CHEMICAL KINETICS.

Introduction

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

Rate of chemical reaction

The rate of a chemical reaction can be defined as amount of product formed (reactant used up) per unit.

Thus, we can write; Rate $\alpha \frac{d[product]}{dt}$ or Rate $\alpha \frac{d[reactant]}{dt}$; where [ ] is concentration in $moll^{-1}$ or $moldm^{-3}$.
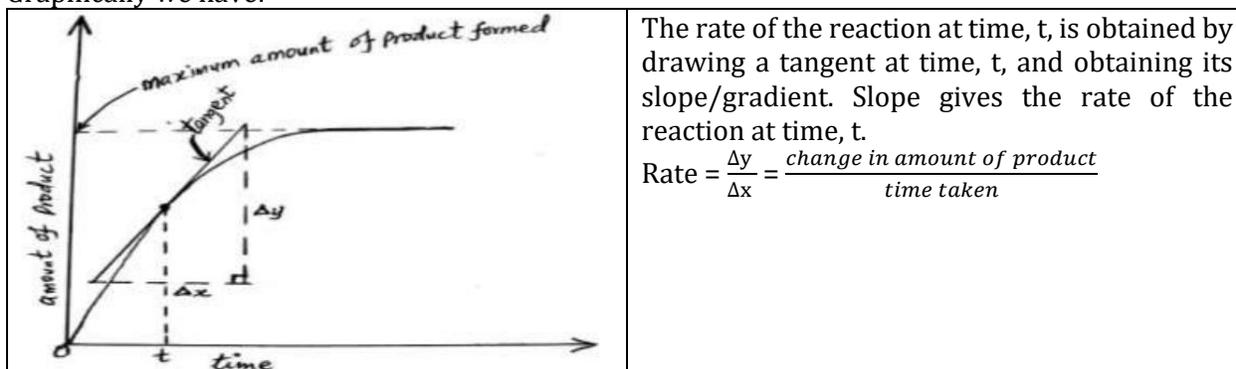
Consider a general reaction; $A + B \rightarrow C + D$
If rate is represented by R, the we can write:

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

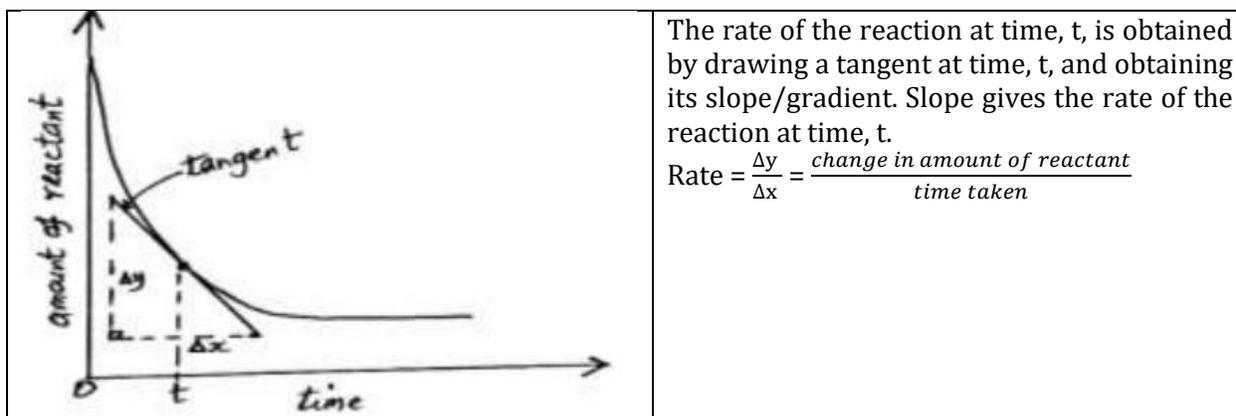The negative sign implies that the concentration of **A or B** is decreasing with time.
Graphically we have:

	The rate of the reaction at time, t, is obtained by drawing a tangent at time, t, and obtaining its slope/gradient. Slope gives the rate of the reaction at time, t. Rate $= \frac{\Delta y}{\Delta x} = \frac{change\ in\ amount\ of\ product}{time\ taken}$

(b) $R = +\frac{d[C]}{dt}$ or $+\frac{d[D]}{dt}$

The positive sign implies that the concentration of **C or D** is decreasing with time.
Graphically we have:

|	
	The rate of the reaction at time, t, is obtained by drawing a tangent at time, t, and obtaining its slope/gradient. Slope gives the rate of the reaction at time, t. Rate $= \frac{\Delta y}{\Delta x} = \frac{change\ in\ amount\ of\ reactant}{time\ taken}$

The common laboratory methods for determining rates of chemical reactions are:
(a) Titrimetric method or simply titration
(b) Measuring the volume of the product if gaseous at regular time intervals
(c) Measuring loss in mass of a reaction mixture due loss of a gaseous product.
(d) Measuring the change in conductivity of the liquid due to the change in the number of conducting ions
(e) Measuring change in pressure if the reaction involves gaseous substances etc.

The law of mass action and order of reaction

The law states that "The rate of a chemical reaction is directly proportional to the molar concentration of the reactants raised to appropriate powers at a constant/particular/given temperature"

Consider the reaction below;

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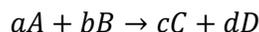
The rate of reaction depends on the concentration of the reacting species.

$$Rate \propto [A]^m \text{ or } Rate \propto [B]^n$$
$$Rate = k[A]^m \text{ or } Rate = k[B]^n$$

- Combining, the overall rate of the reaction is; $Rate = [A]^m[B]^n \dots\dots\dots\dots\dots\dots\dots (i)$
- **k** *is known as the rate constant/velocity constant*
- The above expression is known as rate law/rate expression/rate equation
- The constant **k** *is dependent on* **only** *temperature.*
- The exponents **m** and **n** are experimental quantities which may be zero, positive or negative, fraction or whole numbers and are unrelated to the stoichiometry of the reaction (i.e. the number of moles of the reactant participating in the reaction).
- Thus, we say the rate of the reaction is of order **m** with respect to reactant A and order **n** with respect to reactant B.
- The overall order of the reaction is $(\boldsymbol{m + n})$.
- Thus, the **order of a reaction** is the algebraic sum of the powers to which the concentrations of the reactants are raised to in a given experimental rate equation.
- The **rate constant** refers to the ratio of the rate of a chemical reaction to the product of the concentration of the reactants raised to their appropriate powers in the experimental rate equation at a given temperature.

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

- ✓ The **rate law** is a mathematical expression which expresses the relationship between rate of reaction and concentrations of the reactants raised to their appropriate powers in the slowest/rate determining step of the reaction.
- ✓ The **molecularity** of chemical reaction refers to the total number of chemical species taking part in the rate determining step/slowest step of a chemical reaction.
- ✓ Unlike orders of chemical reactions, molecularity of chemical reactions must be positive whole numbers.
- ✓ In some reactions, only one type of chemical species is involved in the slowest step hence, unimolecular reactions.
- ✓ Bimolecular reactions involve two different type of reacting species.
- ✓ In some cases, the order of a reaction is equal to the molecularity of the reaction.

For example:

(a) Hydrolysis of primary alkyl halides using hot aqueous sodium hydroxide.

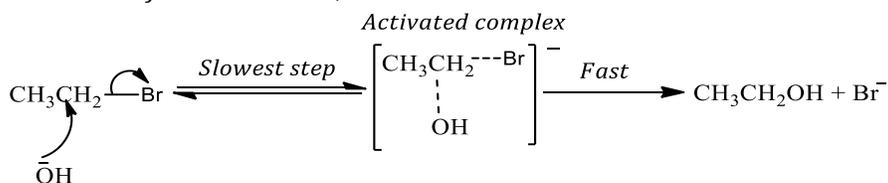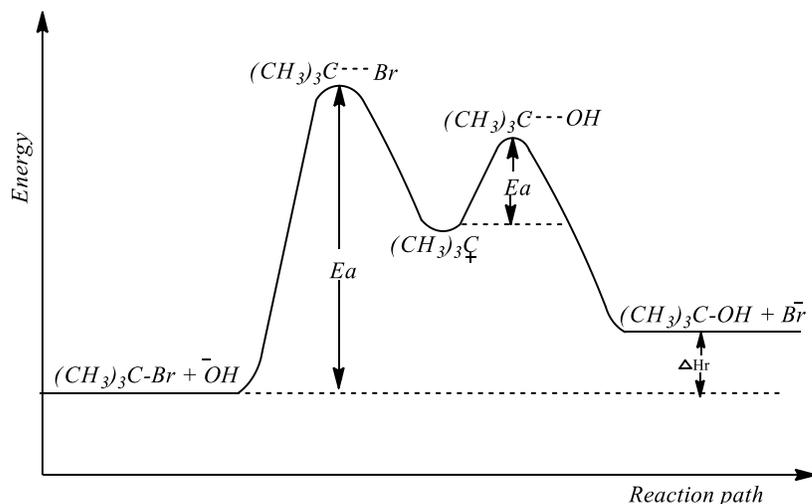$$CH_3CH_2Br + NaOH(aq) \rightarrow CH_3CH_2OH + NaBr$$
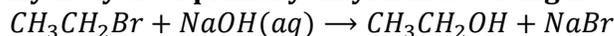
Experiments show that the reaction is first order with respect to bromoethane and first order with respect to sodium hydroxide. Thus, the reaction overall second order and this suggests that the slowest step involves both the alkali and the haloalkane.

The rate expression becomes; $Rate = k[CH_3CH_2Br][OH^-]$

This is a bimolecular reaction. The order and molecularity of the reaction are the same.

Mechanism for the reaction;

The reaction profile diagram for the above reaction takes the form:

Task

1. The kinetics of the hydrolysis of the halogenalkane, **Q** with aqueous sodium hydroxide was studied at 50°C. The following results were obtained:

Expt	$[Q]\ (moldm^{-3})$	$[\bar{O}H]\ (moldm^{-3})$	Initial rate $(moldm^{-3}s^{-1})$
1	0.050	0.10	4.0×10^{-4}
2	0.150	0.10	1.2×10^{-3}
3	0.100	0.20	1.6×10^{-3}

(a) Deduce the order of reaction with respect to **Q** and with respect to the hydroxide ion, $\bar{O}H$.
(b) Hence write the rate equation for the reaction.
(c) Calculate the value of the rate constant for this reaction and state its units.
(d) State the class of the haloalkane, Q.
(e) Draw a well labelled energy profile diagram for the reaction above.

(b) Hydrolysis of tertiary alkyl halides with hot aqueous sodium hydroxide or hot water.
$$(CH_3)_3CBr + NaOH(aq) \longrightarrow (CH_3)_3COH + NaBr$$
Experiments suggest that the reaction is first order with respect to the haloalkane but zero order with respect to the alkali/water.

Thus, the slowest step does include the alkali/water and hence the mechanism of the reaction can be written as follows:

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

$$(CH_3)_3\overset{+}{C} \xleftarrow{} \overset{Fast}{\xrightarrow{\hspace{2cm}}} (CH_3)_3C\text{-}OH$$
$$\bar{O}H$$

The firsts step is the slowest step and the reaction is unimolecular.
The rate law for the reaction can be written as: $Rate = k[(CH_3)_3CBr]$.
Again in this case the order and molecularity of the reaction are the same.
The energy profile diagram for the reaction takes the following form:

Energy

$(CH_3)_3C\text{---}Br$

$(CH_3)_3C\text{---}OH$

Ea

$(CH_3)_3C^{+}$

Ea

$(CH_3)_3C\text{-}OH + \bar{Br}$

ΔHr

$(CH_3)_3C\text{-}Br + \bar{O}H$

Reaction path

Task

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

$$C_4H_9Br(l) + KOH(aq) \longrightarrow C_4H_9OH(aq) + KBr(aq)$$
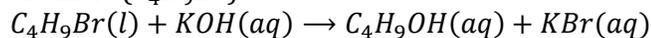
Experiment no.	$[C_4H_9Br](mol\ dm^{-3})$	$[KOH](mol\ dm^{-3})$	Initial rate $(mol\ dm^{-3}\ s^{-1})$
1	1.0×10^{-3}	1.0×10^{-3}	5.0×10^{-8}
2	2.0×10^{-3}	1.0×10^{-3}	1.0×10^{-7}
3	2.0×10^{-3}	2.0×10^{-3}	2.0×10^{-7}

(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.

Pseudo-order reactions

These are reactions whose practical (actual) order is different from that theoretical (expected) one.

For example:

(a) Hydrolysis of esters in the presence of the acid

$$CH_3COOCH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH + CH_3OH$$
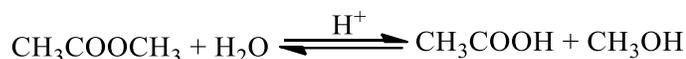
The rate of the reaction above takes the form: $Rate = k[Ester][H_2O][H^+]$ and hence, third order reaction. Molecularity of the reaction is also three.

However, practically, the order of reaction is one under the following assumptions:

➢ Water is in large excess and thus, its concentration remains almost constant and does not affect the rate of the reaction.

➢ Hydrogen ions act as a catalyst. A catalyst is continuously regenerated and so it is concentration remains unchanged.

Thus, the new rate expression of the reaction above takes the form: $Rate = k'[Ester]$; where, $k' = [H_2O][H^+]$.

(b) Hydrolysis of an sucrose in the presence of the acid is also a first order reaction with respect to the sucrose under the similar assumptions above.

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

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$
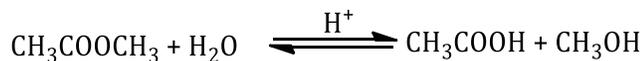
   (a) State the molecularity of the reaction.
   (b) Determine the order of the reaction. (Assume the acid takes part in the reaction).
   (c) State the conditions under which the reaction can be overall first order.
   (d) The rate constant for the hydrolysis of methyl ethanoate in acidic medium at 25°C 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 be hydrolysed.

2. In the 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 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.

Determining orders of chemical reactions

Once data from an experiment for a given chemical reaction is collected, the order of the reaction can be obtained as follows:

A. Initial rate method

In this method, the order of reaction with respect to **one** reactant is determined by comparing the concentrations of the reactant in any two experiments while the concentrations of the other reactants are kept constant.

Examples:

1. The following data were obtained for the reaction; $A + B + C \longrightarrow$ Products at 298K.

Experiment no.	[A] $(moldm^{-3})$	[B] $(moldm^{-3})$	[C] $(moldm^{-3})$	Initial rate $(mol\ l^{-1}s^{-1})$
1	0.5	0.1	0.3	4.0×10^2
2	1.0	0.1	0.3	8.0×10^2
3	2.0	0.1	0.3	16.0×10^2
4	0.5	0.2	0.3	16.0×10^2
5	0.5	0.1	0.6	4.0×10^2

(a) Determine the:
   (i) order of reaction with respect to each of the reactants.
   Let the order with respect to **A** *and* **B** *be m and n respectively*
   $$Rate = k[A]^m[B]^n[C]^p$$
   To determine the order with respect to **A**, *we take experiments* 1 *and* 2 *where* [**B**] *and* [**C**] *are kept constant while* [**A**] *is varying.*

$4.0 \times 10^2 = k(0.5)^m(0.1)^n(0.3)^p \;\ldots(i)$ $8.0 \times 10^2 = k(1.0)^m(0.1)^n(0.3)^p \;\ldots(ii)$ Dividing equations (i) by (ii) $\dfrac{4.0 \times 10^2}{8.0 \times 10^2} = \left(\dfrac{0.5}{0.1}\right)^m \left(\dfrac{0.1}{0.1}\right)^n \left(\dfrac{0.3}{0.3}\right)^p$ $0.5 = 0.5^m$ $m = 1$ The order with respect **A** is 1 Or reaction is of first order with respect to reactant **A**.	*Alternatively:* $\dfrac{4.0 \times 10^2}{8.0 \times 10^2} = \left(\dfrac{0.5}{0.1}\right)^m \left(\dfrac{0.1}{0.1}\right)^n \left(\dfrac{0.3}{0.3}\right)^p$ $0.5 = 0.5^m$ The order with respect **A** is 1 Or reaction is of first order with respect to reactant **A**.

*To determine the order with respect to **B**, we take experiment 1 and 4 where the* [**A**] *and* [**C**] *are kept constant while* [**B**] *is varying.*

$4.0 \times 10^2 = k(0.5)^1(0.1)^n(0.3)^p \;\ldots(i)$

$16.0 \times 10^2 = k(1.0)^1(0.1)^n(0.3)^p \;\ldots(ii)$

Dividing equations (i) by (ii)

$\dfrac{4.0 \times 10^2}{8.0 \times 10^2} = \left(\dfrac{0.5}{0.5}\right)^1 \left(\dfrac{0.1}{0.2}\right)^n \left(\dfrac{0.3}{0.3}\right)^p$

$0.25 = 0.5^n$

$n = 2$

The order with respect **B** is 2 **or** reaction is of second order with respect to reactant **B**.

*To determine the order with respect to **C**, we take experiment 1 and 5 where the* [**A**] *and* [**B**] *are kept constant while* [**C**] *is varying.*

$4.0 \times 10^2 = k(0.5)^1(0.1)^2(0.3)^p \;\ldots(i)$

$16.0 \times 10^2 = k(0.5)^1(0.1)^2(0.6)^p \;\ldots(ii)$

Dividing equations (i) by (ii)

$\dfrac{4.0 \times 10^2}{8.0 \times 10^2} = \left(\dfrac{0.5}{0.5}\right)^1 \left(\dfrac{0.1}{0.1}\right)^2 \left(\dfrac{0.3}{0.3}\right)^p$

$1 = 0.5^n$

$p = 0$

The order with respect **C** is 0 **or** reaction is of zero order with respect to reactant **C**.

    (ii)   overall order of the reaction.
        The overall order of the reaction$= (1 + 2 + 0) = 3$
(b) Write the rate equation for the reaction.
    The rate equation is $Rate = k[A]^1[B]^2[C]^0$ or simply $Rate = k[A][B]^2$

(c) Determine the rate constant for the reaction and state its units.
    To find the rate constant, use any row or experiment from the table. For example, taking experiment **1**;

Using $Rate = k[A]^1[B]^2[C]^0$ $\quad 4.0 \times 10^2 = k(0.5)^1(0.1)^2(0.3)^0$ $\quad k = \dfrac{4.0 \times 10^2}{(0.5)^1(0.1)^2(0.3)^0}$ $\quad\quad = 80{,}000 dm^{-3}mol^{-2}s^{-1}$	Working out units $k = \dfrac{mol\, l^{-1}s^{-1}}{(mol\, dm^{-3})^1(mol\, dm^{-3})^2(mol\, dm^{-3})^0}$ $\quad\quad = dm^{-3}mol^{-2}s^{-1}$

By inspection method; order of a chemical reaction with respect to a given reactant is factor by which the rate changes divided by the factor by which the concentration changes.

- Using experiments 1 and 2; doubling the initial concentrations of A while keeping the initial concentrations of B and C constant, the initial rate also doubles. Thus, the order of reaction with respect to A is 1.
- Using experiments 1 and 4; when the initial concentrations of B is doubled while keeping the initial concentrations of A and C constant, the initial rate quadruples (i.e. the new rate increases to 4 times the initial rate). Thus, the order of reaction with respect to B is 2.
- Using experiments 1 and 5; doubling the initial concentrations of C while keeping the initial concentrations of B and A constant, the initial rate remains the same. Thus, the order of reaction with respect to C is 0.

2. The following data were obtained at 298K or the reaction; $A + B \rightarrow C$.

Experiment no.	[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.

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

$Using\ experiments\ 2\ and\ 3;$

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

$0.25 = 0.5^m$

$log0.25 = mlog0.5$

$m = 2$

The order with respect A is 2,

$Taking\ experiments\ 1\ and\ 2;$

$$\frac{5.25 \times 10^{-4}}{4.20 \times 10^{-3}} = \left(\frac{2.30 \times 10^{-4}}{4.60 \times 10^{-4}}\right)^2 \left(\frac{3.10 \times 10^{-5}}{6.20 \times 10^{-5}}\right)^n$$
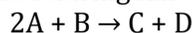
$0.500 = 0.500^n$

$n = 1$

The order with respect B is 1,

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

> Note in this case, there are no two experiments where concentration of A remained constant to determine the order of reaction with respect to B. Thus, we first determine the order of reaction with respect to reactant A.

(b) Determine the rate constant for the reaction and state its units.

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}

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

(ii) rate constant for the reaction and state its units.
(b) Write the rate law for the reaction.
2. The kinetic data for the reaction between X and Y is given in the table below;

Experiment no.	[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) State the:
   (i)   order of reaction with respect to X and Y.
   (ii) overall order of the reaction.
(b) Write the rate equation for the reaction.

3. The table below shows some kinetic data for the following reaction.
$$3A + B \rightarrow 2C$$
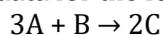
Experiment no.	[A] $(moldm^{-3})$	[B] $(moldm^{-3})$	Initial rate $(moldm^{-3}s^{-1})$
1	0.10	0.20	1.2×10^{-8}
2	0.10	0.60	1.2×10^{-8}
3	0.20	0.60	4.8×10^{-8}

(a) Write the overall rate equation.
(b) Calculate the rate constant and give its units.

Further Task

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

Experiment no.	[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}

Determine
   (a) the order of reaction with respect to each reactant.
   (b) the value of the rate constant and hence the rate equation.
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 no.	[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 no.	[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 another experiment in which the concentration of the ester was $0.24\ mol\,dm^{-3}$, the initial rate of reaction was found to be $2.2 \times 10^{-6}\ mol\,dm^{-3}s^{-1}$.
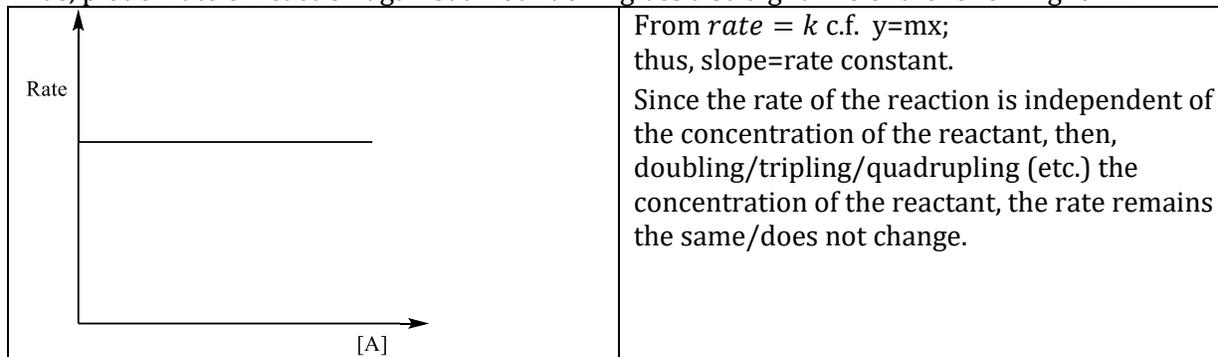Determine the pH of the solution. (Ionic product of water, $Kw = 1.0 \times 10^{-14}\ mol^2 dm^{-6}$).

B. Graphical method

This involves plotting a graph of initial rate ($\frac{1}{t} s^{-1}$) against the amount (partial pressure/volume/mass/moles/concentration) of the reactant.

From $Rate = k[A]^n$

Case 1:

If the reaction is zero order with respective to reactant A (i.e. n=0) the above expression reduces to $Rate = k$.

Thus, plot of rate of reaction against amount of A gives a straight line of the following form:

	From $rate = k$ c.f. y=mx; thus, slope=rate constant.
	Since the rate of the reaction is independent of the concentration of the reactant, then, doubling/tripling/quadrupling (etc.) the concentration of the reactant, the rate remains the same/does not change.

Case 2:

If the reaction is first order with respective to reactant A (i.e. n=1) the above expression reduces to $rate = k[A]^1$ or simply $rate = k[A]$.

Thus, plot of rate of reaction against amount of A (to the **power 1**) gives a straight line through the origin as follows:

	From $rate = k[A]$ c.f. y=mx; thus, slope=rate constant.
Slope $= \frac{\Delta(rate)}{\Delta(amount)} = rate\ constant$	Since the rate of the reaction is directly proportional to the concentration of the reactant, then, doubling the concentration of the reactant doubles the rate/slope. Also, when the concentration of the reactant is tripled, the rate also triples etc.
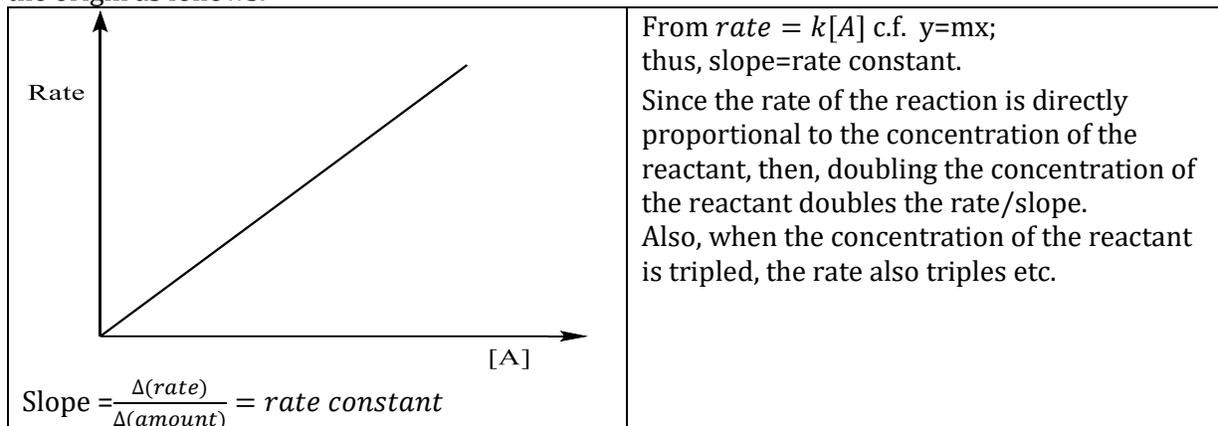
Case 3:

If the reaction is second order with respective to reactant A (i.e. n=2) the above expression reduces to $rate = k[A]^2$.

Thus, plot of rate of reaction against the square of the amount of A (to the **power 2**) gives a straight line through the origin as follows:

	From $rate = k[A]^2$ c.f. y=mx; thus, slope=rate constant. Since the rate of the reaction is directly proportional to the square of concentration of the reactant, then, doubling the concentration of the reactant, the rate/slope quadruples. Tripling the concentration of A causes the rate constant/slope to become 9 times the original.
Rate against [A] graph. Slope $=\dfrac{\Delta(rate)}{\Delta(amount)} = rate\ constant$	
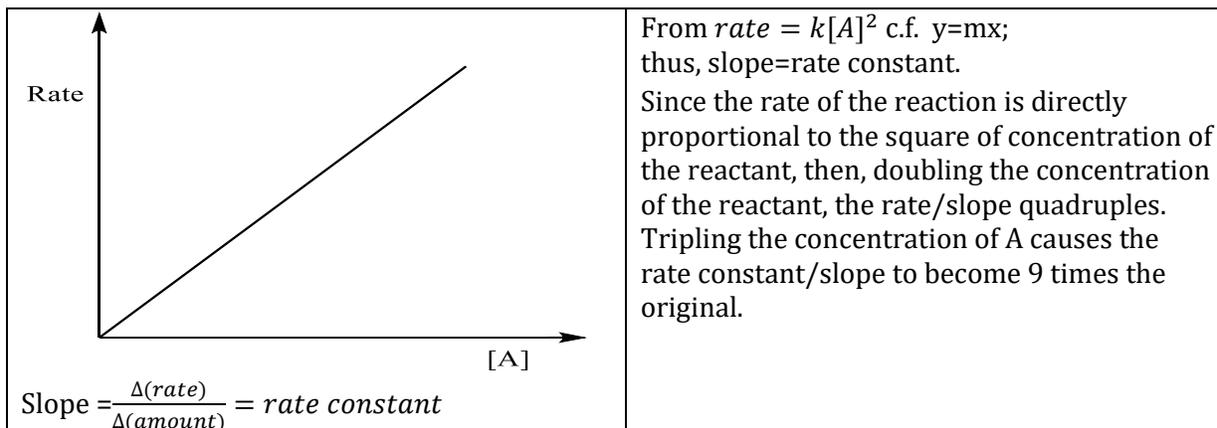
- For first order, the half-life is constant each time the "initial" concentration is reduced to half its previous value.
- For second order' the half-life doubles each time the "initial" concentration is reduced to half its previous value.

Half-life method of deducing the order of a reaction

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

The half-life of a given reaction can be determined from the graph of concentration of reactant against time.

Graphs of concentration (amount) of a reactant against time for both zero and first order reactions take the following form:

Zero order reaction	**First order reaction**
[A] against Time graph (linear decreasing)	[A] against Time graph (exponential decay)
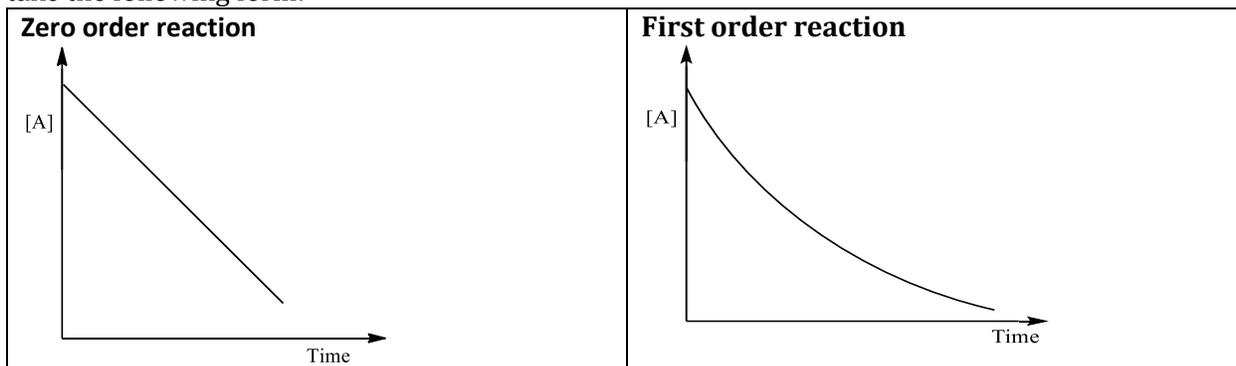
For first order reactions, we can obtain the half-lives directly from the graph of concentration of reactant against time as follows:

	For first order reactions, the half-lives are approximately the same. From the graph, it implies that; $(t_1 - 0) \approx (t_2 - t_1) \approx (t_3 - t_2)$ This implies that the half-life is independent of the initial/ original concentration of the reactant.
Amount against Time graph showing N_0, $\frac{N_0}{2}$, $\frac{N_0}{4}$, $\frac{N_0}{8}$ at times t_1, t_2, t_3.	
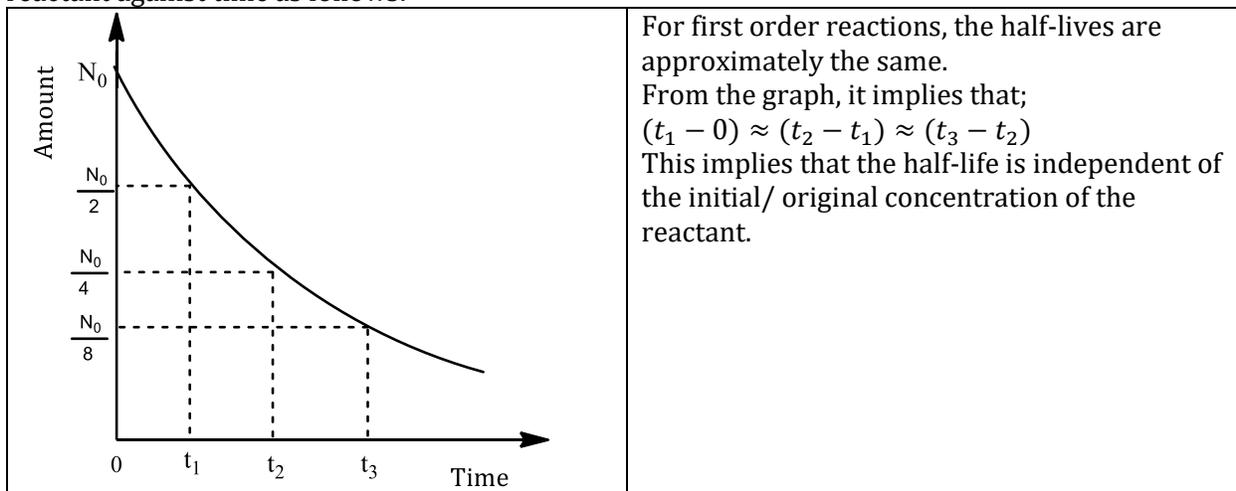
Task

1. Hydrogen iodide gas decomposes at 410°C according to the equation below.
$$2HI(g) \rightarrow H_2(g) + I_2(g)$$
    The data below describes this decomposition:
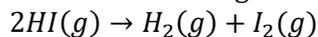
Time (minutes)	0	20	40	60	80
$[HI]$ $(moldm^{-3})$	0.50	0.38	0.31	0.26	0.22

    (a) Plot a graph of concentration against time.
    (b) What is the order of reaction? Explain.
    (c) Determine the half-life of the reaction and hence the rate constant for the reaction and state its units.

2. 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.

3. The table below shows the concentration-time data for the decomposition of ethanol on alumina surface at 600K.

Time (s)	0	100	200	300	400	500
Concentration $(mol\ dm^{-3})$	0.050	0.046	0.042	0.038	0.034	0.030

    (a) Plot a graph of concentration against time.
    (b) What is the order of the reaction? Explain.
    (c) Determine the rate constant and hence the half-life of the reaction.

4. 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.

5. 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.

Integrated rate equations

Zero order reactions

These are reactions which proceed at the same rate regardless of the changes in the concentrations of the reactants.
Consider the reaction:
$$A \rightarrow Products$$
For zero order we can write; $rate = \frac{-d[A]}{dt} = k[A]^0$ or $\frac{-d[A]}{dt} = k. \dots \dots \dots \dots \dots \dots \dots (*)$
Using calculus, it can be shown that: $[A]_t = -kt + [A]_0 \dots \dots \dots \dots (i)$; where $[A]_t$ is the amount of A remaining at time t and $[A]_0$ is the initial amount of A.

Thus, plot of concentration of A against time, t gives a straight line with a negative slope $(-k)$ and y-intercept $[A]_0$.
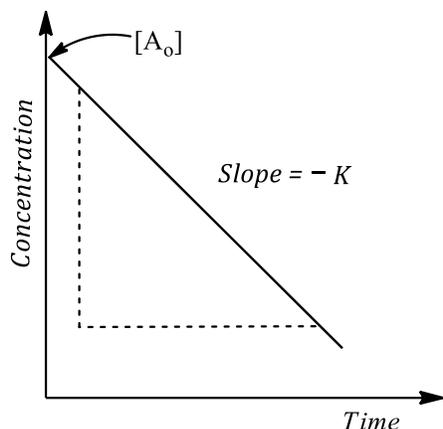
It can be shown that half-life of such reactions can be given by $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$.

An example of a zero-order reaction is the iodination of propanone catalyzed by an acid.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$
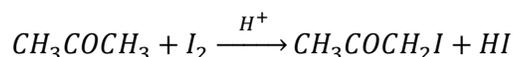
The above reaction is zero order with respect to iodine and first order with respect to propanone.

First order reactions
A first order reaction is one in which the rate of reaction is proportional to the concentration of only one reactant raised to power 1.

Consider the reaction: $A \rightarrow Products$

For a first order reaction, we can write; $Rate = \frac{-d[A]}{dt} = k[A]^1$

If the concentration of A at any time, t is $[A]_t$ while the initial concentration of A is $[A]_0$; the integrated form of the equation becomes:

$ln[A]_t = -kt + In[A]_0$ or $\log_{10}[A]_t = -\frac{kt}{2.303} + \log_{10}[A]_0$ since $lnx = 2.303\log_{10}x$.

Thus, a plot of $In[A]$ or $\log_{10}[A]_t$ against time, t gives a linear (straight) graph with a negative gradient $(-k$ or $-\frac{k}{2.303})$ and $ln[A]_0$ or $\log_{10}[A]_0$ as the y-intercept.
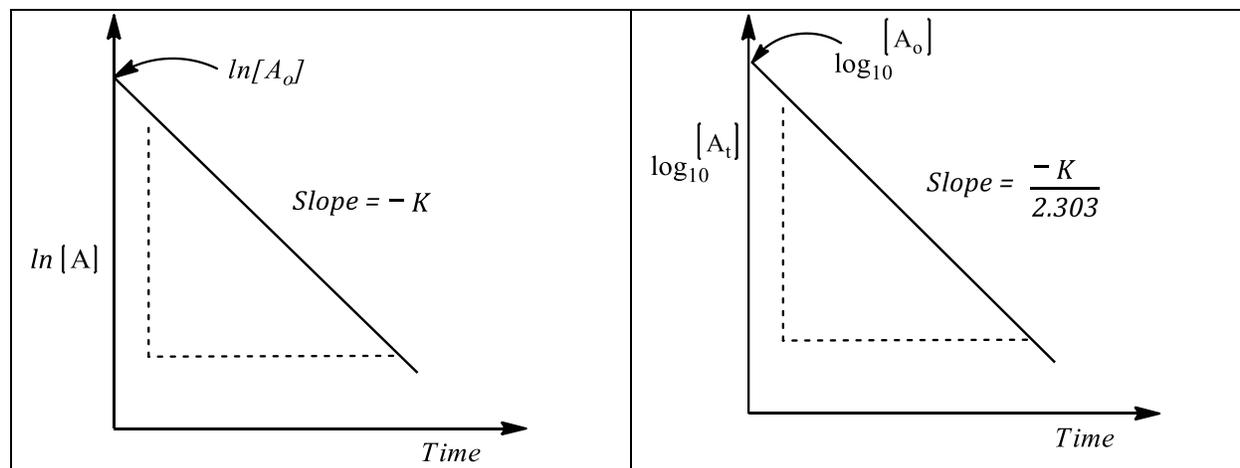
Alternatively, the above equations can be written as $ln\left(\frac{[A]_t}{[A]_o}\right) = -kt$ or $ln\left(\frac{[A]_o}{[A]_t}\right) = kt$ or

$2.303\log_{10}\left(\frac{[A]_t}{[A]_0}\right) = -kt$ or $\log_{10}\left(\frac{[A]_0}{[A]_t}\right) = \frac{kt}{2.303}$

Thus, plotting a graph of $\log_{10}\left(\frac{[A]_0}{[A]_t}\right)$ against time, t yields a straight-line graph with a slope $= \frac{k}{2.303}$
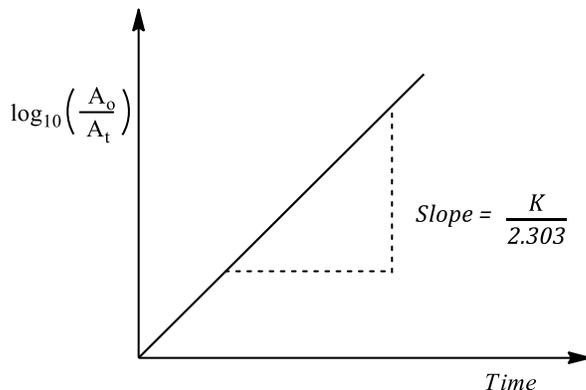
Half-life of first order reactions

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

At half-life; $t = t_{\frac{1}{2}}$, and $[A]_t = \frac{[A]_0}{2}$; substituting these values into any of the above equations gives;

$ln\left(\frac{[A]_0}{\frac{[A]_0}{2}}\right) = kt_{\frac{1}{2}}$ which simplifies to $ln2 = kt_{\frac{1}{2}}$ or $t_{\frac{1}{2}} = \frac{0.693}{k}$

Note use of $\log_{10}[A]_t = -\frac{kt}{2.303} + \log_{10}[A]_0$ or $2.303\log_{10}\left(\frac{[A]_t}{[A]_0}\right) = -kt$ or $\log_{10}\left(\frac{[A]_0}{[A]_t}\right) = \frac{kt}{2.303}$ also gives $t_{\frac{1}{2}} = \frac{0.693}{k}$.

Thus, $t_{\frac{1}{2}}$ for any first order reaction is independent of the initial concentration of the reactant.

Examples of first order reactions are:

- Radioactive disintegration
- Decomposition of hydrogen peroxide

Task
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? [Answer: 3181 days]
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. [Answer: 213 days]
3. The half-life of Bismuth is 20 minutes. Determine the time taken for 16 g of Bismuth to decay to 2 g. [Answer:60 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. [Answer: Half-life=26.07]
(iii) The concentration at time t=0. [Answer: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. [Answer: 42 minutes]
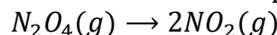(c) Calculate the rate constant, k, for the reaction.

Further 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. The following data are obtained in the decomposition reaction

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

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.

Second order reactions

A second order reaction is one in which the rate of reaction is proportional to the concentration of only one reactant raised to power 2.

Or

A second order reaction which is first order with respect to each of the reactants A and B.

Consider the reaction: $A + B \rightarrow Products$

For a first order reaction, we can write; $Rate = \frac{-d[A]}{dt} = k[A]^2$ or $k[A][B]$

If the concentration of A at any time, t is $[A]_t$ while the initial concentration of A is $[A]_0$; the integrated form of the equation becomes:

……………………………………………

The half-life of the reaction is given by the expression…………………………

# 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 standard 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.

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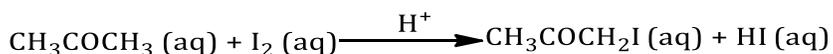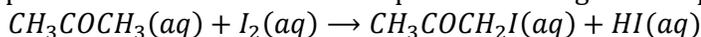
Procedure

- 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 to 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.
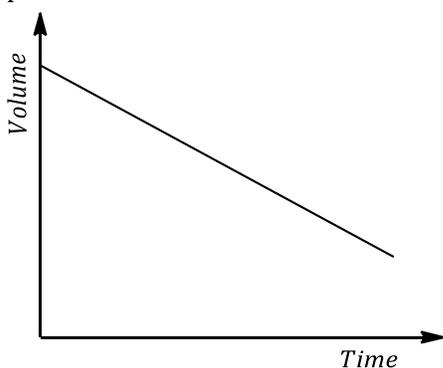
- The graph is a straight line with a negative slope/ gradient which shows that order of the reaction between propanone and iodine is zero order with respect to iodine.
- Or a graph of rate of reaction against concentration of thiosulphate is plotted. From the graph, order of reaction with respect to 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;
$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$
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 $Na_2S_2O_3$ used (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.

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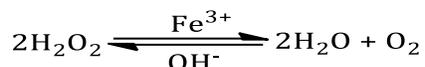
Procedure:

- 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 is pipetted at intervals of time and added to a conical flask containing excess dilute sulphuric acid (to prevent further decomposition of hydrogen peroxide).
- These samples are then titrated with a standard solution of potassium permanganate from the burette.

$$5H_2O_2(l) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$
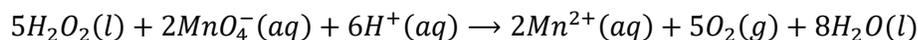
- The concentration of hydrogen peroxide at a given time interval is calculated by backward calculation.
- A graph of concentration of hydrogen peroxide against time is plotted.
- From the graph, the half-lives are determined and are found to be constant showing that the decomposition is first order with respect to hydrogen peroxide.

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.

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$
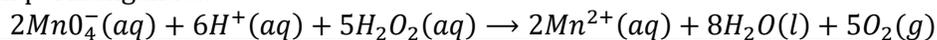
Time (minutes)	0	10	20	30
Vol. of $KMnO_4$ needed for H_2O_2 (cm³)	25.0	16.0	10.5	7.1

   (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;

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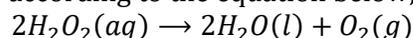
   The table below shows the results obtained when various 20 cm³ samples of hydrogen peroxide solution were titrated with potassium manganate(VII) solution at various times from the start of the reaction.

| 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.

An experiment to show that the reaction between sodium thiosulphate and hydrochloric acid is first order with respect to sodium thiosulphate.
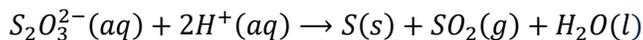
$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$
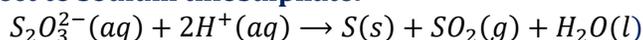
Procedure:

❖ A known volume, V cm³ of a standard solution of sodium thiosulphate is placed in a beaker or conical flask.
❖ The beaker/ conical flask is placed on a white piece of paper with a cross or dot on it. A known volume of a standard solution of hydrochloric acid is added and at the same time stop clock is started.
❖ The mixture is swirled and placed back on the paper with a cross or dot.
❖ The time taken when the yellow precipitate of sulphur blocks (obscure) the cross/ dot from the view is noted.
❖ The procedures are repeated with varied volumes of the same standard solution of sodium thiosulphate, each time making the total volume of the solution V cm³ as before by adding water while keeping that of the acid constant.
❖ A graph of reciprocal of time against concentration of sodium thiosulphate is plotted. A straight line through the origin is obtained an indication that the order of reaction with respect to thiosulphate ion is one i.e. first order.

$\frac{1}{Time}$ (s^{-1})

Slope = k

Concentration of thiosulphate $(mol\ dm^{-3})$
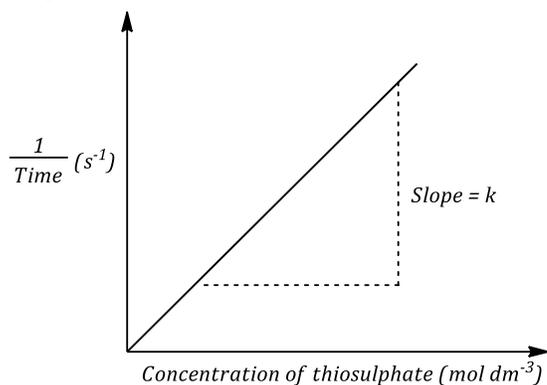
Task

1. Sodium thiosulphate solution reacts with hydrochloric acid according to the following equation.
$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$
(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.

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 is taking place
- Concentration of the reactants
- Surface area of solid reactants
- Presence of a catalyst
- Pressure for reactions involving gases
- Light for photochemical reactions

Effect of catalyst
Catalysts alter the rate of chemical reactions but remain unchanged at the end of the reaction. Catalysts alter the rate of chemical reactions by providing an alternative reaction path with a much lower activation energy.

Catalysis can be either homogeneous or heterogeneous.

A working diagram for a positive catalyst:

Refer to inorganic notes

In homogeneous catalysis; the reactants and products are in the same phase with the catalyst. For example, the reaction between ethanol and ethanoic acid to form an ester and water is catalysed by concentrated sulphuric acid.

In heterogeneous catalysis; the catalyst exists in a different phase from that of the reactants and products. For example, hydrogenation of ethene is catalyzed by tiny particles of metals such as Ni, Pd, or Pt:

$$H_2C{=}CH_2\,(g)\ +\ H_2\,(g) \xrightarrow{\text{Metal catalyst (s)}} CH_3CH_3\,(g)$$
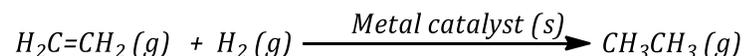
Effect of surface area
This mainly affects reactions in which solids are involved. The larger the surface area of the solid reactant, the faster the rate of reaction.

When the surface area is large, many reactant particles are exposed and there are so close to each other. This results into frequent collisions between the reactant particles and hence faster reaction rate.

For example, the reaction between hydrochloric acid and marble chips (calcium carbonate) is as follows:
$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$
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 surface area than lumps of marble chips.
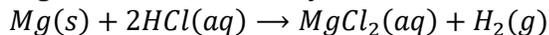
Therefore, if powdered marble chips are used, more carbon dioxide gas is given out compared to a big lump in a given period of time.

Effect of concentration
The higher the concentration of the reactant particles, the faster 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. This results into frequent collisions between the reactant particles and hence faster reaction rate.

Consider the reaction between magnesium ribbon and hydrochloric acid below:
$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$
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.

Effect of pressure
Changes in pressure only affect reactions involving gases.
The higher the pressure of the system, the faster the rate of reaction.
(For explanation see the effect of concentration.)

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

(a) more reacting particles have energy equal to or greater than the activation energy.
(b) the reacting particles move at higher speed, the frequency of collision between the reacting particles increases.
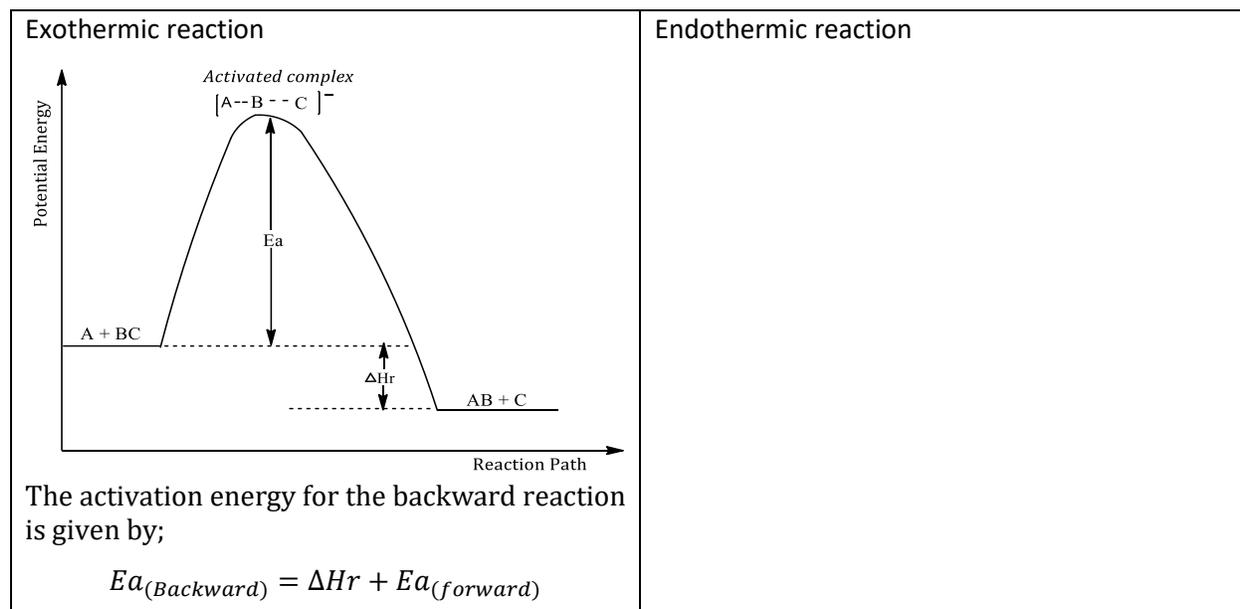
This causes frequent collisions between the reactant particles. More products are formed per unit time and hence the rate of reaction is faster.

The variation of concentration of product with temperature:
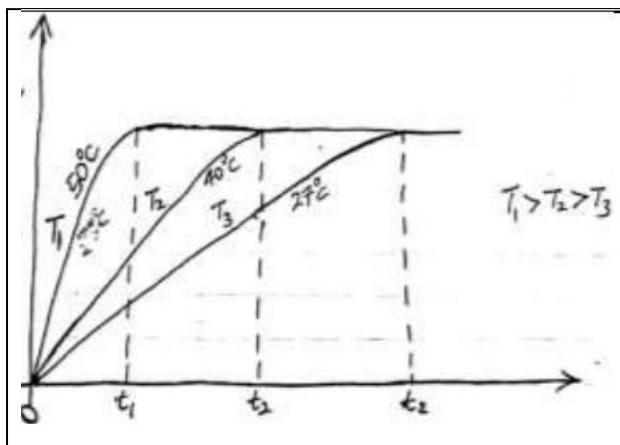
	The graphs show that a reaction at a higher temperature takes a shorter period of time to go to completion while that at a lower temperature takes a longer period of time to go to completion. Thus, the rate of the reaction is faster at T1 than at T2. Similarly, the rate of the reaction is faster at T2 than at T3.

The energy profile diagrams for both exothermic and endothermic reactions are:

Exothermic reaction	Endothermic reaction
The activation energy for the backward reaction is given by; $$Ea_{(Backward)} = \Delta Hr + Ea_{(forward)}$$	

Activation energy is the minimum energy the reactants must possess in order to react and form a product/an activated complex.

Effect of temperature on the rate of reaction.

When reactant particles are heated, their kinetic energy increases. Thus, a larger fraction of the reactant particles will have sufficient energy to overcome the activation barrier, Ea. Hence, faster rate of the reaction since rate constant of the reaction has also increased.

Experiments show that for every 10°C rise in temperature, the rate of the reaction doubles.

The dependence of reaction rate, k on absolute temperature, T was investigated by the Swedish chemist, Arrhenius. He found that:

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

The above expression is called the Arrhenius equation/expression.

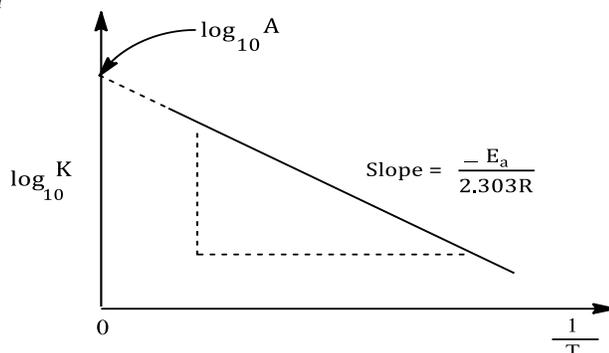**A** is the frequency factor or pre-exponential factor.

R is the gas constant.

Ea is the activation energy.

Taking natural logarithm or logarithm to the base 10 on both sides of equation above;

$$lnk = lnA - \frac{Ea}{RT} \quad \text{or} \quad \log_{10} k = -\frac{Ea}{2.303R}\left(\frac{1}{T}\right) + \log_{10} A$$
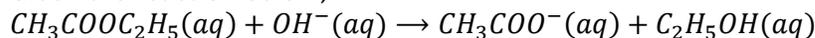
Thus, plot of $\log_{10} k$ against $\frac{1}{T}$ (where T is in Kelvin) yields the graph below:

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

Task

1. Given the reaction below;
   $$CH_3COOC_2H_5(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$$
   The rate of the reaction above was measured at several temperatures, and the following data were collected.

Temperature (°C)	15	25	35	45
K $(mol\ dm^{-3}s^{-1})$	0.0521	0.101	0.184	0.332

   Plot a suitable graph and use it to determine the value of the activation energy.

2. The rate constant for the decomposition of hydrogen iodide 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

   Plot a suitable graph and use it to determine the activation energy for the reaction