Reaction Kinetics (A2)

Methods for following the course of a reaction.

- In order to find out how the rate of reaction changes with time we need to select a suitable method to follow the progress of a reaction.
- This method will measure either the rate of diappearance of a reactant, or the rate of appearance of a product.
- Some methods are as follow.

1. Iodine clock reactions

- The reaction is the oxidation of iodide ions by hydrogen proxide under acidic conditions.

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow I_{2(aq)} + 2H_2O_{(l)}$$

- Iodine also reacts with sodium thiosulfate solution.
- To the reaction mixture (including the starch solution), a very small fixed amount of sodium thiosulfate solution also added.
- The thiosulfate ions will react with the iodine that is initially produced, and so the iodine wont affect the starch, and do not show any blue colour.
- However, when that small amount of sodium thiosulfate has been used up, there is nothing to stop the next lot of iodine produced from reacting with the starch. The mixture then goes blue.

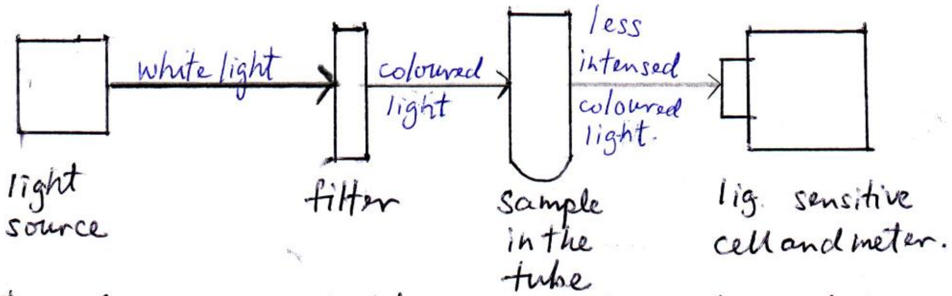
- The experiment can be planned to look at the effect of changing the hydrogen proxide concentration, or the iodide ion concentration, or the hydrogen ion concentration - each time, and must keep other factors constant.

2. <u>Reaction between bromoethane and sodium hydroxide</u>

- $CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$
- During the course of the reaction, both bromoethane and sodium hydroxide will get used up.
- The experiment can be started by mixing equal volume of bromoethane and sodium hydroxide (both at same concentration).
- At regular time intervals during the reaction, a pipette was used to take samples.
- The samples are quenched by adding a known volume (chosen to be an excess) of standard HCl.
- That will use up all the sodium hydroxide in the mixture so that the reaction stops.
- Now titrate the resulting solution with standard sodium hydroxide solution, to find out quantity of HCl leftover in the mixture.
- That lets calculation of quantity HCl used up, which is the same as quantity of sodium hydroxide must have been present in the original reaction mixture.
- This sort of technique is known as a <u>back titration</u>

3. <u>Colorimetry</u>

- In any reaction involving a coloured substance (either reacting or being produced), a colorimeter is used to follow the course of the reaction.



- The colour of the light can be changed by selecting a particular coloured filter. The colour is chosen so that it is the frequency of light which is absorbed by the sample.
- Example reaction between propanone and iodine in the presence of an acid catalyst.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + H^+ + I^-$$

- The solution of iodine in propanone starts off brown, an then fades through orange to yellow then to colourless as the iodine is used up.
- A colorimeter can measure the amount of light which is absorbed as it passes through a solution — recorded as the absorbance of the solution.
- During the experiment, take the reading of absorbance from the meter at regular intervals, and then compared againt calibration curve to convert those values into concentrations.

- The other example reactions are

  1) pale yellow precipitate (sulfur) formation to block the view of cross in the thiosulfate-acid reaction.
  2) gas volume measurement — catalytic decomposition of hydrogen peroxide
  3) conductivity measurements –

     $H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow I_{2(aq)} + 2H_2O_{(l)}$
  4) pressure measurement —

     $C(CH_3)_3I_{(g)} \longrightarrow C(CH_3)_2{=}CH_{2(g)} + HI_{(g)}$

Comparing Sampling Method V.S. Direct Measurement Method

- Direct measurement method do not require the removal of samples from the reacting mixture. The reaction is determined at regular intervals without disturbing the reaction mixture —
- . Sampling Method invite potential contamination to the reaction mixture.
- Sampling method involved many steps and potentially creat more errors.

Rate Equations

- The rate equation methematically links to the concentration of reactants
- can only be found by doing actual experiments, not by looking at the chemical equation.
- Eg the chemical equation:

$$A + 2B + X \longrightarrow C + D$$

- A rate equation:

$$\text{rate} = k[A][B]^2$$

where,

		Units
rate	: rate of reaction	$\frac{\text{conc.}}{\text{time}}$ ($mol\,dm^{-3}s^{-1}$)
k	: rate constant	depend on the rate equation
[ ]	: concentration	$mol\,dm^{-3}$

- *Interpretation*. The above rate equation explains that the rate of reaction is:

proportional to the conc of reactant A	double [A] - will double rate
proportional to the square of the conc B	double [B] - will quadruple rate
not proportional to the conc of X	altering [X] - no effect on rate.

- **Example 1.** - power of conc of reactants not follow stoichiometric equation.

$$2I^-_{(aq)} + S_2O_8^{2-}{}_{(aq)} \longrightarrow I_{2(aq)} + 2SO_4^{2-}{}_{(aq)}$$

$$\text{rate} = k[I^-][S_2O_8^{2-}]$$

(note : rate = $k[I^-]^2 \cdot [S_2O_8^{2-}]$ ✗)

- **Example 2.** - may not include all (or any) reactants in chemical equation written.

$$(CH_3)_3C{-}Cl_{(aq)} + OH^-_{(aq)} \longrightarrow (CH_3)_3C{-}OH_{(aq)} + Cl^-_{(aq)}$$

$$\text{rate} = k[(CH_3)_3C{-}Cl]$$

(note : $[OH^-]$ not appear in the rate equation)

- **Example 3.** - may include substances that are not reactants in the chemical equation.

$$2N_{(g)} \longrightarrow N_{2(g)}$$

$$\text{rate} = k[N]^2 \cdot [N_2]$$

(note : though N_2 is a product in the chemical equation)

Order of reaction

- **Individual order** – The power to which a concentration is raised in the rate equation.
- **Overall order** — The sum of all the individual orders in the rate equation.
- e.g. in the rate equation, $\text{rate} = k[A][B]^2$
- the order with respect to A is 1 (1st order)
- the order with respect to B is 2 (2nd order)
- the overall order is 3 (3rd order)

Generalising the findings

- By doing experiments involving a reaction between A and B, it was found that the rate of the reaction was related to the concentrations of A and B in this way:

$$\underset{\substack{\text{rate in}\\ \text{mol dm}^{-3}\text{s}^{-1}}}{\text{rate}} = \underset{\text{rate constant}}{k}\,\underset{\substack{\text{concentration of A}\\ \text{in mol dm}^{-3}}}{[A]}^{\overset{\substack{\text{order of reaction}\\ \text{with respect to A}}}{m}}\,\underset{\substack{\text{concentration of B}\\ \text{in mol dm}^{-3}}}{[B]}^{\overset{\substack{\text{order of reaction}\\ \text{with respect to B}}}{n}}$$

- The reaction is mth order with respect to A
- The reaction is nth order with respect to B
- The overall order of the reaction is the sum $(m+n)$
- Value(s)
- orders need not be whole numbers. The most likely orders of reaction are 0, 1 or 2. But other values are possible, for example 1.53.

- orders can be zero if the rate is unaffected by how much substance is present.

Important notes

- The rate equation is derived from experimental evidence not by from an equation.
  - species in the stoichiometric equation sometimes aren't in the rate equation.
  - substances not in the stoichiometry equation can appear in the rate equation.
- Rate equations for some reactions:

Stoichiometric equation	rate equation
$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$	$r = k[H_2][I_2]$
$NO_{(g)} + CO_{(g)} + O_{2(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$	$r = k[NO]^2$
$2H_{2(g)} + 2NO_{(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$	$r = k[H_2][NO]^2$
$BrO_3^-{}_{(aq)} + 5Br^-{}_{(aq)} + 6H^+_{(aq)} \longrightarrow 3Br_{2(aq)} + 3H_2O_{(l)}$	$r = k[BrO_3^-][Br^-][H^+]^2$

Example

The reaction $2A + B + C \longrightarrow 2D + E$

rate equation is : rate $= k[A][B]^2$

What are the individual orders and overall order for the above reaction?

The reaction is 1st order with respect to A.

The reaction is 2nd order with respect to B.

The reaction is zero order with respect to C.

The overall order of the reaction is 3.

The rate constant

- The rate constant is constant for a given reaction only if all the changing is the concentration of the reactants and the other factors (eg. temperature, use of catalyst etc) remains unchanged.
- The rate constant varies for a reaction, if there is changes in the temperature of the reaction, add a catalyst, or change the catalyst.

Units of Rate Constants

- The units of the rate constant depend on the order of the reaction.
- First order reactions
- an example of a first order reaction is

$$(CH_3)_3C-Br + OH^- \longrightarrow (CH_3)_3C-OH + Br^-$$

- Experimentally, the rate equation is

$$rate = k \cdot [(CH_3)_3C-Br]$$

- rearranging the rate equation

$$k = \frac{rate}{[(CH_3)_3C-Br]}$$

- Hence the unit of $k = \dfrac{\text{units of rate}}{\text{units of } [(CH_3)_3C-Br]}$

$$= \frac{mol\,dm^{-3}s^{-1}}{mol\,dm^{-3}}$$

$$= s^{-1}$$

- The unit of the rate constant for all 1st order reaction is s^{-1}.

- Second order reactions.
- An example of a second order reaction is

$$HCOOCH_3 + NaOH \longrightarrow HCOONa + CH_3OH$$

- Experimentally, the rate equation is

$$\text{rate} = k.[HCOOCH_3][NaOH]$$

- rearranging the rate equation

$$k = \frac{\text{rate}}{[HCOOCH_3][NaOH]}$$

- Hence the units of $k = \dfrac{\text{units of rate}}{(\text{units of concentrations})^2}$

$$= \frac{mol\,dm^{-3}s^{-1}}{mol^{2}dm^{-6}} = dm^{3}mol^{-1}s^{-1}$$

- The units of the rate constant of all second order reactions are $dm^3mol^{-1}s^{-1}$.

- Third order reactions
- An example of a third order reaction is

$$2NO + Cl_2 \longrightarrow 2NOCl$$

- Experimentally, the rate equation is

$$\text{rate} = k.[NO]^2.[Cl_2]$$

- Hence the units of $k = \dfrac{\text{units of rate}}{(\text{units of concentrations})^3}$

$$= \frac{mol\,dm^{-3}s^{-1}}{mol^{3}dm^{-9}}$$

$$= dm^{6}mol^{-2}s^{-1}$$

- The units for the rate constant of all third order reactions are $dm^6mol^{-2}s^{-1}$.

Example 1

$CH_3-CH=CH_2 + Br_2 \longrightarrow CH_3-CHBr-CH_2Br$.

The rate equation for the above reaction is

$$rate = k[CH_3-CH=CH_2][Br_2]$$

The rate constant, k is 30.0 $dm^3\,mol^{-1}s^{-1}$

a) What is the order of the reaction?

b) What is the rate of reaction when the concentrations of propene and bromine are both 0.02 $mol\,dm^{-3}$?

Answer

a) The order = 1+1 = 2

b) The rate = 30.0 × 0.02 × 0.02 = 0.012 $mol\,dm^{-3}s^{-1}$

Example 2

$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

The rate equation for the reaction is

$$rate = k.[HI]^2$$

At 629 K and at a concentration of 2.00 $mol\,dm^{-3}$, the rate of decomposition of hydrogen Iodide = $24 \times 10^{-5}\,mol\,dm^{-3}s^{-1}$!

a) Calculate the rate constant, k for the reaction at 629 K. Give the units

b) Calculate the number of hydrogen iodide molecules that decompose per second in 1 dm^3 of gaseous hydrogen iodide at 629 K (at concentration 2.00 $mol\,dm^{-3}$).

[Avogadro constant = $6.0 \times 10^{23}\,mol^{-1}$]

Answer

a) $k = \dfrac{\text{rate of reaction}}{[HI]^2} = \dfrac{24.0 \times 10^{-5}}{(2.00)^2} = 6.0 \times 10^{-5}\,dm^3\,mol^{-1}s^{-1}$

b) From the rate of reaction, 24.0×10^{-5} mol of HI is decomposing in 1 dm^3 every second .

Hence the number of molecules decomposing in 1 dm^3 every second $= 24.0 \times 10^{-5} \times 6.0 \times 10^{23}$

$= 1.44 \times 10^{20}$ molecules

Deduce order of a reaction by initial rates and initial concentrations

- Example

$BrO_3^-{}_{(aq)} + 5Br^-{}_{(aq)} + 6H^+{}_{(aq)} \longrightarrow 3Br_{2(aq)} + 3H_2O_{(l)}$

Four experiments were carried out to find out how the rate of the above reaction depends on the concentrations of BrO_3^-, Br^- and H^+. The results are summarised in the following table.

experiment	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Initial rate of reaction
1	x	y	z	r
2	$2x$	y	z	$2r$
3	x	$2y$	z	$2r$
4	x	$2y$	$2z$	$8r$

a) How does the rate of reaction depend on the concentrations of the reactants in the chemical equation?

b) What is the rate equation for the reaction?

c) What is the order of the reaction?

d) What are the units of the rate constant?

Answers.

a) Comparing experiments 1 and 2:

when $[BrO_3^-]$ is doubled, the rate is doubled.

Hence rate $\propto [BrO_3^-]$

Comparing experiments 1 and 3:

when $[Br^-]$ is doubled, the rate is doubled.

Hence rate $\propto [Br^-]$

Comparing experiments 3 and 4:

when $[H^+]$ is doubled, the rate is increased by a factor of 4.

Hence rate $\propto [H^+]^2$

b) The rate equation, rate $= k[BrO_3^-][Br^-][H^+]^2$

c) The order of reaction $= 1+1+2 = 4$

d) The units of the rate constant, $k = \dfrac{\text{Units of rate}}{(\text{units of concentrations})^4}$

$$= \frac{mol\,dm^{-3}s^{-1}}{(mol\,dm^{-3})^4}$$

$$= dm^9\,mol^{-3}\,s^{-1}$$

Calculation of a rate constant using initial rate

- In the presence of hydrogen ions, hydrogen peroxide, H_2O_2 reacts with iodide ions to form water and iodine

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

- The rate equation is : rate $= k[H_2O_2][I^-]$
- The progress of the reaction can be followed by measuring the initial rate of iodine formation.
- The table shows reaction rates obtained using varius initial concentrations of each reactant.

Expt	$[H_2O_2]$/mol dm^{-3}	$[I^-]$/mol dm^{-3}	$[H^+]$/mol dm^{-3}	Initial reaction rate/mol dm^{-3} s^{-1}
1	0.0200	0.0100	0.0100	3.50×10^{-6}
2	0.0300	0.0100	0.0100	5.30×10^{-6}
3	0.0050	0.0200	0.0200	1.75×10^{-6}

- Using the data from experiment 1, calculating the rate constant as shown below:

Step 1: rate $= k[H_2O_2][I^-]$

Step 2: $k = \dfrac{\text{rate}}{[H_2O_2][I^-]}$

Step 3 : Substitute the value

$$k = \frac{3.50 \times 10^{-6}}{(0.02)(0.01)} = 1.75 \times 10^{-2}\ mol^{-1} dm^{3} s^{-1}$$

Note : $[H^+]$ is ignored, because $[H^+]$ not appear in the rate equation. (The reaction is zero order with respect to $[H^+]$

Calculate a rate constant (k) from half-life ($t_{1/2}$)

For a first-order reaction, half-life is related to the rate constant by the expression:

$$\boxed{t_{1/2} = \frac{0.693}{k}} \qquad \left(t_{1/2} = \frac{\log_e 2}{k}\right)$$

$t_{1/2}$: the half-life , unit : second

Rewrite the expression:

$$\boxed{k = \frac{0.693}{t_{1/2}}}$$

Example

For the first-order reaction cyclopropane to propene, its half-life is 17.0 min.

$$t_{1/2} = 17.0 \text{ min} = 17.0 \times 60 \text{ second}.$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{17.0 \times 60} = 6.79 \times 10^{-4} \text{ s}^{-1}$$

Exercise

a. Use the data from experiments 2 and 3 in the table of previous example to calculate the rate constant for the following reaction.

$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \rightarrow 2H_2O_{(l)} + I_{2(aq)}$

The rate equation for this reaction is:

$\text{rate} = k[H_2O_2][I^-]$

(Answers k (experiment 2) $= 0.0177\,dm^3\,mol^{-1}\,s^{-1}$
k (experiment 3) $= 0.0175\,dm^3\,mol^{-1}\,s^{-1}$)

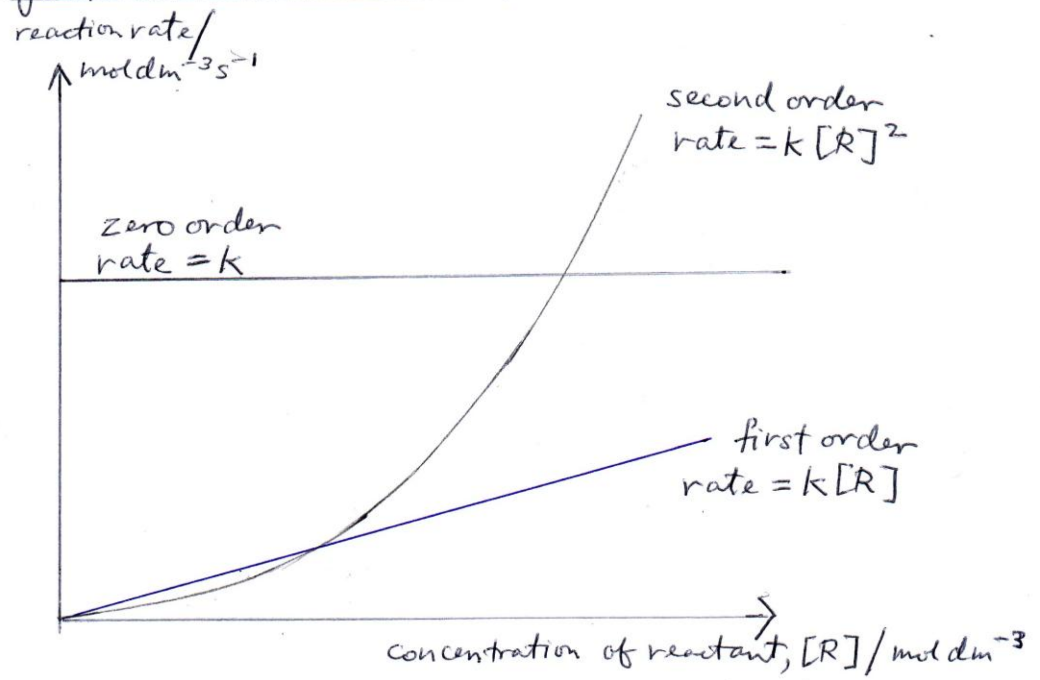
b. Use the formula $t_{1/2} = \frac{0.693}{k}$ to calculate a value for the rate constant of a reaction which is first order and has a half-life of 480 s.

(Answer $k = 1.44 \times 10^{-3}\,s^{-1}$)

c. A first-order reaction has a rate constant of $9.63 \times 10^{-5}\,s^{-1}$. Calculate a value for the half-life of this reaction.

(Answer $t_{1/2} = 7200\,s$)

Graphs rate of reaction against concentration of reactant.



- Graphs show changes in the concentration of a reactant affect the reactan rate of zero-, first- and second-order reactions.

Zero-order reaction

- e.g. $2NH_{3(g)} \xrightarrow{\text{hot tungsten}} N_{2(g)} + 3H_{2(g)}$
- from experiment, rate $= k[NH_3]^0$
- Graph rate of reaction against concentration of reactant — a horizontal straight line.
- the reaction rate does not change with concentration.
- rate $= k$.

First-order reaction.

- e.g. $2N_2O_{(g)} \xrightarrow{gold} 2N_{2(g)} + O_{2(g)}$
- from experiment, rate = $k[N_2O]^1$ (or rate = $k[N_2O]$)
- The plot of reaction rate against concentration of reactant — an inclined straight line going through the origin.
- The rate is directly proportional to the concentration of N_2O.
- Doubling the concentration of N_2O doubles the rate of reaction.

Gradient = rate constant(k)

Second-order reaction

- e.g. $NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$
- from experiment, rate = $k[NO]^2$
- The plot of reaction rate against reactant concentration — an upwardly curved line.
- The reaction rate is directly proportional to the square of the concentration of $NO_{2(g)}$.
- The concentration of $NO_{2(g)}$ doubles, the rate of reaction increases four-fold.
- at 1 mol dm^{-3}, rate = $k(1)^2 = 1k$
  at 2 mol dm^{-3}, rate = $k(2)^2 = 4k$.
- plotting rate vs. $[NO_2]^2$ gives a straight line.

Exercise

Draw sketch graphs of reaction rate against concentration of the reactant underlined for each of the following reactions:

a) $\underline{NO}_{(g)} + CO_{(g)} + O_{2(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$

for which the rate equation is:

rate = $k[NO]^2$

b) $2\underline{HI}_{(g)} \xrightarrow{gold} H_{2(g)} + I_{2(g)}$

for which the rate equation is:

rate = k

Note: the catalyst influences the order here – the order is not the same as for the uncatalysed rxn.

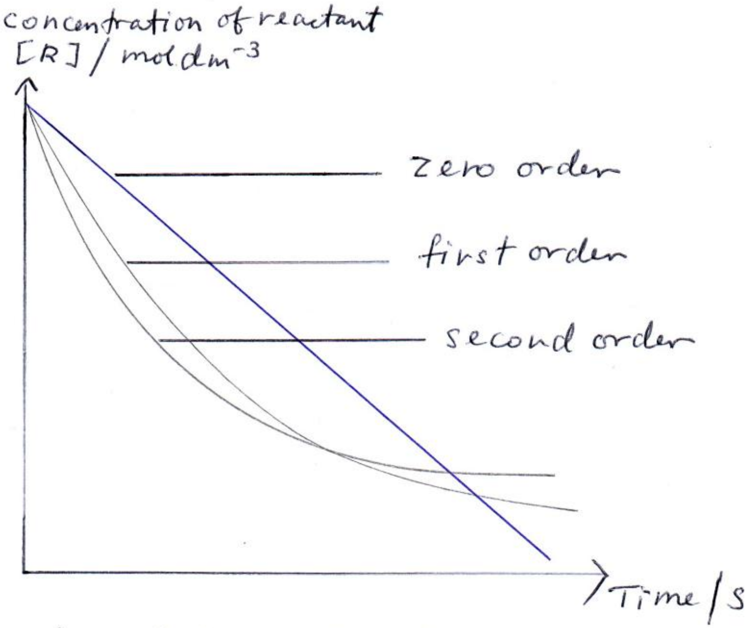
c) $\underline{(CH_3)_3CCl} + OH^- \longrightarrow (CH_3)_3COH + Cl^-$

for which the rate equation is:

rate = $k[(CH_3)_3CCl]$

Graphs reactant concentration against time.

- show the changes in the concentration of a reactant at different times as reaction proceed.



- can distinguish between zero-, first- and second-order reactions.

Zero Order

- the graph is descending straight line
- the rate of reaction is the slope (gradient) of the graph.
- the reaction proceeds at the same rate (constant rate) whatever the concentration of the reactant.

First Order

- declines in a shallow curve.

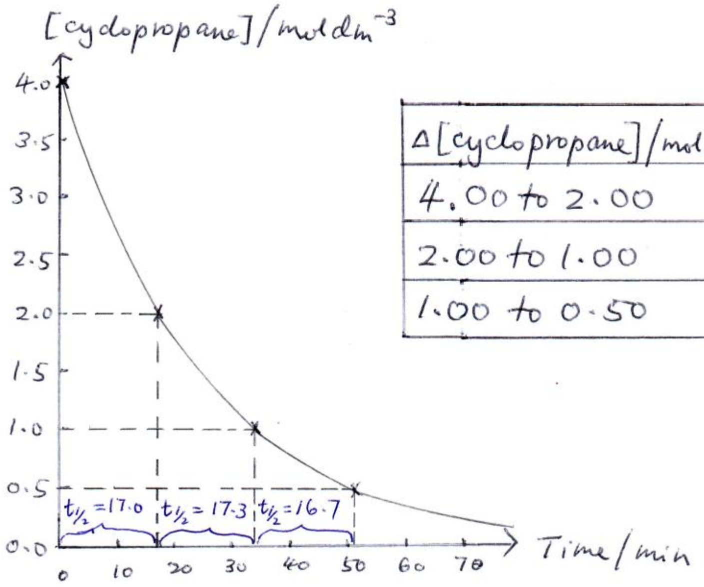
Second Order

- the curve is much deeper than 1st order rxn.
- also appears to have a relatively longer 'tail' as it level off.

Half-life ($t_{1/2}$)

Definition : is the time taken for the concentration of a reactant to fall to half of its original value.

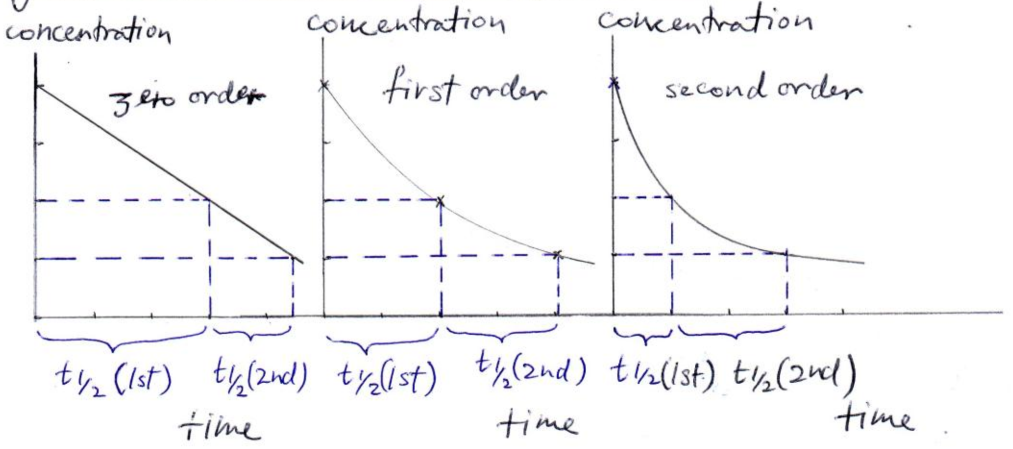
Example : reaction cyclopropane → propene



Δ[cyclopropane]/mol dm^{-3}	Half-life/min
4.00 to 2.00	17.0
2.00 to 1.00	34.3 − 17.0 = 17.3
1.00 to 0.50	51.0 − 34.3 = 16.7

- A constant half-life indicates a first-order rxn.
- In the first order reaction, the half-life is independent of the original concentration of reactant.

Graphs of concentration against time



- Zero-order reaction
  - has successive half-lives which decreases with time.
- First-order reaction
  - has a half-life which is constant.
- Second-order reaction.
  - has successive half-lives which increase with time.
  - higher order for a particular reactant will also show successive half-lives which increase with time.

Example

Benzenediazonium chloride, $C_6H_5N_2Cl$ decomposes at room temperature:

$C_6H_5N_2Cl_{(aq)} + H_2O_{(l)} \longrightarrow C_6H_5OH_{(aq)} + N_{2(g)} + HCl_{(aq)}$

a. Describe how this reaction can be monitored.

b. Using the data in the table, plot a graph of concentration of $C_6H_5N_2Cl$ against time.

Time / s	$[C_6H_5N_2Cl] / 10^{-4}\,mol\,dm^{-3}$
0	5.8
200	4.4
400	3.2
600	2.5
800	1.7
1000	1.2
1200	0.8
1400	0.5
1600	0.3

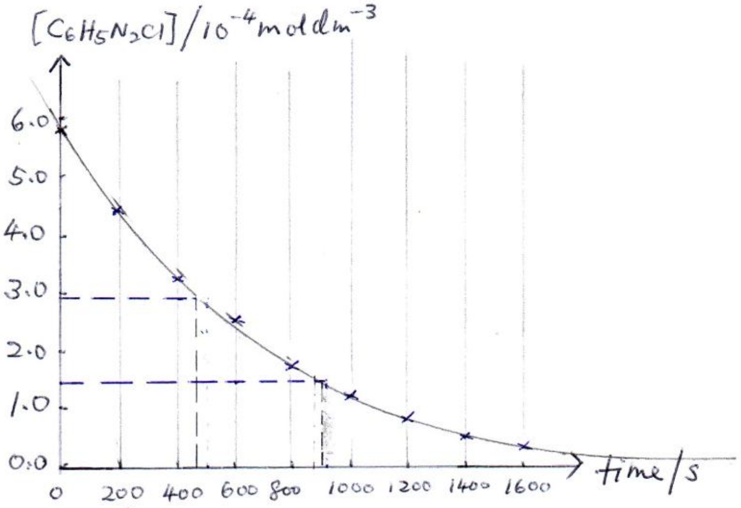
c. From your graph, find the value of two successive half-lives

d. Use the values of these half-lives to deduce the order of the reaction.

Answers.

a) By measuring the volume of nitrogen gas given off with time using a gas syringe.

b)



c) From $[C_6H_5N_2Cl] = 5{\cdot}8\times10^{-4}\,mol\,dm^{-3}$ to $[C_6H_5N_2Cl] = 2{\cdot}9\times10^{-4}\,mol\,dm^{-3}$, 1st $T_{1/2} = 460\,s$

From $[C_6H_5N_2Cl] = 2{\cdot}9\times10^{-4}\,mol\,dm^{-3}$ to $[C_6H_5N_2Cl] = 1.45\times10^{-4}\,mol\,dm^{-3}$, 2nd $T_{1/2} = 440\,S$

d) $T_{1/2}$ (1st) more or less the same as $T_{1/2}$ (2nd), therefore the reaction is first order.

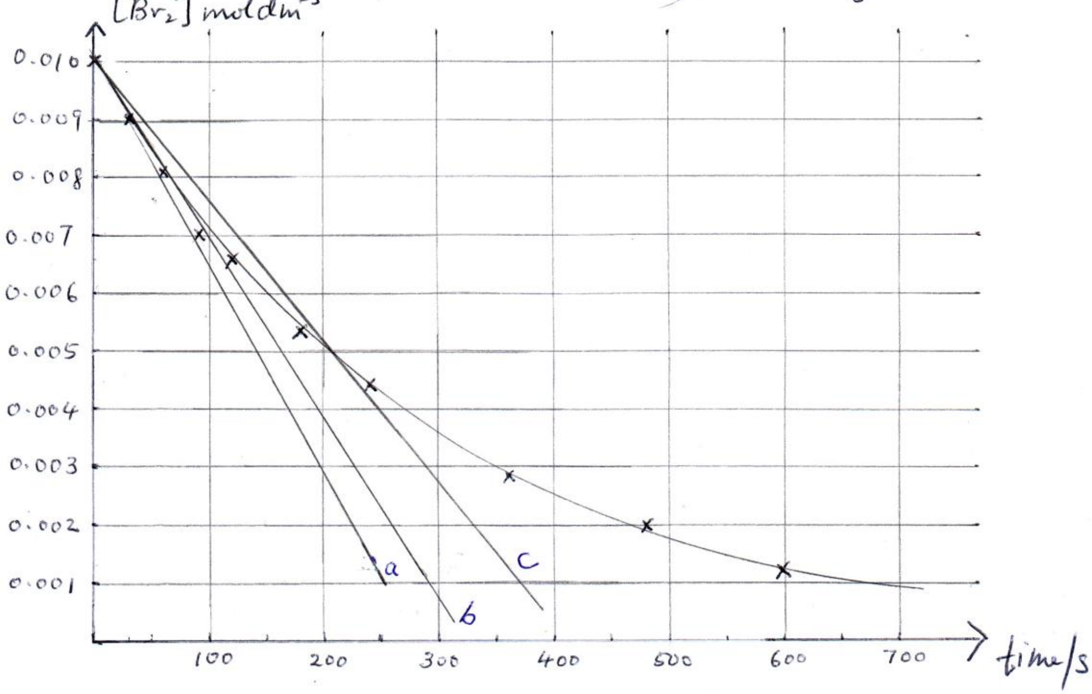
Using concentration-time graph to calculate initial rate

$$Br_{2(aq)} + HCOOH_{(aq)} \xrightarrow{H^+} 2Br^-_{(aq)} + 2H^+_{(aq)} + CO_{2(g)}$$

- The course of reaction can be followed calorimetrically by measuring the intensity of the red-brown bromine at suitable time intervals.
- By plotting a calibration curve of known bromine concentrations against colorimeter readings, the concentrations of bromine from the colorimeter readings can be deduced at various time intervals.
- Results of reaction between bromine and methanoic acid.

Time / s	$[Br_2]$/mol dm^{-3}
0	0.0100
30	0.0090
60	0.0081
90	0.0073
120	0.0066
180	0.0053
240	0.0044
360	0.0028
480	0.0020
600	0.0013

- The concentrations of bromine are plotted against time.



- The concentration of bromine $[Br_2]$ falls during the course of the reaction.
- reaction rate = − rate of change of bromine concentration

$$= -\frac{d[Br_2]}{dt}.$$

- negative sign used because the bromine is being used up.
- In order to obtain the reaction rate at any given time, draw a tangent to the curve at this particular time and measure its gradient.
- gradient of a = true initial rate (at time = 0)
- gradient of b = average reaction rate for 20% completion
- gradient of c = average reaction rate for 50% completion.