## ANDERSON SERANGOON JUNIOR COLLEGE JC1 H2 CHEMISTRY <u>REACTION KINETICS</u>

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#### Learning Outcomes

#### Students must be able to:

- (a) explain and use the terms: rate of reaction; rate equation; order of reaction; rate constant; half-life of a reaction; rate-determining step; activation energy; catalysis
- (b) construct and use rate equations of the form rate = k [A]<sup>m</sup> [B]<sup>n</sup> (limited to simple cases of single step reactions and of multi–step processes with a rate–determining step, for which m and n are 0, 1 or 2), including:
  - (i) deducing the order of a reaction by the initial rates method
  - (ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs
  - (iii) verifying that a suggested reaction mechanism is consistent with the observed kinetics
  - (iv) predicting the order that would result from a given reaction mechanism
  - (v) calculating an initial rate using concentration data
- (c) (i) show understanding that the half-life of a first-order reaction is independent of concentration
- (ii) use the half-life of a first-order reaction in calculations
- (d) calculate a rate constant using the initial rates method
- (e) devise an experimental technique for studying the rate of a reaction, from given information
- (f) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction
- (g) show understanding, including reference to the Boltzmann, of what is meant by the term activation energy
- (h) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on the rate constant (and, hence, on the rate) of a reaction
- (i) (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant
  - (ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution
- (j) outline the different modes of action of homogeneous and heterogeneous catalysis, including:
   (i) the Haber process
  - (ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines
  - (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide (iii) each tig role of  $Folt in the F/S = 0.2^{-2}$  reaction
  - (iv) catalytic role of Fe<sup>3+</sup> in the  $I^-/S_2O_8^{2-}$  reaction
- (k) describe enzymes as biological catalysts which may have specific activity
   (i) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

#### References

- 1. Chemistry for Advanced Level, Cann and Hughes, Murray
- 2. Understanding Advanced Physical Inorganic Chemistry, Jeanne Tan and Kim Seng Chan
- 3. Chemistry, The Molecular Nature of Matter and Change (Fourth Edition), Silberberg, McGraw Hill
- 4. Chemistry & Chemical Reactivity (Sixth Edition), Kotz, Treichel and Weaver, Thomson
- 5. Chemistry The Central Science (Ninth Edition), Brown, LeMay, Bursten, Prentice Hall

#### 1 Introduction

We have been taking a rather simple approach to chemical change, i.e.: reactants mix, and products are formed. A balanced equation is an essential quantitative tool for calculating product yields from reactant amounts, but it tells us nothing about how fast the reaction is.

In energetics, we learnt about energy changes that accompany chemical reactions. While the value of the energy changes may indicate the direction of the chemical change, it does not tell us how fast a reaction proceeds. The rate of reaction can only be determined by experiment.

Reactions occur at a wide range of rates. Some, like a neutralisation, a precipitation, or an explosive redox process, seems to be over as soon as the reactants make contact – in a fraction of a second. Others, such as the reactions involved in rusting or decaying, take a moderate length of time, from minutes to months or even thousands of years.

Kinetics studies are important as it provide information on the rate and economic feasibility of a process in the industry. From there, an optimal set of conditions can be chosen to maximise the output in the shortest time frame. Knowing the mechanism will also allow the modification of processes or reactants, thereby increasing its effectiveness. For example, knowing how quickly a medicine acts or blood clots can make the difference between life and death; how long it takes for cement to harden or polyethylene to form can make the difference between profit and loss.

In general, the rates of these diverse process / reactions depend very much on the same variables, most of which chemist can manipulate to maximise yields within a given time or to slow down an unwanted reaction. In this lecture, you will look at both the quantitative and qualitative aspects of reaction kinetics.

- *Reaction Kinetics* is a study of the *rates* of chemical reactions, the factors which affect them and the mechanism by which chemical reactions occur.
- The rate of chemical reaction varies greatly with different reactions and under different conditions. Factors that can affect the rate of a reaction include:
  - temperature condition of the reaction,
  - concentration of reactants (or pressure, for gaseous reactions),
  - particle size of reactant,
  - presence of catalyst.

We will apply the **Collision Theory** to explain how these various factors affect the rates of chemical reactions (refer to Section 7).

- We can measure the rate of a reaction by monitoring the *rate of change* of an *observable property* in the reaction, such as concentration of reactants or concentration of products, or mass, volume of gas etc. (refer to *Section 10*).
- Kinetic experiments can also be performed to examine quantitatively how the various factors (e.g. change in concentration of a reactant) affect the rate of a reaction. (You will perform some kinetics experiments in the lab).
- Quantitative data from these experiments is used to derive an important equation called the *rate equation* that is unique for a reaction under a set of conditions (refer to *Section 5*).
- The rate equation allows us to determine the factors or conditions to increase (or decrease) the rate of a reaction, and most importantly, provides information on how the chemical reaction takes place at the molecular level, that is, information on the *reaction mechanism* (refer to *Section 6*).

## 2 Expressing the Reaction Rate

• The <u>rate of reaction</u> can be quantitatively expressed as the <u>increase in concentration of</u> <u>a product per unit time</u> or the <u>decrease in concentration of a reactant per unit time</u>.

Rate =  $\frac{\text{change in [product]}}{\text{change in time}} = -\frac{\text{change in [reactant]}}{\text{change in time}}$ 

- The negative sign in the second expression reflects the fact that the concentration of the reactant is decreasing, hence including it will give a positive value for the rate.
- Units for rate of reaction is mol dm<sup>-3</sup> time<sup>-1</sup>
- Common units are mol dm<sup>-3</sup> s<sup>-1</sup> or mol dm<sup>-3</sup> min<sup>-1</sup>

## 2.1 Average, Instantaneous, and Initial Reaction Rates

Examining the rate of a real reaction reveals an important point: *the rate itself varies with time as the reaction proceed.* When investigating the rate of a reaction, we could be interested in measuring either the average rate, the instantaneous rate or the initial rate of the reaction. Let us look at each of these measurements.

#### (a) <u>Average rate</u>

- Average rate refers to the change in concentration of a reactant or product over a <u>specific</u> <u>time interval</u> (e.g. from time t<sub>1</sub> to time t<sub>2</sub>).
- We can carry out experiments to measure the change in concentration of a reactant (or product) with time and use the results to draw a concentration against time graph.

Consider a hypothetical reaction: A (reactant)  $\rightarrow$  B (product)

## Graph of concentration of reactant against time





Graph of concentration of product against time

- A curve obtained for a concentration versus time graph means the rate of the reaction changes as the concentration of the reactant changes during the reaction.
- Thus, a time interval that covers the entire duration of a reaction is not very useful especially if the rate of the reaction is affected significantly by the concentration of the reactant as it does not tell us how fast the concentration is changing at a given instant.
- However, the average rate can still be useful if we measure it over a <u>very short time interval</u> as we will see in **(c)**.

## (b) Instantaneous rate

- Instantaneous rate refers to the rate of a reaction at a specific point of time. It is defined as the rate of change in concentration of a reactant or product <u>at a specific point of time</u> (e.g. at time t<sub>1</sub>)
- The instantaneous rate can be obtained from a concentration-time graph of the reaction by drawing a tangent to the graph at a specific time and determining the <u>gradient</u> (as shown below).

# Graph of concentration of reactant against time

## Graph of concentration of product against time





Instantaneous rate at time t1

$$= \left| \frac{d[A]}{dt} \right| = \text{gradient to the tangent at } t_1$$

Instantaneous rate at time  $t_1$ 

$$= \left| \frac{d[B]}{dt} \right| = \text{gradient to the tangent at } t_1$$

Consider the reaction between hydrogen and iodine to form hydrogen iodide:

 $H_2(g) + I_2(g) \rightarrow 2HI(g)$ 

For every molecule of  $H_2$  that disappears, one molecule of  $I_2$  disappears and two molecules of HI appear. In other words, the rate of  $[H_2]$  decrease is the same as the rate of  $[I_2]$  decrease, but both are only half the rate of [HI] increase.

Fig. 1 shows a plot of the simultaneous monitoring of one reactant (I<sub>2</sub>) and the product (HI).



- By convention, reaction rate is a <u>positive</u> number.
- A negative gradient indicates a decrease in concentration (since reactant is used up) while a positive gradient indicates an increase in concentration (since product is formed).
- Using the example above, it can be seen that for a general equation:

 $aA + bB \rightarrow cC + dD$ 

where *a*, *b*, *c*, and *d* are coefficients of the balanced equation, the rate is related to reactant or product concentrations as follows

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

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## (c) Initial Rate

- Initial rate refers to the instantaneous rate at time zero (t = 0)
- It is the instantaneous rate **at the start of the reaction**, when an infinitely small amount of the reactant has been used up.



 In practice as shown in Fig. 2, the <u>initial rate</u> can be <u>approximated</u> by the <u>average rate</u> if we measure it over a <u>very short time interval / period</u>.



Note: The initial rate of a reaction is often measured in kinetics experiments.

#### **Checkpoint 1**

Cyclobutane ( $C_4H_8$ ) can decompose to form ethene ( $C_2H_4$ ) as given in the following equation:

$$C_4H_8(g) \rightarrow 2C_2H_4(g)$$

The decrease in concentration of cyclobutane with time was monitored in an experiment to yield the following graph:



#### Use the graph to

(i) calculate the average rate of reaction between the first 10 to 50 seconds.



Average rate of reaction between first 10 to 50 s = |(0.04 - 0.18) / (50 - 10)|= (ii) calculate the initial rate of reaction.



Initial rate of reaction = Instantaneous rate of reaction at 0 s = |(0 - 0.24) / (38 - 0)|=

(iii) calculate the instantaneous rate of reaction at time = 30 seconds.



time/s

Instantaneous rate of reaction at 30 s = |(0 - 0.175) / (58 - 0)|=

calculate the rate of formation of ethene  $(C_2H_4)$  30 seconds after the start of the reaction. (iv)

 $C_4H_8(g) \rightarrow 2C_2H_4(g)$ Rate =  $-\frac{d[C_4H_8]}{dt} = \frac{1}{2}\frac{d[C_2H_4]}{dt}$ 

Rate of formation of C<sub>2</sub>H<sub>4</sub> at 30 s

= 2 x rate of decomposition of  $C_4H_8$  at 30 s (note: 1  $C_4H_8 \equiv 2 C_2H_4$ )  $= 2 \times 3.02 \times 10^{-3}$ =

## 3 Rate Equation (or Rate Law), Rate Constant & Order of Reaction

- Changing the concentration of a reactant commonly (**but not always**) will change the rate of reaction.
- The stoichiometric equation (balanced equation) <u>cannot</u> be used to predict the effect of concentration of a reactant on rate for reactions occurring at a fixed temperature.
- The relationship between rate of reaction and the concentration of reactants can only be determined <u>experimentally</u>.

## 3.1 Rate Equation (or Rate Law)

• The equation which describes the mathematical relationship between the rate of a reaction and the concentration of reactants is called the **rate equation or rate law** of the reaction.

Consider the reaction:  $xA + yB \rightarrow zC$ 

If experimental data shows that rate  $\propto$  [A]<sup>m</sup> and rate  $\propto$  [B]<sup>n</sup>, then

the rate equation is

Rate = 
$$\boldsymbol{k}$$
 [A]<sup>m</sup> [B]<sup>n</sup>

where

*k* is the rate constant; *m* is the order of reaction with respect to **A** *n* is the order of reaction with respect to **B** (m + n) is the overall order of reaction

#### Definition:

The rate equation relates the rate of reaction to the concentration of reactants raised to the appropriate power.

• The units for rate of reaction is **mol dm<sup>-3</sup> time<sup>-1</sup> (SI units for time is 's')** 

## 3.2 Order of reaction

#### Definition:

The order of reaction with respect to a given reactant is the <u>power</u> to which the <u>concentration of the reactant</u> is <u>raised</u> in the <u>experimentally determined</u> rate equation.

- Order of a reaction is a number that tells us how a change in concentration of a reactant affects the rate of a reaction.
- The order of a reaction is an experimentally determined value. It is not necessarily equivalent to the stoichiometric coefficient of the reactant in the balanced equation (i.e. **m** and **n** need <u>not necessarily</u> be equal to x and y respectively).
- Orders of reaction are usually <u>integers</u> but for some complex reactions, they can be <u>negative</u> or <u>fractional</u>.
   (Note: For A–level, common values of m or n are 0, 1 and 2.)

• Overall order of reaction is the <u>sum of the individual orders</u> with respect to each of the reactants.

In the above example,

Order of reaction with respect to reactant A:  $\underline{m}$ Order of reaction with respect to reactant B:  $\underline{n}$ Overall order of the reaction = m + n

## 3.3 Rate constant, k

- It is a **constant of proportionality in a rate equation**.
- Its value depends on temperature and the activation energy of the reaction, and is <u>not</u> dependent on the concentration of reactants.
- The <u>units of *k*</u> depend on the <u>overall order</u> of reaction and the <u>time unit</u>. You need to derive the units for *k* mathematically.

## 3.3.1 Effect of Temperature and Catalyst on Rate Constant, k

- (a) Increasing temperature will increase the value of k
- (b) <u>Presence of catalyst</u> (which provides an alternative reaction pathway of lower activation energy) will <u>increase the value of k</u>

These effects can be seen from the Arrhenius Equation.

The Arrhenius Equation is useful in predicting how changes in temperature or addition of catalyst affects the rate constant, k, of a reaction.

$$k = A e^{-\frac{E_a}{RT}}$$

where **k** is the rate constant

**A** is the Arrhenius constant (related to collision frequency and molecular orientation)

*E<sub>a</sub>* is the activation energy of the reaction

R is the universal gas constant

T is the absolute temperature in Kelvin, K

From the equation, it can be seen that rate constant, k, is affected by changes in  $E_a$  and T (and other factors, broadly the frequency factor and the energy factor).

## Note: Rate equation for a gaseous system

$$\begin{split} x \mathbf{A}(g) \ + \ y \mathbf{B}(g) \ \to \ z \mathbf{C}(g) \\ \text{Recall ideal gas law, since } p V = n R T \qquad \Rightarrow \ p = \frac{n}{V} R T \\ \Rightarrow \ p = c R T, \text{ where } c \text{ is the concentration of the gas} \\ \Rightarrow p \propto c \text{ , at constant temperature} \end{split}$$

Hence, the rate equation can be written in terms of partial pressure of the gas:

Rate =  $k p_{A}^{m} p_{B}^{n}$ 

Units of rate will be based on units for pressure, e.g. Pa  $s^{-1}$  or N  $m^{-2} s^{-1}$ . Checkpoint 2

Consider the reaction:  $BrO_3^{-}(aq) + 5Br^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$ Kinetic studies show that rate =  $k [BrO_3^{-}] [Br^{-}] [H^{+}]^2$ 

(a)	State the order of reaction with respect to					
	(i)	BrO <sub>3</sub> <sup>-</sup>	(ii)	Br⁻	(iii)	H⁺

(b) Calculate the overall order of the reaction.

 $m_{\text{prime}}$  (c) Determine the units of k for the reaction.

## Solution:

(a) (i) Order of reaction w.r.t. 
$$BrO_3^-$$
 =

(ii) Order of reaction w.r.t. Br =

- (iii) Order of reaction w.r.t. H<sup>+</sup> =
- (b) Overall order of reaction =
- (c) rate = k [BrO<sub>3</sub><sup>-</sup>] [Br<sup>-</sup>] [H<sup>+</sup>]<sup>2</sup> k = rate / [BrO<sub>3</sub><sup>-</sup>] [Br<sup>-</sup>] [H<sup>+</sup>]<sup>2</sup>

units of k =

 $= mol^{-3} dm^9 s^{-1}$ 



## 4 Understanding Order of Reaction

## 4.1 Zero–Order Reaction

## Definition:

A reaction that is zero–order with respect to a reactant **A** is one whereby the <u>rate of reaction</u> is <u>independent of [A]</u>, i.e. rate is unaffected by changes in the concentration of the reactant.

• Consider the reaction:  $\mathbf{A}$   $\rightarrow$  product

If the experimentally determined rate equation is:

rate =  $k [A]^0$  where k is the rate constant

or rate = 
$$k$$

- Increasing the [A] will not change the rate of the reaction.
- The reaction proceeds at a <u>constant rate</u>, *k* at a constant temperature.
- Units of rate constant, k for zero-order reaction: mol dm<sup>-3</sup> s<sup>-1</sup> or mol dm<sup>-3</sup> min<sup>-1</sup>
- The graphs associated with a zero-order reaction are shown below.

Graph of [A] against time	Graph of [product] against time	Graph of rate against [A]
$[A] / mol dm^{-3}$ Gradient = -k 0 t/s	$[product] / mol dm-3$ Gradient = k $0 \xrightarrow{k/s}$	rate / mol dm <sup>-3</sup> S <sup>-1</sup> $k$ $k$ $0$ [A] / mol dm <sup>-3</sup>

## 4.2 First-Order Reaction

### Definition:

A reaction that is first-order with respect to a reactant **A** is one whereby the rate of reaction is **directly proportional to [A]**, i.e. rate  $\alpha$  [A].

• Consider the reaction:  $\mathbf{A} \rightarrow \text{product}$ 

If the experimentally determined rate equation is:

**rate =** *k* **[A]** where *k* is the rate constant

- when [A] doubles, \_\_\_\_\_ (or, when [A] increases by a factor of 2, rate increases by a factor of 2)
- when [A] triples, \_\_\_\_\_ (or, when [A] increases by a factor of 3, rate increases by a factor of 3)
- Characteristics of a first–order reaction:
  - The rate constant k has units of:  $\frac{\text{mol dm}^{-3} \text{s}^{-1}}{\text{mol dm}^{-3}} = \underline{\textbf{s}^{-1}} \qquad \text{(or min}^{-1} / \text{h}^{-1} \text{ etc.)}$
  - The graph of rate against [A] is a <u>straight line</u> which passes through the origin and has a positive gradient. (refer to Graph 3 below)
  - The reaction has a <u>half-life, t<sub>1/2</sub></u>. (This will be discussed in the next section.)
- The graphs associated with a first-order reaction are shown below.

Graph 1: [A] against time	Graph 2: [product] against time	Graph 3: rate against [A]
[A] / mol dm <sup>-3</sup> [A] <sub>i</sub> $\frac{1}{2}[A]_i$ 	$[P] / mol dm^{-3}$ $[P] \int_{3/4}^{3/4} [P] \int_{1/2}^{1/2} [P] \int_{1$	rate / mol dm <sup>-3</sup> s <sup>-1</sup> Gradient = $k$ 0 [A] / mol dm <sup>-3</sup>

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## 4.2.1 Half-life, t/2

The notion of half-life is one useful concept for describing reaction rate.

## Definition:

The half–life of a reactant is the <u>time taken</u> for the concentration of a reactant to <u>decrease to</u> <u>half its original concentration</u>.

For a first-order reaction,

- the half-life of the reactant is constant, and
- the half-life is independent of the initial concentration of the reactant
- the relationship between half–life,  $t_{1/2}$  and rate constant, k at constant temperature is given by:

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

- We can confirm whether the order of reaction with respect to a reactant is one or not by analysing a <u>concentration against time graph of the reactant or the product</u>.
- If <u>at least two constant half-lives</u> can be obtained from the <u>concentration against time</u> <u>graph</u>, the <u>order</u> with respect to the reactant is <u>one</u>.

## Graphical determination of the for first-order reaction using concentration-time graph



In a first-order reaction where  $X \rightarrow Y$ 

 Another useful equation for <u>first-order reaction</u> relates the <u>fraction of reactant (C/C<sub>o</sub>)</u> remaining after a certain number of half-lives has passed.

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

where

C = concentration of reactant at time t

 $C_o$  = concentration of reactant at t = 0 (i.e. initial concentration) n = no. of half–lives undergone

 $C_{o} \xrightarrow{\mathbf{t}_{1/2}} 1/2 C_{o} \xrightarrow{\mathbf{t}_{1/2}} 1/4 C_{o} \xrightarrow{\mathbf{t}_{1/2}} 1/8 C_{o} \longrightarrow \rightarrow \rightarrow (\mathbf{1/2})^{n} C_{o}$   $(\frac{1}{2})^{1} C_{o} \qquad (\frac{1}{2})^{2} C_{o} \qquad (\frac{1}{2})^{3} C_{o}$ 

#### **Checkpoint 3**

1. The decomposition of a compound **W** is as follows:  $W(g) \rightarrow Y(g) + Z(g)$ The rate equation for the decomposition is found to be:

rate = k [**W**] where the rate constant, k = 0.45 s<sup>-1</sup>.

What is the time taken for W to reach one quarter of its initial concentration of 2.0 mol dm<sup>-3</sup>?

#### Solution:

One quarter of its initial concentration =  $0.25 \times 2.0 = 0.5 \text{ mol dm}^{-3}$ 

2.0 mol dm<sup>-3</sup>  $\xrightarrow{t_{1/2}}$  1.0 mol dm<sup>-3</sup>  $\xrightarrow{t_{1/2}}$  0.5 mol dm<sup>-3</sup>

 $t_{1/2} =$ 

Time taken = = **3.08 s** 

2. Consider the following first–order reaction:  $X \rightarrow Y$ If the half–life of the reaction is 30 min, what fraction of X remains after 100 min?

#### Solution:

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

n = number of half-lives =

## 4.3 Second–Order Reaction

## Definition:

A reaction that is second–order with respect to reactant **A** is one whereby the rate of reaction is **directly proportional to [A]**<sup>2</sup>.

• Consider the reaction:  $\mathbf{A} \rightarrow \text{product}$ 

If the experimentally determined rate equation is:

rate =  $k [A]^2$  where k is the rate constant

- when [A] doubles, rate increases 2<sup>2</sup> = 4 times (quadruples) (or, when [A] increases by a factor of 2, rate increases by a factor of 4).
- when [A] triples, rate increases 3<sup>2</sup> = 9 times (or, when [A] increases by a factor of 3, rate increases by a factor of 9).
- Units of rate constant k for second–order reaction: **mol<sup>-1</sup> dm<sup>3</sup> time<sup>-1</sup>** (time: s, min, h etc)
- The graphs associated with a second–order reaction are shown below.



- For a second-order reaction, <u>half-life</u> is <u>not constant</u>. In fact, the half-life gets greater as the reaction proceeds.
- Hence, the relationship:  $t_{1/2} = \frac{\ln 2}{k}$  **<u>cannot</u>** be used for a second–order reaction.



#### **Checkpoint 4**

- 1. The rate equation for the reaction:  $I^- + CH_3Cl \rightarrow CH_3I + Cl^-$  is rate =  $k[I^-][CH_3Cl]$ . Which one of the following statements is **false**?
  - A The overall order of reaction is 2.
  - **B** The rate of reaction is directly proportional to concentration of iodide ion.
  - **C** The unit for k is mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>.
  - **D** Doubling  $[I^-]$  and  $[CH_3Cl]$  will increase the rate of reaction 2 times.

Solution: \_\_\_\_

<u>Option A</u>: The order of reaction w.r.t. I<sup>-</sup> and CH<sub>3</sub>C*l* is one. Therefore, the overall order of reaction is 2.

<u>Option B</u>: As the order of reaction w.r.t.  $I^-$  is one, increasing  $[I^-]$  will cause the rate to increase by the same factor, i.e. directly proportional.

<u>Option C</u>: units of  $k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^2} = \text{mol}^{-1} \text{dm}^3 \text{ s}^{-1}$ 

<u>Option D</u>: when  $[I^-]$  and  $[CH_3Cl]$  is doubled, the rate of reaction will <u>increase 4 times</u>. Let the initial concentration of  $I^-$  and  $CH_3Cl$  each to be x. rate =  $k [I^-] [CH_3Cl] = kx^2$ 

When the [I<sup>-</sup>] and [CH<sub>3</sub>C*l*] is doubled, the concentration of each will be 2x. Substituting the new concentration into the rate equation, rate =  $k(2x)(2x) = 4kx^2$ = 4k [I<sup>-</sup>] [CH<sub>3</sub>C*l*] Therefore, the rate of reaction increases <u>4 times</u>.

2. Which one of the following graphs will confirm that the decomposition of hydrogen peroxide is first order with respect to hydrogen peroxide?



Solution: \_

For first–order reaction, the rate equation is rate =  $k [H_2O_2]$  which follows the graph of y = mx.

This is a straight–line graph passing through the origin.

#### 4.4 Pseudo first-order reaction

Under certain conditions, some reactions may exhibit a *pseudo first–order kinetics*. Some examples are shown below.

#### (I) Presence of a large excess of a reactant

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

- The rate equation is found to be: rate = k [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] [I<sup>-</sup>], the overall order of reaction = 2
- If <u>initial [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] is much higher than initial [I<sup>-</sup>]</u>, then [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] will hardly change during the reaction relative to the change in [I<sup>-</sup>].
- Thus, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] is <u>relatively constant throughout the reaction</u> and <u>will not affect the rate of</u> <u>reaction</u>.
- Hence, the rate equation can be simplified as:

rate = k' [I<sup>-</sup>] where k' = k [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]

- Under this condition where there is excess of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, this reaction is regarded as a pseudo first-order reaction with respect to Γ.
- In this case, the  $[I^-]$ -time graph will indicate a constant half-life,  $t_{1/2}$ , where:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{k [S_2 O_8^{2}]}$$

## (II) When the Reactant is also a Solvent in the reaction

Consider the hydrolysis of ethyl ethanoate in water.

$$CH_3CO_2C_2H_5(aq) + H_2O(I) \rightarrow CH_3CO_2H(aq) + CH_3CH_2OH(aq)$$

- Given that rate = k [CH<sub>3</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>] [H<sub>2</sub>O], the overall order of reaction = 2
- As water is used as the <u>solvent</u> in this reaction, it is <u>present</u> in a <u>large excess</u>. Hence, [H<sub>2</sub>O] <u>remains relatively constant</u> throughout the reaction.
- Hence, the rate equation can be simplified as:

rate = k' [CH<sub>3</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>] where k' = k [H<sub>2</sub>O]

- This reaction is regarded as a pseudo first-order reaction with respect to CH<sub>3</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>.
- Similarly in this case, the  $[CH_3CO_2C_2H_5]$ -time graph will indicate a constant half-life,  $t_{1/2}$ :

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{\ln 2}{k [H_2 O]}$$

Note: Refer application of this relationship in Example 5 on *page 36*  2024 JC1 H2 Reaction Kinetics

#### (III) Presence of a Catalyst

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

 $\begin{array}{cccc} \mathsf{HC}l \\ \mathsf{C}_{12}\mathsf{H}_{22}\mathsf{O}_{11} & + & \mathsf{H}_2\mathsf{O} & \xrightarrow{\mathsf{HC}l} & \mathsf{C}_6\mathsf{H}_{12}\mathsf{O}_6 & + & \mathsf{C}_6\mathsf{H}_{12}\mathsf{O}_6 \\ \text{sucrose} & & & & & & & & \\ \end{array}$ 

- Experimentally, the rate equation is found to be: rate = k [HCl] [sucrose]
- HCl acts as a catalyst, a substance that increases the rate of the reaction without being consumed in the reaction. It is used and then regenerated. Consequently, the [HCl] remains relatively constant during the reaction, i.e. [HCl] ≈ constant
- Hence, the reaction is pseudo first-order with respect to sucrose and the rate equation can be simplified to:

rate = k' [sucrose] where k' = k [HCl]

#### Summary

• Consider the rate equation, rate =  $k [\mathbf{A}]^m$ , where **A** is a reactant,

and *m* can be 0, 1, 2, 3, ....

т	order of reaction w.r.t. A	key points	
0	zero	<ul> <li>Rate equation: Rate = k [A]<sup>0</sup> = k</li> <li>Rate is independent of [A], i.e. Rate is constant</li> <li>⇒ changing the concentration of the reactant does not affect the rate of reaction</li> <li>Units of k: mol dm<sup>-3</sup> time<sup>-1</sup> (e.g. mol dm<sup>-3</sup> s<sup>-1</sup>, mol dm<sup>-3</sup> min<sup>-1</sup>)</li> </ul>	
1	first	<ul> <li>Rate equation: Rate = k [A]</li> <li>Rate is <u>directly proportional to [A]</u></li> <li>⇒ when concentration of reactant is doubled, rate of reaction is doubled</li> <li>Units of k: time<sup>-1</sup> (e.g. s<sup>-1</sup>, min<sup>-1</sup>)</li> </ul>	
2	second	<ul> <li>Rate equation: Rate = k [A]<sup>2</sup></li> <li>Rate is <u>directly proportional to [A]<sup>2</sup></u></li> <li>⇒ when concentration of reactant is doubled, rate of reaction increased four times</li> <li>Units of k: mol<sup>-1</sup> dm<sup>3</sup> time<sup>-1</sup> (e.g. mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>)</li> </ul>	

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## • Graphical Representation

	zero order	first order	second order
rate of reaction against [reactant] graph	rate 0 [reactant]	rate 0 [reactant]	rate 0 [reactant]
[reactant] against time graph	[A] 0 time	[A] [A] [A] $1/2[A]_i$ $1/4[A]_i$ 0 $t_1$ $t_2$ $t_1$ $t_2$ $t_1 = t_2$ (t <sub>1/2</sub> : constant)	$\begin{bmatrix} A \end{bmatrix} \bullet$ $\begin{bmatrix} A \end{bmatrix}_{i}$ $\frac{1}{2} \begin{bmatrix} A \end{bmatrix}_{i}$ $\frac{1}{2} \begin{bmatrix} A \end{bmatrix}_{i}$ $\frac{1}{4} \begin{bmatrix} A \end{bmatrix}_{i}$ $$
[product] against time graph	[P] 0 time	$\begin{bmatrix} P \\ P \end{bmatrix}_{max}$ $\frac{34[P]_{max}}{1/2[P]_{max}}$ $0$ $t_{1} = t_{2} (t_{1/2}: constant)$ $t_{1/2} = \frac{ln2}{k}$	[P] [P]max 34[P]max 12

<u>FYI</u>

For a zero order reaction involving A,  $t_{\frac{1}{2}} = \frac{[A]_i}{2k}$ For a second order reaction involving a single reactant A,  $t_{\frac{1}{2}} = \frac{1}{k[A]_t}$ 

## 5 Determination of Rate Equation (or Rate Law)

The rate of a reaction can be investigated by **monitoring measurable changes** over time during the course of the reaction, using either **continuous** or **initial rate method** 

## <u>Continuous method</u>

- Only **one set** of experiment is carried out and the **change in concentration** of either the **reactant or** the **product** is **monitored over a period of time**. Some of the methods to measure the change include sampling and titration method, measuring volume of gas produced etc.
- A [reactant]-time or a [product]-time graph is usually drawn and used to determine the orders of reaction and rate equation.

## Initial rate method

- Separate sets of the same experiment are performed by using different starting concentrations of the reactants.
- The initial rate of each set of experiment or the time taken for the reaction to reach the same extent for each set of experiment (e.g. clock reactions) is then determined.
- Such data collected from the different sets of experiments is usually tabulated and directly compared to determine the orders of reaction and rate equation.

[Refer to Section 10 (to be provided with Practical) for the details on these kinetics experiments]

## (a) Examples using data from INITIAL RATE method

## Example 1

The iodination of propanone is carried out in acidic medium as shown:

 $I_2(aq) + CH_3COCH_3(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + HI(aq)$ 

In employing the initial rate method, a series of experiments have been conducted and the following results were obtained:

	[H⁺]	[CH <sub>3</sub> COCH <sub>3</sub> ]	[I <sub>2</sub> ]	Initial rate × 10 <sup>-4</sup>
Experiment	/ mol dm <sup>-3</sup>	/ mol dm <sup>-3</sup>	/ mol dm <sup>-3</sup>	/ mol dm <sup>-3</sup> s <sup>-1</sup>
1	1.0	0.8	0.05	4.4
2	0.5	0.8	0.05	2.2
3	1.0	0.4	0.05	2.2
4	1.0	1.6	0.025	8.8
5	2.0	1.6	0.10	?

(a) Find the order of reaction with respect to each of the three species under investigation.

- (b) Write down the rate equation for this reaction.
- (c) Calculate the value of the rate constant k, specifying its unit.
- (d) Predict the initial rate of reaction for experiment 5.

#### **Solution**

## (a) By inspection / reasoning

(Use this method when there exist <u>2 experiments</u> with the <u>concentration</u> of <u>only one reactant</u> being <u>varied</u>.)

- Comparing experiments <u>1 and 2</u>, [CH<sub>3</sub>COCH<sub>3</sub>] and [I<sub>2</sub>] are kept constant. When [H<sup>+</sup>] doubles (<sup>1.0</sup><sub>0.5</sub> = 2), the rate also <u>doubles</u> (<sup>4.4</sup><sub>2.2</sub> = 2). Thus, the rate of reaction is directly proportional to [H<sup>+</sup>] and the reaction is <u>first order</u> w.r.t. H<sup>+</sup>.
- Comparing experiments <u>1 and 3</u>, [H<sup>+</sup>] and [I<sub>2</sub>] are kept constant, When [CH<sub>3</sub>COCH<sub>3</sub>] doubles (<sup>0.8</sup>/<sub>0.4</sub> = 2), the rate also doubles (<sup>4.4</sup>/<sub>2.2</sub> = 2). Thus, the rate of reaction is directly proportional to [CH<sub>3</sub>COCH<sub>3</sub>] and the reaction is <u>first order</u> w.r.t. CH<sub>3</sub>COCH<sub>3</sub>.

## By calculation

(Use this method when you cannot determine order of reaction by inspection. Whenever possible, try to choose 2 sets of experiments where only the concentration of one reactant changes.)

Let the rate equation be rate =  $k [H^+] [CH_3COCH_3] [I_2]^z$ 

Comparing experiments 1 and 4,

$$\frac{\operatorname{rate}_{4}}{\operatorname{rate}_{1}} = \frac{k(1.0)(1.6)(0.025)^{z}}{k(1.0)(0.8)(0.05)^{z}}$$
$$\frac{8.8 \times 10^{-4}}{4.4 \times 10^{-4}} = 2\left(\frac{0.025}{0.05}\right)^{z}$$
$$z = 0$$

 $\therefore$  Order of reaction w.r.t. I<sub>2</sub> = **0** 

## (b) rate = *k* [H<sup>+</sup>] [CH<sub>3</sub>COCH<sub>3</sub>]

(c) Using experiment 1, find the value of rate constant, k

$$k = \frac{\text{rate}}{[\text{H}^+][\text{CH}_3\text{COCH}_3]} = \frac{4.4 \times 10^{-4}}{(1.0)(0.8)} = \frac{5.50 \times 10^{-4}}{(1.0)(0.8)}$$

units of 
$$k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol}^2 \text{ dm}^{-6}} = \frac{\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}{\text{mol}^2 \text{ dm}^{-6}}$$

(d) rate = 
$$k [H^+] [CH_3COCH_3]$$
 or  
= 5.50 x 10<sup>-4</sup> (2.0) (1.6)  
= 1.76 x 10<sup>-3</sup> mol dm<sup>-3</sup> s<sup>-1</sup>

Compare experiment <u>4 and 5</u>, [CH<sub>3</sub>COCH<sub>3</sub>] is kept <u>constant</u>. When <u>[H<sup>+</sup>] doubles</u> ( $\frac{2.0}{1.0}$  = 2), the rate should <u>double</u>. Initial rate for experiment 5 =2 x 8.8 x 10<sup>-4</sup> = <u>1.76 x 10<sup>-3</sup> mol dm<sup>-3</sup> s<sup>-1</sup></u>

## Example 2 ('lodine Clock' Experiment)

A series of experiments is conducted to determine the order of reaction with respect to iodide ions for the reaction between  $H_2O_2$  and acidified potassium iodide solution. The rate of the reaction is followed by monitoring the rate of formation of iodine,  $I_2$ .

 $2I^{-}(aq) + H_2O_2(aq) + 2H^{+}(aq) \rightarrow 2H_2O(l) + I_2(aq)$  ------ reaction 1  $I_2(aq) + 2Na_2S_2O_3(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$  ------- reaction 2

In each experiment, a small fixed amount of sodium thiosulfate and starch indicator are added to the reaction mixture. The iodine produced in reaction 1 will immediately react in reaction 2 until all the sodium thiosulfate has been used up. At that point, free iodine present in the solution will cause a sudden appearance of a blue–coloured complex in the presence of starch. The time taken for the appearance of the blue–coloured complex is recorded. The following results are obtained.

Experiment	[KI(aq)] / mol dm⁻³	Time (t) / s
Ι	0.004	74
II	0.006	49
III	0.008	37
IV	0.010	30
V	0.012	25

Deduce the order of reaction with respect to iodide ions.



## Important notes on Example 2

- rate =  $\Delta$ [iodine] time taken (t) for appearance of blue colour
- In these experiments, the time taken, t, *from the start of reaction 1 to the appearance of the blue-coloured complex* is a measure of the time taken for a **small**, **fixed amount** of product, **I**<sub>2</sub> **formed**.
- The blue-coloured complex appears when the small, fixed amount of sodium thiosulfate added has completely reacted with a fixed amount of iodine formed in reaction 1.
- Since Δ[iodine] is constant, the reaction occurs to the <u>same extent</u> in each experiment.

Thus,	initial rate $\alpha$	1
		time taken, t

- The faster the iodine is produced in reaction 1, the faster the sodium thiosulfate will be used up in reaction 2, and the shorter the time taken for the appearance of the blue–coloured complex.
- Thus, the <u>fixed (or constant) amount</u> of sodium thiosulfate used in each experiment is to ensure the <u>same extent of reaction</u>.
- Only a <u>small</u> amount of thiosulfate is used to ensure that the reaction is allowed to <u>proceed to a **small**</u> <u>extent</u> such that the rate measured is <u>close to the initial rate of reaction</u> (refer to <u>Section 2.1</u> on page 7).

## **Solution**

Experiment	[Kɪ(aq)] / mol dm⁻³	Time (t) / s	1/t <b>s</b> ⁻¹	Relative Rate
Ι	0.004	74	0.0135	
II	0.006	49	0.0204	
III	0.008	37	0.0270	
IV	0.010	30	0.0333	
V	0.012	25	0.0400	

Since initial rate  $\alpha \frac{1}{\text{time taken for appearance of blue colour}}$ 

Comparing Expt I and III,

when [KI] is **doubled**  $(\frac{0.008}{0.004} = 2)$ ,

rate of formation of iodine is **<u>doubled</u>**  $\left(\frac{2.0}{1.0} = 2\right)$ .

Hence, rate is directly proportional to [KI]

and order of reaction w.r.t. I<sup>-</sup> is  $\underline{1}$ .

	_
S.	
The relationship, Initial rate $\alpha \frac{1}{t}$ where t = time taken for a <b>small</b> , <b>same extent</b> of reaction	
is only valid when comparing reactions which proceed to the same extent.	
<u>Note</u> : the rate is <b>proportional</b> , not equal <b>to</b> , the reciprocal of time taken (rate $\neq \frac{1}{t}$ )	

Note:

For inspection/reasoning method, when the increase in concentration is not a whole number or larger than 4, you may want to use the following phrasing:

When [reactant] increases by a factor of x, the rate increases by a factor of x, thus the rate of reaction is directly proportional to [reactant]. Hence, the order of reaction is 1.

When <u>[reactant]</u> increases by a factor of  $\mathbf{x}$ , the <u>rate increases by a factor of  $\mathbf{x}^2$ </u>, thus the rate of reaction is directly proportional to [reactant]<sup>2</sup>. Hence, the order of reaction is 2.

## Example 3 'Sulfur Clock' Experiment

The table below shows the results of a series of experiments conducted to determine the orders of reaction for the reaction:

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

Expt. No.	Vol. of 1.0 mol dm <sup>-3</sup> HC $l$ (aq) used, V <sub>1</sub> / cm <sup>3</sup>	Vol. of 0.2 mol dm <sup>-3</sup> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (aq) used, $V_2/\ cm^3$	Vol. of water used / cm <sup>3</sup>	Time taken for cross 'X' to be obscured, t / s	$\frac{1}{t} / s^{-1}$
1	30	40	0	16	
2	30	20	20	32	
3	30	10	30	64	
4	40	30	0	19	
5	20	30	20	20	

In these experiments, the time taken, t, for a fixed amount of sulfur solid formed is recorded.

Determine the order of the reaction with respect to (i)  $S_2O_3^{2-}$  (ii) H<sup>+</sup>

<u></u>

## ) Important notes on Example 3

- The rate of reaction between sodium thiosulfate and dilute HC*l* can be studied by measuring the time take for a **fixed**, **small amount** of **sulfur** to be formed.
- How do we quantify this amount? A good gauge is observing sufficient yellow sulfur masking an image (an 'X') on a piece of white paper placed underneath the reaction beaker.
- The volume of water is varied in each experiment to keep the total volume of the reaction mixture constant for the different experiments so that the initial concentration of each reactant in the reaction mixture is directly proportional to its volume used. (refer to explanation below)
  - ⇒ Initial  $[Na_2S_2O_3] \propto volume of Na_2S_2O_3 used$ Initial  $[Na_2S_2O_3] \propto V_2$
  - $\Rightarrow$  Similarly, initial [H<sup>+</sup>]  $\propto$  V<sub>1</sub>



Thus, initial  $[Na_2S_2O_3] \propto volume of Na_2S_2O_3 used.$ 

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### **Solution**

Expt. No.	Vol. of 1.0 mol dm <sup>-3</sup> HC $l$ (aq) used, V <sub>1</sub> / cm <sup>3</sup>	Vol. of 0.2 mol dm <sup>-3</sup> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (aq) used, $V_2$ / cm <sup>3</sup>	Vol. of water used / cm <sup>3</sup>	Time taken for cross 'X' to be obscured, t / s	$\frac{1}{t} / s^{-1}$
1	30	40	0	16	6.25 x 10 <sup>-2</sup>
2	30	20	20	32	3.13 x 10 <sup>-2</sup>
3	30	10	30	64	1.56 x 10 <sup>-2</sup>
4	40	30	0	19	5.26 x 10 <sup>-2</sup>
5	20	30	20	20	5.00 x 10 <sup>-2</sup>

Since initial rate  $\alpha = \frac{1}{\text{time taken, t}}$  (same extent of reaction)

initial  $[Na_2S_2O_3] \propto V_2$  and initial  $[HCl] \propto V_1$ 

Comparing Expt 1 and 2, when [HC/] is constant,

when  $[Na_2S_2O_3]$  <u>doubles</u>  $(\frac{40}{20} = 2)$ , initial rate <u>doubles</u>  $(\frac{6.25 \times 10^{-2}}{3.13 \times 10^{-2}} = 2)$ .

Rate is **directly proportional** to  $[S_2O_3^{2-}]$  and thus, order of reaction w.r.t.  $S_2O_3^{2-}$  is \_\_\_\_\_.

Let the rate equation be rate =  $k [S_2O_3^{2-}] [H^+]^y$ 

Comparing experiments <u>4 and 5</u>,

$$\frac{\operatorname{rate}_{4}}{\operatorname{rate}_{5}} = \frac{k(30)(40)^{y}}{k(30)(20)^{y}}$$
$$\frac{5.26 \times 10^{-2}}{5.00 \times 10^{-2}} = \left(\frac{2}{1}\right)^{y}$$
$$1.052 = \left(\frac{2}{1}\right)^{y} \implies y = 0$$

Rate is **independent** of  $[H^+]$  and thus, the order of reaction w.r.t.  $H^+$  is \_\_\_\_\_.

## (b) Examples using data from CONTINUOUS measurement

## (i) From [reactant] – time graph

#### Example 4 (N91/III/3)

A dilute solution of hydrogen peroxide can be used to bleach hair. It decomposes slowly in aqueous solution according to the following equation:  $2H_2O_2 \rightarrow 2H_2O + O_2$ .

A solution with an original concentration of 3.0 mol dm<sup>-3</sup> was placed in a bottle contaminated with transition metal ions, which act as catalyst for the decomposition. The rate of decomposition was measured by withdrawing 10 cm<sup>3</sup> portions at various times and titrating with acidified 0.1 mol dm<sup>-3</sup> KMnO<sub>4</sub>(aq). (5 moles of peroxide react with 2 moles of KMnO<sub>4</sub>). The following results were obtained.

time / min	0	5	10	15	20	25	30
volume of KMnO <sub>4</sub> / cm <sup>3</sup>	30.0	23.4	18.3	14.2	11.1	8.7	6.8

(a) Confirm that the reaction is first order with respect to the peroxide.

- (b) Write an expression for the rate equation and calculate the rate constant and half-life.
- (c) Calculate the concentration of hydrogen peroxide at the time the first portion was withdrawn. Hence estimate how long the solution had been in the contaminated bottle.
- (d) Suggest a method whereby the shelf-life of hydrogen peroxide solution could be increased.

## **Solution**







from the plotted graph,

time taken for volume of KMnO<sub>4</sub> required to reduce from 30 cm<sup>3</sup> to 15 cm<sup>3</sup> = 14 min time taken for volume of KMnO<sub>4</sub> required to reduce from 15 cm<sup>3</sup> to 7.5 cm<sup>3</sup> = 28 - 14= 14 min

Since <u>half-life</u> of the reaction is approximately <u>constant at 14 min</u>, reaction is <u>first order</u> w.r.t. peroxide.

(b) Rate =  $k [H_2O_2]$ ,  $t_{1/2} = 14.0 \text{ min}$ ,

 $k = \ln 2 / t_{1/2} = 0.05 \text{ min}^{-1}$ 

(c) When first portion of H<sub>2</sub>O<sub>2</sub> was withdrawn, volume of KMnO<sub>4</sub> used is 30 cm<sup>3</sup>

n(KMnO<sub>4</sub>) used =  $\frac{30}{1000}$  x 0.1 = 0.003 mol n(H<sub>2</sub>O<sub>2</sub>) present =  $\frac{5}{2}$  x 0.003 = 0.0075 mol [H<sub>2</sub>O<sub>2</sub>] =  $\frac{0.0075}{\frac{10}{1000}}$  = **0.75 mol dm<sup>-3</sup>** 

3.0 mol dm<sup>-3</sup>  $\longrightarrow$  1.5  $\longrightarrow$  0.75  $t_{\frac{1}{2}}$ 

Solution has been in the bottle for 28 min

Since 
$$\frac{C}{C_o} = \left(\frac{1}{2}\right)^n$$
  
 $\therefore \frac{0.75}{3.0} = \left(\frac{1}{2}\right)^n$   
 $\therefore n = 2$   
 $\therefore \text{ time } = 2 \times 14 = 28 \text{ min}$ 

(d) Keep the solution at **low** temperature / in a **dark** bottle.

Example 5 (N99/I/2)

(a) Ethyl ethanoate undergoes a slow acid-catalysed hydrolysis in water.

 $CH_3CO_2C_2H_5 + H_2O \rightarrow CH_3CO_2H + C_2H_5OH$ 

The reaction was followed twice with different concentrations of HC*l* and the following results were obtained.

Time/min	Experiment 1	Experiment 2		
Time/min	With $[HC] = 0.1 \text{ mol } dm^{-3}$ [ethyl ethanoate] / mol $dm^{-3}$	With [HC/] = 0.2 mol dm <sup><math>-3</math></sup> [ethyl ethanoate] / mol dm <sup><math>-3</math></sup>		
0	0.200	0.200		
25	0.152	0.115		
50	0.115	0.067		
75	0.088	0.038		
100	0.067	0.022		
125 0.051		0.013		

- (i) Plot graphs of these values.
- (ii) Use your graphs
  - 1. to show that the reaction is first order with respect to the ester,
  - 2. to calculate the order of reaction with respect to hydrochloric acid.
- (iii) Deduce the rate equation and calculate the rate constant, giving its units.
- (b) Why is it not possible to determine the order with respect to water in this experiment?

## **Solution**

(a)(i) [refer to plotted graph on the next page]

## (a)(ii) (1) Using half-life method to show that the reaction is first order w.r.t. ester

From the first graph where  $[HCl] = 0.2 \text{ mol dm}^{-3}$ ,

- time taken for [ethyl ethanoate] to be reduced by half from 0.2 to 0.1 mol  $dm^{-3} = 32 min$
- time taken for [ethyl ethanoate] to be reduced by half from 0.1 to 0.05 mol dm<sup>-3</sup> = 64 32

= 32 min

- <u>half–life</u> is a **constant** at **32 min**.
- hence, reaction is *first order* with respect to ethyl ethanoate.



## (a)(ii) (2) To determine order of reaction w.r.t. HCl (initial rates method)

## Method 1: Finding initial rates from graphs



[ethyl ethanoate] is the same for both at t = 0 min

 $\Rightarrow$  any change in initial rate must be due to the change in [HCl]

 $\Rightarrow$  to obtain order of reaction with respect to HCl, compare the initial rates of the reaction for the 2 different [HCl]

Concept: Initial rate = Gradient of graph at  $t = 0 \min$  $\Rightarrow$  Draw a tangent at t = 0 min for both experiments

initial rate when [HC*l*] is 0.1 mol dm<sup>-3</sup> =  $\left| \frac{0.200 - 0}{0 - 104} \right| = 1.92 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$ 

initial rate when [HC*l*] is 0.2 mol dm<sup>-3</sup> =  $\left| \frac{0.200 - 0}{0 - 52} \right| = 3.85 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$ 

Summarising the data,

Expt	[HC <i>l</i> ] / mol dm <sup>-3</sup>	[ethyl ethanoate] / mol dm <sup>-3</sup>	initial rate / mol dm <sup>-3</sup> min <sup>-1</sup>
1	0.1	0.200	1.92 × 10 <sup>-3</sup>
2	0.2	0.200	$3.85  imes 10^{-3}$

When [HC1] doubles from 0.1 mol dm<sup>-3</sup> to 0.2 mol dm<sup>-3</sup>, the rate also doubles  $(\frac{3.85 \times 10^{-3}}{1.92 \times 10^{-3}} \approx \mathbf{\underline{2}}).$ 

Hence, order of reaction w.r.t. HCl is 1.

## Method 2: Finding time taken for reaction to proceed to the same extent

Consider the table of values,

When [HCl] = 0.1 mol dm<sup>-3</sup>, time taken for [ethyl ethanoate] to change from 0.200 to 0.115 is 50 min.

When [HCl] = 0.2 mol dm<sup>-3</sup>, time taken for [ethyl ethanoate] to change from 0.200 to 0.115 is 25 min.

Alternatively, you can also use any other values convenient for you, e.g. half–life From the graph, When [HCl] = 0.1 mol dm<sup>-3</sup>, time taken for [ethyl ethanoate] to change from 0.2 to 0.1 is 64 min.

When [HCl] = 0.2 mol dm<sup>-3</sup>, time taken for [ethyl ethanoate] to change from 0.2 to 0.1 is 32 min.

Hence, when [HCl] doubles,

time taken for the reaction to proceed to the same extent is halved,

that is, the rate doubles (recall: initial rate of reaction  $\alpha \frac{1}{\text{time taken, t}}$ ).

Therefore, order of reaction w.r.t. HCl is 1.

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## (a)(iii) Determine the rate equation and rate constant

From the orders of reaction, it can be deduced that the rate equation for the reaction is

## Rate = k [ethyl ethanoate] [HCl]

To determine the rate constant: Method 1: <u>By substitution</u>

Rate = k [ethyl ethanoate] [HCl] Substituting data from Experiment 1,  $1.92 \times 10^{-3} = k (0.200)(0.1)$  $k = 0.0960 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$  Alternatively, Substituting data from Experiment 2,  $3.85 \times 10^{-3} = k (0.200)(0.2)$  $k = 0.0963 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ 

## Method 2: Use of pseudo first-order to determine k

Since HC*l* is a catalyst, its concentration remains fairly constant and the rate equation can be approximated to

rate = k' [ethyl ethanoate] where k' = k [HCl]

and 
$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{32} \text{ min}^{-1} = 0.02167 \text{ min}^{-1}$$
  
 $\therefore k = \frac{0.02167}{0.2} = 0.108 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$  (similar to value of *k* calculated using Method 1)

(b) Water is used as a <u>solvent</u> and hence it is in <u>large excess</u>. 'Concentration' of water would remain approximately <u>constant</u> as the reaction proceeds and hence it is not possible to determine its order of reaction as its concentration is not changed.

## (ii) From [product] - time graph

#### Example 6

A dilute solution of hydrogen peroxide can be used to bleach hair. It decomposes slowly in aqueous solution according to the following equation:  $2H_2O_2 \rightarrow 2H_2O + O_2$ 

The total volume of O<sub>2</sub> gas liberated was recorded every minute. The results are tabulated below.

time / min	0	1	2	3	4	5	6	7	$\infty$
total volume of $O_2$ gas / cm <sup>3</sup>	0	23.0	36.5	46.0	51.0	54.5	57.0	58.5	60.0

Explain, as fully as you can, why the experimental results indicate that the overall kinetics are first order.

## Solution

From the graph drawn, [recall page 16]

Time / min	0	$\rightarrow$	t <sub>1</sub>	$\rightarrow$	t <sub>2</sub>	$\rightarrow \dots \rightarrow$	Completion
H <sub>2</sub> O <sub>2</sub> (reactant)	Cinitial		$\frac{1}{2}$ C <sub>initial</sub>		1/4 Cinitial		
O <sub>2</sub> (product)	0		¹∕₂ V <sub>max</sub>		¾ V <sub>max</sub>		$V_{max} = 60 \text{ cm}^{3}$
	(0)		(30)		(45)		



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## 6 Reaction Mechanism

- Most chemical reactions occur via a sequence of single reaction steps, one of which has a highest activation energy,  $E_a$ , that determines the overall rate of the reaction.
- The sequence of single reaction steps, called **elementary steps**, by which an overall reaction occurs, is called the *mechanism of the reaction (or simply, reaction mechanism)*.
- The rate equation (or rate law) of a reaction can help to reveal the reaction mechanism.

## Example 7

Consider the reaction:

 $(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$ Reactants Products

The experimentally-determined rate equation for the reaction is

Rate =  $k [(CH_3)_3CCl]$ 

The **mechanism** of the above reaction has been studied and can be represented by the following two steps:

Step 1: $(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^-$ (slow)Step 2: $(CH_3)_3C^+ + OH^- \longrightarrow (CH_3)_3COH$ (fast)

## (a) Some definitions of terms

## (i) <u>Elementary steps</u>

- are the simplest steps in a mechanism which cannot be further broken down into simpler steps;
- do not have the same rate.
- In Example 7 above, Steps 1 and 2 are elementary steps.

## (ii) Intermediate

- is a substance that is formed in one step of the mechanism and consumed in a later one during the overall reaction;
- does not appear in the overall balanced equation.
- In Example 7, (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> is an intermediate.

## (iii) Rate-determining step

- is the slowest elementary step (one with <u>highest activation energy</u>) which governs the overall rate of the chemical reaction.
- Because the rate-determining step limits the overall rate of the reaction, its rate law represents the rate law for the overall reaction.
- In Example 7, Step 1 is the rate-determining step.

- Notice in Example 7 that the <u>rate law for the rate-determining step (Step 1) in the</u> <u>mechanism is consistent with the observed kinetics shown in the rate equation</u>.
- The slow step (Step 1) in the mechanism (which determines the overall rate of the reaction) involves one reactant molecule of (CH<sub>3</sub>)<sub>3</sub>CC*l* and does not involve the OH<sup>-</sup> ion, and is the same as the reaction order as reflected in the rate equation (i.e. first order w.r.t. (CH<sub>3</sub>)<sub>3</sub>CC*l* and zero order w.r.t. OH<sup>-</sup>).

## (iv) Molecularity

The *molecularity* of an elementary step refers to the **number** of **reactant particles** involved in that step.

Unimologylor	One reactant particle.
Unimolecular	In Example 7, the rate-determining step is unimolecular.
Bimolecular	Two reactant particles may collide and result in a rearrangement of chemical bonds.
	Three reactant particles collide simultaneously.
Termolecular	This is extremely rare because the probability of three species colliding at the same time with enough energy and in the right orientation is very small.

## (b) Proposing a Reaction Mechanism

We can suggest a reasonable reaction mechanism by using observations and data from kinetics experiments to hypothesise what the individual steps might be.

Criteria to meet when suggesting a reaction mechanism:

- (i) The <u>order of reaction with respect to each reactant</u> in the experimentally determined rate equation appears as the <u>coefficients of the respective reactants</u> in the <u>rate-determining step</u>.
- (ii) The <u>elementary steps</u> in the mechanism must <u>add up</u> to the <u>overall balanced</u> <u>chemical equation</u>.
- (iii) The rate equation involves the reactants (exclude intermediates) that take part in the **elementary** steps <u>preceding and including the rate-determining step</u>.

## Example 8 Consider a hypothetical reaction between X and Y. $2X + Y \rightarrow X_2Y$ If the rate equation is: rate = $k [X]^2$ , suggest a likely mechanism for the reaction. Solution Note Possible two-step mechanism: • The coefficient of X in the slow step corresponds to the order of reaction w.r.t. X in the rate equation. • Y does not appear in the rate equation, hence it is not involved in the slow step. • By considering Step 1 and the overall chemical equation, Y would be involved in the fast step. -----Example 9 Ozone in the stratosphere breaks down according to the reaction: $2O_3(g) \longrightarrow 3O_2(g) \Delta H$ is negative The rate equation is given by: rate = $k[O_3]$ Is the following mechanism consistent with this rate equation? Step 1: $O_3(g) \longrightarrow O_2(g) + O(g)$ slow, unimolecular Step 2: $O(g) + O_3(g) \longrightarrow 2O_2(g)$ fast. bimolecular

## Solution

The mechanism is **consistent** with this rate equation because:

- the <u>slow step</u> involves <u>1 molecule of O<sub>3</sub></u> which corresponds to the order of reaction w.r.t. O<sub>3</sub> as shown in the rate equation, <u>and</u>
- the elementary steps add up to the overall balanced chemical equation.

#### Example 10

Reaction between nitrogen dioxide and carbon monoxide: NO<sub>2</sub> (g) + CO(g)  $\longrightarrow$  NO(g) + CO<sub>2</sub>(g)

The rate equation is given by: rate =  $k [NO_2]^2$ . Is the following mechanism consistent with this rate equation?

Step 1: NO <sub>2</sub> (g) + NO <sub>2</sub> (g)>	<ul> <li>NO<sub>3</sub>(g) + NO(g)</li> </ul>	slow
Step 2: NO <sub>3</sub> (g) + CO(g) →	$NO_2(g) + CO_2(g)$	fast

#### **Solution**

The mechanism is consistent with this rate equation as

- the <u>slow step</u> involves <u>2 molecules of NO<sub>2</sub></u> which corresponds to the order of reaction w.r.t. NO<sub>2</sub> as shown in the rate equation, and
- the elementary steps add up to the overall balanced chemical equation.

## Example 11

The decomposition of hydrogen peroxide can be catalysed by bromide ions:

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

The rate equation is rate =  $k [H_2O_2] [Br^-]$ Which of the following mechanisms is consistent with this rate equation?

Mechanism 1	
H₂O₂ → 2HO	slow
2HO + Br → BrO + H <sub>2</sub> O	fast
$H_2O_2 + BrO^- \longrightarrow H_2O + O_2 + Br^-$	fast
Mechanism 2	
$H_2O_2 + Br^- \longrightarrow H_2O + BrO^-$	slow
$BrO^- + H_2O_2 \longrightarrow H_2O + O_2 + Br^-$	fast

**Solution** 

Mechanism **2** is **consistent** with this rate equation.

- the <u>slow step</u> involves <u>1 molecule of H<sub>2</sub>O<sub>2</sub></u> and <u>1 Br<sup>-</sup> ion</u> which corresponds to the order of reaction w.r.t. each species in the rate equation, and
- the elementary steps add up to the overall balanced chemical equation.
- Br<sup>-</sup> is used in the slow step and regenerated in the fast step (catalyst).

#### Example 12

Consider a reaction which is proposed with the following mechanism:

Eqn 1:	$NO_2(g) + NO_2(g)$	$\rightarrow$	$NO_3(g) + NO(g)$	(slow)
Eqn 2:	$NO_3(g) + CO(g)$	$\rightarrow$	$NO_{2}(g) + CO_{2}(g)$	(fast)

(a) Determine the overall chemical equation for the reaction.

(b) Deduce the rate equation for the reaction.

#### <u>Solution</u>

(a) To determine overall chemical equation: add up eqn (1) & eqn (2)

Overall equation:  $NO_2(g) + CO \rightarrow NO(g) + CO_2(g)$ (Note:  $NO_3$  is an intermediate which is formed and later consumed in the reaction)

(b) From the <u>rate-determining step</u> (i.e. slow step):  $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ 

Rate equation is  $rate = k [NO_2]^2$ 

#### Example 13

The reaction between nitric oxide and oxygen is an important intermediate step in the industrial production of nitric acid. It is also one of the reactions involved in atmospheric pollution from car exhausts.

Kinetic studies have shown that the reaction is third order overall, and it has been suggested that the mechanism involves the following two steps.

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

Construct a rate equation for this reaction.

For the two-step mechanism, where the first step is fast and reversible, and the second step is slow, we focus on the <u>rate-determining step for the rate law</u>. The intermediate  $N_2O_2$  has a concentration that is quickly established by the equilibrium of the first step:

Rate of forward = Rate of backward

$$k_{\rm f}[\rm NO]^2 = k_{\rm b}[\rm N_2O_2]$$
$$[\rm N_2O_2] = \frac{k_f}{k_b}[\rm NO]^2$$

Based on the slow step, rate =  $k[N_2O_2][O_2]$ .

By substituting [N<sub>2</sub>O<sub>2</sub>] in the rate equation, we get:

rate = 
$$k[N_2O_2][O_2] = k \frac{k_f}{k_b} [NO]^2[O_2]$$

This simplifies to:

rate =  $k'[NO]^2[O_2]$  where  $k = k \frac{k_f}{k_h}$ 

The rate equation for the overall third order reaction will be:

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

If the 1<sup>st</sup> step is not the slow step, the reactants in the overall equation that take part in the elementary steps before and including the slow step will appear in the rate law.

## (c) Energy Profile Diagrams

- Graphical representation of reaction mechanism.
- General energy profile diagrams for <u>single-step</u> mechanisms (mechanisms with only one step) can be represented as follows.



 When there are two steps in the reaction mechanism, the general energy profile diagram of such reactions is as shown.



Note from the above general energy profile diagram that:

- ⇒ Each step in the mechanism has its own transition state.
- ⇒ The intermediate is a reactive, unstable species, so it is higher in energy than the reactants or products.
- $\Rightarrow$  The first step is slower, so its activation energy is larger than that of the second step.
- ⇒ The overall reaction is exothermic, so the products are lower in energy than the reactants.

Steps in drawing an energy profile diagram

- □ Label both axes
- □ Label energy level of reactants and products
- □ Include arrow from reactants to peak of curve for activation energy of forward reaction [from product to peak for reverse reaction; from intermediate to peak for multi-steps]
- □ Label the activation energy
- □ Include arrow from energy level of reactant(s) to product(s) for the enthalpy change of reaction
- □ Label the enthalpy change of reaction



## Example 15

2-bromopropane undergoes nucleophilic substitution with aqueous NaOH via the following mechanism.



Which of the following diagrams represent the energy profile diagram of the reaction?



As step 1 is a slow step, the activation energy will be <u>higher</u> than that for the second step.

## 7 Collision Theory and Factors affecting Rate of Reaction

- The basic tenet of **collision theory** is that reactant particles (atoms, molecules and ions) must collide with each other to react.
- In order for a reaction to take place between two colliding reactant particles,
  - the particles must be <u>correctly orientated</u>
  - the collision must occur with a minimum amount of energy called the <u>activation energy</u>,  $\underline{E}_a$
- Collisions that fulfil both criteria are termed effective collisions.
- An increase in the <u>frequency of effective collisions</u> (i.e. the number of effective collisions per unit time) leads to an <u>increase in rate of reaction</u>.

## Factors affecting the Rate of a Reaction

(a) <u>Reactant particle size / surface area</u> (only for heterogeneous reaction)

*Example:* Reaction between CaCO<sub>3</sub> and HC*l*:

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

CaCO₃ used	Rate
Large chips	Slow
Powdered form	Rapid

## Explanation

For a fixed mass,

- $\Rightarrow$  the smaller the size of reactants
- $\Rightarrow$  the larger the surface area exposed for reaction to occur
- $\Rightarrow$  frequency of effective collisions increases
- $\Rightarrow$  hence <u>rate</u> of reaction <u>increases</u>.

## (b) Concentration

Reaction between CaCO<sub>3</sub> and HC*l*: reaction occurs much faster when a more concentrated HC*l* is used.

#### **Explanation**

An increase in the concentration causes

- $\Rightarrow$  an increase in the <u>number of molecules per unit volume</u>
- $\Rightarrow$  frequency of effective collisions increases
- $\Rightarrow$  hence <u>rate</u> of reaction <u>increases</u>. o

 $\bigcirc$ Does increasing the concentration of a reactant always lead to an increase in the rate of reaction?

(c) <u>Pressure</u> (for reactions involving gaseous reactants)

An increase in pressure of gaseous reactants

- $\Rightarrow$  larger number of molecules per unit volume
- $\Rightarrow$  frequency of effective collisions increases
- $\Rightarrow$  hence <u>rate</u> of reaction <u>increases</u>.

## (d) Effect of Temperature

Increasing the temperature gives the collisions more energy. This increases the frequency of effective collisions resulting in faster rate of reaction. A 10 °C rise in temperature often doubles the rate of reaction.  $\underline{E}_a$  remains unchanged but the <u>rate constant</u>, <u>k</u> of the reaction increases.





Low Temperature

High Temperature

## Maxwell Boltzmann distribution curve

In any chemical system, the particles will possess a range of energies. The Maxwell Boltzmann distribution curve shows the distribution of particles with collision energies at a particular temperature. The diagram below shows how the energy distribution changes for a system when the temperature is increased from  $T_1$  to  $T_2$ .



S.C.

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

When temperature increases from  $T_1$  to  $T_2$ , the <u>average kinetic energy</u> of the molecules <u>increases</u>.

- As shown on the diagram, the number of reactant molecules with <u>energy greater than or equal</u> to the activation energy, *E<sub>a</sub>*, increases significantly.
- This results in an increase in the frequency of effective collisions.
- The rate constant, k, increases and hence rate of reaction increases.

### Additional points to note from the Maxwell–Boltzmann distribution diagram

Observe that when temperature is increased from T<sub>1</sub> to T<sub>2</sub>,

- The <u>maximum</u> of the curve <u>shifts (or displaces) to the right</u> and the kinetic energy of the particles are <u>spread over a wider range</u>, showing that the average kinetic energy of particles increases. More particles are moving at higher speed.
- The maximum is slightly lower because the energies become more spread out.
- The shaded area shows the <u>number of molecules with energy greater than or equal to *E<sub>a</sub>* is <u>higher</u>.</u>
- <u>Total area</u> under the curve at T<sub>2</sub> is the <u>same</u> as the total area under the curve at T<sub>1</sub>.
   (*The total area under the curve represents the total number of molecules in the system, which does not change when temperature is increased*)

## (e) Effect of Catalyst



A catalyst is a substance that increases the rate of the reaction without being consumed in the reaction. It is used and then regenerated.

## (i) **Properties of a Catalyst**

- A catalyst increases the reaction rate by providing <u>an alternative reaction pathway</u> which has a <u>lower activation energy</u>.
- It remains <u>chemically unchanged</u> at the end of the reaction.
- It does not affect the yield of the reaction.
- It increases the rate constant, k of the reaction.

## (ii) Link to Chemical Energetics

- The energy profile below compares the difference in activation energies between a catalysed reaction and an uncatalysed reaction.
- A catalyst provides an alternative reaction pathway of <u>lower activation energy</u>, but it has <u>no effect on the enthalpy change of reaction</u>.



reaction progress

## (iii) Maxwell Boltzmann distribution curve



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

In the **presence of a catalyst** at a certain temperature *T*, the reaction proceeds via <u>an alternative</u> pathway which has lower activation energy  $(E_a' < E_a)$ .

- As shown on the diagram, more molecules have <u>energies greater than or equal to the lowered</u> activation energy <u>E<sub>a</sub></u>.
- This results in an increase in the frequency of effective collisions.
- The rate constant, k, increases and hence rate of reaction increases.

## 8 Catalysis

## (a) Heterogeneous Catalysis

- Heterogeneous catalysts exist in a <u>different phase</u> from the reactants.
- They are often metals or metal oxides interacting with gaseous or liquid reactants.
- The areas where catalysis takes place on the **surface** of the catalysts are known as the <u>active sites</u>.

Stages involved in heterogeneous catalysis (refer to details on next page)

- 1. Adsorption (adhesion of a substance to the surface of another substance) of reactant molecules onto the catalyst surface.
- 2. New bonds are formed between reactant molecules.
- 3. Desorption of product molecules from the catalyst surface.
- \_..\_..
- Rate of reaction increases in the presence of a heterogeneous catalyst because
  - the <u>adsorption increases the concentration of the reactant molecules</u> at the catalyst surface and allows the **reactant molecules to come into close contact with proper orientation** for reaction to take place.
  - the **adsorption weakens the existing bonds within the reactant molecules**, thereby **lowering the activation energy** for the reaction.

## Examples of heterogeneous catalysis

## (i) Haber Process

 $N_2(q) + 3H_2(q) \longrightarrow 2NH_3(q)$  Fe as catalyst





## (ii) Catalytic removal of pollutants from car engines

- Catalysts in catalytic converter consist of platinum (Pt), palladium (Pd), rhodium (Rh).
- Removes 3 main pollutants in car **exhaust gases** CO, NO<sub>x</sub>, unburnt hydrocarbons



Reference: http://mastermuffler.net/catalytic-converter/

Catalyst	Reaction	Less harmful products
Pt, Pd	Oxidation of CO and unburnt hydrocarbons: $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $C_xH_y(g) + (x + \frac{y}{4})O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(g)$	CO <sub>2</sub> , H <sub>2</sub> O
Rh	Reduction of oxides of nitrogen (NO <sub>x</sub> ) by excess CO present: $CO(g) + NO(g) \rightarrow CO_2(g) + \frac{1}{2}N_2(g)$	$N_2$ , $CO_2$

Cars fitted with catalytic converters must be run on unleaded petrol.

\_..\_..

Reason: Lead is preferentially adsorbed on the active sites on catalyst surface prevents the reactions for conversion of pollutants from taking place ⇒ ⇒

de-activation (or poisoning) of catalytic converter by lead

## (b) Homogeneous Catalysis

- Homogeneous catalysts exist in the **same phase** as the reactants.
- The catalyst takes part in the reaction by being converted into a reactive intermediate ion or compound, which is subsequently consumed to form the product.
- The product is formed with the **regeneration** of the **catalyst**.
- The catalyst is able to perform its role due to its ability to exist in more than one oxidation state.

## Examples of homogeneous catalysis

(i) Catalytic role of Fe<sup>3+</sup> in the oxidation of I<sup>-</sup> by peroxodisulfate,  $S_2O_8^{2-}$ 

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

- Slow reaction due to electrostatic repulsion between the two negatively charged ions, thus the reaction has a high activation energy.
- This reaction is catalysed by d-block metal ions, for example  $Fe^{2+}(aq)$ .
- Addition of a small amount of aqueous Fe<sup>2+</sup> ion increases the rate of this reaction.

Mechanism of catalysed reaction:

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

In Step 1,  $Fe^{2+}$  reduces  $S_2O_8^{2-}$ .

In Step 2, Fe<sup>3+</sup> intermediate oxidises I<sup>-</sup>and itself reduced back to Fe<sup>2+</sup>.

- Fe<sup>2+</sup> ion catalyses the reaction by providing an alternative pathway with a lower activation energy via the intermediate Fe<sup>3+</sup> ion.
- The reaction now involves oppositely charged ions to collide with each other, hence lowering the *E*<sub>a</sub> of the reaction. Fe<sup>2+</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions (as well as Fe<sup>3+</sup> and I<sup>-</sup> ions) attract one another and increases the frequency of *effective* collisions.



**Reaction progress** 

## (ii) Catalytic role of oxides of nitrogen in the oxidation of sulfur dioxide in the atmosphere

• Oxidation of sulfur dioxide by moist air to produce sulfuric acid (acid rain).

 $SO_2(g) + \frac{1}{2}O_2(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$ 

• Reaction is exacerbated by catalytic action of nitrogen dioxide as shown:

 $\begin{array}{rcl} SO_2(g) \ + \ \textbf{NO}_2(\textbf{g}) & \longrightarrow & SO_3(g) \ + \ \textbf{NO}(g) \\ NO(g) \ + \ 1_2O_2(g) & \longrightarrow & \textbf{NO}_2(\textbf{g}) \\ SO_3(g) \ + \ H_2O(l) & \longrightarrow & H_2SO_4(aq) \end{array}$ 

## (c) Autocatalysis

- An autocatalytic reaction involves the formation of a **product** that acts as a catalyst for the reaction.
- This product is known as **autocatalyst**.



## <u>Example</u>:

The reaction between  $MnO_4^-$  and  $C_2O_4^{2-}$  in acid solution is catalysed by the  $Mn^{2+}$  formed during the reaction.

 $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ 

- At the beginning, the rate of reaction is slow as it is not catalysed.
- The reaction speeds up as the autocatalyst, Mn<sup>2+</sup> is produced. The purple MnO<sub>4</sub><sup>-</sup> is rapidly decolourised.
- Reaction slows down due to decreasing concentrations of reactants, even though there is an adequate supply of catalyst. Reactions eventually stops when one of the reactants is used up.

## (d) Enzyme Actions ("Lock and Key" Model)

- Enzymes are:
  - naturally occurring biological catalysts
  - normally large protein molecules
  - very specific in the type of reactions they catalyse (i.e. enzymes have specific activity)
  - operate best at a certain optimum temperature (20–50 °C) and pH range (5 8)
  - <u>denatured at high temperature</u>, the 3–dimensional structure of enzyme is altered by heat and its catalytic activity is destroyed. Therefore, for biological reaction, the rate of reaction <u>does not always increase with temperature</u>.
- The catalytic reaction occurs at a certain location on the enzyme called the active site.
- The molecules upon which the enzyme acts are called the substrate molecules.
- The active site has a specific configuration or structure which allows only substrate molecules with complementary structure to bind.
- Upon completion of reaction, products are released and the active site is free to allow action on other substrate molecules.

## Lock-and-key hypothesis (Fischer; 1890)



• Mechanism of enzyme – catalysed reaction:



Reaction profile for an enzyme-catalysed reaction

- Conversion of enzyme-substrate (ES) to enzyme-product (EP) is the <u>rate-determining step</u>.
- Relationship between substrate concentration and the rate of an enzyme-catalysed reaction:



- At <u>low concentration</u> of substrate, the rate increases rapidly with increasing substrate concentration. <u>Rate</u> of reaction is <u>directly proportional</u> to <u>[substrate]</u> since <u>active sites</u> in the enzymes are <u>not fully occupied</u>.
- At <u>high concentration</u> of substrate, <u>rate</u> is <u>independent</u> of <u>[substrate]</u> since all the <u>active</u> <u>sites</u> are <u>fully occupied</u>.
- At and beyond this point, an increase in concentration of substrate does not affect the overall rate.

## 9 Thermodynamic Stability vs. Kinetic Stability

- Thermodynamics explains the tendency for a reaction to occur, while kinetics gives an indication of the rate at which this tendency is realised.
- A thermodynamically spontaneous process will take place so slowly that it practically does not occur over the time period of observation if the activation energy of the process is too high.

Example: Consider the conversion of diamond to graphite



**Reaction progress** 

- The conversion of diamond to graphite is **exothermic** and diamond, having a higher energy content, is **energetically less stable** than graphite.
- The reaction, however, does *not* happen under normal conditions due to the **high activation energy**, *E*<sub>a</sub>, involved.
- Diamond is an example of an energetically unstable, yet kinetically stable, substance.
- The conversion of diamond to graphite is said to be energetically (thermodynamically) feasible but not kinetically feasible.