CHEMICAL KINETICS (*DATA* & *GRAPHICAL INTERPRETAION*)

CHEMICAL KINETICS

Kinetics is the study of reaction rates, determining which products are formed fastest. Kinetics also helps to predict how the rate will change if the reaction conditions are changed.

1. Rate of reaction;

    Some reactions e.g. ionic reactions occur very fast like precipitation of silver chloride by mixing aqueous solver nitrate with sodium chloride solution. 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 chemical reaction can be defined as the change in concentration of a reactant or product per unit time. To be more specific, it can be expressed in terms of;

    ✓ The rate of decrease in concentration of any one of the reactants or

    ✓ The rate of increase in concentration of any one of the products.

2. Rate law: rate law is an expression which gives the relationship between rate of reaction and concentration of the reactants.

Consider a general reaction

$$aA + bB \longrightarrow cC + dD$$
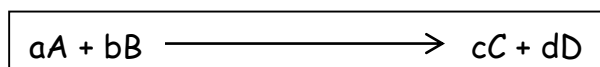
$$\text{Rate} = k[A]^x[B]^y$$

The above equation is known as the rate law or expression. K is known as the rate constant.

NB: 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;

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$
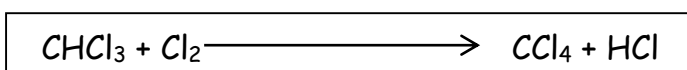
$$\text{Rate} = k[CHCl_3][Cl_2]^{\frac{1}{2}}$$

3. Order of reaction is defined as the exponents of the concentration terms in the experimental rate law of reaction. It can be 1, 2, 3 or fractional.

Or the power to which a concentration is raised in the experimentally determined rate equation.

4. `Overall order of reaction:` the sum of all the individual orders in the experimentally determined rate equation.

Classification of reaction orders.

1. `Zero order.`

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

   Consider the reaction: $A \rightarrow Products$

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

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

   $integrating\ both\ sides\ of\ the\ equation;$

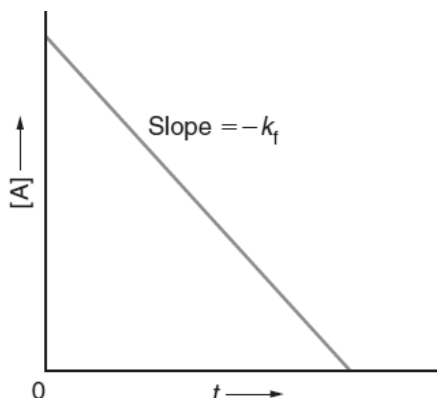 $$\int_{[A]_O}^{[A]_t} d[A] = -k \int_0^t dt$$

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

   $$[A]_t = -kt + [A]_0 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (i)$$

$comparing\ equation\ (i) with\ the\ genral\ line\ of\ the\ equation;$

$y = mx + c;\ \ if\ we\ plot\ a\ garaph\ of\ concentarion\ against\ time, a\ straight\ line\ with\ slope = -k\ and\ intercept = [A]_0$

Note; a plot of $concentarion\ against\ time$ gives a linear (straight) graph and if the graph is not linear, then the reaction is not zero order.

hamzakisubi@gmail.com0701392987

2. First order.

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

Consider the reaction: $A \rightarrow Products$

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

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

integrating both sides of the equation;

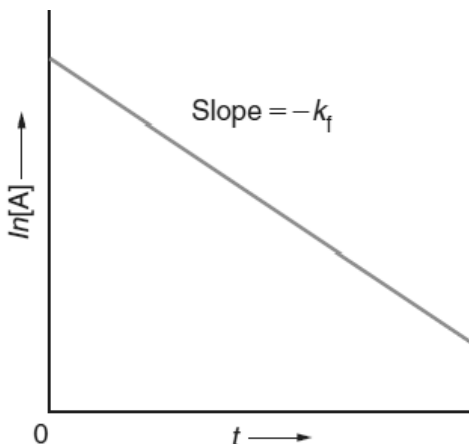$$\int_{[A]_o}^{[A]_t} \frac{d[A]}{[A]} = - k \int_0^t dt$$

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

$$In[A]_t = -kt + In[A]_0 \dots\dots\dots\dots\dots\dots\dots\dots\dots (ii)$$

comparing equation (i) with the genral line of the equation;

$y = mx + c;$ *if we plot a garaph of* $In[A]$ *against time* $(t),$ *a straight line with slope* $= -k$ *an intercept* $= [A]_0$

Note; a plot of $In[A]$ *against time* (t) gives a linear (straight) graph and if the graph is not linear, then the reaction is not first order.

Half-life of a reaction:

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

Half-life for first order reaction;

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

hamzakisubi@gmail.com 0701392987

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

$$This\ implies\ that \quad In\left(\frac{[A]_0}{[A]_t}\right) = kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(iii)$$

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

$$In\left(\frac{[A]_0}{\frac{[A]_0}{2}}\right) = kt_{\frac{1}{2}}\ , simplifying\ gives \quad In2 = kt_{\frac{1}{2}}$$

$$implying\ that\ t_{\frac{1}{2}} = \frac{0.693}{k}$$

Sample calculations.

1. For a general reaction "aA + bB →products," the following initial rates are determined experimentally when reactions are set up with the initial amounts indicated in units of molarity, M.

Expt	[A] (M)	[B] (M)	Initial Rate (MS⁻¹)
1	1.44	0.35	5.37×10^{-3}
2	1.44	0.70	2.15×10^{-2}
3	2.89	0.35	2.69×10^{-3}

Assuming the rate law is written as; $Rate = k[A]^m[B]^n$, determine the value of m, n and k. [Answer is m is -1, n is 2 and k is $6.31 \times 10^{-2}S^{-1}$

2. Using the following data for the reaction illustrated in Equation (35.13), determine the order of the reaction with respect to A and B, and the rate constant for the reaction:

Expt	[A] (M)	[B] (M)	Initial Rate (MS⁻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}

[Answer is wrt A is 2 and wrt B is 1 and rate constant is $3.17 \times 10^{8}M^{-2}S^{-1}$]

3. 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;

| A (MolL^{-1})	0.20	0.20	0.40
B (MolL^{-1})	0.30	0.10	0.05
r_0 (MolL^{-1}S^{-1})	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B?

Experimental determination of reaction rates

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 this reaction, then analyzing the reaction mixture at suitable intervals of time which makes it possible to determine the concentration of both the reactants and products at different time hence obtain a suitable measure of reaction rate.
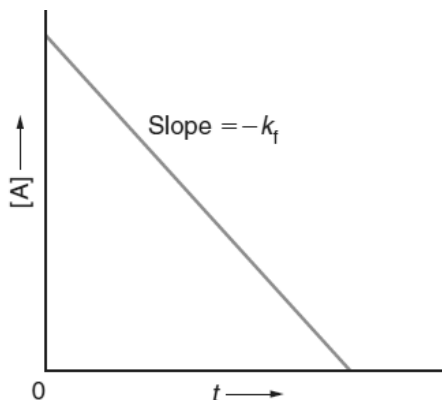
Titrimetric analysis.

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

$$CH_3COCH_{3\,(aq)} + I_{2\,(aq)} \xrightarrow{H^+} CH_3COCH_2I_2(aq) + HI_{(aq)}$$
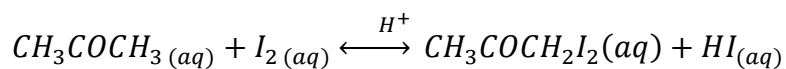
$procedure$

- A known volume of propanone and dilute sulphuric acid are placed in a beaker and then a known volume of iodine is added to this beaker and the stop clock simultaneously started.
- The beaker is shaken for some time and after a given time interval e.g. 5 minutes, a known volume of the reaction mixture is pipetted and removed for analysis by adding it into a conical flask that contains a reagent which quenches (stops) the reaction e.g. sodium carbonate or sodium hydrogen carbonate to neutralize the acid catalyst.

- The quenched mixture is then analyzed by titrating it with a standard solution of sodium thiosulphate using starch indicator. This procedure is repeated at measured time intervals and 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 versus time is plotted.

- 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 because it is a linear graph.

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

$$2H_2O_{2\,(aq)} \underset{OH^-}{\overset{Fe^{3+}}{\rightleftharpoons}} 2H_2O_{(l)} + O_{2\,(g)}$$
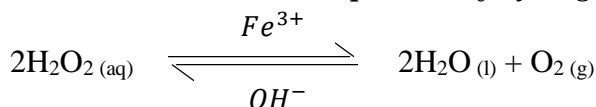
Procedure:

- A known volume of hydrogen peroxide is placed in a beaker followed by a known volume of sodium hydroxide solution.
- A known volume of a catalyst of iron(iii) chloride is added and a stop clock is simultaneously started.
- Samples of the reaction 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.
- The concentration of hydrogen peroxide at a given time interval is calculated by backward calculation and a graph of concentration against time is plotted or a graph of rate against time is plotted.
- The reaction is found to be first order with respect to hydrogen peroxide.

3. **For esterification;**

$$HCOOH_{(aq)} + CH_3OH \underset{Heat}{\overset{H^+}{\rightleftharpoons}} HCOOCH_{3\ (aq)} + H_2O_{(aq)}$$
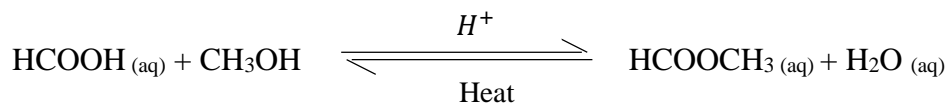
procedure

- A given amount 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 $40^\circ c$.
- 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 measure time intervals, known volumes of the reaction mixtures are pipetted into conical flask and cooled in ice cold water to prevent the reaction.
- Then amount of carboxylic acid formed is then titrated with a standard solution of sodium hydroxide using phenolphthalein indicator.
- A graph of concentration of sodium hydroxide is then plotted against time.

Graphical determination of orders 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.

Examples

1. The table below shows the kinetic data that were obtained for the hydrolysis of the ester, methyl ethanoate in acid solution

Time (min)	0	3600	7200	10800	14400
Concentration of ester (moldm^{-3})	0.2405	0.1565	0.1045	0.0685	0.0455

(i) Plot a graph of concentration of the ester, methyl ethanoate against time.

(ii) Determine the half-life of the reaction.

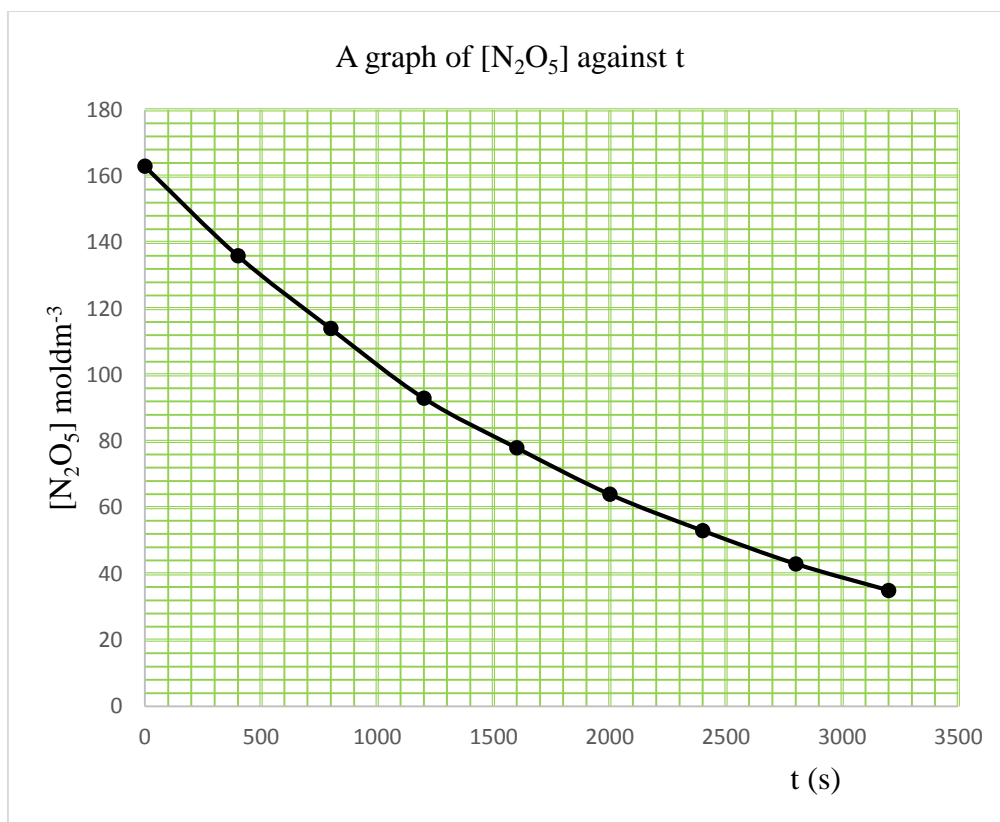**A graph of cncentration of the ester against time**
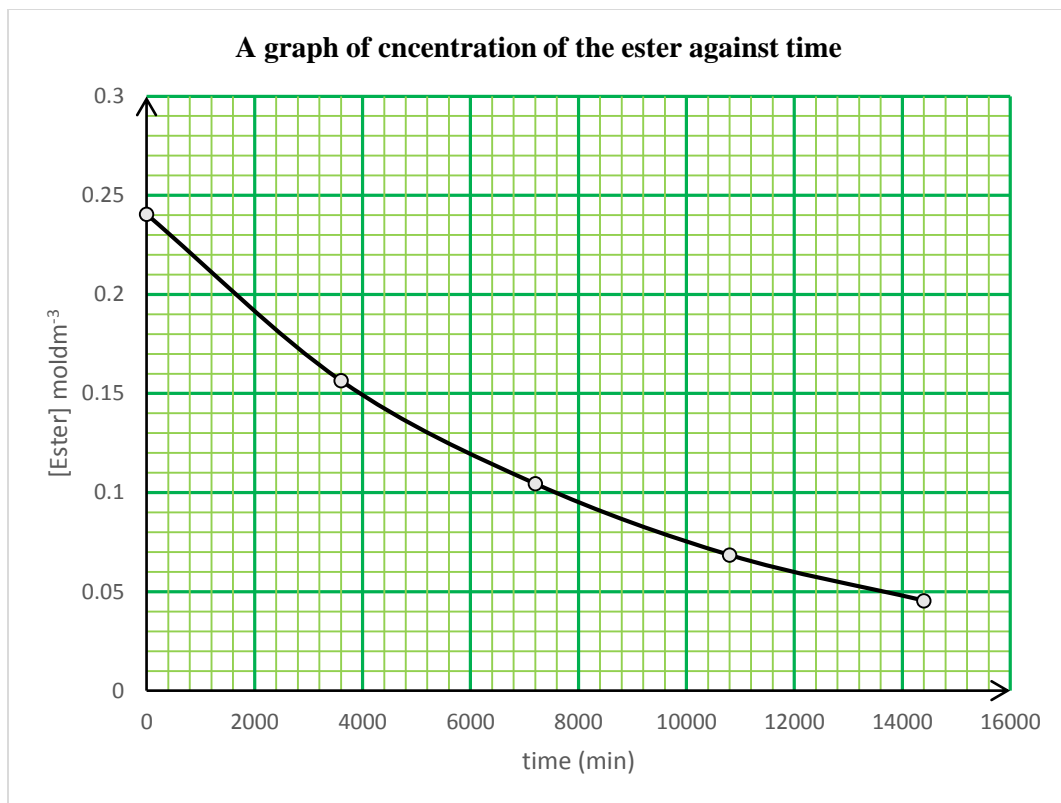
2. The experimental data for decomposition of N₂O₅; $[N_2O_5 \longrightarrow 4NO_2 + O_2]$ in gas phase at 318K are given below;

t (s)	0	400	800	1200	1600	2000	2400	2800	3200
$[N_2O_5]\ moldm^{-3}$	163	136	114	93	78	64	53	43	35

   (i)   Plot [N₂O₅] against *t*.

   (ii) Find the half-life period for the reaction.

*(See next page for solution)*

A graph of [N$_2$O$_5$] against t

From the graph, Time corresponding to the concentration, $\frac{163}{2} = 81.5 \, moldm^{-3}$ is the half-life. From the graph, the half-life is 1450s also the successive half-lifes are constant implying that the reaction is first order.

3. For the gas phase (Dimerization) reaction at 300^Oc, $2C_2F_4 \rightarrow C_4F_8$, the following concentration of C2F4 were obtained.

t (s)	0	250	750	1750	3750
$[C_2F_4] \, moldm^{-3}$	0.0500	0.0250	0.0125	0.00625	0.00312

Plot a graph of concentration against time, determine the half-life and order of reaction giving a reason for your answer.

(See next page for solution)
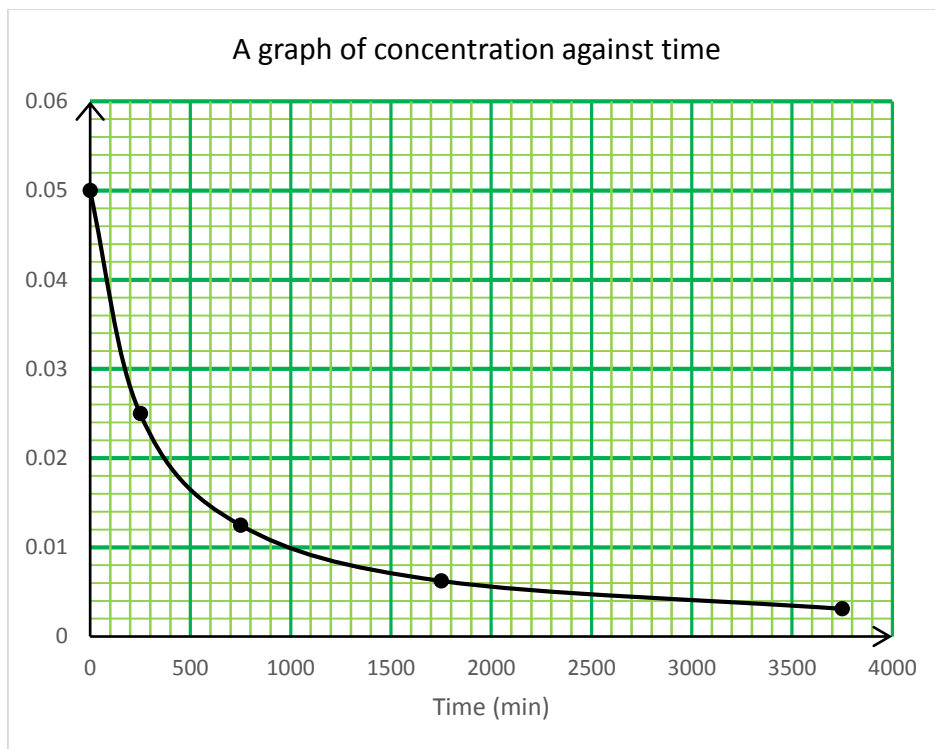
A graph of concentration against time

The half-life doubles each time the "initial" concentration is reduced to half its previous value. This behavior indicates a second-order reaction.

END