Techniques to measure rate of reaction

[4.3b]

The rate of chemical reactions – and the factors affecting the rate of chemical change – have been studied closely for many years. Why do chemists study reaction rates (kinetics)?

• The fact that reactions can occur at very different rates is intriguing and chemists want to understand what is going on.
• Chemists need to understand how to change the rate of a reaction. In industry, it is essential to understand rates of reaction to help work out the economics of a manufacturing process.
• Reaction rates can provide evidence of the mechanism of a chemical reaction – the individual steps by which a reaction takes place.

The ability to manipulate the rate of a chemical reaction is as vital in the school lab as it is in the chemical industry. As you saw in your AS level Chemistry book (pages 196–7), concentration, pressure, temperature, the surface area of the reacting substances and catalysts all affect the rate at which chemical reactions happen. Using the chemistry of fireworks as an example, it is important that a firework fuse burns for long enough to allow the person who lit the firework to get out of the way. However, it mustn’t burn too long or people are tempted to go back and make sure it hasn’t gone out. The Health and Safety Executive has fixed the minimum burn time at 5 seconds, and the maximum at 15 seconds. The ‘blue touch paper’ which acts as a fuse is paper impregnated with potassium nitrate – it will burn even in wet, windy conditions. The speed at which it burns is controlled by the potassium nitrate content of the paper – the higher the concentration, the faster it burns.

To understand and control the rate of chemical reactions, chemists need to be able to measure how fast reactions occur. You can calculate the rate of a reaction by measuring the change in concentration of one of the reactants or products and the time taken:

\[
\text{rate of reaction} = \frac{\text{change in concentration}}{\text{change in time}}
\]

or \[rate = \frac{\Delta c}{\Delta t}\]

A number of different methods can be used to collect the data we need to measure the rate of a reaction. They all investigate changes in concentration, either directly or indirectly. As you saw in your AS course, the techniques largely depend on measuring either how quickly the reactants are used up or how quickly the products are formed. You will be considering and using many of these methods.
Measuring the volume of a gas produced

In a reaction in which a gas is given off, the progress of the reaction can be measured by monitoring the rate at which the gaseous product is given off. The technique you use will depend on the level of accuracy demanded – the simplest is simply to count the number of bubbles produced in a certain time.

For more accurate results you can measure the volume of gas given off at regular time intervals, collecting the gas in a measuring cylinder by water displacement – particularly useful for larger volumes of gas – or in a gas syringe (fig. 1.1.2). You plot a graph of the total volume of gas produced against time to show how the rate of reaction changes. By changing the reaction conditions – for example the concentrations of the reactants or the temperature – you can investigate how these factors affect reaction rates.

Measuring the change in mass of a reaction mixture

This technique also depends on having gaseous substances as products of the reaction. You measure the decrease in mass of the total reacting mixture as the reaction proceeds (fig. 1.1.3). It is relatively easy to carry out in the laboratory, needing only a sensitive balance, but there are many opportunities for experimental error to creep in unless great care is taken to avoid splashes etc.

Monitoring a colour change (colorimetry)

The techniques involved in using colour changes to measure reaction rate range from simple observation to the use of a colorimeter (fig. 1.1.4). The appearance of a coloured product, or the loss of a coloured reactant, is used. By changing the reaction conditions and measuring the effect on the appearance or loss of colour, the impact of the change on the rate of the reaction can be measured. The iodine clock, an experimental technique you will look at later, is an example where you use your eyes – iodine is formed in a reaction and this reacts with starch indicator to form a noticeable blue-black colour.

In a similar investigation, the reaction of potassium iodide with potassium peroxodisulfate is carried out in a colorimeter. As the oxidation takes place and iodine is produced, the brown colour of the iodine is monitored extremely precisely in the colorimeter. The change detected by the colorimeter is far more subtle than the human eye could observe.
Titrimetric analysis

This involves removing small portions (aliquots) of the reacting mixture at regular intervals. These aliquots are usually added to another reagent, which immediately stops or quenches the reaction.

Alternatively, the reaction is slowed by immersing the portion in an ice bath, so that there are no further changes to the concentrations in the reacting mixture until further analysis can be carried out. The quenched aliquots are then titrated to find the concentrations of known compounds in them.

In a reaction in which acid is being used up, titration could be carried out with a standard solution of sodium hydroxide. A similar technique of titrimetric analysis is useful for investigating the reaction between iodine and propanone (fig. 1.1.5), which is catalysed by acid. The samples are run into excess sodium hydrogen carbonate to stop the reaction. By titrating with sodium thiosulfate you can measure the concentration of iodine in the reacting mixture (see page 14):

\[
\text{CH}_3\text{COCH}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_2\text{I}(\text{aq}) + \text{H}^+(\text{aq}) + \text{I}^- (\text{aq})
\]

\[
2\text{Na}_2\text{S}_2\text{O}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{Na}_2\text{S}_4\text{O}_6(\text{aq}) + 2\text{NaI}(\text{aq})
\]

Conductimetric analysis

The number and type of ions in a solution affect its electrical conductivity. As some chemical reactions take place in solution, the ionic balance changes and the resulting change in conductivity can be used to measure the rate of the reaction (fig. 1.1.6). These reflect the changes in the ions present in the solution and so can be used to measure the changes in concentration of the various components of the mixture. For example, when bromoethane reacts with hydroxide ions in alkaline solution, the small, mobile hydroxide ions in the starting solution are replaced by larger, slower moving bromide ions as the reaction progresses. This is reflected in a change in the conductivity of the solution as the ionic concentrations change – which in turn gives us a measure of the rate at which the reaction is taking place.
HSW  Reaction rates and brewing beer

Understanding reaction rates and how to change them is very important in the brewing industry. There are many different types of beers, from fruit beers to dark stouts, light lagers and heavy ales. One important factor affecting their alcohol content and taste is the rate at which the fermentation takes place. Fermentation – the conversion of sugar into ethanol – is the key reaction in making beer. It is brought about by the zymase enzyme found in yeast; controlling the rate of this reaction is crucial to the beer-making process. Brewers want fermentation to be as economical as possible while producing a good, drinkable beer. Within limits, increasing the temperature of the fermenting mixture would speed up the process so the beer could be made and sent for sale more quickly – but it isn’t that easy!

Scientists have identified two main factors affecting the fermentation reaction in a commercial vat. The start temperature – the temperature of the reaction mixture (or wort) when the yeast (catalyst) is added – is very important. Too low and the fermentation rate will be too slow; too high and the yeast will be ‘shocked’, producing beer with poor flavour.

The maximum temperature of the process is also crucial to the taste and flavour of the beer. Too low and not enough fermentation takes place – the beer tastes sweet with low alcohol levels because lots of sugar is left. Too high and too much fermentation occurs – the beer tastes ‘thin’ with high alcohol levels. And if it is really hot then the yeast is ‘killed’ and fermentation halts completely. Most fermentations are carried out at 14–22 °C, depending on the type of beer wanted. The alcohol concentration in the beer is also very important – if excessive the yeast will be inhibited and fermentation will stop. By using different strains of yeast, brewers can vary the alcohol levels of the beers they produce.

Scientists have developed several different ways of monitoring the rate of a fermentation in commercial breweries. The temperature is monitored constantly, the rate of carbon dioxide production is measured using chemical sensors, the amount of yeast in the brew can be measured by its turbidity (cloudiness) using a colorimeter and the pH, oxygen levels and more can all be recorded to make sure that the rate of the reaction is always as close as possible to ideal.

**Questions**

1. How would you change the conditions to control the following reaction rates:
   a. slow down the souring of milk
   b. speed up the fermentation of sugar to carbon dioxide and ethanol
   c. slow down the reaction of iron with air and water
   d. slow down the rate of carbon dioxide formation in the reaction between calcium carbonate and hydrochloric acid?

2. Suggest suitable experimental techniques to obtain rate data for the following reactions and explain your choices:
   a. magnesium with dilute hydrochloric acid
   b. ethyl ethanoate with sodium hydroxide: 
      \[ \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{NaOH}(aq) \rightarrow \text{CH}_3\text{COONa}(aq) + \text{C}_2\text{H}_5\text{OH}(aq) + \text{H}_2\text{O}(l) \]
   c. copper(II) ions with ammonia molecules:
      \[ \text{Cu}^{2+}(aq) + 4\text{NH}_3(aq) \rightarrow \text{Cu(NH}_3)_4^{2+}(aq) \]

3. Why would the method involving measuring the mass of the reaction vessel not work well in the reaction of magnesium and dilute hydrochloric acid? Think about the density of hydrogen.

4. a. Which method in fig. 1.1.2 do you think is likely to give the more accurate results?
   b. If the gas produced were soluble, which method would be better and why?
Rate equations, rate constants and the order of a reaction [4.3a]

When measuring the rate of reaction, a chemist will investigate the increase in the concentration of one of the products or a decrease in the concentration of one of the reactants.

So in the reaction

\[ A + B \rightarrow C + D \]

the results might show that the rate is related to the concentrations of \( A \) and \( B \) as follows:

\[ \text{rate} = k[A]^m[B]^n \]

This is known as a rate equation. \([A]\) and \([B]\) represent the concentrations of \( A \) and \( B \) in mol dm\(^{-3}\), and \( k \) is called the rate constant.

The indices \( m \) and \( n \) are usually whole numbers \((1, 2 \ldots)\) but they can be fractional or zero. The index \( m \) is called the order of reaction with respect to \( A \).

The overall order of a reaction is the sum of the indices \((m + n)\).

Many reactions involve several steps. The slowest step controls the overall rate of a reaction and this is called the rate-determining step. A useful way of visualising the idea of a rate-determining step is to imagine that a teacher has prepared some pages of notes and wants to collect them into sets with the help of three students. The pages of the notes are arranged in 10 piles. The first student collects a page from each of the piles (step 1). The second takes this set of 10 pages from the first and tidies them ready for stapling (step 2). The third student staples this sets of notes together (step 3). It is not hard to see that the overall rate of the process (the rate at which the sets of notes are prepared) depends on step 1, the collecting of the sheets of notes, because this is the slowest step. It does not matter, within reason, how quickly the tidying or the stapling is done.

The overall order of the reaction is related to the molecularity of the rate-determining step – that is the number of particles involved. In a reaction between \( A \) and \( B \), if the rate-determining step involves the collision of one particle of \( A \) with one particle of \( B \), the molecularity is 2.

Clock reactions

By far the best way to study the effect of changing the concentration of the reactants on the reaction rate is to carry out some experiments. A reaction that is easy to follow experimentally is the reaction between iodide ions and hydrogen peroxide in the presence of an acid, starch and sodium thiosulfate – often referred to as an iodine ‘clock’ reaction.

Iodine clock reaction

This is an experiment first devised by Hans Heinrich Landolt in 1886. Two colourless solutions are mixed and at first there is no visible reaction, but after a short time delay the liquid suddenly turns dark blue (sometimes described as blue-black) (fig. 1.1.7).

The time, \( t \), is measured from mixing until the first formation of the blue colour. The rate of reaction is proportional to \( \frac{1}{t} \).

![fig. 1.1.7 An iodine clock reaction.](image)
One of the reactants is a solution of potassium iodide. This is acidified with dilute sulfuric acid and small quantities of starch and sodium thiosulfate are added. The final reactant is a solution of hydrogen peroxide. Hydrogen peroxide reacts with acidified potassium iodide to produce iodine:

\[ \text{Step 1} \]
\[ \text{H}_2\text{O}_2(\text{aq}) + 2\text{I}^- (\text{aq}) + 2\text{H}^+ (\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq}) \]

As soon as any iodine is produced, it reacts with sodium thiosulfate, forming iodide ions again:

\[ \text{Step 2} \]
\[ \text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{I}^- (\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq}) \]

When all the sodium thiosulfate is used up, a blue colour is suddenly formed because the iodine forms a complex with the starch that has been added.

In this reaction, step 2 has no effect on the overall rate – it is much faster than step 1. Step 1 is the rate-determining step.

By repeating the experiment using several different concentrations of hydrogen peroxide, the effect on the rate of changing the concentration of hydrogen peroxide can be investigated. The rate equation can be represented as:

\[ \text{rate} = k[\text{H}_2\text{O}_2]^{x}[\text{I}^-]^{y}[\text{H}^+]^{z} \]

The order with respect to one reactant (for example \( \text{H}_2\text{O}_2 \)) can be determined by using a large excess of the other reactants (\( \text{I}^- \) and \( \text{H}^+ \)) so that their concentrations remain effectively constant throughout the reaction.

Under these conditions the rate of reaction can be expressed as:

\[ \text{rate} = k'[\text{H}_2\text{O}_2]^{x} \]

where \( k' \) is a modified rate constant that includes the constant concentration of the other reactants.

The units of a rate constant depend on the form of its rate equation. For example, if rate = \( k[A] \) then the units of the rate constant are \( \text{s}^{-1} \) because:

\[ k = \frac{\text{rate}}{[A]} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1} \]

**Worked examples**

1. The reaction of peroxodisulfate ions and iodide ions can be represented as:
   \[ \text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^- (\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \]
   The rate equation determined by experiment is:
   \[ \text{rate} = k[S_2O_8^{2-}][I^-] \]
   The values of the order indices are both 1 in this reaction – so the order of reaction with respect to peroxodisulfate ions is 1, and with respect to iodide ions is also 1. The overall order of the reaction is 2. You can see the order is not related to the equation.

2. The reaction of hydrogen and bromine can be represented by:
   \[ \text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g}) \]
   The rate equation determined by experiment is:
   \[ \text{rate} = k[H_2][Br_2]^{0.5} \]
   The order with respect to hydrogen is 1, and with respect to bromine is 0.5 (or \( \frac{1}{2} \)). The overall order of reaction is \( 1\frac{1}{2} \). Notice that the order of reaction can be a whole number or a fraction – whatever fits the mathematical relationship.

**Questions**

1. Why is it important in the iodine clock reaction that there is only a small quantity of sodium thiosulfate?
2. The reaction between \( \text{NO}(\text{g}) \) and \( \text{Cl}_2(\text{g}) \) has been studied at 50 °C.
   \[ \text{NO}(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NOCl}(\text{g}) \]
   The table shows the initial concentrations of reactants and the initial rate of formation of \( \text{NOCl}(\text{g}) \).

| [\text{NO}(\text{g})]/\text{mol dm}^{-3} | [\text{Cl}_2(\text{g})]/\text{mol dm}^{-3} | \text{Initial rate}/\text{mol dm}^{-3}\text{s}^{-1} | \hline
| 0.250 | 0.250 | 1.43 \times 10^{-6} | \hline
| 0.250 | 0.500 | 2.86 \times 10^{-6} | \hline
| 0.500 | 0.500 | 11.44 \times 10^{-6} | \hline

a What is the order of reaction with respect to \( \text{Cl}_2(\text{g}) \)?
b What is the order of reaction with respect to \( \text{NO}(\text{g}) \)?
c What is the overall order of reaction?
d Write the rate equation for this reaction.
e Calculate the value of the rate constant \( k \). Give its units.
Determining the order of a reaction and the rate equation from experimental data [4.3f (ii), (iii)]

We have seen that rate constants appear in rate equations, and that the units of rate constants can vary. In this section we are going to find out how to calculate a rate of reaction graphically by drawing tangents to the curve of its reaction rate graph. Then we can use the data to calculate the order of the reaction and the rate constant.

It is not possible to predict the order of reaction from a balanced equation. It has to be found out by experiment.

**Interpreting experimental data**

Once the changes in concentration have been measured in an experiment, the reaction rate can be obtained by plotting concentration against time. **Figure 1.1.8** shows a graph of the concentration of A against time for a slow reaction, $\text{A(aq) + B(aq) \rightarrow C(aq) + D(aq)}$.

You will notice that the graph is steepest at the start of the reaction, and it gradually gets less steep as the reaction progresses. If such a graph becomes horizontal then the reaction has finished. The rate of reaction decreases with time because the number of particles of A and B decrease and so there are fewer collisions.

To find the rate of reaction at a particular time, a tangent has to be drawn to the curve at that time and its gradient calculated, as shown in **fig. 1.1.9**.

To draw a tangent, hold a ruler to the curve so that it just touches the curve at the time required. Draw a long straight line – a large triangle is required to get accurate results. In the example in **fig. 1.1.9**, the rate at 400 minutes is $-1.09 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$:

$$\text{Gradient} = \frac{y}{x} = \frac{-1.60 \text{ mol dm}^{-3}}{1470 \text{ min}} = -1.09 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$$

The value of the rate of reaction is negative and this indicates that the concentration of A is decreasing as time goes on.
Worked example

The equation for the decomposition of sulfur dichloride oxide, \( \text{SO}_2\text{Cl}_2 \), is:

\[
\text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_2(g) + \text{Cl}_2(g)
\]

The rate of this reaction can be followed by monitoring the pressure of the gases in the reaction vessel. This will increase because the number of moles of gas doubles on going from left to right.

The pressure results were used to calculate the concentration of sulfur dichloride oxide at certain times – the results are summarised in table 1.1.1. Figure 1.1.10 shows the graph of concentration against time.

The graph shows how \([\text{SO}_2\text{Cl}_2(g)]\) falls during the reaction. We can therefore write an expression for the rate of this reaction with respect to \([\text{SO}_2\text{Cl}_2]\):

\[
\text{rate} = -\frac{\Delta [\text{SO}_2\text{Cl}_2]}{\Delta t}
\]

The negative sign in this expression is necessary because \([\text{SO}_2\text{Cl}_2] \) decreases with time, so the change in \([\text{SO}_2\text{Cl}_2] \) divided by the change in time is negative. By definition, a rate of reaction is positive and the negative sign ensures that this is so. Now look at the graph in fig. 1.1.11 and table 1.1.2. The values in the right-hand column were calculated by drawing tangents to the curve at each point and calculating the gradient.

### Data for fig. 1.1.10.

<table>
<thead>
<tr>
<th>Time/s</th>
<th>Concentration of ( \text{SO}_2\text{Cl}_2 )/mol dm(^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2000</td>
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<tr>
<td>3000</td>
<td>0.20</td>
</tr>
<tr>
<td>4000</td>
<td>0.15</td>
</tr>
</tbody>
</table>

### Data for fig. 1.1.11.

<table>
<thead>
<tr>
<th>Concentration of ( \text{SO}_2\text{Cl}_2 )/mol dm(^{-3} )</th>
<th>(-\frac{\Delta [\text{SO}_2\text{Cl}_2]}{\Delta t})/mol dm(^{-3} ) s(^{-1} )</th>
</tr>
</thead>
<tbody>
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<td>0.45</td>
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<td>0.23</td>
<td>6.90 \times 10^{-5}</td>
</tr>
<tr>
<td>0.18</td>
<td>5.40 \times 10^{-5}</td>
</tr>
</tbody>
</table>
UNIT 4 General principles of chemistry I – Rates, equilibria and further organic chemistry

The graph of $\frac{-\Delta [SO_2Cl_2]}{\Delta t}$ against time in Fig. 1.1.11 on the previous page is a straight line. Since reaction rate is plotted on the y-axis of the graph and [SO$_2$Cl$_2$(g)] is plotted on the x-axis, it follows that

rate = $k[SO_2Cl_2(g)]$

Graphs are extremely useful for finding and confirming relationships between different variables – for example, the variation of the volume of a gas with its temperature. The simplest type of relationship is one which is linear, in which a graph of one variable against another is a straight line.

The graph in Fig. 1.1.11 is an example of a linear graph. The reaction rate is plotted on the vertical axis (referred to as the $y$-axis or the ordinate) and the concentration of SO$_2$Cl$_2$(g) is plotted on the horizontal axis (referred to as the $x$-axis or the abscissa).

The general form of the equation for a straight line is:

$y = mx + c$

where $m$ is the slope or gradient of the line and $c$ is the intercept on the $y$-axis (where the line crosses the $y$-axis).

In this case $c = 0$, so the equation has the form:

$y = mx$

Rate expressions

The rate of dissociation of SO$_2$Cl$_2$ follows a law which can be written as:

rate = $k[SO_2Cl_2(g)]^1$

or

rate = $k[SO_2Cl_2(g)]$

The reaction is said to be first order with respect to SO$_2$Cl$_2$ because the concentration of SO$_2$Cl$_2$ appears in the rate expression raised to the power of 1.

We can calculate the rate constant for the reaction from gradient of the graph in Fig. 1.1.11.

The coordinates for points A and B are (0.26 mol dm$^{-3}$, 7.8 $\times$ 10$^{-5}$ mol dm$^{-3}$ s$^{-1}$) and (0.35 mol dm$^{-3}$, 1.05 $\times$ 10$^{-4}$ mol dm$^{-3}$ s$^{-1}$) respectively, so

$k = \frac{1.05 \times 10^{-4} \text{mol dm}^{-3} \text{s}^{-1} - 7.8 \times 10^{-5} \text{mol dm}^{-3} \text{s}^{-1}}{0.35 \text{mol dm}^{-3} - 0.26 \text{mol dm}^{-3}}$

$= 3.0 \times 10^{-4} \text{s}^{-1}$

Remember that the rate constant for a reaction varies with temperature, so the value of $k$ calculated from a particular investigation applies only to the temperature at which the investigation was carried out.

For reactions with more than two reactants, the rate expression can be extended. For example, the reaction:

$2\text{HCrO}_4^-(aq) + 3\text{HSO}_3^-(aq) + 5\text{H}^+(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 3\text{SO}_4^{2-}(aq) + 5\text{H}_2\text{O}(l)$

has the rate expression:

rate = $k[\text{HCrO}_4^-](\text{aq})][\text{HSO}_3^-](\text{aq})^2[\text{H}^+(\text{aq})]$

Notice that this reaction is fourth order overall – first order with respect to HCrO$_4^-$ and to H$, and second order with respect to HSO$_3^-$. 

AS a general rule, it is not possible to obtain the rate expression for a reaction from its balanced equation. This is because a great many reactions happen in several steps – for example, the decomposition of ozone (O$_3$) to oxygen (O$_2$) occurs in two steps – the first of which is rapid, the second of which is much slower:

O$_3$ $\rightleftharpoons$ O$_2$ + O

O + O$_3$ $\rightleftharpoons$ 2O$_2$

The second step is slow, and therefore determines the rate of the reaction – it is the rate-determining step. We can now write a rate expression for this reaction, since the rate of formation of O$_2$ will depend on [O] and [O$_3$]:

rate = $k[O][O_3]$

From this we can deduce that the rate of decomposition of ozone in the upper atmosphere increases as the concentration of ozone increases. Since ozone is used up in the second step, this is a means of ensuring that the level of ozone does not become too high.
In the SO₂Cl₂ example opposite, we saw that a straight line graph of rate against concentration shows that the reaction is first order with respect to one reactant. If a reaction is not first order then the graph will be a curve.

To find out if it is second order, you have to plot a graph of rate of reaction against (concentration)². If this is a straight line the reaction is second order with respect to that reactant. Obviously this is a very long method involving the use of trial and error to find the order of reaction. Figure 1.1.12 shows the typical shapes of concentration against time curves for zero order, first order and second order reactions. It also shows the typical shapes of rate against concentration for these examples.

When plotting a graph of rate against concentration (e.g. fig. 1.1.11), you have to measure the gradient of a curve at a number of different points. Why would only two points lead to uncertainty?

In the gas phase, molecule A decomposes to molecules B and C at high temperatures. A chemist suspects that this reaction is first order with respect to A. In an experiment to explore the kinetics of the reaction, the data in the table were obtained for the decomposition at 800 K.

<table>
<thead>
<tr>
<th>Time/s</th>
<th>Partial pressure of A/kPa (see page 55)</th>
</tr>
</thead>
<tbody>
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<td>1300</td>
</tr>
<tr>
<td>20</td>
<td>1051</td>
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<td>191</td>
</tr>
<tr>
<td>200</td>
<td>154</td>
</tr>
</tbody>
</table>

**Questions**

1. When plotting a graph of rate against concentration (e.g. fig. 1.1.11), you have to measure the gradient of a curve at a number of different points. Why would only two points lead to uncertainty?

2. In the gas phase, molecule A decomposes to molecules B and C at high temperatures. A chemist suspects that this reaction is first order with respect to A. In an experiment to explore the kinetics of the reaction, the data in the table were obtained for the decomposition at 800 K.

   **a** If the reaction is first order with respect to A, write down the rate equation.
   **b** By using a graph, find out if this reaction really is first order with respect to A.
   **c** Calculate the rate constant for the reaction. What are its units?
   **d** What does the rate equation tell you about its mechanism?
Why do the orders of reactions and rate equations matter so much? When chemical engineers design new reactors or chemical plants, they need to know exactly how the rate of the reaction varies with the concentrations of the reactants. This not only informs them about the ideal starting concentrations for the reactants, but also helps them to plan the best possible places to collect the products or to restock the reaction vessels with one or more of the reactants. This is just one reason why it is so important to be able to represent kinetic measurements as accurately as possible.

Order of reaction from initial rate of reaction

A series of experiments is carried out using different initial concentrations of the reagent under consideration, with every other factor, such as concentration and the temperature, unchanged. It is important that only one variable is changed.

For each experiment and product, a concentration against time graph is plotted (fig. 1.1.14). A tangent is drawn to the curve at \( t = 0 \) and, using a large triangle for maximum accuracy, the gradient is calculated. This is the initial rate of the reaction.

When sufficient initial rate values have been obtained, a graph of initial rate against concentration is drawn (fig. 1.1.15).

Bromate(V) and bromide reaction

The following reaction was studied:

\[
\text{BrO}_3^-(aq) + 5\text{Br}^- (aq) + 6\text{H}^+ (aq) \rightarrow 3\text{Br}_2 (aq) + 3\text{H}_2\text{O}(l)
\]

Three series of experiments were carried out. The results are shown in tables 1.1.3–1.1.5.
From these data, it is clear that rate $\propto [\text{BrO}_3^-\text{(aq)}]$ because doubling the concentration of $[\text{BrO}_3^-]$ doubles the rate. So the reaction is first order with respect to bromate(V) ions.

From these data it can be concluded that rate $\propto [\text{Br}^-\text{(aq)}]$. So the reaction is first order with respect to bromide ions.

From these data it can be concluded that rate $\propto [\text{H}^+\text{(aq)}]^2$ because doubling the concentration of $\text{H}^+(\text{aq})$ quadruples the rate of reaction. So the reaction is second order with respect to hydrogen ions.

The rate equation for this reaction is therefore:

$$\text{rate} = k[\text{BrO}_3^-\text{(aq)}][\text{Br}^-\text{(aq)}][\text{H}^+\text{(aq)}]^2$$

**Half-life**

A convenient way to measure the rate of a reaction, particularly of first order reactions, is to use the half-life of the reaction. This is the time taken for half of a reactant to be used up during a reaction process.
Half-life of a first order reaction

On page 17 the decomposition of sulfur dichloride oxide was investigated:

\[ \text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g}) \]

Figure 1.1.16 shows a graph of concentration of \( \text{SO}_2\text{Cl}_2(\text{g}) \) against time.

[Graph showing concentration of \( \text{SO}_2\text{Cl}_2(\text{g}) \) against time with time in s on the x-axis and concentration in mol dm\(^{-3}\) on the y-axis, with half-lives marked at various concentrations.]

This graph shows that the reaction has a constant half-life – that is, the time taken for the concentration of \( \text{SO}_2\text{Cl}_2 \) to halve is always constant (at a given temperature). All first order reactions behave like this.

Look at fig. 1.1.16 carefully. The time it takes the concentration of \( \text{SO}_2\text{Cl}_2 \) to halve is marked on it. Notice that this time is constant – in other words, it takes the same time for the concentration to fall from 0.50 mol dm\(^{-3}\) to 0.25 mol dm\(^{-3}\) as it takes for it to fall from 0.25 mol dm\(^{-3}\) to 0.125 mol dm\(^{-3}\). The time taken for the concentration to halve is known as the half-life \( (t_\text{½}) \) of the reaction. It is the length of time for half of a given reactant to disappear. If the half-life is short, the reaction is rapid; if the half-life is long, the reaction is slow. The half-life is independent of concentration.

All first order reactions have constant half-lives at a given temperature. You have met the idea of half-life before, in connection with radioactive decay during your AS Chemistry course – radioactive decay is another example of a first order reaction.

Half-life and radioactive decay

Radioactive decay is an example of a first order reaction because its rate is independent of the concentration of the radioactive material. Half-lives vary from a tiny fraction of a second (the decay of polonium-212 has \( t_\text{½} = 3 \times 10^{-7} \) s) to millions of years (the decay of uranium-238 has \( t_\text{½} = 4.5 \times 10^9 \) years).

Many radioactive elements have very long half-lives and scientists use these to help to work out the age of rocks in the Earth’s crust. For example, some rocks would have originally contained \( \frac{^{238}\text{U}}{^{82}\text{Pb}} \) but none of the decay product, \( \frac{^{206}\text{Pb}}{^{82}\text{Pb}} \). As time passed and the uranium decayed, the levels of lead began to build up. By analysing the present-day ratio of \( \frac{^{238}\text{U}}{^{82}\text{Pb}} \) to \( \frac{^{206}\text{Pb}}{^{82}\text{Pb}} \), scientists can estimate the approximate age of the rocks. Current estimates for the age of the Earth based on this method put it at around 4000 million years old.

For working out the age of material that was once living or – in the case of some trees – is still living, scientists use radiocarbon dating. This relies on the half-life of the radioactive isotope carbon-14, which is around 5730 years. This method can produce some very accurate dates, especially when linked to mass spectrometry. However, there are issues with really old material – the technique seems to be effective only over a limited timespan.

Write a short piece of prose to explain, in simple language, the science behind carbon-dating based on counting data, its limitations and why modern methods based on mass spectroscopic measurement of carbon isotope ratios are now used.

Half-life in second order reactions

The half-life of a first order reaction is independent of the initial concentration of the reactants. However, the half-life of a second order reaction does depend on the initial concentrations of the reactants.

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In fig. 1.1.17, the initial HI concentration is 0.10 mol dm\(^{-3}\) and it takes 125 seconds for the concentration to drop to 0.05 mol dm\(^{-3}\) – in other words, the half-life for this first part is 125 seconds. But if you think of 0.05 mol dm\(^{-3}\) as the new ‘initial concentration’, you will see that it takes 250 seconds to fall to 0.025 mol dm\(^{-3}\). So in second order reactions, halving the initial concentration doubles the half-life. In other words, in second order reactions the half-life is inversely proportional to the initial concentration of the reactants. It is related to the rate constant by the following equation:

\[
\frac{1}{t_{1/2}} = \frac{k}{[\text{reactant}]_{\text{initial}}}
\]

**Graphs of concentration against time and rate against concentration**

When you carry out kinetics experiments, characteristic graph shapes are obtained. These shapes are determined by the order of the reaction (see fig. 1.1.12). It is useful to be able to recognise them.

**Figure 1.1.18** shows concentration against time graphs for zero, first and second order reactions.

**Questions**

1. The equation for the reaction of bromine and methanoic acid is:

\[
\text{Br}_2(\text{aq}) + \text{HCOOH}(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{CO}_2(\text{g})
\]

   a  Suggest a way of keeping the concentration of methanoic acid virtually constant.

   b  The results of an experiment in which the concentration of bromine was monitored throughout a reaction are shown in the table. Plot a graph of [Br\(_2\)(aq)] against time. Show that this reaction is first order by working out three values for half-life.

   2. The half-life of radioactive iodine-131 is 8.0 days. What fraction of the initial amount of iodine-131 would be present in a patient after 24 days, if none were eliminated through natural body processes?
You will know from Edexcel AS Chemistry chapter 2.6 that substances have to have sufficient energy before they can start reacting – this is called the **activation energy**, $E_A$.

Many reactions appear not to take place at room temperature – the particles involved don’t have sufficient energy when they collide to overcome the activation energy barrier. Raising the temperature can help the molecules to achieve sufficient energy – much depends on the height of the barrier.

**Figure 1.1.20** shows the reaction profile for an exothermic reaction. The higher the activation energy barrier, the slower the reaction is likely to be.

The effect of using a catalyst is shown in **fig. 1.1.21**. Here the reaction profile shows the energy changes during an uncatalysed reaction (a) and a catalysed reaction (b). You will notice that the effect of the catalyst is to lower the overall activation energy. More colliding particles will possess sufficient energy and so the reaction will be faster.

**Catalysts**

It has been estimated that 90% of all chemicals produced in industry today use a catalyst at some stage in the manufacturing process.

Catalysts do not make impossible reactions take place – they merely make possible reactions faster. The simple definition of a catalyst is that it is a substance that alters the speed of a reaction without being used up. In practice, catalysts are often used up in secondary reactions.

Catalysts can be divided into two types – homogeneous catalysts and heterogeneous catalysts.

**Homogeneous catalysts**

A **homogeneous catalyst** is in the same phase (solid, liquid, solution or gas) as the reactants – for example, a gaseous catalyst in a mixture of gases or a liquid catalyst in a mixture of liquids.

Chlorine free radicals act as a homogeneous catalyst in the gas phase. Chlorine free radicals are produced when ultraviolet light from the Sun breaks up chlorine molecules. They are breaking down ozone in the upper atmosphere into oxygen (see Edexcel AS Chemistry page 214):

\[
\text{Cl}^\cdot (g) + \text{O}_3(g) \rightarrow \text{ClO}^\cdot (g) + \text{O}_2(g)
\]

\[
\text{ClO}^\cdot (g) + \text{O}_3(g) \rightarrow \text{Cl}^\cdot (g) + 2\text{O}_2(g)
\]

Notice that the chlorine free radicals are destroyed, and then regenerated.

The hydrolysis of esters by acid catalysis is an example of homogeneous catalysis with all the reactants, products and the catalyst being dissolved in water:

\[
\text{CH}_3\text{COOCH}_3(aq) + \text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{COOH(aq)} + \text{CH}_3\text{OH(aq)}
\]

Modern examples of homogeneous catalysis include Ziegler–Natta catalysts used to polymerise alkenes (see Edexcel AS Chemistry page 134). These catalysts are organometallic compounds containing both a transition metal (e.g. titanium) and an alkyl group.
Heterogeneous catalysts

A heterogeneous catalyst is in a different phase from the reactants. For example, in the Haber process the solid iron catalyst catalyses the reaction between two gases, hydrogen and nitrogen.

In a catalytic converter in a car, hot gases from the engine react on the metal surface. The catalysts are used to reduce the amounts of carbon monoxide, unburnt hydrocarbons and nitrogen oxides in the exhaust gases. The first stage is reduction – nitrogen oxides are reduced to nitrogen. The second stage is oxidation – carbon monoxide and unburnt hydrocarbons are oxidised to form carbon dioxide and water.

Heterogeneous catalysts are frequently transition metals – for example iron, platinum and nickel. The reacting mixtures are usually adsorbed onto the surface of the catalyst, so the catalyst is usually given a very large surface area to maximise its effect on the reaction rate – a large ingot of iron would have little effect compared to the same mass in finely divided form.

Inorganic catalysts such as these are used to catalyse a wide range of different reactions. Although catalysts are not permanently altered during the reactions that they catalyse, they can be poisoned by some impurities and will not work again.

Figure 1.1.22 shows how a heterogeneous catalyst works in a catalytic converter. Reactant molecules are adsorbed onto the surface of the catalyst and the molecules break down. Reaction takes place on the surface and the product molecules are desorbed from the surface.

HSW Catalytic converters

When it is three years old, every car has to have a Ministry of Transport test (MOT) to ensure that it is roadworthy. The test has to be repeated every 12 months. Part of the test involves analysing the gases escaping from the exhaust system. In order to reduce harmful emissions, modern cars have been designed to control carefully the amount of fuel they burn. There are sensors mounted before and after the catalytic converter to do this (see over). The main emissions of a modern car engine are shown in table 1.1.6.

<table>
<thead>
<tr>
<th>Gas</th>
<th>How formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen gas</td>
<td>Most passes right through the car engine unchanged</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Produced when fuel burns in the engine</td>
</tr>
<tr>
<td>Water vapour</td>
<td>Produced when fuel burns in the engine</td>
</tr>
</tbody>
</table>

table 1.1.6

These three gases can be regarded to be acceptable in the atmosphere, although we now realise that carbon dioxide emissions are believed to contribute to global warming. However, because the combustion process is never perfect, smaller amounts of more harmful emissions are also produced in car engines:

- carbon monoxide – a poisonous gas that is colourless and odourless.
- hydrocarbons or volatile organic compounds (VOCs) – produced mostly from unburnt fuel that evaporates. Sunlight breaks these down to form oxidants, which react with oxides of nitrogen to cause ground level ozone, a major component of pollution.
- oxides of nitrogen – contribute to smog and acid rain, and also cause irritation to human mucus membranes.
Most modern cars are equipped with a three-way catalytic converter as part of the exhaust system. ‘Three-way’ refers to the three regulated emissions it helps to reduce – carbon monoxide, unburnt hydrocarbons and nitrogen oxides.

The first stage of the catalytic converter is the reduction catalyst. It uses platinum and rhodium to help to reduce the nitrogen oxide emissions. When such molecules come in contact with the catalyst, the oxygen is removed. Nitrogen atoms bond with other nitrogen atoms, forming nitrogen gas.

The second stage is the oxidation catalyst. This reduces the unburnt hydrocarbons and carbon monoxide by oxidising them over a platinum and palladium catalyst. This catalyst aids the reaction of carbon monoxide and hydrocarbons with the remaining oxygen in the exhaust gas to form carbon dioxide and water.

Both catalysts consist of a ceramic structure coated with the metal catalyst. The idea is to create a structure that exposes the maximum surface area of the catalyst to the exhaust stream, while also minimising the amount of catalyst required (they are very expensive).

The third stage in the converter is a control system that monitors the exhaust stream using two heated oxygen sensors (also called Lambda sensors) and uses this information to control the fuel injection system. The first of these sensors measures the amount of oxygen in the exhaust gas and this data is used to adjust the composition of fuel and oxygen entering the engine. The second sensor monitors the efficiency of the catalyst in the converter. The goal is to keep the air-to-fuel ratio very close to the ‘stoichiometric’ point, which is the calculated ideal ratio of air to fuel. Theoretically, at this ratio all the fuel will be burned using all the oxygen in the air. For petrol, the stoichiometric ratio is about 14.7 to 1, meaning that for each kilogram of fuel, 14.7 kilograms of air are burned. The fuel mixture actually deviates from the ideal ratio quite a bit during driving. Sometimes the mixture can be ‘lean’ (an air-to-fuel ratio higher than 14.7); at other times the mixture can be ‘rich’ (an air-to-fuel ratio lower than 14.7).

The catalytic converter does a great job of reducing pollution – but there is room for improvement. One of the converter’s biggest shortcomings is that it only works at a fairly high temperature. When you start your car cold, the catalytic converter does almost nothing to reduce the pollution in your exhaust. This is an important point to bear in mind when taking your car for its MOT – make sure that it has had a good steady run to heat up the system to working temperature or the car could fail its emissions test.

A simple solution to this problem is to move the catalytic converter closer to the engine. This means that hotter exhaust gases reach the converter and it heats up faster, but this may also reduce the life of the converter by exposing it to extremely high temperatures. Most car makers position the converter under the front passenger seat, far enough from the engine to keep the temperature down to levels that will not harm it. Preheating the catalytic converter using electric resistance heaters could be a good way of reducing emissions. Unfortunately, the 12-volt electrical system on most cars just does not provide enough energy to heat the catalytic converter fast enough.
Catalytic converters could not be used if cars used leaded petrol. Suggest why.

Why are small quantities of a homogeneous catalyst sufficient for a reaction?

Tetraethyl lead (TEL) is an organometallic compound with the formula \((CH_3CH_2)_4Pb\).

It was discovered in 1921 by Thomas Midgley, working for General Motors Research. Due to its extreme toxicity, many early TEL researchers, including Midgley, became poisoned by lead and dozens died.

Tetraethyl lead was once used extensively as an additive in petrol for its ability to increase the octane rating of the fuel. TEL is still the most effective additive for increasing the octane rating of gasoline. A high enough octane rating is required to prevent premature detonation (or ‘knocking’). Anti-knock agents allow the use of higher compression ratios for greater engine efficiency. One of the greatest advantages of TEL over other anti-knock agents is the very low concentration needed – typical formulations called for 1 part of TEL to 1260 parts of untreated petrol. Its use in petrol, particularly during the Second World War, was important.

The most important feature of the TEL molecule is the weakness of its four C–Pb bonds. At the temperatures found in internal combustion engines, \((CH_3CH_2)_4Pb\) reacts with oxygen and decomposes completely into carbon dioxide, water and lead:

\[
(CH_3CH_2)_4Pb + 13O_2 \rightarrow 8CO_2 + 10H_2O + Pb
\]

along with combustible, short-lived ethyl radicals.

The lead can oxidise further to give species such as lead(II) oxide:

\[
2Pb + O_2 \rightarrow 2PbO
\]

Lead and lead oxide remove radical intermediates in the combustion reactions. This prevents ignition of unburnt fuel during the engine’s exhaust stroke. Lead itself is the reactive anti-knock agent.

The lead and lead(II) oxide would accumulate quickly and destroy an engine. For this reason, compounds such as 1,2-dibromoethane are used with TEL. This forms volatile lead(II) bromide, which is lost from the engine through the exhaust.

TEL is no longer used as a petrol additive in most of the world because of the toxicity of lead, and because lead compounds would poison the catalyst inside the converter of a modern car. It is still used as a fuel additive in piston-engined aircraft.
Investigating the activation energy of a reaction [4.3f(v), g]

Activation energy

You know that a certain amount of energy is needed before a reaction can occur. This is called the activation energy. You also know that the rate constant in a reaction is constant only at constant temperature. In this section, we are going to investigate the effect on the rate constant of changing the temperature.

In the mid-nineteenth century, Ludwig Boltzmann and James Clark Maxwell were working quite independently of each other in Vienna, Austria, and Cambridge, England. The two scientists developed a statistical treatment of the distribution of energy amongst a collection of particles. This led to a greater understanding of the way in which the macroscopic behaviour of matter may be related to the microscopic particles of which it is composed, and to the development of the kinetic theory through a branch of the sciences now called statistical mechanics.

The work of Maxwell and Boltzmann on the distribution of the speeds of particles in a gas underpins much of the understanding of the rate at which chemical reactions occur. Yet Boltzmann's theories on the behaviour of matter were far from accepted at the time. Coming soon after the work of Darwin, many scientists saw Boltzmann's work as threatening the purposeful, God-given workings of the Universe, for if it could be shown that the behaviour of matter on a grand scale could be understood by studying its behaviour on a much smaller scale, what scope was left for the Creator? Stung by the scorn of his fellow scientists, Boltzmann committed suicide.

About 1930, Zartmann and Ko devised an experiment to measure the molecular speeds of gas molecules at different temperatures. They heated tin in an oven and directed the gaseous atoms towards a rotating disc with a slit in it. Any atoms that travelled through the slit hit a second disc behind the first and solidified on it. They found that the tin deposits were not uniform and had different thickness on different parts of the second disk. This meant that there was a spread of velocities and that their distribution was uneven.

Only when these experiments could be carried out could the truth of the work of Maxwell and Boltzmann be verified.

Figure 1.1.25 shows a distribution of the kinetic energies of particles in a sample of gas at a constant temperature. In this graph, $E_A$ represents the activation energy. The area under the curve represents the total number of particles and the shaded area under the curve represents the number of particles with sufficient energy to react – that is, more than the activation energy.

$$\text{fraction of particles with greater than } E_A = \frac{\text{shaded area beneath curve}}{\text{total area beneath curve}}$$
Investigating the activation energy of a reaction

fig. 1.1.25 Distribution of the kinetic energies of particles in a sample of gas.

Using kinetic theory and probability theory, it can be shown that the fraction of molecules with greater energy than \( E_A \) J mol\(^{-1} \) is given by \( e^{E_A/RT} \), where \( R \) is the gas constant (8.314 J K\(^{-1} \) mol\(^{-1} \)), \( T \) is the absolute temperature and \( e \) is the exponential constant.

From this we can say that at a given temperature:

rate of reaction \( \propto e^{E_A/RT} \)

But as the rate constant, \( k \), is a measure of the rate of reaction we can write:

\[ k \propto e^{E_A/RT} \text{ or } k = A e^{E_A/RT} \]

\( A \) is called the Arrhenius constant. The relationship between temperature and rate constant was proposed by the Swedish chemist Svante Arrhenius. He applied natural logarithms throughout:

\[ \ln k = -\frac{E_A}{R} T + \text{a constant} \]

A straight line can be represented by \( y = mx + c \).

So, from \( \ln k = -\frac{E_A}{R} T + \text{a constant} \), plotting a graph of \( \ln k \) (that’s \( y \)) against \( \frac{1}{T} \) (that’s \( x \)) gives a straight line graph, the gradient (\( m \)) of which is \(-\frac{E_A}{R} \) (see fig.1.1.26).

From this value for the gradient, you can work out the value for \( E_A \) using the value \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \).

Note also that this type of graph cuts the \( y \)-axis at a certain value – this is the value for the Arrhenius constant, \( A \), for the reaction.

**Questions**

1. Use the Arrhenius equation to explain:
   a. the higher the temperature, the faster is the reaction
   b. a reaction with a large activation energy has a slow rate of reaction.

2. The table gives the rate constant for the decomposition of hydrogen peroxide into water and oxygen at different temperatures.

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>Rate constant/s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>4.93 ( \times ) 10(^{-4} )</td>
</tr>
<tr>
<td>305</td>
<td>1.4 ( \times ) 10(^{-3} )</td>
</tr>
</tbody>
</table>

Estimate the activation energy for the reaction.
You will know from AS Chemistry that increasing the concentration of a reactant often increases the rate of a chemical reaction. The exact relationship between rate of reaction and concentration can be determined experimentally.

Most chemical reactions take place in a series of steps rather than in a single step. The different steps in a multi-step process have different speeds – some are faster than others. In a multi-step reaction, the slowest step is called the rate-determining step and this determines the speed of the overall reaction.

A reaction mechanism worked out for a reaction is only a theory, because in most cases chemists cannot detect or isolate the proposed intermediates. It has to be ‘guessed’ from the raw data. So to support a model of the mechanism of a particular reaction, the predicted rate law from the mechanism must match the rate law achieved from experimental data. If they don’t match, however elegant the mechanism proposed, it is wrong!

The mechanism of substitution reactions
In Edexcel AS Chemistry (page 226) there are data to support a discussion of the nucleophilic substitution of two halogenoalkanes – bromoalkanes A and B – with hydroxide ions. These data are shown again in tables 1.1.7 and 1.1.8.

In the case of bromoalkane A, the rate of reaction is directly proportional to the concentration of A. So doubling the concentration of A doubles the rate of reaction, and tripling [A] triples the rate of reaction.

The rate of reaction is independent of the concentration of hydroxide ions, so increasing [OH–] does not make the reaction faster. This means that hydroxide ions do not feature in the rate-determining step.

When 2-iodo-2-methylbutane is refluxed with aqueous potassium hydroxide solution, the first step is the heterolytic fission of the carbon–iodine bond to form a tertiary carbocation. Tertiary carbocations are relatively stable. This step is slow and is the rate-determining step.

The second step involves a rapid reaction between the carbocation and hydroxide ions.

The process is summarised in fig. 1.1.27. The rate-determining step involves only the 2-iodo-2-methylbutane and so the rate equation does not involve hydroxide ions. This is called an SN1 reaction (substitution / nucleophilic / first order or unimolecular).

**Bromoalkane A**

<table>
<thead>
<tr>
<th>Concentration of bromoalkane A /mol dm⁻³</th>
<th>Concentration of hydroxide ions /mol dm⁻³</th>
<th>Initial rate /mol dm⁻³s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>1.11 x 10⁻⁵</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1</td>
<td>2.22 x 10⁻⁵</td>
</tr>
<tr>
<td>0.3</td>
<td>0.1</td>
<td>3.33 x 10⁻⁵</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>1.11 x 10⁻⁵</td>
</tr>
<tr>
<td>0.1</td>
<td>0.3</td>
<td>1.11 x 10⁻⁵</td>
</tr>
</tbody>
</table>

*table 1.1.7 Reaction rate data for bromoalkane A.*

**Bromoalkane B**

<table>
<thead>
<tr>
<th>Concentration of bromoalkane B /mol dm⁻³</th>
<th>Concentration of hydroxide ions /mol dm⁻³</th>
<th>Initial rate /mol dm⁻³s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>1.50 x 10⁻⁵</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1</td>
<td>3.00 x 10⁻⁵</td>
</tr>
<tr>
<td>0.3</td>
<td>0.1</td>
<td>4.50 x 10⁻⁵</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>3.00 x 10⁻⁵</td>
</tr>
<tr>
<td>0.1</td>
<td>0.3</td>
<td>4.50 x 10⁻⁵</td>
</tr>
</tbody>
</table>

*table 1.1.8 Reaction rate data for bromoalkane B.*
In the case of bromoalkane B, the rate of reaction doubles when the concentration of B doubles (and the concentration of hydroxide ions is unchanged). It also doubles when [OH\(^-\)] doubles (and [B] is unchanged). This can be expressed as:
\[
\text{rate} \propto [B][OH^-]
\]
This can then be represented as a rate equation:
\[
\text{rate} = k[B][OH^-]
\]
The kinetics of this reaction suggest that the rate-determining step involves both the halogenoalkane and the hydroxide ion.

An example of this mechanism is the reaction of bromomethane with aqueous potassium hydroxide solution. The explanation for this was first given by Christopher Ingold. He suggested that the hydroxide ion joined onto the central carbon atom at the same time as the bromine atom was leaving. Part of the energy required to break the C–Br bond was supplied by the energy released on producing the C–OH bond. Calculations show that the approach of the hydroxide ion along the line of centres of the carbon and bromine atoms is that of lowest energy requirement.

This process is summarised in fig. 1.1.28. The rate-determining step involves both bromomethane and hydroxide ions. This is called an S\(_N\)2 reaction (substitution / nucleophilic / second order or bimolecular).

![fig. 1.1.28 The S\(_N\)2 substitution reaction mechanism.](image)

Studying kinetics alone can, in some cases, be insufficient to be sure just which mechanism is being followed – unless the reaction is studied thoroughly under more than one set of conditions.

For example, the hydrolysis of a halogenoalkane R–X in water can lead to confusing results. Water acts as a nucleophilic reagent. If the reaction is S\(_N\)2 the rate equation would be:
\[
\text{rate} = k[RX][H_2O]
\]
But the water is in excess so [H\(_2\)O] is effectively constant – so the rate equation would become:
\[
\text{rate} = k[RX]
\]
This might lead you to think the reaction was S\(_N\)1.

**Questions**

1. The reaction between nitrogen dioxide and carbon monoxide fits the following overall equation:
   \[
   \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(s)
   \]
   a. If the rate equation suggested a single-step mechanism, what would be the rate equation?
   b. The rate equation for this reaction is in fact:
   \[
   \text{rate} = k[\text{NO}_2]^2
   \]
   A possible mechanism is:
   \[
   2\text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \quad \text{step 1}
   \]
   \[
   \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \quad \text{step 2}
   \]
   Which of these steps do you think is the rate-determining step? Explain your answer.

2. Under certain conditions, hydrolysis of 1-bromobutane can produce 2-methylpropan-2-ol. Using your understanding of nucleophilic substitution, suggest how this happens.
Iodine and propanone react, in the presence of acid, in a substitution reaction to form iodopropanone. The reaction can be represented by:

\[
\text{CH}_3\text{COCH}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{CH}_2\text{ICOCH}_3(\text{aq}) + \text{H}^+(\text{aq}) + \text{I}^-(\text{aq})
\]

Kinetic experiments can be carried out using different concentrations of propanone, iodine and hydrogen ions.

**By titration**

During the experiment small aliquots (samples) of the reaction mixture are removed with a pipette.

The withdrawn sample is put in a flask and excess sodium hydrogencarbonate is added. This effectively stops the reaction so no further change in iodine concentration occurs during titration. The aliquots are titrated with a standard solution of sodium thiosulfate using starch indicator near the end-point. The measured values for the [I\(_2\)] can be used to calculate the concentrations of the other substances involved. **Table 1.1.9** summarises the results of such an experiment. We can conclude that:

- doubling the concentration of iodine has no effect on the relative rate of the reaction (experiments 1 and 2)
- doubling the concentration of propanone doubles the relative rate of the reaction (experiments 1 and 4)
- doubling the concentration of hydrogen ions doubles the relative rate of the reaction (experiments 1, 3 and 5).

Using this we can write the rate equation:

\[
\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]
\]

The reaction is first order with respect to propanone and hydrogen ions, but zero order with respect to iodine. The overall order of the reaction is two. What does this tell us about the mechanism of the reaction?

The reaction involves various steps and the slowest step, the rate-determining step, does not involve iodine. This is why iodine does not appear in the rate equation. Hydrogen ions act as a catalyst – they are regenerated during the reaction.

**Table 1.1.9** The rate of reaction depends on the concentration of propanone and on that of hydrogen ions, but not on the iodine concentration.
A possible mechanism for the reaction of iodine and propanone in acid solution is given below.

**Step 1**
An H⁺ ion protonates the oxygen atom in propanone:

\[(\text{CH}_3)_2\text{C}=\text{O} + \text{H}_3\text{O}^+ \rightleftharpoons (\text{CH}_3)_2\text{C}=\text{O}^+\text{H} + \text{H}_2\text{O}\]

This is a reversible reaction involving proton transfer (acid–base reaction). Remember that a protonated water molecule, H₃O⁺, behaves as an H⁺ ion.

**Step 2**
The electrons in the C=O bond partly shift to form a carbocation – i.e. the positive charge is transferred from the oxygen to the carbon:

\[(\text{CH}_3)_2\text{C}=\text{O}^+\text{H} \rightleftharpoons (\text{CH}_3)_2\text{C}^+\text{OH}\]

**Step 3**
This carbocation loses a proton and slowly changes into the enol form. The enol has both alkene and alcohol functional groups and is isomeric with the original ketone:

\[(\text{CH}_3)_2\text{C}^+\text{OH} + \text{H}_2\text{O} = \text{CH}_3\text{C(OH)}=\text{CH}_2 + \text{H}_3\text{O}^+\]

This involves breaking a strong C–H bond, hence this step has a high activation energy and slow speed. The positive charge on the adjacent carbon of the carbocation facilitates in ‘pulling’ the C–H bond pair to form the C=C bond and releases the proton to form an H₃O⁺ ion.

The rate of formation of the enol thus depends on the concentrations of the ketone and the acid.

**Step 4**
The iodine molecule acts as an electrophile and undergoes a quick electrophilic addition reaction (like other alkenes). This produces a protonated iodoketone:

\[\text{CH}_3\text{C(OH)}=\text{CH}_2 + \text{I}_2 \rightarrow \text{CH}_3\text{C(=O+H)}=\text{CH}_2\text{I} + \text{I}^-\]

**Step 5**
A water molecule then rapidly removes the proton in another acid–base reaction to form the iodoketone:

\[\text{CH}_3\text{C(=O+H)}=\text{CH}_2\text{I} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{H}_3\text{O}^+\]

The whole process is summarised in fig.1.1.30.

In this example the slow, rate-determining steps 1, 2 and 3 are the first stage in the reaction and need only \(\text{CH}_3\text{COCH}_3\) and H⁺. The remaining steps happen very quickly. This is also the case when oxygen and hydrogen bromide react together at 700 K. However, the slowest reaction is not always the first.

In the reaction between bromide ions and bromate(V) ions in acid solution (see pages 20–21) the most likely mechanism is that HBr and HBrO₃ are made very rapidly before the third, relatively slow, reaction between the two of them takes place. This is the rate-determining reaction, and is followed by two more rapid steps to complete the reaction.

**Questions**

1. These questions refer to the methods used to carry out the reaction of iodine and propanone in acid solution.
   a) Suggest advantages of the method that uses a colorimeter.
   b) In the titration method, why is a pipette used to remove aliquots?
   c) Why does sodium hydrogencarbonate effectively stop the reaction?

2. Why does I₂ not appear in the rate equation?