

# Pioneer Junior College

## Higher 2 Chemistry (9647)

### Reaction Kinetics (Tutor's Copy)

#### References

1. Chemistry In Context (5<sup>th</sup> edition) by Hill and Holman
2. A level Chemistry (4<sup>th</sup> edition) by E.N. Ramsden

#### Syllabus content

- Simple rate equations; orders of reactions; rate constants
- Concept of activation energy
- Effect of concentration, temperature, and catalysts on reaction rate
- Homogeneous and heterogeneous catalysis
- Enzymes as biological catalysts

#### Assessment objectives

Candidates should be able to:

- (a) explain and use the terms: rate of reaction, rate equation, order of reaction, rate constant, half-life of a reaction, rate-determining step, activation energy, catalysis.
- (b) construct and use rate equations of the form  $\text{rate} = k[A]^m[B]^n$  (limited to simple cases of single step reactions and of multi-step processes with a rate-determining step, for which  $m$  and  $n$  are 0, 1 or 2), including:
  - (i) deducing the order of a reaction by the initial rates method;
  - (ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs;
  - (iii) verifying that a suggested reaction mechanism is consistent with the observed kinetics;
  - (iv) predicting the order that would result from a given reaction mechanism;
  - (v) calculating an initial rate using concentration data.

[Integrated forms of rate equations are **not** required.]
- (c)
  - (i) show understanding that the half-life of a first-order reaction is independent of concentration.
  - (ii) use the half-life of a first-order reaction in calculations.
- (d) calculate a rate constant using the initial rates method.
- (e) devise a suitable experimental technique for studying the rate of a reaction, from given information.
- (f) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction.
- (g) show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy.
- (h) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and, hence, on the rate) of a reaction.
- (i)
  - (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant.
  - (ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution.
- (j) outline the different modes of action of homogeneous and heterogeneous catalysis, including :
  - (i) the Haber Process
  - (ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engine
  - (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulphur dioxide
  - (iv) catalytic role of  $\text{Fe}^{3+}$  (or  $\text{Fe}^{2+}$ ) in the  $\text{I}^-/\text{S}_2\text{O}_8^{2-}$  reaction
- (k) describe enzymes as biological catalysts (proteins) which may have specific activity.
- (l) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

- (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.

## 1. Introduction

**Reaction kinetics** is the study of the rates of chemical reactions, the factors that affect the rates of chemical reactions and the mechanisms (sequence of steps) by which chemical reactions occur.

## 2. Rate of a Reaction

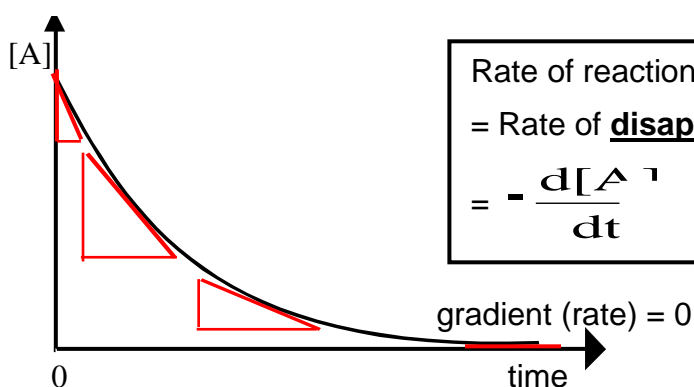
### 2.1 Definition

The **rate of a chemical reaction** is the change in concentration of a reactant or a product per unit time and measures how fast a reaction proceeds.

The unit for the rate of reaction is **always**  $\text{mol dm}^{-3} \text{ t}^{-1}$  (where time, t, is either in seconds or minutes).

### 2.2 Concentration-time graphs for reaction : $A \rightarrow B$

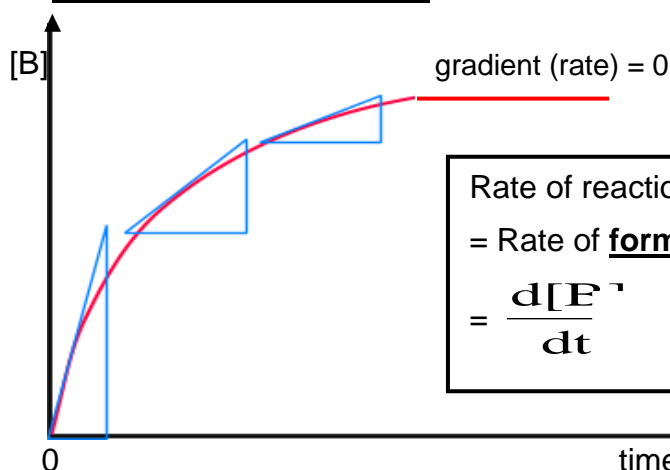
#### i) [Reactant]-Time Graph



Rate of reaction at time, t  
 = Rate of disappearance of reactant A at time, t  

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

#### ii) [Product]-Time Graph



Rate of reaction at time, t  
 = Rate of formation of reactant B at time, t  

$$= \frac{d[B]}{dt}$$

- magnitude of the slope (gradient) of the curve = rate of the reaction (slope can be negative but rate is never negative, rate simply decreases or increases).
- slope gets less steep (showing the rate is slowing down) as the reaction proceeds
- slope (rate) becomes zero when reactant A is used up and [B] becomes constant
- **slope** at the start of the reaction will give the **INITIAL RATE**
- initial rate is usually the fastest (steepest slope) for most reactions

**Example 1:**

Given  $2A + B \rightarrow 3C$ , write the rate in terms of changes in [A], [B] and [C]

For every mol of B used up, 2 mol of A would have been used and 3 mol of C would have formed.

Mathematical relationship of the rates of reaction:

$$\left(-\frac{d[B]}{dt}\right) = \left(-\frac{d[A]}{dt}\right)\left(\frac{1}{2}\right) = \left(\frac{d[C]}{dt}\right)\left(\frac{1}{3}\right)$$

- (b) construct and use rate equations of the form  $\text{rate} = k[A]^m[B]^n$  (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.]

### 3 The Rate Law (Rate Equation)

#### Definition 1 – Rate Law

The **rate law or rate equation** of a chemical reaction is a mathematical expression that defines the rate as the product of a rate constant and the concentration(s) of the reactant(s) raised to appropriate power(s).

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

$k$  is the rate constant

$n$  is order of reaction with respect to reactant

The rate equation is found by doing experiments and not by looking at the stoichiometric equation

E.g. The equation  $2A + 3B + C \longrightarrow D + E$ , might have:

$$\text{Rate Equation: } \text{Rate} = k[A][B]^2$$

#### Definition 2 – Rate constant

The **rate constant**,  $k$ , is the **constant of proportionality** in the rate equation

The **rate constant**,  $k$ ,

- is **constant** for a particular reaction at a given temperature
- is determined experimentally and has no fixed units

**NOTE :**

$$\text{unit of } k = \frac{\text{unit of rate}}{(\text{unit of concentration})^n}, \text{ where } n = \text{overall order}$$

- generally **increases** with (1) increase in temperature and (2) the use of catalyst
- if it is larger, rate of reaction is **higher**.

### Definition 3 – Order of reaction

The **order of reaction** with respect to a reactant is the **power** to which the concentration of that reactant is raised in the rate equation.

E.g. rate =  $k[A]^1[B]^2$  then the order of reaction w.r.t A is 1 and the order of reaction w.r.t B is 2.

#### Order indicates how a change in concentration of a reactant affects the rate

E.g. Rate =  $k[A]^1[B]^2$  - Doubling [A], doubles the rate ( $= 2^1$ )  
Halving [A], halves the rate ( $= 0.5^1$ )

Doubling [B], quadruples the rate ( $= 2^2$ )

Halving [B], rate will be  $\frac{1}{4}$  of the original rate ( $= 0.5^2$ )

### Definition 4 – Overall order

The **overall order** of the reaction is the sum of all the powers of the concentration terms in the rate equation. E.g. rate =  $k[A]^1[B]^2[C]^1$  then the overall order is 4.

**Example 2:** Given  $\text{BrO}_3^- (\text{aq}) + 5 \text{Br}^- (\text{aq}) + 6 \text{H}^+ (\text{aq}) \rightarrow 3 \text{Br}_2 (\text{aq}) + 3 \text{H}_2\text{O} (\text{l})$

The reaction kinetics of the reaction was studied experimentally using the **initial rates method** and the results are:

Mixtures	Initial concentration			Relative rate
	$[\text{BrO}_3^-] / \text{mol dm}^{-3}$	$[\text{Br}^-] / \text{mol dm}^{-3}$	$[\text{H}^+] / \text{mol dm}^{-3}$	
A	0.05	0.25	0.30	1
B	0.10	0.25	0.30	2
C	0.10	0.50	0.30	4
D	0.10	0.50	0.60	16

- (a) Find the order of reaction w.r.t each reactant and state the overall order.  
 (b) Write the rate law for the reaction.  
 (c) Determine the unit for the rate constant,  $k$ , in this case.

### Using Inspection method

Compare mixtures A and B in which  $[\text{Br}^-]$  &  $[\text{H}^+]$  are **constant**, doubling  $[\text{BrO}_3^-]$  **doubles** the rate. Therefore, **rate**  $\propto$   **$[\text{BrO}_3^-]$** .

Order of reaction with respect to bromate(V) ion = 1

Compare mixtures B and C in which  $[\text{BrO}_3^-]$  &  $[\text{H}^+]$  are **constant**, doubling  $[\text{Br}^-]$  **doubles** the rate. Therefore, **rate**  $\propto$   **$[\text{Br}^-]$** .

Order of reaction with respect to bromide ion = 1

Compare mixtures C and D in which  $[\text{Br}^-]$  &  $[\text{BrO}_3^-]$  are **constant**, doubling  $[\text{H}^+]$  **quadruples** the rate. Therefore, **rate**  $\propto [\text{H}^+]^2$ .

Order of reaction with respect to hydrogen ion = 2

Overall order of reaction =  $1 + 1 + 2 = 4$

(b) Therefore,  $\text{rate} \propto [\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$  and  $\text{rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$ .

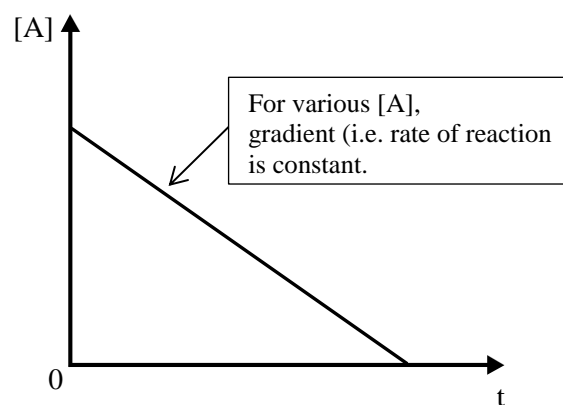
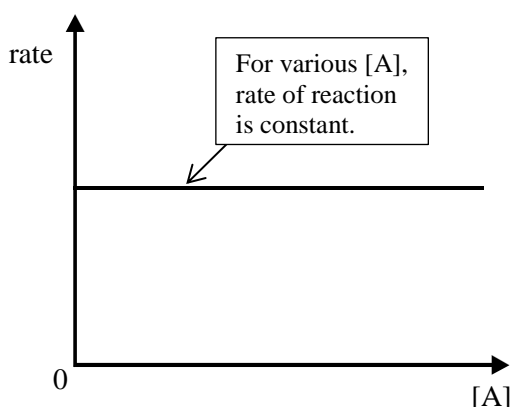
(c) Unit of  $k = \frac{\text{unit of rate}}{(\text{unit of concentration})^n}$  where  $n$  = overall order  
 $= \frac{\text{mol dm}^{-3} \text{s}^{-1}}{(\text{mol dm}^{-3})^4}$ , since overall order of reaction is 4  
 $= \text{mol}^{-3} \text{dm}^9 \text{s}^{-1}$

### 3.1 Zero Order Reaction

Consider the reaction  $\text{A} \rightarrow \text{products}$  where the rate law is  $\text{rate} = k[\text{A}]^n$

If  $n = 0$  (rate of reaction is zero order w.r.t to A), then  $\text{rate} = k[\text{A}]^0 = k$   
 i.e. the rate of reaction is **constant and independent of the [A]**

The unit for  $k$  is  $\text{mol dm}^{-3} \text{s}^{-1}$  or  $\text{mol dm}^{-3} \text{min}^{-1}$ .



### 3.2 First Order Reaction

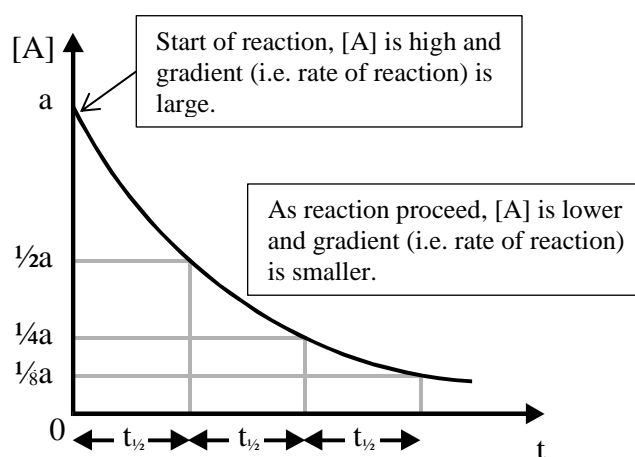
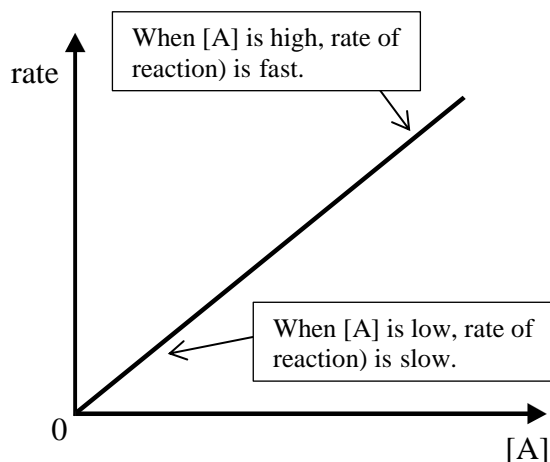
Consider the reaction  $\text{A} \rightarrow \text{products}$  where the rate law is  $\text{rate} = k[\text{A}]^n$

If  $n = 1$  (rate of reaction is first order w.r.t to A), then  $\text{rate} = k[\text{A}]^1$   
 i.e. the rate of reaction is **directly proportional to [A]**.

The unit for  $k$  is  $\text{s}^{-1}$  or  $\text{min}^{-1}$ .

**Example 3:**Complete the following table for a reaction where rate =  $k[A]$ .

Initial [A]	Initial Rate
x	y
2x	2y
3x	3y
$\frac{1}{2}x$	$\frac{1}{2}y$



**Half-life**,  $t_{1/2}$ , is the time taken for the reactant concentration to decrease to half of its original value.

For a first order reaction, the half-life is a **constant** and is independent of concentration of reactant(s).

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

**Pseudo first order reactions**

E.g. hydrolysis of ester:  $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5(l) + \text{H}_2\text{O}(l) \longrightarrow \text{CH}_3\text{CO}_2\text{H}(l) + \text{CH}_3\text{CH}_2\text{OH}(l)$   
ethyl ethanoate

Rate law is rate =  $k[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5][\text{H}_2\text{O}]$  from experimental studies.

If water is present in **large excess**, the amount of water used up would be a small fraction of the amount of water present initially, that is,  $[\text{H}_2\text{O}]$  is essentially **constant**.

$$\text{rate} = k[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5][\text{H}_2\text{O}] = k'[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] \quad \text{where } k' = k[\text{H}_2\text{O}]$$

The reaction **appears** to be zero order with respect to water and first order with respect to the ester, hence a **pseudo first-order reaction**.

**Note :** Given rate =  $k[A][B]$  for a reaction which is first order w.r.t each of the two reactants, the reaction will be pseudo first-order if the concentration of one of the reactants is so **large** that it is effectively **constant** or if one of the reactants is a **catalyst**.

### 3.3 Second Order Reaction

Consider the reaction  $A \rightarrow \text{products}$  where the rate law is  $\text{rate} = k[A]^n$

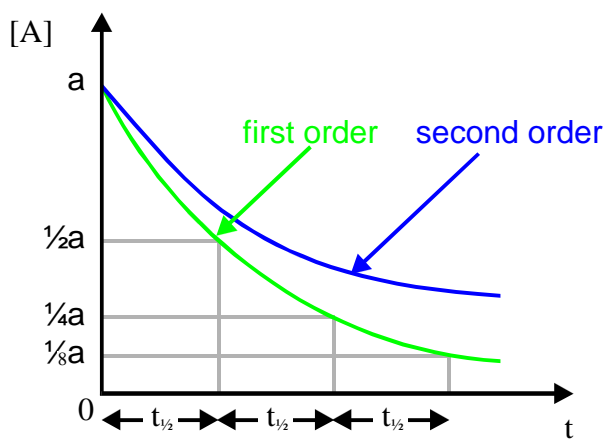
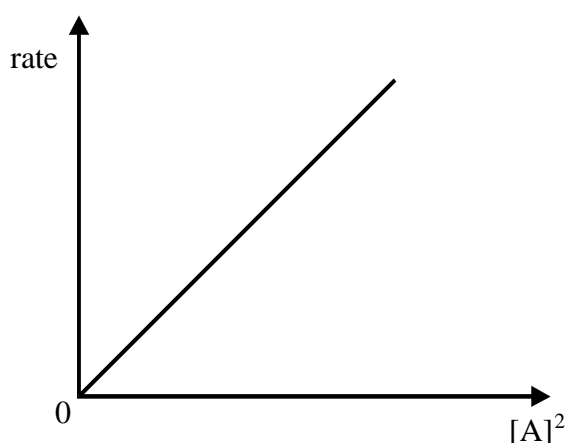
If  $n = 2$  (order of reaction is two wrt A), then  $\text{rate} = k[A]^2$   
 i.e. the rate of reaction is **directly proportional** to the  $[A]^2$

The unit for  $k$  is  $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$  or  $\text{mol}^{-1} \text{dm}^3 \text{min}^{-1}$ .

#### Example 4:

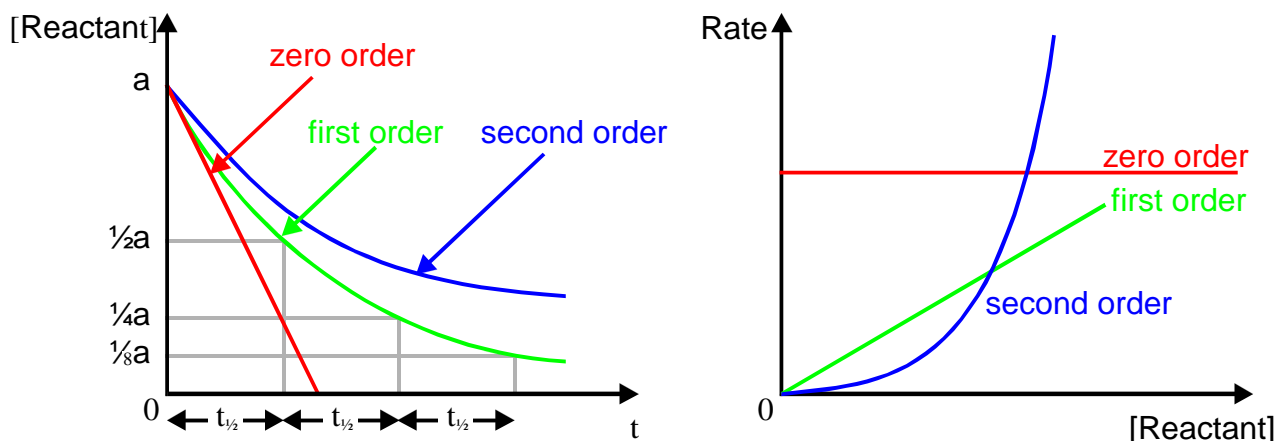
Complete the following table for a reaction where  $\text{rate} = k[A]^2$ .

Initial [A]	Initial Rate
x	y
2x	4y
3x	9y
$\frac{1}{2}x$	$\frac{1}{4}y$

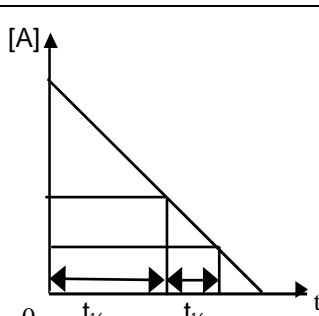
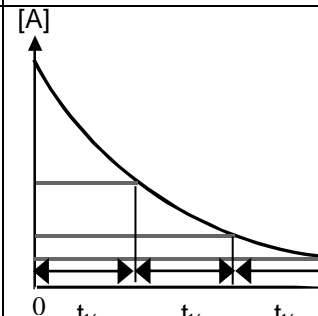
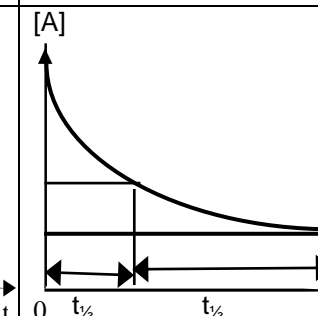
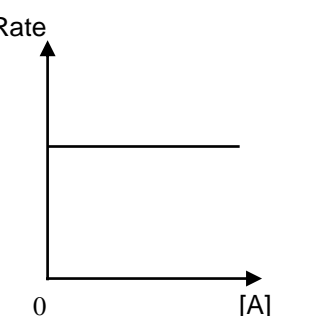
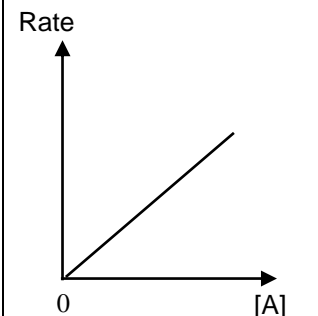
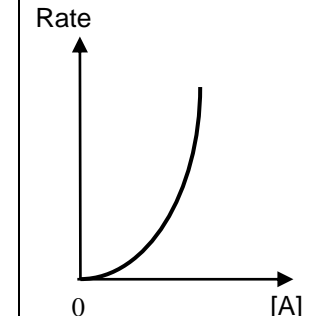


Note: The half-life of a second order reaction is **not constant**.

### 3.4 Summary



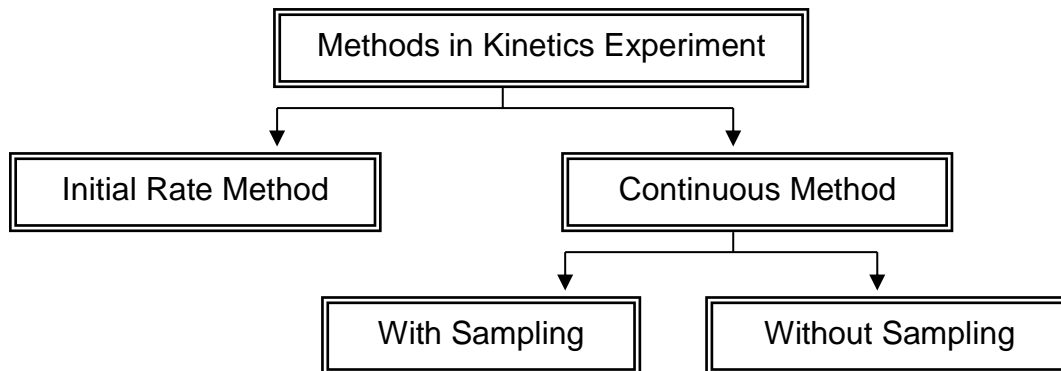
# Order is usually 0, 1 or 2 although it can be a negative integer or a fraction

Order of Reaction <sup>#</sup>	Zero $A \rightarrow \text{products}$	First $A \rightarrow \text{products}$	Second $A \rightarrow \text{products}$
Rate Law/ Equation	Rate = $k[A]^0$	Rate = $k[A]^1$	Rate = $k[A]^2$ Or Rate = $k[A][B]$ for $A + B \rightarrow \text{products}$
Unit of k	$\text{mol dm}^{-3} \text{s}^{-1}$	$\text{s}^{-1}$	$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
Graph of [reactant] vs time	 <p>Straight line graph with a negative slope</p>	 <p>Downward sloping curve with constant <math>t_{1/2}</math></p>	 <p>Downward sloping curve; <math>t_{1/2} \neq \text{constant}</math></p>
Graph of Rate vs [reactant]	 <p>Horizontal straight line graph</p>	 <p>Straight line graph passing thru' origin with a positive slope k</p>	 <p>Upward sloping curve</p>
Half-life, $t_{1/2}$	decreases with time	$t_{1/2} = \frac{\ln 2}{k}$ is a constant	increases with time



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

#### 4 Experimental Determination of Reaction Rates



### 4.1 Initial Rate Method

- A few sets of experiments are conducted for a reactant R, varying  $[R]$  and keeping the concentration of all other reactants constant.
- Temperature is kept constant for all experiments.
- Principle of initial rate method with constant volume system:

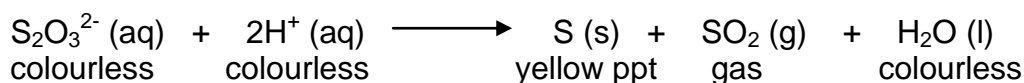
Keep the total volume of mixture constant by making up the total volume with water. **WHY?**

If the total volume of the reaction mixture is kept constant, **[reactant]  $\propto$  volume of the reactant.**

- There are two types of measurements can be taken for initial rate method:
  - 1) Time taken for the formation of a fixed [product], or
  - 2) Time taken for reactant to be used up

Time taken for a fixed [product] to be formed	Time taken for reactant to be used up
<u>Colourless reactants</u> form <u>coloured product</u>	<u>Coloured reactant</u> forms <u>colourless products</u> .
Rate $\propto \frac{1}{time}$	Rate $\propto \frac{V_{\text{coloured reactant}}}{time}$
<p>Examples:</p> <p>1) <math>\text{Na}_2\text{S}_2\text{O}_3 (\text{aq}) + 2\text{HCl} (\text{aq}) \longrightarrow \text{S} (\text{s}) + \text{SO}_2 (\text{g}) + 2\text{NaCl} (\text{aq}) + \text{H}_2\text{O} (\text{l})</math>  <span style="margin-left: 40px;">↑</span>            yellow ppt</p> <p>2) <math>2\text{HBr} + \text{conc H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O}</math>  <span style="margin-left: 180px;">↑</span>            reddish brown</p>	<p>Examples:</p> <p>1) <math>\text{CH}_3\text{COCH}_3 (\text{aq}) + \text{I}_2 (\text{aq}) \xrightarrow{\text{H}^+} \text{CH}_3\text{CICOCH}_3 (\text{aq}) + \text{HI} (\text{aq})</math>  <span style="margin-left: 150px;">↑</span>            brown</p> <p>2) <math>\text{CH}_2=\text{CH}_2 + \text{Br}_2 \longrightarrow \text{CH}_2\text{BrCH}_2\text{Br}</math>  <span style="margin-left: 120px;">↑</span>            reddish brown</p>

**Example 5:** The reaction between  $\text{HCl}$  and thiosulfate ions can be investigated by varying the concentration of the two reactants and measuring the time taken by the product sulfur to obscure a marked cross placed under the reaction mixture.



Various volumes of water are added to the four mixtures below to ensure that the total volumes of all four mixtures are the same.

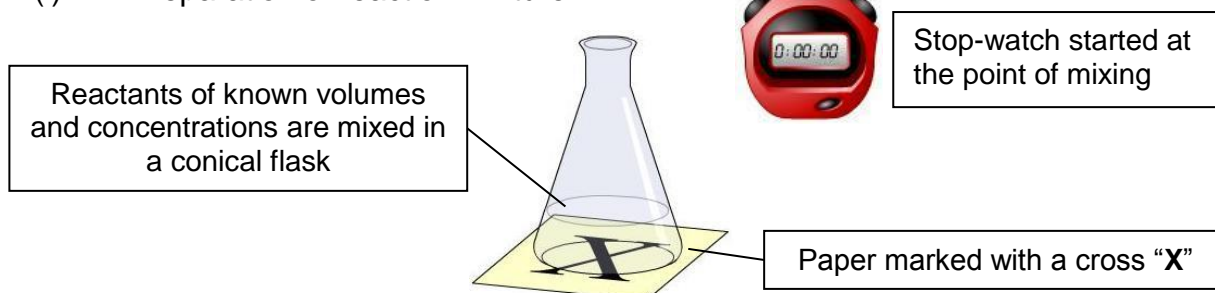
Expt. No.	Vol. of $\text{HCl}/\text{cm}^3$	Vol. of $\text{S}_2\text{O}_3^{2-}/\text{cm}^3$	Vol. of $\text{H}_2\text{O}/\text{cm}^3$	Time taken to obscure 'cross'/ s
1	25	30	0	8
2	25	10	20	24
3	15	10	30	24

- (a) Describe the experimental procedure required to perform the experiment to obtain the results in the table above.  
 (b) Determine the rate equation by analysing the data in the table.

**Ans:**

(a) Experimental Procedure:

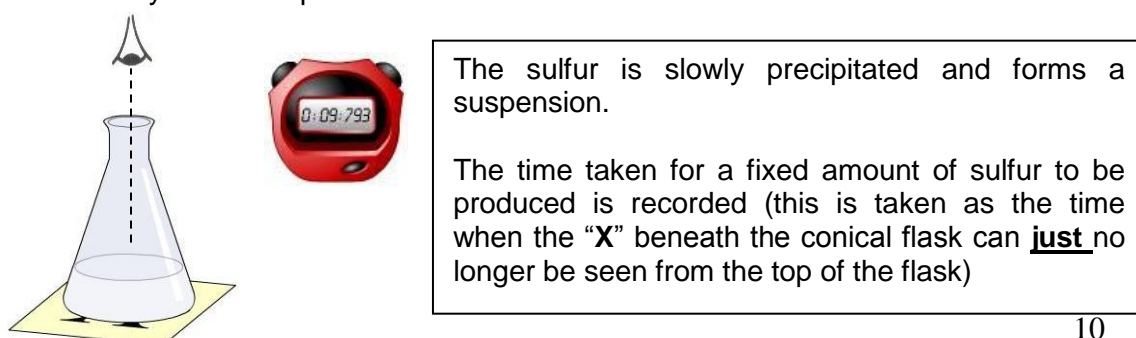
(i) Preparation of reaction mixture



- Add stated volumes of thiosulfate followed by water and finally  $\text{HCl}$  into conical flask.
- Add solutions quickly but carefully to avoid any spillage.
- Start the stopwatch simultaneously as the last solution is added, with one hand pouring the solution and the other, starting the stopwatch.
- Swirl the reaction flask 1-2 times and leave it on top of the "X". Be consistent in the number of times you swirl the flask for all the experiments.

(ii) Observation of reaction mixture and time measurement

- Look from the top of the flask to judge the obscurity. Stop the stopwatch when the "X" is just obscured by the sulfur produced in the reaction.



(b) Determine the rate equation by analysing the data in the table.

Since the total volume of mixture is kept constant,  $[\text{reactant}] \propto \text{vol}_{\text{reactant}}$

$$\text{Initial rate} = \frac{\text{fixed amount of sulfur}}{\text{time taken to obscure 'X'}}$$

$$\text{Thus, Initial rate} \propto \frac{1}{\text{time taken to obscure X}}$$

Expt. No.	Vol. of HCl/cm <sup>3</sup>	Vol. of S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> /cm <sup>3</sup>	Vol. of H <sub>2</sub> O/cm <sup>3</sup>	Time taken to obscure 'cross'/ s	1 / t /s <sup>-1</sup>	Relative initial rate
1	25	30	0	8	1/8	3
2	25	10	20	24	1/24	1
3	15	10	30	24	1/24	1

### Comparing Expt 2 and 1

[H<sup>+</sup>] kept constant, when [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] is increased three times.

Relative initial rate increased **three** times

Thus, rate  $\propto$  [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] and reaction is **first order** w.r.t S<sub>2</sub>O<sub>3</sub><sup>2-</sup>

### Comparing Expt 3 and 2

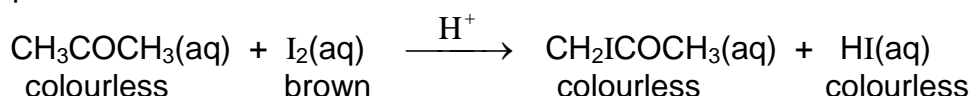
[S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] kept constant, when [HCl] increased 5/3 times,

Relative initial rate is **unchanged**. (Increased (5/3)<sup>0</sup> = 1 time )

Thus, rate  $\propto$  [HCl]<sup>0</sup> and reaction is **zero order** w.r.t HCl.

$$\text{Overall Rate} = k [\text{S}_2\text{O}_3^{2-}] [\text{HCl}]^0 = k [\text{S}_2\text{O}_3^{2-}]$$

**Example 6:** The kinetics of the acid-catalysed reaction of propanone with iodine can be investigated experimentally by varying the concentrations of the three reactants involved (propanone, acid & iodine) and determining the time for the colour of iodine to disappear.



The following results were obtained in such an experiment.

Expt	Vol. of propanone /cm <sup>3</sup>	Vol. of iodine /cm <sup>3</sup>	Vol. of H <sub>2</sub> SO <sub>4</sub> /cm <sup>3</sup>	Vol. of water /cm <sup>3</sup>	Relative time for I <sub>2</sub> colour to disappear	Relative rate of reaction
1	8	4	8	0	1	4
2	8	4	4	4	2	2
3	4	4	8	4	2	2
4	8	2	8	2	0.5	4

Complete the initial rate for each experiment and find the rate equation.

### Solution:

Since the total volume of mixture is kept constant,  $[I_2] \propto \text{Vol of } I_2$

Thus, initial rate  $\propto \frac{\text{volume of iodine used}}{\text{time taken for iodine colour to disappear}}$

### **Comparing Expt 1 and 3,**

$[I_2]$  &  $[H^+]$  kept constant, when  $[CH_3COCH_3]$  is **halved**, rate is **halved**.

Thus, rate  $\propto$   $[CH_3COCH_3]$  and reaction is **first order** w.r.t propanone.

### **Comparing Expt 1 and 4,**

$[CH_3COCH_3]$  &  $[H^+]$  kept constant, when  $[I_2]$  is **halved**, rate remains **unchanged**.

Thus, rate  $\propto$   $[I_2]^0$  and reaction is **zero order** w.r.t iodine.

### **Comparing Expt 1 and 2,**

$[CH_3COCH_3]$  &  $[I_2]$  kept constant, when  $[H^+]$  is **halved**, rate is **halved**.

Thus, rate  $\propto$   $[H^+]$  and reaction is **first order** w.r.t  $H^+$ .

$$\text{Rate} = k [CH_3COCH_3] [H^+]$$

## **4.2 Continuous Method**

- **Only one experiment** is conducted for a reactant R and the rate is measured by following changes in [reactant] left or [product] formed or some **physical property** that is proportional to the [reactant] left or [product] formed as the reaction progresses.
- Any physical property (e.g. volume of gas, pressure, colour, electrical conductivity, mass etc.) can be used to measure rate.

Example:  $P + Q \rightarrow R$

- If two or more reactants are involved, make the reactant **P limiting** and the rest in **great excess** so that the graph of the measured property plotted against time reflects the order of reaction w.r.t **P**. Order of reaction w.r.t other reactants e.g. **Q** may then be found by performing an experiment in which **Q** is limiting.
- Plot a graph of the measured property against time. From the graph, rate of reaction at various times, order of reaction w.r.t reactant R and the rate constant may be found.
- Continuous method may be performed with or without sampling.

## 4.2.1 Continuous Method with Sampling (Titration Method)

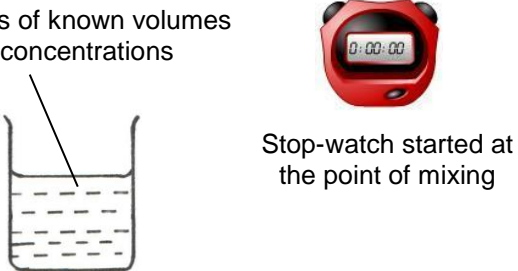
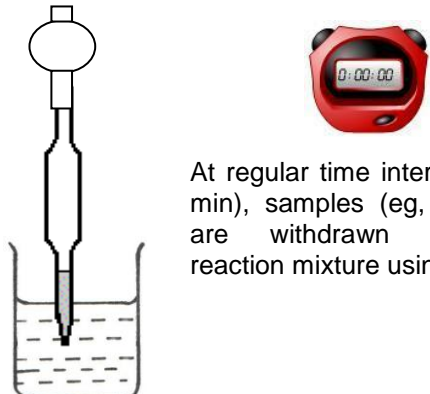
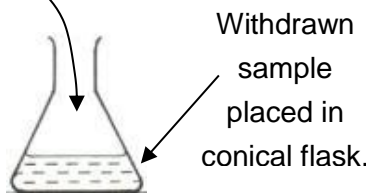
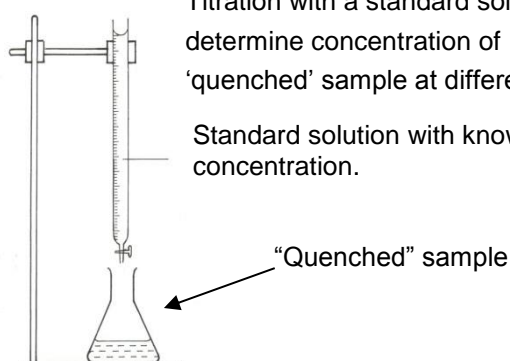
### Experimental Procedure:

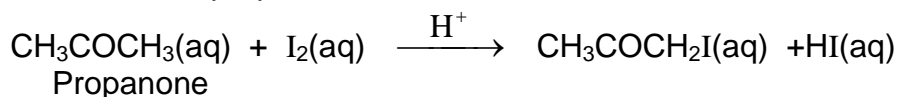
- Solutions of reactants of known concentrations are mixed at constant temperature and a stop watch is started.
- After  $t$  minutes, a sample of the reaction mixture is pipetted out and the reaction is stopped by **quenching** using:
  - \* **sudden cooling**
  - \* **sudden dilution**
  - \* **adding a quenching agent.** e.g.  $\text{NaHCO}_3$  (e.g. for a reaction that requires an acidic medium, the quenching reagent can be  $\text{NaOH}$  or  $\text{NaHCO}_3$ , provided it does not catalyse or take part in the reaction.)

**Quenching stops the reaction so that the concentration of the substance under study does not change further.**

- The quenched mixture is then titrated against a suitable reagent to find the concentration of the reactant left or the concentration of product formed at the particular time.
- Repeat steps (b) and (c) at regular time intervals of  $t$  minutes.
- Plot a graph of concentration of reactant (or product) against time. The rate of reaction at various time intervals can be determined by obtaining the respective gradients.

### Procedure Schematics:

(a) Preparation of reaction mixture	(b) Withdrawal of samples for analysis
<p>Reactants of known volumes and concentrations</p>  <p>Stop-watch started at the point of mixing</p> <p>The reaction vessel should be kept in a constant-temperature water bath</p>	 <p>At regular time intervals (eg, 5 min), samples (eg, <math>10.0 \text{ cm}^3</math>) are withdrawn from the reaction mixture using a pipette</p>
(c) Quenching of reaction in sample	(d) Analysis of quenched sample mixture
<p>Addition of 'quenching' reagent</p>  <p>Withdrawn sample placed in conical flask.</p> <p>The exact time at which the reaction is quenched is noted.</p>	 <p>Titration with a standard solution to determine concentration of 'quenched' sample at different time.</p> <p>Standard solution with known concentration.</p> <p>"Quenched" sample</p>

**Example 7:** Iodination of propanone

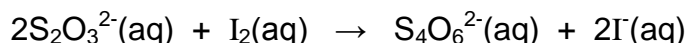
Reaction takes place slowly at room temperature and is catalysed by  $\text{H}^+$  ions. The course of the reaction can be followed by measuring the  $[\text{I}_2]$  left at regular time intervals.

**Note:**

1. Since the reaction is catalysed by acid, the withdrawn sample is quenched by adding sodium hydrogencarbonate to remove the acid catalyst.



2. The concentration of iodine left at the various time intervals is determined by titrating with aqueous sodium thiosulfate.



3. Volume of thiosulfate  $\propto [\text{I}_2]$
4. A graph of iodine concentration (vol of  $\text{S}_2\text{O}_3^{2-}$ ) against time is plotted.
5. From the graph, rate of reaction at various times, order of reaction wrt reactant  $\text{I}_2$  and the rate constant may be found.

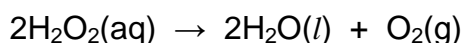
**4.2.2 Continuous Method Without Sampling (Physical Method)**

- Method is preferred over titration as the physical property can be monitored continuously without disturbing the reaction mixture.

**(a) Volume Measurement**

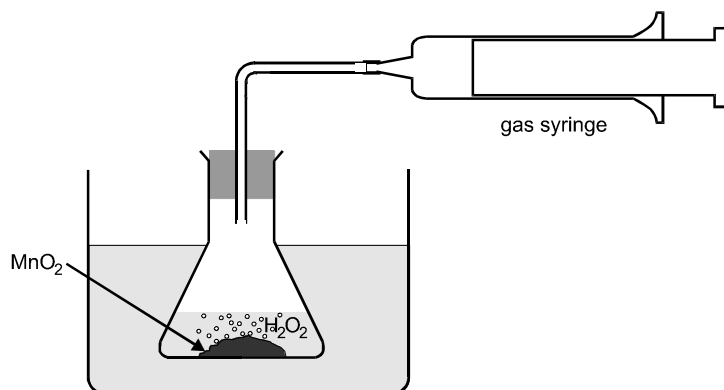
- This method is suitable for reactions which produce **gaseous** product(s).
- Examples of reactions:
  - Action of dilute acid on a carbonate (e.g.  $\text{CaCO}_3$ )
  - Action of dilute acid on reactive metals
  - Catalytic decomposition of  $\text{H}_2\text{O}_2$

Experimental procedures: Catalytic decomposition of hydrogen peroxide.



1. Set up the apparatus as shown setting the syringe to zero.
2. Hydrogen peroxide of known concentration is added to the catalyst ( $\text{MnO}_2$ ) and a stop watch is started.
3. Volume of gas collected in the syringe is measured at regular intervals

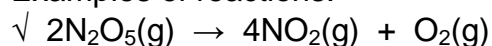
4. Plot volume collected against time. From the graph, rate of reaction at various times, order of reaction w.r.t reactant  $\text{H}_2\text{O}_2$  and the rate constant may be found.



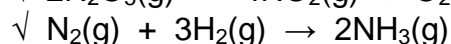
### (b) Changes in Gas Pressure

- This method is suitable for reactions whereby the no. of moles of **gaseous product** is **different** from the no. of moles of **gaseous reactants**.
- Pressure**  $\propto$  **number of moles of gaseous molecules** at constant temperature and volume. Hence reaction rate can be followed by measuring the change in total pressure at regular time intervals.

Examples of reactions:

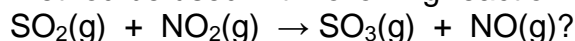


$$\Delta n = 5 - 2 = 3$$



$$\Delta n = 2 - 4 = -2$$

Can this method be used with following reaction:

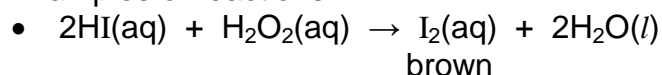


**Ans:** No.  $\Delta n = 0$

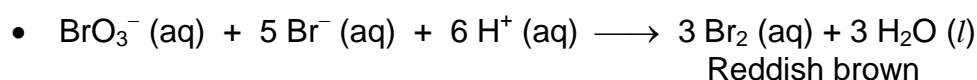
### (c) Colorimetric method

- This method is suitable for reactions with **coloured** reactants and/or products.
- The rate of reaction is followed by measuring the amount of light transmitted through the solution at regular time intervals during the course of the reaction.
- Colour intensity of a chemical species is directly proportional to its concentration.**

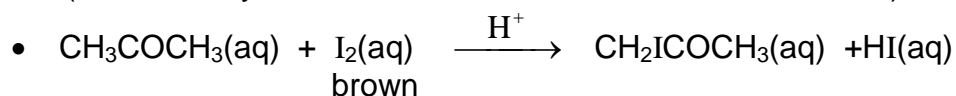
Examples of reactions:



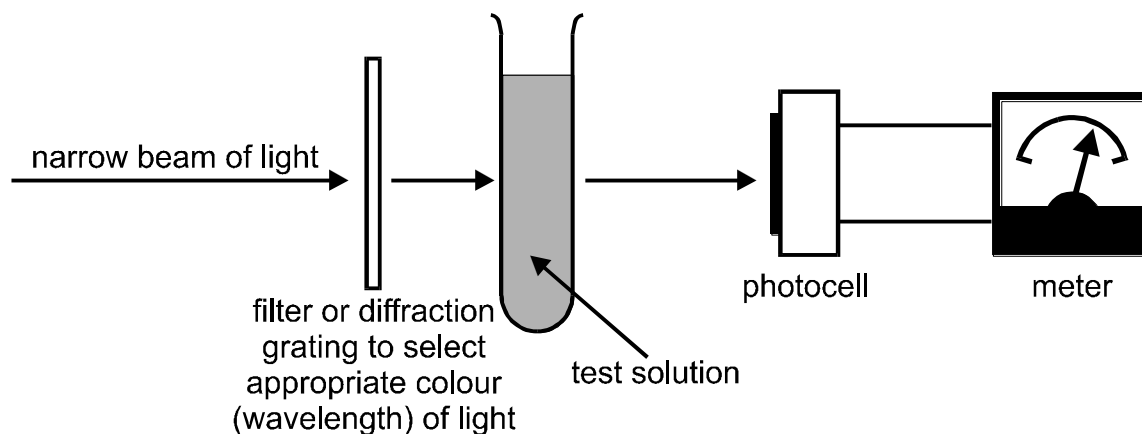
(The intensity of brown colour **increases** with time)



(The intensity of reddish brown colour **increases** with time)

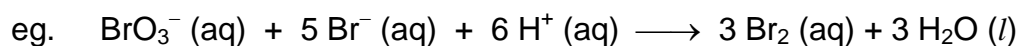


(The intensity of brown colour **decreases** with time)



#### (d) Conductometric method

- This method is suitable for reactions involving ions in which there is a change in the number of ions as the reaction proceeds.



- The rate of reaction is followed by measuring the electrical conductivity with time since conductivity  $\propto$  [ions]

### 4.3 Further Examples

**Example 8:** The reaction kinetics of the decomposition of hydrogen peroxide was studied experimentally and the results are shown below:

Experiment	Initial $[\text{H}_2\text{O}_2]$ / $\text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.0600	$0.350 \times 10^{-3}$
2	0.120	$0.700 \times 10^{-3}$
3	0.180	$1.05 \times 10^{-3}$
4	0.300	$1.75 \times 10^{-3}$

Find the rate law for the reaction and the rate constant.

**Ans:**

#### Inspection method:

Comparing experiments **1 & 2**, when the initial concentration of hydrogen peroxide is **doubled**, the rate of reaction is **doubled**.

Therefore, rate  $\propto [\text{H}_2\text{O}_2]$

The reaction is first order with respect to hydrogen peroxide.

Therefore, the rate law is rate =  $k[\text{H}_2\text{O}_2]$

**OR**



**Substitution method:**

Let the rate law be  $\text{rate} = k [\text{H}_2\text{O}_2]^m$ , substituting rate and  $[\text{H}_2\text{O}_2]$  into rate equation,

Results of expt 1:  $0.350 \times 10^{-3} = k (0.0600)^m$  ..... (1)

Results of expt 2:  $0.700 \times 10^{-3} = k (0.120)^m$  ..... (2)

$$(2) \div (1) \quad \left( \frac{0.120}{0.0600} \right)^m = \left( \frac{0.700 \times 10^{-3}}{0.350 \times 10^{-3}} \right)$$

$$\Rightarrow (2)^m = 2.00$$

$$\Rightarrow m = 1$$

**To find the rate constant, choose any set of experimental data and substitute into the previously determined rate equation,  $\text{rate} = k [\text{H}_2\text{O}_2]$**

E.g. Using data of experiment 1:

$$0.350 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1} = k (0.0600 \text{ mol dm}^{-3}) \Rightarrow k = 5.83 \times 10^{-3} \text{ s}^{-1}$$

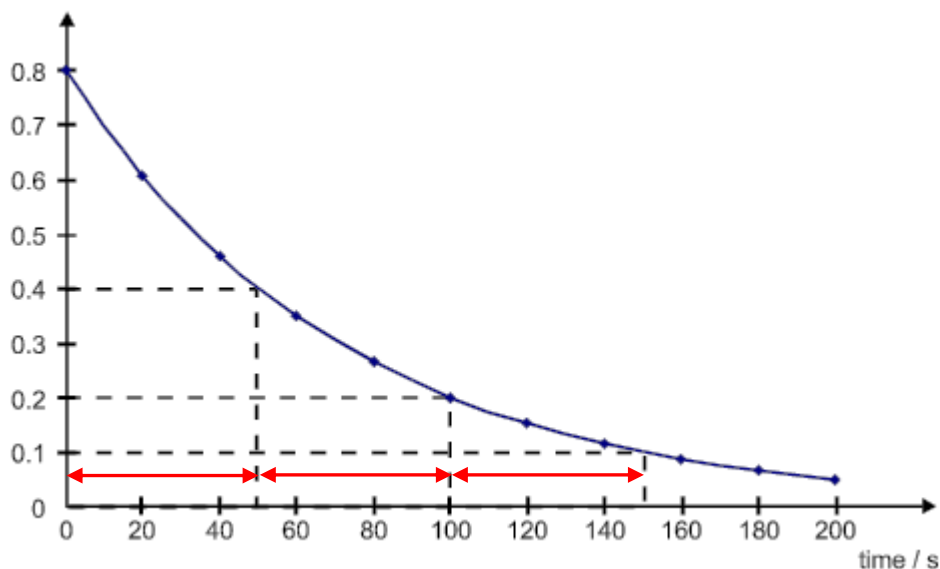
**Example 9:** For a reaction  $\text{A} \rightarrow \text{B}$ , the following results were obtained

Time / s	0	20	40	60	80	100	120	140	160
[A] / $\text{mol dm}^{-3}$	0.800	0.606	0.459	0.348	0.264	0.200	0.152	0.115	0.087

Find the rate constant.

**Ans:**

concentration/ $\text{mol dm}^{-3}$



From the graph, half-life =  $t_{1/2} = 50 \text{ s}$ .

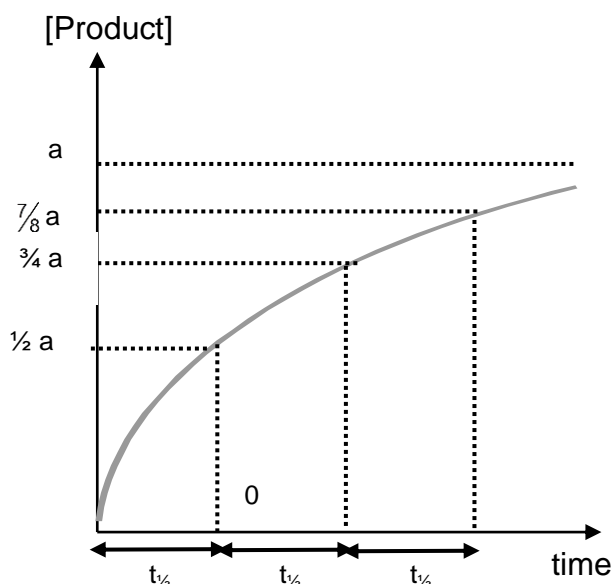
The half-lives are **constant**.

Reaction is **first order** with respect to A.

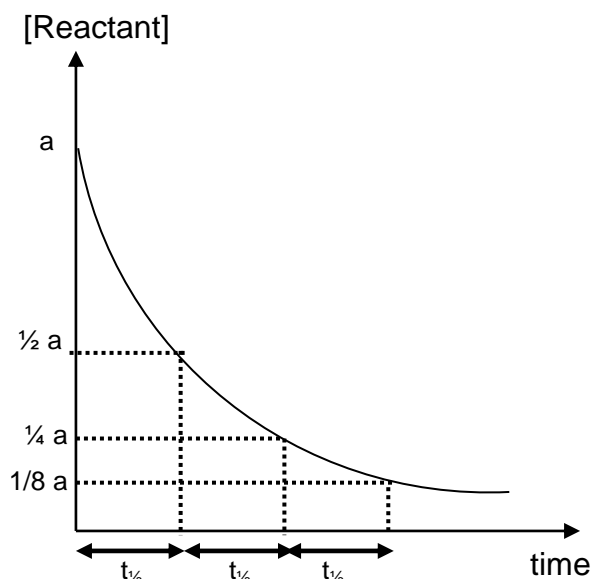
For 1<sup>st</sup> order reaction, the rate constant,  $k = \ln 2 / t_{1/2} = 0.0139 \text{ s}^{-1}$ .

**Qn : How to find  $t_{1/2}$  from a [product] – time graph for a first order reaction?**

E.g. For reaction: 1 Reactant  $\rightarrow$  1 Product



1<sup>st</sup> half-life: Total [product] =  $\frac{1}{2} a$   
 2<sup>nd</sup> half-life: Total [product] =  $\frac{1}{2} a + \frac{1}{4} a$   
 3<sup>rd</sup> half-life: Total [product] =  $\frac{1}{2} a + \frac{1}{4} a + \frac{1}{8} a$



1<sup>st</sup> half-life: Increase in [product] =  $\frac{1}{2} a$   
 2<sup>nd</sup> half-life: Increase in [product] =  $\frac{1}{4} a$   
 3<sup>rd</sup> half-life: Increase in [product] =  $\frac{1}{8} a$

## 5 Reaction Mechanism

The **reaction mechanism** of a chemical reaction is a **sequence of steps** by which the reaction occurs.

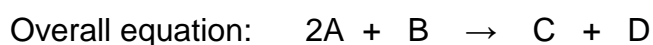
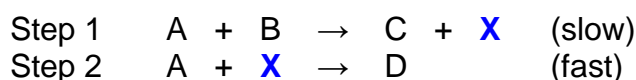
The **molecularity** of each step is the **number of reactant particles** (molecules, atoms or ions) taking part.

- A unimolecular step involves one reactant species.
- A bimolecular step involves two reactant species.
- A termolecular step involves three reactant species.

Consider the reaction:  $2A + B \rightarrow C + D$

It could occur in **one step** and is then known as an **elementary reaction**

It could occur through a **sequence of steps** as shown below:



(Sum of all the steps in the mechanism gives the overall equation)

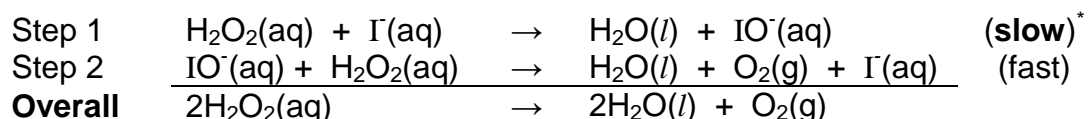
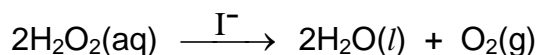
The **slow step** is called the **rate-determining step** (rds).

**Overall rate of reaction = rate of the slow step (rds)**

**Note:**

1. **X** does not appear in the overall equation. **X** is known as an **intermediate**.
2. The **rate-determining step** is the **slowest step** in a reaction mechanism.
3. **The rate equation for a reaction is obtained from the stoichiometry of the rate-determining step (rds)**. Thus, the rate law for the reaction is  $\text{rate} = k [\text{A}][\text{B}]$ .
4. The **overall order** of the reaction = 2 (**equals the molecularity in the rds**)

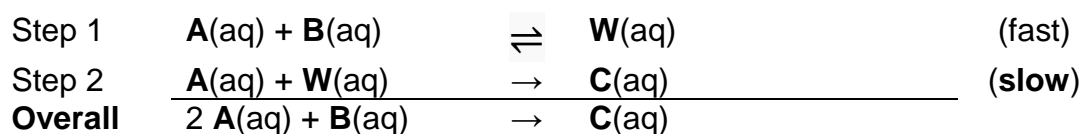
**Example 10:** Decomposition of hydrogen peroxide catalysed by iodide ions



The rate-determining step (step 1) shows that **rate =  $k [\text{H}_2\text{O}_2][\text{I}^-]$**

\* **Note:** The rate-determining step is not necessarily always step 1 (see E.g. 11)

**Example 11:**  $2 \text{A}(\text{aq}) + \text{B}(\text{aq}) \longrightarrow \text{C}(\text{aq})$



Determine the rate equation for this reaction.

**Ans:**

From the slow step,  $\text{rate} = k [\text{A}][\text{W}]$

However, rate equation cannot be expressed in terms of intermediate (e.g. **W**).  
The value of **[W]** needs to be substituted by another value.

Since  $K_c = \frac{[\text{W}]}{[\text{A}][\text{B}]}$ ,  $[\text{W}] = K_c [\text{A}][\text{B}] \text{ ----- (1)}$

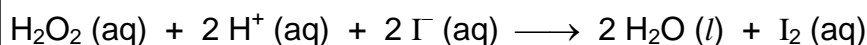
Substitute (1) into rate equation,

$$\begin{aligned} \text{rate} &= k [\text{A}] (K_c [\text{A}][\text{B}]) \\ &= [(k)K_c] [\text{A}]^2[\text{B}] \\ &= k' [\text{A}]^2[\text{B}], \text{ where } k' = [(k)(K_c)] \end{aligned}$$

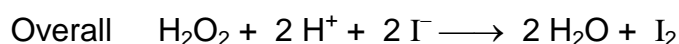
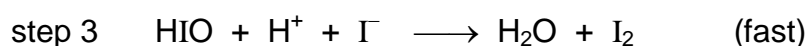
## 5.1 Relating order of reaction to mechanism

### Example 12:

Given rate =  $k[\text{H}_2\text{O}_2][\text{I}^-]$  for the reaction between  $\text{H}_2\text{O}_2$  & hydrogen iodide :



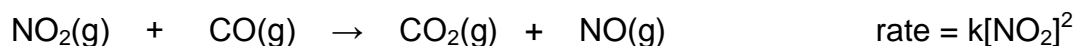
Is the following mechanism consistent with the given rate law?



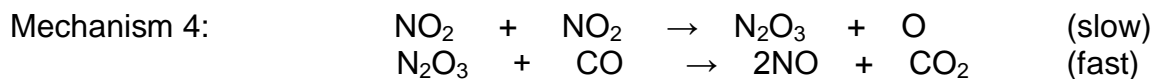
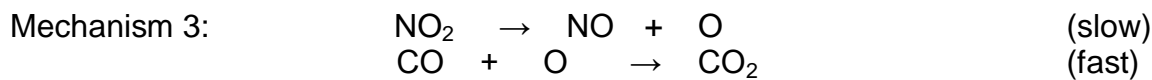
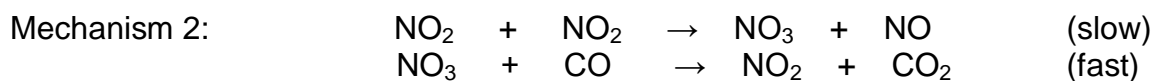
**Answer:**

**Yes, since the slow (rate-determining) step involves one molecule of  $\text{H}_2\text{O}_2$  colliding with one  $\text{I}^-$  ion.**

### Example 13



Which of the following mechanisms best agrees with the experimentally determined rate law?



**Ans: Mechanism 2**

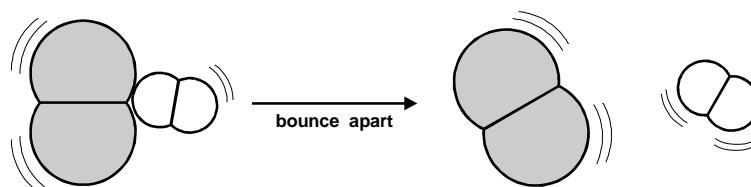
## 6 Theories of Reaction Rates

### 6.1 Collision Theory

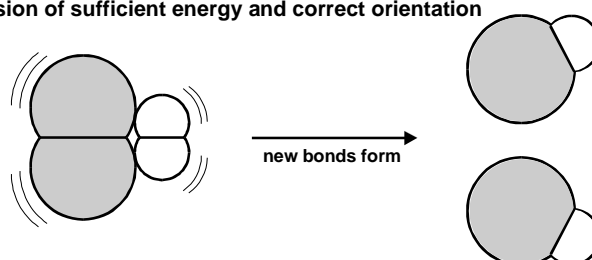
In order to react, reactant particles must **collide**:

1) with the correct orientation to each other

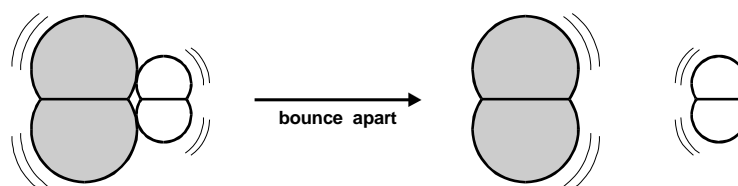
Collision of incorrect orientation



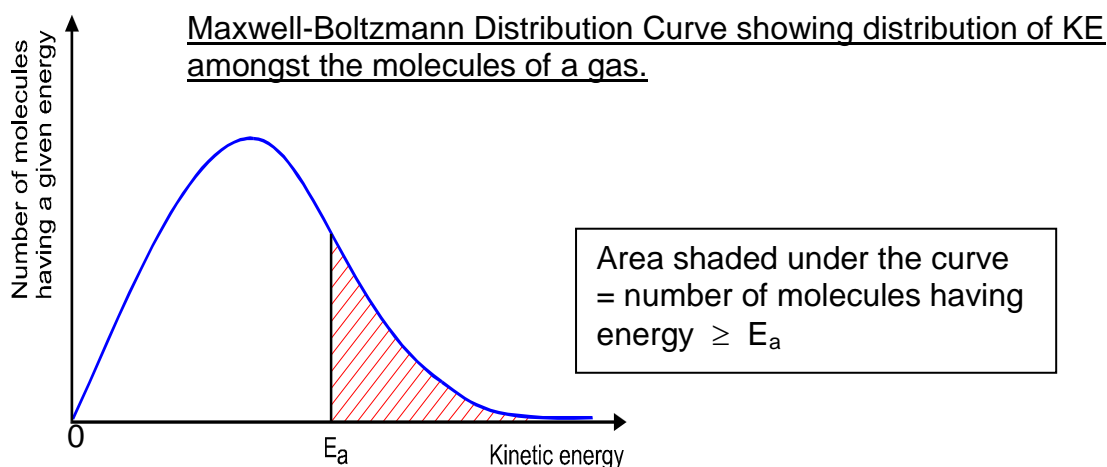
Collision of sufficient energy and correct orientation



Collision of insufficient energy



2) with a certain **minimum** amount of (kinetic) energy, known as **activation energy**,  $E_a$



**Note:** It is **INCORRECT** to draw a symmetrical Maxwell-Boltzman Distribution Curve. The curve must tail off on the **right**. This is because at any temperature, there are more molecules with extremely low energy than molecules with extremely high energy level.

**Definition**

**Activation energy,  $E_a$** , is the minimum amount of kinetic energy required for an effective collision resulting in a reaction.

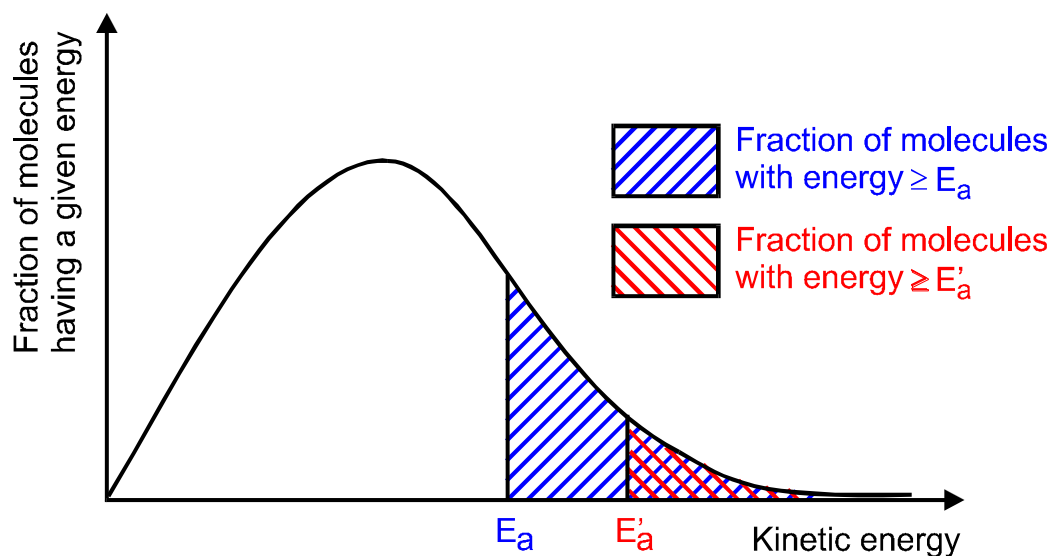
\*An effective collision is a collision with **BOTH** sufficient energy and **correct orientation**.

Hence, it is statistically unlikely for an elementary reaction to be termolecular (difficult for 3 reactant molecules to collide with **BOTH** sufficient energy and correct orientation).

Reactions with low  $E_a$  are fast at room temperature as a large proportion of molecules will have energy  $\geq E_a$ .

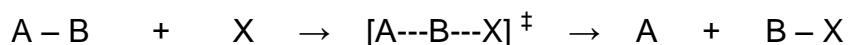
Reactions with high  $E'_a$  are slow and need higher temperature to react as a small proportion of molecules will have energy  $\geq E'_a$  at room temperature.

**At the same temperature, reaction with higher  $E'_a$  thus proceeds at a slower rate than one with lower  $E_a$ .**

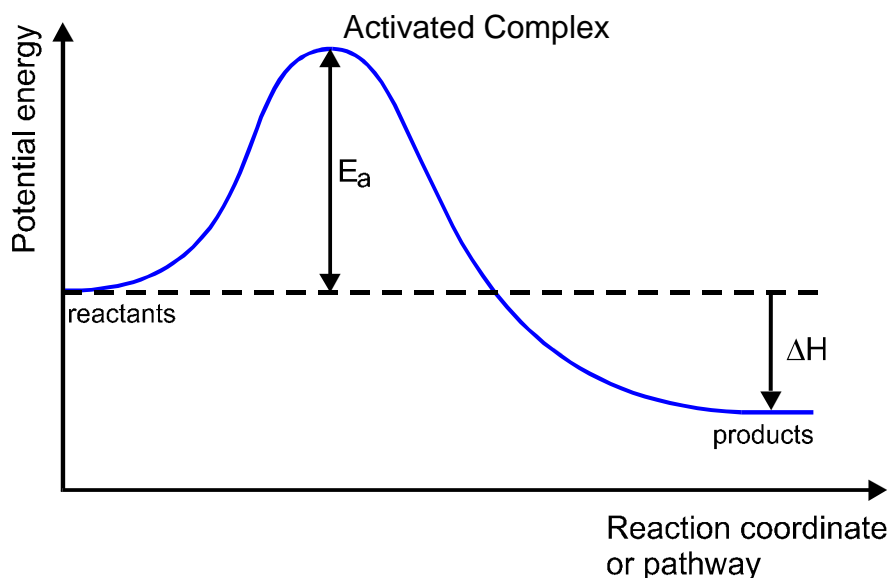
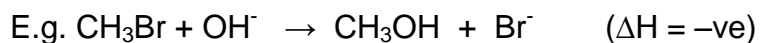


## 6.2 Transition State Theory

Reacting molecules with enough energy will form a **transition state** or **activated complex** which can then decompose to form products.

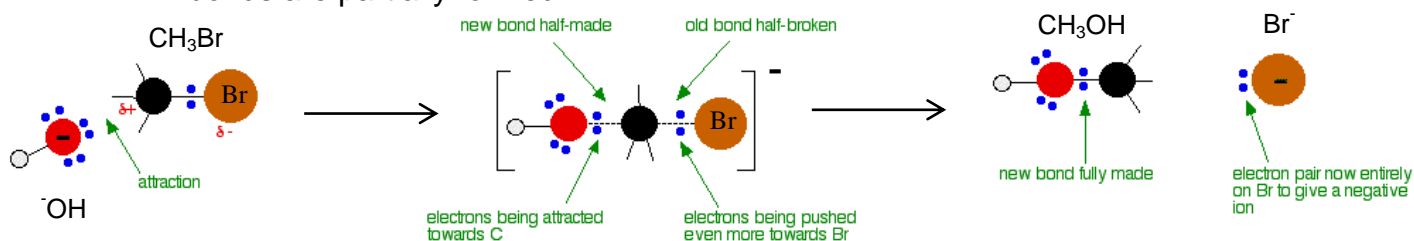


### Energy profile for a single-step reaction



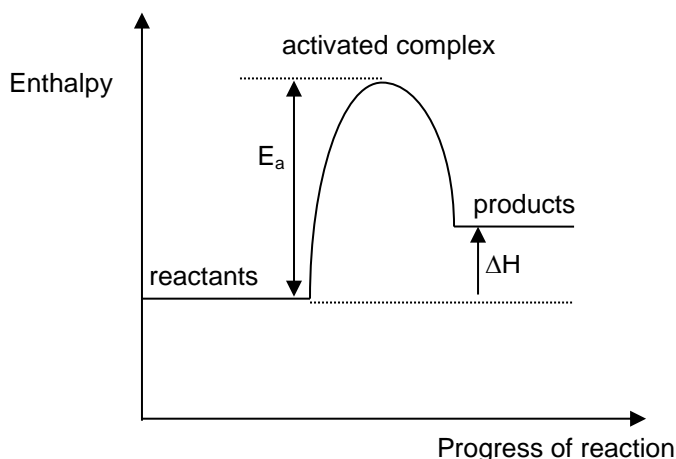
For information only:

- Reactant molecules approach each other and begin to slow down, due to mutual repulsion in their electron clouds. Kinetic energy is converted to potential energy.
- Potential energy increases until a maximum when an activated complex is formed.
- In the activated complex, the old bonds are partially broken and the new bonds are partially formed.

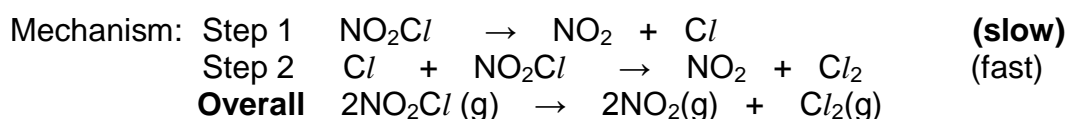
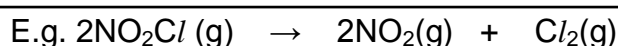
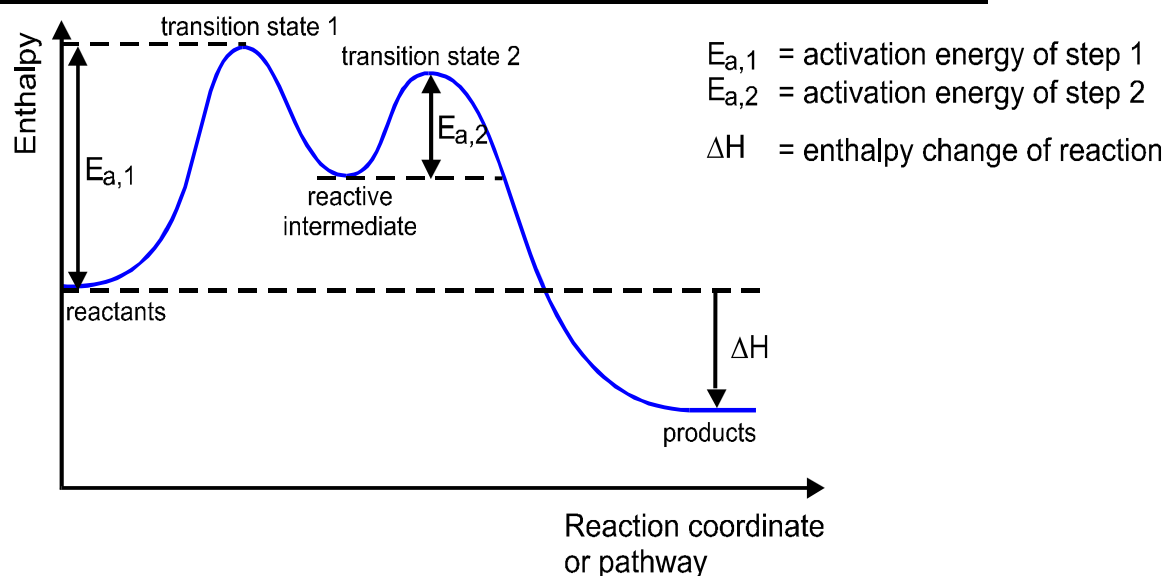


- The energy required to form the activated complex is the activation energy,  $E_a$ .  $E_a$  thus represents an energy barrier that the reactants must overcome to become products.
- Heat released in bond formation greater than heat absorbed in bond breaking. This results in exothermic reaction ( $\Delta H -ve$ )
- The activated complex
  - ✓ has the maximum energy
  - ✓ is very unstable
  - ✓ is a **transient state** - it cannot be isolated as a compound

**Example 14:** Sketch the energy profile for a single-step endothermic reaction.



**Energy profile for a reaction with multiple step reaction mechanism**



The decomposition reaction of  $\text{NO}_2\text{Cl}$  in which rate =  $k[\text{NO}_2\text{Cl}]$

Note:  $\text{Cl}$  is known as a **reactive intermediate**.

- The (reactive) **intermediate**
  - ✓ although a short-lived species, is **stable enough to be isolated**.
  - ✓ is not found in the overall reaction
  - ✓ is formed in one step and then consumed in a subsequent step
- 2 steps reaction –  $2 E_a$   
 n steps reaction –  $n E_a$
- **Activation energy** for the slow step is the **highest** amongst *all* the steps



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

## 7 Factors Affecting the Rate of a Chemical Reaction

1. Concentration of reactants
2. Temperature
3. Catalyst
4. Nature of Reactants (ions or molecules)
5. Light (photochemical reaction)

### 7.1 Effect of Concentration on Rate of Reaction

An **increase** in the **concentration** of the reactants (or pressure if the reactants are gaseous) will **increase the rate of a reaction**. (Exception: zero order reaction)

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

An **increase in concentration** leads to:

- increase in number of reacting particles per unit volume
- an increase in the number of reacting particles having energy  $\geq E_a$
- an increase in the frequency of collisions between reacting particles
- resulting in a greater number of effective collisions per unit time
- an increase in rate of reaction

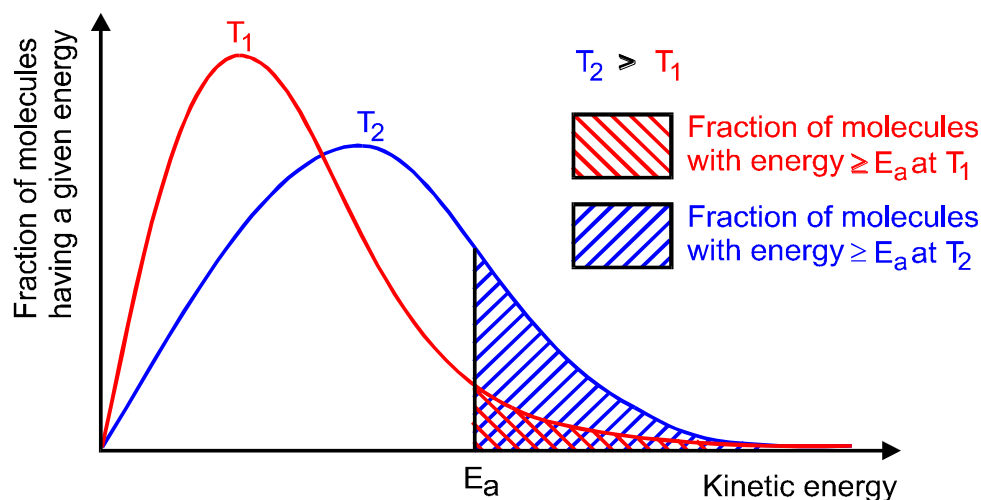
### 7.2 Effect of Temperature on Rate of Reaction

The rate of a reaction increases **exponentially** with increase in temperature.

Rate of reaction approximately **doubles** for a **10K** rise in temperature.

When temperature is increased, there is:

- an increase in the average kinetic energy of the particles, resulting in,
- an increase in the number of reacting particles with energy  $\geq E_a$
- an increase in the frequency of collisions between reacting particles
- resulting in a greater number of effective collisions per unit time
- an increase in rate of reaction



**Note:** At higher temperature  $T_2$ , the curve shifts right with a lower peak since **average kinetic energy** of particles **increase**. The **total number of particles** (area under the curve) remains the **same**.

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

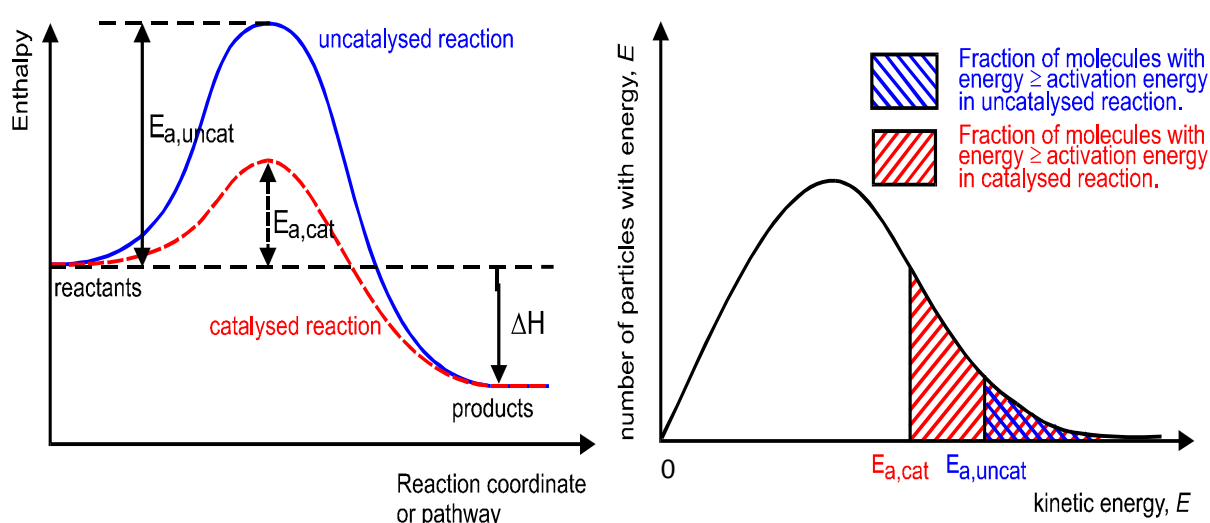
### 7.3 Effect of Catalyst on Rate of Reaction

#### Definition 6 – Catalyst

A **catalyst** is a substance which **alters** (generally increases) the rate of a chemical reaction while remaining chemically unchanged at the end of the reaction. Hence, it is not consumed in the reaction and only a small amount is needed.

A catalyst:

- increases the rate of a chemical reaction (positive catalyst).
- provides an **alternative reaction pathway** with a **lower activation energy**.



Hence, when a catalyst is used in a reaction, it:

- increases the rate of the reaction by providing an alternative reaction pathway with lower activation energy
- increases the number of reacting particles with energy  $\geq E_a$
- (there is **NO** increase in frequency of collisions between reacting particles!)
- increases the number of effective collisions per unit time
- increases the rate of reaction

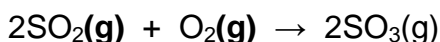
**Note:** The **enthalpy change of reaction,  $\Delta H$** , is **not affected** by the presence of a catalyst.

- (j) outline the different modes of action of homogeneous and heterogeneous catalysis, including :
- the Haber Process
  - the catalytic removal of oxides of nitrogen in the exhaust gases from car engine
  - the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulphur dioxide
  - catalytic role of  $\text{Fe}^{3+}$  (or  $\text{Fe}^{2+}$ ) in the  $\text{I}^-/\text{S}_2\text{O}_8^{2-}$  reaction

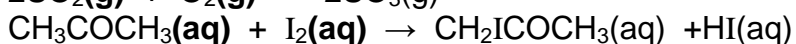
#### 7.3.1 Homogeneous Catalyst (Covered in greater detail in Transition Elements)

A **homogeneous** catalyst is in the **same phase** as the **reactants**.

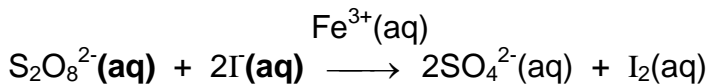
Examples:



Catalyst :  $\text{NO}(\text{g})$



Catalyst :  $\text{H}^+(\text{aq})$

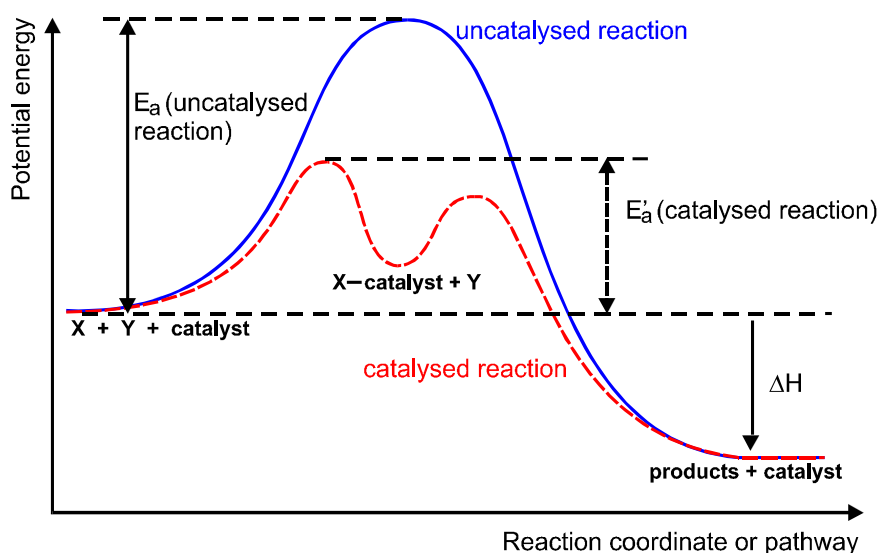
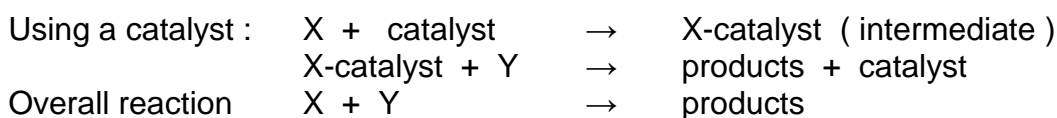


Catalyst:  $\text{Fe}^{3+}(\text{aq})$

### Mechanism:

**Homogeneous catalyst is converted into an intermediate and is then regenerated at the end of the reaction**

Consider the elementary reaction  $\text{X} + \text{Y} \rightarrow \text{products}$



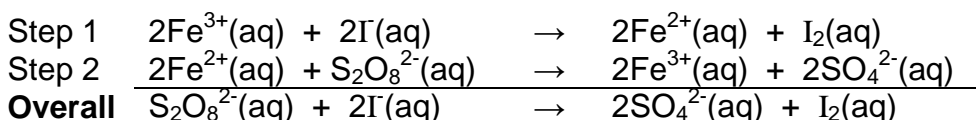
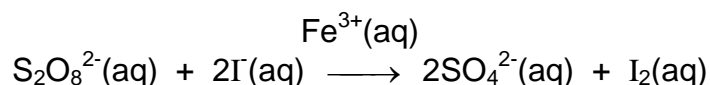
### Note:

The catalysed reaction has an **alternative** reaction mechanism from that of the uncatalysed reaction.

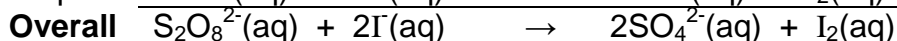
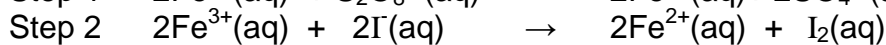
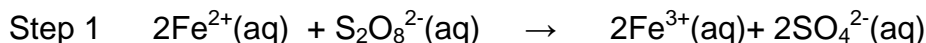
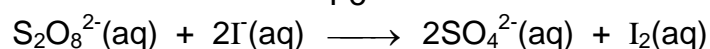
The catalysed reaction can have 2 or more steps. The activation energy of **each** of these steps is **lower than** that of the **uncatalysed** reaction.

Examples:

Oxidation of  $\text{I}^-$  by  $\text{S}_2\text{O}_8^{2-}$  catalysed by  $\text{Fe}^{3+}$



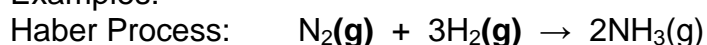
### Oxidation of $I^-$ by $S_2O_8^{2-}$ catalysed by $Fe^{2+}$



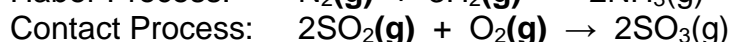
### 7.3.2 Heterogeneous Catalyst (Covered in greater detail in Transition Elements)

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

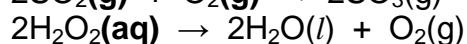
Examples:



Catalyst : Fe (s)



Catalyst :  $V_2O_5$  (s)



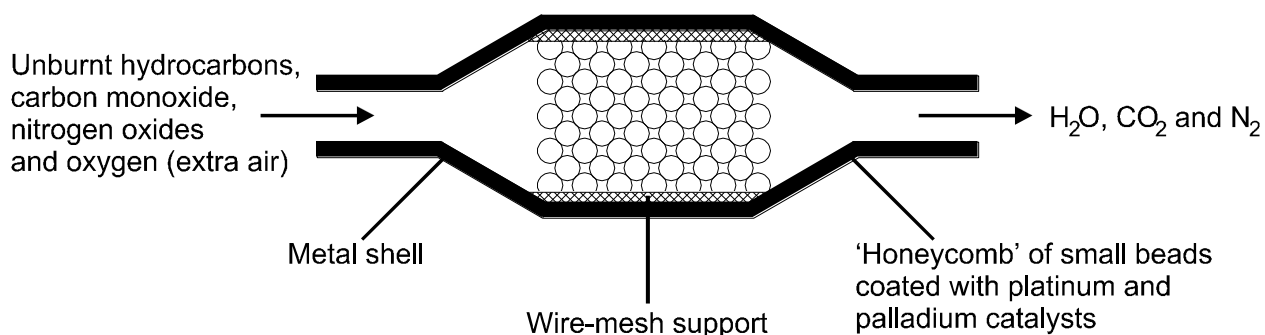
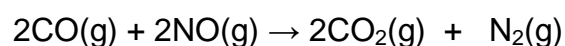
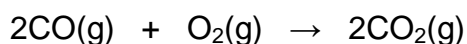
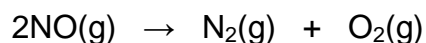
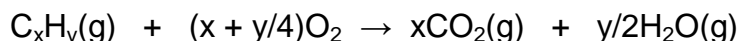
Catalyst :  $MnO_2$  (s)

Heterogeneous catalysts

- normally transition metals or their compounds
  - provide a surface area for the **adsorption**\* of reactant molecules.
- \*Adsorption: The reactants are first adsorbed onto the surface of the catalyst, the metal chosen must adsorb the reactants easily but not so strongly that the products do not come off again.
- Reaction: the reactants are held on the surface in such a position that they can readily react together.
- Desorption: the products leave the surface.

### Catalytic removal of pollutant gases in exhaust gas of cars

Unburnt hydrocarbons, carbon monoxide and oxides of nitrogen are present in exhaust gases, causing environmental pollution. Catalytic converters are fitted in cars to convert these gases into carbon dioxide, water and nitrogen.



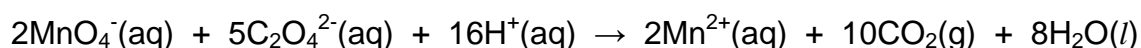
Lead, if present, in petrol is adsorbed on the catalytic surface containing Pt and Pd and decreases the number of active sites for the **adsorption** of reactant molecules. The catalyst is said to be poisoned and no longer functions as a catalyst.

Cars fitted with **catalytic converters** must use lead-free petrol.

### 7.3.3 Autocatalysis

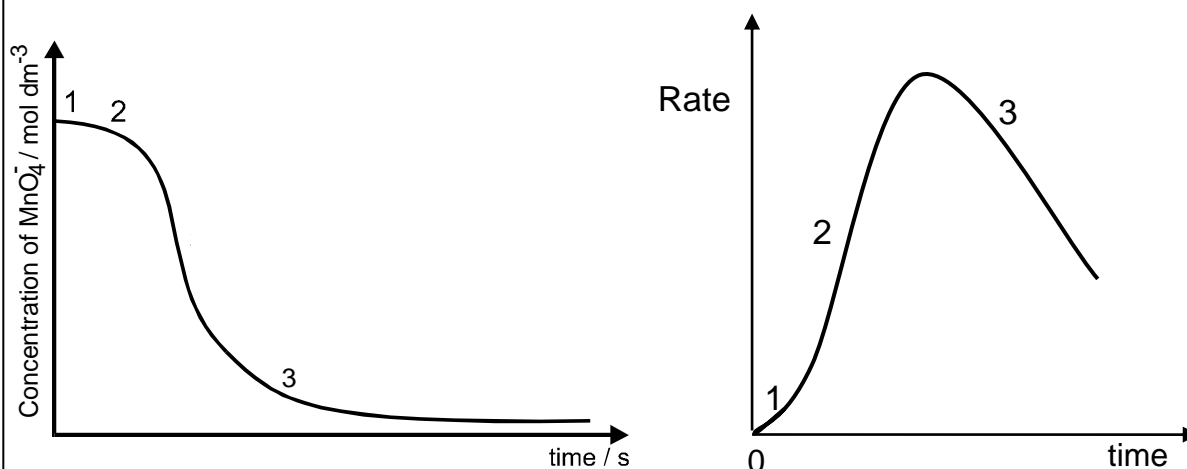
**Autocatalysis** is a type of catalysis whereby **one of the products** of the reaction catalyses the reaction.

E.g. Reaction between manganate(VII) ions and acidified ethanedioate ions:



The  $\text{Mn}^{2+}$  ions formed acts as a catalyst for the reaction.

1. The rate of reaction is **slow** at the beginning of the reaction.
2. As the reaction proceeds,  **$[\text{Mn}^{2+}]$  increases**. The rate of reaction **increases**.
3. The **rate** of reaction will eventually **decrease** as **[reactants] decreases** to very low levels despite the increasing concentration of the  $\text{Mn}^{2+}$  catalyst.



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

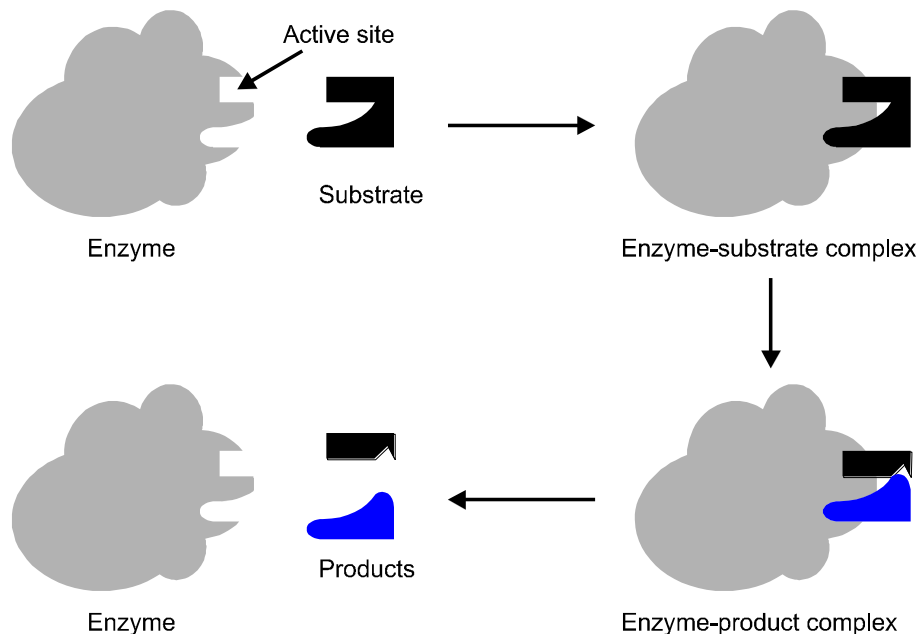
### 7.3.4 Biological Catalysts (Enzymes)

Enzymes are:

- essentially **proteins** which catalyse reactions in living organisms
- highly specific as each enzyme has an **active site** which **only one type of substrate of matching shape and size can fit into**
- regenerated during their catalytic activities and are **highly efficient**

### Mechanism (Lock and key):

An enzyme-substrate complex is formed and this weakens the **intramolecular bonding** within the substrate, **lowering** the **activation energy**. The products are no longer of the right shape to remain in the active site and the complex breaks up, releasing the products and freeing the enzyme for further catalytic reaction.

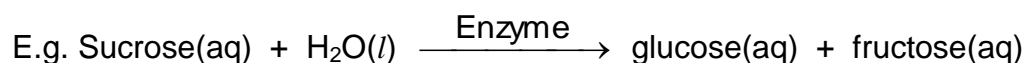


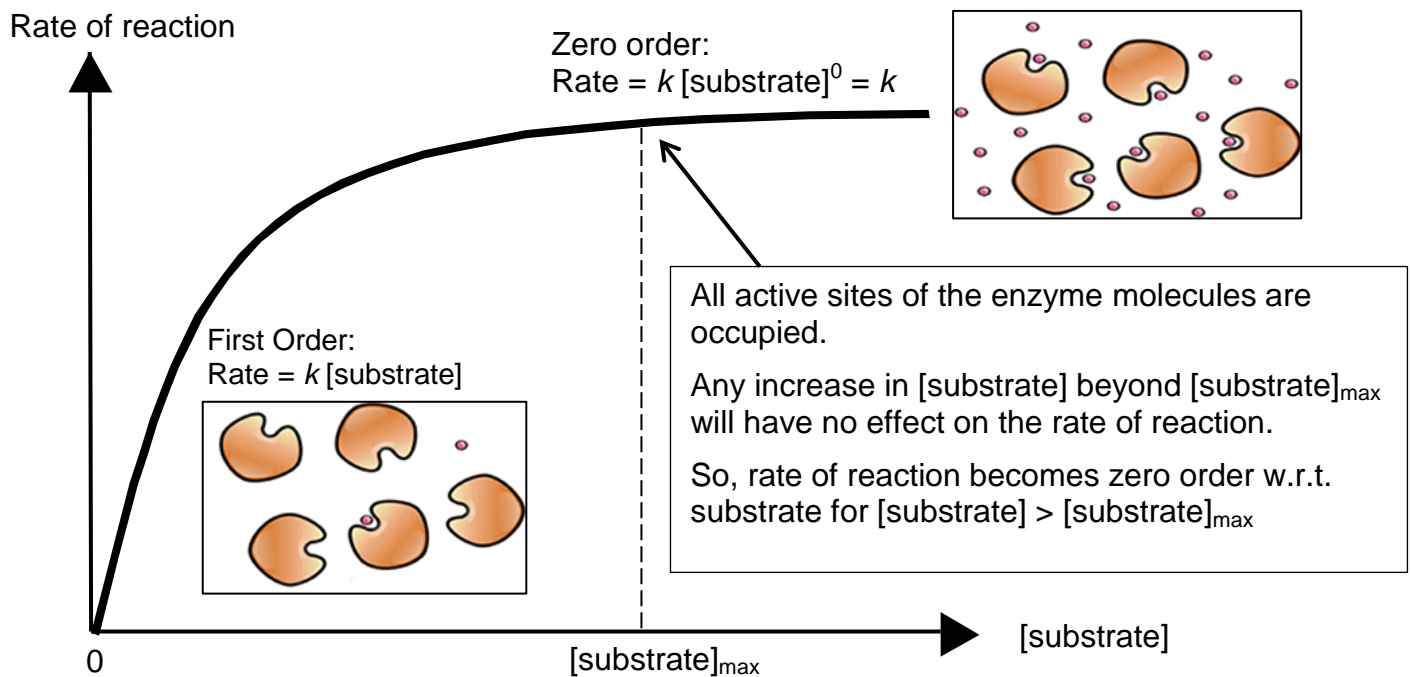
- (1) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

### Factors affecting enzymic activities:

#### (a) **Substrate (reactant) concentration**

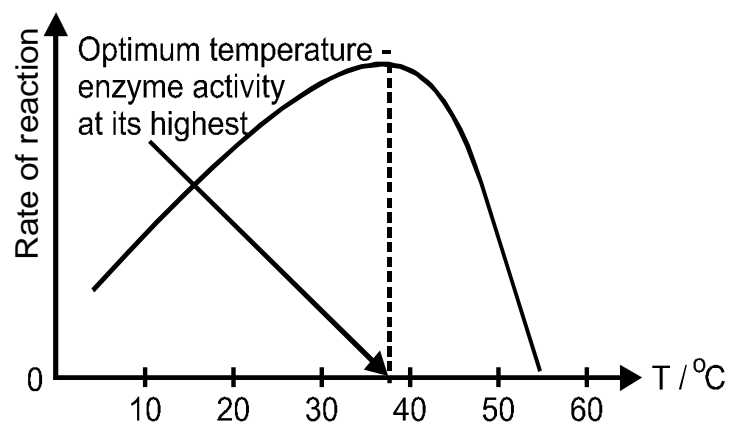
- The rate of enzyme-catalysed reaction increases with substrate concentration (reaction is **first order** with respect to the substrate) until a maximum when all the active sites of the enzyme molecules are occupied.
- Further increase in substrate concentration does not increase the rate of reaction and the reaction becomes **zero order** with respect to the substrate.





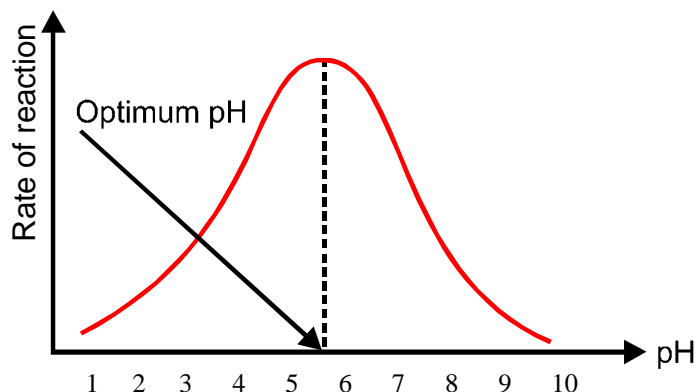
## Temperature

- Enzymes work well over a narrow temperature range (about 25°C – 40°C).
- At a **higher temperature**, the protein structure of the enzyme is **denatured** and the enzyme loses its catalytic property.



## (c) pH

- Enzymes work well over a narrow pH range (about 5 – 8).
- The rate of an enzyme-catalysed reaction reaches a maximum value at a particular pH (optimum pH) which is characteristic of that enzyme.



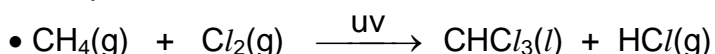
## 7.4 Effect of Physical Nature of Reactants on Rate of Reaction

- Generally, **reactions involving oppositely charged ions can proceed at a high rate:**  
e.g.  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
- For reactions involving solids, **the larger the total surface area, the greater will be the number of effective collisions per unit time** (i.e. faster rate of reaction).  
E.g. powdered  $\text{CaCO}_3$  reacts much faster with acid than lumps of it.
- Many organic reactions are generally slow as covalent bonds need to be broken and rearranged to form products. E.g. esterification reaction.

## 7.5 Effect of Light on Rate of Reaction

- Light **increases** the rate of **photochemical** reactions (reactions that absorb light).
- Such reactions are slow in the dark but the rate can be increased by raising the temperature or by illumination with visible light or ultra-violet and usually involve **radicals** (species with unpaired electron(s)).
- Reaction becomes fast once it is initiated leading to a chain reaction.

Examples:



- Destruction of ozone by CFCs (CFC molecules broken up by uv to form  $\text{Cl}\bullet$ )