CHEMICAL KINETICS.

This deals with the study of reaction rates, factors which influence them and the mechanism by which the reactions occur.

Kinetics also helps to predict how the rate will change if the reaction conditions are changed.

This study is practically important because the knowledge gained can be used to adjust the reaction conditions to the greatest advantage.

Rate of reaction

Some reactions e.g. ionic reactions like precipitation of silver chloride by mixing aqueous solver nitrate with sodium chloride solution occur very fast. On the other hand, some reactions are very slow e.g. rusting of iron in the presence of air and moisture.

The rate/ speed of a chemical reaction is the speed with which the reactants are converted into products per unit time. It may be expressed in terms of;

- decrease in concentration of any one of the reactants per unit time or
- increase in concentration of any one of the products per unit time.

Therefore the rate of reaction measures the rate of change of the concentration of either the products or the reactants. It can therefore be expressed as a rate of increase in concentration of products or rate of decrease in the concentration of reactants.

Consider the reaction; $A \rightarrow B$

$$Rate = \frac{d}{dt}([B]) \; or \; Rate = -\frac{d}{dt}([A])$$

The negative sign implies that the concentration of A is decreasing with increase in time.

Note: the reaction rate is not constant but decreases over time, as the reactant(s) concentration goes down.

Order of reaction

Order of reaction is the sum of the powers to which the concentration of the reactants are raised to in the experimental rate equation.

Consider the reaction below;

$$aA + bB \rightarrow cC + dD,$$
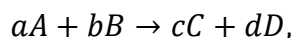
The rate of reaction depends on the concentration of the reacting species.

$$Rate \propto [A]^m \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (i)$$

$$Rate \propto [B]^n \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (ii)$$

Combining the two equations gives;

$$Rate \propto [A]^m[B]^n \ldots \ldots \ldots \ldots \ldots \ldots \ldots (iii)$$

Removing the proportionality sign yields the equation below;

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n \dots\dots\dots\dots\dots\dots (iv)$$

Where:

K *is known as the rate constant/ velocity constant,*

m *is the order of reaction with respect to A and*

n *is order of reaction with respect to B.*

Rate law

Equation (iv) is known as the rate law or expression/ equation.

The rate law gives the relationship between rate of reaction, concentration of the reactants and the power to which the concentrations are raised to in the experimentally determined equation.

The rate law states that the rate of a reaction is directly proportional to the molar concentration of reactants raised to appropriate powers at a given temperature.

Rate constant

This refers to the ratio of the rate of reaction to the product of the concentration of the reactants present at the slow (rate determining) step of the reaction when the concentration of the reactants are raised to their appropriate powers.

$$k = \frac{\text{Rate}}{[\text{A}]^m[\text{B}]^n} \dots\dots\dots\dots\dots\dots\dots\dots\dots (v)$$

The larger the rate constant, faster the reaction and this depends on temperature. The unit depends on overall order of reaction.

The sum; $(m + n)$ gives the overall order of reaction.

NOTE: Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation (it has nothing to do with stoichiometric ratios i.e. theoretically) but it is determined experimentally, for example consider the equation below;

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$
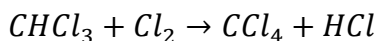
$$\text{Rate} = k[CHCl_3][Cl_2]^{\frac{1}{2}} \dots\dots\dots\dots\dots\dots (vi)$$

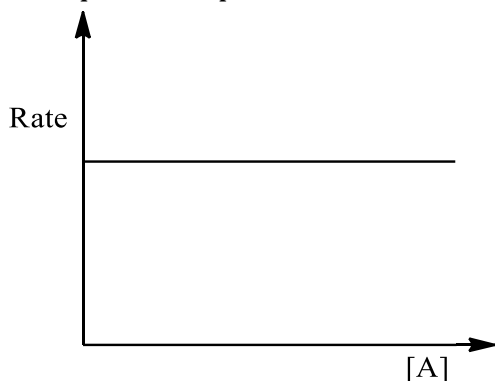## Classification of reactions based on their orders.

Zero order.

The rate of reaction is proportional to zero power of the concentration of the reactants. Consider the reaction:

$A \rightarrow Products$

$$Rate = \frac{-d[A]}{dt} = k[A]^0$$

$$\frac{-d[A]}{dt} = k. \ldots \ldots \ldots \ldots \ldots \ldots \ldots (*)$$

The above equation implies that the rate is independent of the concentration of reactants.

Separating variables in equation (*),
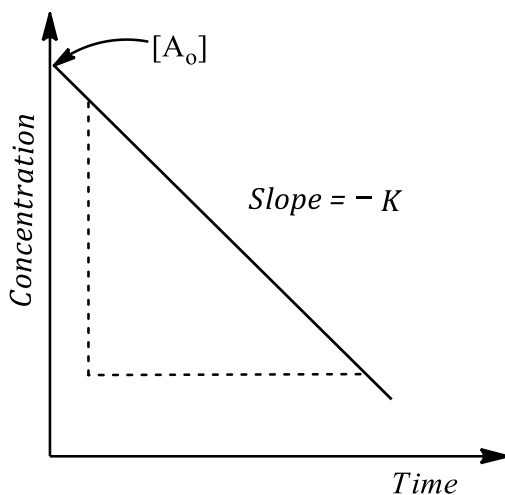
$$\Rightarrow d[A] = -kdt$$

Integrating both sides of the equation;

$$\int_{[A]_O}^{[A]_t} d[A] = -k \int_0^t dt$$

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

$$[A]_t = -kt + [A]_0 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (i)$$
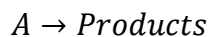
A plot of concentration against time gives a linear (straight) line graph with a negative slope $(-k)$ and $[A]_0$ as the y-intercept.

First order.

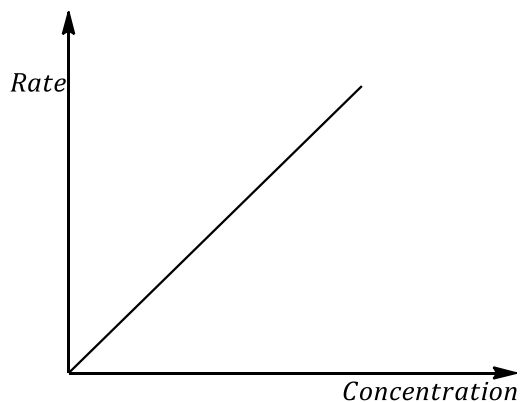The rate of reaction is proportional to first power of the concentration of the reactants.

Consider the reaction:

$$A \rightarrow Products$$

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

Physical processes like radioactive disintegration follows first order kinetics.

A graph of rate i.e. $\left(\frac{1}{t}\right)$ against concentration for first order reaction is shown below.

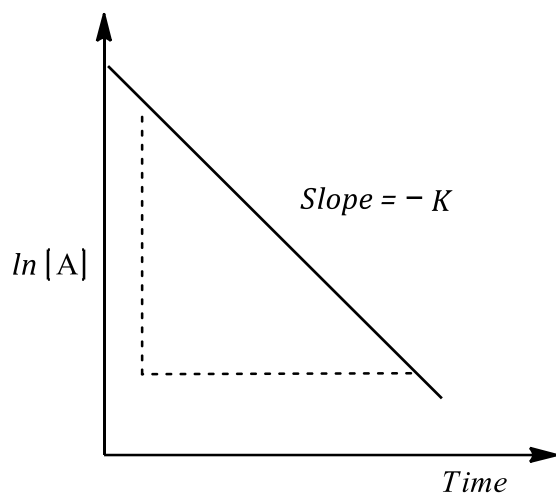$$\frac{-d[A]}{dt} = k[A], \qquad \Rightarrow \frac{d[A]}{[A]} = -kdt$$

Integrating both sides of the equation;

$$\int_{[A]_O}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

$$ln[A]_t - ln[A]_0 = -kt \ldots \ldots \ldots \ldots \ldots (ii)$$

$$ln[A]_t = -kt + In[A]_0 \ldots \ldots \ldots \ldots \ldots (iii)$$

A plot of $In[A]$ against time(t) gives a linear (straight) graph with a negative gradient.

Alternative graphs for first order reactions:

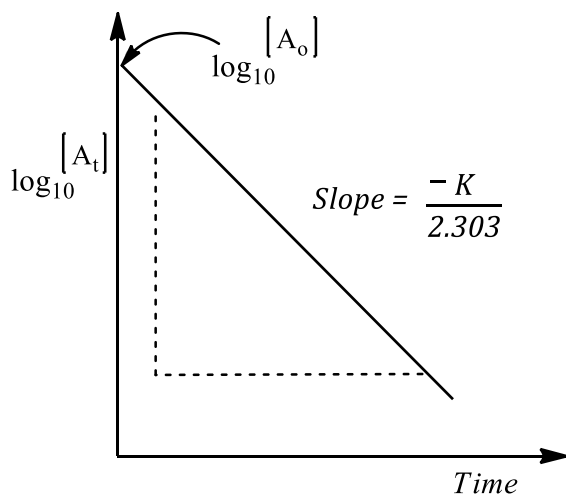(a) Using equation (ii); $ln[A]_t - ln[A]_0 = -kt$

Note: $lnx = 2.303 \log_{10} x$

$$\Rightarrow 2.303 \log_{10}[A]_t - 2.303 \log_{10}[A]_0 = -kt$$

$$2.303 \log_{10}[A]_t = -kt + 2.303 \log_{10}[A]_0$$

$$\log_{10}[A]_t = -\frac{kt}{2.303} + \log_{10}[A]_0$$

Plotting a graph of $\log_{10}[A]_t$ against t yields a straight line graph with a slope equals to $-\frac{k}{2.303}$ and the y-intercept equals to $\log_{10}[A]_0$.
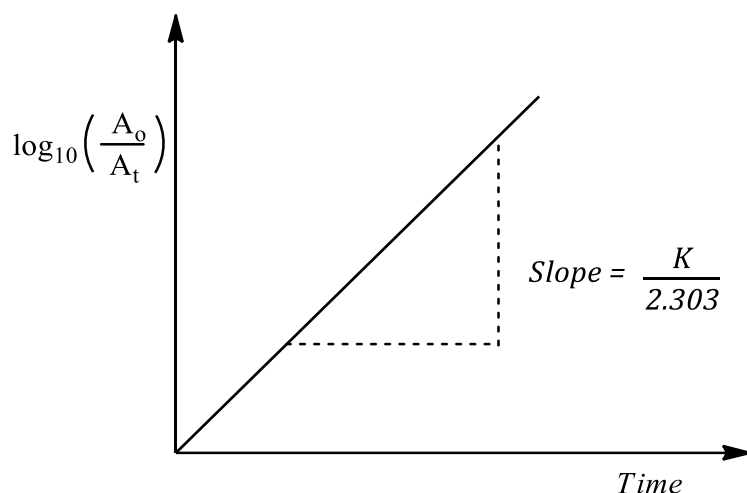

(b) Using still equation (ii); $ln[A]_t - ln[A]_0 = -kt$

$$ln\left(\frac{[A]_t}{[A]_o}\right) = -kt$$

$$2.303\log_{10}\left(\frac{[A]_t}{[A]_o}\right) = -kt$$

$$\log_{10}\left(\frac{[A]_o}{[A]_t}\right) = \frac{kt}{2.303}$$

Plotting a graph of $\log_{10}\left(\frac{[A]_o}{[A]_t}\right)$ against t yields a straight line graph with a slope equals to $\frac{k}{2.303}$

Half-life of a first order reaction:

This is the time taken for the concentration of the reactant to reduce to one half (50%) of its initial (original) concentration. It is denoted by $t_{\frac{1}{2}}$.

From; $ln[A]_t - ln[A]_0 = -kt$

$$ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

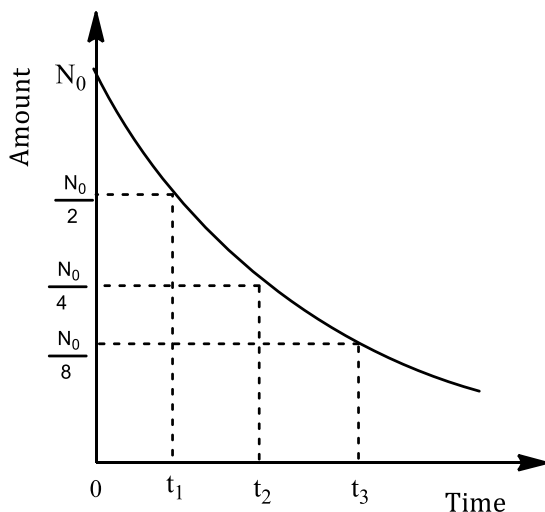This implies that; $ln\left(\frac{[A]_0}{[A]_t}\right) = kt \dots (iii)$

At half-life; $t = t_{\frac{1}{2}}, and\ [A]_t = \frac{[A]_0}{2}$; substituting these values into equation (iii) gives;

$$ln\left(\frac{[A]_0}{\frac{[A]_0}{2}}\right) = kt_{\frac{1}{2}} \dots \dots \dots \dots \dots \dots \dots (iv)$$

Simplifying equation (iv) yields $ln2 = kt_{\frac{1}{2}} \Rightarrow t_{\frac{1}{2}} = \frac{0.693}{k}$

The decay curve for a first order reaction

The decay curve shows how the mount of a sample varies with time.

For a first order reaction, the half-lives are the same. This implies that the half-life is independent of the initial/ original concentration of the reactant.

Using the graph, it implies that;

$$(t_1 - 0) \approx (t_2 - t_1) \approx (t_3 - t_2)$$

Examples

1. The half-life of radium is 1590. How long will it take a sample of radium to decay to 25% of its original activity?

Solution

$$ln\left(\frac{N_o}{N_t}\right) = kt$$

$$k = \frac{ln2}{t_{\frac{1}{2}}} = \frac{0.693}{1590} = 4.358 \times 10^{-4}$$

$$ln\left(\frac{100}{25}\right) = (4.358 \times 10^{-4})t,$$

$$t = 3181$$

2. When a radioactive isotope was left to stand, it decayed by 15% of its original value in 50 days. Calculate the half-life of the radioisotope.

Solution

$$ln\left(\frac{N_o}{N_t}\right) = kt$$

$$ln\left(\frac{100}{85}\right) = 50k,$$

$$k = 3.25 \times 10^{-3} day^{-1}$$

$$t_{\frac{1}{2}} = \frac{ln2}{k} = \frac{0.693}{3.25 \times 10^{-3}}$$

$$= 213.23 \text{ days}$$

The half-life of the radioactive isotope is 213.23 days.

3. The half-life of Bismuth is 20 minutes. Determine the time taken for 16 g of Bismuth to decay to 2 g.

Solution

$$k = \frac{ln2}{t_{\frac{1}{2}}} = \frac{0.693}{20} = 0.03465 \text{ minute}^{-1}$$

From; $ln\left(\frac{N_o}{N_t}\right) = kt$

$$\Rightarrow ln\left(\frac{16}{2}\right) = (0.03465)t,$$

$$t = 60 \text{ minutes.}$$

4. The table below shows the variation of concentration of substance **A** with time.

Time (minutes)	10	15	20	25	30
[A] $(moldm^{-3})$	2.14	1.86	1.66	1.44	1.28

(a) plot a graph of $ln[A]$ against time.
(b) From your graph, determine;
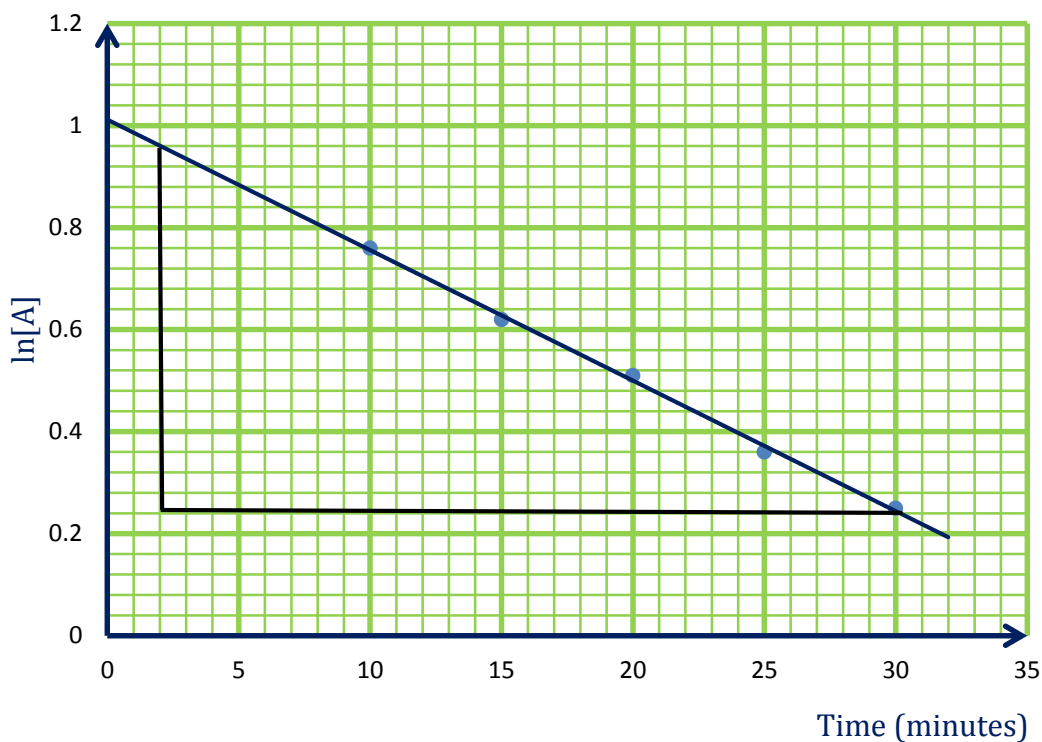   (i)   The rate constant.
   (ii) The half-life.
   (iii) The activity at time t=0.

Solution

Time (minutes)	10	15	20	25	30
$ln[A]$		0.76	0.62	0.51	0.36	0.25

(a) A graph of $ln[A]$ against time

(b) Using the graph to determine;

   (i)   Rate constant, k

       From the graph, the slope is -0.0256

       $-k = -0.0256$

       $k = 0.0256$

   (ii) Half-life

$$t_{\frac{1}{2}} = \frac{ln2}{k} = \frac{0.693}{0.0256} = 26.07$$

   (iii) Activity at time t=0

       The activity at time t=0 is equal to the intercept value

       From the graph, the intercept is 1

       $ln[A_o] = 1$

       $[A_o] = 2.72$

5. The following data was obtained for the decomposition of compound **Q** at 40°C.

Time (minutes)	0	20	40	60	80
Concentration $(moldm^{-3})$	0.40	0.29	0.21	0.15	0.11

    (a) Plot a graph of concentration against time.

    (b) Use the graph to determine the half-life and order of the reaction.

    (c) Calculate the rate constant, k, for the reaction.

Solution

(a) A graph of concentration against time.

(b) Half-life of the reaction

From the graph; $t' = 42$ and $t'' = 42$

Half-life$= \left(\frac{42+42}{2}\right) = 42$ minutes

(c) Rate constant, k for the reaction

$$k = \frac{ln2}{t_{1/2}} = \left(\frac{0.693}{42}\right) = 0.0165 \; minute^{-1}$$

Task

1. The following kinetic data were obtained by a student for a certain reaction.

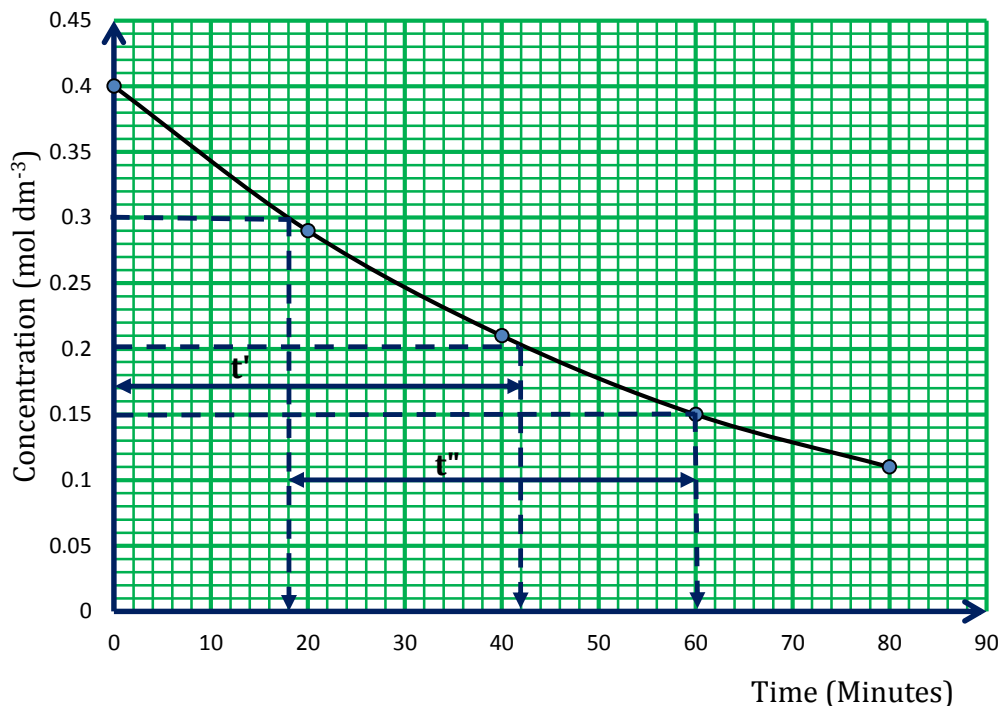| Time (seconds)	0	100	150	300	400	600	800
Concentration $(moldm^{-3})$	1.00	0.80	0.70	0.50	0.40	0.25	0.15

(a) Plot a graph of concentration against time.

(b) Use the graph to determine the half-life and order of the reaction.

(c) Calculate the rate constant, k, for the reaction.

2. In a pseudo first order hydrolysis of an ester in water, the following results are obtained.

Time (minutes)	0	20	40	60	80
[Ester] $(moldm^{-3})$	0.40	0.29	0.21	0.15	0.11

(a) Plot a graph of concentration against time.

(b) Use the graph to determine the half-life and order of the reaction.

(c) Calculate the rate constant, k, for the reaction.

3. The following data are obtained in the decomposition reaction
$$N_2O_4(g) \longrightarrow 2NO_2(g)$$
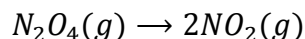
Time (s)	0	200	400	600	800
$[N_2O_4]$ $(moldm^{-3})$	1.59	1.42	1.27	1.12	1.00

(a) Plot a graph of $\log_{10}[N_2O_4]$ against time.

(b) Use your graph to determine the order of the reaction.

(c) Determine the rate constant for the above decomposition reaction.

Ways of determining orders of reaction

There are several ways/ methods of determining order(s) of reaction(s). Among them are the following;

▪ Graphical method

▪ Initial rate method

▪ Integrated rate equations.

Determination of orders of reaction using initial rate method.

During a course of chemical reaction, different set of the initial rate with its concentration data is obtained. Then by keeping the concentration of one of the reactants constant and varying the other one(s), the effect on the rate can be studied and used to determine the order of a given reaction.

The rate law is applied in which the power or exponent will give the order of reaction. When the order is known, the overall rate constant for the reaction can also be obtained.

Examples:

1. For the reaction; $A + B \longrightarrow$ Products

The following data were obtained at 298K

Experiment	$[A]$ $(moldm^{-3})$	$[B]$ $(moldm^{-3})$	Initial rate $(mol^{-1}S^{-1})$
1	0.1	0.1	5.0×10^{-4}
2	0.05	0.1	2.5×10^{-4}
3	0.05	0.05	1.25×10^{-4}

(a) Determine the order of reaction with respect to each reactant.

Solution

With respect to A:

Let the order with respect to A *and* B *be m and n respectively*
$$Rate = k[A]^m[B]^n$$

To determine the order with respect to A, we take experiment 1 and 2 where the [B] is kept constant while [A] is varying.

$$5.0 \times 10^{-4} = k[0.1]^m[0.1]^n \dots\dots\dots\dots\dots\dots\dots\dots (i)$$

$$2.5 \times 10^{-4} = k[0.05]^m[0.1]^n \dots\dots\dots\dots.\dots\dots\dots (ii)$$

Dividing equation (i) by (ii)

$$\frac{5.0 \times 10^{-4}}{2.5 \times 10^{-4}} = \left(\frac{0.1}{0.05}\right)^m \left(\frac{0.1}{0.1}\right)^n$$

$$2 = 2^m$$

$$m = 1$$

The order with respect A is 1,

With respect to B:

To determine the order with respect to B, we take experiment 2 and 3

where the [A] is kept constant while [B] is varying.

$$2.5 \times 10^{-4} = k[0.05]^m[0.1]^n \dots\dots\dots\dots\dots\dots\dots.\dots (iii)$$

$$1.25 \times 10^{-4} = k[0.05]^m[0.05]^n \dots\dots\dots\dots.\dots\dots\dots (iv)$$

Dividing equation (iii) by (iv)

$$\frac{2.5 \times 10^{-4}}{1.25 \times 10^{-4}} = \left(\frac{0.05}{0.05}\right)^m \left(\frac{0.1}{0.05}\right)^n$$

$$2 = 2^n$$

$$n = 1$$

The order with respect B is 1,
Therefore the rate equation becomes; $Rate = k[A][B]$

(b) Determine the overall order of the reaction.

Solution

The overall order of the reaction $= 1 + 1$

Overall order of the reaction is 2

(c) Determine the rate constant for the reaction.

Solution

To find the rate constant, you use any row or experiment from the table.

Taking experiment 1 and taking the respective concentrations,

$$5.0 \times 10^{-4} = k[0.1]^1[0.1]^1$$

$$k = \frac{5.0 \times 10^{-4}}{(0.1 \times 0.1)} = 0.05$$

Note

i. Zero order: $m = 0$, rate is independent of the concentration of the reactant. Doubling the concentration of the reactant does not affect the rate.

ii. First order: $m = 1$, rate is directly proportional to the concentration of the reactant. Doubling the concentration of the reactant doubles the rate.

iii. Second order: $m = 2$, rate is proportional to the square of the concentration of the reactant. Doubling the concentration of the reactant increases the rate by a factor of 4.

Task

1. The following results have been obtained during kinetic studies of the reaction;

$$2A + B \rightarrow C + D$$
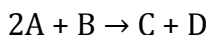
Experiment	$[A](Moll^{-1})$	$[B](Moll^{-1})$	Initial rate $(Moll^{-1}S^{-1})$
1	0.1	0.1	6.0×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.40×10^{-2}

Determine

(i) The order of reaction with respect to each reactant.

(ii) The rate constant for the reaction and,

(iii) the rate law.

2. The kinetic data for the reaction between X and Y is given in the table below;

Experiment	[X] (moldm⁻³)	[Y] moldm⁻³	Rate (moldm⁻³s⁻¹)
1	3.0×10^{-1}	1.5×10^{-1}	1.5×10^{-2}
2	3.0×10^{-1}	3.0×10^{-1}	3.0×10^{-2}
3	6.0×10^{-1}	3.0×10^{-1}	6.0×10^{-2}
4	6.0×10^{-1}	6.0×10^{-1}	12.0×10^{-2}

(a) Determine the order of reaction with respect to X and Y.

(b) Determine the overall order of the reaction.

(c) Write the rate equation for the reaction.

3. The table below shows some kinetic data for the following reactions.

$$3A + B \rightarrow 2C$$
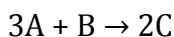
Exp't	$[A] (Moldm^{-3})$	$[B] (Moldm^{-3})$	Initial Rate $(Moldm^{-3}S^{-1})$
1	0.10	0.20	1.2×10^{-8}
2	0.10	0.60	1.2×10^{-8}
3	0.20	0.60	4.8×10^{-8}

(a) Write the overall rate equation.

(b) Calculate the rate constant and give its units.

NOTE: Sometimes, the concentration of one reactant may not remain constant like in the example below;

1. For the reaction; $A + B \longrightarrow C$

   The following data were obtained at 298K

Exp't	[A] ($Moldm^{-3}$)	[B] ($Moldm^{-3}$)	Initial Rate ($Moldm^{-3}S^{-1}$)
1	2.30×10^{-4}	3.10×10^{-5}	5.25×10^{-4}
2	4.60×10^{-4}	6.20×10^{-5}	4.20×10^{-3}
3	9.20×10^{-4}	6.20×10^{-5}	1.68×10^{-2}

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

Solution

With respect to A:

Let the order with respect to A *and* B *be m and n respectively*

$Rate = k[A]^m[B]^n$

To determine the order with respect to A, we take experiment 2 and 3 where the [B] *is kept constant while* [A] *is varying.*

$4.20 \times 10^{-3} = k[4.60 \times 10^{-4}]^m[6.20 \times 10^{-5}]^n$ ... ... (i)

$1.68 \times 10^{-2} = k[9.20 \times 10^{-4}]^m[6.20 \times 10^{-5}]^n$ ... ... (ii)

Dividing equation (i) by (ii)

$$\frac{4.20 \times 10^{-3}}{1.68 \times 10^{-2}} = \left(\frac{4.60 \times 10^{-4}}{9.20 \times 10^{-4}}\right)^m \left(\frac{6.20 \times 10^{-5}}{6.20 \times 10^{-5}}\right)^n$$

$0.25 = 0.5^m$

Introducing *log* on both sides,

$log0.25 = mlog0.5$

$m = 2$

The order with respect A is 2,

With respect to B:

To determine the order with respect to B, we take experiment 1 *and* 2 *where the* [B] *is varying while using the value of m, 2 obtained above.*

$5.25 \times 10^{-4} = k[2.30 \times 10^{-4}]^m[3.10 \times 10^{-5}]^n$ ... ... (iii)

$4.20 \times 10^{-3} = k[4.60 \times 10^{-4}]^m[6.20 \times 10^{-5}]^n$ ... ... (iv)

Dividing equation (iii) by (iv)

$$\frac{5.25 \times 10^{-4}}{4.20 \times 10^{-3}} = \left(\frac{2.30 \times 10^{-4}}{4.60 \times 10^{-4}}\right)^2 \left(\frac{3.10 \times 10^{-5}}{6.20 \times 10^{-5}}\right)^n$$

$$0.500 = 0.500^n$$

$$n = 1$$

The order with respect B is 1,

Therefore the rate equation becomes; $Rate = k[A]^2[B]$

(b) Determine the rate constant for the reaction.

[Taking experiment 1, Rate constant is $3.17 \times 10^8 M^{-2} S^{-1}$]

Task

1. For the reaction in which A and B form C, the following data were obtained from three experiments.

Experiment	$[A](mol\ L^{-1})$	$[B](mol\ L^{-1})$	Initial rate $(mol\ L^{-1}\ s^{-1})$
1	0.03	0.03	0.3×10^{-4}
2	0.06	0.06	1.2×10^{-4}
3	0.06	0.09	2.7×10^{-4}

(a) Determine the order of reaction with respect to each reactant.

(b) Determine the value of the rate constant and hence the rate equation.

[Answer: $Rate = 3.33 \times 10^{-2}[B]^2$]

2. In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below;

Experiment	$[A]mol\ L^{-1}$	$[B]mol\ L^{-1}$	$r_0\ (mol\ L^{-1}\ s^{-1})$
1	0.20	0.30	50.7×10^{-5}
2	0.20	0.10	50.7×10^{-5}
3	0.40	0.05	1.43×10^{-4}

Determine the order of the reaction with respect to A and B.

3. The following data relate to the base catalysed hydrolysis of an ester, E

Experiment	$[E]\ moldm^{-3}$	$[\bar{O}H]\ moldm^{-3}$	Initial rate of reaction $(moldm^{-3}S^{-1})$
1	0.071	0.239	1.4×10^{-6}
2	0.142	0.241	2.7×10^{-6}
3	0.142	0.481	5.4×10^{-6}

(a) Determine the rate equation for the reaction.

(b) In an experiment in which the concentration of the ester was $0.24\ moldm^{-3}$, the initial rate of reaction was found to be $2.2 \times 10^{-6}\ moldm^{-3}S^{-1}$. Determine the pH of the solution. (Ionic product of water, $Kw = 1.0 \times 10^{-14}\ mol^2 dm^{-6}$).
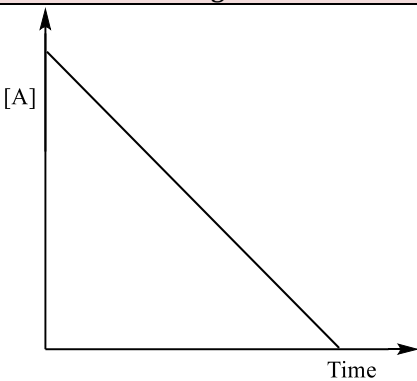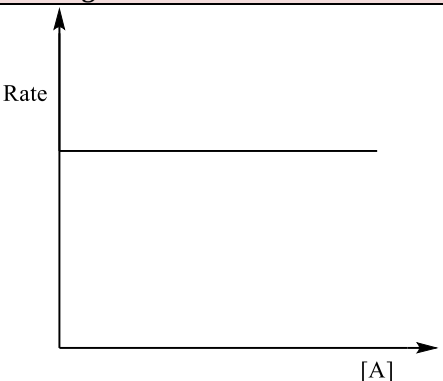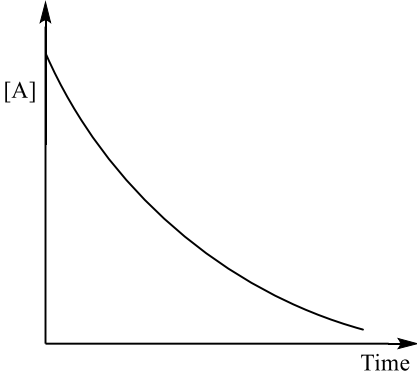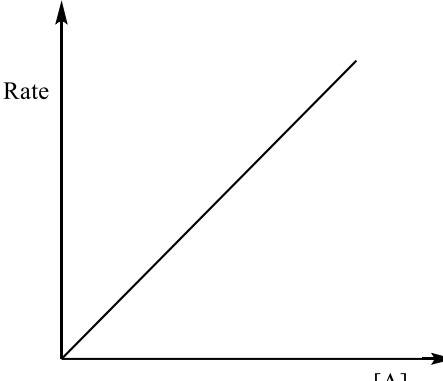
[Answer≅ 13]

Graphical determination of order of reaction

NOTE: If a graph of concentration is plotted against time,

- For first order, the half-life is constant each time the "initial" concentration is reduced to half its previous value.

- For second order' the half-life doubles each time the "initial" concentration is reduced to half its previous value.

order	Half-life	Graph of ;	
		Concentration against time	*Rate against concentration*
$[A]^0$	Decreases with time		
$[A]^1$	Constant		

Note: For Second order; successive half-life increases with time.
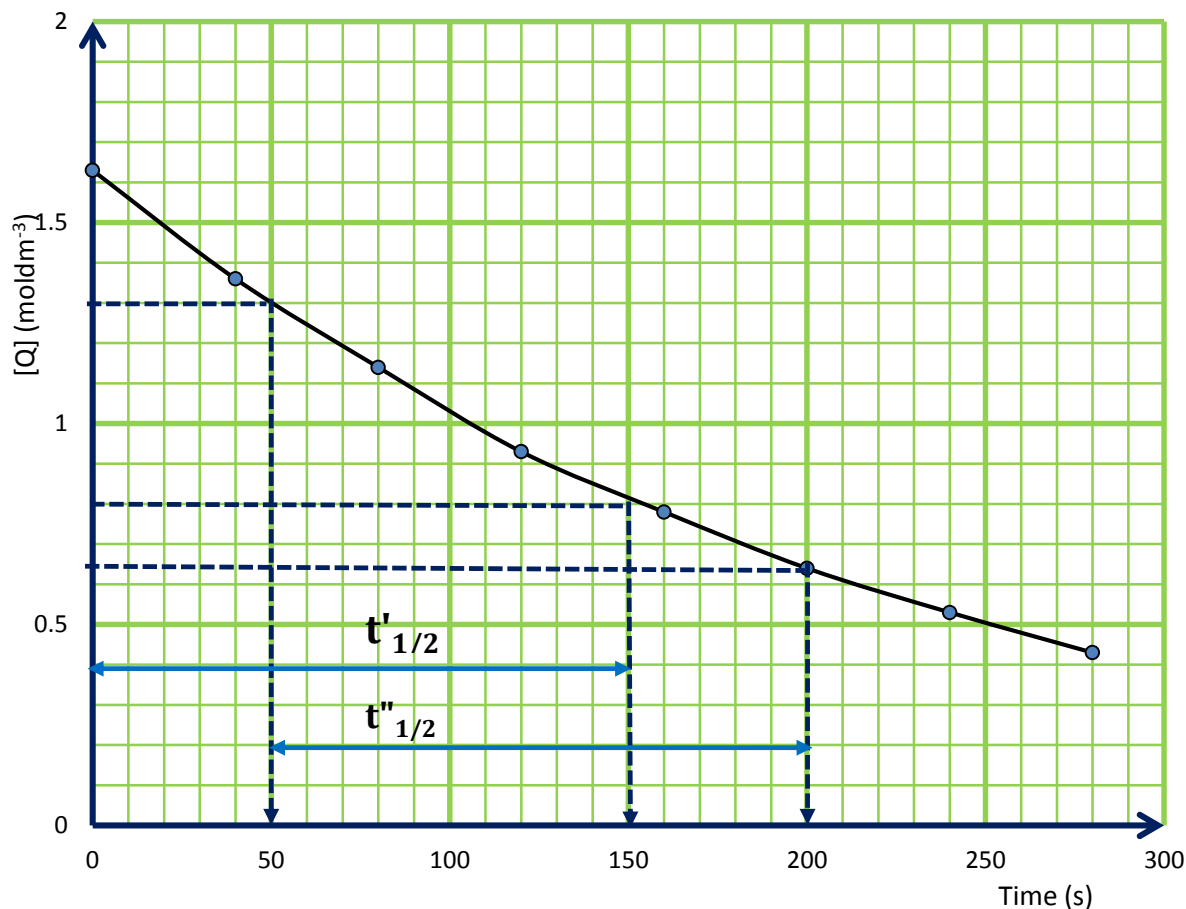
Examples:

1. The experimental data for decomposition of compound Q in gas phase at 318K are given below;

Time, t (s)	0	40	80	120	160	200	240	280
$[Q]$ $(moldm^{-3})$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43

    (a) Plot a graph of [Q] against *t*.

    (b) Use the graph to determine the half-life period for the reaction.

    (c) Calculate the rate constant.

Solution:

(a) A graph of [N₂O₅] against t

(b) From the graph, $t'_{1/2} = 150$ and $t'_{1/2} = 150$.

   Therefore half-life is $\left(\frac{150+150}{2}\right) = 150$ s.

(c) From the expression; $k = \frac{0.693}{t_{\frac{1}{2}}}$

$k = \dfrac{0.693}{150} = 4.62 \times 10^{-3} \ s^{-1}$

Task

1. The decomposition of aqueous hydrogen peroxide in a given concentration of catalyst yielded the following data;

Time (minutes)	0.0	5.0	10.0	15.0
$[H_2O_2]$ (Moldm^{-3})	0.1000	0.0804	0.0648	0.0519

(a) Plot a graph of $\log_{10}[H_2O_2]$ versus time.

(b) State the order of reaction and give a reason for your answer.

(c) Use your graph to determine the rate constant for the decomposition of hydrogen peroxide.

(d) Determine the half-life for the decomposition of hydrogen peroxide.

2. The table below shows the variation of concentration of substance **Q** with time.

Time (s)	0	400	800	1200	1600
Concentration ($Moldm^{-3}$)	5.8	3.2	1.7	0.8	0.3

(a) Using the values in the table above, plot a graph of concentration of **Q** against time.

(b) State the order the above reaction.

(c) Deduce the half-life of the reaction hence determine the rate constant of the reaction.

Using integrated rate equations to determine order of reaction

A simple data of concentration and time is used to find out the order of reaction. Different set of data is substituted into the kinetic equations of various orders at various intervals to determine the rate constants. The equation which gives the most consistent values for the rate constant is the one corresponding to the order of reaction.

Example

1. A solution of hydrogen peroxide titrated against acidified potassium manganate(VII) solution at different time intervals, gave the following results;

Time (minutes)	0	10	20
Volume of acidified $KMnO_4$ used (cm³)	23.8	14.7	9.1

(a) Show that the decomposition of hydrogen peroxide is first order.

Solution

For a first order reaction, $ln\left(\frac{N_o}{N_t}\right) = kt$

The volume of hydrogen peroxide is used as a measure of concentration of hydrogen peroxide in solution.

$$ln\left(\frac{23.8}{14.7}\right) = k \times 10 ; \quad k = 0.0481 \; minute^{-1}$$

$$ln\left(\frac{14.7}{9.1}\right) = k \times 10 ; \quad k = 0.0480 \; minute^{-1}$$

$$ln\left(\frac{23.8}{9.1}\right) = k \times 20 ; \quad k = 0.04807 \; minute^{-1}$$

Since the rate constant is almost the same (constant), the decomposition of hydrogen peroxide is therefore first order.

(b) Calculate the half-life of the decomposition of hydrogen peroxide.

Solution

$$t_{1/2} = \frac{ln2}{k} = \left(\frac{0.693}{0.048}\right) = 14.44 \text{ Minutes}$$

## Experimental determination of orders of reaction.

The rate of a chemical reaction can be obtained by following some property of the reaction e.g. concentration of the reactant or product which changes with extent of the reaction, then analyzing the reaction mixture at suitable intervals of time by titration with a suitable reagent which makes it possible to determine the concentration of both the reactants and products at different time. This provides a suitable measure of reaction rate.

Experiment to show that iodination of propanone is zero order with respect to iodine.

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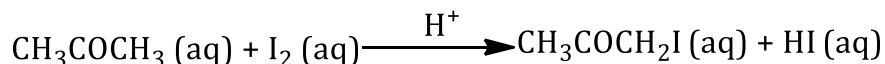
Procedure

- A known volume of a standard solution of propanone and dilute sulphuric acid are mixed in a beaker.

- A known volume of a standard solution of iodine is added in the above mixture and the stop clock is started immediately or simultaneously.

- The mixture is shaken and allowed to settle at a constant temperature.

- After specific equal time intervals, a given volume of the reaction mixture is pipetted into a conical flask containing excess sodium carbonate or sodium hydrogen carbonate to stop or quench the reaction between propanone and iodine.

- The quenched mixture is then analyzed by titrating it with a standard solution of sodium thiosulphate using starch indicator. The volume of sodium thiosulphate required to reach endpoint is noted and is proportional to the concentration of the iodine after a given time interval.
- The procedure is repeated at measured time intervals.
- Since volume of sodium thiosulphate gives a measure of amount of iodine remaining in the reaction mixture at given time interval, a graph of volume of thiosulphate used against time is plotted.
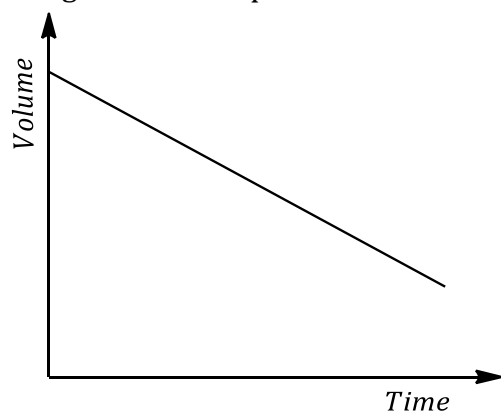
- The graph is a straight line with a negative slope/ gradient which shows that order of the reaction between propanone and iodine is zero order with respect to iodine.
- Or a graph of rate of reaction against concentration of thiosulphate is plotted. From the graph, order of reaction with respect to iodine is zero.

Task

(a) Explain what is meant by the term order of a reaction.

(b) Describe an experiment that can be carried out to show that the iodination of propanone is zero order with respect to iodine.

(c) The iodination of propanone in acidic solution takes place according to the equation;

$$CH_3COCH_3(aq) + I_2(aq) \longrightarrow CH_3COCH_2I(aq) + HI(aq)$$
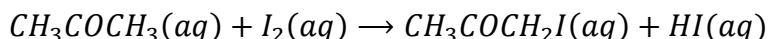
The rate of the reaction was followed by withdrawing 10 cm³ samples from the reaction mixture, quenching and titrating against standard sodium thiosulphate solution. The following results were obtained.

| Time (minutes)	0	10	20	30	40
Volume of $Na_2S_2O_3$ (cm³)	8.0	6.5	5.0	3.5	2.0

(i)   Plot a graph of volume of sodium thiosulphate used against time.

(ii) What is the order of the reaction with respect to iodine? Explain your answer.

(iii) Write an expression for the rate of the reaction if the reaction is first order overall.

(iv) What would be the effect on the gradient of your graph if the initial concentration of iodine is doubled? Give a reason for your answer.

Experiment to show that decomposition of hydrogen peroxide is first order.

$$2H_2O_2 \underset{OH^-}{\overset{Fe^{3+}}{\rightleftharpoons}} 2H_2O + O_2$$
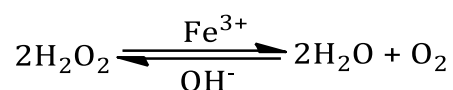
Procedure:

- A known volume of standard solution of hydrogen peroxide is placed in a beaker followed by a known volume of standard solution of sodium hydroxide.

- A known volume of a catalyst of Iron(III) chloride is added and a stop clock is simultaneously started. The mixture is allowed to stand at room temperature.

- A known volume of the reaction mixture are pipetted and added to a conical flask containing excess dilute sulphuric acid (to prevent further decomposition of hydrogen peroxide) at given time intervals.

- These samples are then titrated with a standard solution of potassium permanganate from the burette.

$$5H_2O(l) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$
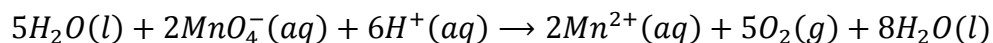
- The concentration of hydrogen peroxide at a given time interval is calculated by backward calculation.

- A graph of concentration of hydrogen peroxide against time is plotted.

- From the graph, the half-lives are determined and are found to be constant showing that the decomposition is first order.

Alternatively:
- A graph of rate against concentration is plotted.
- The graph is a straight line with a positive slope through the origin. Implying that the decomposition is first order.
- The rate constant for the reaction is obtained by determining the slope of the graph.

Task

1. The data below was obtained from the decomposition of hydrogen peroxide. The volume of hydrogen peroxide left after a given time interval was obtained by titration using acidified potassium permanganate.

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$
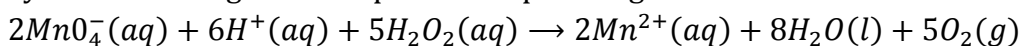
Time (minutes)	0	10	20	30
Vol. of $KMnO_4$ needed for H_2O_2 (cm³)	25.0	16.0	10.5	7.10

(a) Plot a graph of volume of potassium permanganate used against time.

(b) What is the order of reaction with respect to hydrogen peroxide? Explain your answer.

2. Hydrogen peroxide decomposes according to the equation below;

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$
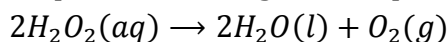
The table below shows the results obtained when various 20 cm³ samples of hydrogen peroxide solution were titrated with potassium manganate(VII) solution at various times from the start of the reaction.

Time (minutes)	0	5	10	15	20	25	30
Volume, V, of $KMnO_4$ (cm³)	24.0	18.7	14.6	11.3	8.8	6.9	5.4

(a) Write the equation for the reaction between hydrogen peroxide and potassium manganate(VII) solution.

(b) Plot a graph of $\log_{10} V$ against time.

(c) State the order of reaction with respect to hydrogen peroxide, giving a reason for your answer.

(d) Write the rate equation for the reaction.

(e) Use the graph to determine the rate constant for the reaction.

For hydrolysis of an ester;

$$CH_3COOCH_3 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOH + CH_3OH$$
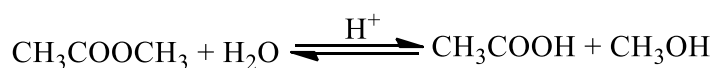
Procedure

- A known volume of a standard solution of the ester is added to a given amount of water in a beaker.

- The mixture is heated to a given temperature i.e. above 40ºC. A few drops of concentrated sulphuric acid are added and the stop clock is started simultaneously.

- The beaker is shaken for some minutes and at measured time intervals, known volumes of the reaction mixtures are pipetted into conical flask and cooled in ice cold water to prevent/ stop the reaction.

- The reaction mixture is then titrated with a standard solution of sodium hydroxide using phenolphthalein indicator to determine the amount of carboxylic acid formed.

- A graph of concentration of sodium hydroxide is then plotted against time.

Example:

1. The table below shows the kinetic data that were obtained for the hydrolysis of the ester, methyl ethanoate in acid solution. The concentration of ethanoic acid formed in the reaction mixture was recorded at intervals of time. The original concentration of methyl ethanoate was 0.2405M.

Time (minutes)	0	3600	7200	10800	14400
$[CH_3COOH]$ (moldm^{-3})	0	0.084	0.136	0.172	0.195

   (a) Plot a graph of concentration of the ester (methyl ethanoate) against time.
   (b) Determine the half-life of the reaction.
   (c) Determine the order of reaction with respect to the ester, give a reason for your answer.
   (d) Determine the rate constant for the reaction and indicate its units.

Solution:

(a) If x moles of ethanoic acid were formed, then the concentration of the ester can be determined from $(0.2405 - x)$ as shown below;

| Time (min)	0	3600	7200	10800	14400
[Ester] (moldm^{-3})	0.2405	0.1565	0.1045	0.0685	0.0455
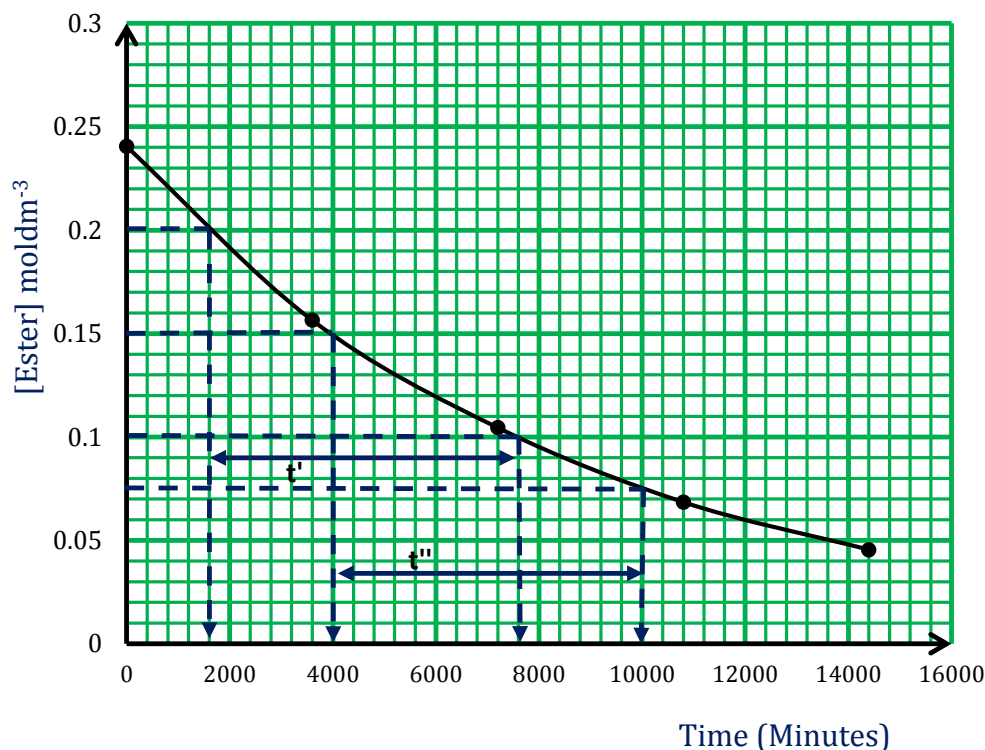
(b) From the graph, half-life is 6000 minutes and the order of reaction is first order with respect to ester since the successive half-lives are constant.

(c) The rate constant is determined by using the expression $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{6000} = 1.155 \times 10^{-4} \ Minute^{-1}$$

An experiment to show that the reaction between sodium thiosulphate and hydrochloric acid is first order with respect to sodium thiosulphate.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$
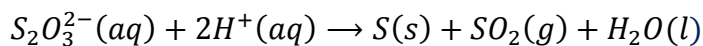
Procedure:

❖ Known volumes of known concentrations of sodium thiosulphate are prepared from the stock solution and placed in different beakers or conical flasks.

❖ The beakers are placed on a white piece of paper with a cross or dot on them. A known (fixed) volume of dilute hydrochloric acid is measured using measuring cylinder.

❖ When dilute hydrochloric acid is added to the solution of sodium thiosulphate, a stop clock is started. The mixture is swirled while being viewed from above. The time

taken when the yellow precipitate of sulphur blocks (obscure) the cross/ dot from the view is noted.

❖ The experiment is repeated with different concentrations of sodium thiosulphate and times recorded.

❖ A graph of reciprocal of time against concentration of sodium thiosulphate is plotted. A straight line graph from the origin is obtained an indication that the order of reaction with respect to thiosulphate ion is one i.e. first order.

Concentration of thiosulphate (mol dm⁻³)
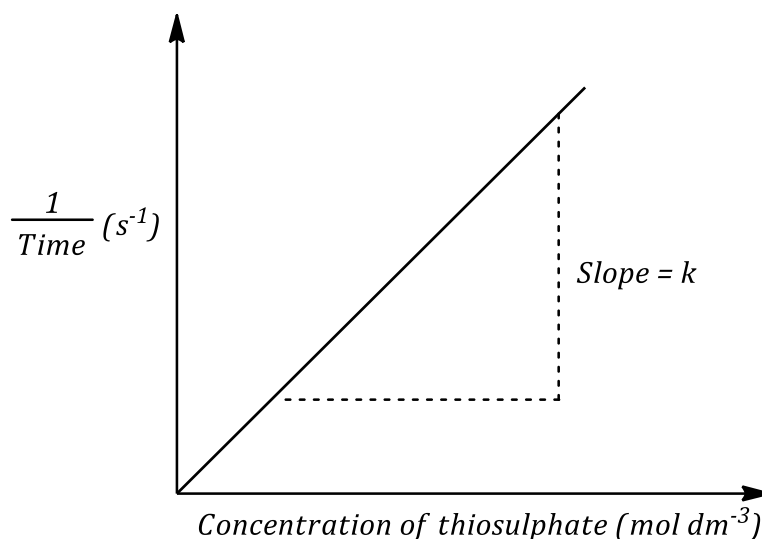
Task

1. Sodium thiosulphate solution reacts with hydrochloric acid according to the following equation.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$$
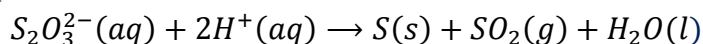
(a) The kinetic data for the above reaction at 25°C is shown in the table below.

| Expt	$[S_2O_3^{2-}]$ $(mol\ dm^{-3})$	$[H^+]$ $(mol\ dm^{-3})$	Initial rate $(mol\ dm^{-3}\ s^{-1})$
1	0.40	0.20	7.00×10^{-4}
2	0.40	0.60	6.30×10^{-3}
3	0.80	0.60	1.26×10^{-2}

(i)   Differentiate between **order** and **rate constant** of reaction.

(ii) Determine the order of the reaction with respect to $S_2O_3^{2-}$ and H^+ions.

(iii) Write an expression for the rate law.

(iv) Calculate the rate constant for the reaction at 25°C and indicate its units.

(b) Using the above reaction, describe an experiment that can be carried out to determine the order of reaction with respect to $S_2O_3^{2-}$ ions.

ACTIVATION ENERGY AND THE ACTIVATED COMPLEX.

All elementary (single step) reactions occur via a transition step e.g. Consider a simple substitution reaction such below;

$$A(g) + BC(g) \longrightarrow AB(g) + C(g)$$
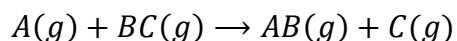
The reaction proceeds via;

$$A + B \leftrightharpoons [A \cdots B \cdots C] \rightarrow AB + C$$
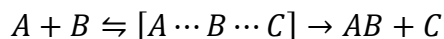
In order to form a transition step, $[A \cdots B \cdots C]$, the reactants must acquire some energy which must be equal to the threshold value for the products to be formed. This energy is called the activation energy. It is denoted by Ea.

Activation energy;

This is the minimum energy which the reactants must possess before they can react to form products.

If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

Since the transition step is energy rich, it cannot be isolated and therefore the transition step is referred to as the activated complex which may decompose to give either the products or original reactants.

Activated complex;

This is an unstable intermediate state in which the bonds are partially broken and the bonds between the products are partially formed.

Energy variation during the formation of an activated complex is shown below;
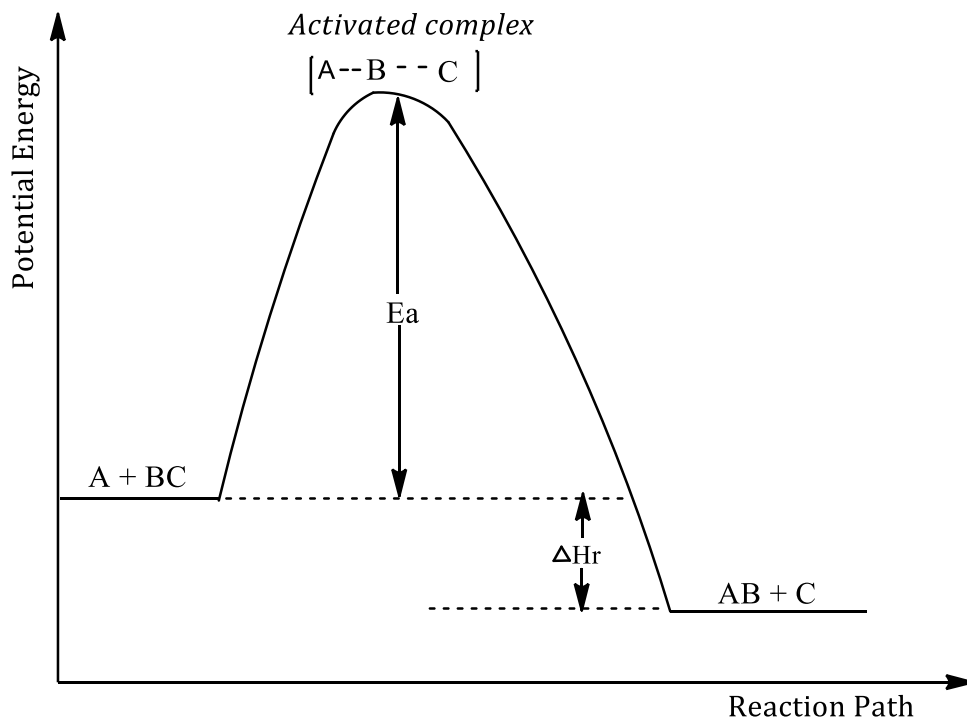
For the above particular case, the reaction is exothermic because the products are at a lower energy level than the reactants.

The activation energy for the backward reaction is given by;

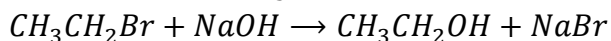$$Ea_{(Backward)} = \Delta Hr + Ea$$

Molecularity of a reaction.

This refers to the number of reacting species (atoms, ions, or molecules) taking part in the rate determining step/ slowest step/ activated complex formation in a chemical reaction.

Molecularity is always a whole number and determined from the stoichiometry of the reaction equation.
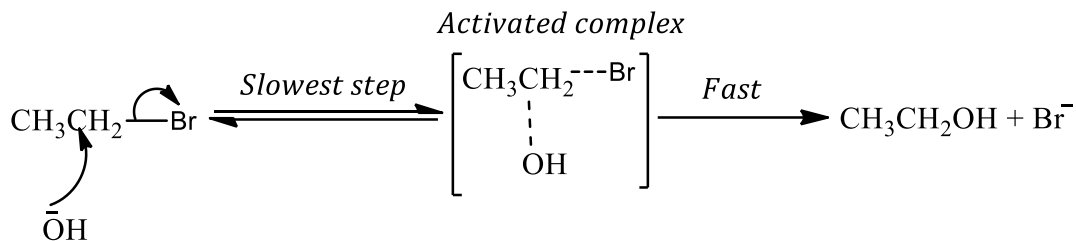
The reactions are termed as unimolecular, bimolecular or trimolecular depending upon the number of reacting particles as 1, 2, 3, etc. in the rate determine step. Simultaneous collisions involving more than three molecules are very rare and hence reactions with molecularity more than three are also rare.

Example:
  (a) Reaction of a primary alkylhalide e.g. CH_3CH_2Br with sodium hydroxide.
$$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$$
  Mechanism for the reaction;

Activated complex

$$CH_3CH_2\text{—Br} \xrightleftharpoons{\textit{Slowest step}} \left[\begin{array}{c} CH_3CH_2\text{---Br} \\ \vdots \\ OH \end{array} \right] \xrightarrow{\textit{Fast}} CH_3CH_2OH + Br^-$$
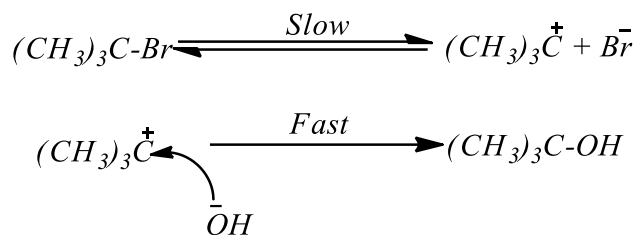
$$Rate = kCH_3CH_2Br][OH^-]$$

- The reaction is first order with respect to is OH^-.
- The reaction is also first order with respect to CH_3CH_2Br
- The molecularity of the reaction is 2 i.e. the reaction is Bimolecular hence SN₂ mechanism.
- The reaction profile for the above reaction is shown below;
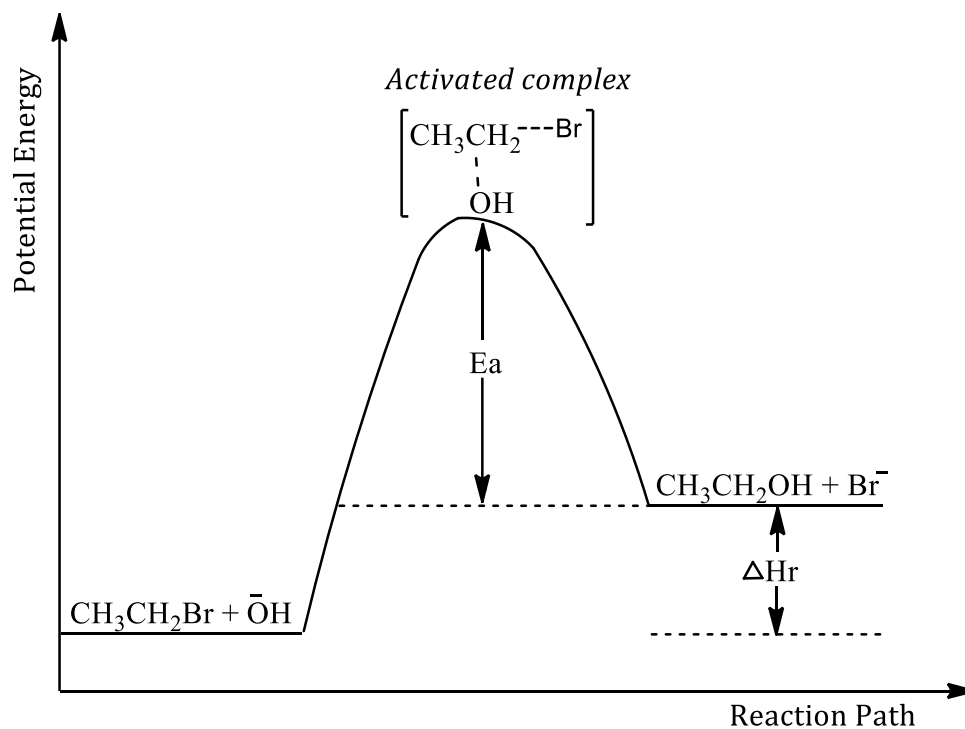

(b) Reaction of a tertiary alkylhalide with sodium hydroxide.
   There are number of reactions which are complex in nature and occur in several steps; the molecularity of such reactions is determined by the slowest step. Thus, molecularity depends upon the mechanism of the reaction.

Mechanism of reaction:

$$(CH_3)_3C\text{-}Br \underset{\xrightarrow{\hspace{2cm}}}{\overset{Slow}{\longleftarrow}} (CH_3)_3\overset{+}{C} + \overset{-}{Br}$$

$$(CH_3)_3\overset{+}{C} \xrightarrow{\hspace{0.3cm}Fast\hspace{1cm}} (CH_3)_3C\text{-}OH$$
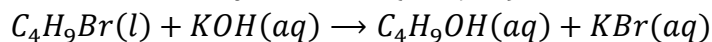
$$\overset{-}{OH}$$

in the above mechanism the slowest step involves one reactant, therefore the molecularity of the above reaction is one, the energy profile for the reaction is as shown below;
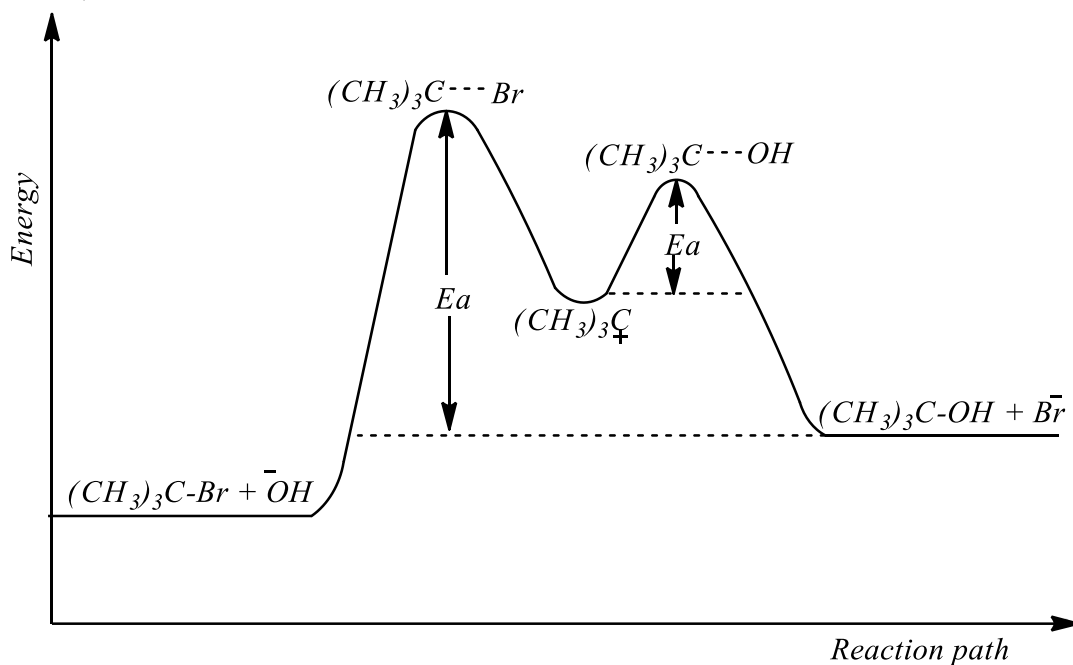
Task

1. The table below shows the kinetic data for the reaction between hot aqueous potassium hydroxide and an alkyl bromide (C_4H_9Br).

$$C_4H_9Br(l) + KOH(aq) \rightarrow C_4H_9OH(aq) + KBr(aq)$$

Expt	$[C_4H_9Br](mol\ dm^{-3})$	$[KOH](mol\ dm^{-3})$	Initial rate ($mol\ dm^{-3}\ s^{-1}$)
1	1.0×10^{-3}	1.0×10^{-3}	5.0×10^{-8}
2	2.0×10^{-3}	1.0×10^{-3}	1.0×10^{-7}
3	2.0×10^{-3}	2.0×10^{-3}	2.0×10^{-7}

(a) Determine the overall order of reaction.

(b) Identify the alkyl halide.

(c) Write the mechanism for the reaction above.

(d) Draw a well labelled energy level diagram for the reaction mechanism illustrated in (c) above.

FACTORS AFFECTING THE RATE OF REACTION

According to the collision theory, the rate of reaction will increase if:

- the frequency of collision and effective collision increases
- the proportion of particles with energy greater than activation energy increases

The following are the factors that can affect rate of a chemical reaction:

- Temperature at which the reaction are taking place.
- Concentration of the reactants.
- Surface area of the reactants.
- Presence of a catalyst.

Catalyst

Catalysts increase the rate of chemical reactions but remain unchanged at the end of the reaction.

For a given chemical reaction, the same amount of products are formed but within a shorter period of time.

Catalysts increase the rate of chemical reaction by lowering the activation energy of the reactants by providing an alternative path to the reaction.

Effect of surface area.

This mainly affects reaction systems in which solids are involved. The larger the surface area of the reactant particles, the higher the rate of reaction.

This is because the surface area exposed for collision is larger, frequency of collision between the reactant particles increases and hence the frequency of effective collision also increases. More products are formed per unit time and hence the rate of reaction increases.

For example, the reaction between hydrochloric acid and marble chips (calcium carbonate) is as follows:

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$$
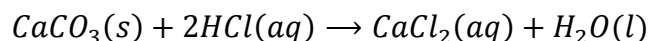
The powdered marble chips react faster than big lumps of marble chips. The powdered marble chips are smaller in size and hence have a larger total surface area.

Therefore if powdered marble chips are used, more carbon dioxide gas is given out compared to a big lumps in a given period of time.

Effect of concentration.

The higher the concentration of the reactant particles, the higher the rate of reaction. This is because in a more concentrated solution, there are more reactant particles per unit volume. The particles become so close to one another.

The frequency of collision between the reactant particles increases and hence the frequency of effective collision also increases. More products are formed per unit time and hence the rate of reaction is higher.

Consider the reaction between magnesium ribbon and hydrochloric acid is as follow;

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(aq)$$
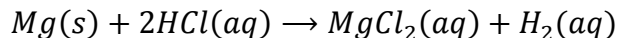
The rate of reaction can be found by measuring the time taken for the magnesium ribbon to disappear from sight. When hydrochloric acid of higher concentration is used, the time taken for the magnesium ribbon to disappear is shorter.

NB: Rate of reaction is inversely proportional to time, the shorter the time, the higher the rate of reaction.

Effect of pressure
The higher the pressure of the system, the higher the rate of reaction, the explanation is the same as the one in the effect of concentration. However, increasing the pressure will only increase the rate of a reaction involving gases. Changing the pressure of a reaction which involves only solid or liquid has no effect on it.

Effect of temperature.
The higher the temperature of the reacting system, the higher the rate of reaction, this is because at higher temperature, the average kinetic energy of the particles increases, so:

(a) more reacting particles have energy equal to or greater than the activation energy (This is the major reason)
(b) the reacting particles move at higher speed, the frequency of collision between the reacting particles increases (This is the minor reason)

This causes the frequency of effective collision to increase. More products are formed per unit time and hence the rate of reaction is higher.

NB: The rate of reaction doubles for every increase in 10 °C. The effect of temperature on rate of reaction can be shown in a Maxwell-Boltzmann distribution curve.

Effect of temperature on the rate of reaction.
When molecules are heated, their kinetic energy increases, which means that a larger fraction of them will have sufficient energy to overcome the activation barrier, Ea and thus the rate of reaction increases which also increases the rate constant since the two are directly proportional.

NOTE: increase in temperature does not affect the activation energy of the reactants instead it increases the number of molecules possessing the activation energy and thus more products are formed.

For many reactions, raising the reaction temperature by 10°C doubles or triples the rate i.e. the rate increases by a factor of 2 to 3.

The Swedish chemist Arrhenius noticed the dependence of reaction rate k on temperature T. He found that his measured data conformed to the equation below;

$$k = Ae^{\left(\frac{-Ea}{RT}\right)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(i)$$

The above expression is called the Arrhenius equation/ expression.

A is the frequency factor or pre-exponential factor which is only obtained by experiment. It is related to the frequency of collisions and the orientation of the reacting molecules.

R is the gas constant. This is equal to 8.314 and
Ea is the activation energy.
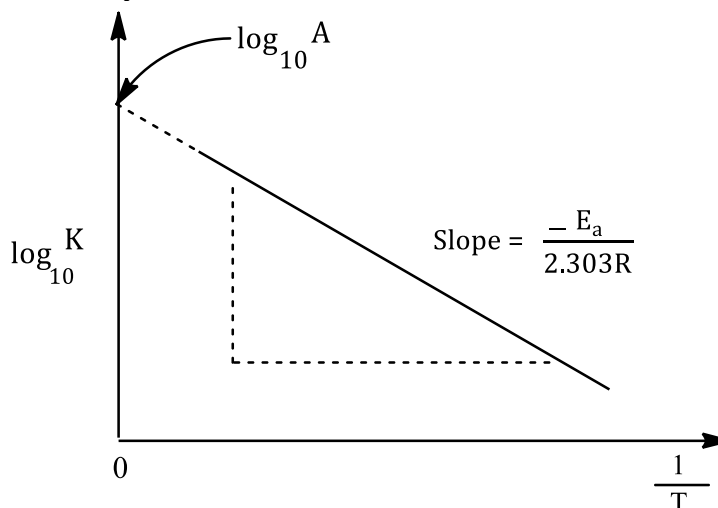Taking natural logarithm on both sides of equation (i) above;

$$lnk = lnA - \frac{Ea}{RT}$$

$$2.303 \log_{10} k = 2.303 \log_{10} A - \frac{Ea}{RT}$$

$$\log_{10} k = -\frac{Ea}{2.303R}\left(\frac{1}{T}\right) + \log_{10} A \dots\dots\dots\dots\dots..(ii)$$

Compare equation (ii) $with\ y = mx + c$

A plot of $\log_{10} k$ against $\frac{1}{T}$ (where T is in Kelvin) yields the graph below;

From the graph, we can obtain the activation energy **Ea** for a given reaction.

Suppose for a reaction at T_1, the rate constant is K_1 while at T_2, the rate constant is K_2 where T_2 is greater than T_1 and K_2 is greater than K_1.

$$\log_{10} k_2 = -\frac{Ea}{2.303R}\left(\frac{1}{T_2}\right) + \log_{10} A \dots\dots\dots\dots\dots\dots..(iii)$$

$$\log_{10} k_1 = -\frac{Ea}{2.303R}\left(\frac{1}{T_1}\right) + \log_{10} A \dots \dots \dots \dots \dots \dots \dots . (iv)$$
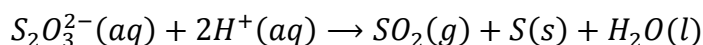
Subtracting (iv) from (iii),

$$\log_{10} k_2 - \log_{10} k_1 = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \dots \dots \dots \dots \dots \dots \dots . (v)$$

Examples:

1. The table below shows a student's work on the acid catalysed disproportionation of thiosulphate ions.

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

Temperature (K)	Time (s)
294	87
303	48
316	24
325	16
333	09

The rate of reaction was measured by a clock method. The measured event was for the time for the sulphur precipitate to obscure a black dot viewed through a reaction vessel.

Reciprocals of the the times are taken as being proportianal to the rates.
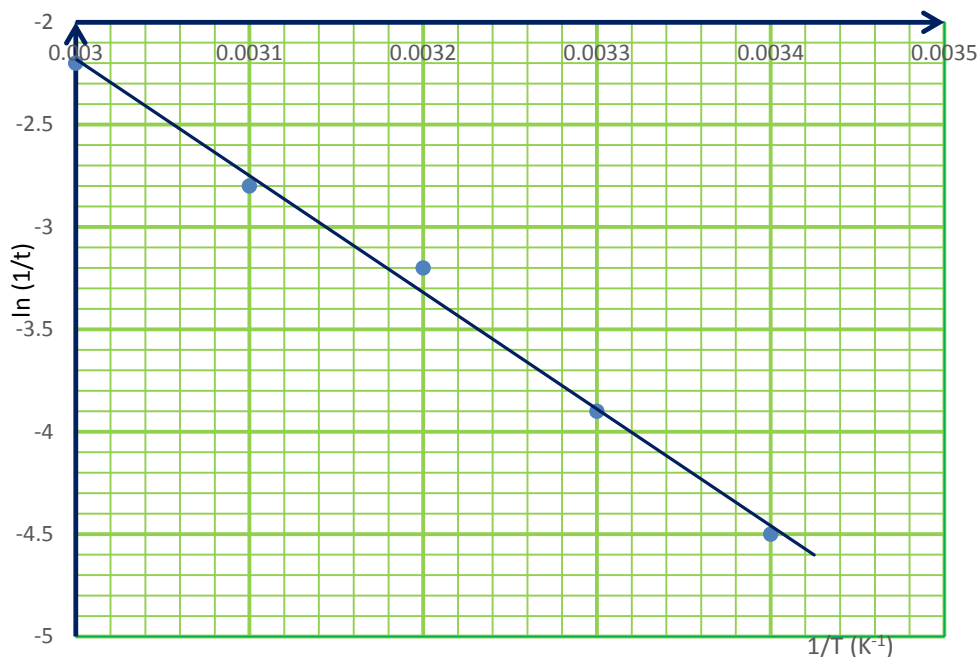
(a) Convert the time data into numbers that are proportianal to rate.

(b) Plot a graph of $ln(Rate)$ against 1/T.

(c) Use your graph to determine the activation energy of the reaction.

Solution

Temperature, T (K)	Time, t (s)	$\frac{1}{t}$ ($\propto Rate$) $(10^{-2}s^{-1})$	$ln\left(\frac{1}{t}\right)$	$\frac{1}{T}$ $(10^{-3}K^{-1})$
294	87	0.011	-4.5	0.0034
303	48	0.021	-3.9	0.0033
316	24	0.042	-3.2	0.0032
325	16	0.063	-2.8	0.0031
333	9	0.111	-2.2	0.003

$$Slope = \frac{(-2.2 - (-4.5))}{(0.003415 - 0.003)} = -5542$$

$$slope = -\frac{E_a}{R}$$

$$-5542K = -\frac{E_a}{8.314}$$

$$E_a = 46076.188 \, Jmol^{-1}$$

2. The variation of the rate constant with temperature for decomposition of hydrogen iodide gas to hydrogen gas and iodine gas is given below.

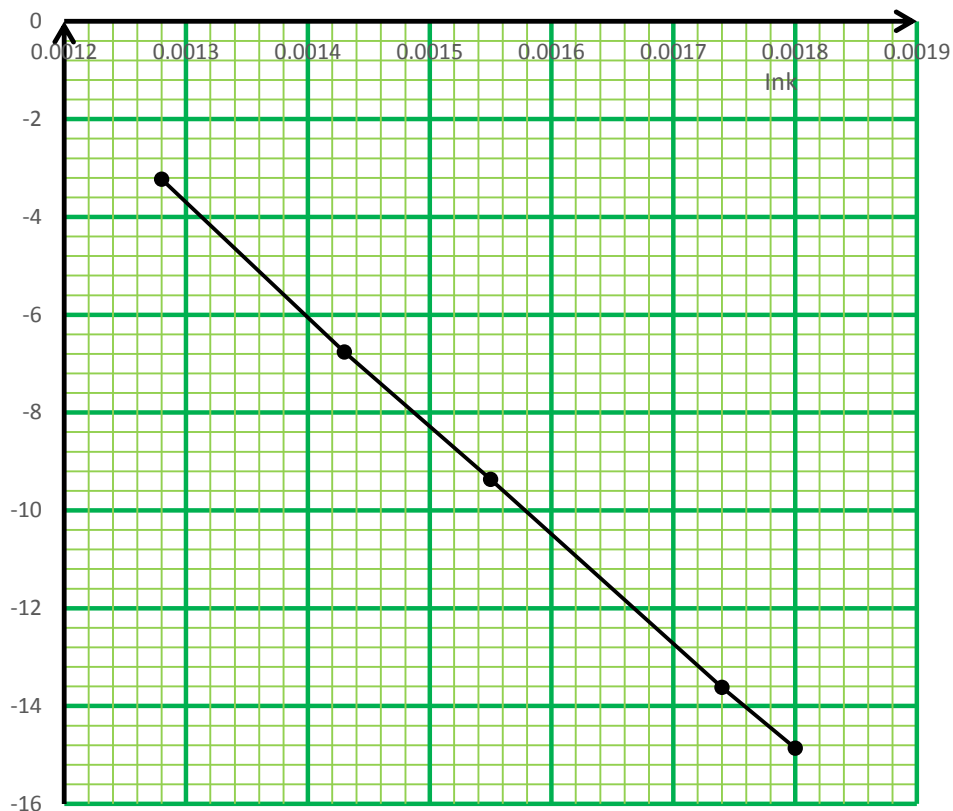| T (K)	555	575	645	700	781
K	3.52×10^{-7}	1.22×10^{-6}	8.59×10^{-5}	1.16×10^{-3}	3.95×10^{-2}

(a) Plot a graph of $\frac{1}{T}$ against InK

(b) Use the graph to determine the activation energy.

Solution

(a)

$\frac{1}{T}$	1.80×10^{-3}	1.74×10^{-3}	1.55×10^{-3}	1.43×10^{-3}	1.28×10^{-3}
InK	-14.860	13.617	-9.362	-6.759	-3.231

(b) From the graph, slope $= 22000$

But $slope = \frac{\Delta(InK)}{\Delta\left(\frac{1}{T}\right)} = -\frac{E_a}{R}$

Implying that $-\frac{E_a}{R} = 22000$

$E_a = -22000 \times 8.314 = 18290.8 \, Jmol^{-1}$

$E_a = 18.2908 \, kJmol^{-1}$

Task

The rate constant for the decomposition of HI to yield hydrogen gas and iodine gas follows the following temperature dependence.

k $(dm^3mol^{-1}s^{-1})$	3.16×10^{-6}	7.90×10^{-5}	3.20×10^{-3}	0.10
T (K)	550	625	700	830

Determine the activation energy for the reaction
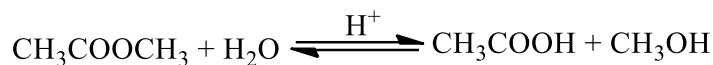
Pseudo-order reactions

Reactions whose actual order is different from that expected using rate law expression are called pseudo-order reactions.

Pseudo-first order reactions.

These are reactions which are practically first order but theoretically are of higher orders. Examples of pseudo-first order reactions are;

- Hydrolysis of sucrose in the presence of the acid
- Hydrolysis of an ester in the presence of the acid.

Consider the hydrolysis of the ester below,

$$CH_3COOCH_3 + H_2O \xrightleftharpoons{H^+} CH_3COOH + CH_3OH$$

$$Rate = k[Ester][H_2O][H^+]$$

Practically, the order of reaction is one, but theoretically 3.

Conditions for pseudo-first order reactions to take place;

- When one of the reactants is in excess. The concentration of the excess reactant remains practically unchanged. Therefore the rate of reaction will not be affected by such concentrations in large excess but it will depend on the concentration of that reactant which tends to be a minimum.

- When one of the reactants is a catalyst. A catalyst is continuously regenerated and so its concentration remains unchanged.

Task

1. Methyl ethanoate is hydrolysed by water in the presence of an acid according to the following equation.

$$CH_3COOCH_3 + H_2O \xrightleftharpoons{H^+} CH_3COOH + CH_3OH$$
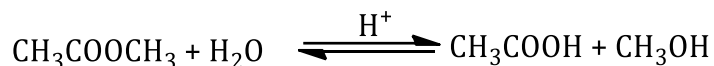
(a) State the molecularity of the reaction.
(b) Determine the order of the reaction. (Assume the acid takes part in the reaction).
(c) State the conditions under which the reaction can be overall first order.
(d) The rate constant for the hydrolysis of methyl ethanoate in acidic medium at 25°C is $1.26 \times 10^{-4} s^{-1}$. Determine;
   (i) The half-life of methyl ethanoate at 25°C.
   (ii) How long it will take for 85% of the methyl ethanoate to react.

2. The table below shows the kinetic data obtained for hydrolysis of an ester in acidic media.

Time (Minutes)	0	15	30	45	60	75	90
$[Ester]$ $(moldm^{-3})$	0.55	0.42	0.31	0.23	0.17	0.12	0.09

(a) Plot a graph of concentration of ester against time.
(b) Using the graph in (a), determine the;
   (i) half-life of the reaction.

(ii) Order of the reaction with respect to the ester. Give a reason for your answer.