8 Reaction Kinetics

The investigation of the factors that affect the rate of a chemical reaction is important in the study of physical chemistry. The temperature and the addition of a catalyst can both affect the progression of a chemical reaction.

8.1 Simple rate equations; orders of reaction; rate constants ☐

8.2 Effect of temperature on reaction rates and rate constants; the concept of activation energy ☐

8.3 Homogeneous and heterogeneous catalysts including enzymes ☐

REACTION KINETICS

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	Learning outcomes Candidates should be able to:
8.1 Simple rate equations; orders of reaction; rate constants	a) explain and use the term *rate of reaction* b) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction **c) explain and use the terms *rate equation, order of reaction, rate constant, half-life of a reaction, rate-determining step*** **d) construct and use rate equations of the form rate =** $k[A]^m[B]^n$ **(for which *m* and *n* are 0, 1 or 2), including:** **(i) deducing the order of a reaction, or the rate equation for a reaction, from concentration-time graphs or from experimental data relating to the initial rates method and half-life method** **(ii) interpreting experimental data in graphical form, including concentration-time and rate-concentration graphs** **(iii) calculating an initial rate using concentration data** **(integrated forms of rate equations are not required)** **e) (i) show understanding that the half-life of a first-order reaction is independent of concentration** **(ii) use the half-life of a first-order reaction in calculations** **f) calculate the numerical value of a rate constant, for example by using the initial rates or half-life method** **g) for a multi-step reaction:** **(i) suggest a reaction mechanism that is consistent with the rate equation and the equation for the overall reaction** **(ii) predict the order that would result from a given reaction mechanism (and vice versa)** **h) devise a suitable experimental technique for studying the rate of a reaction, from given information**
8.2 Effect of temperature on reaction rates and rate constants; the concept of activation energy	a) explain and use the term *activation energy*, including reference to the Boltzmann distribution b) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on the rate of a reaction **c) explain qualitatively the effect of temperature change on a rate constant and hence the rate of a reaction**

8.3 Homogeneous and heterogeneous catalysts including enzymes	a) explain and use the term *catalysis* b) explain that catalysts can be homogenous or heterogeneous c) (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy (ii) interpret this catalytic effect in terms of the Boltzmann distribution d) describe enzymes as biological catalysts (proteins) which may have specificity **e) outline the different characteristics and modes of action of homogeneous, heterogeneous and enzyme catalysts, including:** **(i) the Haber process** **(ii) the catalytic removal of oxides of nitrogen from the exhaust gases of car engines (see also Section 15.3(b)(i))** **(iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide (see also Section 13.1(f))** **(iv) the catalytic role of Fe^{2+} or Fe^{3+} in the $I^-/S_2O_8^{2-}$ reaction** **(v) the catalytic role of enzymes (including the explanation of specificity using a simple lock and key model but excluding inhibition)**

INCREASING THE RATE

According to collision theory, to increase the rate of reaction you need:

more frequent collisions

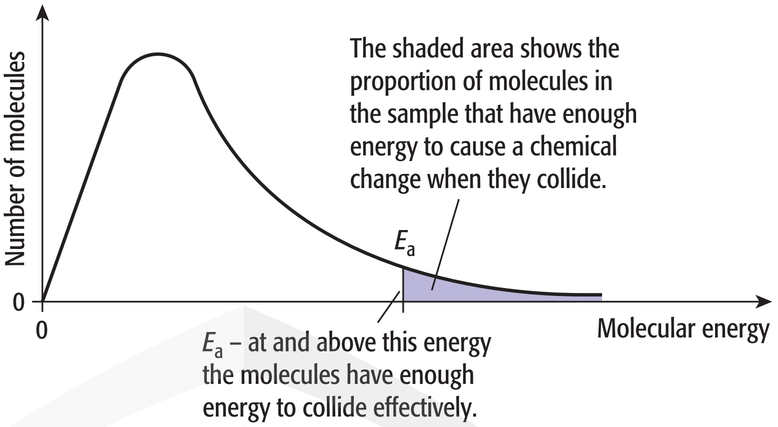
increase particle speed

have more particles present

more successful collisions

give particles more energy

lower the activation energy



RATE OF A REACTION

The rate of a reaction is a measure of the rate at which reactants are used up or the rate at which products are formed. The units of rate are mol $dm^{-3}s^{-1}$.

The factors that affect the rate of a reaction are:

increase the surface area of **solids**

increase the temperature

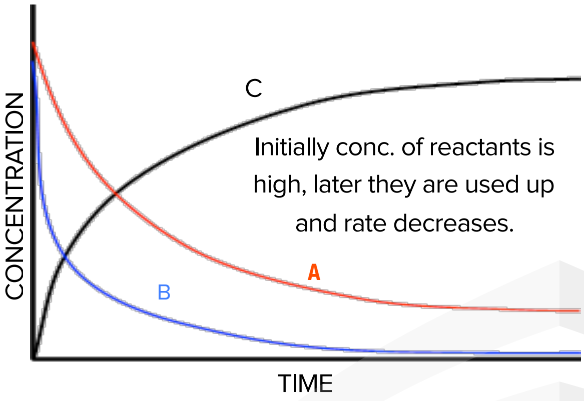
add a catalyst

increase the pressure of any **gases**

increase the concentration of reactants

RATE CHANGE DURING A REACTION

In a reaction such as A + 2B → C the concentrations might change as shown



Initially conc. of reactants is high, later they are used up and rate decreases.

The steeper the curve the faster the rate of the reaction

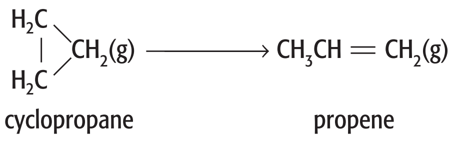
The higher the gradient, the faster the rate of reaction

Reactions start off quickly because of the greater likelihood of collisions

Reactions slow down with time as there are fewer reactants to collide with.

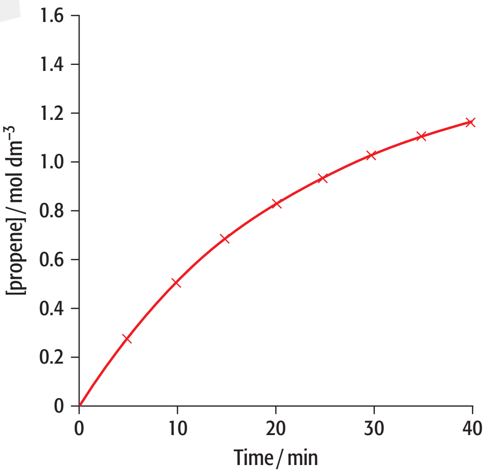
MEASURING THE RATE

Taking the isomerisation of cyclopropane to propene as an example:



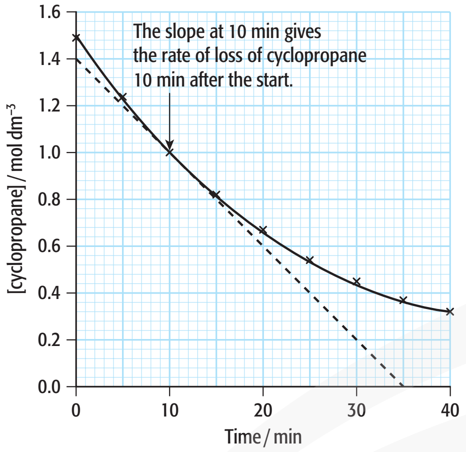
$CH_3CH=CH_2(g)$

The graph on the right shows how the concentration of propene (the product) changes with time.



MEASURING THE RATE

The rate of decrease of cyclopropane (the reactant) concentration over times as the reaction proceeds.



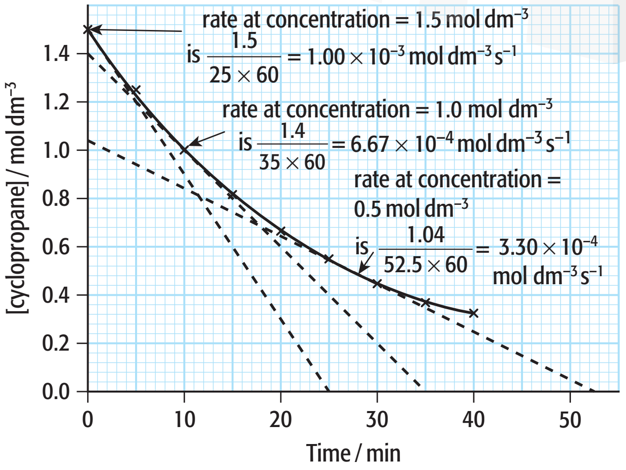
The rate of change of concentration is found from the slope (gradient) of the curve by drawing a tangent at a point.

The gradient at the start of the reaction will give the initial rate

CHANGES IN RATE AS THE REACTION PROCEEDS

The graph shows tangents drawn at several points along the graph.

The gradient of tangents gets less. This shows that the rate is slowing down as the reaction proceeds.



CHANGES IN RATE AS THE REACTION PROCEEDS

Rates of decrease for cyclopropane at different concentrations

[cyclopropane] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}	$\frac{\text{rate}}{[\text{cyclopropane}]}$ / s^{-1}
1.50	1.00×10^{-3}	6.67×10^{-4}
1.00	6.67×10^{-4}	6.67×10^{-4}
0.50	3.30×10^{-4}	6.60×10^{-4}

From the above table:

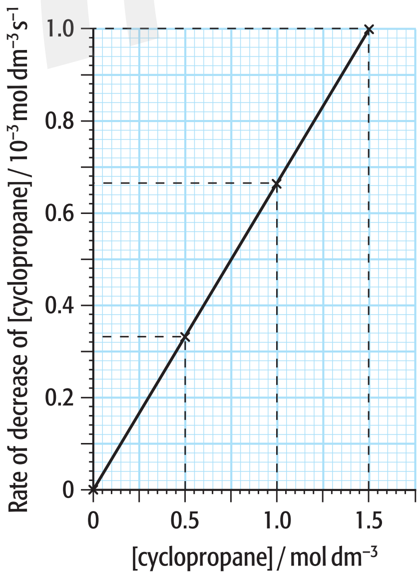
if the concentration of cyclopropane is doubled the rate of reaction is doubled and

if the concentration of cyclopropane falls by one-third, the rate of reaction falls by one-third

CHANGES IN RATE AS THE REACTION PROCEEDS

A graph of rate of reaction against concentration of cyclopropane shows us that

the rate is directly proportional to the concentration of cyclopropane.



THE RATE EQUATION

It is an equation showing the relationship between the rate constant and the product of those reactants which affect the rate of reaction.

For the equation $A + B \rightarrow C + D$

might have a rate equation like this: $R = k[A][B]^2$

R	rate of reaction	units	conc. / time mol dm^{-3} s^{-1}
k	rate constant	units	depends on the rate equation
[ ]	concentration	units	mol dm^{-3}

THE RATE EQUATION

$R = k[A][B]^2$

The above rate equation tells you that the rate of reaction is:

proportional to the concentration of reactant A: doubling [A] doubles rate

proportional to the square of the concentration of B: doubling [B] quadruples (2^2) rate

Note: The rate equation is derived from experimental evidence not by looking at an equation.

ORDER OF REACTION

Order is the power to which the concentration of a reactant is raised in the rate equation.

If the concentration does not affect the rate,the reaction is zero order.

If the rate is directly proportional to the reactant concentration, the reaction is first order.

If the rate is directly proportional to the square of the reactant concentration, the reaction is second order.

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.

EXAMPLE

In the rate equation $R = k[A][B]^2$,

the order with respect to A is	1	1st Order
the order with respect to B is	2	2nd Order
and the overall order is	3	3rd Order

Note: Order values need not be whole numbers and can be zero if the rate is unaffected by how much of a substance is present.

THE RATE CONSTANT (K)

Definition: The proportionality constant in the rate equation.

Units: The units of k depend on the overall order of reaction. For example,

if the rate equation is rate = k $[A]^2$ the units of k will be $mol^{-1}\ dm^3\ s^{-1}$

in the rate equation r = k [A] k will have units of s^{-1}

in the rate equation r = k [A] $[B]^2$ k will have units of $mol^{-2}\ dm^6\ s^{-1}$

Divide the rate by as many concentrations as appear in the rate equation.

RATE EQUATION - SAMPLE CALCULATION

In an experiment between A and B the initial rate of reaction was found for various starting concentrations of A and B.

Calculate:

(a) the individual orders for A and B

(b) the overall order of reaction

(c) the value of the rate constant (k)

(d) the units of the rate constant

	[A]	[B]	Initial Rate
1	0.5	1	2
2	1.5	1	6
3	0.5	2	8

RATE EQUATION - SAMPLE CALCULATION

(a) Calculating order wrt A

Choose any two experiments where:

[A] is changed and, more importantly,

[B] is **kept the same**

	[A]	[B]	Initial Rate
1	0.5	1	2
2	1.5	1	6
3	0.5	2	8

See how the change in [A] affects the rate

Hence, compare Experiments 1 & 2:

[A] changes & [B] is the same

[A] is 3 x greater and the rate is 3 x bigger $\therefore$ rate $\propto$ [A]

$\therefore$ order wrt to A is 1

RATE EQUATION - SAMPLE CALCULATION

(b) Calculating order wrt B

Choose any two experiments where:

[B] is changed and, more importantly,

[A] is **kept the same**

	[A]	[B]	Initial Rate
1	0.5	1	2
2	1.5	1	6
3	0.5	2	8

See how the change in [B] affects the rate

Hence, compare Experiments 1 & 3:

[B] changes & [A] same

[B] is 2 x greater, rate is 4 x greater $\therefore$ rate $\propto$ $[B]^2$

$\therefore$ order with respect to B is 2

RATE EQUATION - SAMPLE CALCULATION

(c) Overall rate equation

rate $\propto$ [A] & rate $\propto$ $[B]^2$

By combining the two relationships you can construct the overall rate equation

Therefore, **rate = k [A] $[B]^2$** where k is the rate constant

(d) Value of the rate constant and (e) Units of the rate constant

Chose one experiment (e.g. Experiment. 3) and substitute its values into the rate equation to find the value of k

$$k = \frac{8}{(0.5)\,(2)^2} = 4\ \text{mol}^{-2}\ \text{dm}^{6}\ \text{s}^{-1}$$

RATE EQUATION - EXAMPLE 1

In an experiment between A and B the initial rate of reaction was found for various starting concentrations of A and B.

Calculate

(a) the individual orders for A and B

(b) the rate equation

(c) the value of the rate constant (k)

(d) the units of the rate constant

	[A]	[B]	Initial Rate
1	0.25	0.25	4
2	0.25	0.50	8
3	0.50	0.25	8

RATE EQUATION - EXAMPLE 1

Experiments 1 & 2:

[A] is constant, [B] x 2 and Rate x 2

∴ rate ∝ [B] 1st order wrt B

Experiments 1 & 3:

[B] is constant, [A] x 2 and Rate x 2

∴ rate ∝ [A] 1st order wrt A

Rate equation is R = k[A][B]

	[A]	[B]	Initial Rate
1	0.25	0.25	4
2	0.25	0.50	8
3	0.50	0.25	8

RATE EQUATION - EXAMPLE 2

In an experiment between C and D the initial rate of reaction was found for various starting concentrations of C and D.

Calculate

(a) the individual orders for C and D

(b) the overall order of reaction

(c) the value of the rate constant (k)

(d) the units of the rate constant

	[C]	[D]	Initial Rate
1	0.40	0.40	0.16
2	0.20	0.40	0.04
3	0.40	1.20	1.44

RATE EQUATION - EXAMPLE 2

Experiments 1 & 3:

[C] is constant, [D] x 3 and rate is 9 x greater

$\therefore$ rate $\propto [D]^2$ 2nd order wrt D

Experiments 1 & 2:

[D] is constant, [C] is halved and rate is quartered

$\therefore$ rate $\propto [C]^2$ 2nd order wrt C

Therefore, the rate equation is $R = k\,[C]^2[D]^2$

	[C]	[D]	Initial Rate
1	0.40	0.40	0.16
2	0.20	0.40	0.04
3	0.40	1.20	1.44

RATE EQUATION - EXAMPLE 3

In an experiment between E and F the initial rate of reaction was found for various starting concentrations of E and F.

Calculate

(a) the individual orders for E and F

(b) the overall order of reaction

(c) the value of the rate constant (k)

(d) the units of the rate constant

	[E]	[F]	Initial Rate
1	0.40	0.40	0.16
2	0.80	0.80	0.32
3	0.80	1.20	0.32

RATE EQUATION - EXAMPLE 3

Experiments 2 & 3:

[E] is constant and [F] x 1.5

Rate is constant that is, it's unaffected

∴ ZERO order wrt F

Experiments 1 & 2:

[E] x 2 and [F] x 2

Rate x 2 ∴ rate $\propto$ [E] 1st order wrt E

	[E]	[F]	Initial Rate
1	0.40	0.40	0.16
2	0.80	0.80	0.32
3	0.80	1.20	0.32

Although both concentrations have been doubled, we know [F] has no effect. The change must be all due to [E].

SKILL CHECK

Hydrogen gas reacts with nitrogen monoxide gas to form steam and nitrogen. Doubling the concentration of hydrogen doubles the rate of reaction. Tripling the concentration of NO gas increases the rate by a factor of nine.

(a) Write the balanced equation for the reaction.

(b) Write the rate equation for the reaction.

SKILL CHECK

Hydrogen reacts with iodine at 450°C to give hydrogen iodide. The results from several experiments designed to find rate equation for the reaction are given in table below.

Initial $[I_2]$ /mol dm^{-3}	Initial $[H_2]$ /mol dm^{-3}	Relative Initial rate
0.001	0.001	1
0.003	0.001	3
0.001	0.004	4

(a) Find the order of reaction with respect to each of the reactants.

(b) Write the rate equation for the reaction

25

SKILL CHECK

This data refers to the reaction of the halogenoalkane 1-bromobutane (here represented as RBr) with hydroxide ions.

Experiment	[RBr] /mol dm^{-3}	$[OH^-]$ /mol dm^{-3}	Rate of reaction /mol dm^{-3} s^{-1}
1	0.020	0.020	1.36
2	0.010	0.020	0.68
3	0.010	0.005	0.17

(a) Deduce the rate equation for the reaction.

(b) Calculate the value of rate constant.

26

SKILL CHECK

This data refers to the reaction of the halogenoalkane 2-bromo-2-methylpropane (here represented as R'Br) with hydroxide ions.

Experiment	**[R'Br] /mol dm^{-3}**	**[OH−] /mol dm^{-3}**	**Rate of reaction /mol dm^{-3} s^{-1}**
1	0.020	0.020	40.40
2	0.010	0.020	20.19
3	0.010	0.005	20.20

(a) Deduce the rate equation for the reaction.

(b) Calculate the value of rate constant.

ORDER OF REACTIONS

We can identify the order of a reaction in three ways:

plot a graph of reaction rate against concentration of reactant

plot a graph of concentration of reactant against time

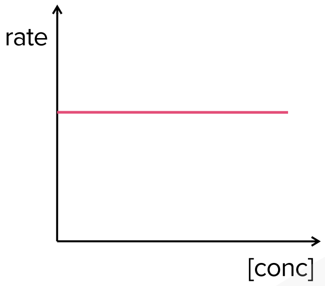
deduce successive half-lives from graphs of concentration against time

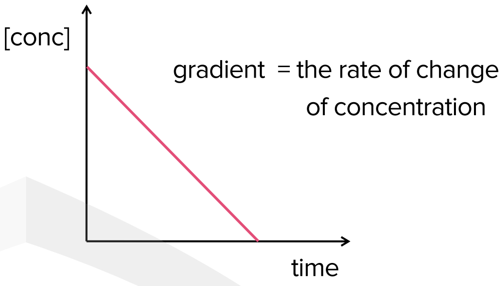
ZERO ORDER REACTIONS

$$R \propto [A]^0$$

$$R = k[A]^0 = k$$

$$y = c$$





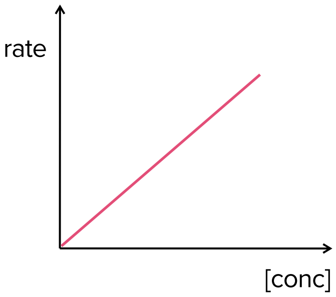
gradient = the rate of change of concentration

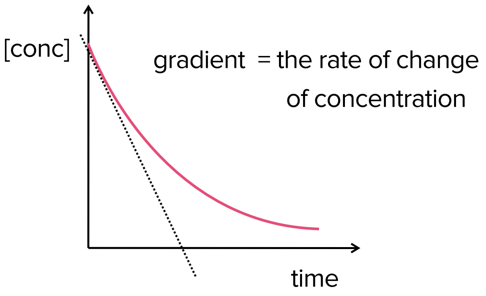
FIRST ORDER REACTIONS

$$R \propto [A]^1$$

$$R = k[A]$$

$$y = mx$$





gradient = the rate of change of concentration

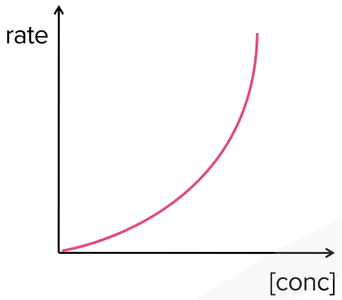
Constant half life

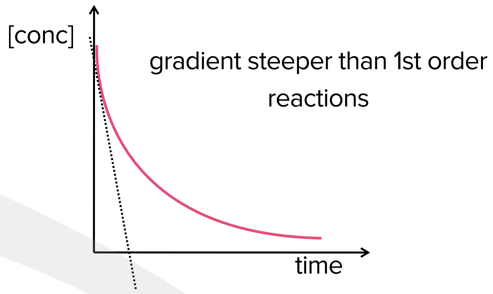
SECOND ORDER REACTIONS

$R \propto [A]^2$

$R = k[A]^2$

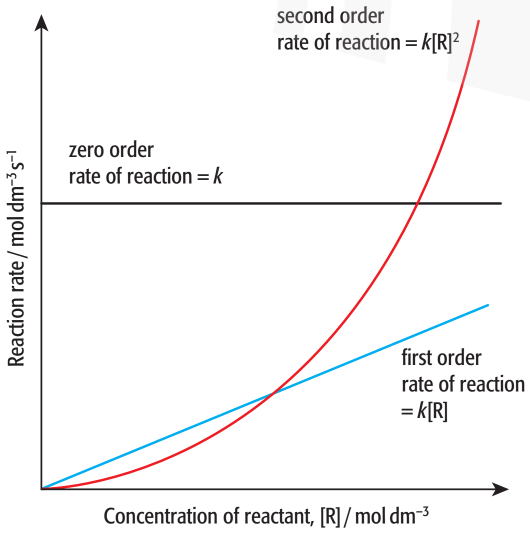
$y = mx^2$





gradient steeper than 1st order reactions

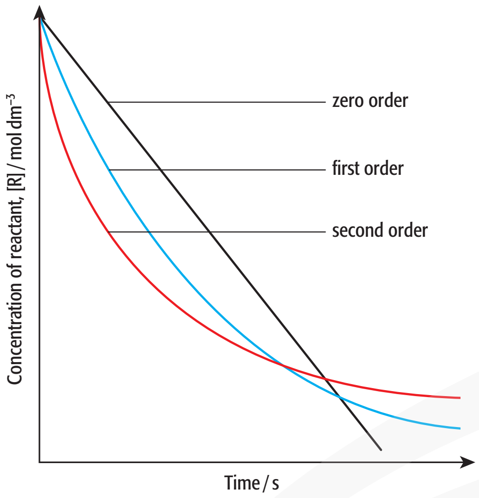
ORDER OF REACTION



A graph of reaction rate against concentration tells us whether a reaction is zero, first, second or third order with respect to a particular reagent (or overall).

It is very rare to obtain an order with respect to a particular reagent higher than second order.

ORDER OF REACTION GRAPHS



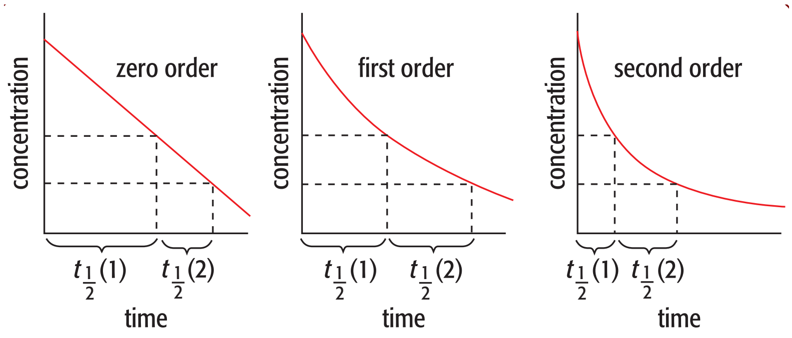
The order of reaction can be found by measuring the rate at different times during the reaction and plotting the rate against either concentration or time.

The shape of the curve provides an indication of the order.

Zero order: The constant rate of decline
First order: Declines in a shallow curve
Second order: A deeper curve which then levels out

ORDER AND HALF-LIFE

Half-life, $t_{1/2}$, is the *time taken for the concentration of a reactant to fall to half of its original value*. We can distinguish zero, first and second order reactions from their successive half-lives.



$t_1 > t_2$ t1 = t2 t1 < t2

ORDER AND HALF-LIFE

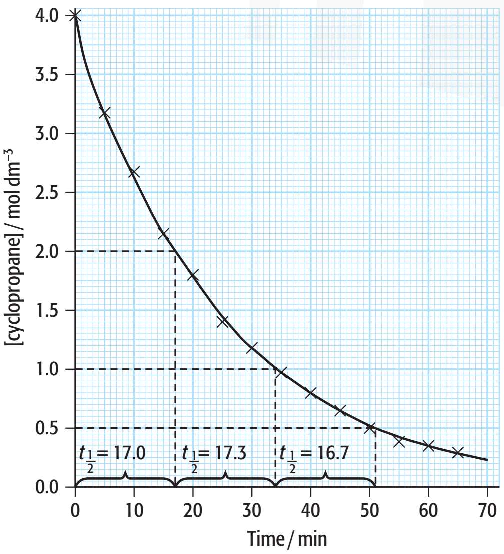
A zero-order reaction has successive half-lives which decrease with time.

A first-order reaction has a half-life which is constant.

Second-order reactions have successive half-lives which increase with time.

An increase in successive half-lives also applies to reactions with a higher order for a particular reagent.

FIRST ORDER REACTIONS AND HALF LIFE



One characteristic of a **first order reaction** is that it is similar to radioactive decay. It has a half-life that is independent of the concentration.

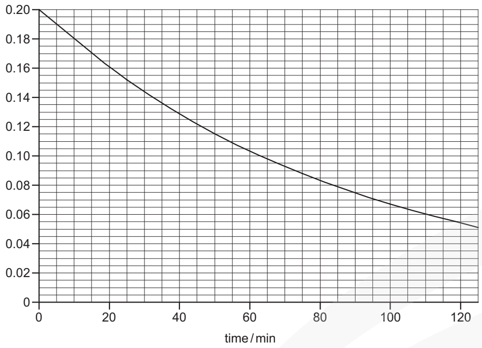
It should take the same time to drop to one half of the original concentration as it does to drop from one half to one quarter of the original.

DETERMINING ORDERS USING GRAPHS

Ethyl ethanoate is hydrolysed slowly by water in the following acid-catalysed reaction.

$$CH_3CO_2CH_2CH_3 \quad + \quad 2H_2O \xrightarrow{H^+} CH_3CO_2H \quad + \quad CH_3CH_2OH$$

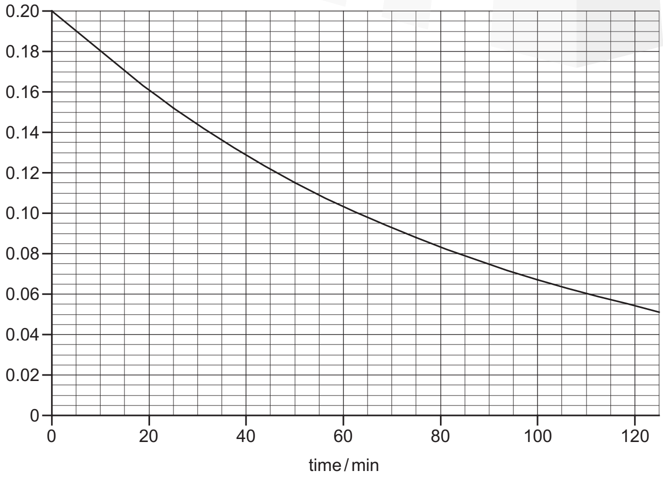
The concentration of ethyl ethanoate was determined at regular time intervals as the reaction progressed using [HCl] = 0.1 mol dm^{-3}



Calculate the order with respect to $CH_3CO_2CH_2CH_3$

DETERMINING ORDERS USING GRAPHS

Ethyl ethanoate is hydrolysed slowly by water in the following acid-catalysed reaction.



Draw construction lines at conc. 0.10 and 0.05 moldm^{-3} and find their corresponding times, t_1 & t_2

If $t_1 = t_2$, then the half lives are constant and the reaction is first order with respect to $CH_3CO_2CH_2CH_3$

DETERMINING ORDERS USING GRAPHS

When the experiment was carried out using [HCl] = 0.2 mol dm^{-3}, the following results were obtained

time /min	$CH_3CO_2CH_2CH_3$ / mol dm^{-3}
0	0.200
10	0.160
25	0.115
50	0.067
75	0.038
100	0.022
125	0.013

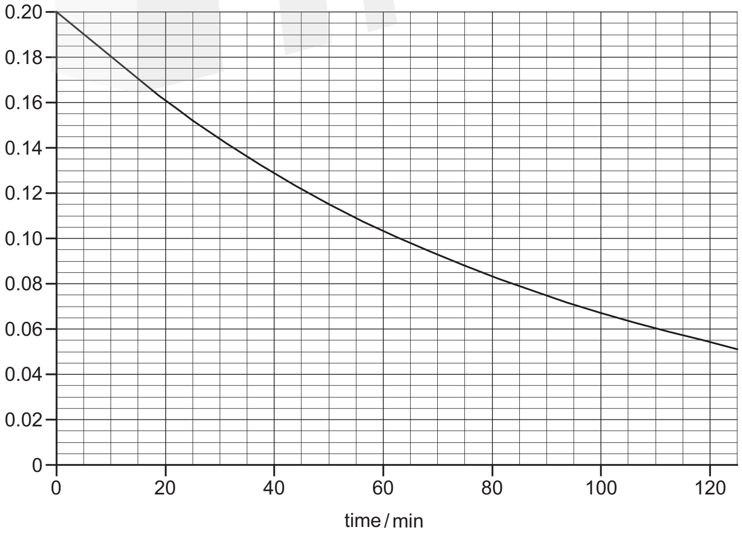
Plot these data on the axes, and draw a line (curve) of best fit.

Draw tangents on conc. 0.20 moldm^{-3} on both the curves and find the gradients for both lines.

39

DETERMINING ORDERS USING GRAPHS

time /min	**$CH_3CO_2CH_2CH_3$ / mol dm^{-3}**
0	0.200
10	0.160
25	0.115
50	0.067
75	0.038
100	0.022
125	0.013



40

DETERMINING ORDERS USING GRAPHS

Draw tangents on conc. 0.20 $moldm^{-3}$ on both the curves.

The gradient of the tangents gives the rate of the equation.

$[CH_3CO_2CH_2CH_3]$ is constant and [HCl] × 2 and rate × 2. Thus rate [HCl] and 1st order wrt [HCl].

as the [HCl] doubled the initial rate (found through tangents) doubled.

RATE DETERMINING STEP

Many reactions consist of a series of separate stages.

Each step has its own rate and rate constant.

The overall rate of a multi-step process is governed by the slowest step

This step is known as the **RATE DETERMINING STEP.**

If there is more than one step, the rate equation may not contain all the reactants in its format.

RATE DETERMINING STEP

$$A + B \xrightarrow{D} AB \text{ (product)}$$

Mechanism

step 1. $A + D \longrightarrow AD$

step 2. $AD + A \longrightarrow A_2D$

step 3. $A_2D + B \longrightarrow AB + A + D$

If Step 1 is the slowest step:

$R \propto [A][D]$

If Step 2 is the slowest step:

$R \propto [AD][A]$

$R \propto [A][D][A]$

$R \propto [A]^2[D]$

If Step 3 is the slowest step:

$R \propto [A_2D][B]$

$R \propto [AD][A][B]$

$R \propto [A][D][A][B]$

$R \propto [A]^2[D][B]$

RATE DETERMINING STEP - EXAMPLES

The reaction **$2N_2O_5 \longrightarrow 4NO_2 + O_2$** takes place in 3 steps:

Step 1: $N_2O_5 \longrightarrow NO_2 + NO_3$ Slow

Step 2: $NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$ Fast

Step 3: $NO + NO_3 \longrightarrow 2NO_2$ Fast

The rate determining step is Step 1 since it's the slowest step.

$\therefore$ rate = $k[N_2O_5]$

RATE DETERMINING STEP - EXAMPLES

The reaction **$H_2O_2 + 2H_3O^+ + 2I^- \longrightarrow I_2 + 4H_2O$** takes place in 3 steps:

Step 1: $H_2O_2 + I^- \longrightarrow IO^- + H_2O$ Slow

Step 2: $IO^- + H_3O^+ \longrightarrow HIO + H_2O$ Fast

Step 3: $HIO + H_3O^+ + I^- \longrightarrow I_2 + 2H_2O$ Fast

The rate determining step is Step 1 as it is the slowest:

$\therefore$ rate = $k[H_2O_2][I^-]$

If step 2 is slow	If step 3 is slow
$R \propto [H_2O_2][I^-][H_3O^+]$	$R \propto [H_2O_2][I^-]^2[H_3O^+]^2$

REACTION BETWEEN PROPANONE & IODINE

Iodine and propanone react in the presence of acid:

$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$

The rate equation is: $R = k[CH_3COCH_3][H^+]$

Why do H^+ ions appear in the rate equation?

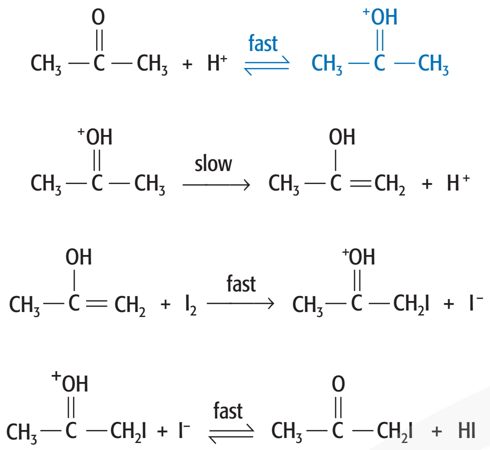
The reaction is catalysed by acid $[H^+]$ affects the rate but is unchanged overall

Why does I_2 not appear in the rate equation?

The rate determining step doesn't involve I_2

Catalysts appear in the rate equation because they affect the rate but they do not appear in the stoichiometric equation because they remain chemically unchanged.

REACTION BETWEEN PROPANONE & IODINE



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H^+ \xrightleftharpoons{\text{fast}} CH_3-\overset{\overset{^+OH}{\|}}{C}-CH_3$$

$$CH_3-\overset{\overset{^+OH}{\|}}{C}-CH_3 \xrightarrow{\text{slow}} CH_3-\overset{\overset{OH}{|}}{C}=CH_2 + H^+$$

$$CH_3-\overset{\overset{OH}{|}}{C}=CH_2 + I_2 \xrightarrow{\text{fast}} CH_3-\overset{\overset{^+OH}{\|}}{C}-CH_2I + I^-$$

$$CH_3-\overset{\overset{^+OH}{\|}}{C}-CH_2I + I^- \xrightleftharpoons{\text{fast}} CH_3-\overset{\overset{O}{\|}}{C}-CH_2I + HI$$

The slow step (the rate-determining step) does not involve either propanone or H^+ directly.

The intermediate is derived from substances which react together to form it. So both $[CH_3COCH_3]$ and $[H^+]$ appear in the rate equation.

The reaction between I_2 and the intermediate is fast and I_2 molecules are not involved in the mechanism until after the rate-determining step. So the rate of reaction does not depend on $[I_2]$

HYDROLYSIS OF HALOALKANES

Haloalkanes (general formula RX) are hydrolysed by hydroxide ion to give alcohols.

$$RX + OH^- \longrightarrow ROH + X^-$$

With primary haloalkanes the rate equation is:

$$R = k\,[RX][OH^-] \quad \text{(second order)}$$

This is because both the RX and OH^- must collide for a reaction to take place in **one step**.

Hence it is an S_N2 mechanism (Overall order = 2)

HYDROLYSIS OF HALOALKANES

With tertiary haloalkanes, it only depends on [RX]:

$R = k\,[RX]$ (first order)

The reaction has taken place in two steps:

1. The first involves breaking an R-X bond
   $RX \rightarrow R^+ + X^-$ *Slow*
2. The second step involves the two ions joining
   $R^+ + OH^- \rightarrow ROH$ *Fast*

The first step is slower as it involves bond breaking and energy has to be put in. This is the SN_1 mechanism (Overall order=1)

EFFECT OF TEMPERATURE ON RATE CONSTANT

In AS we saw that temperature increases the rate of a chemical reaction and that this temperature effect can be explained in terms of the kinetic-molecular theory.

Increasing the temperature increases the rate of reaction because:

- the increased energy results in particles moving around more quickly, which increases the frequency of collisions
- the proportion of successful collisions (i.e. those that result in a reaction) increases because the proportion of particles exceeding the activation energy increases. This is the more important factor.

This increase of rate of a reaction due to temperature results in an increase in the reaction rate constant, **k**.

CATALYSIS

Catalysts increase the rate of a chemical reaction. They do this by providing an alternative pathway for the reaction with lower activation energy.

We can divide catalysts into two main classes.

Catalysis

Homogeneous Catalysis

Occurs when the catalyst is in the same phase as the reaction mixture. For example: hydrogen ions catalyse the hydrolysis of esters.

Heterogeneous Catalysis

Occurs when the catalyst is in a different phase to the reaction mixture. For example, decomposition of aqueous hydrogen peroxide catalysed by manganese(IV) oxide.

HOMOGENEOUS CATALYSIS

Homogeneous catalysis often involves changes in oxidation number of the ions involved in catalysis.

Ions of transition elements are often good catalysts because of their ability to change oxidation number.

Examples:

1. The catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide.
2. Catalytic role of Fe^{3+} in the $I^-/S_2O_8^{2-}$ reaction.

THE IODINE–PEROXODISULFATE REACTION

$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

Peroxodisulfate (persulfate) ions, $S_2O_8^{2-}$, oxidise iodide ions to iodine. This reaction is very slow. These are both anions, and so repel each other, hence need a higher Ea.

$Fe^{3+}(aq)$ ions catalyse this reaction. The catalysis involves two redox reactions:

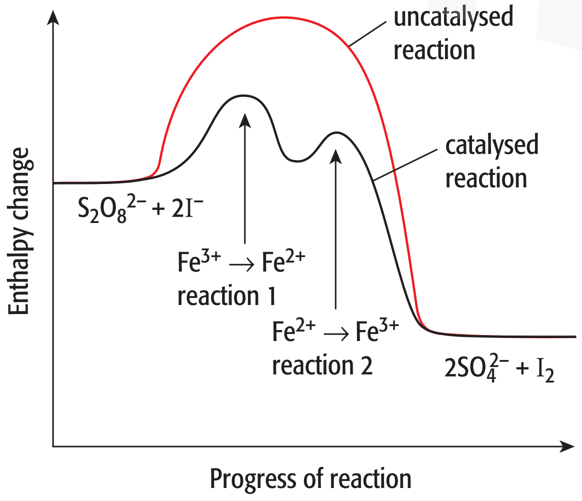
Reaction 1: Reduction of Fe^{3+} ions to Fe^{2+} ions by I^- ions:

$2Fe^{3+}(aq) + 2I^- \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 2: Oxidation of Fe^{2+} ions back to Fe^{3+} by $S_2O_8^{2-}$ ions:

$2Fe^{2+}(aq) + S_2O_8^{2-} \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}$

THE IODINE–PEROXODISULFATE REACTION



The figure shows an energy level profile for the catalysed and the uncatalysed reactions.

Notice that the catalysed reaction has two energy ‘humps’ because it is a two-stage reaction.

OXIDES OF NITROGEN AND ACID RAIN

One of the steps in the formation of acid rain is the oxidation of sulfur dioxide to sulfur trioxide.

$$SO_2(g) + 1/2O_2(g) \rightarrow SO_3(g)$$

This oxidation is catalysed by a wide variety of mechanisms. Nitrogen (IV) oxide present in the atmosphere from a variety of sources can catalyse the oxidation of sulfur dioxide. The nitrogen(IV) oxide is reformed by reaction with atmospheric oxygen:

$$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$$

$$NO + 1/2O_2 \rightarrow NO_2\ (g)$$

HETEROGENEOUS CATALYSIS

The mechanism of this catalysis can be explained using the theory of adsorption. Chemical adsorption (also called chemisorption) occurs when molecules become bonded to atoms on the surface of a solid.

You must be careful to distinguish between the words **adsorb** and **absorb**. Adsorb means to bond to the surface of a substance. Absorb means to move right into the substance – rather like a sponge absorbs water.

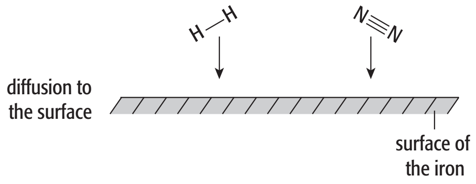
Examples:

1. Iron in the Haber Process
2. Transition elements in catalytic converters

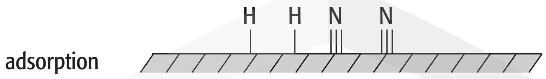
IRON IN THE HABER PROCESS

This heterogeneous catalysis occurs in five steps:

1. **Diffusion**: Nitrogen gas and hydrogen gas diffuse to the surface of the iron.



2. **Adsorption:** The reactant molecules are chemically adsorbed onto the surface of the iron.



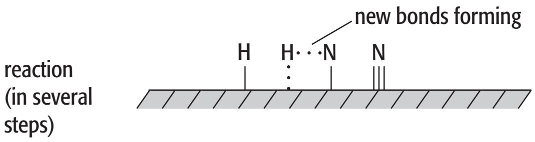
IRON IN THE HABER PROCESS

The bonds formed between the reactant molecules and the iron are:

strong enough to weaken the covalent bonds within the nitrogen and hydrogen molecules so the atoms can react with each other

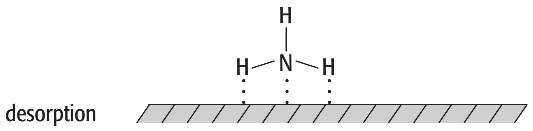
weak enough to break and allow the products to leave the surface.

3. **Reaction:** The adsorbed nitrogen and hydrogen atoms react on the surface of the iron to form ammonia.

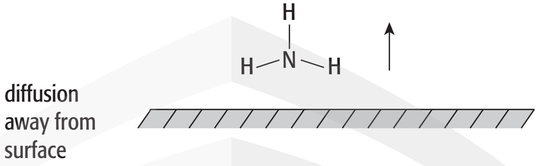


IRON IN THE HABER PROCESS

4. **Desorption**: the bonds between the ammonia and the surface of the iron weaken and are eventually broken.



5. **Diffusion**: Ammonia diffuses away from the surface of the iron.



CATALYTIC CONVERTERS

Catalytic converters convert harmful nitrogen oxides and carbon monoxide present in the exhaust gases from car engines to harmless gases.

$$2CO + 2NO \longrightarrow 2CO_2 + N_2$$

Catalytic converters can be affected by catalyst poisoning. Lead is a familiar catalyst poison for catalytic converters. It coats the honeycomb of expensive metals and stops it working.

The 'honeycomb' structure inside the catalytic converter contains small beads coated with platinum, palladium or rhodium. This maximises the surface area and keeps the amount of metal used to a minimum.

TRANSITION ELEMENTS IN CATALYTIC CONVERTERS

Possible steps in the catalytic process include:

adsorption of nitrogen oxides and carbon monoxide onto the catalyst surface

weakening of the covalent **bonds** within the nitrogen oxides and carbon monoxide

formation of new bonds between adjacent nitrogen atoms (to form nitrogen molecules) and carbon monoxide and oxygen atoms to form carbon dioxide

desorption of nitrogen molecules and carbon dioxide molecules from the surface of the catalyst.