Edexcel

A - Level

Chemistry

CODE: (WCH11)

Topic 11

Kinetics

11A 1 Techniques for measuring the rate of reaction

RATE OF REACTION

The **rate of reaction** can be expressed in two ways:

(1) How the concentration of a product *increases* with time.

$$\text{rate} = \frac{\text{change in concentration of product}}{\text{time}}$$

(2) How the concentration of a reactant *decreases* with time.

$$\text{rate} = -\frac{\text{change in concentration of reactant}}{\text{time}}$$

Rate is measured in units of concentration per unit time, and the most common units are mol dm^{-3} $s^{-1.}$

The expressions in calculus notation are:

$$\text{rate} = \frac{d[\text{product}]}{dt}$$

$$\text{rate} = -\frac{d[\text{reactant}]}{dt}$$

This **rate of reaction** is sometimes called the 'overall rate of reaction'.

TECHNIQUES FOR MEASURING THE RATE OF REACTION

Before investigating the rate of a particular reaction, it is necessary to know the overall equation, including state symbols, for the reaction so that we can decide what technique to use to follow the reaction.

There are various techniques available to use, such as:

1 measuring the volume of a gas evolved
2 measuring the change in mass of a reaction mixture
3 monitoring the change in intensity of colour of a reaction mixture (colorimetry)
4 measuring the change in concentration of a reactant or product using titration
5 measuring the change in pH of a solution
6 measuring the change in electrical conductivity of a reaction mixture.

However, the reaction between propanone and iodine in aqueous solution,

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

could not be followed by measuring the change in mass because all products of the reaction remain in solution. It would be possible, however, to follow the reaction by monitoring the decrease in intensity of colour of the reaction mixture, since $I_2(aq)$ is the only coloured species present (technique 3).

TECHNIQUE 1: MEASURING THE VOLUME OF A GAS EVOLVED

The two most common techniques for collecting and measuring the volume of a gas evolved during a reaction are:

1 collection over water into a measuring cylinder (fig A), and

2 collection using a gas syringe (fig B).

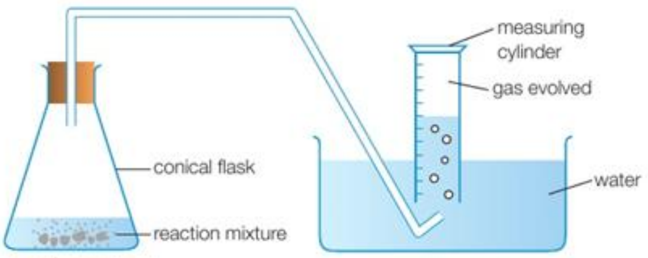


fig A Collecting a gas over water.

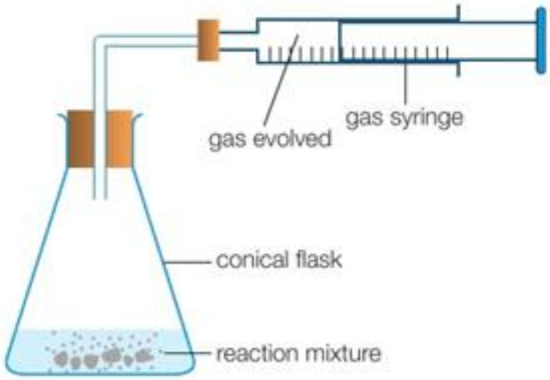


fig B Collecting a gas in a gas syringe.

TECHNIQUE 2: MEASURING THE CHANGE IN MASS OF A REACTION MIXTURE

This is another technique applicable to reactions in which a gas is evolved.
The reaction flask and contents are placed on a digital balance and the decrease in mass is measured as the reaction proceeds (fig C).

This technique is most precise when the gas given off has a relatively high density, such as with carbon dioxide. With a low-density (i.e. low relative molecular mass) gas such as hydrogen, the mass changes are so small that the measurement uncertainties become significant.

TECHNIQUE 3: MONITORING A COLOUR CHANGE (COLORIMETRY)

Colour change can sometimes be monitored using observation only. However, using a colorimeter gives more precise results (fig D). A colorimeter can detect far more subtle changes than the human eye can observe, and provides a quantitative (rather than a subjective) measurement.

fig D A colorimeter.

TECHNIQUE 4: ANALYSIS BY TITRATIO

Quenching is a technique used to stop or slow down a reaction in an aliquot using a pipette. It involves removing small samples from a reaction mixture, adding another substance, or immersing it in an ice bath. The aliquot is then titrated to determine the concentration of a reactant or product species. This method is used to investigate acid-catalyzed reactions.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

fig E Titrating iodine against sodium thiosulfate.

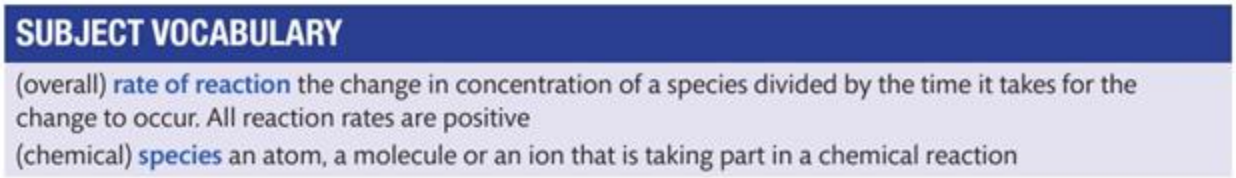
TECHNIQUE 5: MEASURING THE ELECTRICAL CONDUCTIVITY

If the total number, or type, of ions in solution changes during a reaction, it might be possible to follow the reaction by measuring changes in the electrical conductivity of the solution using a conductivity meter. For example, it could be used to follow this reaction:

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

TECHNIQUE 6: MEASURING ANY OTHER PHYSICAL PROPERTY THAT SHOWS A SIGNIFICANT CHANGE

Possible physical properties that have not already been mentioned include changes in the volume of liquid ('dilatometry'), chirality and refractive index.



SUBJECT VOCABULARY

(overall) **rate of reaction** the change in concentration of a species divided by the time it takes for the change to occur. All reaction rates are positive

(chemical) **species** an atom, a molecule or an ion that is taking part in a chemical reaction

11A 2 RATE EQUATIONS, RATE CONSTANTS AND ORDERS OF REACTION

RATE EQUATION

WHAT IS A RATE EQUATION?

The usual relationship between the rate of reaction and the concentration of a reactant is that the rate of reaction is directly proportional to the concentration. In other words, as the concentration is doubled, the rate of reaction doubles.

Let us consider the simple relationship where the rate is directly proportional to the concentration of a reactant, say A. We can represent this by the expression:

or:

$$\text{rate} \propto [A]$$

or:

$$\text{rate} = k[A]$$

where k is the proportionality constant.

This is called the first order rate equation. The constant k is called the rate constant.

- Every reaction has its own particular rate equation and its own rate constant.
- Rate constants will only change their value with a change in temperature.

Other common rate equations with respect to an individual reactant are:

second order rate equation: $\text{rate} = k[A]^2$

zero order rate equation: $\text{rate} = k[A]^0$ or $\text{rate} = k$

Zero order reactions do not occur very often, and it might be difficult at this stage for you to imagine why they should occur at all. However, you will find out shortly why they can occur.

If two or more reactants are involved, then it is possible to have a third order rate equation:

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

THE UNITS OF RATE CONSTANTS

Table A shows the units for rate constants, using mol dm^{-3} as the unit of concentration and seconds as the unit of time. You find the units by rearranging the rate equation.

ORDER	UNIT
Zero	mol dm^{-3} s^{-1}
First	s^{-1}
Second	dm^3 mol^{-1} s^{-1}
Third	dm^6 mol^{-2} s^{-1}

table A

EXAM HINT

The values for orders of reaction in rate equations will only ever be 0, 1 or 2 at International A Level.

The majority of reactions involve two or more reactants. If we call the reactants A, B and C, then the reaction may be first order with respect to A, first order with respect to B and second order with respect to C. The overall rate equation will be:

rate = $k[A][B][C]^2$

and the overall order of the reaction is four (1 + 1 + 2). Note that you are adding the powers.

For a general reaction in which the orders are m, n and p, we have:

rate = $k[A]^m[B]^n[C]^p$

The overall order of the reaction is m+n+p.

REACTION MECHANISMS

Many reactions can be represented by a stoichiometric equation containing many reactant particles. For example, the reaction between manganate(VII) ions and iron(II) ions in acidic solution can be represented by:

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

The reaction is fast even at room temperature, requiring a series of steps to occur. The probability of 14 particles colliding with the correct orientation and energy is extremely rare. The orders of reaction of individual reactants can help suggest a possible mechanism, but the mathematical relationship between rate and reactant concentration cannot be inferred from the stoichiometric equation.

Consider the reaction:

$$A + B + C \rightarrow D + E$$

for which the experimentally determined rate equation is:

rate = $k[A][B]$

Step 1: $A + B \rightarrow Z$ SLOW

Step 2: $Z + C \rightarrow D + E$ FAST

Since only Step 1 is rate-determining, then only changes in [A] and [B] will affect the overall rate of reaction. Changes in the rate at which Step 2 occurs, owing to changes in [C], will be negligible.
Important points to remember are that:

- The slowest step in a reaction determines the overall rate of the reaction.
- The slowest step is known as the rate-determining step of the reaction.

We will return to the concept of reaction mechanisms, and consider them in much more detail, in Section 11A.4.

SUBJECT VOCABULARY

rate equation an equation expressing the mathematical relationship between the rate of reaction and the concentrations of the reactants

order (of a reactant species) the power to which the concentration of the species is raised in the rate equation

overall order (of a reaction) the sum of all the individual orders

rate-determining step (of a reaction) the slowest step in the mechanism for the reaction

11A 3 DETERMINING ORDERS OF REACTION

HOW CAN WE DETERMINE THE RATE EQUATION?

This question can equally be phrased 'How can we determine the order of reaction with respect to each reactant?' There are two methods for determining orders of reaction. They are both experimental. Indeed, orders of reaction can only be determined by experiment.

The first is sometimes called the 'continuous method'.
The second is sometimes called the 'initial-rate method'.

THE CONTINUOUS METHOD

In this method, one reaction mixture is made up and samples of the reaction mixture are withdrawn at regular time intervals. The reaction in the sample is stopped, if necessary, by quenching. The concentration of the reactant is then determined by an appropriate experimental technique, such as titration.

- The first step is to draw a 'concentration-time' graph.
- The second step is to find out the half-life for the reaction at different concentrations.

If the half-life has a constant value, then the reaction is first order with respect to the reactant.

The 1st half-life, for the change in concentration from 120 to 60 units, is 100s (fig A).

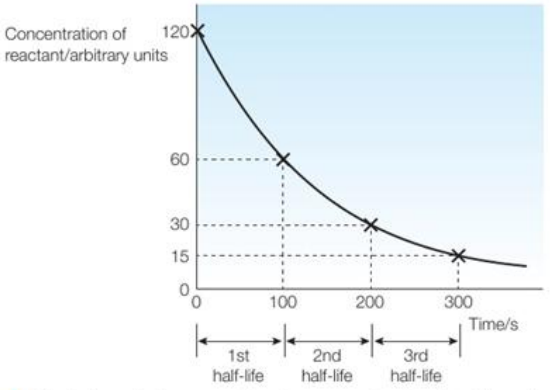


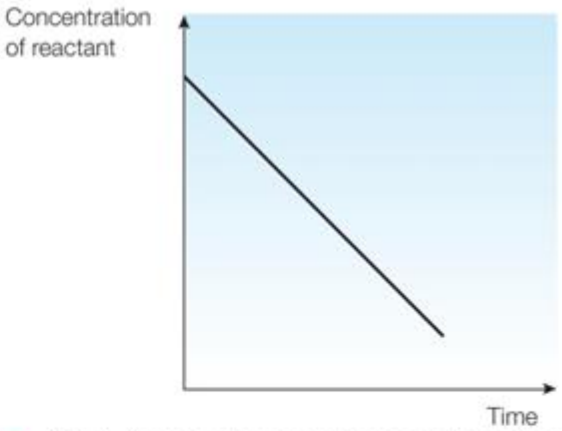
fig A A graph of concentration of reactant against time for a first order reaction.

The 2nd half-life, for the change in concentration from 60 to 30 units, is 100 s.
The 3rd half-life, for the change in concentration from 30 to 15 units, is 100 s.

Since all three half-lives are the same, the reaction is first order with respect to the concentration of the reactant plotted.

If the half-life doubles as the reaction proceeds, then the reaction is second order.

If the graph is a straight line with a negative gradient, then the rate of reaction is constant no matter what the concentration of the reactant (fig B). In other words, the reaction is zero order with respect to the reactant.



▲ **fig B** A graph of concentration against time for a zero order reaction.

A typical set of results is shown in **table A** for the reaction:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

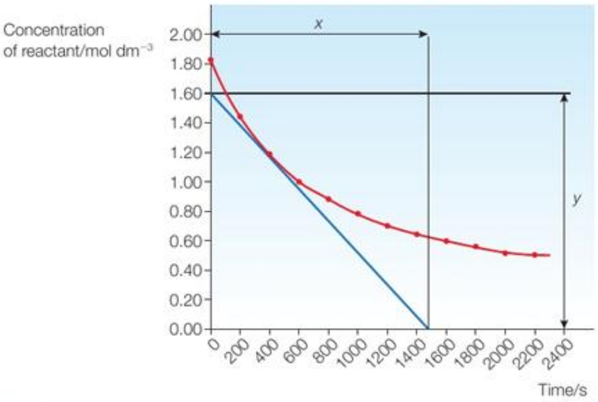
TIME/min	0	10	20	30	40	50	60	70	80	90
$[N_2O_5]/10^{-3}$ mol dm^{-3}	22.90	16.27	12.29	9.35	6.89	4.88	3.68	2.74	2.16	1.85

table A

If you plot a graph of $[N_2O_5]$ against time using the above data, you will find that the line is curved and the half-life is constant; as a result, the reaction is first order with respect to N_2O_5.

CALCULATING RATE FROM A CONCENTRATION-TIME GRAPH

The rate of reaction at any given time can be determined from a concentration-time or volume-time graph by drawing a tangent to the curve at the given time and calculating the gradient of the tangent. Fig C shows the change in concentration of a reactant with time.



▲ **fig C** Determining an instantaneous rate of reaction from a graph of concentration of reactant against time.

A tangent to the curve has been drawn at time = 400 s.

To find the rate at this time point, draw as large a triangle as possible and then measure x and y.

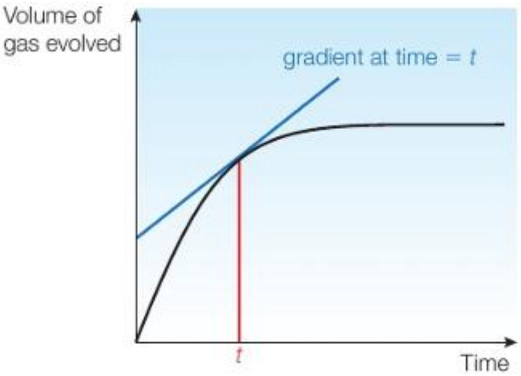
$x = 1470\,\text{s}$ and $y = -1.60\,\text{mol dm}^{-3}$.

$$\text{rate} = -\frac{\text{change in concentration of reactant}}{\text{time}}$$

$$= -\frac{-1.60\,\text{mol dm}^{-3}}{1470\,\text{s}} = 1.09 \times 10^{-3}\,\text{mol dm}^{-3}\,\text{s}^{-1}$$

CALCULATING RATE FROM A VOLUME-TIME GRAPH

The procedure is exactly the same for a volume-time graph for a gas evolved (Section 11A.1). This time the curve will slope upwards not downwards (fig D).



▲ **fig D** Determining an instantaneous rate of reaction from a graph of volume of gas evolved against time.

The rate of reaction obtained in this way is sometimes called the **instantaneous reaction rate**.

THE INITIAL-RATE METHOD FOR DETERMINING THE RATE EQUATION

In this method, several reaction mixtures are made up and the initial rate (i.e. the time taken for a fixed amount of reactant to be used up or for a fixed amount of product to be formed) is measured. From these times, it is then possible to calculate the mathematical relationship between the rate of the reaction and the concentration of the reactant.

A typical set of results is shown in table B for the reaction:

$$A + B \rightarrow C$$

EXPERIMENT	$[A]/\text{mol dm}^{-3}$	$[B]/\text{mol dm}^{-3}$	INITIAL RATE OF FORMATION OF $C/\text{mol dm}^{-3}\,\text{s}^{-1}$
1	0.1	0.1	0.02
2	0.1	0.2	0.04
3	0.2	0.1	0.04
4	0.2	0.2	0.08

table B

If we now look at experiments 1 and 3, we can see that [A] has doubled while [B] has remained constant. The rate of reaction has also doubled. This indicates that the reaction is first order with respect to A and, as a result, we can write:

$$\text{rate} \propto [A]$$

If we now look at experiments 1 and 2, or experiments 3 and 4, we can see that [B] has doubled while [A] has remained constant. The initial rate of reaction has also doubled. This indicates that the rate of reaction is directly proportional to [B]. That is, the reaction is first order with respect to B. As a result, we can write:

$$\text{rate} \propto [\text{B}]$$

The overall order of the reaction is two, and the complete rate law (rate equation) is:

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

DETERMINING ORDER FROM A RATE-CONCENTRATION GRAPH

The method for determining initial rates with changing concentrations produces approximate values, but this approximation is generally acceptable. In an initial rates experiment, the time measured is proportional to the reciprocal of the time, t, measured for a fixed amount of product or reactant.

That is:

$$\text{rate} \propto \frac{1}{t}$$

It might be possible to determine orders of reaction from just a few measurements. However, it is usual to record a range of results and plot a graph of 1/t against concentration of reactant.

The shape of the graph in table C indicates the order of reaction.

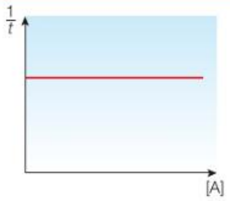
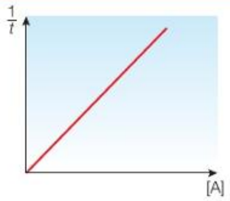
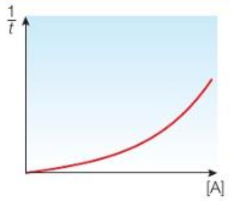
ZERO ORDER WITH RESPECT TO A $1/t\,(\propto \text{RATE}) = k[\text{A}]^0$	FIRST ORDER WITH RESPECT TO A $1/t\,(\propto \text{RATE}) = k[\text{A}]^1$	SECOND ORDER WITH RESPECT TO A $1/t\,(\propto \text{RATE}) = k[\text{A}]^2$
		

table C

EXAM HINT

Be careful to check the units on the axes of graphs. Graphs with the same shape will have different meanings if there are different units on the axes!

It is impossible to determine directly by sight from a rate–concentration graph that the reaction is second order. If the graph is a curve as shown, then it is necessary to then plot $\frac{1}{t}$ against $[\text{A}]^2$. If this produces a straight line passing through the origin, then the reaction is second order with respect to A.

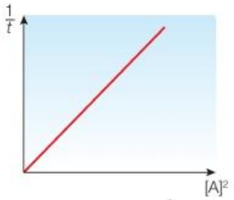


fig E A graph of $\frac{1}{t}$ against the square of the concentration of a reactant for a second order reaction.

SUBJECT VOCABULARY

half-life (of a reaction) the time taken for the concentration of the reactant to fall to one-half of its initial value

instantaneous reaction rate the gradient of a tangent drawn to the line of the graph of concentration against time. The instantaneous rate varies as the reaction proceeds (except for a zero order reaction)

11 A 4 Rate equations and mechanisms

REACTION MECHANISMS

You will remember from Book 1 that the basic view as to how a reaction takes place at a particulate level is that particles (atoms, molecules, ions or radicals) first have to collide in the correct orientation and with sufficient energy for products to be formed.

For the following reaction:
P+Q→ products

we expect the rate law to be:
rate = k[P][Q]

ELEMENTARY REACTIONS

A reaction taking place in this manner (a single collision between the two reactant particles) is described as being elementary.

If we know that a reaction is elementary, then we can deduce the rate law directly from the stoichiometric equation. For example, the following reaction is known to be elementary:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

so the rate equation is:

$$\text{rate} = k[NO][O_3]$$

The reaction takes place when a molecule of NO collides with a molecule of O3.
If the reaction is not elementary, it is not possible to deduce the rate equation by simply looking at the stoichiometric equation for the reaction.

A reaction that is not elementary takes place via a series of interconnected elementary reactions that are collectively called the mechanism for the reaction. You will have already come across a number of such mechanisms in your study of organic chemistry.

For example, the radical substitution reaction between methane and chlorine to form chloromethane (CH_3Cl) is thought to have the following mechanism:

Step 1: $Cl_2 \rightarrow 2Cl\bullet$

Step 2: $Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3$

Step 3: $Cl_2 + \bullet CH_3 \rightarrow Cl\bullet + CH_3Cl$

The overall stoichiometric equation for the reaction is:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

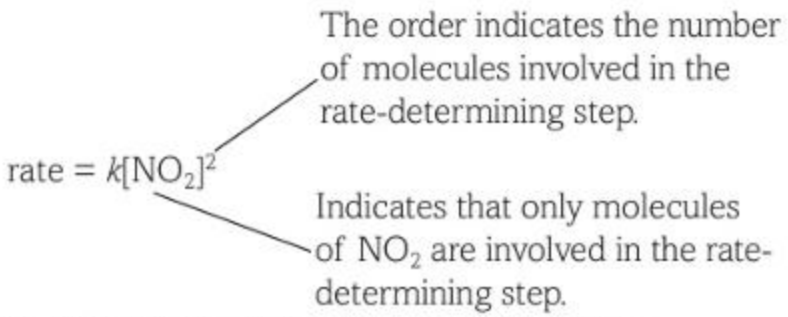
The species Cl• and •CH3 are called intermediates. They do not appear in the overall equation for the reaction, but are involved in reactions that ultimately result in the reactants being converted into the products.
If the experimentally determined rate equation does not match the overall stoichiometry, then it is almost certain that the reaction is not elementary.
For example, the rate equation for the following reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

is:

$$\text{rate} = k[NO_2]^2$$

This suggests that only molecules of NO_2 are involved in the rate-determining step, and that *two* molecules of NO_2 are involved in this step.



$\text{rate} = k[NO_2]^2$

The order indicates the number of molecules involved in the rate-determining step.

Indicates that only molecules of NO_2 are involved in the rate-determining step.

fig A Molecules involved in the rate-determining step.

Using our knowledge of molecules that do exist, two possible rate-determining steps are:

1 $NO_2 + NO_2 \rightarrow N_2O_4$, or

2 $NO_2 + NO_2 \rightarrow 2NO + O_2$

Both of these reactions are equally valid, and we have no way of knowing, without carrying out further investigations, which is the more likely to be taking place.

We also have no way of knowing what is involved in the remaining steps, but we do know that the sum of all the steps must add up to the overall stoichiometric equation.

Using the second of the two possible rate-determining steps, the following mechanism is consistent with the data:

$NO_2 + NO_2 \rightarrow 2NO + O_2$ SLOW

$CO + O_2 \rightarrow CO_2 + O$ FAST

$NO + O \rightarrow NO_2$ FAST

This shows how the particles in the proposed mechanism cancel to produce the overall equation:

$$\begin{array}{rcl} NO_2 + \cancel{NO_2} & \rightarrow & \cancel{NO} + NO + \cancel{O_2} \\ CO + \cancel{O_2} & \rightarrow & CO_2 + \cancel{O} \\ \cancel{NO} + \cancel{O} & \rightarrow & \cancel{NO_2} \\ \hline NO_2 + CO & \rightarrow & NO + CO_2 \\ \hline \end{array}$$

As it happens, further investigations into this reaction have identified the mechanism as:

$$NO_2 + NO_2 \rightarrow NO_3 + NO \quad \text{SLOW}$$
$$NO_3 + CO \rightarrow NO_2 + CO_2 \quad \text{FAST}$$

This is not what we would immediately suspect as the mechanism because the existence of NO3 is not something with which we would be familiar.

Even if the experimentally determined rate equation is simple, it does not necessarily follow that the reaction proceeds in a single elementary step. For example, the rate expression for the following gas-phase reaction:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

is:

$$\text{rate} = k[N_2O_5]$$

Yet, the reaction is thought to involve several steps and a number of intermediates.

ALKALINE HYDROLYSIS OF HALOGENOALKANES

The hydrolysis of halogenoalkanes by hydroxide ions is a reaction we introduced in Topic 10 (Book 1: IAS). The hydroxide ion acts as a nucleophile and replaces the halogen in the halogenoalkanes. The reaction, therefore, can also be described as nucleophilic substitution.

HYDROLYSIS OF A TERTIARY HALOGENOALKANE

The equation for the alkaline hydrolysis of 2-chloromethylpropane is:

$$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$$

The experimentally determined rate equation for this reaction is:

$$\text{rate} = k[(CH_3)_3CCl]$$

The reaction is first order with respect to 2-chloromethylpropane, but zero order with respect to the hydroxide ion.

The sensible conclusion to reach is that the 2-chloromethylpropane undergoes slow ionisation as the rate-determining step. This is then followed by a very fast step involving attack by the hydroxide ion on the carbocation formed in Step 1.

Step 1: $(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$ SLOW
Step 2: $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ FAST

This type of mechanism is named S_N1, i.e. *S*ubstitution *N*ucleophilic *uni*molecular.

The rate-determining step is said to be *uni*molecular because there is only *one* reactant particle present, $(CH_3)_3CCl$.

The carbocation, $(CH_3)_3C^+$, formed in Step 1 is an *intermediate* (see **Section 11A.6**).

HYDROLYSIS OF A PRIMARY HALOGENOALKANE

The equation for the alkaline hydrolysis of 1-chlorobutane is:

$$CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Cl^-$$

The experimentally determined rate equation for this reaction is:

$$\text{rate} = k[CH_3CH_2CH_2CH_2Cl][OH^-]$$

The accepted mechanism for the reaction is:

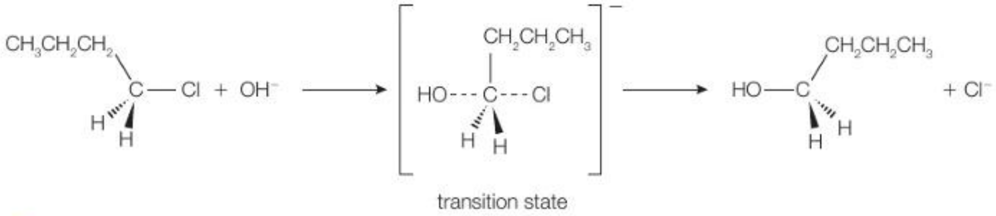


fig B S_N2 mechanism of the alkaline hydrolysis of 1-chlorobutane.

11A 5 Activation energy and catalysis

The activation energy, E_a

The activation energy, E_a is the minimum energy required for a reaction to occur, requiring particles to reach the transition state's energy level. Once there, they can react to form products and release energy.

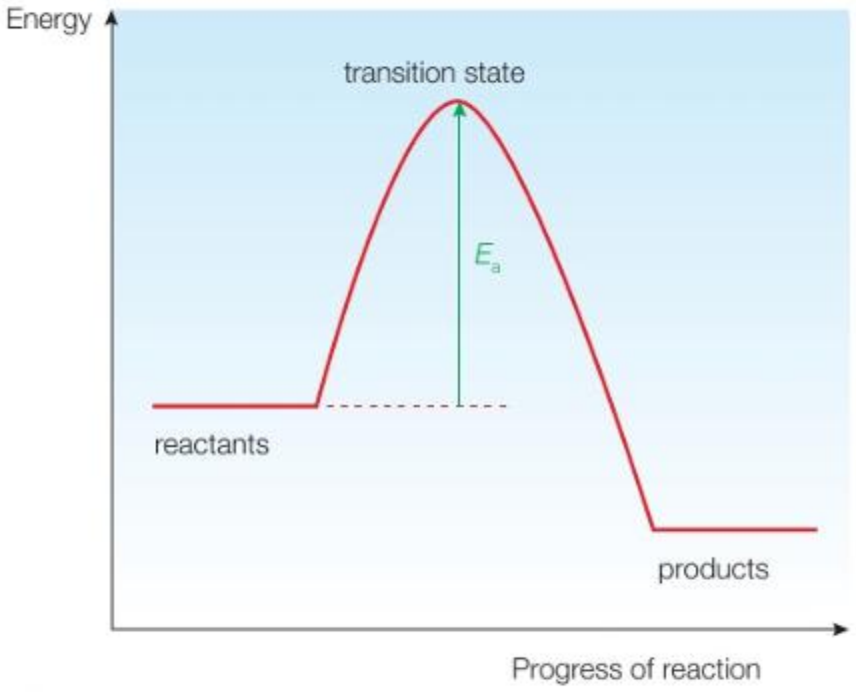


fig A A reaction profile for an elementary exothermic reaction.

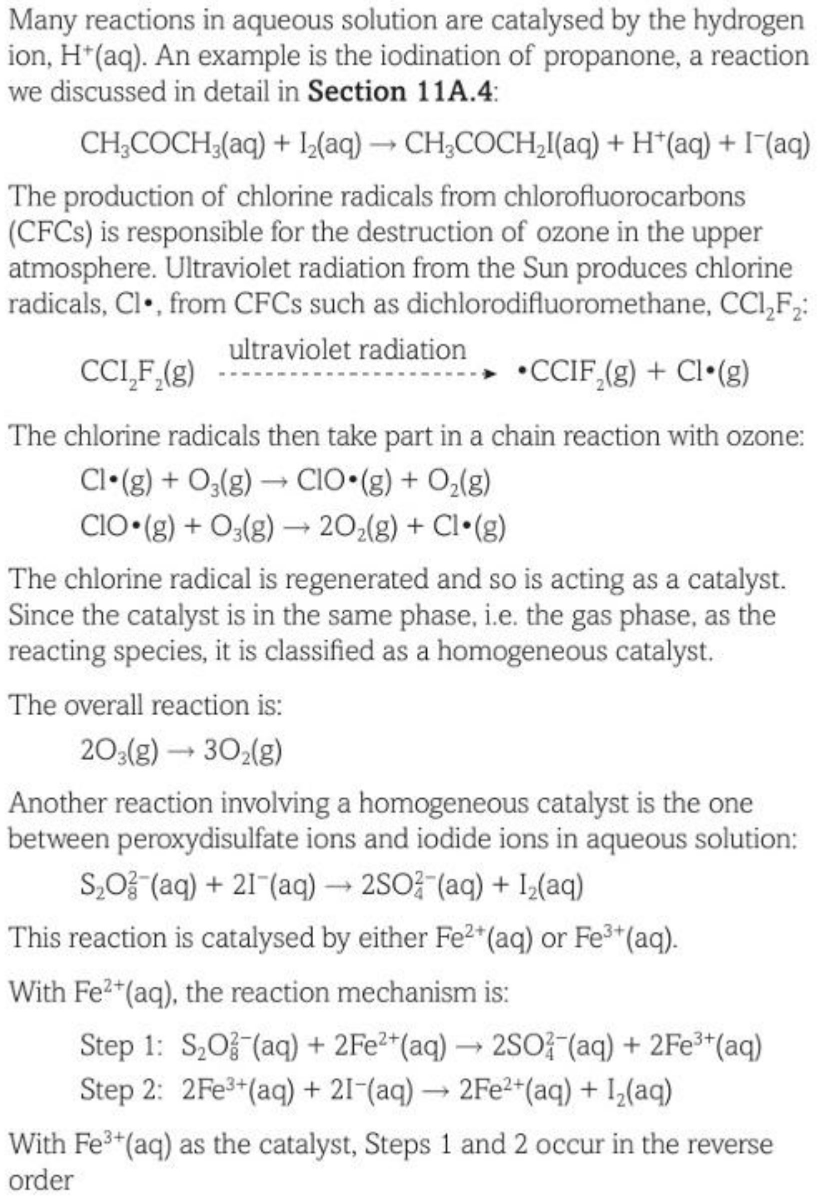
CATALYSTS

Catalysts can be divided into two groups:

- homogeneous catalysts
- heterogeneous catalysts.

HOMOGENEOUS CATALYSTS

A homogeneous catalyst is in the same phase (solid, liquid, solution or gas) as the reactants.



Many reactions in aqueous solution are catalysed by the hydrogen ion, $H^+(aq)$. An example is the iodination of propanone, a reaction we discussed in detail in **Section 11A.4**:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The production of chlorine radicals from chlorofluorocarbons (CFCs) is responsible for the destruction of ozone in the upper atmosphere. Ultraviolet radiation from the Sun produces chlorine radicals, Cl•, from CFCs such as dichlorodifluoromethane, CCl_2F_2:

$$CCl_2F_2(g) \xrightarrow{\text{ultraviolet radiation}} \bullet CClF_2(g) + Cl\bullet(g)$$

The chlorine radicals then take part in a chain reaction with ozone:

$$Cl\bullet(g) + O_3(g) \rightarrow ClO\bullet(g) + O_2(g)$$
$$ClO\bullet(g) + O_3(g) \rightarrow 2O_2(g) + Cl\bullet(g)$$

The chlorine radical is regenerated and so is acting as a catalyst. Since the catalyst is in the same phase, i.e. the gas phase, as the reacting species, it is classified as a homogeneous catalyst.

The overall reaction is:

$$2O_3(g) \rightarrow 3O_2(g)$$

Another reaction involving a homogeneous catalyst is the one between peroxydisulfate ions and iodide ions in aqueous solution:

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

This reaction is catalysed by either $Fe^{2+}(aq)$ or $Fe^{3+}(aq)$.

With $Fe^{2+}(aq)$, the reaction mechanism is:

Step 1: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

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

With $Fe^{3+}(aq)$ as the catalyst, Steps 1 and 2 occur in the reverse order

HETEROGENEOUS CATALYSTS

Heterogeneous catalysts, in different phases, are used in industry for Haber and Contact processes. Solid vanadium oxide is used in Contact, while solid iron is used in Haber for nitrogen gas-hydrogen gas reaction.

Iron acts as a catalyst by forming an interstitial hydride with hydrogen molecules, allowing hydrogen atoms to react with nitrogen molecules adsorbbed onto the metal surface.

1. Adsorption - the reactants are first adsorbed onto the surface of the catalyst.

2. Reaction - the reactant molecules are held in positions that enable them to react together.

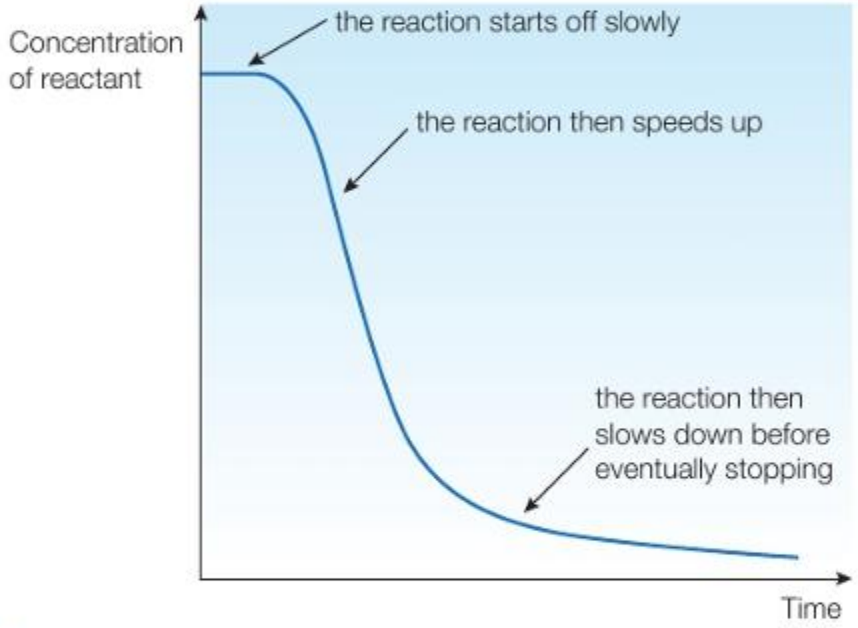
3. Desorption- the product molecules leave the surface.

OXIDATION OF ETHANEDIOIC ACID BY MANGANATE(VII) IONS

In autocatalysis, the reaction is catalysed by one of its products. One of the simplest examples of this is the oxidation of ethanedioic acid by acidified potassium manganate(VII). The equation for the reaction is:

$$5(COOH)_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

The reaction is very slow at room temperature, but is catalysed by manganese(II) ions, Mn2+. The Mn2+ ions are not present initially, so the reaction starts off extremely slowly at room temperature.



▲ **fig B** A graph of concentration against time for an autocatalysed reaction.

SUBJECT VOCABULARY

adsorption the adhesion of atoms, molecules or ions to the surface of a solid

autocatalysis when a reaction product acts as a catalyst for the reaction

RELATIONSHIP BETWEEN TEMPERATURE AND RATE OF REACTION

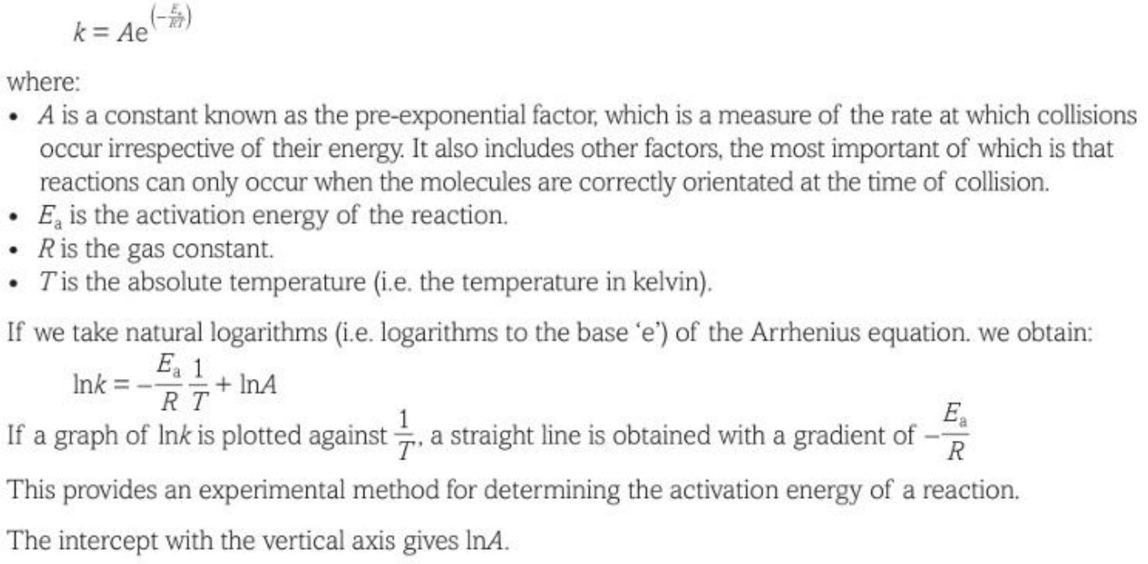
In Book 1 we discussed qualitatively why an increase in temperature increased the rate of a reaction. There are two reasons for this:

- an increase in the fraction of molecules with energy equal to or greater than the activation energy for the reaction
- an overall increase in the frequency of collisions between the reacting molecules.

The second effect is considerably less significant than the first and means that we can effectively ignore the overall increase in the frequency of collisions.

THE ARRHENIUS EQUATION

In 1889, Svante Arrhenius, a Swedish chemist, proposed a quantitative relationship between temperature and the rate constant, k, for a reaction. This is described by the Arrhenius equation and is usually expressed in the form:



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

where:

- A is a constant known as the pre-exponential factor, which is a measure of the rate at which collisions occur irrespective of their energy. It also includes other factors, the most important of which is that reactions can only occur when the molecules are correctly orientated at the time of collision.
- E_a is the activation energy of the reaction.
- R is the gas constant.
- T is the absolute temperature (i.e. the temperature in kelvin).

If we take natural logarithms (i.e. logarithms to the base 'e') of the Arrhenius equation. we obtain:

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

If a graph of $\ln k$ is plotted against $\frac{1}{T}$, a straight line is obtained with a gradient of $-\frac{E_a}{R}$

This provides an experimental method for determining the activation energy of a reaction.

The intercept with the vertical axis gives $\ln A$.