CHEMICAL KINETICS

Chemical kinetics is the study of rates of reaction and factors affecting rates of reaction.

Rates of reaction

Is the *rate of change in concentration of one of the products or reactants*.

Rate of reaction decreases as the reaction proceeds and the reactant is gradually used up.

Consider a reaction A $\longrightarrow$ B;

Rate of decrease in concentration of A $= -\dfrac{d[A]}{dt}$

Rates of increase in concentration of B $= \dfrac{d[B]}{dt}$

Units of reaction rates is **concentration per time** e.g. moles per dm^3 per second $(moldm^{-3}s^{-1})$

The rate at the start of the reaction, when an infinitesimally small amount of the reactant has been used up is called the **initial rate.**

Variation of concentration of reactants and products with time

## Variation of concentration of reactants and products with time

Time(s)
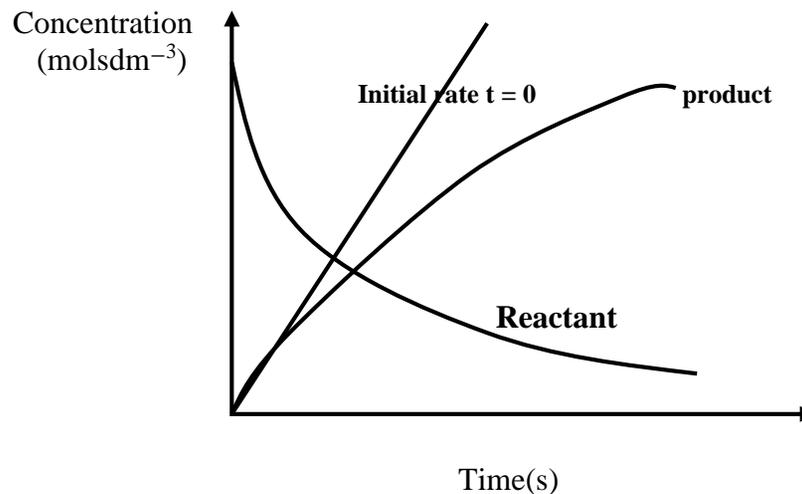
Initial rate of reaction can be obtained by finding the slope/ tangent to the curve at time, t = 0.

METHODS OF FINDING THE RATES OF CHEMICAL REACTIONS

a) **Chemical analysis**
- Here, the reaction is carried out in a thermostatically controlled water bath.
- Solutions of the reactants of known concentration are mixed and a stop clock started.
- A sample of a reaction mixture is withdrawn with a pipette and the reaction is stopped/ quenched by either cooling or dilution into a freezing mixture or into an excess of solvent.

- Titration is performed to find the concentration of one of the reactants or products. E.g. oxidation of Iodide to Iodine by hydrogen peroxide.

$$H_2O_2 \text{ (aq)} + I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow I_2 \text{ (aq)} + 2H_2O \text{ (}l\text{)}$$
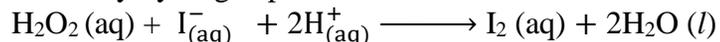
- Solutions of hydrogen peroxide, acid and Iodine of known concentrations are allowed to reach the temperature of the thermostat bath.
- Solutions are mixed and the time of mixing noted.
- At measured time intervals, sample of reaction mixtures are extracted by pipette.
- Reaction in each sample is quenched by diluting in ice cold water.
- Each sample is titrated against standard aqueous sodium thiosulphite and the concentration of Iodine is calculated.

b) **Electrical conductivity:**
- Conductivity of a reaction mixture may be monitored overtime by carrying out the reaction in a conductivity cell.
- Conductivity apparatus is calibrated with solutions of known concentration
- Conductivity of a solution is proportional to the concentration of its ions and the charges they bear.
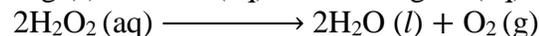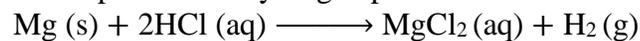
c) **Colorimetry**
- Applicable to reaction mixtures that show a steady colour as the reaction as the proceeds.
- Colorimeter indicates concentration by measuring the intensity of light shining through a coloured reaction mixture.
- Photocell is calibrated with solutions of known concentrations
- Light of fixed wavelength is directed through the reaction mixture and into the photocell.

- Photocell develops an emf proportional to the intensity of the light.
- Emf can then be converted to concentration values.

d) **Change in gas volume:**

- For reactions involving gases, the rate of reaction may be monitored by measuring the volume of gas evolved after various time intervals.
- The measured volume of gas may then be used to calculate the corresponding concentration of the reactant. e.g. reaction of a metal with acid and the decomposition of hydrogen peroxide.

$$Mg \text{ (s)} + 2HCl \text{ (aq)} \longrightarrow MgCl_2 \text{ (aq)} + H_2 \text{ (g)}$$
$$2H_2O_2 \text{ (aq)} \longrightarrow 2H_2O \text{ (}l\text{)} + O_2 \text{ (g)}$$

a) **Change in pressure**
- An increase or decrease in gaseous pressure can be used to follow many gaseous reactions e.g.

  i. The reaction: $N_2O_5 \text{ (g)} \longrightarrow N_2O_4 \text{ (g)} + \frac{1}{2} O_2 \text{(g)}$

- It involves an increase in the number of moles of gas and an increase in pressure can be followed.

  ii. The reaction: $H_2 \text{ (g)} + O_2 \text{ (g)} \longrightarrow H_2O \text{ (}l\text{)}$ is accompanied by a decrease in the number of moles, and decrease in pressure at constant volume.

b) **Spectrophotometry**
- Applicable for the reactions which are extremely rapid.
- Uses a very short burst of light from a laser to start reaction that is sensitive to light.
- Spectroscopic techniques then monitor the concentration of the reactive intermediate formed.

SOME COMMON TERMS

i. **Rate law:**
- States that, "*the rate of any chemical reaction at a constant temperature is directly proportional to the molar concentration of the reactants raised to appropriate power whose value is experimentally determined*."
- It summarises the relationship between rate of a chemical reaction and the concentration of the reactants.

ii. **Rate equation:**
- Expresses the rate of reaction in terms of the concentration of each reactant raised to a specific power. Consider a reaction $A + B \longrightarrow$ Products
From Rate law; Rate $\propto [A]^x[B]^Y$ Rate $= k [A]^x[B]^Y$

Where k = rate constant/ coefficient

X = order of reaction with respect to A

Y = Order of reaction with respect to B

iii. **Rate constant / Rate coefficient:**
Is the ratio of the rate of a chemical reaction to the products of the concentration of the reactants raised to appropriate powers as in the rate equation.
Units vary according to the overall order i.e.
From Rate $= k [A]^x[B]^Y$
$K = \dfrac{Rate}{[A]^x[B]^Y}$

iv. **Order of reaction**
Is the power to which the concentration terms are raised in the experimental rate equation

v. **Overall order equation**
Is the sum of the powers to which the concentration terms are raised in the experimental rate equation.
From Rate $= k [A]^x[B]^Y$
Overall order $= x + y$

vi. **Molecularity of a reaction:**
Is the total number of species (ions/ molecules) involved in a particular reaction i.e the number of species involved in the rate determining step for those reactions occurring in stages.

Difference between molecularity and order of a reaction

Molecularity	Order of equation
• Only whole numbers and is never zero	Can be a fraction, zero or a whole number
• Determined from a Stoichiometric equation	Experimentally determined
• Number of species that take part in the rate determining state	Power to which the concentration of the reactant is raised in the experimental rate equation

vii. **Rate determining step/Rate limiting step:**
Is the slowest step in a multi step chemical reaction through which the reactants are converted to the products.

viii. **Elementary reactions:**
These are reactions that involve one step path or route from reactants to products.

For elementary reactions, molecularity is equal to the order of reaction.

However, the reactions which are not elementary, molecularity may not be equal to order of reaction. E.g. in hydrolysis of a reactant such as ester/ sucrose in presence of a large excess of water.

Consider hydrolysis of sucrose;

Sucrose + water $\longrightarrow$ Glucose + Fructose

$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Molecularity of above reaction is two because both sucrose and water are involved in the rate determining step.

However, the overall order of this reaction is *first order* when experimentally determined.

Reason

- Water is present in large excess, its concentration remains unaffected and hence doesn't contribute to the order of the reaction.
- Only sucrose concentration changes during the course of a reaction, affecting the rate of reaction with an order one.

NB: *Such reactions where water is in excess making its concentration zero is referred to as pseudo – first order reaction*.

DETERMINATION OF ORDER OF REACTION FROM INITIAL RATE METHOD

In this method, the order of reaction with respect to a given reactant is determined by comparing the initial rate for the experiments in which the concentration of only the reactant whose order of reaction is to be determined is changing while the other reactant concentrations are kept constant.

It therefore requires more than one reactant.

For zero order reaction;
- ✓ the rate of reaction is not affected by change in initial concentration of the reactant e.g. doubling the concentration of the reactant has no effect on the rate.

For all 1st order reactions;
- ✓ doubling the initial concentration of the reactant also doubles the rate,
- ✓ Trebling it also trebles the rate i.e. increasing the concentration of reactant by factor y also increases the rate by some factor y.

For second order reactions;
- ✓ doubling or trebling initial concentration of the reactant increases the rate by 4 or 9 times respectively.

Example:
The result shown refers to oxidation of Bromine ion by Bromate ion in acidic solution.

$5Br^-$ (aq) + BrO_3^- (aq) + $6H^+$ (aq) $\longrightarrow$ $3Br_2$ (aq) + $3H_2O$ (l)
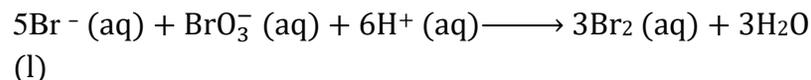
[5Br⁻](mol dm⁻³)	BrO_3^- (mol dm⁻³)	H⁺(mol dm⁻³)	Initial rate (mol dm⁻³)
i. 0.10	0.10	0.10	8×10^{-4}
ii. 0.10	0.20	0.10	1.6×10^{-3}
iii. 0.20	0.20	0.10	3.2×10^{-3}
iv. 0.10	0.10	0.20	3.2×10^{-3}

a) Find the order of the reaction with respect to Br^-, BrO_3^-, H^+
b) State the overall order of reaction
c) Write the rate equation
d) Calculate the value of rate constant and state its units.
e) Calculate the rate reaction when concentration of all three reactants is $0.2 mol\ dm^{-3}$

Solution

 a) (i) Br^-

Let the order of the reaction with respect to Br^- be **x**

Let the order of reaction with respect to **BrO_3^-** be **y**

Let the order of reaction with respect to H⁺ be z

Taking experiments (ii) and (iii)

$Rate = K[Br-]^X [Br_3^-]^y [H^+]^z$

$1.6 \times 10^{-3} = K [0.10]^x[0.2]^y [0.10]^z$ ------------------------ (i)

$3.2 \times 10^{-3} = K [0.2]^x[0.2]^y[0.1]^z$ _____ (ii)

  Dividing equation (ii) by (i)

$\dfrac{3.2 \times 10^{-3}}{1.6 \times 10-3} = \dfrac{K[0.2]^x[0.2]^y[0.1]^z}{K [0.10]^x[0.2]^y [0.10]^z}$

$\dfrac{3.2 \times 10^{-3}}{1.6 \times 10-3} = \left(\dfrac{0.2}{0.1}\right)^X$

$2^1 = 2^x$

X = 1

Order of reaction with Br⁻ is 1

Reason:

Doubling the concentration of Br^- doubles the initial rate

(ii) BrO_3^-

Taking experiments (i) and (ii)

$Rate = K[Br-]^X [Br_3^-]^y [H^+]^z$

For (i); $8 \times 10^{-4} = K [0.1]^X [0.1]^y [0.1]^z$ _____(i)

For (ii); $1.6 \times 10^{-3} = K[0.1]^X [0.2]^y [0.1]^z$ _____(ii)

  Dividing equation (ii) by (i)

$\dfrac{1.6 \times 10-3}{8 \times 10-4} = \dfrac{K[0.1]^X [0.2]^y [0.1]^z}{K [0.1]^X [0.1]^y [0.1]^z}$

$\dfrac{1.6 \times 10-3}{8 \times 10-4} = \left(\dfrac{0.2}{0.1}\right)^y$

$2^1 = 2^y$

Y = 1

The order of reaction with respect to BrO_3^- is 1

Reason:

Doubling the concentration of BrO_3^- doubles the rate.

(iii)   H⁺

  Taking experiment (i) and (iv)

$Rate = K[Br-]^X [Br_3^-]^y [H^+]^z$

For (i); $8 \times 10^{-4} = K [0.1]^X [0.1]^y [0.1]^z$ _____ (i)

For (iv): $3.2 \times 10^{-3} = K [0.1]^x[0.1]^y[0.2]^z$ _____(ii)

Dividing (ii) by (i)

$$\frac{3.2 \times 10^{-3}}{8 \times 10^{-4}} = \frac{K[0.1]^x[0.1]^y[0.2]^z}{K[0.1]^x[0.1]^y[0.1]z}$$

$4 = 2^z$

$2^2 = 2^z$

Z = 2; Order of reaction with respect to H+ is 2

Reason;

Doubling the reaction with respect to H+ rate increases by factor four (4) (rate quadruples)

b) Rate = $K[Br-]^1 [Br_3^-]^1 [H^+]^2$
   Overall order = 2 + 1 + 1 = 4
c) Rate = $K[Br-]^1 [Br_3^-]^1 [H^+]^2$
d) From rate = $K[Br-]^1 [Br_3^-]^1 [H^+]^2$

$$K = \frac{\text{Rate}}{[Br-]^1 [Br_3^-]^1 [H+]2} =$$

$$\frac{3.2 \times 10{-3} \; (\text{mol dm}{-3})}{(0.2)(0.2)(0.1)^2 \; (\text{mol dm}{-3})(\text{mol dm}{-3})(\text{mol dm}{-3})}$$

$$= 8 \text{mol} - 3 \, dm^4 s^{-1}$$

e) Rate = $8 (0.2)(0.2) (0.2)^2$
   = 0.0128mol dm⁻³s⁻¹

Example

2. For the reaction A + B ⟶ C, the following results were obtained for kinetic run at the same temperature.

[A](mol dm⁻³)	[B] (mol dm⁻³)	Initial rate (mol dm⁻³s⁻¹)
0.20	0.10	0.2
0.40	0.20	0.8

0.40	0.20	0.8

Find:

a) Rate equation of reaction
b) Rate constant
c) Initial rate of reaction when [A] = 0.6moldm⁻³ and [B] = 0.3 moldm⁻³

Solution:

a) Doubling the concentration of **A** quadruples the rate giving order 2.
   For B, doubling the concentration has no effect on rate hence zero order.
   Rate = k [A]²

(b) $K = \frac{\text{rate}}{[A]^2} = \frac{0.20}{(0.20)^2} = $ **5 mol⁻¹dm³s⁻¹**

(c) Rate = $k [A]^2[B]^0$

$= 5[0.6]^2$
= 1.8 mol dm⁻³s⁻¹

Exercise

1. The table below shows some data for the reactions;

[A](mol dm⁻³)	[B] (mol dm⁻³)	Initial rate (mol dm⁻³s⁻¹)
1.00 × 10⁻²	2.8 × 10⁻³	2.2
5.00 × 10⁻³	2.8 × 10⁻³	1.1

1.00 × 10^{-2}	5.6 × 10^{-3}	4.4

a) Determine the order of reaction with respect A and B, giving reasons for your answers.
b) Write the rate equation of reaction
c) Calculate the rate constant and find its unit
d) Calculate the rate reaction when concentration of A and B is A = 8.5 × 10^{-3} moldm^{-3}, B = 3.83 × 10^{-3} moldm^{-3}

2. 2 – Bromo – 2 – methylpropane, $(CH_3)_3CBr$ and NaOH react together according to the following equation

$(CH_3)_3CBr + \bar{O}H \longrightarrow (CH_3)_3COH + Br^-$

The following data gives the results of three experiments used to determine the rate equation from the reaction at 25°C.

Experiment	Initial $(CH_3)_3CBr$ (moldm^{-3})	Initial $[\bar{O}H]$ (moldm^{-3})	Initial rate of reaction (moldm^{-3})
1	1.0 × 10^{-3}	2.0 × 10^{-1}	3.0 × 10^{-3}
2	4.0 × 10^{-3}	2.0 × 10^{-1}	6.0 × 10^{-3}
3	5.0 × 10^{-3}	4.0 × 10^{-1}	6.0 × 10^{-3}

From these results, it can be deduced that the rate equation is;

Rate = K $[(CH_3)_3CBr]$

i. Show how the data can be used to determine/ deduce that the reaction is 1st order with respect to $(CH_3)_3CBr$ and zero order with respect to $\bar{O}H$.

ii. Calculate the value of the rate constant at this temperature and state its units.
iii. Calculate the initial rate of reaction when the initial concentration of $(CH_3)_3CBr$ is 4.0 × 10^{-3} moldm^{-3} and the initial concentration of $\bar{O}H$ is 1.0 × 10^{-1} moldm^{-3}

b) Name and outline a mechanism for the reaction of tertiary haloalkane $(CH_3)_3CBr$ with aqueous NaOH.

CLASSIFICATION OF CHEMICAL REACTIONS ACCORDING TO OVERALL ORDER

Zero Order Reactions

- Rate of reaction is independent of the concentration of the reactant
- The rate equation for the zero order reaction is given by;
  Rate = K $[A]^0 \Rightarrow$ Rate = K (constant)
  Where A is a constant in the determining step.
  A plot of rate of reaction against concentration of reactant

Rate

Concentration of reaction
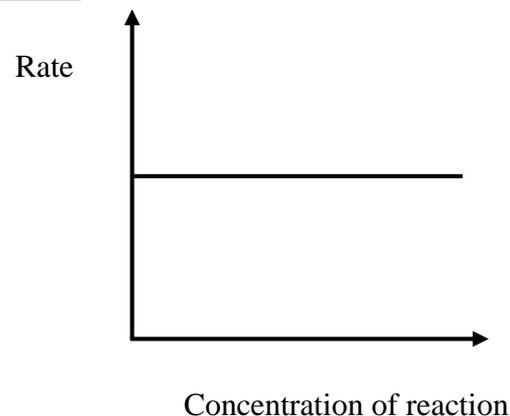
From Rate $= -\dfrac{d[A]}{dt} = K[A]^O$

$$= -\dfrac{d[A]}{dt} = K$$

$$-d[A] = Kdt$$

Integrate from A_0 at $t = 0$ to A_t at time $t = t$
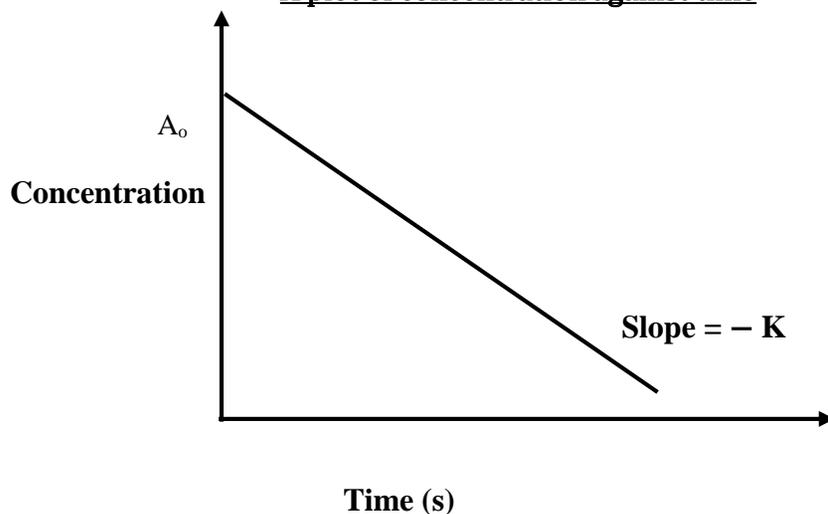
$$-\int_{A0}^{At} d[A] = K\int_{t=0}^{t=t} dt$$

- $[A]\Big|_{A0}^{At} = Kt\Big|_{t=0}^{t=t}$
- $A_t - (-A_0) = Kt$
- $A_t + A_o = Kt$

$A_t = -Kt + A_0 \quad (y = mx + c)$

A plot of concentration against time

Examples of zero order reactions

✓ *Iodination of Propanone*; in which the reaction is zero order with respect to Iodine.
✓ *Reactions between gases*; where rate of reaction with respect to one of the reactants is zero order; indicating that this reactant has been adsorbed on the surface of the vessel and the rate only depends on the frequency of collision between the non adsorbed gas with the inside of the vessel e.g. decomposition of NH_3 (g) to Nitrogen and Hydrogen in the presence of a hot tungsten wire.

### Experiment: To determine order of reactions with respect to Iodine in the Iodination of propanone catalysed by H_2SO_4

Procedure:

- Fixed volumes of propanone and sulphuric acid are measured into a clean flask.
- A fixed volume of standard solution of iodine is then added to the flask. The time at which the iodine is added is being noted.
- After a few minutes, a sample of the reacting mixture is pipetted into a conical flask and added a solution of Sodium hydrogen Carbonate solution to stops the reaction instantly by neutralizing the acid.
- The time at which the reaction stops is noted.
- The resultant mixture is then titrated with a standard solution of Sodium thiosulphite to determine the amount of Iodine that remains.
- The procedure is repeated at intervals of 5 minutes to determine the amount of Iodine that has remained.
- Initial concentration of iodine is determined

- Since titre values at various times will be proportional to the concentration of iodine left at those times, a plot of volume of thiosulphite against the time elapsed since the start of reaction, gives a straight line from which the value of rate constant(K) can be determined.

A plot of volume of Sodium thiosulphite against time
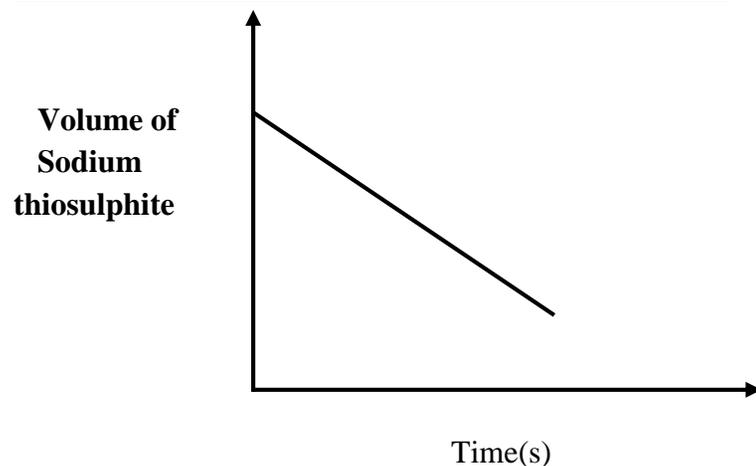
Rate of the reaction remains constant as the iodine concentration decreases.

Example (QUIZ)

a) Describe an experiment to show Iodination of Propanone follows a zero order reaction with respect to Iodine.

b) Propanone reacts with Iodine in the presence of an acid catalyst according to the equation

$$CH_3COCH_3 \text{ (aq)} + I_2 \text{ (aq)} \xrightarrow{\quad H+ \quad} CH_3COCH_2I + HI$$
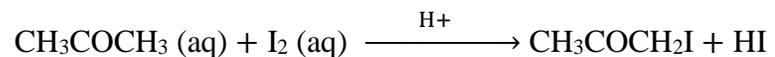
The reaction is first order with respect to Propanone and independent of the concentration of Iodine. Briefly describe how the order of reaction with respect to Iodine can be determined.
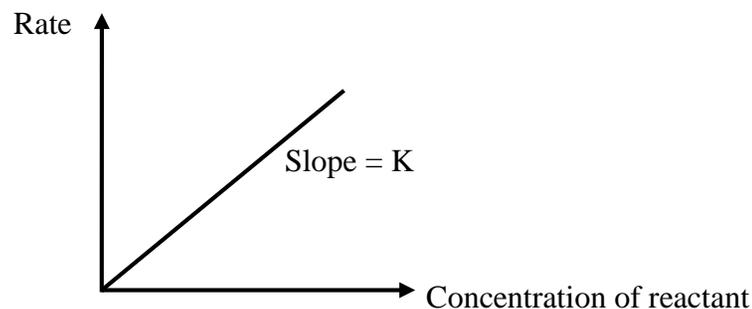
2. **First Order Reactions**

- Rate of reaction is proportional to the first power of concentration of single reactants.
- Consider a reaction, $A \longrightarrow$ products

$$Rate = -\frac{d[A]}{dt} = K\,[A]^1$$

Rate = k [A], from y = mx + c, c = 0

A graph of rate against concentration of reactants

Examples of first order reactions

- Hydrolysis of sucrose in presence of acid.
- Acid catalysed hydrolysis of an ester.
- Radioactive decay
- Decomposition of nitrogen pentaoxide, N_2O_5
- Decomposition of Benzene diazonium chloride.

Radioactive decay and half life

Half life:

Is the time taken for the concentration to fall to half its original value.

Rate of reaction $= -\dfrac{d[A]}{dt} = K[A]$

Separating variables;

$-\dfrac{d[A]}{[A]} = K\,dt$

Integrating between the limits A_o at times $t = 0$ to A_t at $t = t$

$-\int_{Ao}^{At} \dfrac{d[A]}{[A]} = k\int_{t=0}^{t=t} dt$

$-\ \ln[A]\ \begin{vmatrix} At \\ Ao \end{vmatrix} = kt\ \begin{vmatrix} t=t \\ t=0 \end{vmatrix}$

$-\ \ln A_t - (-\ \ln A_0) = kt$

$\ln\left(\dfrac{Ao}{At}\right) = kt$

But $\ln = 2.303\log_{10} \Longrightarrow \boxed{2.303\log\dfrac{Ao}{At} = kt}$ --------- (i)

At $t = t_{\frac{1}{2}}$; $A_t = \dfrac{Ao}{2}$

$2.303\log\dfrac{Ao}{\frac{Ao}{2}} = kt_{\frac{1}{2}}$

$t_{\frac{1}{2}} = 2.303\log 2 = \dfrac{0.693}{K}$

$\therefore\ \boxed{t_{\frac{1}{2}} = \dfrac{0.693}{K}}$ ------------------------- (ii)

For 1st order reactions, *half life is constant and independent of the initial concentration of the reactant.*
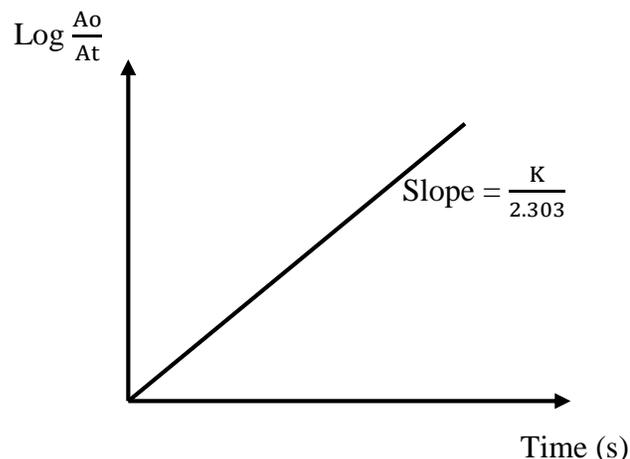
A graph of concentration of A against time
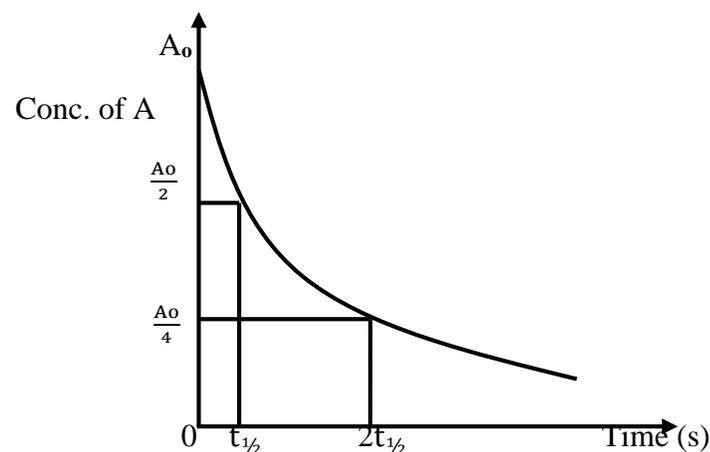
First order reaction $(t_{\frac{1}{2}} - 0) = (2t_{\frac{1}{2}} - t_{\frac{1}{2}})$

Also from $2.303\log\dfrac{Ao}{At} = kt$

$\Longrightarrow \log\dfrac{Ao}{At} = \dfrac{kt}{2.303}$

A plot of $\frac{Ao}{At}$ against time

$Log \frac{Ao}{At}$

Slope $= \frac{K}{2.303}$

Time (s)

Also from $\quad log\frac{Ao}{At} = \frac{K}{2.303}$

$$log A_o - log A_t = \frac{K}{2.303}$$

$$log A_t = log A_o - \frac{K}{2.303}$$

Ao

Slope $= -\frac{K}{2.303}$

$log A_t$

Time(s)
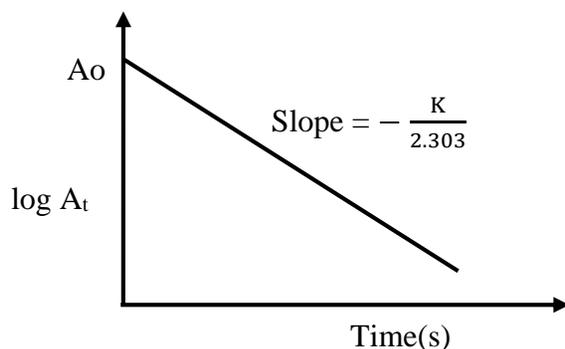
1. The table below shows the kinetic data that was obtained for the conversion of sucrose to glucose in acid solution.

Conc. of sucrose (mol dm^{-3})	0.08	0.06	0.04	0.02	0.01
Rate of reaction (moldm^{-3})	0.004	0.003	0.002	0.001	0.0005

  i. Plot a graph of rate of reaction against the concentration of sucrose.
  ii. State the order of the reaction. Give a reason for your answer.
  iii. Determine the rate constant for the reaction and indicate its units.
  iv. Calculate the rate of the reaction when the concentration of sucrose was 0.12moldm^{-3}.

2. Compound B undergoes a reaction to form compound W. The course of the reaction can be followed by adding excess KI solution to a fixed volume of the reactant. B reacts with a standard solution of Sodium thiosulphate. The volume of the Sodium thiosulphite solution is a measure of the concentration of B remaining at time T. The table below shows the volume of Sodium thiosulphite, V required at various times.

V(cm^3)	24.70	17.80	12.90	9.25	5.50	3.60
t (mins)	0	60	120	180	240	300

a) Plot a graph of V against time
b) From the graph in (a), deduce the time for B; to

i. be reduced to half the original value
ii. be reduced to $\frac{1}{4}$ the original value
c) What is the order of the reaction with respect to B?
d) Write the rate equation for the reaction in which B is converted to W.
e) Determine the rate constant for the reaction.

NB: When only time and the concentration of the product is given, the concentration of the reactant at each time is got by subtracting the concentration of the product at that time from the concentration of the product at the end of the reaction. i.e.

[Reactants]t = [product]end − [product]t

A plot of the concentration of reactant and time is then made e.g. given;

W + H$_2$O ⟶ products

| Time(s)	0	20	40	60	∞
[products]/moldm^3	30	90	120	135	150

Experimental determination of order of catalyzed decomposition of H$_2$O$_2$

Procedure:

- A known fixed volume of H$_2$O$_2$ solution is pipette.
- NaOH solution is added to it followed by FeCl$_3$ solution and the stop clock simultaneously started.
- Mixture is shaken and allowed to stand for 3 minutes.
- A known volme reaction mixture is withdrawn, excess dilute H$_2$SO$_4$ is added to it stop the decomposition.
- The resultant mixture is then titrated with a standard solution of KMnO$_4$.
- The procedure is repeated at intervals of 3 minutes before adding H$_2$SO$_4$ and the titre values V$_t$ noted.
- Initial concentration of H$_2$O$_2$ before decomposition is obtained by titrating the original H$_2$O$_2$, with KMnO$_4$ and volume of the potassium permanganate used V$_o$ is recorded.
- A graph of **log ($\frac{V_o}{V_t}$)** against time is plotted, a straight line is obtained.

Solution:

Time (s)	0	20	40	60	∞
[Product] (moldm^{-3})	30	90	120	135	150
[reactant] (moldm^{-3})	(150 − 30) 120	(150− 90) 60	(150− 120) 30	(150− 135) 15	(150− 150) 0

t (min)	0	5	10	15	20	25	30	35	40	45
Vt (cm^3)	12.30	9.20	6.90	5.20	3.90	2.90	2.20	1.60	1.20	1.15

Treatment of results

Volume ofVo
KMnO$_4$ (cm^3)

Time (s)

log V$_t$

log $\frac{Vo}{Vt}$

Slope $= \frac{k}{2.303}$

Time (s)
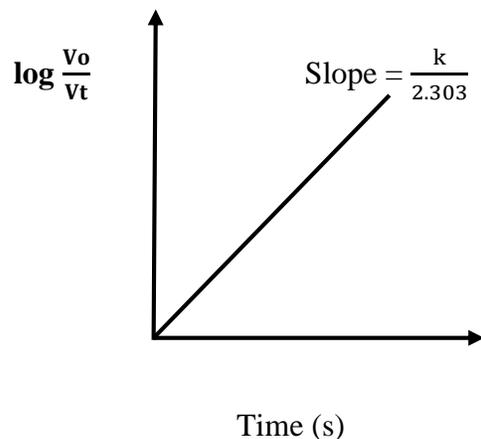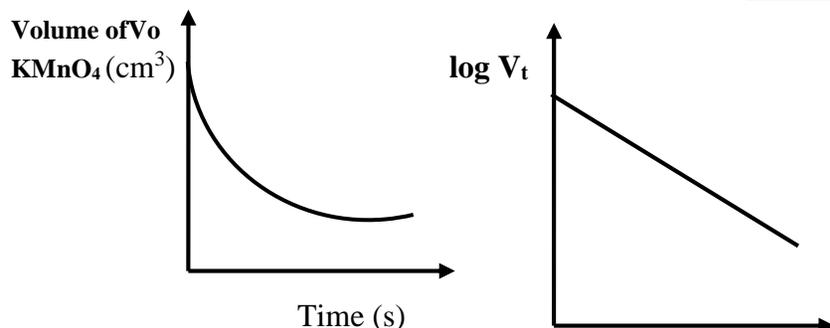
i. Tabulate values of log Vt
ii. Plot a graph of log Vt against time
iii. State order of reaction with respect hydrogen peroxide. Give reason for your answer.
iv. Determine the rate constant for the reaction
v. Calculate the half life for the reaction

2. Describe an experiment to show that catalytic decomposition of H_2O_2 is a first order reaction.

NB: Conditions for first order reaction

- If one of the reactants is in large excess that only a small fraction of it will be used up in the reaction.
- Use of acid as catalyst; where its concentration doesn't change during the course of the reaction e.g acid catalysed hydrolysis of esters and sucrose.

3. **SECOND ORDER REACTION**

Rate of reaction is proportional to the ,

✓ products of the concentration of reactants each raised to power one
✓ square of the concentration of a single reactant.

For A $\longrightarrow$ Products , rate $= k[A]^2$
For A + B $\longrightarrow$ Products, Rate $= k[A]^1 [B]^1$

Graphs of second order reactions

UNEB 2011

1. A certain volume of H_2O_2 solution was decomposed in the presence of platinum. The amount of H_2O_2 after time t was found by withdrawing aliquot portions of solution, adding dilute sulphuric acid and titrating with Potassium manganate (VII) solution. The volume Vt of Potassium manganate (VII) solution were as follows;

Rate of
Rxn

Concentration of reactant
concentration

Rate of
rxn
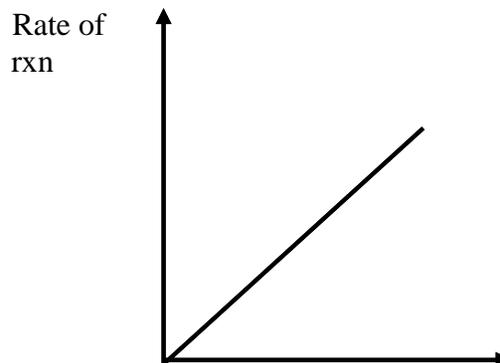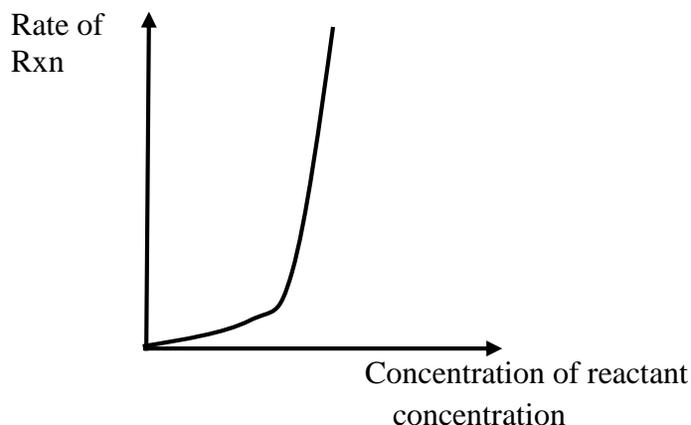
Half life:

For second order reactions, half life is inversely proportional to the concentration. i.e . It almost doubles for every successive decrease in concentration of the reactant by half

Concentration Ao   **b > a**

A½

A¼

a   b
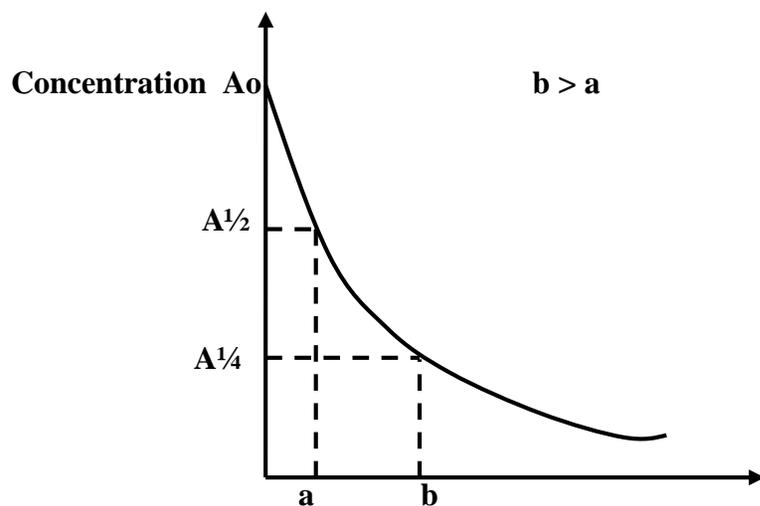
Examples of 2nd order reactions

− Hydrolysis of ethyl ethanoate by aqueous NaOH
− Oxidation of I^- to I_2 by H_2O_2

FACTORS AFFECTING RATES OF REACTION

These include

   i.   Concentration of reactants in solution
   ii.   Temperature
   iii. Pressure of gaseous reactants
   iv.   Light
   v.   Catalyst
   vi.   Surface area/size of particle of a solid reactant.

Surface area:

   − For reactions involving solids, breaking the solid into smaller pieces increases its total surface area.

- Increase in SA of the reactants increases the rate of reaction by exposing more reactant molecules to react with another.

Light;

- Photosensitive reactions e.g. photosynthesis and formation of Ag and Ag salts which take place when a photographic film is exposed to light, their rates increase with exposure to light.
- Light of sufficient energy breaks the bonds in one of the reactants creating a reactive intermediate from which the products are formed.

Pressure of gaseous reactants:

Increase in pressure of gases pushes the gaseous molecules close together; increasing on their frequency of collision and thus reacting more rapidly.

Concentration;

- Increasing the concentration of the reactants increases the rate of reaction and vice versa
- This is because at greater concentration, there are more molecules in a given volume, close distance between these molecules are reduced and there is an increased number of collisions per unit volume.

Example:

1. The rate equation for $2A + B \longrightarrow C$ is given by Rate = $k[A] [B]^2$. How will the rate of reaction alter if concentration of

i. A is doubled but concentration of B is kept constant
ii. Concentration of B is halved but concentration of A is kept constant
iii. Both Concentration of A and concentration of B are doubled

Solution:

i. Rate = $k[A] [B]^2$
   $= k[2A] [B]^2$
   $= 2k [A] [B]^2$
   New rate is twice the initial rate
ii. Rate = $k[A] [½B]^2$
   $= (½)^2 k [A] [B]^2$
   $= ¼ k [A] [B]^2$
   New rate is ¼ times the initial rate
iii. From Rate = $k[A] [B]^2$
   Rate = $k [2A] [2B]^2$
   $= (2)(4) k[A] [B]^2$
   $= 8 k[A] [B]^2$
   new rate is 8 times the initial rate

ACTIVITY

The rate of a certain reaction is Rate = $k[A] [B]^2[C]$ where [ ] is the concentration in moles per litre and k is the rate constant. State how the rate of the reaction will change if;

i. Concentration of B and C is doubled and A is kept constant
ii. Concentration of A and C were kept constant and concentration of B is halved
iii. [A] and [C] were kept constant and [B] was doubled.

iv. Concentration of A, B and C were doubled.

Temperature:

− Increasing the temperature of the reactants increases the rate of a reaction.
− At higher temperatures, the ions/ molecules of the reactants have more energy moving with greater average velocity and collide more frequently and with more force.
− Increased collision frequency results in a higher rate of reaction.

MAXWELL – BOLTZMANN DISTRIBUTION OF MOLECULAR ENERGY,E

- Maxwell – Boltzmann stated that; *Rate of reaction doubles for every $10^0C/10k$ rise in temperature* as shown below.

A plot of fraction of number of molecules with energy E against molecular energy E

T_1 $T_2 > T_1$

No. of Molecules with Energy, E

T_2 Ea
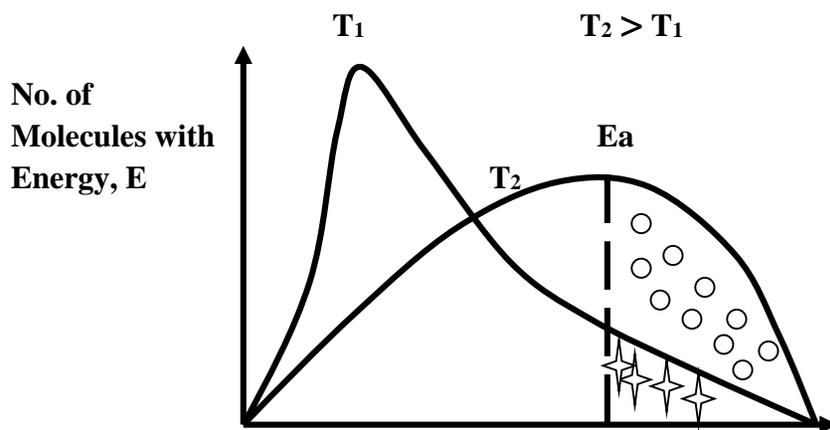
Molecular energy,E

Interpretation

- At lower temperature (T_1), a very large fraction of the molecules have energy close to the average energy, only a very small fraction of the molecules having very high or very low energies.
- At higher temperature (T2), there is a wide range of molecular energies; proportion of molecules with energy greater than or equal to average is greater; increasing the likelihood of successive collision increasing the rate of reaction.

Qn: Explain with the help of Maxwell - distribution diagram why the rate of some reactions approximately doubles when the temperature is increased by 10^0C around room temperature.

Relationship between the rate constant, K and temperature

- Arrhenius equation relates the magnitude of the rate constant and the temperature
- The equation can be used to calculate the activation energy from the rates of reactions at different temperatures.
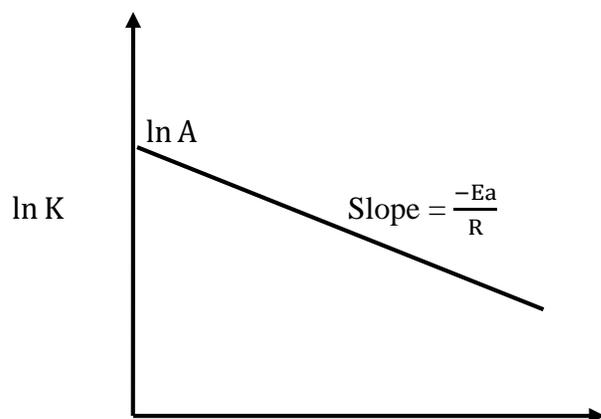
$K = Ae^{-Ea/_{RT}}$

$InK = InA - \frac{Ea}{RT}$

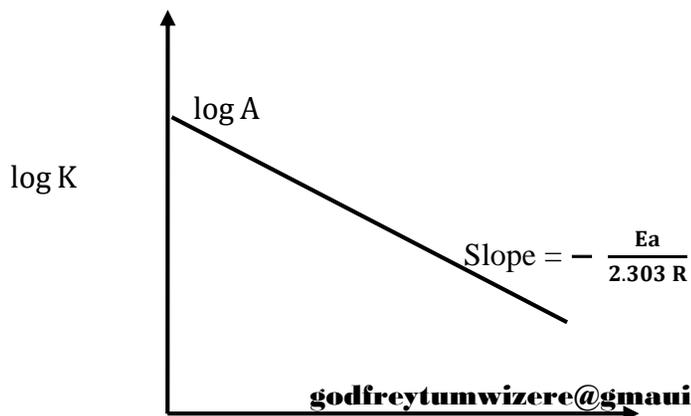Where A = Arrhenius factor (pre exponential factor)

K = Rate constant

Ea = Activation energy

T = absolute temperature

R = Gas constant

A plot of ln K against temperature

$\frac{1}{\text{Temp}}\ (K^{-1})$

A Plot of log K against $^1/_T$ (log K = log A − $\frac{Ea}{2.303\ RT}$)

$\frac{1}{T}\ (K^{-1})$

- If K_1 is the rate constant at temperature T_1 and K_2 is the rate constant at temperature T_2

From $\ln K = \ln A - \frac{Ea}{RT}$

$K_1 \rightarrow T_1,\ K_2 \rightarrow T_2$

$$\ln K1 = \ln A - \frac{Ea}{RT1} \text{ ----------------------- (i)}$$

$$\ln K2 = \ln A - \frac{Ea}{RT2} \text{ ----------------------- (ii)}$$

(i) − (ii)

$$\ln K1 - \ln K2 = -\frac{Ea}{RT1} - \left(-\frac{Ea}{RT2}\right)$$

$$\ln \frac{K1}{K2} = \frac{Ea}{RT2} - \frac{Ea}{RT1}$$

$$\Rightarrow \ln \frac{K1}{K2} = \frac{Ea}{R}\left(\frac{T1-T2}{T2T1}\right) \text{ _____ (i)}$$

OR

$$\ln \frac{K2}{K1} = \frac{Ea}{R}\left(\frac{T2-T1}{T2T1}\right) \text{ _____ (ii)}$$

But $\ln K = 2.303 \log_{10}$

$$\mathbf{\log \frac{K_1}{K_2} = \frac{Ea}{2.303R}\left(\frac{T_1 - T_2}{T_2 T_1}\right)}$$

Example

1. The activation energy for a certain reaction is 50kJmol^{-1}. What is the effect on the rate constant of increasing the temperature by 10K around room temperature (assumed to be 15^{0}C)

Solution:

$T_1 = (15 + 273) = 288K$

$T_2 = 288 + 10 = 298K$

From $\log \frac{K_2}{K_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$

$\log \frac{K_2}{K_1} = \frac{5000}{2.303 \times 8.314}\left(\frac{298 - 288}{298 \cdot 288}\right)$

$\log \frac{K_2}{K_1} = 0.30426871$

$\frac{K_2}{K_1} = \log^{-1}(0.30426871) = \mathbf{\underline{2.0149}}$

$\mathbf{\frac{K_2}{K_1} \approx 2}$

The final rate is twice the initial rate

ACTIVITY

The rate $2N_2O_5 \longrightarrow 2N_2O_4 (g) + O_2 (g)$ was studied at various temperatures and the rate constants were determined at those temperatures as shown in the table below.

Temp ^{o} C	20	35	45	65
Rate constant	1.76×10^{-4}	1.35×10^{-4}	4.94×10^{-4}	4.87×10^{-3}

Calculate the activation energy Ea for the reaction.

Vi) Catalyst:

- Is a substance that alters the rate of chemical reaction but remains chemically unchanged at the end of the reaction.
- They speed up the rate of chemical reaction by providing an alternative route of lower activation energy from reactants to products

Reaction profile of uncatalysed and catalysed reactions
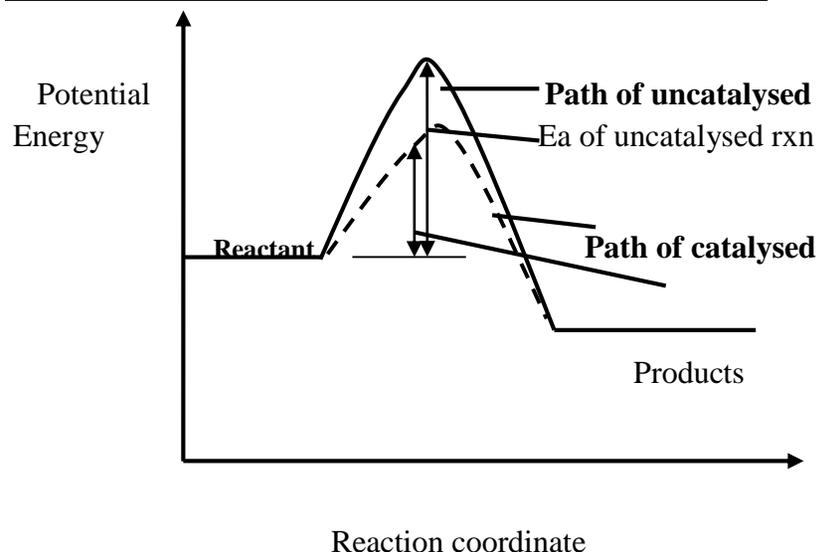
Reaction coordinate

i. Using the same axis, draw a labeled diagram for energy – reaction coordinate for a catalysed and uncatalysed. reactions
ii. State the difference in your diagrams
iii. State how a catalyst increases the rate of a reaction.

Classification of catalyst

Classified according to the physical state it is in compared to the reactant namely.

a) Heterogeneous catalyst
b) Homogenous catalyst
a) Heterogeneous catalyst
- Catalysts and reacting substances are in different states

- Examples include.
  i. Using of Fe in the Haber Process
  ii. Nickel catalyst in the in the hardening of vegetable oils in the production of Margarine.
  iii. Vanadium (v) oxide in the contact process

$$2SO_2 (g) + O_2(g) \underset{\longleftarrow}{\overset{V_2 O_5 (s)}{\longrightarrow}} SO_3(g)$$
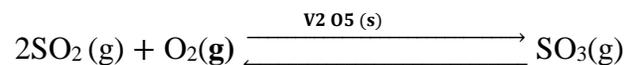
Heterogeneous catalyst takes place at the surface of the Catalyst.

Reactants are adsorbed onto the surface of the catalyst, bonds are broken and new bonds formed. The products are desorbed from the surface

b) Homogenous catalyst
- Catalyst and reacting substances are in the same physical states. E.g. include
  i. Acid catalysed hydrolysis
  ii. Peroxidase enzyme in the mammalian liver.
  iii. Use of Aq. $CoCl_2$ in the reaction between H_2O_2 and aqueous solution of Sodium – Potassium 2, 3 – dihydroxybutandioate.

Features of Catalysts

i. Very specific to a single reaction or to class of very similar reactions.
ii. Catalyse both forward and backward reaction at the same extent and therefore have no effect on equilibrium constant or equilibrium position.
iii. Small quantities can usually achieve a huge increase in rate of reaction.

iv. Catalyst maybe poisoned by some other substances e.g. lead, Arsenic and cyanide.

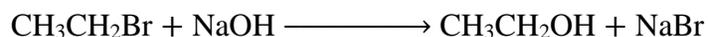**Determination of a mechanism of a reaction**

- Reaction mechanism is a detailed step by step description of the pathways followed by reactants in forming products.
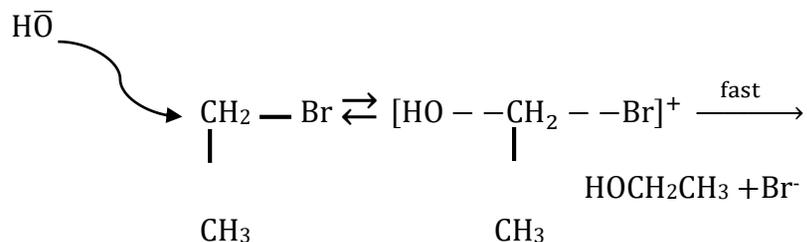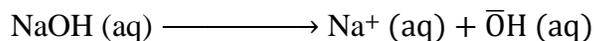- It specifies all intermediate stages and all intermediate species formed.

Examples;

i. Hydrolysis of primary alkyl halide.
- The reaction is first order with respect to Hydroxyl ion and also first order with respect Bromoethane ; giving an overall order of 2.

Equation:

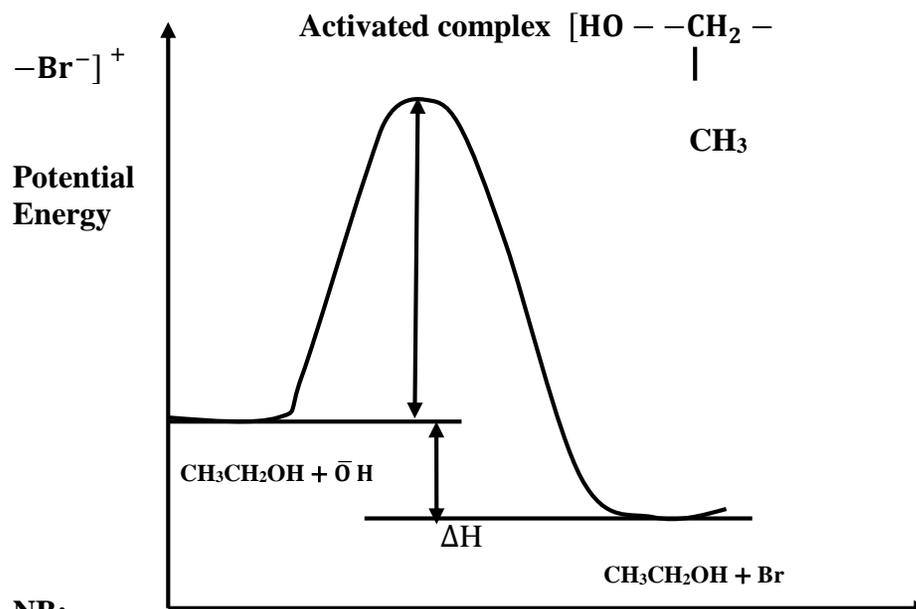$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$

Mechanism:

$NaOH \text{ (aq)} \longrightarrow Na^+ \text{ (aq)} + \overline{O}H \text{ (aq)}$

$H\overline{O}$

$\underset{\underset{CH_3}{|}}{CH_2} - Br \rightleftarrows [HO - -\underset{\underset{CH_3}{|}}{CH_2} - -Br]^+ \xrightarrow{\text{fast}}$

$HOCH_2CH_3 + Br^-$

Reactants   activated complex
products

$Rate = K [\overline{O}H] [CH_3 CH_2Br]$

Reaction profile for substitution Nucleophilic (SN₂)

Activated complex $[HO - -CH_2 -$
$-Br^-]^+$

CH_3

Potential
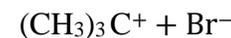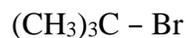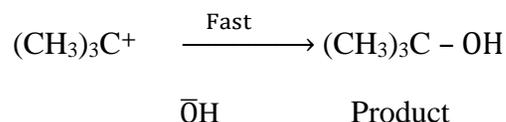Energy

$CH_3CH_2OH + \overline{O} H$

ΔH

$CH_3CH_2OH + Br$

NB:
Activated complex is an *"unstable intermediate in which bonds of the reactant molecules are partially breaking while the new bonds of the product molecules are partially being formed."*
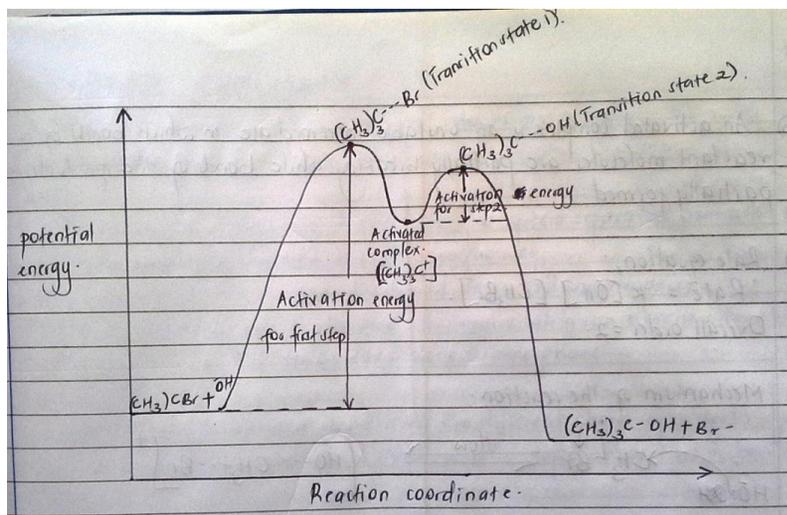
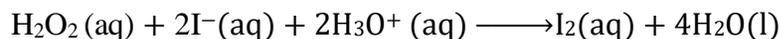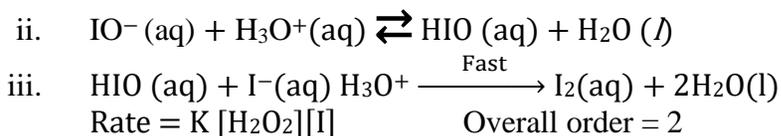ii. **Hydrolysis of tertially alkyl halides (2 – Bromo – 2 – methyl propane)**
Equation:

$(CH_3)_3C - Br \qquad (CH_3)_3 C^+ + Br^-$

$$(CH_3)_3C^+ \xrightarrow{\text{Fast}} (CH_3)_3C - OH$$

$$\overline{O}H \qquad\qquad \text{Product}$$

Reaction profile of substitution Nucleophilic Unimolecular (SN₁)

iii. Oxidation of Iodide to Iodine by H_2O_2

$$H_2O_2 (aq) + 2I^-(aq) + 2H_3O^+ (aq) \longrightarrow I_2(aq) + 4H_2O(l)$$

Mechanism

i. $H_2O_2 (aq) + I^-(aq) \underset{\text{Fast}}{\overset{\text{slow}}{\rightleftarrows}} IO^-(aq) + H_2O(l)$

ii. $IO^- (aq) + H_3O^+(aq) \rightleftarrows HIO (aq) + H_2O (l)$

iii. $HIO (aq) + I^-(aq) H_3O^+ \xrightarrow{\text{Fast}} I_2(aq) + 2H_2O(l)$

Rate $= K [H_2O_2][I]$ Overall order $= 2$
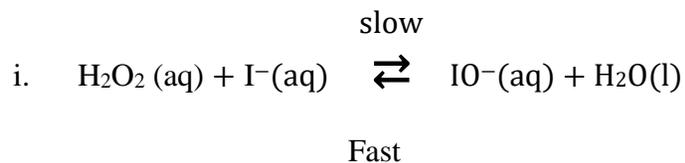
Questions (UNEB 1999 QN 14)

1. 2 – Bromo – 2- methyl propane reacts with aqueous NaOH to form 2 – methyl – propan – 2 – ol
   a) Write the rate equation for the reaction.
   b) Draw an energy diagram for the reaction
      Write the mechanism for the reaction
   c) State the;
      i. Rate determining step of the reaction
      ii. Technique which was used to study the reaction
2. Bromo – methane reacts with aqueous NaOH according to the following equations
   $CH_3Br + OH (aq) \longrightarrow CH_3OH (aq) + Br^-(aq)$ $\Delta H = ^-VE$.
   The overall order is 2
      a) Draw a fully labeled diagram of energy versus reaction pathway for the reaction.
      b) Explain what is meant by the term activated complex.
      i. Write the rate equation for the reaction
      ii. Outline a mechanism for the reaction.

NOTE:

- Transition state is a state of maximum potential energy during a chemical reaction in which the substance present at that state can now form the products of the reaction or can give back the reactants.

- Activation energy is the minimum energy which colliding molecules need in order to react forming products.

Assignment

Theories of reaction rates

- Collision theory(**Ramsden, 287-290, 307-308; understanding chem., 165-166**)
- Transition state theory(**Ramsden, 308-310; understanding chem.; 166-167**)