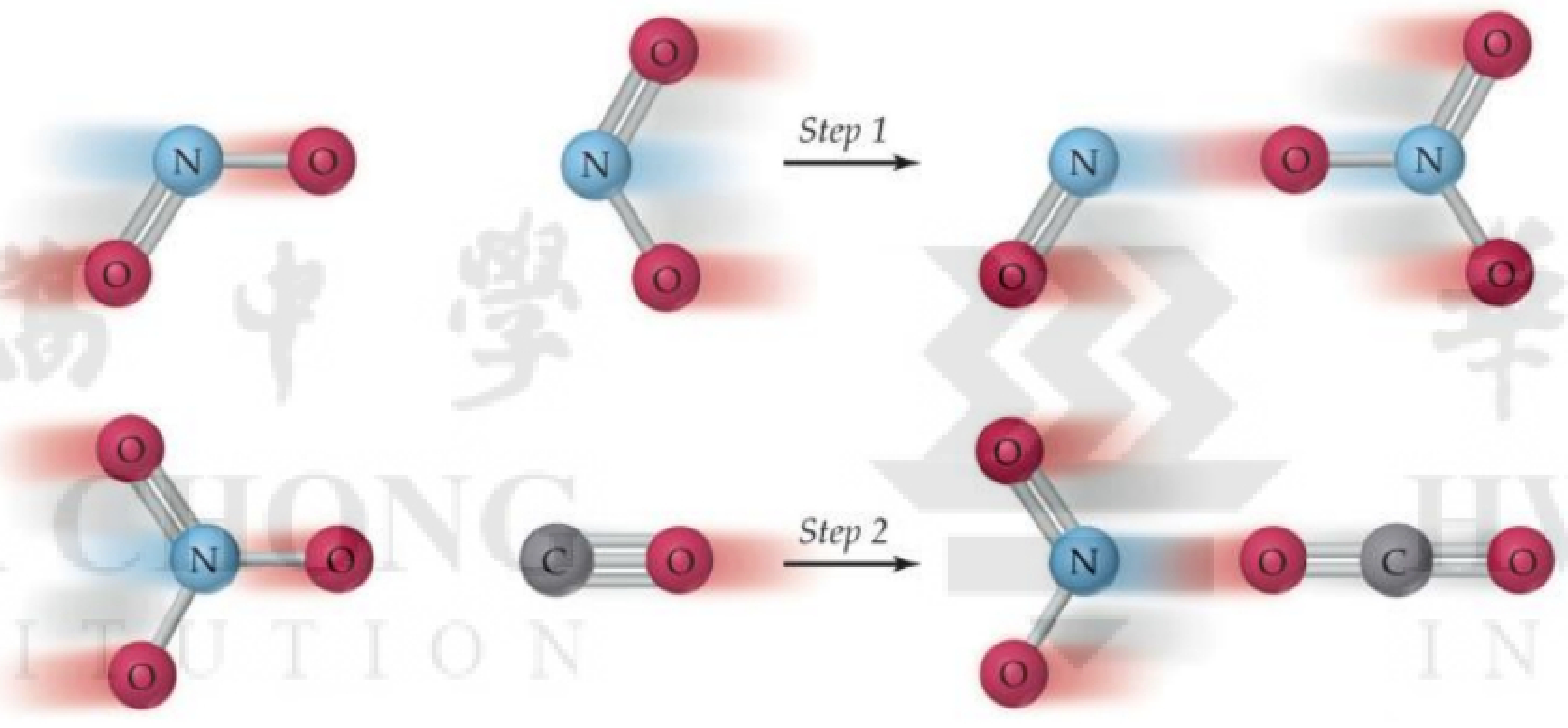
1. Cann & Hughes, *Chemistry for Advanced Level*, Chapters 8 & 11.
2. Martin S. Silberberg, *Chemistry The Molecular Nature of Matter and Change*, 6th Ed., Chapter 16
3. Petrucci & Harwiidm *General Chemistry – Principles and Modern Applications,* 6th Ed., Chapter 15

1 INTRODUCTION

LOOKING BACK

Topic 5 Chemical Energetics looked at energy changes of reactions, in terms of enthalpy, entropy and Gibbs' free energy. While the sign of $\triangle G$ may indicate the direction of chemical change, it gives no information on how fast a reaction occurs. A thermodynamically spontaneous reaction (where $\triangle G$ is negative) may be so slow that no significant reaction could be observed in our lifetime. The study of the rates of chemical reactions is called kinetics. The rate of reaction depends on a number of factors, each of which can be studied separately, and can only be determined by experiment.

Kinetics, derived from the Greek word κίνησις (kinesis), means movement or the act of moving. Indeed, **chemical reactions** involve the movement, or rather, **collisions** between **reactant particles**.



In the industry or everyday life, some reactions need to be fast, for example, those which goes inside your body when you take a pain reliever; while some reactions should be as slow as possible, like the rusting of iron in machinery and motor vehicles.

pressure cooker cooks fast

fast-acting panadol

at what rate is the car rusting?

The study of kinetics may be divided into two areas:

(1) at the *macroscopic level*

- **what reaction rate means**
- how to **determine the reaction rate** and **rate equation experimentally**
- and how factors such as **temperature**, reactant **concentration** and the use of a **catalyst** influence rate

(2) at the *particulate level*

- which is **reaction mechanism** about
- the detailed pathway taken by atoms and/or molecules as a reaction proceeds

Studying kinetics helps chemists to select the best conditions to control the speed at which a reaction proceeds.

2 COLLISION THEORY AND ACTIVATION ENERGY

2.1 Collision theory

In order for a reaction to take place, reactant particles or molecules must:

- **collide**,
- with **sufficient energy to overcome the activation energy (E_a)**,
- in the **correct orientation** that can lead to rearrangement of the atoms.

} needed for **effective** collision

Collisions which satisfy these conditions are said to be **effective** and they give the product particles. Otherwise, the colliding particles will simply "bounce off" each other without reaction.

At the molecular level, the rate of reaction depends on:

- how often the reactant molecules collide with each another – the **collision frequency**, and
- what **proportion of the particles have sufficient energy to overcome the activation energy**.

2.2 Maxwell-Boltzmann distribution curve

For most chemical reactions, the activation energy is quite large and only a small fraction of colliding particles are well-oriented and have that minimum energy to overcome the activation energy. The reactant particles in a gas or liquid undergo an enormous number of collisions per second with one another. If each collision were effective, all reactions would be over in an instantaneous explosion!

The particles in a sample have a range of energies. In order to estimate what fraction of collisions will have sufficient energy to overcome the activation energy barrier, we need to know how many particles in a sample have various different energies – in other words what their energy distribution is. This was first calculated by James Clerk Maxwell and Ludwig Boltzmann.

The **Maxwell-Boltzmann energy distribution curve** that results is shown below (refer to Topic 3 The Gaseous State for explanation on the shape of the curve).

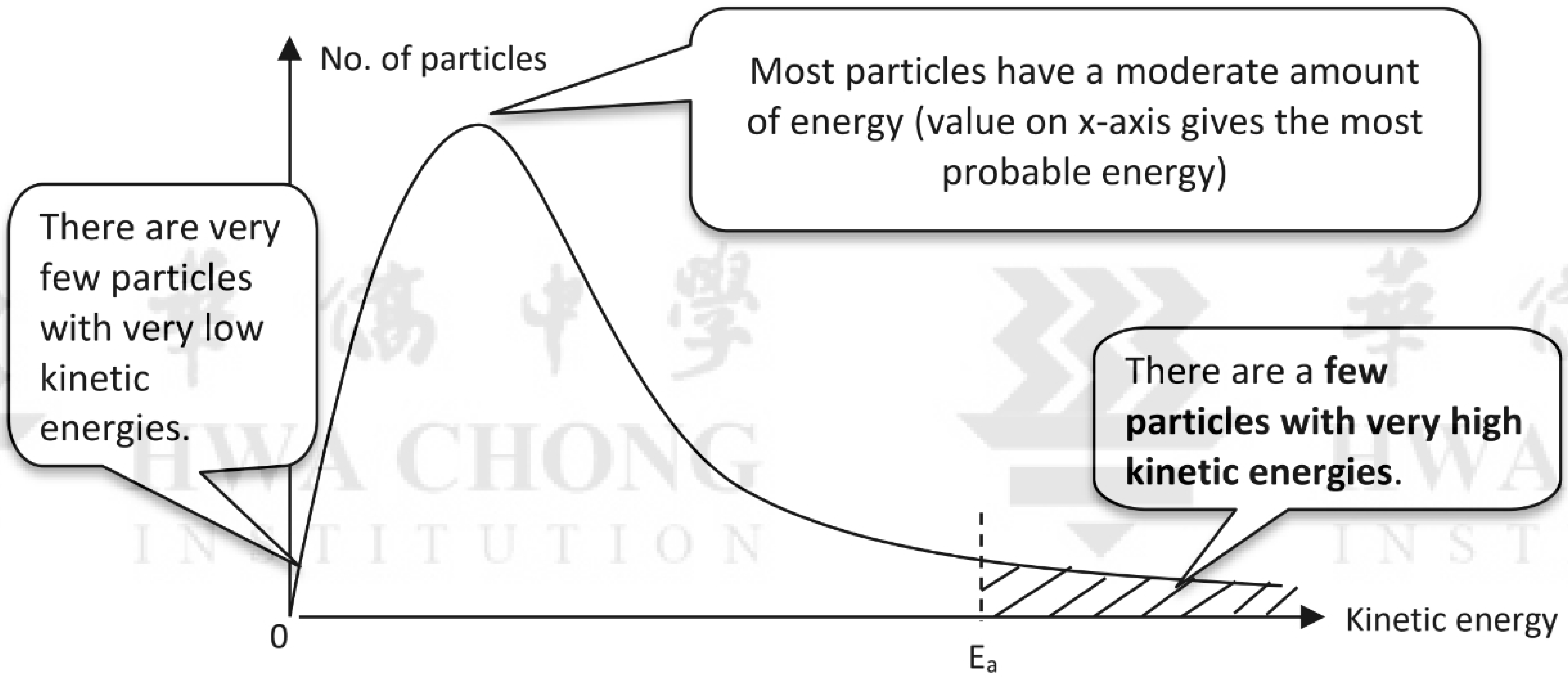


Figure 1. The Maxwell-Boltzmann energy distribution curve.

The **total area under the graph represents the total number of particles present**. The line E_a is marked, showing an activation energy for a particular reaction. The **shaded area represents the fraction of molecules that have kinetic energies greater than or equal to this E_a.**

2.3 Molecular orientation

The figures below illustrate the importance of molecular orientation using the example:

$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$$

where collision between a NO_2Cl molecule and a Cl atom forms a NO_2 molecule and a Cl_2 molecule.

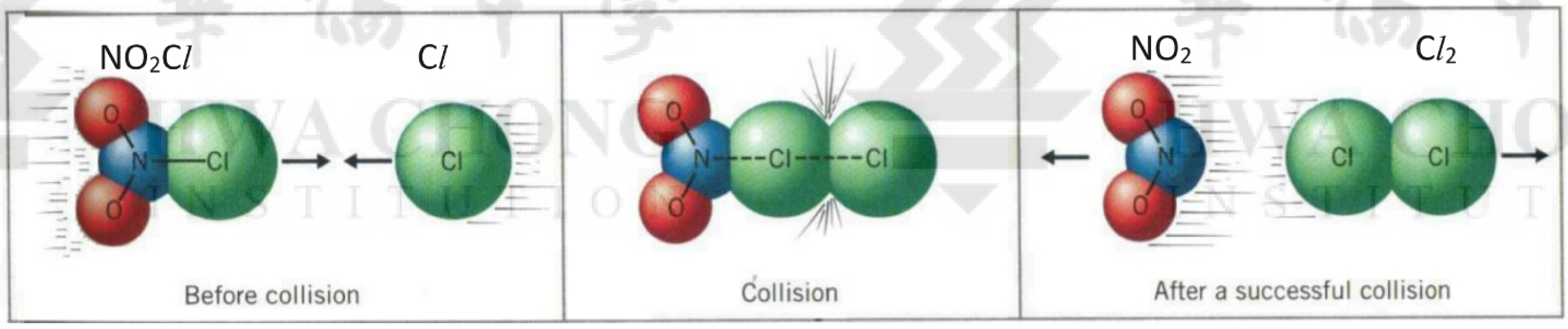


Figure 2a. A correctly oriented collision. The two reactant particles approach each other with sufficient energy and in the correct orientation such that the Cl–Cl bond can form while the N–Cl bond breaks.

In a correctly oriented collision, contact occurs between the atoms that will become bonded in the product.

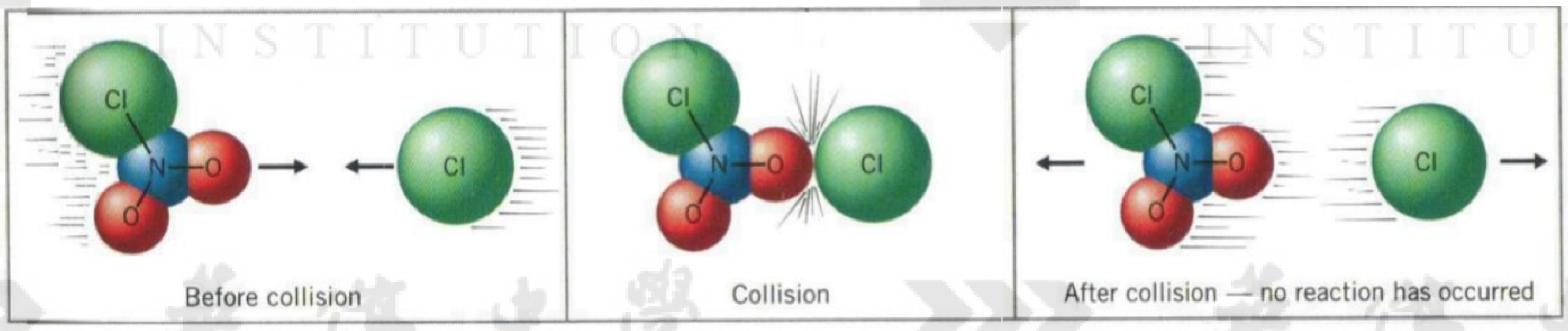


Figure 2b. A poorly oriented collision.

In a poorly oriented collision, the two colliding particles "bounce off" without any reaction.

2.4 Activation energy and reaction profile diagrams

The concept of activation energy and reaction profile diagrams (or energy profile diagrams) have most likely been introduced to you in secondary school chemistry as they are part of the O-level syllabus. Note that the information presented here outlines the A-level treatment of these two concepts. Please read through to refresh your memory as your understanding of these concepts will be used in later sections.

Let's revisit the concept of activation energy, starting with a definition.

*The **activation energy** of a reaction (E_a) is the **minimum energy** which the reacting particles must possess in order to **overcome the energy barrier** before the formation of the products.*

The following examples dramatically illustrate the presence of this energy barrier to a reaction:

- A mixture of methane and oxygen shows no sign of reaction at room temperature and pressure even though the reaction is highly exergonic ($\Delta G_r^\ominus$ = –801 kJ mol^{-1}). However, when a spark is introduced, the reaction occurs explosively.
- On the other hand, the reaction between hydrochloric acid and aqueous sodium hydroxide takes place practically instantaneously even though the reaction is only moderately exergonic ($\Delta G_r^\ominus$ = –80 kJ mol^{-1}).

Conclusion: ΔG cannot be used to tell us about the rate of reaction because **there is an activation energy barrier between the reactants and products that has to be overcome**. The magnitude of the activation energy barrier does not depend on the magnitude of ΔG. A thermodynamically spontaneous process will take place very slowly if the activation energy of the process is too high.

Some points to note:

- Reactions with **low E_a** are **fast** because a large proportion of molecules have the necessary energy to overcome the energy barrier. (kinetically favourable)

- Reactions with **high E_a** are **slow** because only a small proportion of molecules have the necessary energy to overcome the energy barrier. (kinetically unfavourable)

- Generally, reactions with **high** activation energy include:
  - reactions between two neutral molecules or involve breaking strong covalent bonds
  - reactions between ions of similar charge
  - reactions where a bond breaks to form free radicals (which are usually highly unstable)

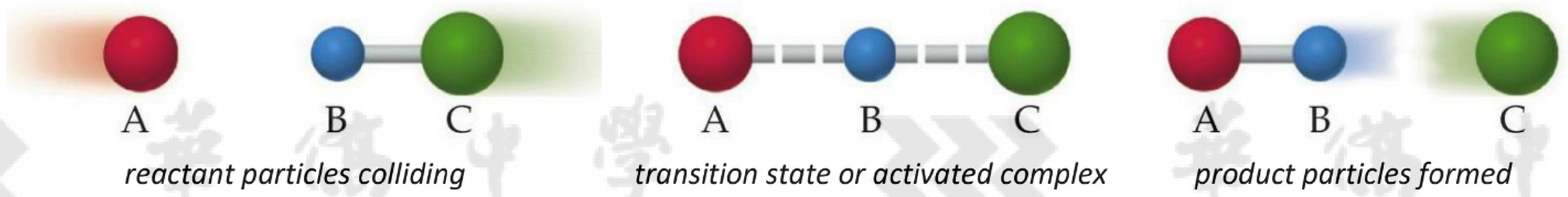
- Generally, reactions with **low** activation energy include:
  - reactions between two free radicals
  - reactions between ions of opposite charge
  - acid-base (neutralisation) reactions

The changing energies of a reaction may be summed up in a reaction pathway diagram. This diagram traces the rise and fall of the total energies of the system as a reaction progresses. The enthalpy change of the reaction as well as the activation energy of a reaction is also reflected in such a diagram. For this reason, this diagram may also be referred to as an energy profile diagram or a reaction profile diagram or a reaction pathway diagram.

Consider a **one-step reaction**:

$\mathbf{A + BC \rightarrow AB + C}$ $\Delta H < 0$ (exothermic)

Here is a simplified representation of the *progress of the reaction*:



The reaction pathway diagram for an exothermic <u>single-step reaction</u> is as follows:

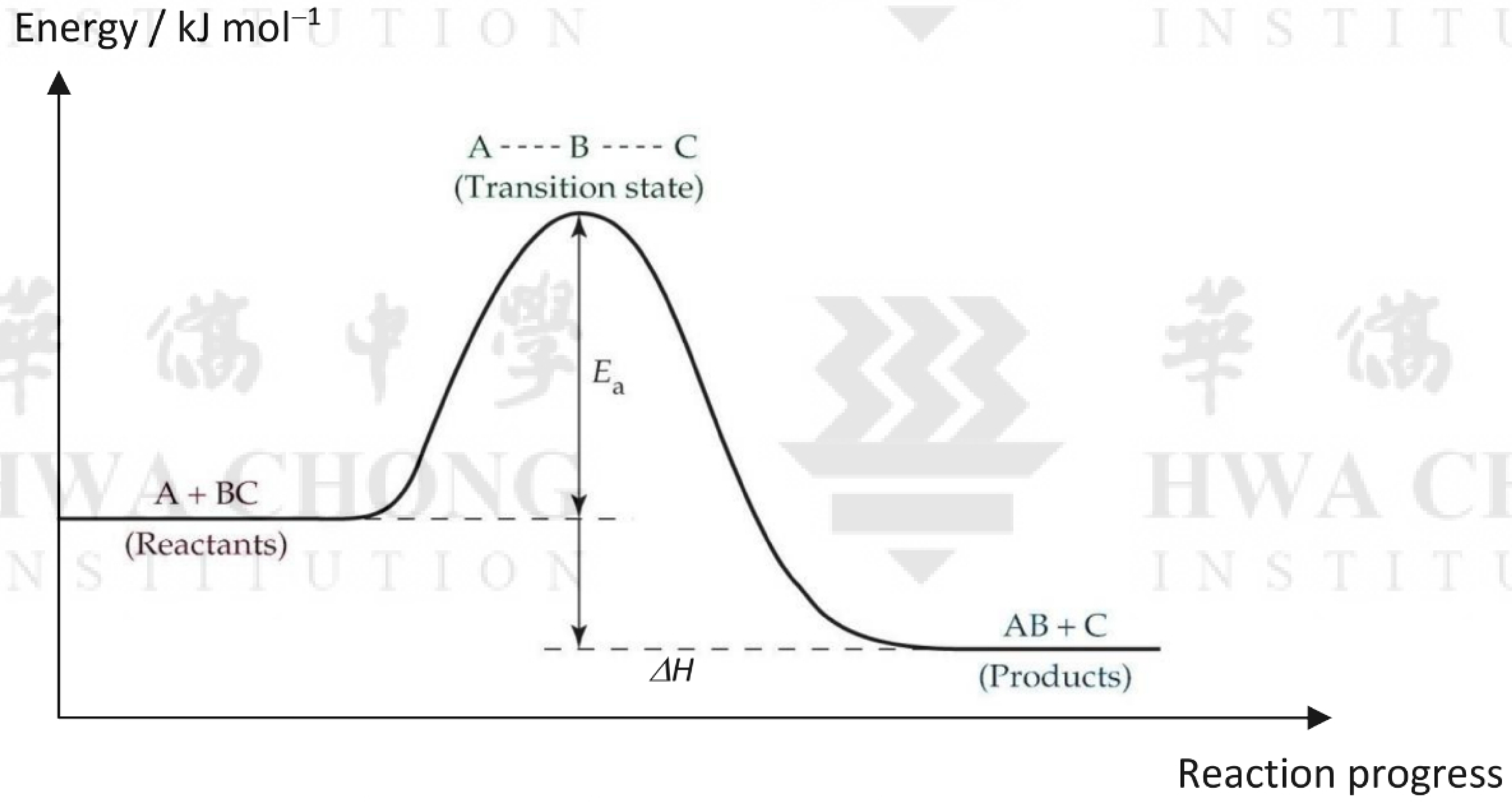


Figure 3. Reaction pathway diagram for a one-step, exothermic reaction, $\mathbf{A + BC \rightarrow AB + C}$*.*

<u>Some points to note:</u>

- A **transition state** or **activated complex** is the arrangement of atomic nuclei and bonding electrons at the **maximum potential energy**. It can either be broken up to form the products or converted back into the original reactant molecules. Due to its high unstability, it **cannot** be isolated as a compound.

- The **activation energy**, $\mathbf{E_a}$, is measured from the energy level of the reactants to the energy level of the transition state.

- <u>Recall:</u> **Enthalpy change, ΔH** is the difference in energy level between the products and reactants.
  - When $\Delta H > 0$, it is an **endothermic** reaction. The products are *energetically* less stable than the reactants.
  - When $\Delta H < 0$, it is an **exothermic** reaction. The products are *energetically* more stable than the reactants.

Note that having an **exothermic** enthalpy change of reaction **does not ensure** that a reaction will take place. This is because the **activation energy may be very high** and thus the **rate of reaction is negligible** at room temperature, for example, the conversion of diamond to graphite does not occur at a visible rate ($\Delta H_r^\ominus = -2$ kJ mol^{-1}).

3 THE RATE OF A CHEMICAL REACTION

3.1 Rate of reaction

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

Mathematically,

$$\text{rate} = \frac{d[\text{product}]}{dt} \quad \text{or} \quad \text{rate} = -\frac{d[\text{reactant}]}{dt} \qquad \textbf{[ ]: concentration in mol dm}^{-3}$$

Why is there a negative sign here?

By definition, the **rate of a reaction is always positive**. Since [reactant] decreases during a reaction, *d*[reactant]/*dt* is negative. The negative sign is added to the expression to give a positive value for the rate.

Units of rate: **mol dm^{-3} s^{-1}** (or other units of time, e.g. mol dm^{-3} min^{-1})

For a simple reaction: $A \rightarrow B$,

$$\text{rate} = -\frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt}$$

This is a simple case as the product concentration increases at the same rate as the reactant concentration decreases.

However, when there are **different stoichiometric coefficients** in the overall balanced equation, it is usual, though not necessary, to express the rate in terms of the substance with a coefficient of **one**.

Consider the reaction: $H_2 + I_2 \rightarrow 2HI$

For every mole of H_2 that is consumed in the reaction, one mole of I_2 is also consumed and 2 moles of HI are formed.

In other words, the rates of consumption of H_2 and I_2 are the same, but the rate of formation of HI is two times faster.

If we use H_2 and I_2 as our reference, then we can express the rate as:

$$\text{rate} = -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = \frac{1}{2}\frac{d[\text{HI}]}{dt}$$

If, instead, we use HI as our reference, then we obtain:

$$\text{rate} = \frac{d[\text{HI}]}{dt} = -2\frac{d[\text{H}_2]}{dt} = -2\frac{d[\text{I}_2]}{dt}$$

Note that this expression would give a rate that is double the numerical value of the previous one. Thus, **the expression and numerical value for the rate of a reaction depends on which substance we use as the reference**.

In conclusion, we need to take into account the stoichiometric coefficients in the balanced equation to express the quantitative relationship between rate of change of concentration of different reactants and/or different products.

In general, to avoid ambiguity, we express the general rate of reaction as follows:
For a reaction: $a\mathbf{A} + b\mathbf{B} \rightarrow c\mathbf{C} + e\mathbf{E}$

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

Self-practice 3.1

For the reaction, $\text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+(aq) \rightarrow 3\text{Br}_2(aq) + 3\text{H}_2\text{O}(l)$, which of the following relationships are correct?

1 $\dfrac{d[\text{Br}_2]}{dt} = \dfrac{d[\text{H}_2\text{O}]}{dt}$

2 $\dfrac{d[\text{Br}_2]}{dt} = -\dfrac{d[\text{BrO}_3^-]}{dt} \times 3$

3 $-5\dfrac{d[\text{Br}^-]}{dt} = -6\dfrac{d[\text{H}^+]}{dt}$

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

3.2 Average, Instantaneous and Initial Rates

The change in rate in a chemical reaction can be seen by plotting the reactant/product concentration-time graphs. Figure 4 shows the concentration-time graph for the decomposition of dinitrogen tetraoxide into its monomers: $N_2O_4\,(g) \rightarrow 2\,NO_2\,(g)$.

General features of the graph:

- The **gradient** (of the tangent) of a concentration-time graph at time *t* gives the rate of reaction at that time.

- The downward sloping line represents the **reactant concentration-time graph**. It falls with time as expected since the reactant is used up during the reaction. The curve will fall to zero reactant concentration after some time as the reaction reaches completion. At completion, gradient = 0, ∴ rate = 0.

- The upward sloping line represents the **product concentration-time graph**. It rises with time as expected since the product is formed during the reaction. At the end of the reaction, the reactant is used up completely and the rate is then zero (gradient = 0). At completion, the product concentration reaches a maximum and the curve plateaus off.

- It is possible to determine from Figure 4, by comparing the gradients, that the rate of appearance of NO_2 is twice as fast as the rate of disappearance of N_2O_4.

Figure 4. Concentration-time graphs for the reaction, $N_2O_4\,(g) \rightarrow 2NO_2\,(g)$.

From a concentration-time graph, it is possible to extract the following information about reaction rates:

The **initial rate of reaction** is the rate at the start of a reaction, i.e., when *t* = 0. It can be determined from the gradient of the tangent at *t* = 0.

The **instantaneous rate of reaction** is the rate at a specified time, *t*. It can be determined from the gradient of the tangent at time *t*.

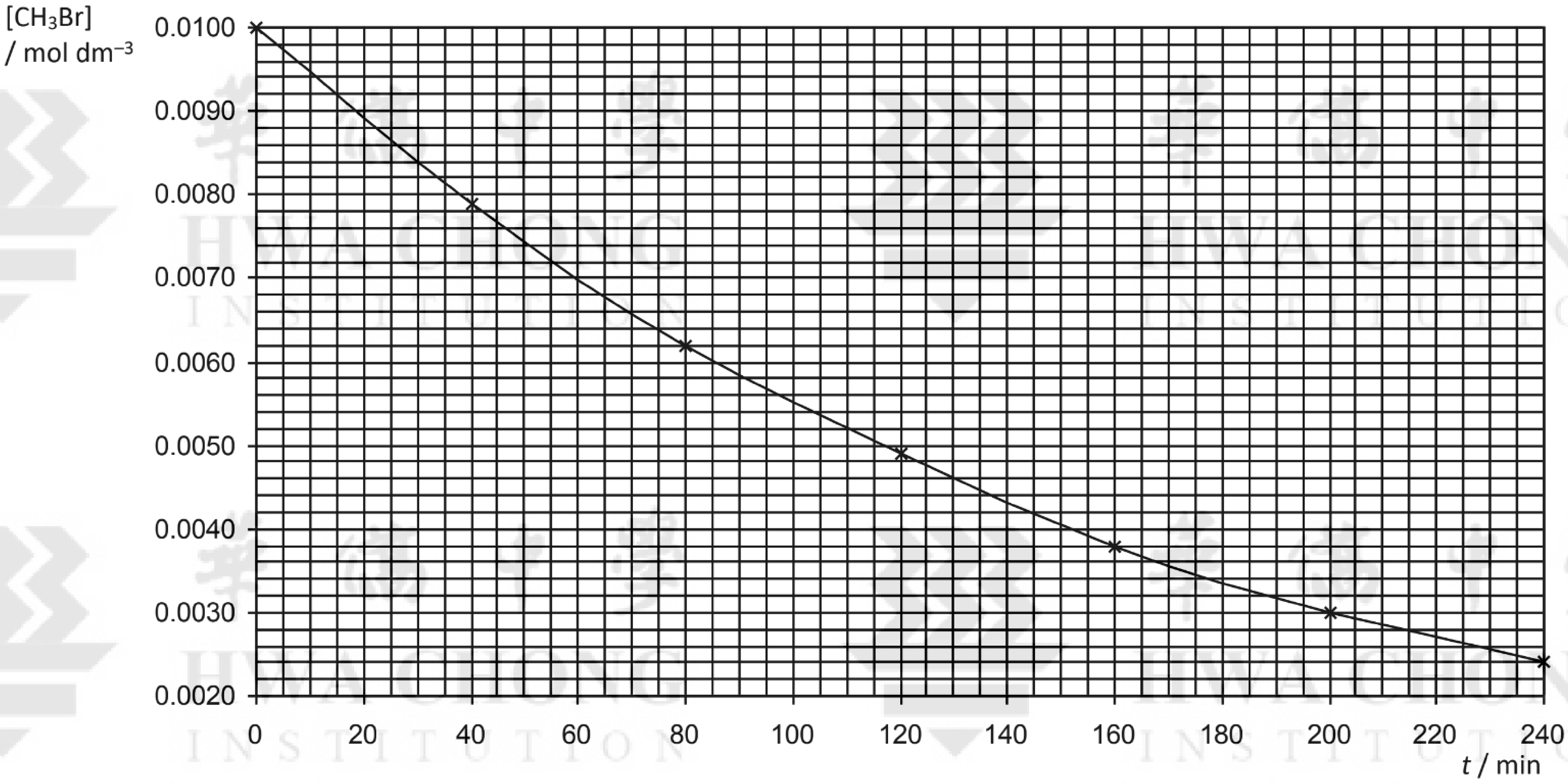
The **average rate of reaction** is the change in concentration of a reactant or a product over a specified time interval.

Lecture Exercise 3.1

The following data and graph were obtained for the reaction, $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$.

time *t* /min	0	40	80	120	160	200	240
$[CH_3Br]$ /mol dm^{-3}	0.0100	0.0079	0.0062	0.0049	0.0038	0.0030	0.0024

[source: N2000/1/3]



(a) Determine the initial rate of the above reaction.

[Ans range: 4.80 to 6.00 × 10^{-5} mol dm^{-3} min^{-1}]

Note that the units of rate follows the unit of time on the x-axis in the concentration-time graph

(b) Determine the instantaneous rate of the above reaction at *t* = 120 min.

[Ans range: 2.50 to 3.10 × 10^{-5} mol dm^{-3} min^{-1}]

(c) Determine the average rate of the above reaction for the first 120 min.

4 RATE EQUATION, RATE CONSTANT AND ORDER OF REACTION

4.1 The rate equation

Knowing *how* the concentration of reactants affect the rate of a chemical reaction is a central part of kinetic study. We obtain this data experimentally and summarise it in the form of a **rate equation**, or rate law. The rate equation predicts how the concentration of reactants affect the rate of reaction.

For a general reaction:

$$a\mathbf{A} + b\mathbf{B} + \ldots \rightarrow \text{products}$$

the rate equation is:

$$\textbf{Rate} = k\,\underbrace{[\mathbf{A}]^{m}\,[\mathbf{B}]^{n}\ldots}$$

This power is called the **order of reaction** with respect to reactant **A**.

This power is called the **order of reaction** with respect to reactant **B**.

The sum of all the exponents $m + n + \ldots$ is the **overall order of reaction**

This proportionality constant is called the **rate constant**. Its value does not change as the reaction proceeds, but it does change with temperature or presence of a catalyst.

Two key points to remember:

- The balancing coefficients *a*, *b*, etc… in the reaction equation are **not** necessarily related to the values of the orders *m*, *n*, etc…
- All the components of the rate equation (i.e. rate, *k*, *m*, *n*, etc…) **must be found experimentally**.

4.2 Understanding order of reaction

We first need to understand what is meant by *order of reaction*.
A reaction has both an *individual* order with respect to each reactant in the chemical reaction, and an *overall* order, which is the sum of each individual order.

Let's consider the simplest case – a reaction with only one reactant, **A**:

$$a\mathbf{A} \rightarrow \text{products}$$

In order to find the order with respect to **A**, we must carry out experiments to determine how the rate changes as the concentration of **A** is varied.

❖ *First order*. Suppose the rate doubles when [A] is doubled. This means that the rate depends on [**A**] raised to the first power, $[\mathbf{A}]^1$ or [**A**] (since we usually omit the power of ^{1}). Thus, the reaction is first order with respect to **A**, and since **A** is the only reactant in the reaction, the overall order is also first order.

$$\text{Rate} \propto [\mathbf{A}] \quad \Rightarrow \quad \text{Rate} = k[\mathbf{A}]$$

Qn: What would happen to the rate if [A] is increased 5 times?
Increases 5 times

- *Second order*. If the rate quadruples (i.e. x4) when [**A**] is doubled, this means that the rate depends on [**A**] squared, $[\mathbf{A}]^2$. Here, the reaction would thus be second order with respect to **A**, and since **A** is the only reactant in the reaction, the overall order is also second order.

$$\text{Rate} \propto [\mathbf{A}]^2 \quad \Rightarrow \quad \text{Rate} = k[\mathbf{A}]^2$$

Qn: What would happen to the rate in this case if [**A**] is tripled?

Increases $3^2 = 9$ times

- *Zero order*. If the rate does not change when [**A**] is doubled, this means that the rate **does not depend** on [**A**]. Mathematically, we say that the rate depends on [**A**] raised to the zero power, $[\mathbf{A}]^0$. The reaction is thus zero order with respect to **A**, since **A** is the only reactant in the reaction, the overall order is also zero order.

$$\text{Rate} \propto [\mathbf{A}]^0 \quad \Rightarrow \quad \text{Rate} = k[\mathbf{A}]^0 = k$$

Note that the rate is not usually independent of *all* the reactants in the chemical reaction, the concentration of at least one of them must affect the rate.

In summary,

Order of reaction with respect to **A**

- If [**A**] doubles, rate doubles => **First order**
- If [**A**] doubles, rate increases 4 times => **Second order**
- If [**A**] doubles, rate is constant => **Zero order**

Let's look at some actual examples.

- For the reaction between nitrogen monoxide and ozone,

$$NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

the rate equation is experimentally found to be:

$$\text{Rate} = k[NO][O_3]$$

The reaction is first order with respect to NO and first order with respect to O_3, so it is second order overall (∵ 1 + 1 = 2).

- For the reaction between NO and hydrogen gas,

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

the rate equation is experimentally found to be:

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

The reaction is thus second order with respect to NO and first order with respect to H_2, so it is third order overall ($\because$ 2 + 1 = 3). Note that this example reinforces the fact that order of reaction **cannot be deduced from the stoichiometry of the balanced equation**, but must be determined from experimental data.

Self-practice 4.1
For the reaction between hydrogen peroxide and acidified iodide ions,

$$H_2O_2\ (aq)\ +\ 3\ I^-\ (aq)\ +\ 2\ H^+\ (aq)\ \rightarrow\ I_3^-\ (aq)\ +\ 2\ H_2O\ (l)$$

the rate equation is experimentally found to be:

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

(a) State the order of reaction with respect to

- H_2O_2
- I^-
- H^+

(b) State the overall order of reaction.

Fractional or negative orders of reaction

- Although reaction orders are usually whole numbers or zero, they can also be fractional or negative.

  For example, in the reaction

$$CHCl_3\ (g) + Cl_2\ (g)\ \rightarrow\ CCl_4\ (g)\ +\ HCl\ (g)$$

  the rate equation is experimentally found to be:

$$\text{Rate} = k[CHCl_3][Cl_2]^{1/2}$$

  This would mean that if, for example, $[Cl_2]$ is quadrupled, the rate would increase $(4)^{1/2}$ = 2 times. The overall order of this reaction is 3/2.

- In the case of the following reaction

$$2\ O_3\ (g) \rightleftharpoons\ 3\ O_2\ (g)$$

  the rate equation is

$$\text{Rate} = k[O_3]^2[O_2]^{-1}$$

  A negative reaction order means the rate actually decreases with an increase in the concentration of the reactant in question. Negative orders are often seen when the rate equation includes products, such as in some equilibrium reaction, as seen in this case. Here if we double the concentration of oxygen gas, the reaction will proceed at half the speed. The overall order in this case would be 1 ($\because$ 2 + (−1) = 1).

4.3 The rate constant

We know intuitively that factors such as increased temperature and presence of catalysts, for example, are able to increase the rate of a reaction. So where do these effects feature in the rate equation? They are included in the value of the rate constant, k.

The **Arrhenius equation**

$$\boxed{k = Ae^{-Ea/RT}}$$

where, A = pre-exponential factor (relatively constant for the same reaction),
E_a = activation energy of the reaction,
R = molar gas constant,
T = absolute temperature

As there are no concentration terms included, we can see that the **value of the rate constant, *k*, is not affected by any changes in concentrations of reactants or products**.

Factors affecting rate constant, k

- Temperature (Refer to **Section 7.3**)
- Presence of a catalyst (Refer to **Section 7.4**)
- Presence of light for photochemical reactions (Refer to **Section 7.5**)

- The **larger** the rate constant, the **faster** is the rate of reaction.

- The units for k are dependent on the **overall order** of the reaction.

  If the overall order is N,

$$\underbrace{\text{mol dm}^{-3}\ \text{s}^{-1}}_{\textit{units of rate}} = \text{units of } k \times \underbrace{(\text{mol dm}^{-3})^{N}}_{\textit{units of concentration terms "combined"}}$$

$$\therefore \text{units of } k: \quad (\text{mol dm}^{-3})^{1-N}\ \text{s}^{-1}$$

  The time component may be in s, min or h. You should always double-check and follow the units used for the data given in the question.

Self-practice 4.2

What are the units of the rate constant k for the following? Use seconds as your time units.

- Overall first order reaction:

- Overall second order reaction:

- Overall third order reaction:

4.4 Summary of definitions

Question: What do you understand by the terms "rate equation", "order of reaction" and "rate constant"?

Suggested answers

The **rate equation** is an experimentally determined equation that relates the rate of reaction to the concentrations of the reactants raised to appropriate powers.

The **order of reaction with respect to a reactant** is the power on its concentration term in the rate equation. The order of reaction must be determined experimentally.

The **overall (or total) order of reaction** is the sum of the individual orders.

The **rate constant**, ***k***, is the proportionality constant in the experimentally-determined rate equation. It is a constant at a given temperature.

Alternative answers

Consider a reaction: $a\mathbf{A} + b\,\mathbf{B} \rightarrow$ products

The experimentally determined **rate equation** for this reaction is given by: rate = $k\,[\mathbf{A}]^m\,[\mathbf{B}]^n$

The powers, m and n, are the **orders of reaction** with respect to reactants **A** and **B** respectively. The order of reaction must be determined experimentally.

$m + n$ gives the **overall (or total) order of reaction**

The proportionality constant, k, is called the **rate constant**. It is a constant at a given temperature.

4.5 Obtaining information about order of reaction from graphs

Plotting concentration-time graphs, rate-time graphs, rate-concentration graphs (or variations of these graphs) and looking at their shapes can also give us information about the order of the reaction.

Again, let's consider the simplest case, a reaction with only one reactant, **A**:

$$a\mathbf{A} \rightarrow \text{products}$$

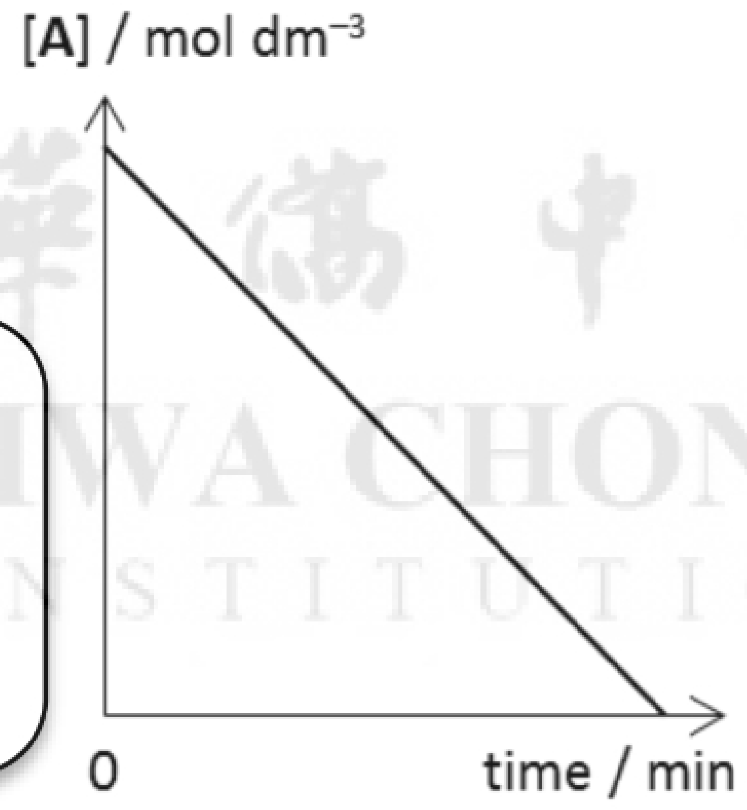
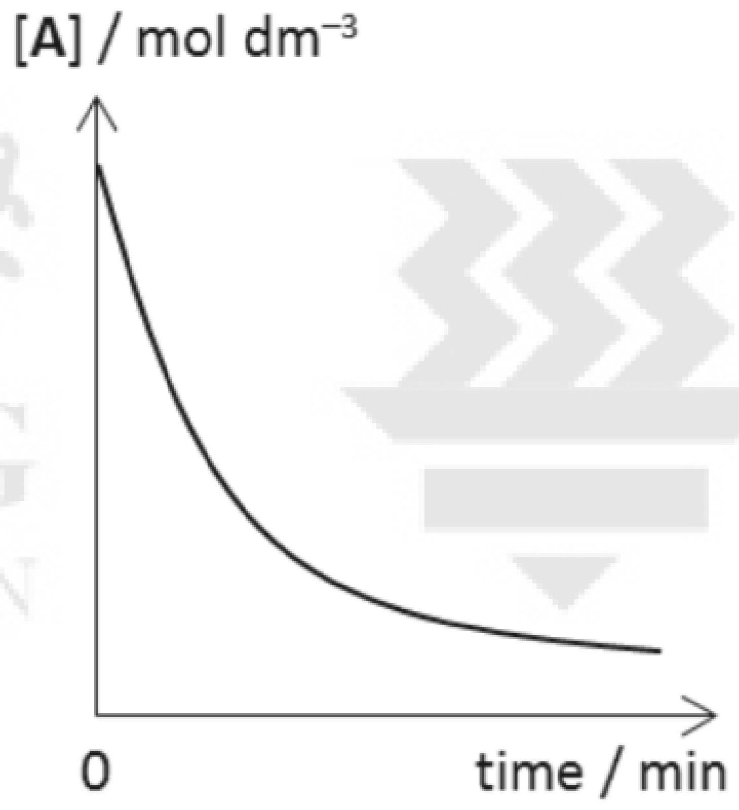
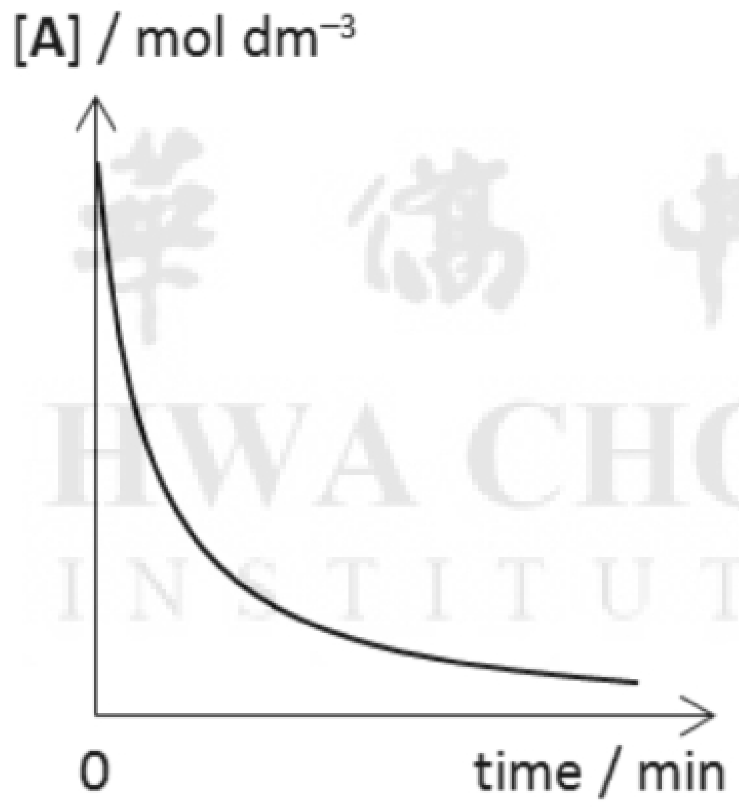
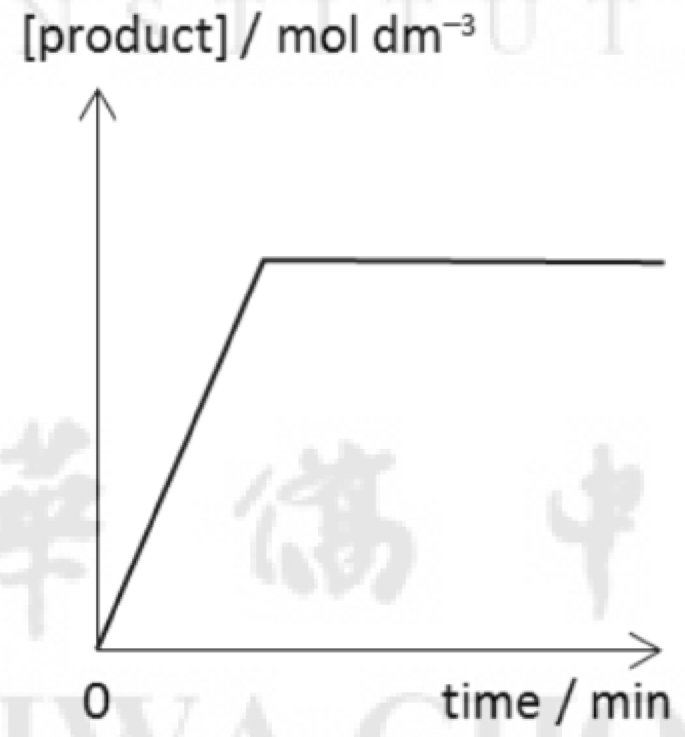
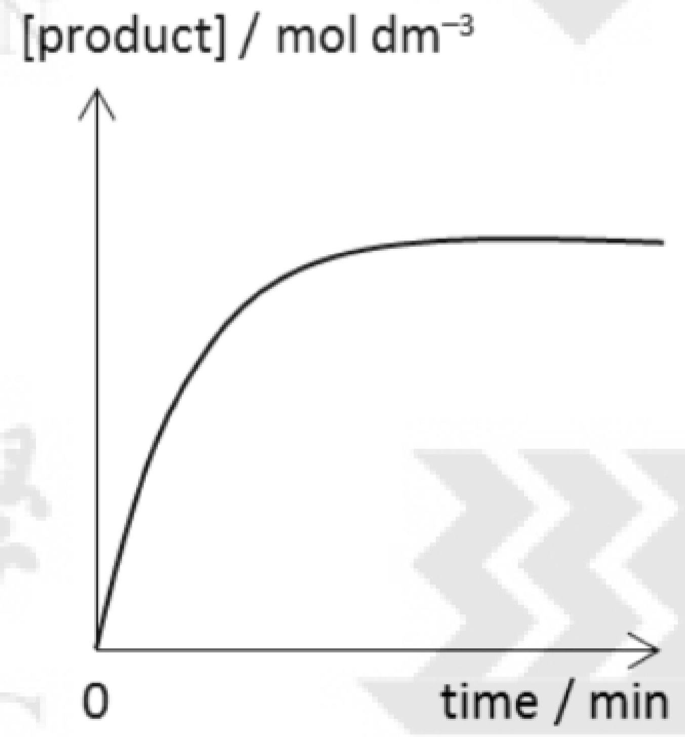
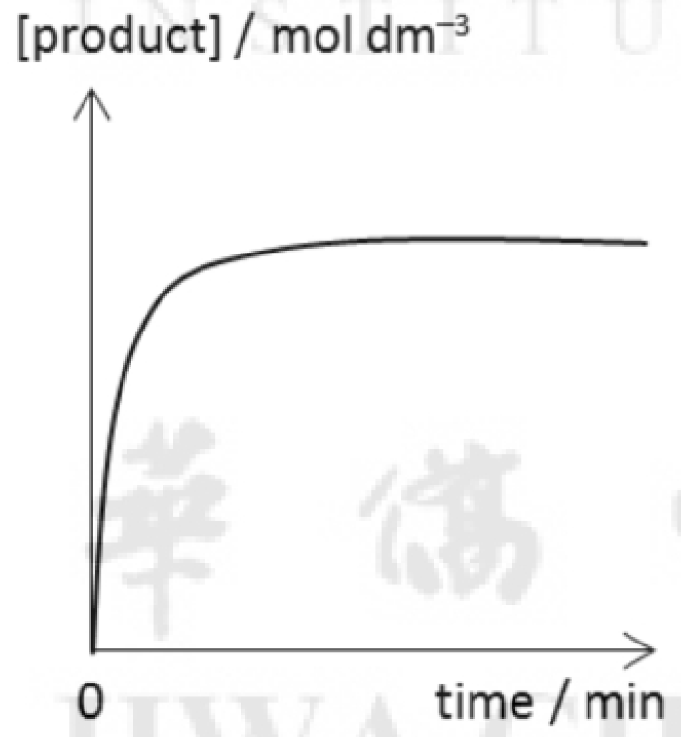
The rate equation would thus be

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

where *m* is the order of reaction with respect to **A** that we wish to determine.

Concentration-time graphs

Let's first look at the **concentration-time graphs** where *m* in the above rate equation is 0, 1 and 2:

order	$m = 0$	$m = 1$	$m = 2$
Rate equation	Rate = $k[A]^0 = k$	Rate = $k[A]$	Rate = $k[A]^2$
[A]-time graphs			
General shape:	straight line (constant gradient)	curve (slope becomes gentler as the reaction progresses) with a **constant half-life** (see next page)	similar shape to first order reaction, but half-lives are **not** constant
To note:	[A] decreases at a constant rate and reaches zero when the reaction is completed or when reagents are used up. The falling [A] has no effect on rate, so the rate remains unchanged (seen by the constant gradient) at the value of *k* throughout the reaction.	[A] decreases exponentially with time and reaches zero when reaction is completed. The falling [A] causes rate to decrease over time (as seen by the curve with decreasing gradient).	The gradient at the start is steeper and later becomes gentler than that of a first order reaction with the same value of *k*.
The corresponding [product]-time graphs:			

Recall: the gradient of a concentration-time graph at any time t represents the instantaneous rate of reaction at t.

Look again at the concentration-time plots for a first vs a second order reaction. The key distinguishing factor is the fact that an **overall first order reaction has a constant half-life**.

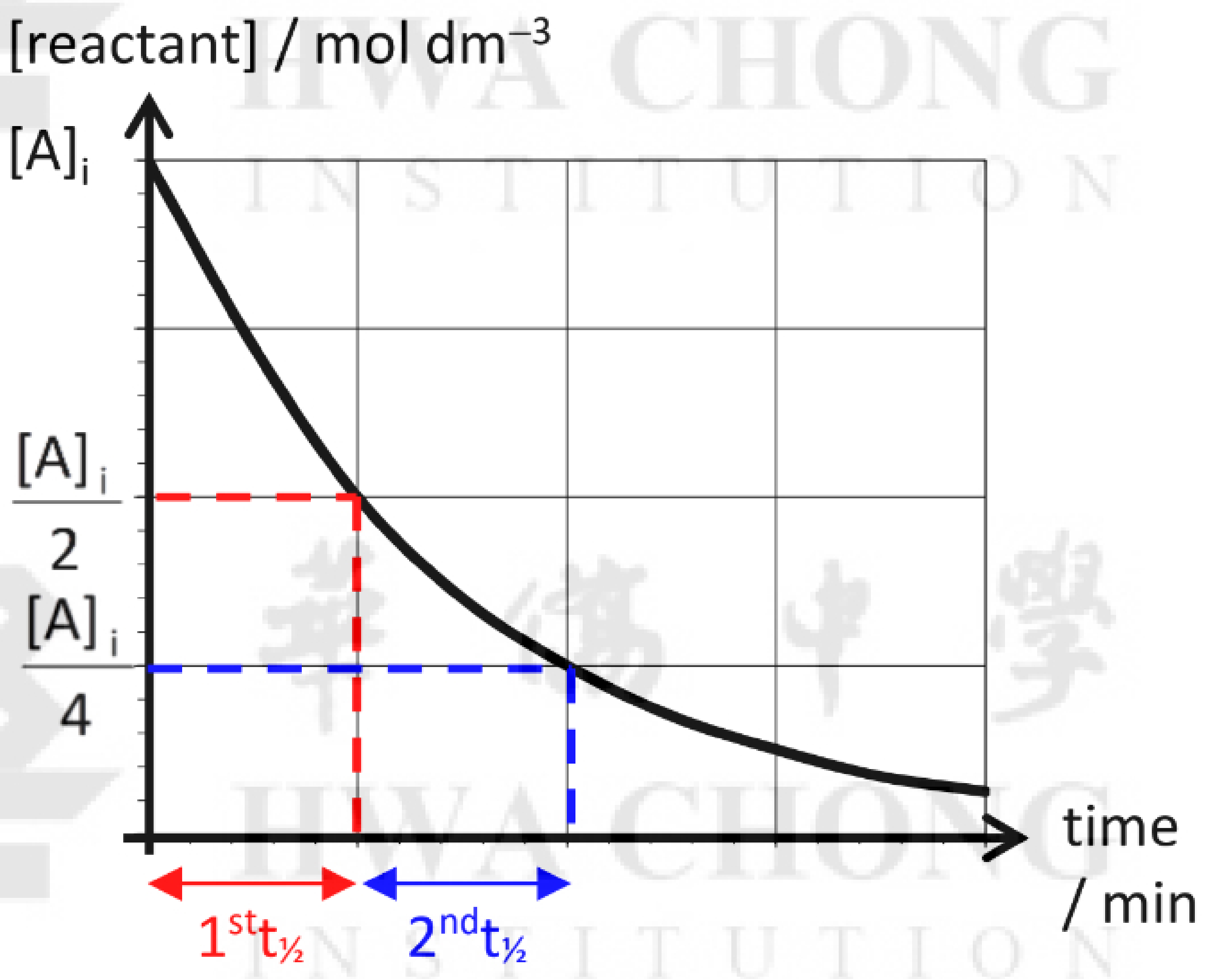
> *The **half-life**, $t_{½}$, of a reaction is the **time taken for the concentration of a reactant to decrease to half its initial value.***

> For an **overall first-order reaction**: $t_{½} = \dfrac{\ln 2}{k}$

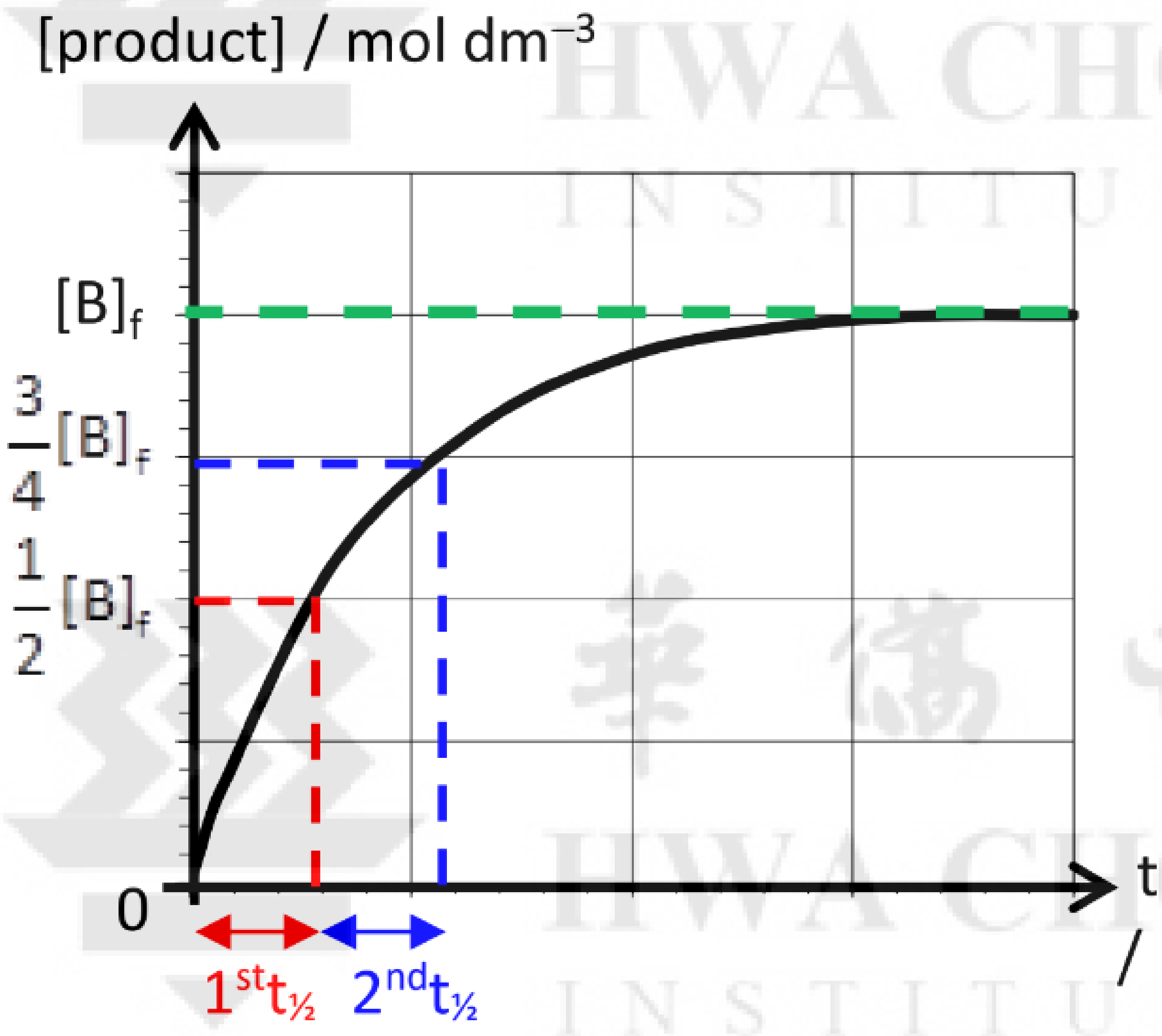
where *k* is the rate constant

Because no concentration term appears in this expression, the half-life of an overall first order reaction is **independent of reactant concentration**. Thus, its value is characteristic of a given first order reaction at a given temperature.

Half-life has units of time. To confirm that a reaction is first order, consecutive half-lives can be shown to be the same on a [reactant]-time graph or [product]-time graph as follows:



- $[A]_i$ is the initial concentration of the reactant, **A**
- The first half-life is the time needed for $[A]_i$ to decrease to $\frac{[A]_i}{2}$, while the second half-life is the time needed for $\frac{[A]_i}{2}$ to decrease to $\frac{[A]_i}{4}$.
- The half-life will be constant, meaning that for any [A] chosen, the time taken to half it will be the same, hence if the graph does **not** have a value for $\frac{[A]_i}{4}$, you can use any [A] to find the second half-life.



- $[B]_f$ is the final concentration of the product, **B**. This value may be calculated via **stoichiometric calculations** if it is not given in the question.
- The first half-life is the time needed to increase from 0 to $\frac{1}{2}[B]_f$, while the second half-life is the time needed for $\frac{1}{2}[B]_f$ to increase to $\frac{3}{4}[B]_f$.

Let's consider the simplest case, a first order reaction with only one reactant, **A** and one product, **B** in a 1:1 ratio:

$$\mathbf{A} \rightarrow \mathbf{B}$$

Let the initial concentration of **A** be $[A]_i$ mol dm^{-3} and the final concentration of **B** be $[B]_f$. After the first half-life, half of A is consumed to form product B, hence [A] will be $\frac{1}{2}[A]_i$ mol dm^{-3} and [B] will be $\frac{1}{2}[B]_f$ mol dm^{-3}. After the second half-life, [A] will be $\frac{1}{4}[A]_i$ mol dm^{-3}, hence [B] will be $\frac{3}{4}[B]_f$ mol dm^{-3}.

		1st $t_{1/2}$		2nd $t_{1/2}$		3rd $t_{1/2}$	
[A] after each half-life/ mol dm^{-3}	$[A]_i$	→	$\frac{1}{2}[A]_i$	→	$\frac{1}{4}[A]_i$	→	$\frac{1}{8}[A]_i$
[B] after each half-life/ mol dm^{-3}	0	→	$\frac{1}{2}[B]_f$	→	$\frac{3}{4}[B]_f$	→	$\frac{7}{8}[B]_f$

$$\boxed{[A] \text{ after n number of half-lifes} = [A]_i \times (\tfrac{1}{2})^n}$$

Self-practice 4.3

(a) 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 a rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1:3?

[PromoNYJC12/I/18]

(b) The rate of removal of the pain–killing drug paracetamol from the body is a first order reaction with a rate constant, $k = 0.26$ hr^{-1}. How long will it take to remove 75% of the paracetamol that a patient consumes?

[PrelimIJC14/I/15]

(c) Quarter-life, $t_{1/4}$, of a radioactive isotope is defined as the time taken for the sample to decay to ¼ its original amount. Potassium-argon dating is used to determine the age of a rock. ^{40}K is a radioactive isotope of potassium and it decays to ^{40}Ar with a constant $t_{1/4}$ of 2.50×10^9 years. A sample of moon rock was found to contain 6.25% of the original amount of ^{40}K. How old is the rock?

[PrelimRIJC14/I/10]

Lecture Exercise 4.1 – Determining order of reaction from concentration-time data

[N91/3/3] A dilute solution of hydrogen peroxide can be used to bleach hair. It decomposes slowly in aqueous solution according to the following equation:

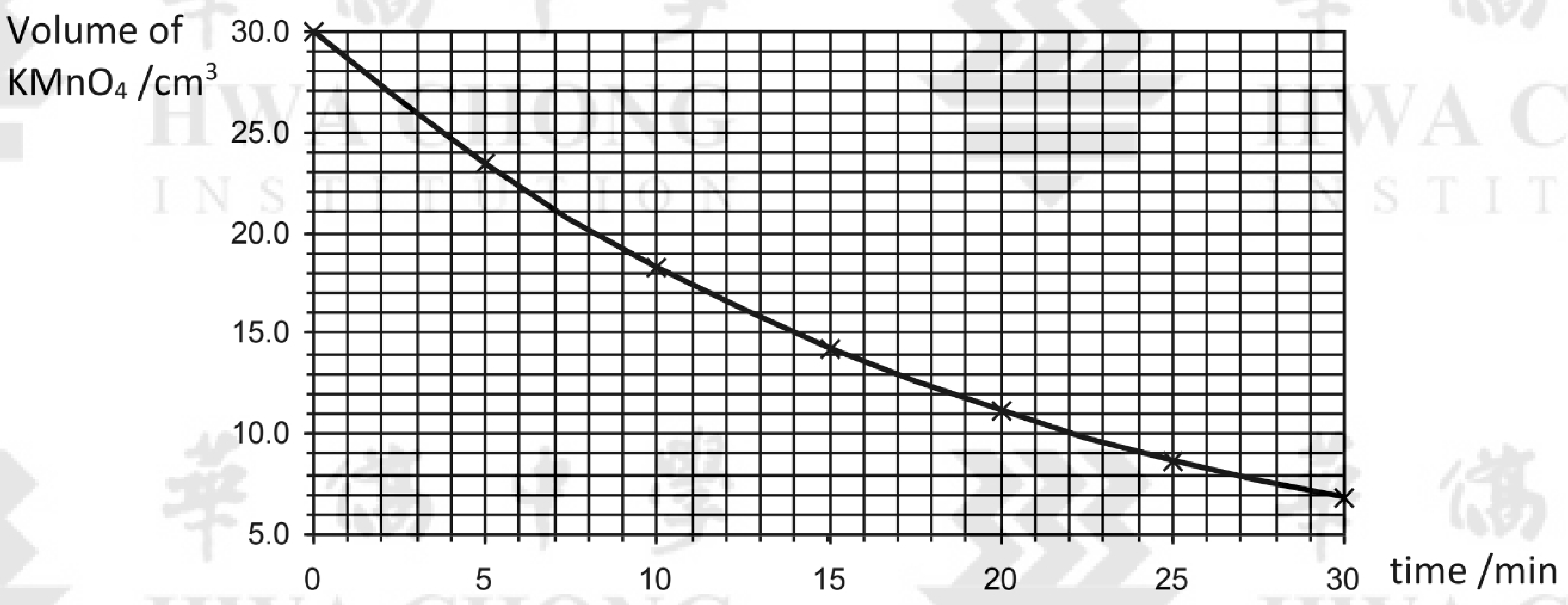
$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

A solution with an original concentration of 3.0 mol dm^{-3} was placed in a bottle contaminated with transition metal ions, which act as catalysts for the decomposition. The reaction was followed by withdrawing 10.0 cm^3 portions at various times and titrating with acidified 0.1 mol dm^{-3} $KMnO_4$(aq). (5 mol of H_2O_2 react with 2 mol of $KMnO_4$.)

The following results were obtained:

Time /min	0	5	10	15	20	25	30
Volume of $KMnO_4$ /cm^3	30.00	23.40	18.30	14.20	11.10	8.70	6.80

The graph was plotted for you.



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

(b) Write an expression for the rate equation and calculate the rate constant, indicating units.

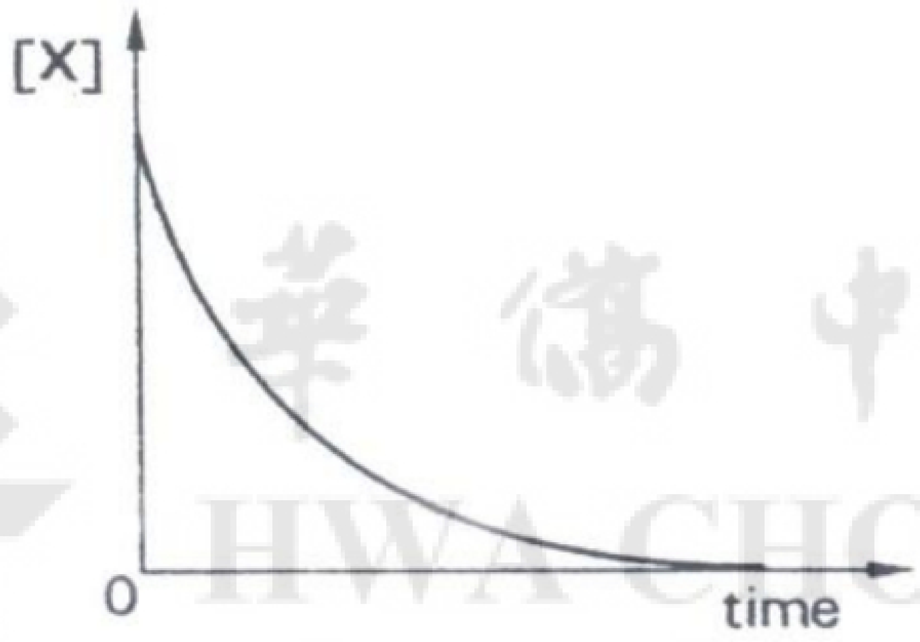
(c) Calculate the concentration of the H_2O_2 at the time the first portion was withdrawn. Hence estimate how long the solution had been in the contaminated bottle.
[5 mol of H_2O_2 react with 2 mol of $KMnO_4$.]

(d) Suggest a method whereby the shelf-life of hydrogen peroxide solutions could be increased.

Self-practice 4.4

(a) The following reaction was believed to be of first order.

$$\mathbf{X} \rightarrow \text{products}$$



In an experiment, [**X**], the concentration of **X**, varied with time as shown in the graph.
What can the graph be used for?

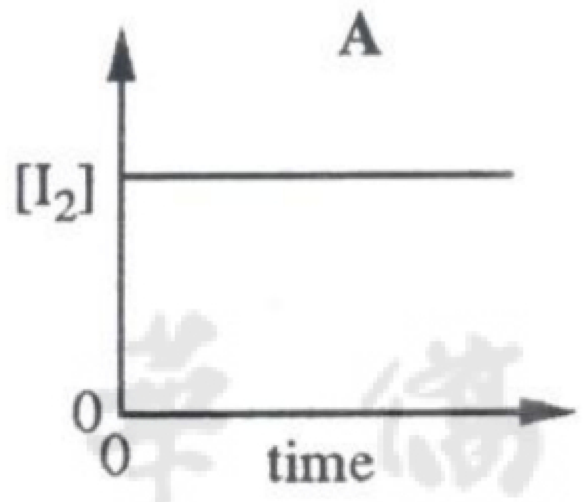
1 to determine the rate of reaction at any given instant
2 to check whether the reaction is of first order throughout
3 to determine the half-life of the reaction

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

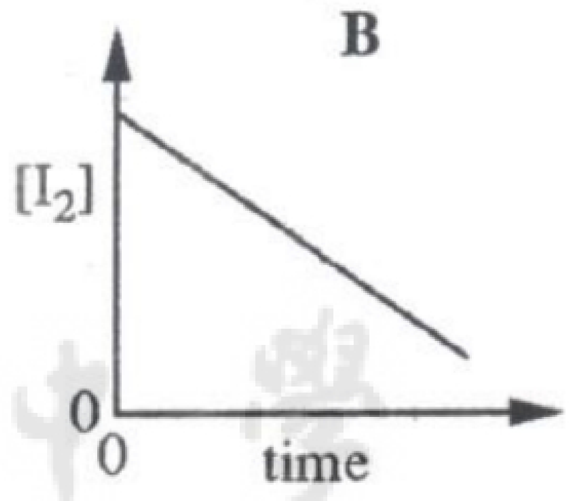
[N92/4/34]

(b) The reaction of iodine with propanone in the presence of aqueous acid is zero order with respect to iodine. Which diagram represents the variation of $[I_2]$ with time?

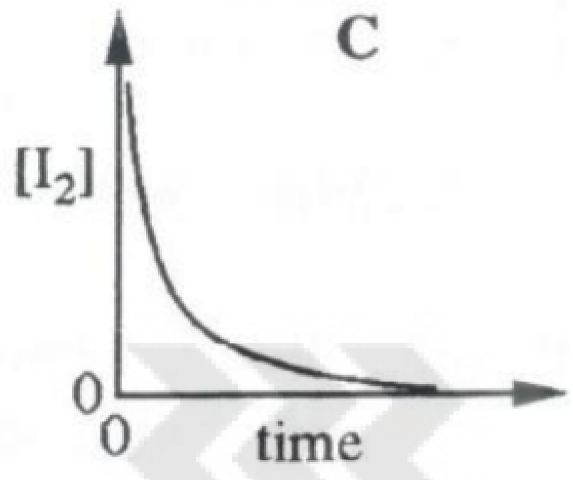
A



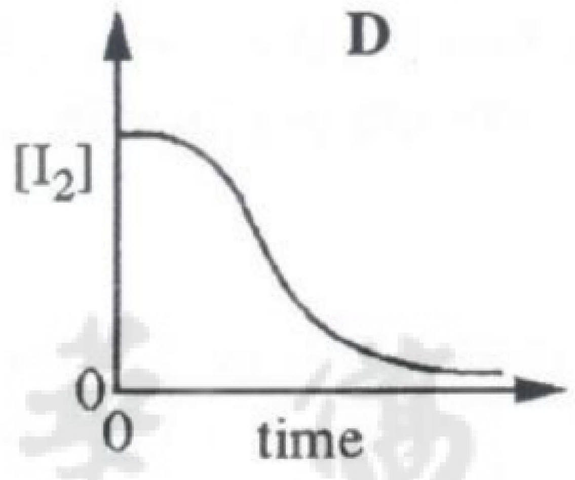
B



C



D



[J98/3/12]

Rate-concentration graphs

Besides concentration-time graphs, we can check the order by plotting a **rate-concentration graph**. The data to plot this graph can be obtained in the following ways:

(1) by measuring the gradient at various points in the concentration-time graph and plotting these rates against their corresponding reactant concentration; or

(2) by carrying out the reaction a few times with different initial [A] and determining the initial rate in each case by obtaining gradient at t = 0 from a concentration-time graph (refer to section 4.6 Method 2).

Zero order

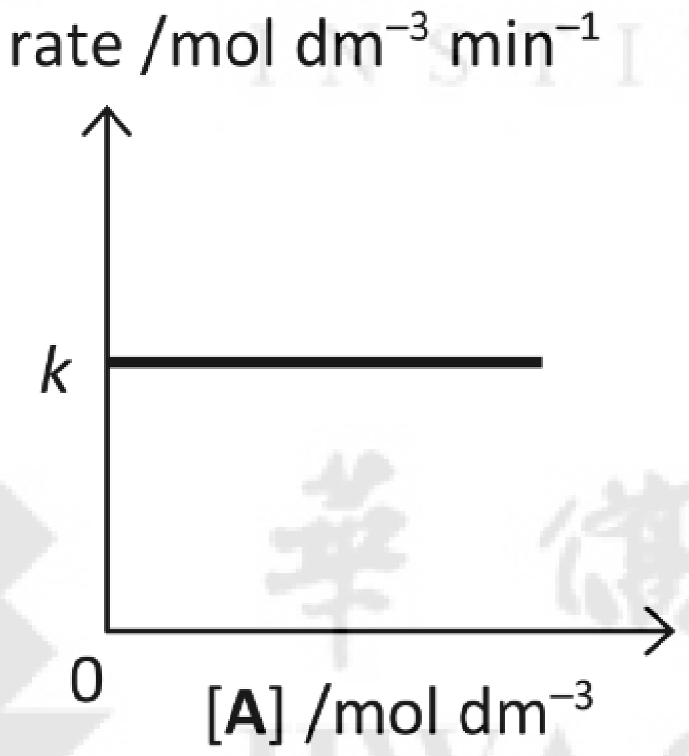
$$\underset{\underset{y}{\uparrow}}{\text{Rate}} = \underset{\underset{m}{\uparrow}}{k}[A]^0$$

$\because [A]^0 = 1 \implies$ **Rate = *k*,**

$\therefore$ **Rate = *k*** at all values of [A]

⇓

a straight line parallel to the x-axis:

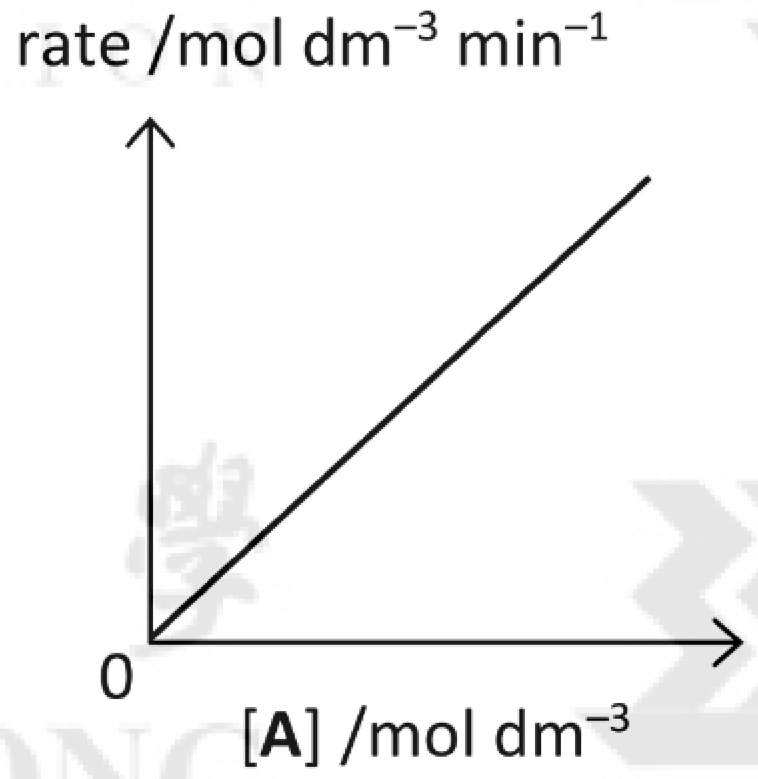


First order

$$\underset{\underset{y}{\uparrow}}{\text{Rate}} = \underset{\underset{m}{\uparrow}}{k}\underset{\underset{x}{\uparrow}}{[A]}$$

⇓

a straight line, with gradient *k*, passing through the origin:

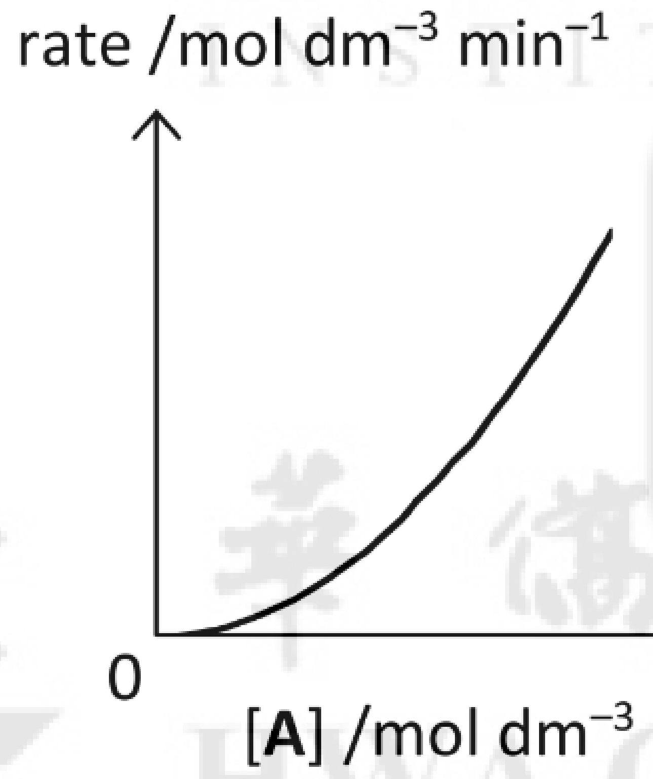


Second order

$$\underset{\underset{y}{\uparrow}}{\text{Rate}} = \underset{\underset{m}{\uparrow}}{k}\underset{\underset{x^2}{\uparrow}}{[A]^2}$$

⇓

a parabola starting at the origin:



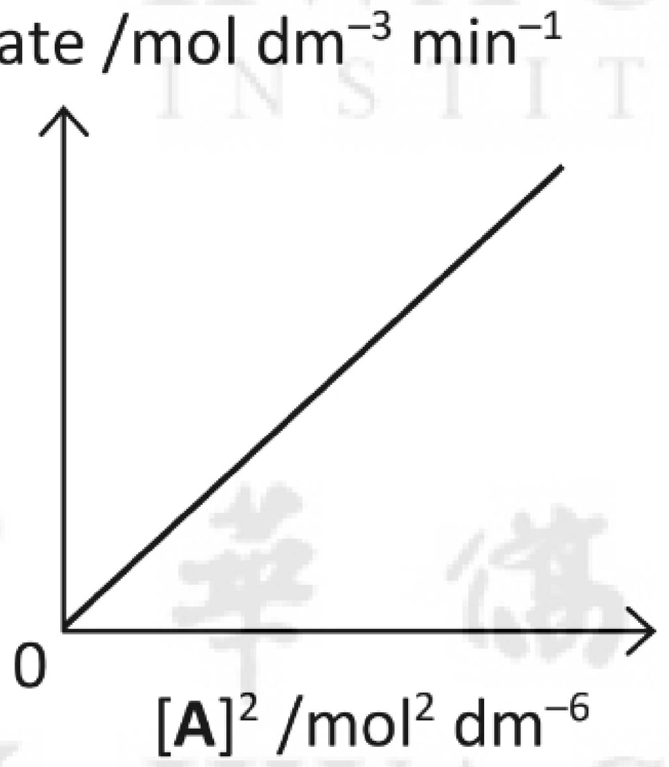
The shape of this graph ***cannot*** *be used to confirm the order with respect to reactant A.*

A better way to confirm a second order reaction would be to plot **rate** against **[A]^2**:

$$\underset{\underset{y}{\uparrow}}{\text{Rate}} = \underset{\underset{m}{\uparrow}}{k}\underset{\underset{x}{\uparrow}}{[A]^2}$$

⇓

a straight line, with gradient *k*, passing through the origin:



This is a better graph to plot if you have to confirm that a reaction is second order with respect to reactant A

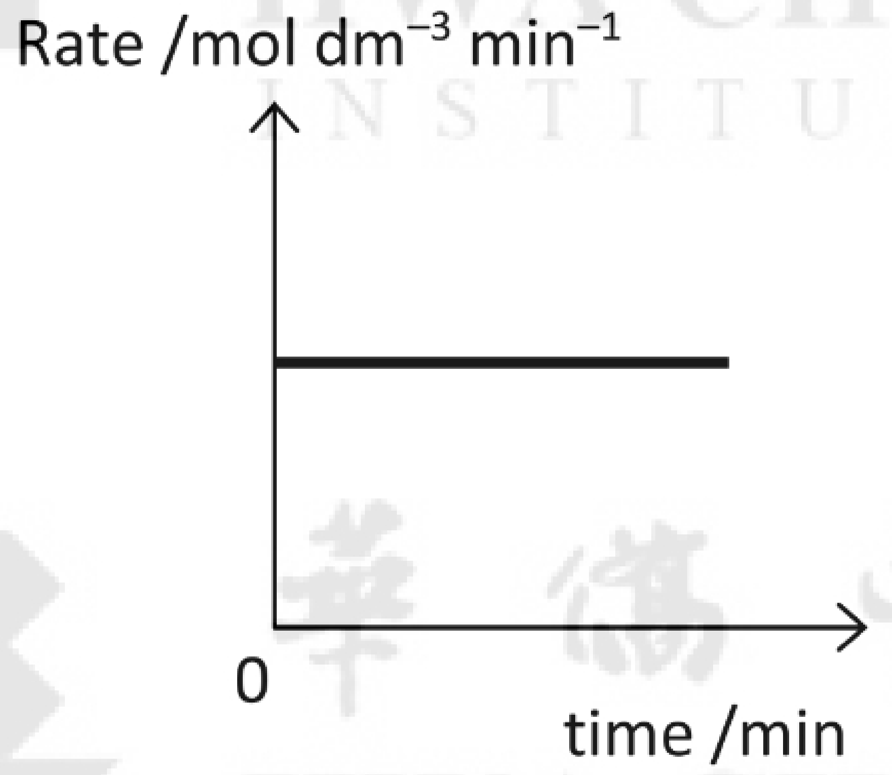
Rate-time graphs

Rate-time graphs are not usually used to deduce the order of a reaction because they do not offer much more information than the concentration-time graphs on which they are based. To obtain a rate-time graph, we find the gradient of different points on the concentration-time graph and obtain the rate at each timing. It is, however, still useful to understand their shapes.

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

Zero order

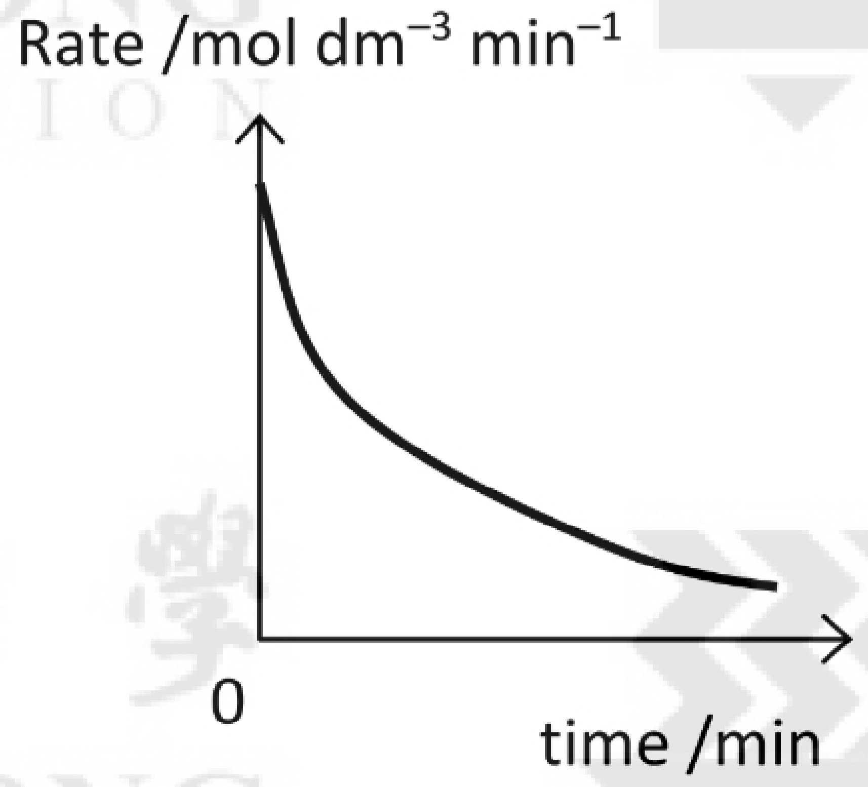
$m = 0$



- rate remains constant during the reaction, except when the reaction is completed

First order

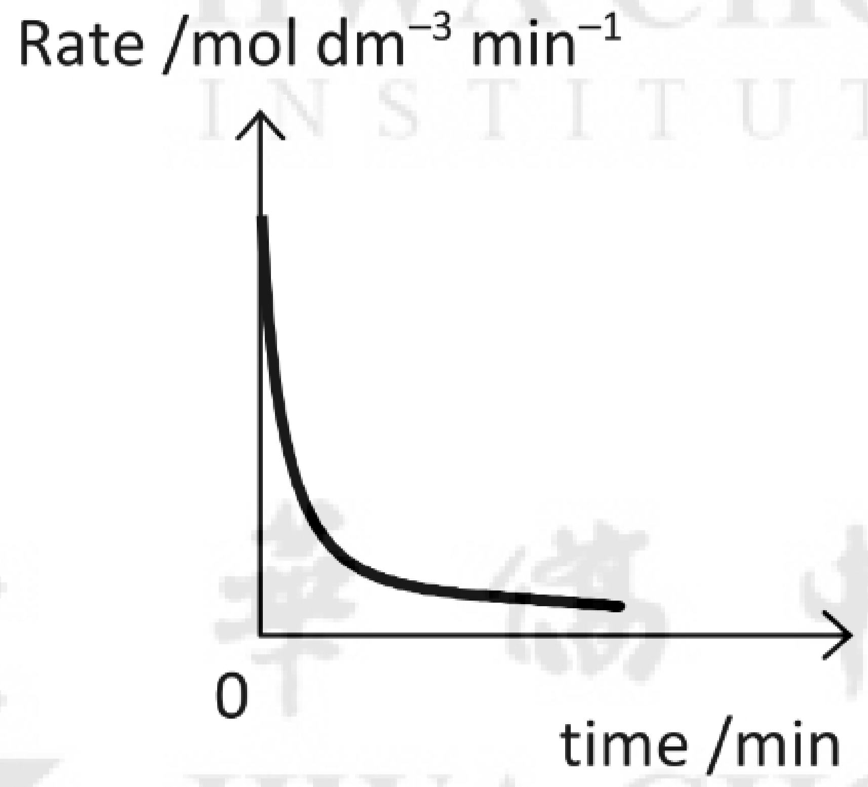
$m = 1$



- rate decreases exponentially with time

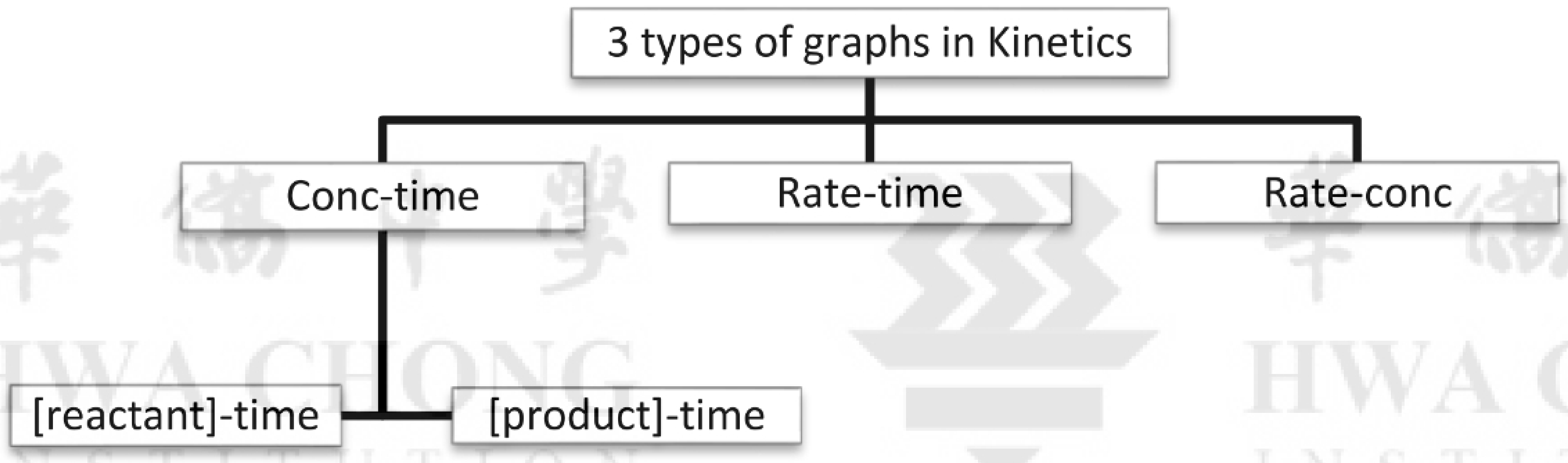
Second order

$m = 2$



- rate decreases exponentially with time
- resembles a first order reaction curve, although for the same value of *k*, the rate falls faster

In summary,



4.6 Studying the rates and orders of reactions

So far we have looked at the simple case of reactions with only one reactant, $a\mathbf{A} \rightarrow$ products. However, there are many reactions which involve more than one reactant. In these cases we need to "isolate" the reactant under study so that we can determine the order of reaction with respect to that reactant alone. There are two general methods that could be used to obtain rates and orders of reactions.

Method 1: Keep all reactants in excess except the one being studied

This is done by ensuring that all other reactants are present in ***large excess*** (i.e. their concentrations should be around 10 times larger than that of the reactant being isolated for study) such that their concentrations don't appear to change significantly and may be regarded as constant during the course of the reaction. We are thus creating an artificial situation in which these other reactants do not seem to influence the rate of the reaction. We call this ***pseudo-zero order*** with respect to the reactants that are in excess. (see Section 5.3)

Say we want to find out the order of reaction with respect to each reactant in the following reaction:

$$\mathbf{A}(aq) + \mathbf{B}(aq) + \mathbf{C}(aq) \rightarrow \text{products}$$

In order to find the order with respect to **A**, we would ensure that the concentrations of **B** and **C** are in large excess compared to [**A**]. Thus, the overall order of reaction obtained would *appear* to reflect the order with respect to **A** as the orders with respect to both **B** and **C** would *appear* to be zero. We can then monitor the **concentration of A vs time graph** to obtain the order with respect to **A**.

Method 2: Initial rate method

In this method, we measure the rate of several reaction mixtures, in which a different initial concentration of one reactant is used, while the initial concentrations of all other reactants are kept the same. Note that other variables (e.g. temperature) should be kept constant as well.

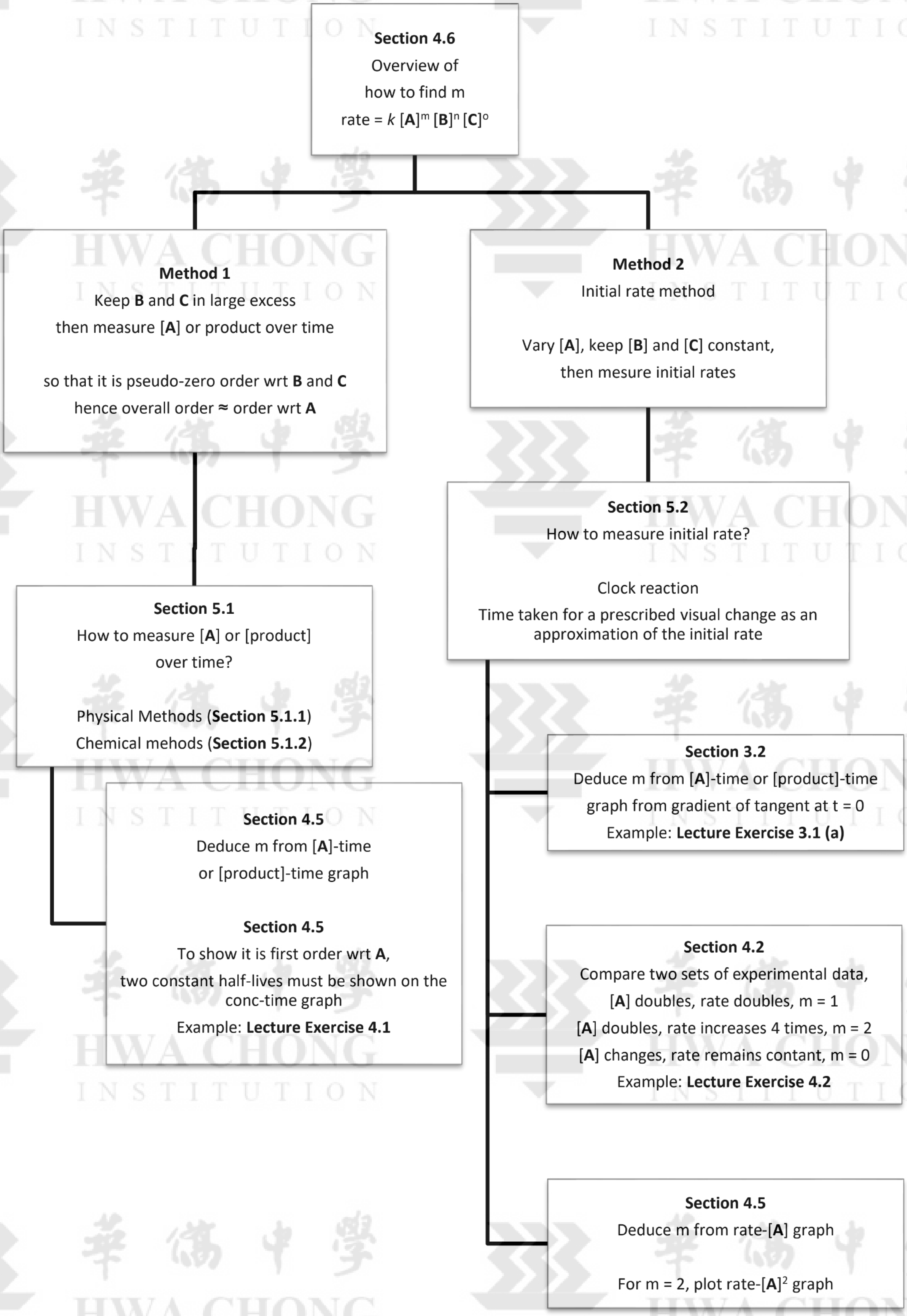
Using the same reaction,

$$\mathbf{A}(aq) + \mathbf{B}(aq) + \mathbf{C}(aq) \rightarrow \text{products}$$

To find the order with respect to reactant **A**, we measure the initial rate of several reaction mixtures using varying initial concentrations of **A** and constant concentrations of **B** and **C**.

If the initial rate is found to double when the initial concentration of **A** doubles, the order of reaction with respect to **A** will be 1. Alternatively, the graph of initial rate vs initial concentration of **A** can be plotted and the order with respect to **A** obtained according to the shape of the graph. Refer to previous section of rate-concentration graphs.

In summary,



Section 4.6
Overview of
how to find m
rate = k [**A**]^m [**B**]^n [**C**]^o

Method 1
Keep **B** and **C** in large excess
then measure [**A**] or product over time

so that it is pseudo-zero order wrt **B** and **C**
hence overall order ≈ order wrt **A**

Section 5.1
How to measure [**A**] or [product]
over time?

Physical Methods (**Section 5.1.1**)
Chemical mehods (**Section 5.1.2**)

Section 4.5
Deduce m from [**A**]-time
or [product]-time graph

Section 4.5
To show it is first order wrt **A**,
two constant half-lives must be shown on the conc-time graph
Example: **Lecture Exercise 4.1**

Method 2
Initial rate method

Vary [**A**], keep [**B**] and [**C**] constant,
then mesure initial rates

Section 5.2
How to measure initial rate?

Clock reaction
Time taken for a prescribed visual change as an approximation of the initial rate

Section 3.2
Deduce m from [**A**]-time or [product]-time
graph from gradient of tangent at t = 0
Example: **Lecture Exercise 3.1 (a)**

Section 4.2
Compare two sets of experimental data,
[**A**] doubles, rate doubles, m = 1
[**A**] doubles, rate increases 4 times, m = 2
[**A**] changes, rate remains contant, m = 0
Example: **Lecture Exercise 4.2**

Section 4.5
Deduce m from rate-[**A**] graph

For m = 2, plot rate-[**A**]^2 graph

Lecture Exercise 4.2 Initial rate method

In investigations of the reaction, 2**A**(aq) + 2**B**(aq) + **C**(aq) → products, the following results are obtained.

Experiment	Initial concentration /mol dm^{-3}			Initial rate of reaction /mol dm^{-3} s^{-1}
	[**A**]	[**B**]	[**C**]	
1	0.010	1.00	0.50	2.0×10^{-3}
2	0.030	1.00	0.50	6.0×10^{-3}
3	0.030	2.00	0.50	2.4×10^{-2}
4	0.030	2.00	0.25	2.4×10^{-2}
5	0.040	2.50	0.40	?

(a) Determine the order of reaction with respect to **A**, **B** and **C**.

(b) Write the rate equation for the reaction.

(c) Calculate the rate constant for the reaction, indicating units.

(d) Calculate the initial rate for Experiment 5.

Self-practice 4.5

(a) Hydrogen peroxide reacts with acidified iodide ions, liberating iodine. In investigations of this reaction, the following results were obtained.

Initial concentrations of reactants/ mol dm^{-3}			**Initial rate of formation of iodine/ mol dm^{-3} s^{-1}**
[H_2O_2]	**[I^-]**	**[H^+]**	
0.010	0.010	0.10	2.0×10^{-6}
0.030	0.010	0.10	6.0×10^{-6}
0.030	0.020	0.10	1.2×10^{-5}
0.030	0.020	0.20	1.2×10^{-5}

Which statements follow from these results?

1 The rate equation for the reaction can be written: rate = $k[H_2O_2][I^-]$.

2 The reaction is zero order with respect to the acid.

3 The rate constant is 2×10^{-1} mol^{-2} dm^6 s^{-1}.

A **1**, **2** and **3** are correct

B **1** and **2** only are correct

C **2** and **3** only are correct

D **1** only is correct

[N96/IV/34]

(b) Trichloromethane reacts with aqueous sodium hydroxide according to the equation shown below.

$$2CHCl_3 + 7OH^- \rightarrow CO + HCO_2^- + 6Cl^- + 4H_2O$$

Some data were recorded in order to study the kinetics of the reaction:

Expt	Initial [$CHCl_3$] / mol dm^{-3}	Initial [OH^-] / mol dm^{-3}	Initial rate / mol dm^{-3}s^{-1}
1	0.100	0.120	1.0×10^{-4}
2	0.050	0.240	1.0×10^{-4}
3	0.050	0.480	2.0×10^{-4}

If k is the rate constant, what is the rate equation?

A rate = $k[OH^-]$

B rate = $k[CHCl_3][OH^-]$

C rate = $k[CHCl_3]^2[OH^-]$

D rate = $k[CHCl_3][OH^-]^2$

(c) The table shows experimental results obtained for the following reaction:

$$2XO(g) + O_2(g) \rightarrow 2XO_2(g)$$

Partial pressure of XO (in arbitrary units)	Partial pressure of O_2 (in arbitrary units)	Relative rate
100	100	1.00
100	25	0.25
50	100	0.50
50	?	0.125

What is the missing value of the partial pressure of O_2 in the table?

A 25 **B** 40 **C** 50 **D** 75

[N90/1/13]

5 EXPERIMENTAL TECHNIQUES FOR STUDYING RATE OF REACTION AND ORDER OF REACTION

Let's look at how to carry out actual experiments that aim to obtain the rate of a reaction.

Simple observation tells us that some reactions go faster than others, but to actually *measure* the rate of a reaction, we must be able to monitor how fast the product is being produced or how fast the reactant is disappearing over time. A change in time can easily be measured with a stopwatch or other timing device, but how can a change in concentration of the reactants and/or products be measured during a chemical reaction?

5.1 Measuring the concentration of reactant/product over time

There are two different ways in which we can follow the progress of a chemical reaction over time:

(1) Physical methods
By measuring some *physical* property of the reaction which changes as the reaction continues (e.g. the volume of gas produced, intensity of colour of the reaction mixture, change in conductivity, etc.) and relating these to changes in concentration of a reactant or product.

(2) Chemical methods
By taking samples of the reaction mixture at specific time intervals and finding out *chemically* how the concentration of one of the reagents or products is changing.

Note that the two methods do not directly give rate but *concentration data* over time instead. The reaction rate itself still needs to be extracted from this data. We often do this by plotting the experimental data in the form of a **concentration-time graph**.

Note that in all methods of analysis, the *time must always be carefully monitored*.

5.1.1 Physical methods of analysis

Recall that, even though we aim to measure the changes in *concentration* of a reactant or product over time, in practice, it is often easier to measure a physical change that relates to these changes in concentration, such as volume or pressure of gas, colour intensity, etc., since physical methods of analysis do not interfere with the reaction being studied.

The following examples are some of the more common methods employed to measure rate of reaction via changes in a physical property.

5.1.1.1 Measuring volume of gas produced

This method is useful for reactions which produce gaseous products.

For example, the reaction, $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$, may be studied by measuring the volume of O_2 gas produced using a gas syringe or via the water displacement method.

For diagrams and possible experimental set-ups on gas collection techniques, please refer to the Planning section in Topic 3 The Gaseous State.

Generic procedure for obtaining volume–time graphs by gas collection

The generic procedure is similar to the ones stated in the Planning section in Topic 3 The Gaseous State. In that section, two different set-ups were shown. We shall use set-up A as an example:

1. Using an electronic balance, weigh accurately about (mass) g of (solid reactant) in a weighing bottle.
2. Using a measuring cylinder, transfer (volume) cm^3 of (aqueous reactant) into a 250 cm^3 conical flask.
3. Carefully lower the weighing bottle containing (solid reactant) into the conical flask, ensuring the reactants do not mix. Insert the stopper to ensure a closed set-up.
4. **Set up** the apparatus as shown in the diagram (draw an appropriate diagram – refer to Planning section in Topic 3 The Gaseous State).
5. Record the **initial reading** (x cm^3) on the gas syringe.
6. **Shake** the conical flask to mix the reactants and continue swirling the conical flask to thoroughly mix the reactants. **Start the stop–watch at the same time**.
7. At ___(each of your chosen times)___, **record the reading** on the gas syringe and **calculate the volume of the gas** collected.

By recording the volume of gas at several time intervals, we can obtain the rate of reaction by plotting volume of gas produced against time. Because, in our example, the *volume* of O_2 produced is proportional to the *concentration* of O_2 at any time, *t*, the gradient of the volume-time graph at time *t* is **proportional** to rate of reaction at time *t*.

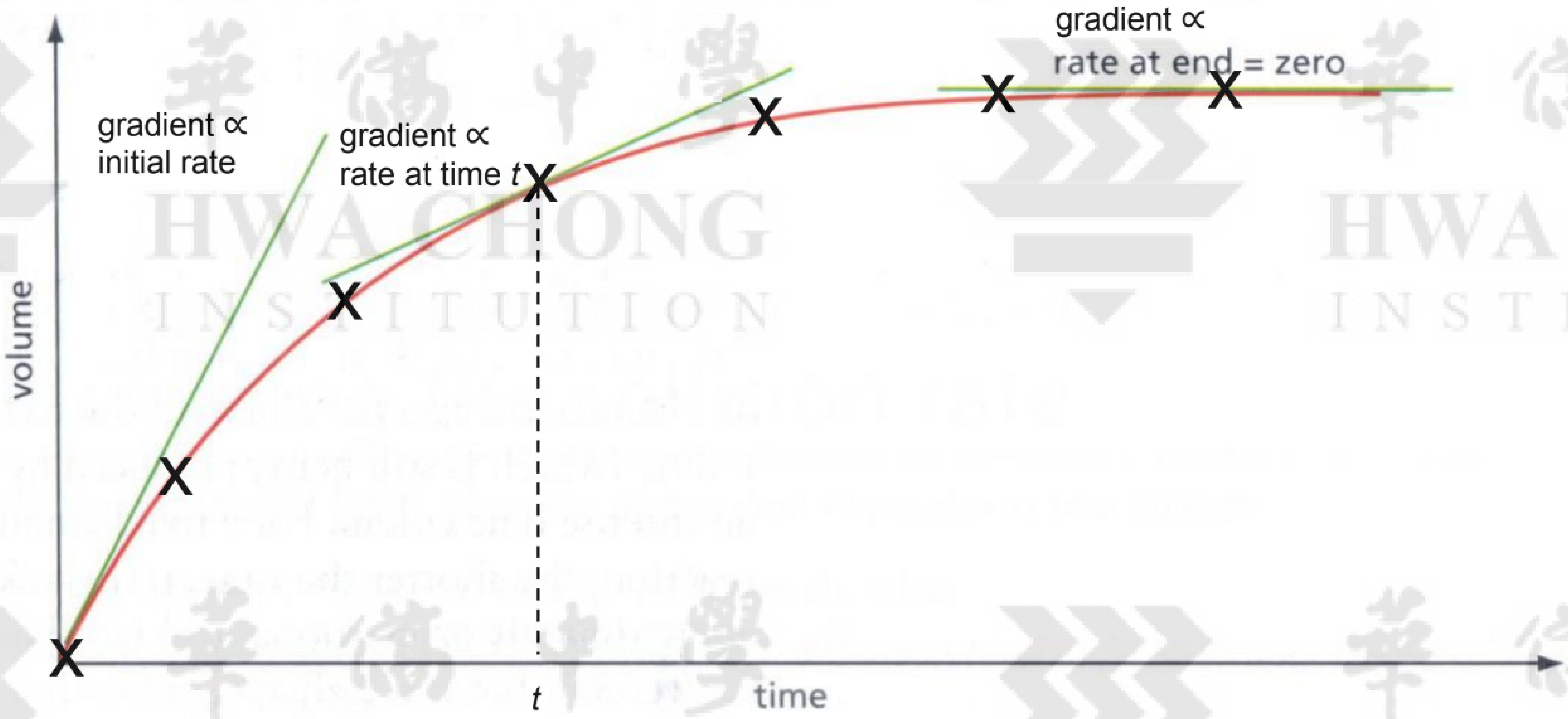


Figure 5. A typical graph of volume against time for a reaction that gives off a gas.

The order of reaction may also be found by plotting **rate against ($V_n – V_t$)** or by plotting **($V_n – V_t$) against time**, and looking at the shape of the graph, where:

V_t = volume of gas produced after time *t*
V_n = volume of gas produced at the end of the reaction
$(V_n – V_t) \propto$ amount of unreacted reactant remaining at time *t.*

This would be equivalent to plotting **rate against [reactant]** or **[reactant] against time** respectively.

5.1.1.2 Measuring the decrease in mass

An alternative method of monitoring reactions which produce gaseous products involves carrying out the reaction in an **open flask** placed on top of an electronic mass balance. As the gas is given off, the mass of the flask and its contents decreases. The total mass can thus be recorded throughout the experiment to plot a mass-time graph.

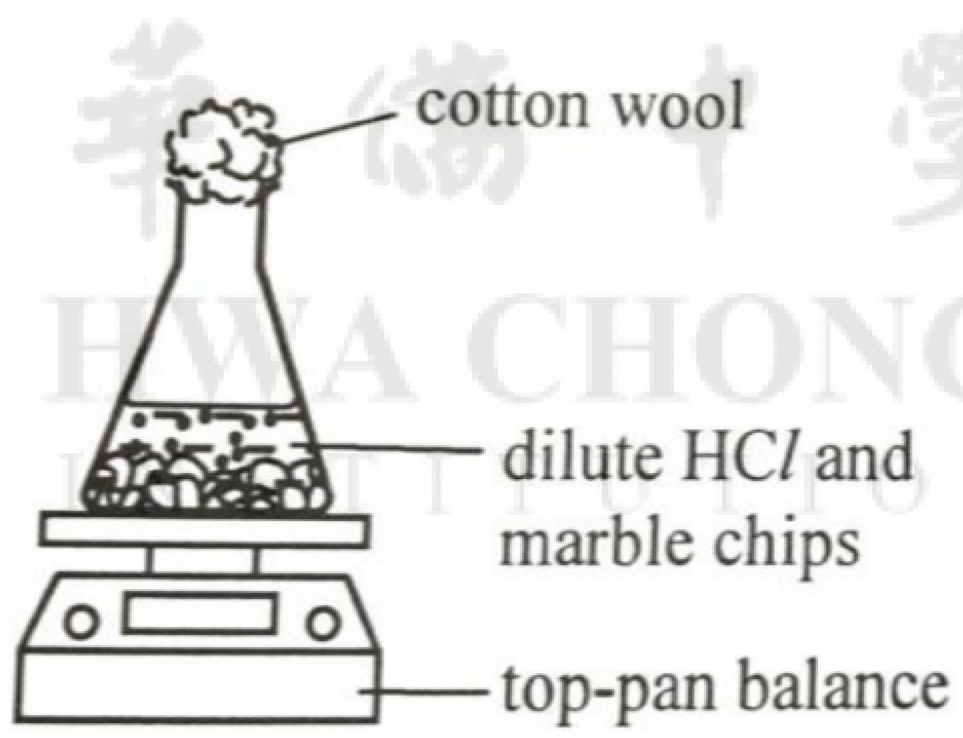


Figure 6a. Experimental setup for the reaction between HCl and $CaCO_3$ (marble chips). Cotton wool is placed at the mouth of the conical flask to prevent the reaction mixture from splashing out from the flask.

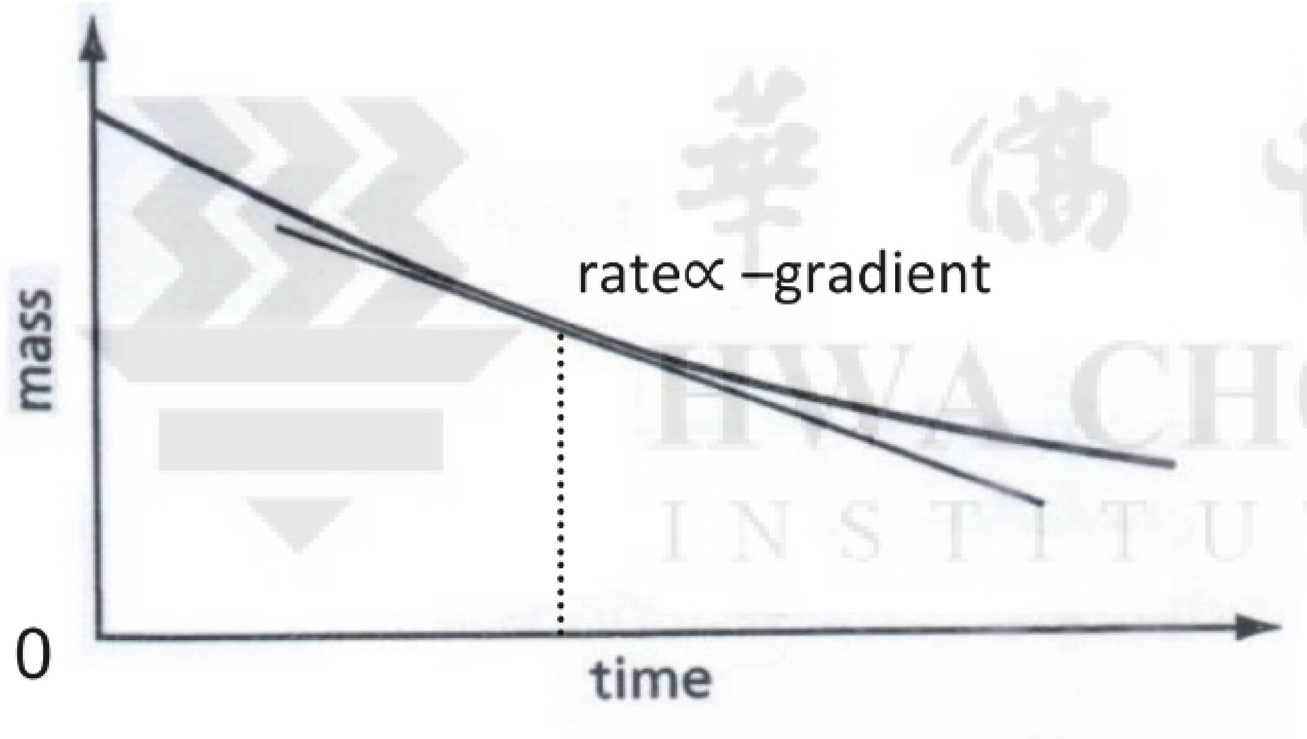


Figure 6b. A typical graph of mass against time for a reaction that "loses" a gas to the atmosphere. The rate of reaction at any time is directly proportional to the negative gradient of the graph at that time.

5.1.1.3 Following a change in gas pressure

This method is suitable for reactions which involve a change in the **number of moles of gases** (hence total pressure). For example, each reaction below shows a reduction in number of moles of gases, hence total pressure decreases as the reaction proceeds.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The total pressure of the reacting system is measured at regular time intervals by connecting the reaction flask to a **manometer**. The gaseous system is kept in a fixed-volume reactor maintained at constant temperature. Rate of reaction is directly proportional to the rate of change in pressure.

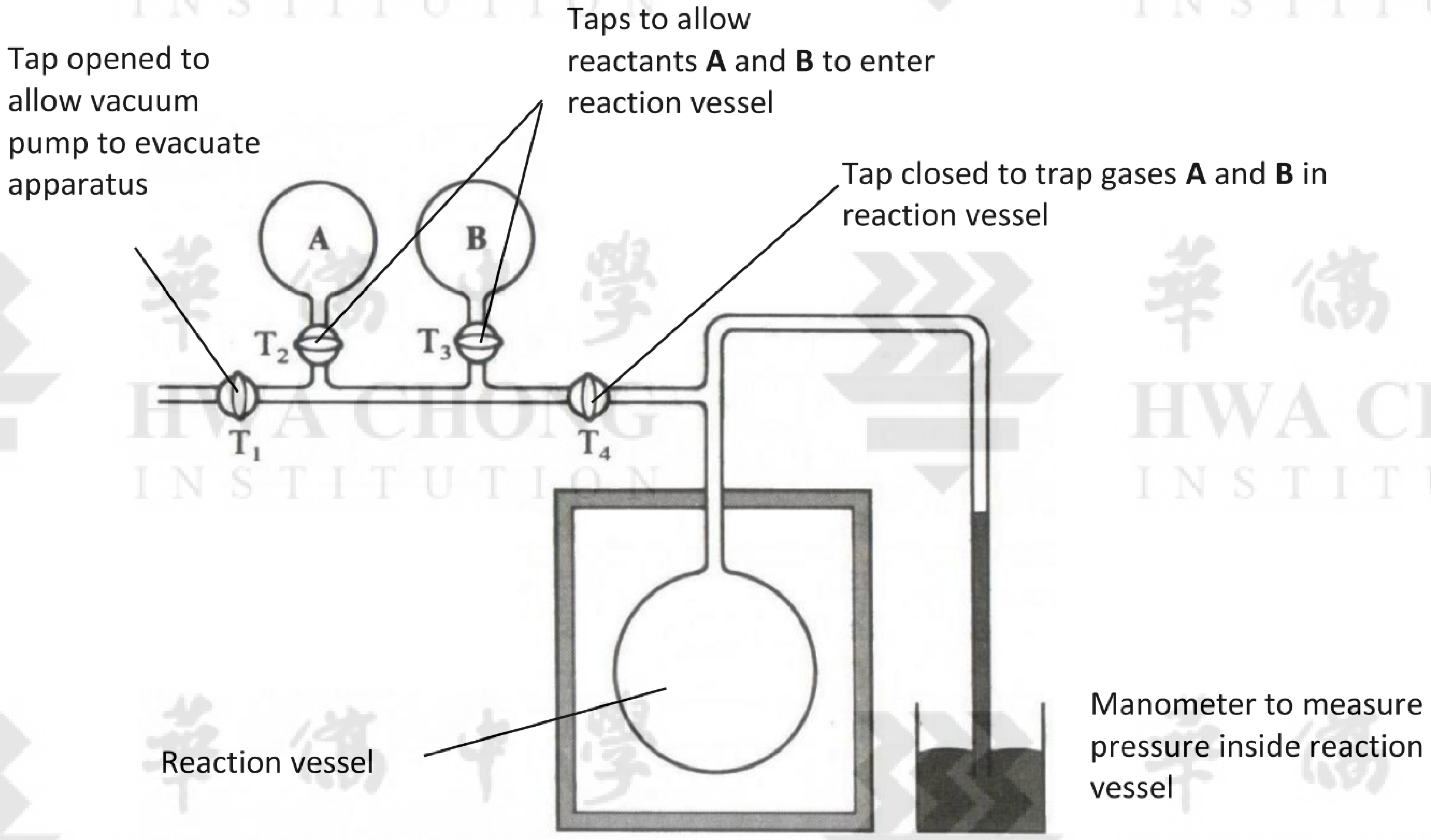


Figure 7. Set-up to measure changes in gas pressure over time.

5.1.1.4 Following a change in electrical conductivity

This method is applicable for a reaction in aqueous solution in which there is a change in the **concentration of ions** (hence electrical conductivity) as the reaction proceeds.

For example, in the redox reaction between bromate(V) and bromide ions, a decrease in concentration of ions is observed during the reaction.

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

On the other hand, in the nucleophilic substitution of *tert*-butyl bromide with water, the concentration of ions increases.

$$(CH_3)_3CBr(l) + H_2O(l) \rightarrow (CH_3)_3COH(l) + H^+(aq) + Br^-(aq),$$

The electrical conductivity of the aqueous solution can be measured at regular time intervals using a conductivity meter, and the rate of reaction is directly proportional to the rate of change in conductivity.

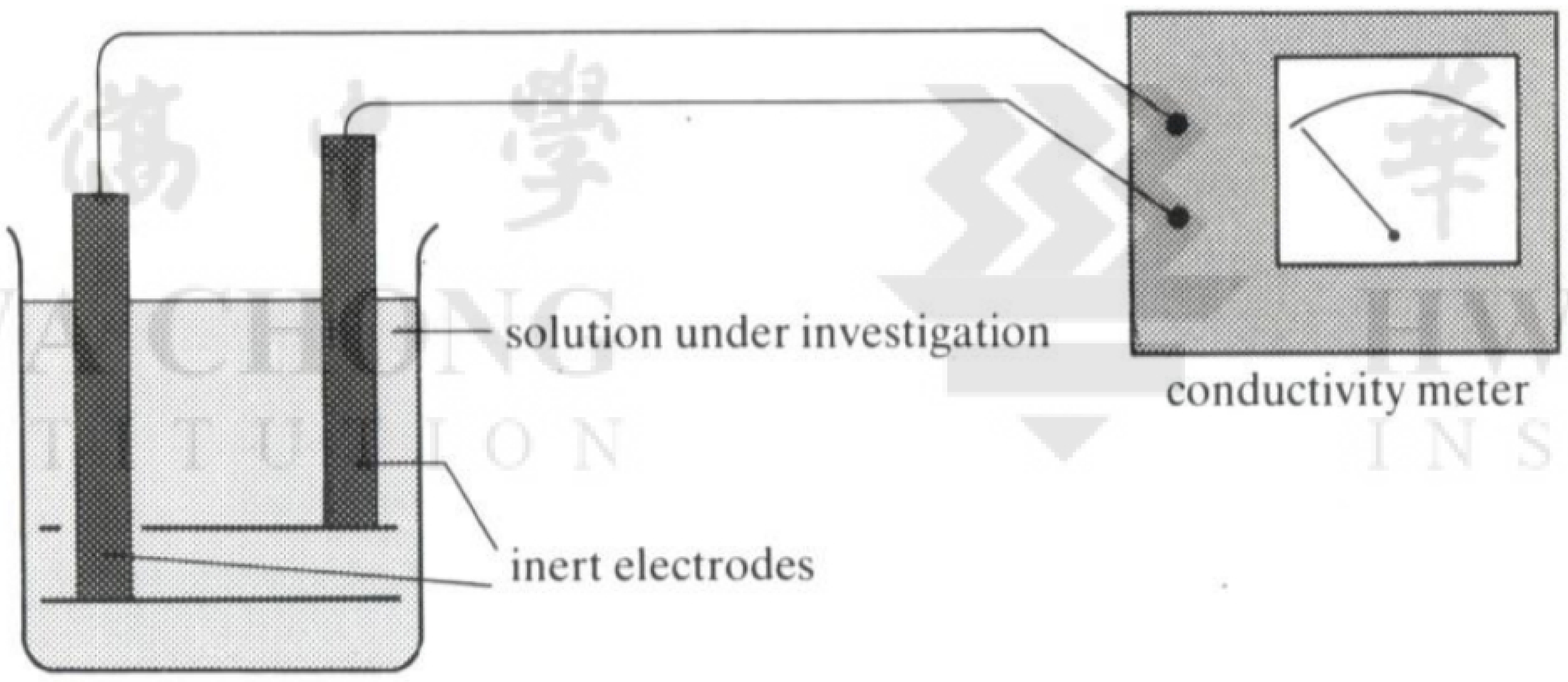


Figure 8. Following the change in electrical conductivity of a solution with time.

5.1.1.5 Following a change in absorbance using a colorimeter

This method is suitable for a reaction in which one of the substances (reactant or product) is coloured or has a different colour from the others. For example, each of the reaction below involves a coloured substance.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow \underset{\text{yellow-orange}}{3Br_2(aq)} + 3H_2O(l)$$

$$CH_3COCH_3(aq) + \underset{\text{brown}}{I_2(aq)} \xrightarrow{H^+} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

A colorimeter measures the amount of light which is absorbed as it passes through a coloured solution – recorded as the absorbance of the solution. The more concentrated the coloured species is in the solution, the more light it will absorb and the greater the absorbance. The absorbance can be measured at regular time intervals using the colorimeter, and the rate of reaction is directly proportional to the rate of change in absorbance.

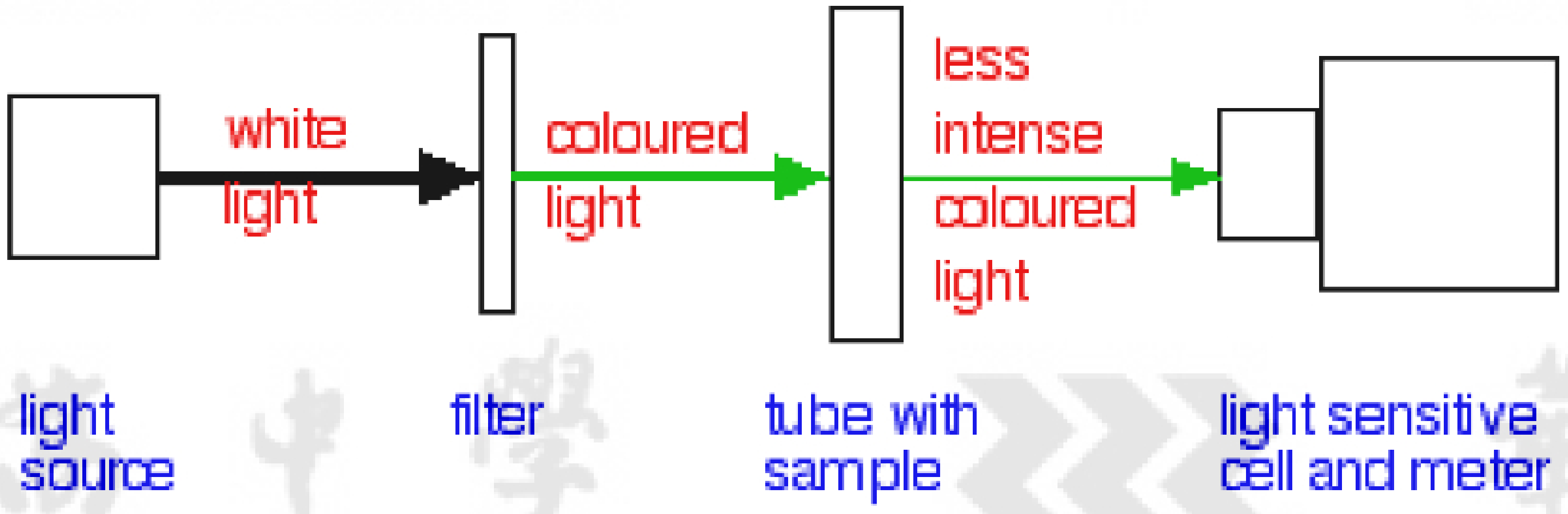


Figure 9. A simplified diagram of a colorimeter

5.1.2 Chemical methods of analysis

Chemical methods of analysis typically interfere with the reaction being studied. Because of this, we must either extract small amounts of the reaction mixture, called samples, and carry out the analysis on them (Section 5.2.1), or alternatively we set up a new reaction mixture for each measurement we take (Section 5.2.2).

5.1.2.1 Sampling and titrimetric method

In this method, a large quantity of reactants is placed in a suitable reaction vessel and the reaction allowed to go to completion. The progress of the reaction is monitored by **extracting a small fixed volume** sample of the reaction mixture at various times, followed by **quenching** the reaction in the sample. Quenching refers to stopping the reaction.

Some methods of quenching include:

- adding a suitable base to neutralise an acidic reacting mixture and vice-versa;
- sudden, rapid dilution with large quantity of water or any suitable solvent;
- sudden, rapid cooling by plunging the mixture into ice.

The quenched sample is then titrated against a suitable reagent (of known concentration) to determine the amount of a reactant that remains or the amount of a product, at the time of quenching. The titration is then repeated for other samples withdrawn at further times. Since the titre volume is proportional to the concentration of the reactant (or product), we can be plot titre volume vs time, effectively giving us the concentration-time graph.

The sampling method is suitable for moderately slow reactions. (Why?)

Generic procedure for obtaining concentration-time graphs by titration

1. To prepare the reaction mixture, **measure** (volume) cm^3 of (reactant X) into a 250 cm^3 beaker (or conical flask) using a (volume) cm^3 measuring cylinder.
2. **Measure** (volume) cm^3 of (last reactant) using a measuring cylinder. **Add** (last reactant) to the mixture and **start the stop–watch at the same time**. Swirl to ensure mixing.
3. Before (your chosen time, say 5 min from the start of the reaction), pipette 10.0 cm^3 of the reaction mixture into a conical flask.
4. **At (your chosen time), quench** the withdrawn sample by adding to it (volume) cm^3 of (suitable quenching reagent). Record the exact time of quenching (but don't stop the stop-watch!).
5. Carry out the **titration** of the quenched sample. (Details of titration steps needed. Refer to the Planning section in Topic 4 Reactions & Stoichiometry)
6. Before (each of your subsequent chosen times), repeat steps 3 and 4. Carry out the **titration** of each quenched sample. (At least 5 samples are collected to obtain data points to plot the graph.)

Note:

- Only one accurate titration is possible for each withdrawn sample.
- The reactant under study should be isolated, i.e. the other reactants should be in large excess (around 10 times more concentrated), so that the order of reaction with respect to that reactant alone can be determined.

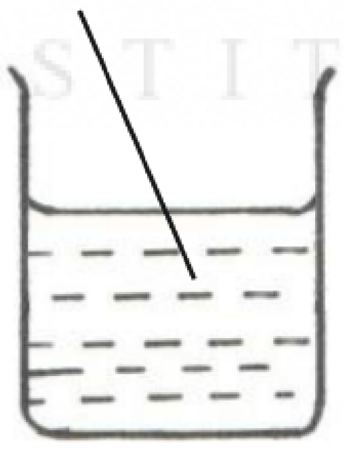
For example, the acid-catalysed iodination of propanone

$$\underset{\text{propanone}}{CH_3COCH_3(aq)} + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

can be followed this way:

Step 1 Preparation of reaction mixture

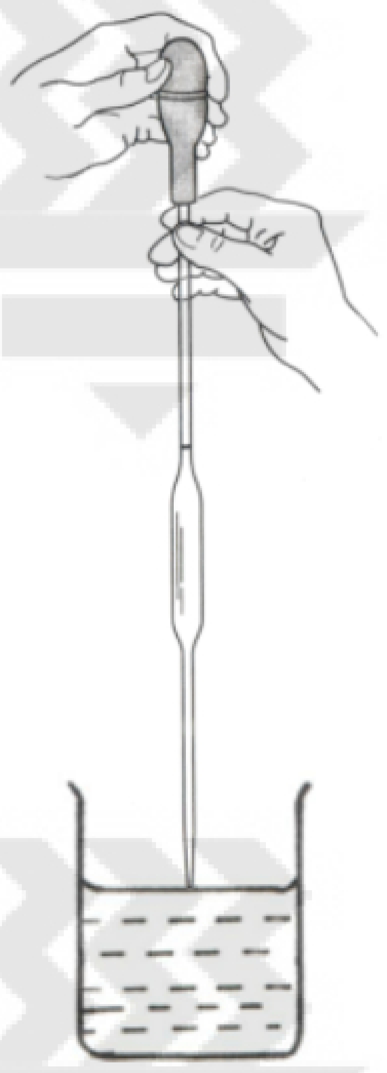
Reactants and acid catalyst of known volumes and concentrations mixed together



Stop-watch started at the instant of mixing

The reaction container should be placed in a constant-temperature water bath

Step 2 Withdrawal of sample

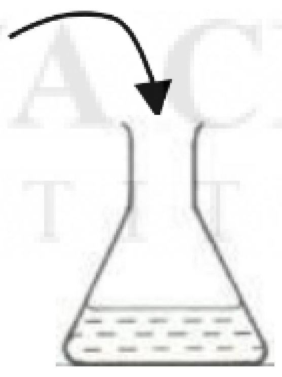


A sample e.g. 10.0 cm^3 is withdrawn from the reaction mixture using a pipette before the time of 5 min (e.g.)

Step 3 Quenching of reaction in sample

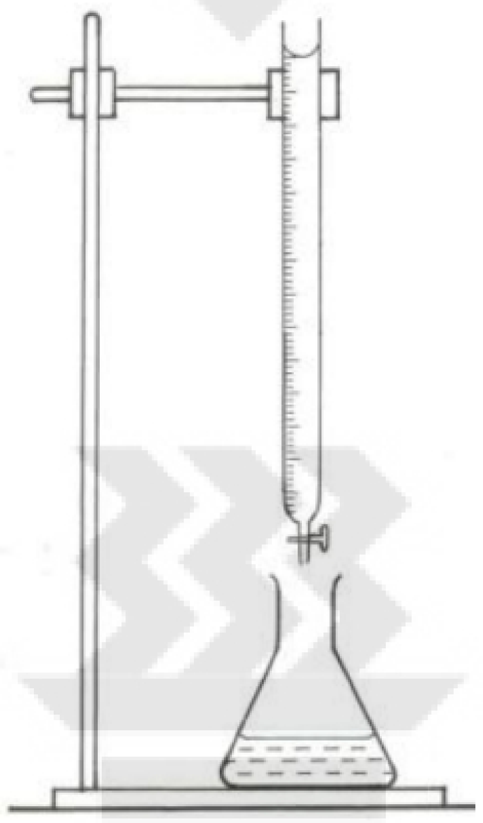
At exactly 5 min (in this e.g.), excess $NaHCO_3$(aq) is added into the withdrawn sample, which removes the acid catalyst. For the reaction between propanone and iodine, the rate is very slow without an acid catalyst. Thus, the reaction immediately falls to a very slow rate such that it may be regarded as virtually stopped.

excess $NaHCO_3$(aq)



Withdrawn sample placed in conical flask

Step 4 Analysis of sample by titration



Titrate iodine remaining in the quenched sample with aqueous sodium thiosulfate, $Na_2S_2O_3$(aq), of known concentration, using starch as indicator.

Steps 2 to 4 repeated at 10 min, 15 min, etc., to collect sufficient number of data points.

5.2 Measuring initial rate via clock reaction

A 'clock reaction' refers to a reaction set up to produce a *sudden change* (usually visual) when a **small, fixed** amount of a product is formed. To study the rate of such reactions, the **time taken for the prescribed visual change to occur** is measured. This time taken **may be used as an approximation of the initial rate of the reaction**.

5.2.1 Reaction of $S_2O_8^{2-}$ and I^- (iodine clock)

For example, the reaction between $S_2O_8^{2-}$ and I^- can be followed using this method. The two reactants are mixed with a known amount of sodium thiosulfate, $Na_2S_2O_3$, and a little starch indicator.

The I^- ions react with $S_2O_8^{2-}$ to form I_2 as shown in the equation below.

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq) \qquad \text{(Reaction 1)}$$

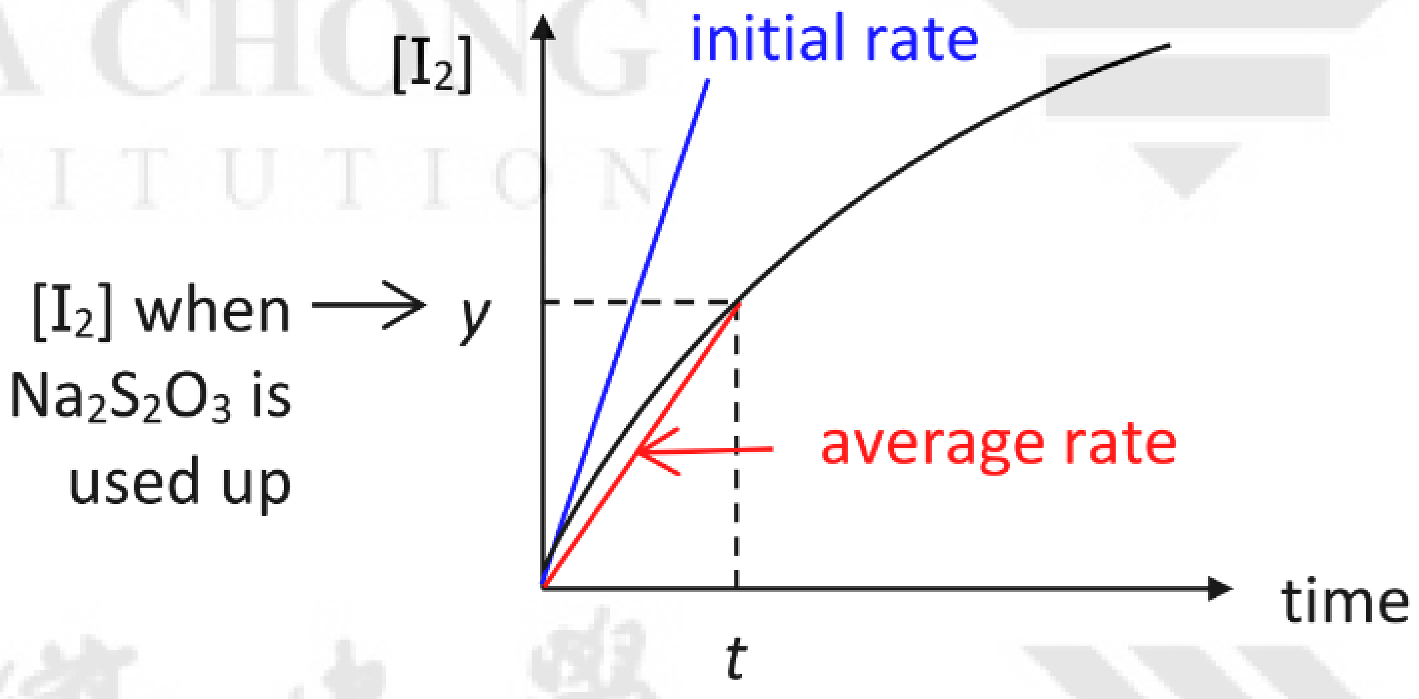
As the reaction proceeds, the I_2 formed will in turn react with $Na_2S_2O_3$ to form I^-.

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

When all $Na_2S_2O_3$ has been used up, the iodine which is still being produced by Reaction 1 reacts with the starch to give a blue-black colour.

For a **fixed** amount of $Na_2S_2O_3$ added, the time taken for the blue-black colour to appear (i.e. for a fixed amount of I_2 to be formed), *t*, is an approximate measure of initial rate. The faster the rate of Reaction 1, the smaller *t* is.

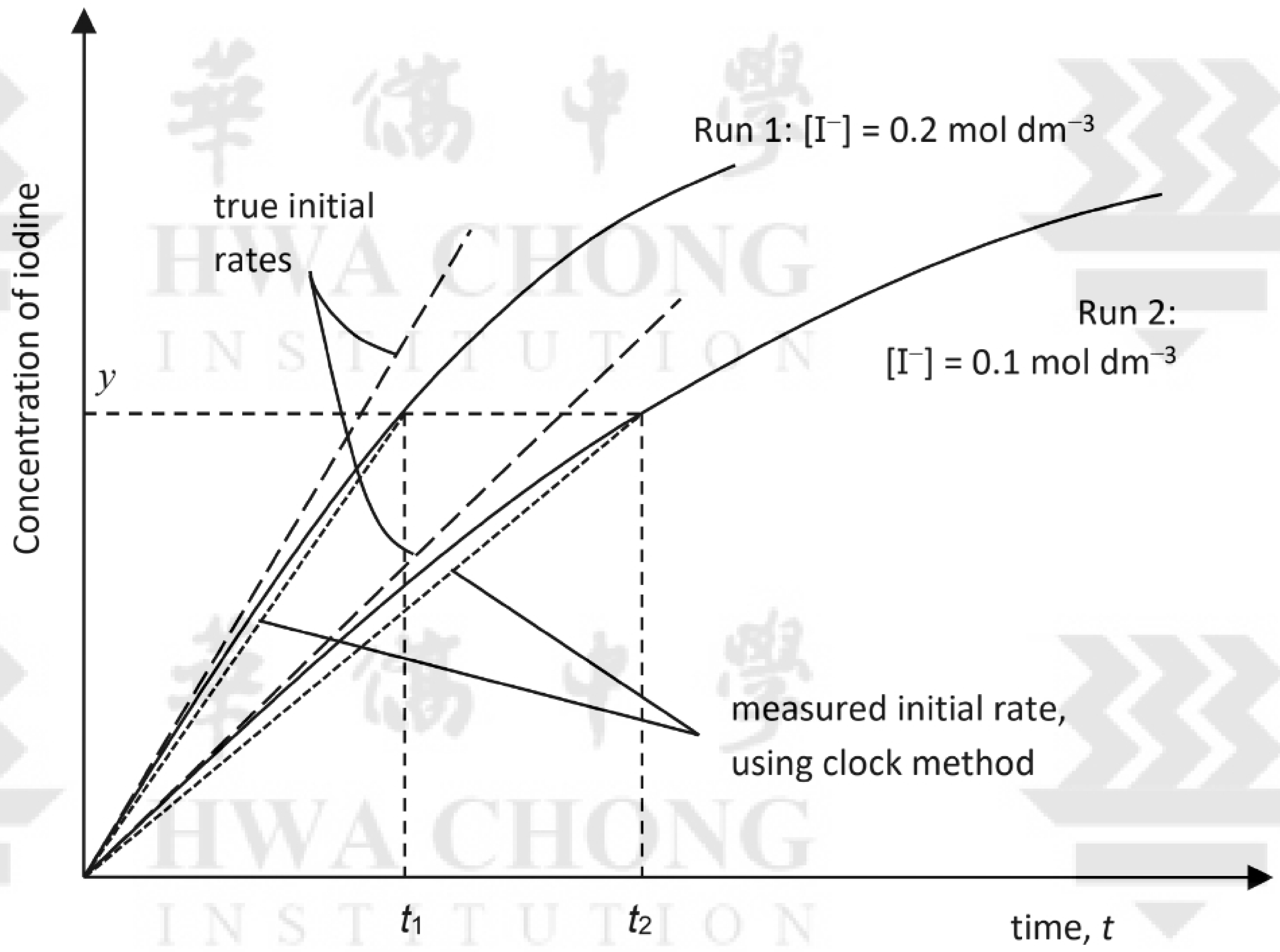
The approximation is <u>only valid if y is **small**</u>, i.e. the reaction is allowed to proceed to a *small extent*, such that we can assume that the concentration-time graph is a straight line right up to the point when the blue-black colour appears (i.e point *y*).



$$\text{Initial rate} = \frac{d[I_2]}{dt} \approx \text{average rate} = \frac{y}{t}$$

As y is fixed by using a fixed amount of $Na_2S_2O_3$, initial rate $\propto \frac{1}{t}$

Say we wish to first find the order of reaction with respect to I^-, we will need to carry out a series of experiments in which the initial concentration of I^- is changed without varying the initial concentration of the other reagents (see Generic Procedure on the next page). For example, we can carry out the reaction twice – the first time with $[I^-] = 0.1$ mol dm^{-3}, then with $[I^-] = 0.2$ mol dm^{-3}. This is able to give us the timings t_1 and t_2, which help to *approximate* the initial rate of each reaction.



Run	Time for blue-black colour to appear	Average rate
1	t_1	y/t_1
2	t_2	y/t_2

Figure 10. Graph showing the difference in true initial rate and the average rate taken using a clock method.

Qn: is the value obtained for the initial rate via the 'clock' method lower or higher than the true value?

5.2.2 Reaction of $S_2O_3^{2-}$ and H^+

Another reaction whose rate may be studied by a clock reaction is the reaction of $Na_2S_2O_3$ with dilute HC*l*.

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

The rate of reaction can be determined by measuring the time taken for sufficient precipitate of sulfur to be formed to obscure a "cross" marked on a piece of paper below the reaction vessel.

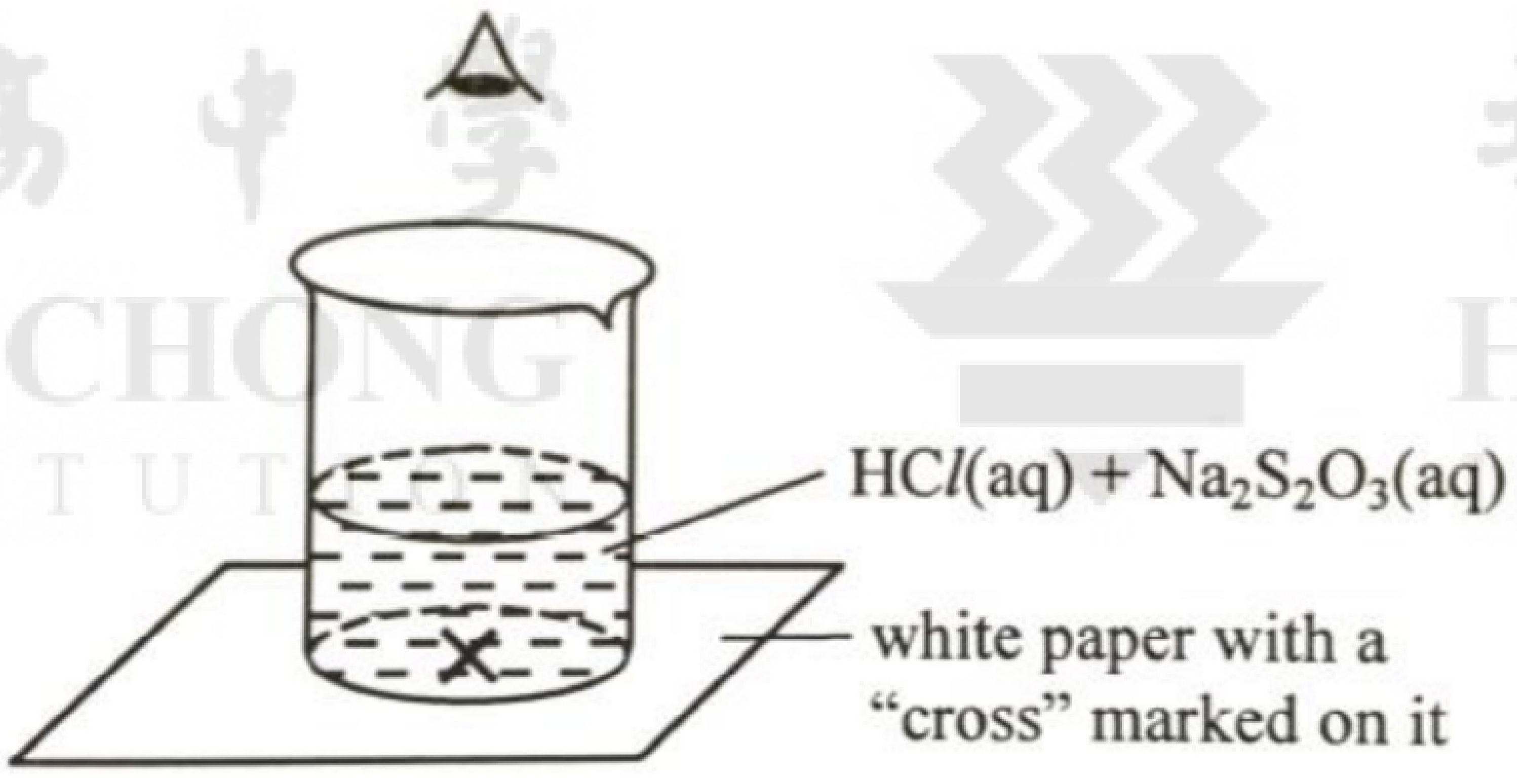


Figure 11. Experimental setup for the reaction between $Na_2S_2O_3$(aq) and HCl(aq).

Rate of reaction is inversely proportional to the time taken, *t*, i.e. rate $\propto \frac{1}{t}$.

To determine the order of reaction with respect to a reactant **A**, we measure the initial rates for a number of experiments in which the concentration of **A** is varied while keeping the concentrations of other reactants constant. Initial rates are often obtained by timing the appearance of a ***small, fixed*** amount of product.

Generic procedure to obtain initial rates via clock reactions

1. To prepare the reaction mixture, **measure** (volume) cm^3 of (reactant X) into a 250 cm^3 beaker (or conical flask) using a measuring cylinder.
   Repeat for all other reactants except for the last reactant which kick–starts the reaction.
2. **Measure** (volume) cm^3 of (last reactant) using a measuring cylinder. **Add** (last reactant) to the mixture and **start the stop–watch at the same time**. Swirl to ensure mixing.
3. **Stop the stop–watch** when (state distinct visual change) is observed. Record the time taken, t.
4. **Repeat** steps 1 to 3 with **different volumes** of (reactant studied) and deionised water, keeping the **total volume constant**. (Use a table to show the list of different volumes to use in each experiment.)

Note:

- The distinct visual change can be when sufficient precipitate is formed to just obscure a mark; or when a particular colour first appears.
- The total volume of the mixture is kept constant so that [**A**]$_{\text{initial}}$ is directly proportional to the volume of reactant **A**. E.g., when volume of **A** is doubled, [**A**]$_{\text{initial}}$ is doubled; when volume of **A** is unchanged, [**A**]$_{\text{initial}}$ is kept the same.
- $\frac{1}{t}$ obtained in this way is a measure of the initial rate of reaction, hence comparing the values of $\frac{1}{t}$ and volume of **A** can give us the order w.r.t. **A** e.g. when volume of A is doubled and $\frac{1}{t}$ is also doubled, it shows that the reaction is first order w.r.t **A**. Alternatively, plotting the values of $\frac{1}{t}$ vs volume of **A** will effectively give us the rate-concentration graph, the shape of which will allow us to determine the order w.r.t. **A** (see Section 4.5).
- Measuring cylinders are usually used to measure the volumes of liquids (common capacities: 10 cm^3, 25 cm^3, 50 cm^3, 100 cm^3). A burette may be used if a chemical is to be added in a small quantity which has to be *exactly* the same quantity for all experiments. However, a burette cannot be used to add the last reactant (Step 2) which has to be added *rapidly*.

5.3 Case study on determination of order of reaction

Propanone and iodine react together in aqueous acidic solution according to the equation:

$$\underset{\text{propanone}}{CH_3COCH_3(aq)} + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

We use the stoichiometric equation to decide which substance to follow during a reaction in order to measure the rate. In this case, the concentration of I_2 is most easily measured, either using a colorimeter (physical method of analysis, Section 5.1.1.5) or by titration with aqueous sodium thiosulfate (chemical method of analysis, Section 5.1.2.1). As we are investigating the effect of concentration on the rate of reaction, all other factors that might affect the rate should be kept constant e.g. the temperature during the reaction.

Figure 12. A thermostatic water bath keeps the temperature of the reaction constant.

In this case study, a physical method of analysis is utilised. The absorbance is measured, at regular time intervals, using a colorimeter.

$[I_2]$ remaining in the reaction mixture at time $t \propto$ absorbance at that time

Rate of reaction $\propto$ rate of decrease in absorbance

From the equation (above), we have three chemical species whose concentration may affect the rate: I_2, propanone and H^+.

So the rate equation may be written as: rate = $k\,[I_2]^x\,[\text{propanone}]^y\,[H^+]^z$.

The objective of this exercise is to determine the order of reaction with respect to each species.

Experiment 1 (Aim: To determine order of reaction w.r.t. I_2)

Design of experiment: Keeping all reactants in excess except the one being studied

In this experiment, the initial concentrations of propanone and H^+ used (listed in the table below) are much higher than that of I_2.

Substance	Initial concentration /mol dm^{-3}	Concentration at the end of the reaction /mol dm^{-3}
I_2	0.002	0
propanone	0.4	0.398
H^+	0.4	0.402

(H^+ is not used up during the reaction because it is a catalyst; its concentration increases because it is also being produced by the reaction.)

Recall (from Section 4.6 Method 1) that if a particular reactant is present in **large excess** (concentration of at least 10 times) compared to the other reactants, **its concentration does not change significantly** compared to the other reactants during the reaction and **may be regarded as constant**. This applies to propanone and H^+ for Experiment 1. The table of values above illustrates why this is the case. The **rate of reaction will *appear* to be independent of propanone and H^+**. This simplifies our investigation because analysis of the experimental results – the graph of $[I_2]$ against time shown at the next page – **reflects the order of reaction with respect to *only* I_2**.

Further discussion in terms of the mathematics:

The rate equation is: rate = $k\,[I_2]^x\,[\text{propanone}]^y\,[H^+]^z$.

If we make the concentrations of propanone and H^+ much higher than that of I_2, then during the course of the reaction, [propanone] and $[H^+]$ change so little -- *compared to* $[I_2]$ -- that they may be regarded as *constant*.

The rate equation can then be simplified as: rate = $k'\,[I_2]^x$
where the new proportionality *constant*, $k' = k\,[\text{propanone}]^y\,[H^+]^z$

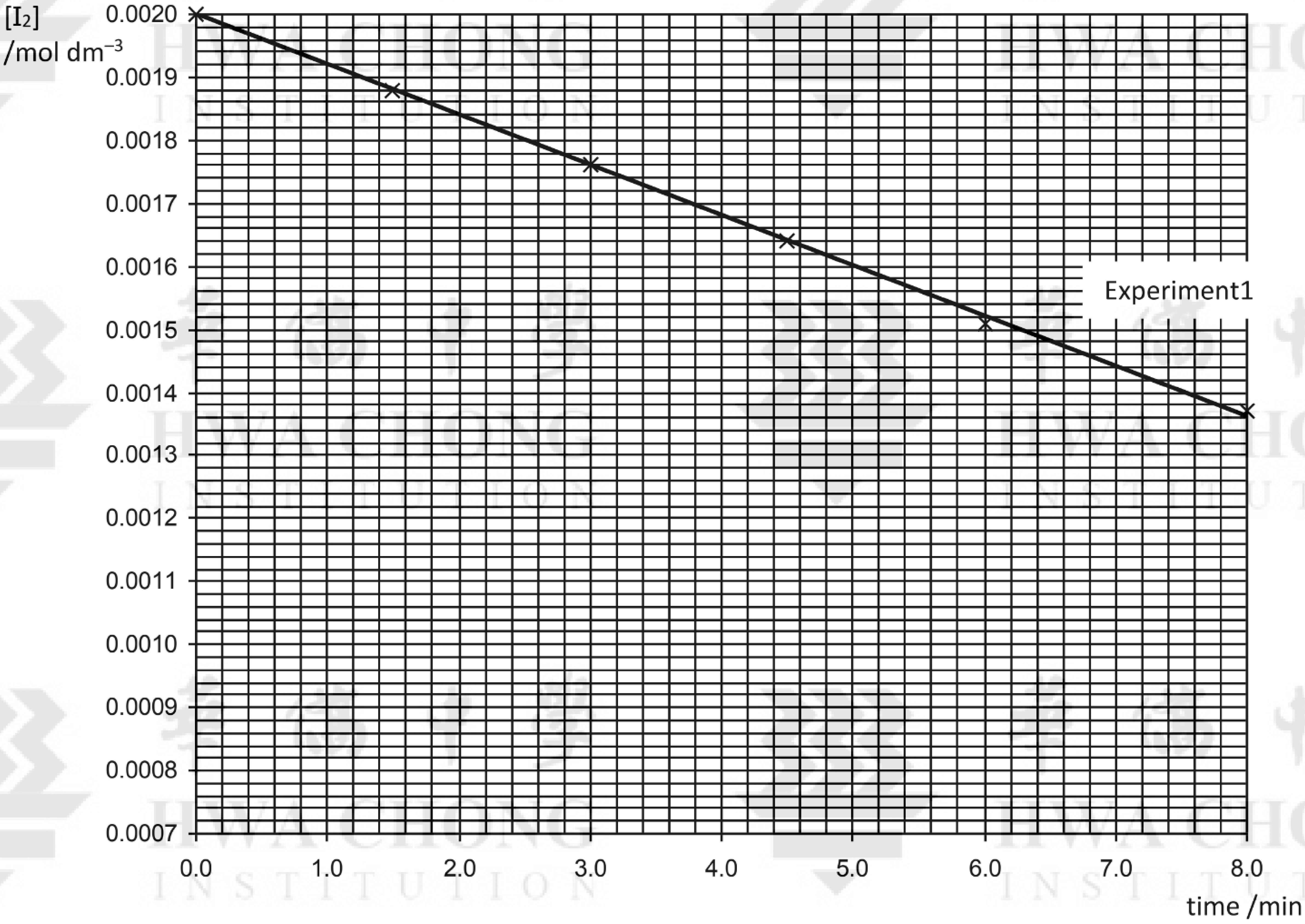
For the "new" simplified rate equation, rate = $k'\,[I_2]^x$, we consider the reaction as **pseudo zero order** with respect to each of propanone and H^+, and is **pseudo x^{th} order overall**.

Procedure and treatment of results

A mixture of propanone and sulfuric acid is placed in a thermostatically controlled water bath. A solution of iodine is also placed in the bath in a separate container. At the start of the experiment, the two solutions are mixed, shaken well and a stopwatch started.

At regular time intervals, $[I_2]$ is found (by measuring absorbance) and a graph of $[I_2]$ against time is then plotted:

Graph 1: initial $[I_2] = 0.002$ mol dm^{-3}, [propanone] = 0.4 mol dm^{-3}, $[H^+] = 0.4$ mol dm^{-3}



Self-practice 5.1

(i) How is the rate of reaction found from a graph of concentration of reactant against time?

(ii) Explain why **Graph 1** shows that the reaction is zero order with respect to I_2.

Experiments 2 & 3 (Aim: To determine order of reaction w.r.t. propanone and H$^+$)

Design of experiment: Comparing initial rates by keeping initial concentrations of all reactants the same while varying the one under investigation

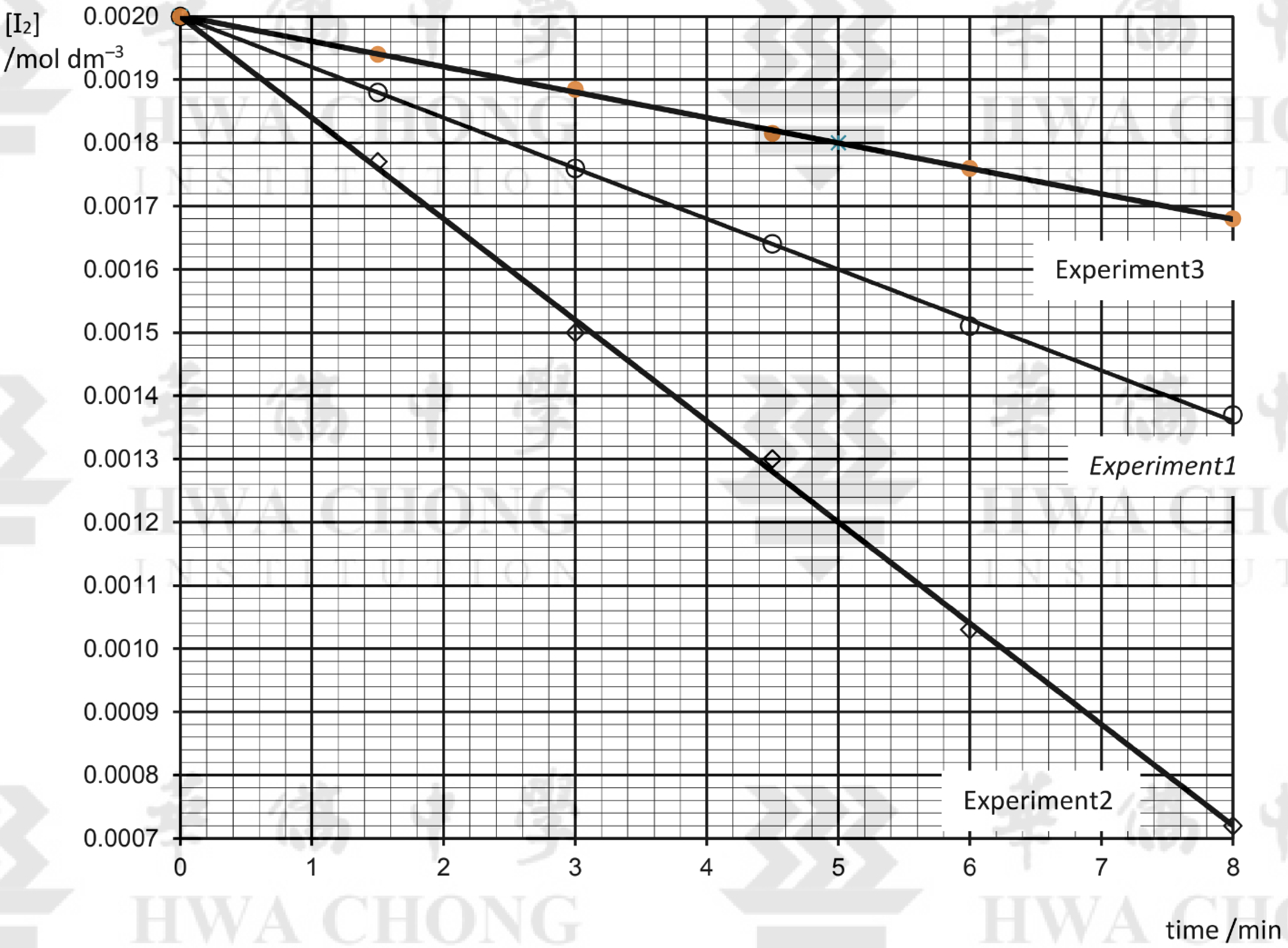
Experiment 1 is repeated using a different initial concentration of propanone (Experiment 2), and once more using a different initial concentration of H$^+$ (Experiment 3):

Experiment	Initial concentration /mol dm^{-3}		
	[I$_2$]	[propanone]	[H$^+$]
1	0.002	0.4	0.4
2	0.002	0.8	0.4
3	0.002	0.4	0.2

Procedure and treatment of results

Again at regular time intervals, [I$_2$] is measured and two more graphs of [I$_2$] against time are plotted:

Graphs 2 & 3



Self-practice 5.2

(i) Comparing Experiments 1 and 2, only the initial concentration of propanone is changed, therefore any difference in initial rates must be due to propanone. Determine the initial rates for Experiments 1 and 2, and hence deduce the order of reaction with respect to propanone.

(ii) Comparing Experiments 1 and 3, only the initial concentration of H^+ is changed, therefore any difference in initial rates must be due to H^+.Determine the initial rate for Experiment 3 and hence deduce the order of reaction with respect to H^+.

(iii) Using the information from Self-practice 5.1 (ii) and your answers above, write a full rate equation for the reaction, using the rate constant, *k*.

(iv) What is the overall order of the reaction?

(v) Calculate a value of the rate constant, indicating units.

Review of case study

There are two main ways of designing experiments to determine the order of reaction with respect to each of the reactants in a reaction.

Method 1. Monitor the concentration of one reactant (or product) present in one reaction mixture over time, while keeping **all other reactants in excess.**

This method is used in Experiment 1 to determine the order of reaction w.r.t. I_2, and its significance or underlying principle has been explained previously. The **reaction is carried out only once** and the experimental results are usually given as follows:

Time /s	0	90	180	270	360	480
$[I_2]$ /mol dm^{-3}	0.00200	0.00188	0.00176	0.00164	0.00151	0.00137

The concentration-time data is usually plotted and its shape is used to deduce order (Section 4.5). In this case, a straight line graph of $[I_2]$ against time is obtained and the conclusion of zero order with respect to I_2 is made. **What should you do if a curve is obtained?**

Method 2. The initial rate method.

This method is used in Experiments 2 and 3 to determine the order of reaction for propanone and that for H^+. The **reaction is carried out a few times** (total of 3 times in the case study) and the experimental results are usually presented in the generic format shown below: The initial rate may be found from the gradient of the concentration-time graph for each experiment.

Experiment	Initial concentration /mol dm^{-3}			Initial rate of reaction /mol dm^{-3} min^{-1}
	[**A**]	[**B**]	[**C**]	
1	0.50	0.002	0.50	2.0×10^{-5}
2	0.30	0.002	0.50	1.2×10^{-5}
3	0.10	0.002	0.50	4.0×10^{-6}
4	0.50	0.002	0.30	1.2×10^{-5}
5	0.50	0.002	0.10	4.0×10^{-6}

Usually, we can identify pairs of experiments in which the **initial concentrations of all the reactants are the same while the one under investigation is varied**. By studying how the initial rate changes when the concentration of this one reactant is changed, we can deduce the order with respect to that reactant (Lecture Exercise 4.2).

6 REACTION MECHANISMS

6.1 Important terminology

A chemical equation only tells us about the identities and ratios of each particle involved in the reaction. It does not tell us exactly how the reactant particles interact with each other at the molecular level. Chemists are interested to know exactly how the various bonds are broken and made in a chemical reaction.

The **reaction mechanism** details how the atoms in the reactants rearrange to form the products and thus gives us some information about the order in which bonds are broken and formed. In other words, reaction mechanisms show how the reaction occurs at the *particulate* level.

A reaction does not always occur in a single step where all the reactants collide at one go and form the products. Instead, we can think of a reaction as occurring in a series of simple steps, called **elementary steps**. These steps **cannot be broken down into simpler steps.** It is the sequence of these elementary steps that we refer to when we use the term '*reaction mechanism*'.

One of these steps has a higher activation energy that determines the overall rate of the reaction. This particular step is called the **rate-determining step (r.d.s.)**. It is the **slowest step** in a multi-step reaction mechanism. (In a single-step mechanism, the only step must be the rate-determining step.)

Example:
The reaction mechanism for the nucleophilic substitution of 2-bromo-2-methylpropane with hydroxide ions. (Do not worry if this reaction is unfamiliar to you. We will learn the mechanism in detail in Topic 13 Halogen Derivatives).

Step 1: $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ **(slow)**

Step 2: $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ **(fast)**

Overall equation: $(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

The **overall reaction** between 2-bromo-2-methylpropane, $(CH_3)_3CBr$, and hydroxide ion, OH^-, to form 2-methylpropan-2-ol, $(CH_3)_3COH$, and bromide ion, Br^-, is postulated to occur via a sequence of two reaction steps as shown above. The two elementary steps, "Step 1" and "Step 2", constitute the mechanism of this reaction. As shown in the example, the **elementary steps in the mechanism "add up" to give the overall equation**.

Notice that elementary steps usually involve one or two (or very occasionally, three) reactant molecules. The **molecularity** of a step counts the number of particles (molecules or ions or atoms) that must collide to produce the reaction indicated **in an elementary step**.

- Unimolecular reactions involve only 1 reactant particle. (E.g. Step 1)
- Bimolecular reactions involve the collision of 2 reactant particles. (E.g. Step 2)
- Termolecular reactions are extremely rare since it requires a collision of three particles at the same time with sufficient energy and with the correct orientation to form the products.

Note: molecularity **only** applies to elementary steps, and **cannot** be assigned to an *overall reaction*.

In the example above, the $(CH_3)_3C^+$ ion is an **intermediate** in the reaction. An intermediate is a chemical species produced in an early step of a mechanism and consumed in a later step. It is neither a reactant nor an ultimate product of the overall reaction. It may be stable enough to be detected or isolated. Intermediates do not appear in the overall balanced equation, nor in the overall rate equation.

6.2 The relationship between reaction mechanism and the rate equation

Possible mechanisms for a given reaction must always relate to experimental data. We can hypothesise the elementary steps of a reaction, and then test the hypothesis against evidence from rate experiments. If the evidence supports the suggested mechanism, we can accept it; if not, we have to propose a different mechanism. In other words, we can never really prove that an accepted mechanism is the actual mechanism, but we can show that it is consistent with the data.

When proposing a reaction mechanism for a reaction, the following three criteria must be met:

1) The elementary steps must add up to the **overall** balanced equation.
2) The elementary steps must be physically **reasonable**. For example, it typically does not involve a collision between 3 particles (very rare) or a collision between ions of the same charge (possible but rare).
3) The mechanism must be consistent with the **experimentally-determined rate equation**.

6.2.1 Constructing a rate equation from a given reaction mechanism

If the reaction mechanism is given in a question, the overall order of reaction can simply be deduced from the molecularity of the rate-determining step (r.d.s.). We can then easily write the rate equation for the overall reaction: **the coefficients of the reactants in the r.d.s. are used as the order w.r.t. each reactant**. Thus, molecularity of the r.d.s. is equal to the overall order of the reaction.

- **Single-step reaction mechanisms**
  For a single-step reaction, there is **only one elementary step**. This step will therefore determine the rate of the reaction.

Example 1: $N_2O_4\ (g) \rightarrow 2NO_2\ (g)$
Rate = $k[N_2O_4]$

Example 2: $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$
Rate = $k[CH_3CH_2Br][OH^-]$

- **Multi-step reaction mechanisms**
  For a multi-step reaction, the rate equation is derived directly from the stoichiometry of the **slowest step,** i.e. the **r.d.s.**:
  - Reactant species that react *before* or *in* the r.d.s. will appear in the rate equation.
  - Reactant species that react *after* the r.d.s. will **not** appear in the rate equation.

➢ Cases when the rate-determining step is the first step:

Example 1: *Nucleophilic substitution of 2-bromo-2-methylpropane*

Overall $(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

Step 1: $(CH_3)_3CBr \rightleftharpoons (CH_3)_3C^+ + Br^-$ (slow)
Step 2: $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ (fast)

$\therefore$ Rate = $k[(CH_3)_3CBr]$

<u>Example 2</u>: *The mechanism for the reaction between nitrogen dioxide and fluorine*

Overall: $2NO_2 + F_2 \rightarrow 2NO_2F$

Step 1: $NO_2 + F_2 \rightarrow NO_2F + F$ (slow)
Step 2: $NO_2 + F \rightarrow NO_2F$ (fast)

$\therefore$ Rate = $k[NO_2][F_2]$

Notice that in both examples 1 and 2, the rate equation cannot be deduced from the stoichiometry of the *overall* balanced chemical equation.

- <u>Cases when the rate-determining step is ***not*** the first step:</u>

If the rate-determining step is not the first step, it will likely involve an intermediate. Recall that intermediates do not appear in the rate equation; instead, the reactants producing this intermediate should appear in the rate equation. There is a need to do some simple substitution based on the elementary steps that occur *before* the rate-determining step.

<u>Example 3</u>: *The proposed mechanism for the oxidation of nitrogen monoxide*

Overall: $2NO + O_2 \rightarrow 2NO_2$

Step 1: $NO + O_2 \rightleftharpoons NO_3$ (reversible, fast)
Step 2: $NO_3 + NO \rightarrow 2NO_2$ (slow)

Since step 2 is the rate-determining step, we may write:
rate = $k_1[NO_3][NO]$ ….. (1)

However, NO_3 is an intermediate which does not appear in the overall chemical equation for reaction and therefore should not appear in the rate equation. We need to substitute $[NO_3]$ with the concentration of reactants that produced this intermediate.

From Step 1, $K_c = \dfrac{[NO_3]}{[NO][O_2]}$

Rearranging, $[NO_3] = K_c[NO][O_2]$ …..(2)
Substitute (2) into (1): rate = $k_1K_c[NO][O_2][NO] = k_1K_c[NO]^2[O_2]$
$\therefore$ rate = $k[NO]^2[O_2]$ where $k = k_1K_c$

Note that it is purely coincidental that the individual orders match the stoichiometry of the overall chemical equation. K_c will be discussed in greater details in Topic 7 Chemical Equilibria.

6.2.2 Verifying that a suggested reaction mechanism is consistent with the observed kinetics

Lecture Exercise 6.1

In the hypothetical reaction between **X** and **Y**,

$$\mathbf{X} + 2\mathbf{Y} \rightarrow \mathbf{XY_2}$$

the experimental rate equation is found to be:

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

Which of the following possible mechanisms is/are consistent with the experimental results?

A. $\mathbf{X} + \mathbf{Y} \rightarrow \mathbf{XY}$ (slow)
$\mathbf{XY} + \mathbf{Y} \rightarrow \mathbf{XY_2}$ (fast)

B. $2\mathbf{Y} \rightarrow \mathbf{Y_2}$ (slow)
$\mathbf{Y_2} + \mathbf{X} \rightarrow \mathbf{XY_2}$ (fast)

C. $2\mathbf{Y} \rightleftharpoons \mathbf{Y_2}$ (fast)
$\mathbf{Y_2} + \mathbf{X} \rightarrow \mathbf{XY_2}$ (slow)

For your information

Testing the mechanism

The example above only shows a possible mechanism that is consistent with the kinetic data for the reaction between **X** and **Y**. This is very different from saying that the mechanism is the most likely one. Scientists need to carry out further experiments to confirm the mechanism. Some of the techniques are described below.

- Isotopic labeling – if an atom is labeled with an isotope, the label may indicate which bond has been broken in a reaction. For example, when esters labeled with ^{18}O are reacted with water (a hydrolysis reaction), the ^{18}O appears in the alcohol and not in the carboxylic acid group. This shows that the C–O bond (1), and not the C–O bond (2), is the one that is broken.

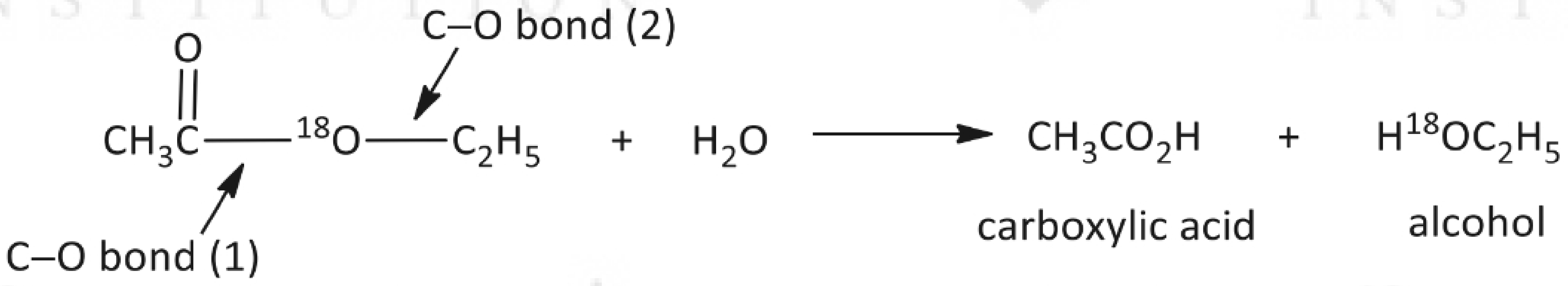


Figure 13. Hydrolysis of ethyl ethanoate to give ethanoic acid and ethanol.

- Kinetic isotope effect – deuterium behaves slightly differently from hydrogen, for example, the C–D bond is slightly harder to break than the C–H bond. This means that if this bond is broken during the rate-determining step, a compound containing C–D bonds reacts more slowly than a compound with C–H bonds.

  On the other hand, if the reaction rate is the same rate for both compounds, it implies that the breakage of this bond does not occur in the slow step. For example, the fact that C_6H_6 and C_6D_6 reacts with NO_2^+ at the same rate shows that the rate-determining step is the initial attack by NO_2^+, and not the elimination of the proton, H^+. The mechanism for the nitration of C_6H_6 is shown below.

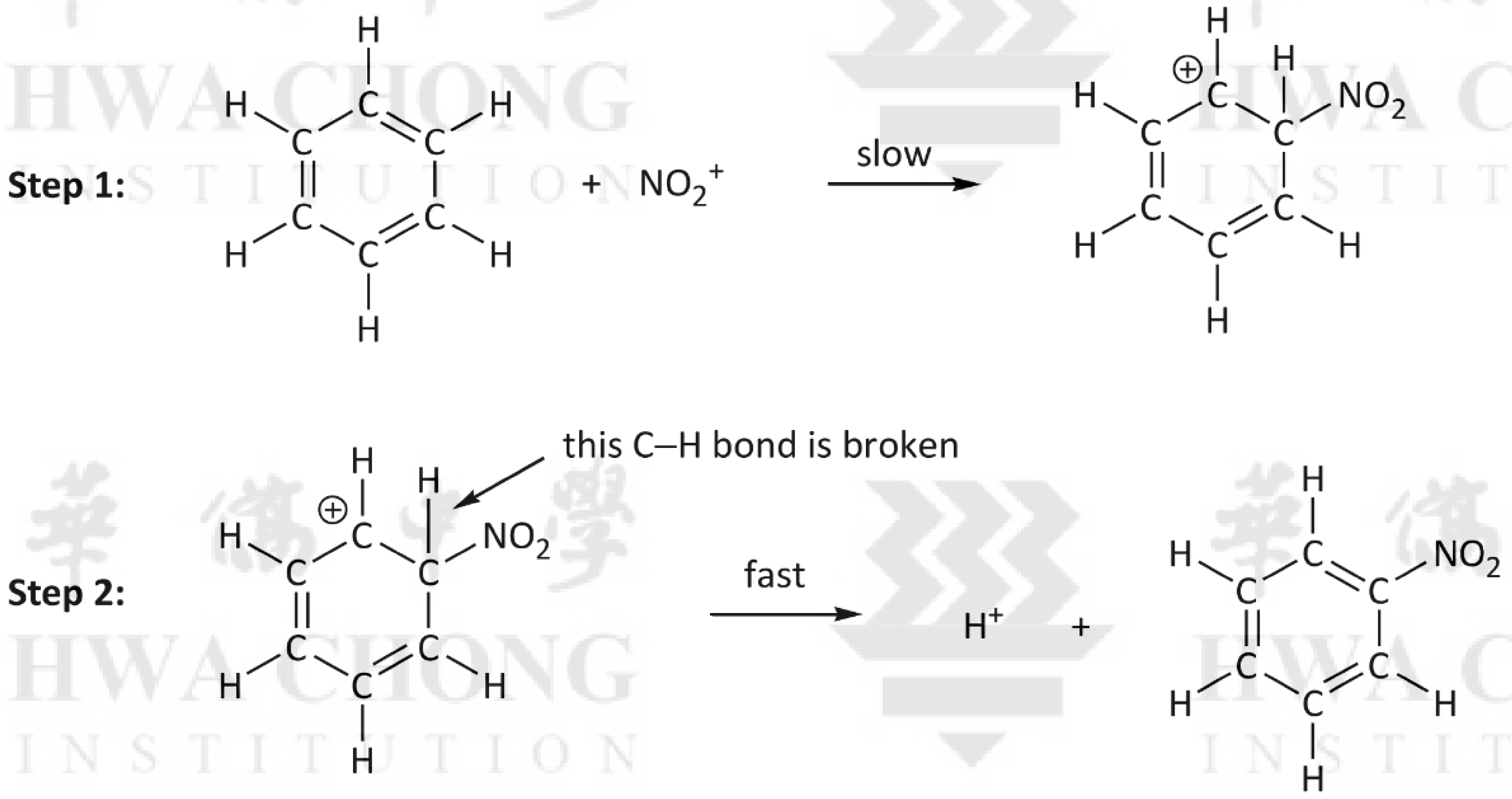


Figure 14. Mechanism for the nitration of benzene.

Self-practice 6.1

(a) The dissociation of dinitrogen tetroxide to nitrogen dioxide, $N_2O_4(g) \rightarrow 2NO_2(g)$, is a single-step reaction.
Write the rate equation for this reaction.

(b) Which suggested mechanism is consistent with the experimentally determined rate equation?

	rate equation	suggested mechanism	
1	Rate = $k_1\,[NO]^2[H_2]$	$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$	(slow) (fast)
2	Rate = $k_2\,[H_2][I_2]$	$H_2(g) \rightarrow 2H(g)$ $2H(g) + I_2(g) \rightarrow 2HI(g)$	(slow) (fast)
3	Rate = $k_3\,[HBr][O_2]$	$2HBr(g) + O_2(g) \rightarrow 2HBrO(g)$ $HBrO(g) + HBr \rightarrow H_2O(g) + Br_2(g)$	(slow) (fast)

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

[N1999/3/33]

(c) The two steps involved in the gas-phase reaction, $X + 2Y \rightarrow XY_2$ are

$$X + Y \xrightarrow{\text{slow}} XY$$
$$XY + Y \xrightarrow{\text{fast}} XY_2$$

What is the rate equation for the overall reaction?

A Rate = $k\,[X]^0\,[Y]^1$
B Rate = $k\,[X]^0\,[Y]^2$
C Rate = $k\,[X]^1\,[Y]^1$
D Rate = $k\,[XY]^1\,[Y]^1$

[J85/3/11, N89/3/9]

(d) The reaction between nitric oxide, NO, and oxygen is one of the reactions involved in atmospheric pollution from car exhausts.
Kinetics studies have shown that the reaction is third order overall, and it has been suggested that the mechanism involves the following two steps.

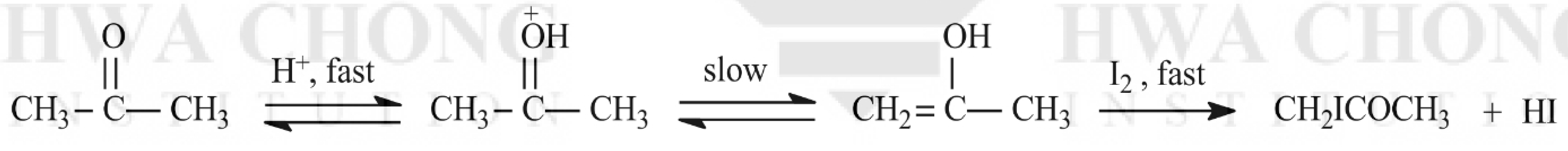
$$2NO \xrightarrow{\text{fast}} N_2O_2$$
$$N_2O_2 + O_2 \xrightarrow{\text{slow}} 2NO_2$$

What is the rate equation for the overall reaction?

A Rate = $k\,[NO]^2\,[N_2O_2]$
B Rate = $k\,[N_2O_2]\,[O_2]$
C Rate = $k\,[NO]^2\,[O_2]$
D Rate = $k\,[N_2O_2]^2\,[O_2]$

[N05/3/1]

(e) The mechanism for the iodination of propanone in aqueous acid is thought to be as follows.



$$CH_3COCH_3 \underset{}{\overset{H^+,\ \text{fast}}{\rightleftharpoons}} CH_3C(=\overset{+}{O}H)CH_3 \overset{\text{slow}}{\rightleftharpoons} CH_2{=}C(OH)CH_3 \xrightarrow{I_2,\ \text{fast}} CH_2ICOCH_3 + HI$$

What are the orders of reaction with respect to iodine and to propanone?

	iodine	*propanone*
A	0	1
B	0	2
C	1	0
D	1	1

[N98/3/12, J01/3/11]

6.3 Depicting reaction profiles of multi-step reactions

A **two-step reaction** could have the reaction profiles depicted in Figure 15. Note that both examples show an overall exothermic reaction, so the products are lower in energy than the reactants.

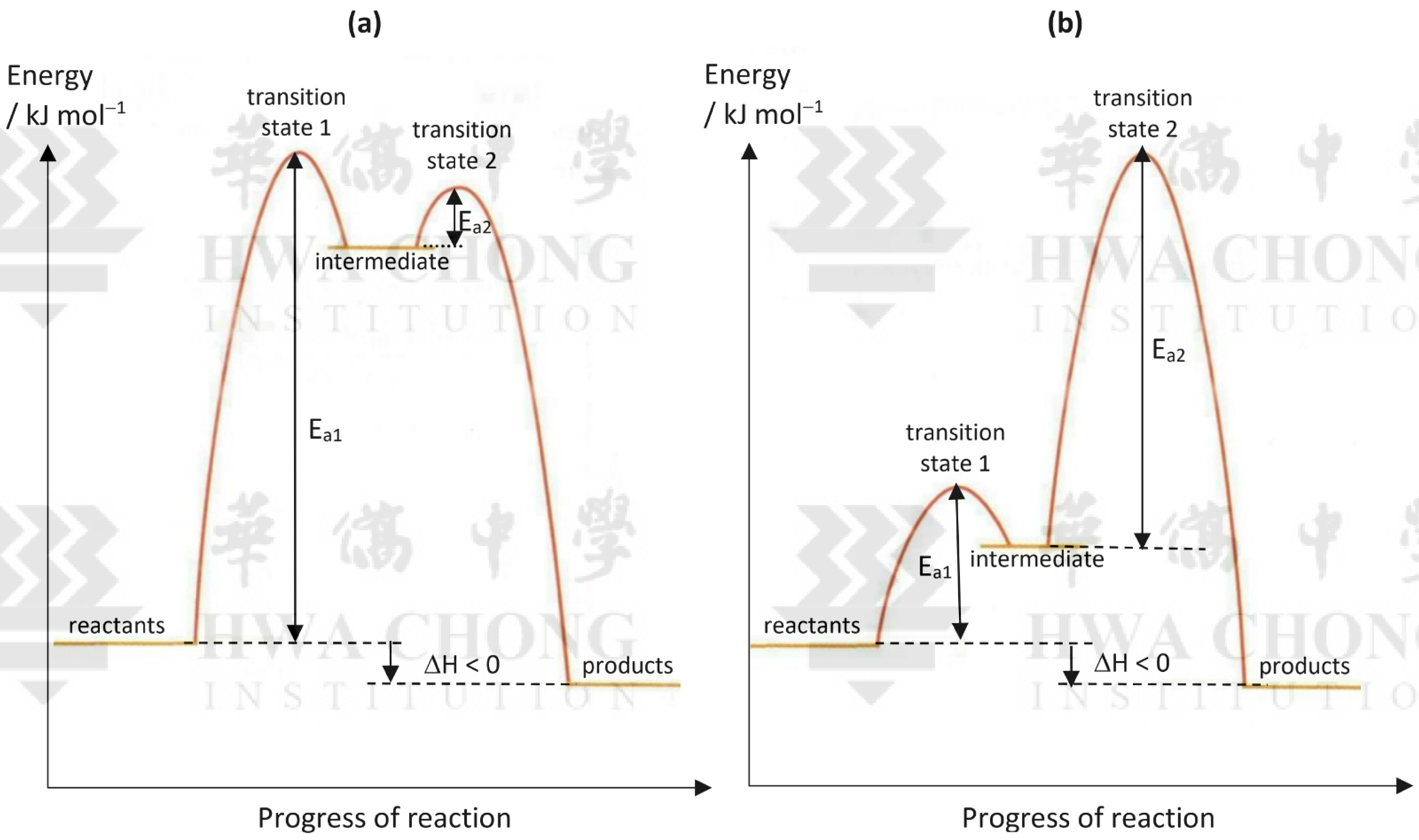


*Figure 15. Reaction pathway diagrams for a two-step reaction. There is one intermediate and two transition states. In **(a)**, the first step is rate-determining. In **(b)**, the second step is rate-determining.*

Some points to note:

- **A transition state is different from an intermediate**. A transition state, at the top of the energy curve, occurs at an **energy maximum**. An intermediate occurs at an **energy minimum**, but, because it is a relatively reactive species, it has higher energy than the reactants or products. A transition state has no permanent lifetime of its own – it exists for just a few femtoseconds (10^{-15} s) when the molecules are in contact with each other. An intermediate is a definite chemical species that exists for a finite length of time. Even a reactive intermediate, with a lifetime of only a microsecond, has a longer lifetime in comparison with the time that colliding particles are in contact.

7 FACTORS AFFECTING RATES OF REACTION

Recall that, according to the collision theory, a reaction occurs only if the particles collide with the correct energy and orientation. At the molecular level, the rate of a reaction depends on two things:

- the **collision frequency** (i.e. how often the reactant molecules collide with each another); and
- the **proportion of the particles that have sufficient energy to overcome the activation energy**.

By changing the physical parameters of a reaction (such as concentration, temperature, etc.), we can effectively modify these two factors, leading to a change in the rate of reaction.

For most chemical reactions, only a tiny fraction of the collisions that take place have enough energy to overcome the activation energy barrier. These collisions are called **effective collisions**. A typical fraction might be one in ten thousand million (1 in 10^{10}). This is why many reactions are slow at room temperature. In general, any change that increases the collision rate will inevitably lead to an increase in effective collisions.

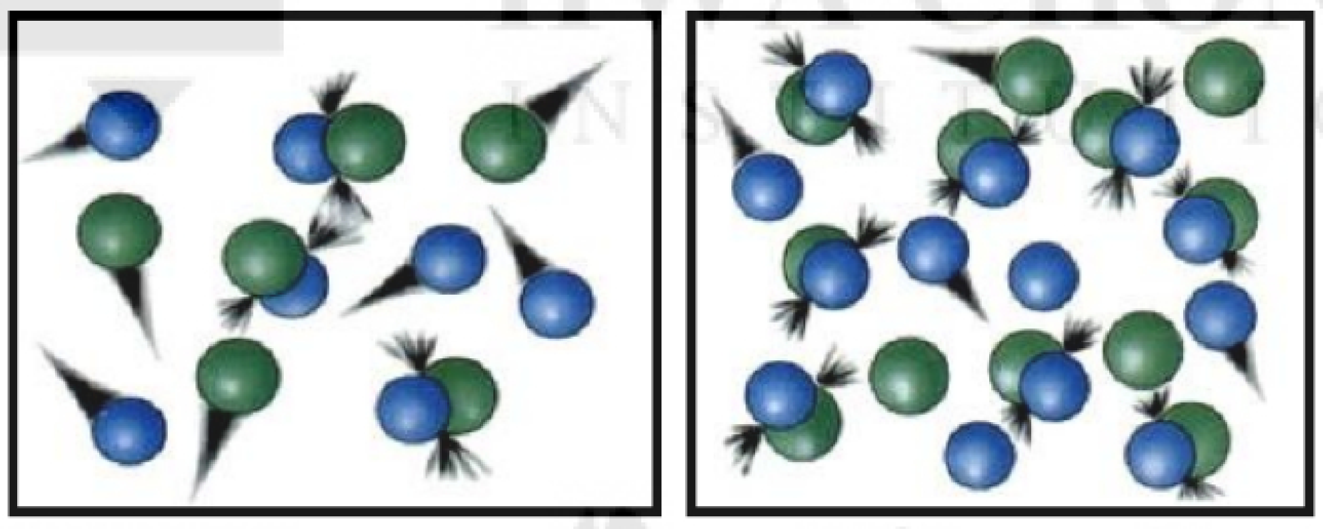
7.1 Effect of concentration or pressure

Usually, rate of reaction increases when the reactant concentration is increased.

At a higher concentration, there are **more reactant particles per unit volume**, therefore,

- **reactant particles are closer together**
- **reactant particles collide more frequently**
- **thus, frequency of effective collisions increases**
- **rate of reaction increases**

(Note: All the above points are necessary in explaining the effect of concentration on reaction rate)



Low concentration, fewer collisions. *High concentration, more collisions.*

Figure 16. Depiction of collision frequency as a function of concentration.

The rate of reaction will increase only if the concentration of reactants that appear in the rate equation is increased.

E.g. $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C}$ rate = $k[\mathbf{A}]$

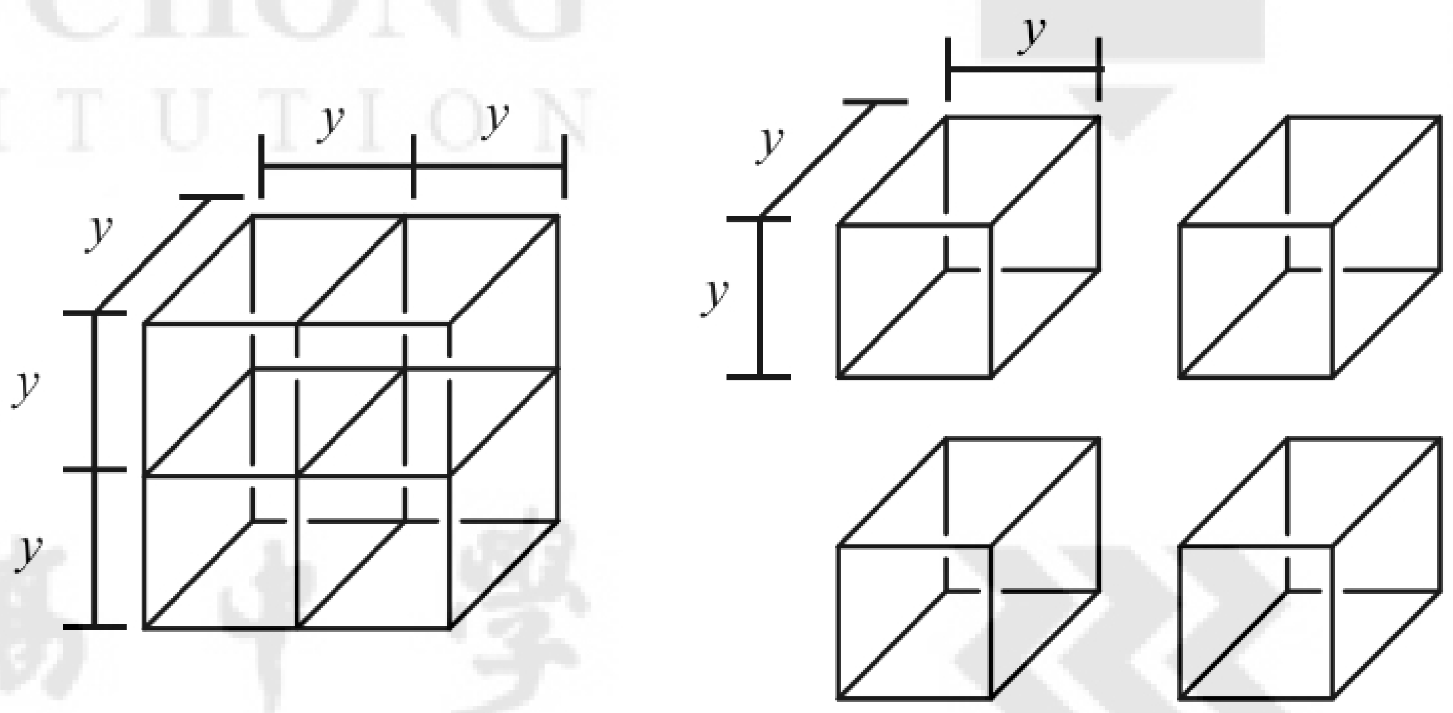
The rate of the above reaction will increase if [**A**] is increased. However, the rate of reaction will not increase if [**B**] is increased as the reaction is zero order with respect to **B**.

The same effect is observed if we increase the **pressure** for a **gaseous** reaction. The molecules are closer together, leading to an increase in collision frequency as well.

However, changing the pressure has virtually no effect on the rate for solid or liquid phase reactions because the volume of a solid or liquid changes very little when put under pressure, so their particles do not move closer together.

7.2 Effect of surface area (solids)

For a chemical reaction involving a **solid**, only the particles on its surface are available for reaction. If the solid reactant is in a more finely divided state, the **surface area** over which the solid can come into contact with liquid or gaseous reactants is larger. Hence, **collision frequency increases**, reaction rate increases.



Large particle size
Surface area
$= (y \times y) \times 16$
$= 16y^2$

Small particle size
Surface area
$= (6 \times y \times y) \times 4$
$= 24y^2$

Figure 17. Illustration showing the effect of smaller particle size on surface area available for reaction.

Self-practice 7.1

Consider the reaction: $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$.

State how the rate of reaction will change under each of the following situations:

i) increasing the concentration of HC*l* (aq),
ii) increasing the total pressure of the system,
iii) using zinc powder instead of zinc granules.

Reactions can be made to go faster by increasing the fraction of reacting particles with enough energy to overcome the activation energy barrier. This is a more important factor than simply increasing frequency of collision. There are two ways in which we can increase this fraction:

- increase the energy of the collisions;
- find another route with a lower activation energy.

7.3 Effect of Temperature

The usual way of increasing the energy of the collisions is to increase the temperature.

A minor effect of increasing the temperature is that the reactant particles move faster as they now have higher kinetic energies, so they collide more frequently.

However, the main effect is that a higher proportion of the particles now have enough energy to overcome the activation energy barrier, thus the **frequency of *effective* collisions** increases.

A good gauge of the effect of temperature increase is the following:
a **10 °C increase in temperature** roughly **doubles** the rate of reaction

➢ Effect of changing temperature on the rate constant

The increase in rate of reaction with an increase in temperature can also be predicted by the Arrhenius equation. According to the Arrhenius equation (Section 4.3), the rate constant increases exponentially with temperature.

$$k = \mathrm{A}e^{-\mathrm{Ea}/\mathrm{RT}}$$

Even without knowing the Arrhenius equation, knowing that an increase in temperature alone can increase the rate of a reaction (all other factors remaining identical), we can easily see that an increase in temperature must have effected an increase in the value of the rate constant, *k*.

To help remember this relationship (between temperature and the rate constant), you can follow the following line of thought.

Recall a general rate equation,

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

If [A] and [B] are kept the same for two identical experiments in which only temperature is changed, then rate $\propto k$.

Our reasoning can follow these lines:

∵ increasing the temperature increases rate
and rate $\propto k$ (∵ [**A**] and [**B**] are kept the same)
∴ increasing the temperature must have increased *k*

Conversely, decreasing the temperature would decrease the value of the rate constant.

Qualitatively, the explanation is better understood with the help of the Boltzmann distribution curve, as outlined in the next self-practice.

Self-practice 7.2

With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of a chemical reaction.

Self-practice 7.3

It is often said that the rate of a typical reaction is roughly doubled by raising the temperature by 10 °C.

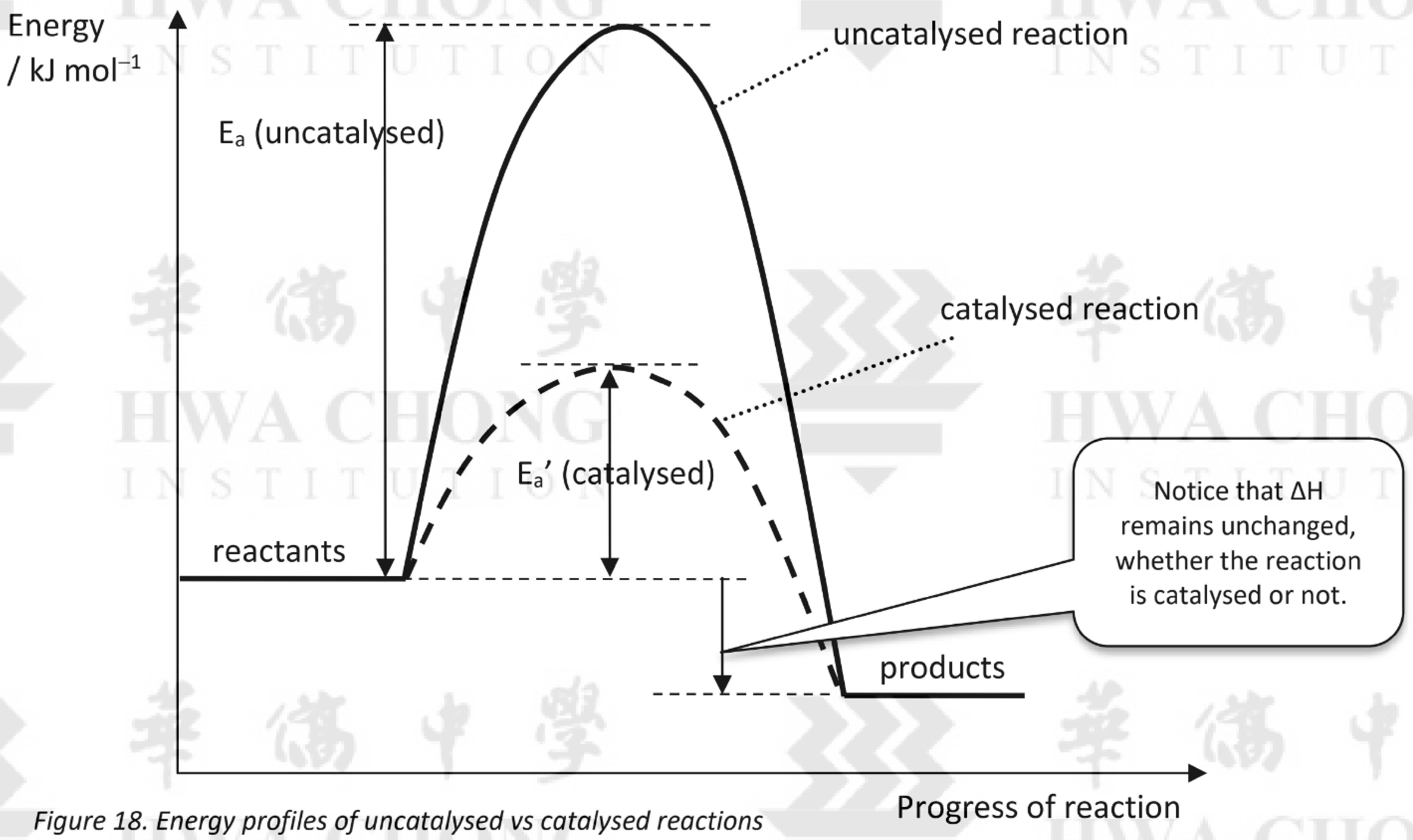
What explains this observation?

A Raising the temperature by 10 °C doubles the average energy of each molecule.
B Raising the temperature by 10 °C doubles the velocity of each molecule.
C Raising the temperature by 10 °C doubles the number of molecular collisions in a given time.
D Raising the temperature by 10 °C doubles the number of molecules having more than a certain minimum energy.

7.4 Effect of Catalysts

Lowering the activation energy is another way of increasing the fraction of reacting particles with enough energy to overcome the activation energy barrier. This is most easily achieved by using a catalyst.

> *A **catalyst** is a substance that **speeds up a chemical reaction by providing an alternative reaction pathway of lower activation energy**, while **remaining chemically unchanged at the end of the reaction**.*



Notice that ΔH remains unchanged, whether the reaction is catalysed or not.

Figure 18. Energy profiles of uncatalysed vs catalysed reactions

➢ Effect of adding a catalyst on the rate constant

Recall that, according to the Arrhenius equation for the rate constant, k, is:

$$k = Ae^{-Ea/RT}$$

So, when E$_a$ decreases due to the presence of a catalyst, the value of k will increase (due to the negative power), thus the rate will increase as well.

Without referring to the Arrhenius equation, we can again work out that the presence of a catalyst gives a larger value of k.

Recall the general rate equation,

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

If all other conditions remain unchanged in two experiments (same initial [A] and [B], and for the same reaction, m and n are identical) where one is catalysed, and one uncatalysed, then rate $\propto k$.

Our reasoning can follow these lines:

$\because$ a catalyst, by definition, increases rate of reaction,
and rate $\propto k$ ($\because$ [**A**] and [**B**] are kept the same)
$\therefore$ adding a catalyst must have increased k

Qualitatively, the explanation is better understood with the help of the Boltzmann distribution curve, as outlined in the next self-practice.

Self-practice 7.4

With the aid of a sketch of the Boltzmann distribution, explain how the presence of a catalyst affects the rate of a chemical reaction.

7.5 Effect of light

Reactions that are affected by the action of light are called **photochemical reactions**. When the reactant molecules absorb light energy, the average kinetic energy of the particles increases, hence increasing the fraction of reacting particles with enough energy to overcome the activation energy barrier.

Examples of photochemical reactions:

- Breakdown of silver bromide to silver and bromine (used in black-and-white photography):
$$AgBr \rightarrow Ag + \tfrac{1}{2} Br_2$$
- Reaction of hydrogen with chlorine which is slow in the dark but explosive in sunlight:
$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$
- Chlorination of alkanes:
$$CH_4 + Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$$

Such reactions tend to be slow in the dark but take place rapidly in the presence of light.

Did you know?

Photochromic sunglasses darken on exposure to ultraviolet (UV) radiation. Photochromic or photochromatic lenses have millions of particles of substances such as silver chloride embedded in them. The particles are transparent to visible light in the absence of UV light. But when exposed to UV rays, as in direct sunlight, the particles undergo a chemical reaction that causes them to change shape. The new structure absorbs portions of the visible light, causing the lenses to darken. The number of particles that change shape varies with the intensity of the UV rays. When you go indoors and out of the UV light, a different chemical reaction takes place. The absence of UV radiation causes the particles to "snap back" to their original shape, resulting in the loss of their light absorbing properties. In both directions, the entire process happens very rapidly.

[Source: http://science.howstuffworks.com/innovation/science-questions/question412.htm]

Self-practice 7.5

When light is shone for a fixed amount of time into a solution of CH_2ICH_2I and I_2 in tetrachloromethane at 100°C, the following reaction occurs:

$$CH_2ICH_2I \rightarrow CH_2{=}CH_2 + I_2$$

Experiment	Relative initial concentrations		Relative light intensity	Relative initial rate of formation of iodine
	CH_2ICH_2I	I_2		
1	2	1	4	2
2	2	1	1	1
3	1	1	4	1
4	1	2	4	1

From the data in the table, the rate of formation of iodine is

1 proportional to $\sqrt{\text{light intensity}}$.

2 independent of initial concentration of I_2.

3 proportional to initial concentration of $C_2H_4I_2$.

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

8 CATALYSIS

Catalysis is especially important to industrial chemists. It allows them to increase the rate of reactions without resorting to increasing temperature which may involve higher cost and possibility of decomposition of reactants or products.

Generally, there are two main types of catalyst: **homogeneous** and **heterogeneous** catalysts. The **type of catalyst** is determined by the **phase** in which the **catalyst** and the **reactants are in**.

The term **phase** as used in chemistry refers to a **physically distinctive form of matter**, such as a **solid, liquid, gas or plasma**. A phase of matter is characterised by having relatively uniform chemical and physical properties. Phases are *different* from states of matter. The states of matter (e.g., liquid, solid, gas) are phases, but matter can exist in different phases yet possess the same state of matter. For example, water and oil are in the same liquid state but when added together exist in different phases (oil phase and aqueous phase) as they do not mix.

8.1 Homogeneous catalysis

A **homogeneous catalyst** acts in the **same phase as the reactants** and is uniformly mixed with them.

Homogeneous catalysis usually involves the formation of an **intermediate** between the catalyst and one of the reactants. The catalyst is then regenerated in a later step of the reaction.

The catalysed reaction may involve two or more steps, each of which must has a lower activation energy than the uncatalysed reaction.

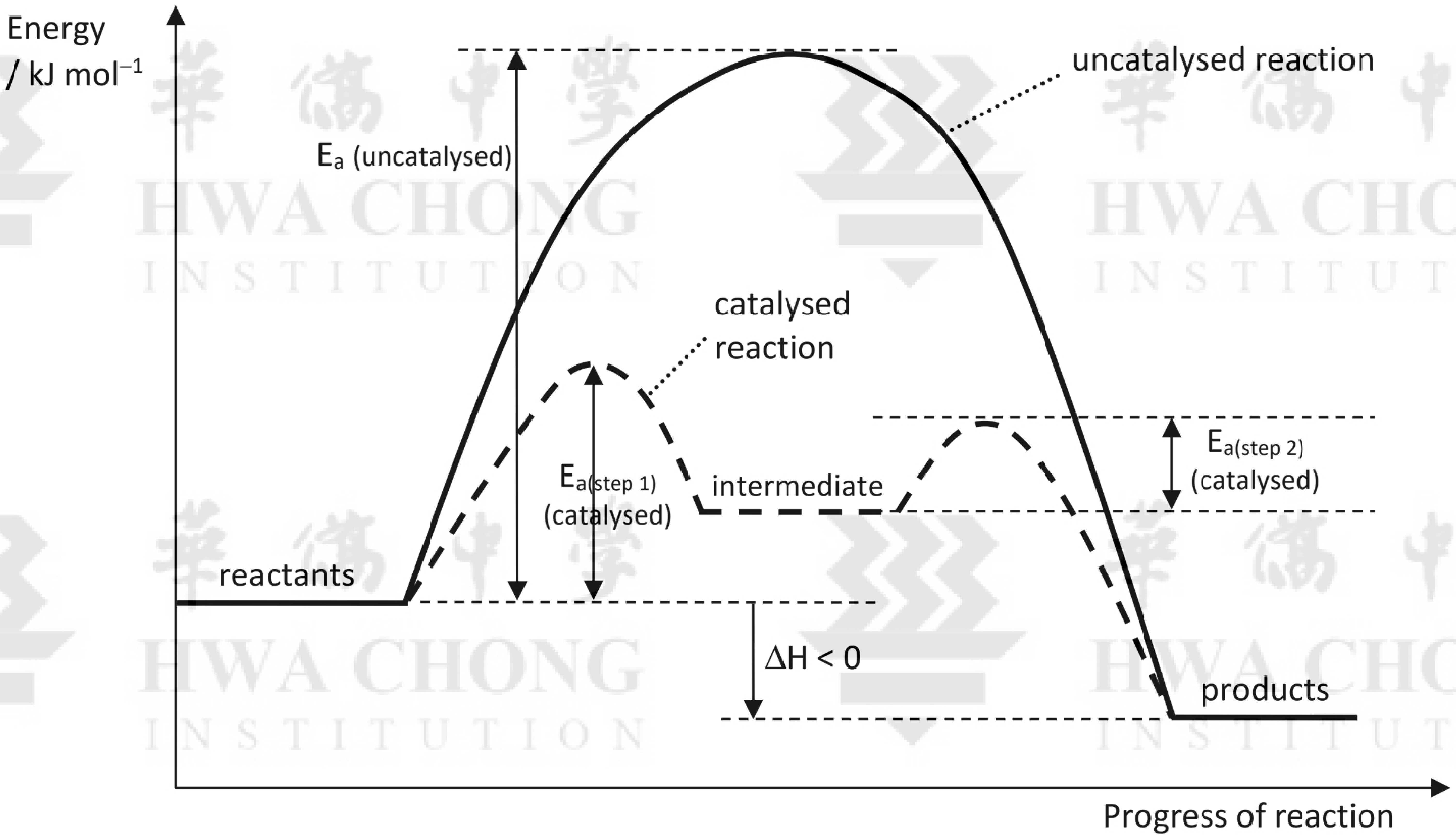


Figure 19. A possible set of energy profiles for a reaction with and without a homogeneous catalyst. In the presence of a catalyst, the reaction has a different reaction pathway which involves lower activation energy. Notice that the catalyst does not alter the final products and the enthalpy change of reaction.

A homogeneous catalyst must be involved in the rate-determining step in order for it to affect the rate of reaction. As such the concentration of the homogeneous catalyst usually appears in the rate equation for the catalysed pathway, even though it does not appear in the overall balanced stoichiometric equation.

Example: The iodination of propanone catalysed by H^+ ions:

$$\underset{\text{propanone}}{CH_3COCH_3(aq)} + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

has the rate equation, rate = $k[CH_3COCH_3][H^+]$.

8.1.1 Catalytic role of Fe^{2+} in the I^- / $S_2O_8^{2-}$ reaction

Iodide ions react with peroxodisulfate ions in the redox reaction:

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

The reaction requires collision between I^- and $S_2O_8^{2-}$ which are both negatively charged and therefore tend to repel. Thus, the reaction has high activation energy and proceeds slowly.

Fe^{2+} ion can be used as a homogeneous catalyst for the reaction. The catalysed pathway involves the following steps:

Step 1:	$2Fe^{2+}(aq)$	+	$S_2O_8^{2-}(aq)$	$\rightarrow$	$2Fe^{3+}(aq)$	+	$2SO_4^{2-}(aq)$
Step 2:	$2Fe^{3+}(aq)$	+	$2I^-(aq)$	$\rightarrow$	$2Fe^{2+}(aq)$	+	$I_2(aq)$
Overall equation:	$2I^-(aq)$	+	$S_2O_8^{2-}(aq)$	$\xrightarrow{Fe^{2+}(aq)}$	$I_2(aq)$	+	$2SO_4^{2-}(aq)$

The catalyst Fe^{2+} and the intermediate Fe^{3+}, being positively charged, easily attract the negative $S_2O_8^{2-}$ and I^- respectively. Thus, in the catalysed pathway, each step has a lower activation energy than the uncatalysed reaction.

Do you think Fe^{3+} ion can act as a homogeneous catalyst for the same reaction?

Yes, step 2 first followed by step 1.

8.1.2 Catalytic role of oxides of nitrogen in the formation of acid rain

Nitrogen dioxide may catalyse the oxidation of SO_2 to SO_3 in the atmosphere and hence speed up the formation of acid rain. The catalysed pathway is given by the following two steps:

Step 1: $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$
Step 2: $NO(g) + ½O_2(g) \rightarrow NO_2(g)$
Overall equation: $SO_2(g) + ½O_2(g) \rightarrow SO_3(g)$

SO_3 reacts readily with moisture in air or rainwater to give sulfuric acid:

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

Sulfuric acid is a strong acid and it forms acid rain when dissolved in rainwater.

8.1.3 Other examples of homogeneous catalysis

1. Production of ozone from O_2 near the ground, catalysed by NO_2:

$$O_2(g) + NO_2(g) \rightarrow NO(g) + O_3(g)$$
$$NO(g) + \tfrac{1}{2}O_2(g) \rightarrow NO_2(g)$$

2. Catalytic destruction of ozone in the upper atmosphere by chlorine atoms (radicals) from CFCs:

$$Cl\bullet(g) + O_3(g) \rightarrow ClO\bullet(g) + O_2(g)$$
$$ClO\bullet(g) + O(g) \rightarrow Cl\bullet(g) + O_2(g)$$

(O atoms are present naturally in the upper atmosphere)

3. Esterification, from carboxylic acid and alcohol, catalysed by H^+ ions from concentrated H_2SO_4:

$$CH_3CO_2H(l) + CH_3OH(l) \xrightleftharpoons{\text{conc. } H_2SO_4} CH_3CO_2CH_3(l) + H_2O(l)$$

Self-practice 8.1

(a) A reversible reaction is catalysed.
Which of the following statements about this system are correct?

1 The catalyst alters the mechanism of the reaction.
2 The catalyst reduces the energy of activation (the energy barrier) for both the forward and backward reactions.
3 The catalyst alters the amounts of products obtained at equilibrium.

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

[J93/4/33]

(b) Sulfur dioxide in the atmosphere can be responsible for the formation of acid rain. It can be converted into sulfur trioxide by the action of nitrogen dioxide in a polluted atmosphere. The nitrogen dioxide reacts according to the following equations.

$$NO_2(g) + SO_2(g) \rightarrow NO(g) + SO_3(g)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

What is the role of the nitrogen dioxide?

1 an acid
2 a homogeneous catalyst
3 an oxidising agent

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

[J99/3/36]

8.2 Heterogeneous catalysis

A **heterogeneous catalyst** acts in a **different physical phase from the reactants**.

This type of catalysis most often involves a solid interacting with gaseous or liquid reactants.

Since solids do not have a ‘concentration’, heterogeneous catalysts *do not* appear in the rate equation in this form. Instead, their effect is included in the value of the rate constant, *k*.

Catalytic action occurs **on the surface** of the solid catalyst at what is called ‘**active sites’**. Thus a **larger surface area** is more advantageous in increasing the rate of reaction since it exposes more active sites. The catalyst is usually made into pellets, wire gauze or finely-powdered form spread on ceramic, silica or asbestos support.

Many heterogeneous catalysts are transitions metals or their compounds:

Reaction	Catalyst
Manufacture of ammonia (Haber Process) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Finely divided Fe(s) or $Fe_2O_3(s)$
One of the reactions involved in the **manufacture of sulfuric acid** (Contact Process): $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$V_2O_5(s)$
Hydrogenation of alkenes $CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g)$	Ni(s) or Pt(s)
Removal of oxides of nitrogen, CO and unburnt hydrocarbons in the exhaust gases from car engines	Pt(s), Pd(s), Rh(s) in the catalytic converter

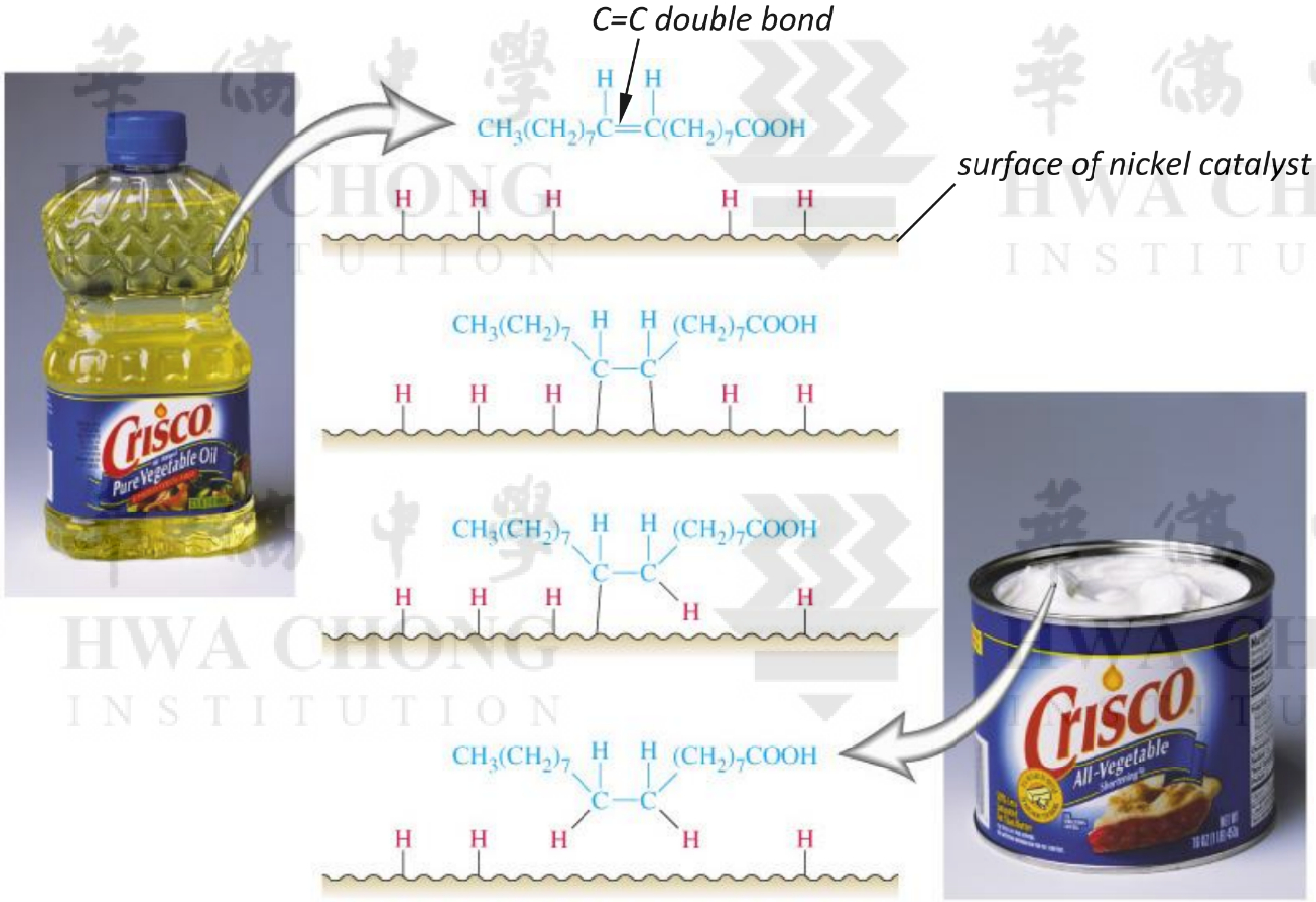


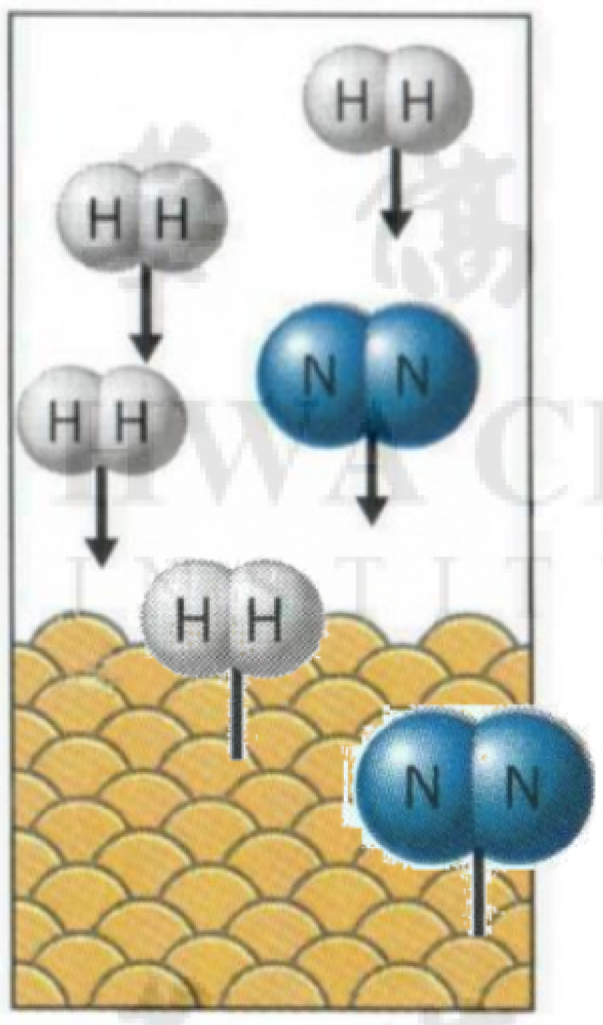
Figure 20. Catalytic hydrogenation of alkenes is used in the conversion of inedible vegetable oils to edible margarine. A solid catalyst usually functions by promoting a reaction on its surface.

8.2.1 Mode of action of heterogeneous catalysts

The mode of action of heterogeneous catalysts is explained below with reference to the reaction in the Haber process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, which is normally catalysed by iron metal.

The figures below illustrate the three stages involved:

(a)

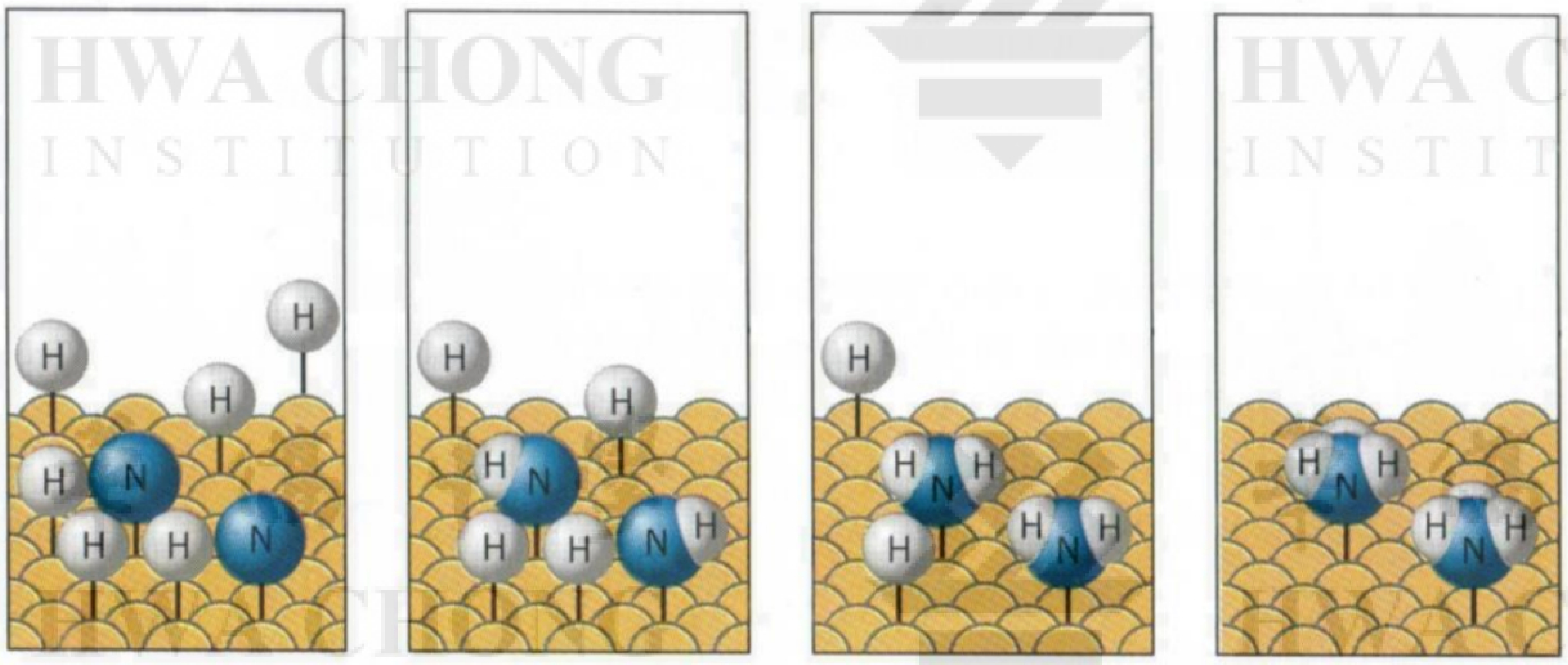


surface of Fe metal

Adsorption. The reactant molecules, N_2 and H_2, **diffuse** towards the surface of the Fe catalyst and are **adsorbed** onto the **active sites** at the surface. This involves the formation of weak attraction forces.

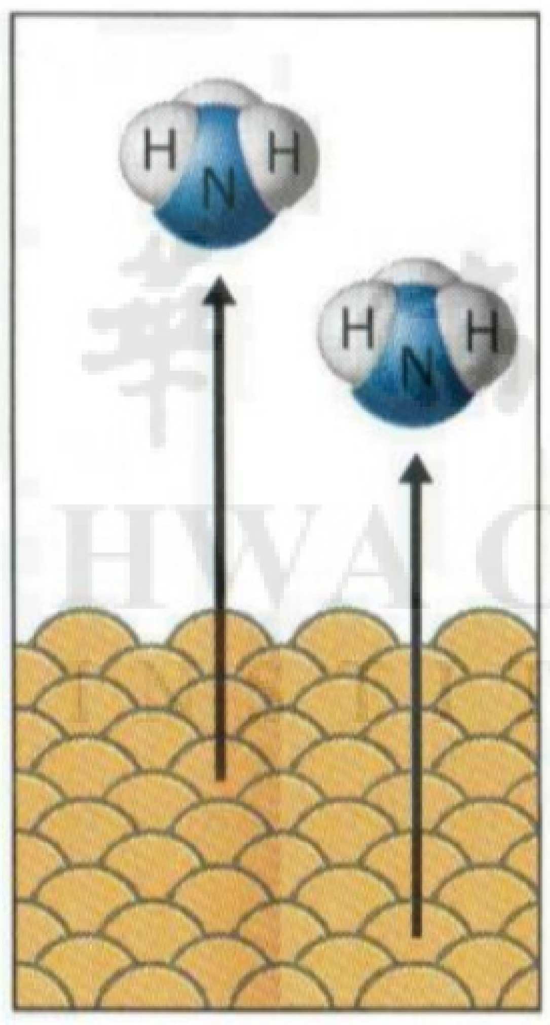
The adsorption process brings reactant molecules closer together. The process also **weakens the bonds in the reactant molecules**, thus **lowering the activation energy**. The reactant molecules are also **correctly orientated** for reaction to occur.

(b)



Reaction. Chemical reaction occurs: bonds break and new bonds form.

(c)



Desorption. Product molecule, NH_3, **desorbs** and diffuses away from the catalyst surface. The active sites become free to adsorb "new" reactant molecules.

The rate of reaction is controlled by how fast the gaseous reactants are adsorbed and how fast the products are desorbed. When the active sites are fully occupied (i.e. when the catalyst is **saturated**), there is no increase in reaction rate even if the pressure of the system is increased.

Qn: What is the order of reaction (with respect to the reactant molecules) when the catalyst is saturated?

Catalyst is saturated, reactants can no longer be adsorbed onto catalyst active sites, rate no longer be affected by [reactant], zero order with respect to reactant.

Figure 21. Mode of action of heterogeneous catalysts, explained with reference to the reaction in the Haber process.

8.2.2 Application of heterogeneous catalysis: Catalytic converters in vehicles to convert harmful emissions to less harmful products

Ideally, the hydrocarbons in petrol would be completely converted into carbon dioxide and water when burned in a car engine. These are non-polluting products, though the CO_2 added into the atmosphere does have an effect on the earth's climate. In practice, however, complete conversion does not occur and three other products are formed which are immediately harmful:

- unburnt hydrocarbons,
- carbon and carbon monoxide from incomplete combustion of the fuel,
- oxides of nitrogen from the reaction between N_2 and O_2 from the air, under the high temperatures in the car engine.

To reduce the amounts of these pollutants, car engines are fitted with **catalytic converters**. The exhaust gases are passed through a ceramic honeycomb or bed of small beads made from alumina (Al_2O_3), coated with platinum (Pt), palladium (Pd), and rhodium (Rh) catalysts. These help to catalyse the following reactions:

- Reduction of NO to N_2

$$CO(g) + NO(g) \rightarrow CO_2(g) + \tfrac{1}{2}N_2(g)$$

- Oxidation of CO to CO_2

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g)$$

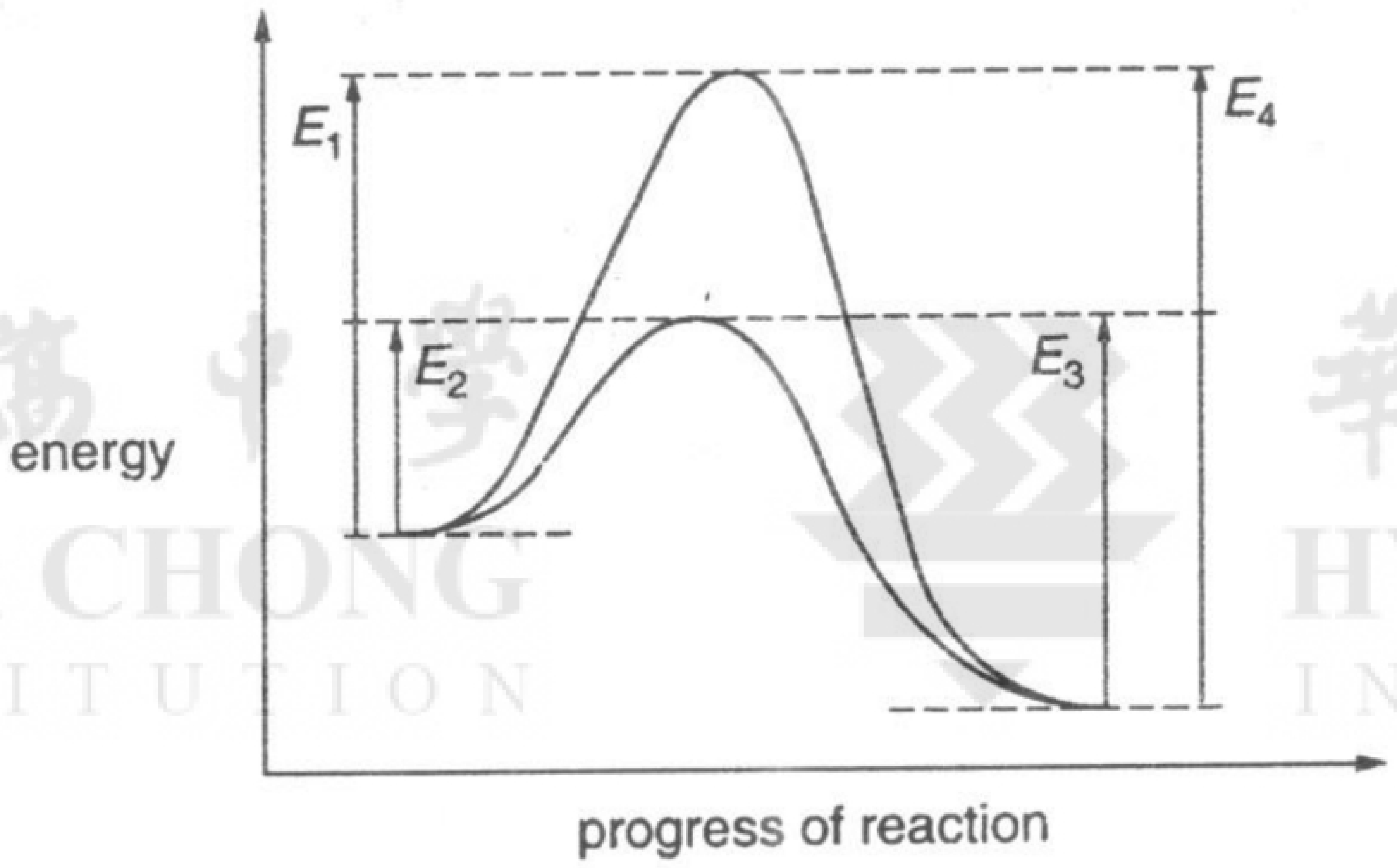
- Oxidation of unburnt hydrocarbons to CO_2 and H_2O

$$\text{unburnt hydrocarbon} + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Because lead poisons the catalysts (therefore rendering them ineffective), it is essential to use unleaded petrol in a car fitted with a catalytic converter.

Self-practice 8.2

(a) The energy diagram represents the reaction occurring with and without a catalyst.

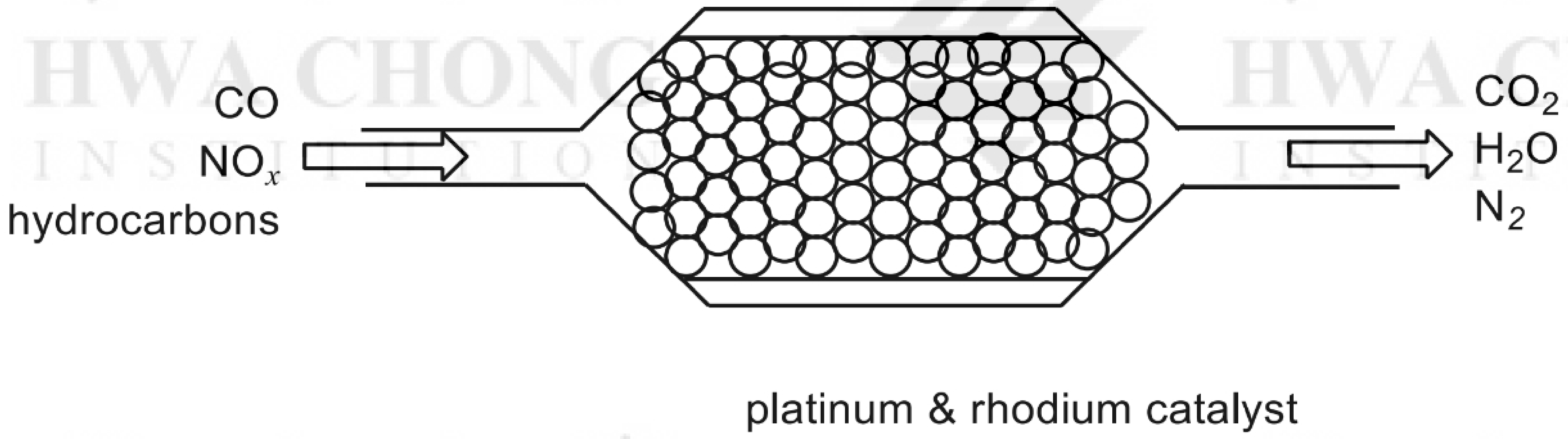


Which of the following statements are correct?

1 E_2 is the activation energy for the catalysed reaction.
2 The enthalpy change of reaction is ($E_2 - E_3$).
3 The enthalpy change of reaction is reduced by using a catalyst.

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

(b) The diagram represents a section of a catalytic converter on the exhaust system of a car. Harmful gases are converted into carbon dioxide, nitrogen and water vapour.



Which processes take place in this catalytic converter?

1 Carbon monoxide and hydrocarbons react together.
2 Carbon monoxide and nitrogen oxide react together.
3 Platinum and rhodium catalyse redox reactions.

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

[J95/IV/39]

8.3 Autocatalysis

In autocatalysis, one of the products of the reaction is a catalyst for the reaction itself.

Examples:

- Mn^{2+} ions catalyse the reaction between manganate(VII) ions and ethanedioate ions:

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

- Hydrolysis of an ester produces ethanoic acid, which can ionise slightly in the aqueous mixture to give H^+ ion which acts as a catalyst for the reaction itself:

$$\underset{\text{ester}}{CH_3CO_2CH_3} + H_2O \rightleftharpoons \underset{\text{ethanoic acid}}{CH_3CO_2\mathbf{H}} + CH_3OH$$

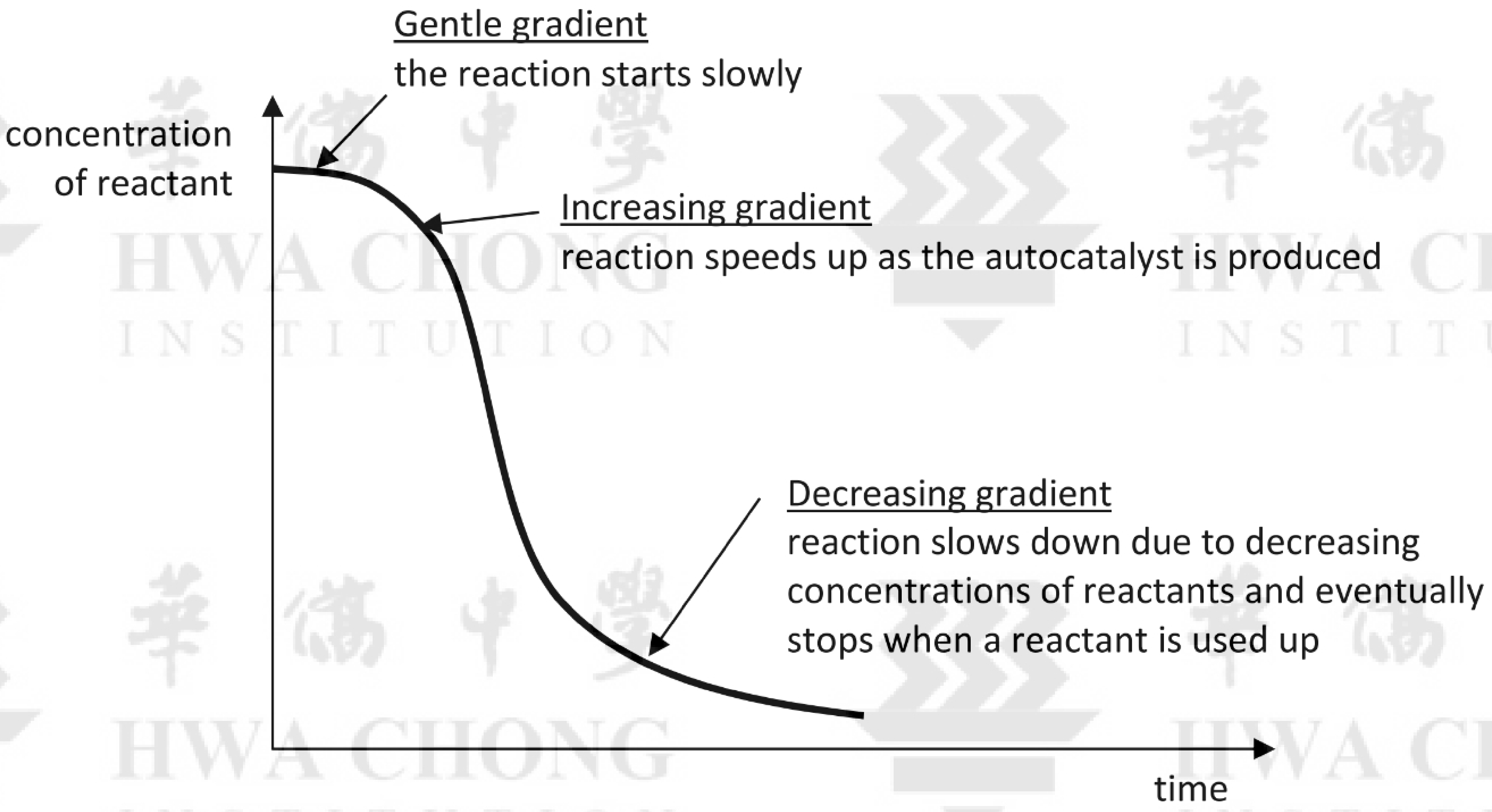
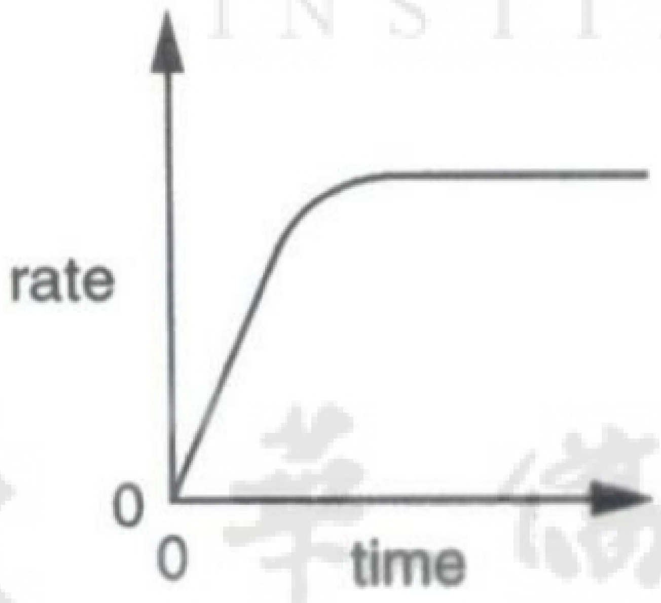


Figure 22. Typical concentration-time graph for a reaction in which autocatalysis occurs.

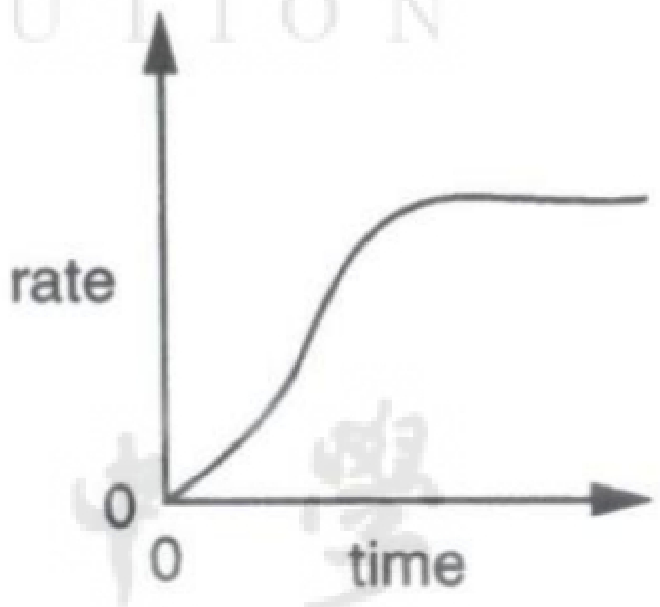
Self-practice 8.3

Which curve is obtained if the rate of reaction is plotted against time for an autocatalytic reaction (i.e. a reaction in which one of the products catalyses the reaction)?

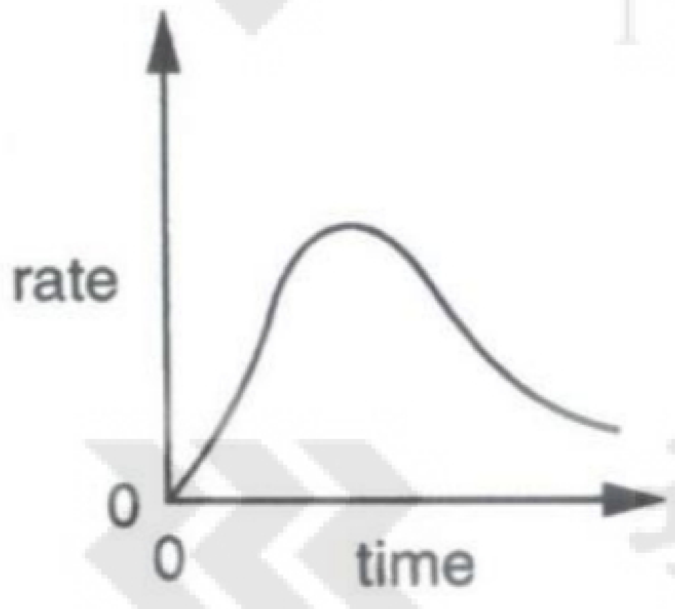
A



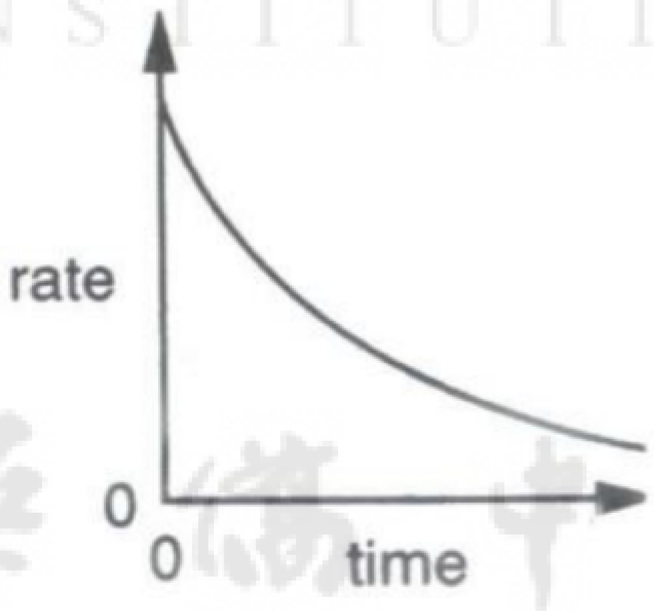
B



C



D



[J02/I/11, N89/3/10]

8.4 Biological catalysts – Enzymes

What is an enzyme?

Chemical reactions that take place in living cells are remarkably fast, especially since they usually take place just above room temperature and at very low concentrations. This is because they are catalysed by very efficient catalysts called enzymes.

Enzymes are **biological catalysts that speed up reactions in living systems** while remaining unchanged at the end of the reaction. Enzymes are very **specific** in their action. **Most enzymes catalyse only one reaction or one group of similar reactions** e.g. proteases are enzymes which break peptide bonds between amino acids of proteins, amylases are enzymes which break down starch.

Enzymes are **proteins**, which are polymers made up of units called amino acids. These units are joined in a chain, like beads in a necklace. A typical enzyme may contain 500 amino acids and has a relative molecular mass of 50,000. The amino acid chain of an enzyme coils and folds into an approximately spherical shape. We thus classify them as globular proteins. Globular proteins are soluble in water.

Catalytic action of enzymes

An enzyme has features of both a homogeneous and a heterogeneous catalyst. Since globular proteins are soluble in water, enzymes thus act in the same "aqueous phase" as the reactants in living systems, so enzymes are homogeneous catalysts. But their mode of action resembles that of heterogeneous catalysts in that the reaction takes place at a specific point on their surface called the **active site**.

The reactant that binds to the enzyme's active site is called the **substrate**. In most cases, a substrate binds to the active site through **intermolecular attractions** such as **hydrogen bonds or dispersion forces**. Usually, only one type of substrate can fit into the active site of an enzyme – so enzymes are **highly specific**.

Some enzymes are so efficient that one enzyme molecule can catalyse the reaction of 10,000 reactant molecules every second! This means that virtually every collision of the substrate with the active site leads to reaction, showing that the **enzyme-catalysed reaction has very low activation energy**.

Examples of enzyme-catalysed reactions:

- Yeast contains a mixture of enzymes called zymase that converts sucrose into ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{4CH_3CH_2OH(aq)} + 4CO_2(g)$$

- Hydrogen peroxide is produced in many metabolic reactions and is harmful to cells. It is rapidly decomposed to water and oxygen in the presence of the enzyme, catalase:

$$H_2O_2(aq) \xrightarrow{\text{catalase}} H_2O(l) + \tfrac{1}{2}O_2(g)$$

Table 1 – Activation energies for the decomposition of hydrogen peroxide (for your information)

	uncatalysed	catalyst: platinum	enzyme: catalase
E_a /kJ mol^{-1}	76	50	8

8.4.1 Mechanism of enzyme action

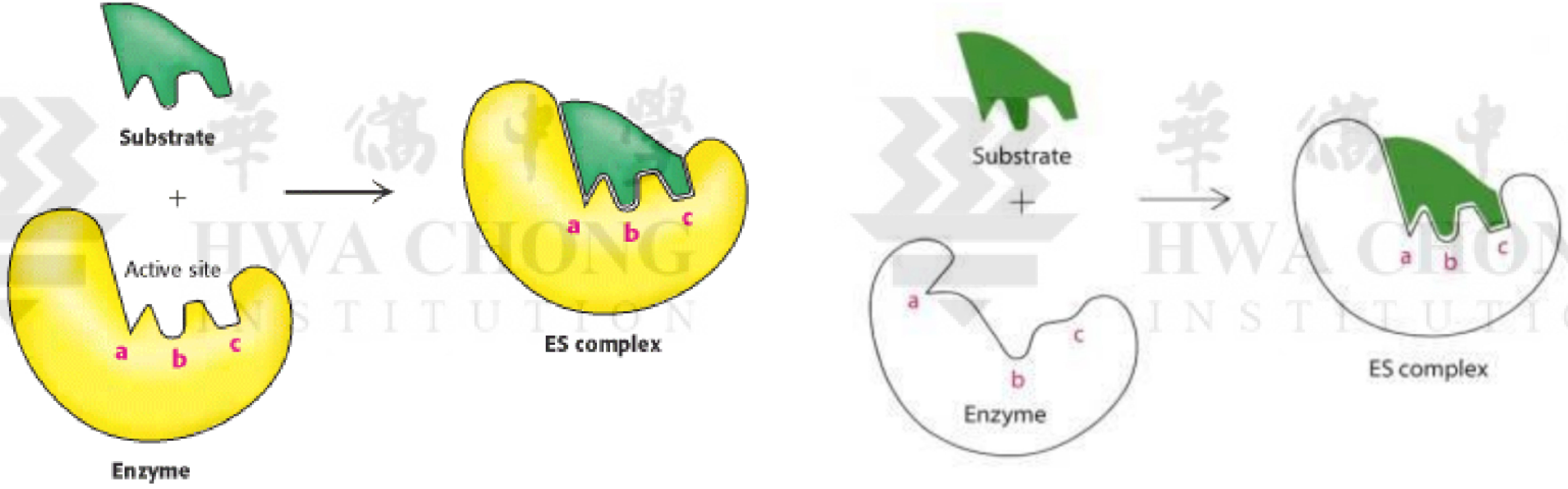
The mechanism may be simplified as the following two steps:

enzyme + substrate ⇌ enzyme–substrate complex (fast)
enzyme–substrate complex → enzyme + products (slow, rate-determining)

The substrate binds to the active site of the enzyme to form the **enzyme–substrate complex**.

Within the complex, the substrate molecule then undergoes chemical change that may involve bond reorganisation and/or reaction with other molecules. Once the products are formed, they will be released from the enzyme and diffuse away. The enzyme's active site is empty again and ready to take in another substrate.

There are two models of enzyme action:



(a) lock-and-key model **(b) induced-fit model**

*Figure 23. Two models of enzyme action. **(a)** In the lock-and-key model, the active site is thought to be an exact fit for the substrate. **(b)** In the induced-fit model, the active site is thought to change shape to fit the substrate.*

8.4.2 Relationship between [substrate] and rate of an enzyme-catalysed reaction

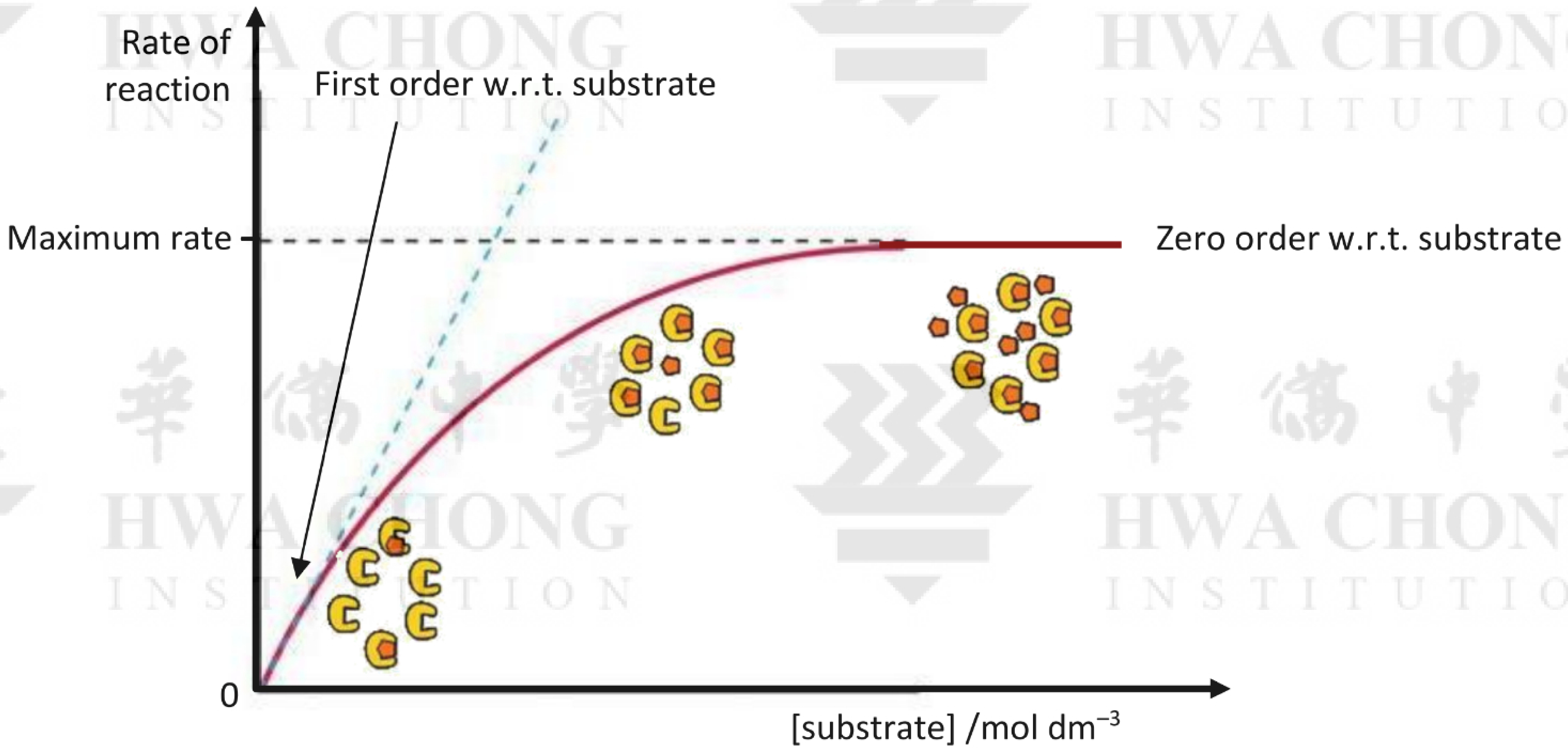


Figure 24. Graph of rate of an enzyme-catalysed reaction against substrate concentration.

At **low [substrate]**, the enzyme concentration is greater than substrate concentration, so the rate of reaction increases proportionally with increasing substrate concentration. The reaction is **first order** with respect to the substrate.

At **high [substrate]**, all the active sites are filled with substrate molecules (i.e. saturation point), so any further increase in [substrate] does not affect the rate. The reaction is now **zero order** with respect to the substrate.

This behaviour is characteristic of enzyme-catalysed reactions.

To overcome the saturation point and further increase the maximum rate of reaction, the [enzyme] has to be increased.

8.4.3 Effects of temperature and pH on enzyme activity

Each enzyme has an optimum set of temperature and pH at which it functions best.

Example: salivary amylase has the following optimum working conditions:

- optimum temperature: 37 °C (human body temperature)
- optimum pH: 6.8

Changes in these conditions will cause enzymes to lose their effectiveness. If the changes are extreme, enzymes will lose their globular structure and will no longer be able to function as catalysts – a process we call **denaturation**. For example, salivary amylase would be denatured above 40 °C. This is because, at this temperature, the attraction forces holding the specific three-dimensional shape of the enzyme molecule are overcome. The denatured enzyme has a random structure and the active site has been irreversibly destroyed.

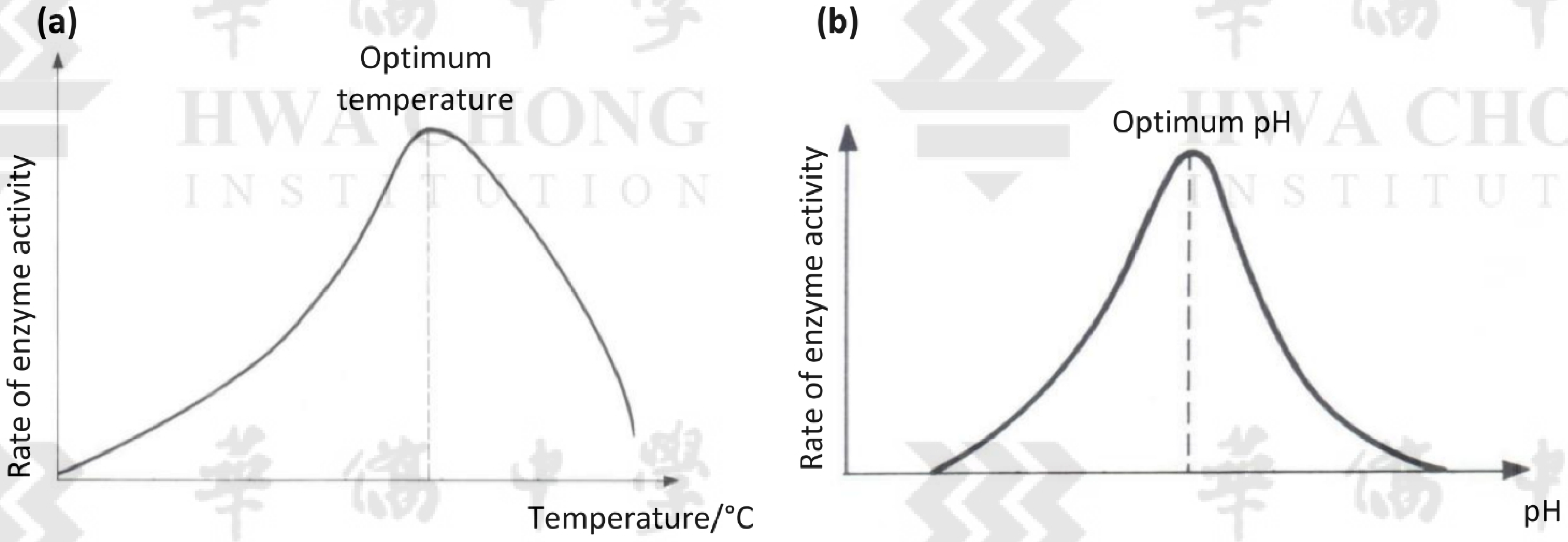


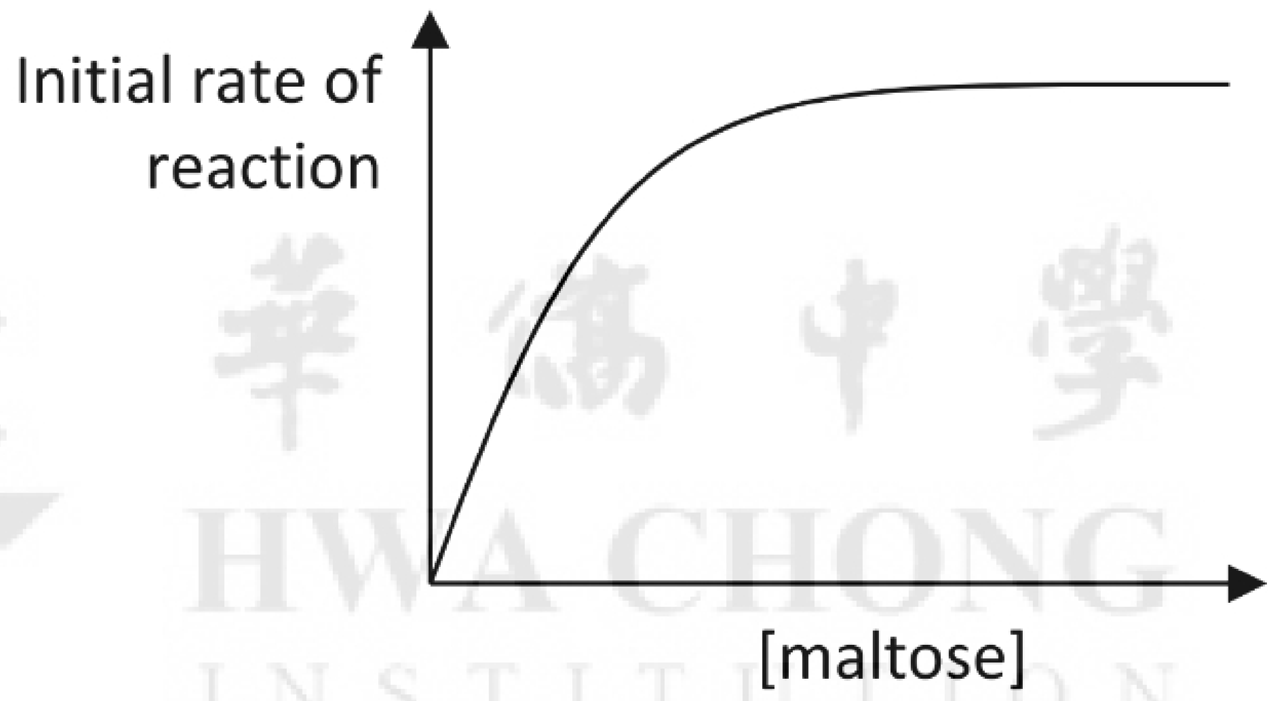
*Figure 25. Enzyme activity is affected by **(a)** temperature and **(b)** pH.*

8.5 Substances affecting catalyst activity

Catalysts with active sites, whether biological or not, are vulnerable to **poisons** which may preferentially bind to the active site. Once bound, these poisons have an inhibitive effect on the action of the catalyst, even when present in small amounts. For example, enzymes are easily poisoned by molecules similar to the substrate, while metal catalyst such as platinum can be poisoned by lead additives in petrol, which are preferentially adsorbed onto the catalyst surface.

Self-practice 8.4

The graph shows the results of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied but that of amylase was kept constant.



Which conclusions can be deduced from these results?

1 When [maltose] is low, the rate is first order with respect to [maltose].
2 When [maltose] is high, the rate is independent of [maltose].
3 When [maltose] is high, the rate is independent of [amylase].

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

[N2001/III/34]

LOOKING AHEAD

Transformation of matter involves the study of the spontaneity (thermodynamics), rate (kinetics) and extent of chemical reactions (concept of equilibrium). The concepts in chemical energetics and kinetics will help us understand the extent to which a reaction proceeds and the position of equilibrium. Theoretically, all reactions are reversible, and the notion of dynamic equilibrium will be introduced in the next topic: Chemical Equilibria