

21 Quantitative kinetics

Topic 8 gave an overview of how to measure rates of reaction, and what factors increase the number of collisions with enough energy to overcome the activation energy barrier. In this topic, we look at rates of reaction quantitatively. The analysis of the collision theory, the simplest model to explain kinetic data, is developed. Analysing the effects of concentration changes on the reaction rate enables us to write a rate equation, and from this we can obtain information about the mechanism of the reaction.

Learning outcomes

By the end of this topic you should be able to:

- 8.1c)** explain and use the terms *rate equation*, *order of reaction*, *rate constant*, *half-life of a reaction*, *rate-determining step* (see also Topic 8)
- 8.1d)** construct and use rate equations of the form $\text{rate} = k[\text{A}]^m[\text{B}]^n$ (for which m and n are 0, 1 or 2), including:
 - deducing the order of a reaction, or the rate equation for a reaction, from concentration–time graphs or from experimental data relating to the initial rates method and half-life method
 - interpreting experimental data in graphical form, including concentration–time and rate–concentration graphs
 - calculating an initial rate using concentration data
- 8.1e)** show understanding that the half-life of a first-order reaction is independent of concentration and use the half-life of a first-order reaction in calculations
- 8.1f)** calculate the numerical value of a rate constant, for example by using the initial rates or half-life method
- 8.1g)** for a multi-step reaction, suggest a reaction mechanism that is consistent with the rate equation and the equation for the overall reaction and predict the order that would result from a given reaction mechanism (and vice versa)
- 8.1h)** devise a suitable experimental technique for studying the rate of a reaction, from given information
- 8.2c)** explain qualitatively the effect of temperature change on a rate constant and hence the rate of a reaction
- 8.3e)** outline the different characteristics and modes of action of homogeneous, heterogeneous and enzyme catalysts, including the Haber process, the catalytic removal of oxides of nitrogen from the exhaust gases of car engines (see also Topic 13), the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide (see also Topic 10), the catalytic role of Fe^{2+} or Fe^{3+} in the $\Gamma/\text{S}_2\text{O}_8^{2-}$ reaction, and the catalytic role of enzymes (including the explanation of specificity using a simple lock and key model but excluding inhibition).

21.1 The rate of a reaction

An expression for the rate of a reaction

In Topic 8, several different ways to measure the rate of a reaction were seen. Examples included the gradient of a graph of volume of gas produced against time (see page 156) and the gradient of a graph of absorbance against time (see page 157). In order to study rates of reaction quantitatively, a precise definition of **rate** is needed. This may be expressed either as how the concentration of a product P increases with time, or how the concentration of a reactant R decreases with time.

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

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

The negative sign in the second expression reflects the fact that the concentration of the reactant is decreasing and therefore produces a positive value for the rate, as it should. The expressions above may be written:

$$\text{rate} = \frac{\Delta[\text{P}]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{-\Delta[\text{R}]}{\Delta t}$$

Using calculus notation, this becomes:

$$\text{rate} = \frac{d[\text{P}]}{dt} \quad \text{or} \quad \text{rate} = \frac{-d[\text{R}]}{dt}$$

Rate is measured in units of concentration per unit time, $\text{mol dm}^{-3} \text{s}^{-1}$.

Calculus notation

Although we are not going to use calculus in this topic, its notation is useful in representing the slope of a line at a particular point.

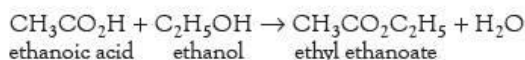
The expression $\frac{\Delta[\text{P}]}{\Delta t}$ means that during the time interval Δt (which may be of any length, for example 1 second, 20 minutes, etc.), between the two times t_1 and t_2 , the concentration of P, written as [P], has changed from $[\text{P}]_1$ to $[\text{P}]_2$:

$$\frac{\Delta[\text{P}]}{\Delta t} = \frac{([\text{P}]_2 - [\text{P}]_1)}{(t_2 - t_1)}$$

$\frac{\Delta[\text{P}]}{\Delta t}$ therefore measures the *average* rate of reaction over this time interval. As we decrease the time interval Δt to smaller and smaller values, the value of $\Delta[\text{P}]$ will become smaller and smaller too, and the ratio $\frac{\Delta[\text{P}]}{\Delta t}$ will approximate more and more to the exact slope of the concentration-time graph at a particular point. In the limit, when Δt is (virtually) zero, the ratio becomes the *exact* rate at a particular point. The expression is then written as $\frac{d[\text{P}]}{dt}$.

Measuring rates by physical and chemical analysis

Before investigating the rate of a particular reaction, we need to know the overall (stoichiometric) equation so that we can decide what method can be used to follow it. For example, if we were studying the following esterification reaction:



the decrease in the amount of ethanoic acid, as found by titration, could be followed.

The rate at a given time t is then:

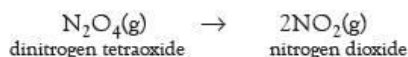
$$\frac{-\Delta[\text{CH}_3\text{CO}_2\text{H}]}{\Delta t} \quad \text{or} \quad \frac{-d[\text{CH}_3\text{CO}_2\text{H}]}{dt}$$

We could also express the rate as any of the following:

$$\frac{-d[\text{C}_2\text{H}_5\text{OH}]}{dt} \quad \text{or} \quad \frac{+d[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5]}{dt} \quad \text{or} \quad \frac{+d[\text{H}_2\text{O}]}{dt}$$

All of these would give the same numerical value of the rate.

For the reaction:



however,

$$\frac{-d[\text{N}_2\text{O}_4]}{dt} \neq \frac{+d[\text{NO}_2]}{dt}$$

because *two* moles of nitrogen dioxide are produced for each *one* mole of dinitrogen tetroxide used up. When there are different coefficients in the equation like this, it is usual to define the rate in terms of the substance with a coefficient of 1.

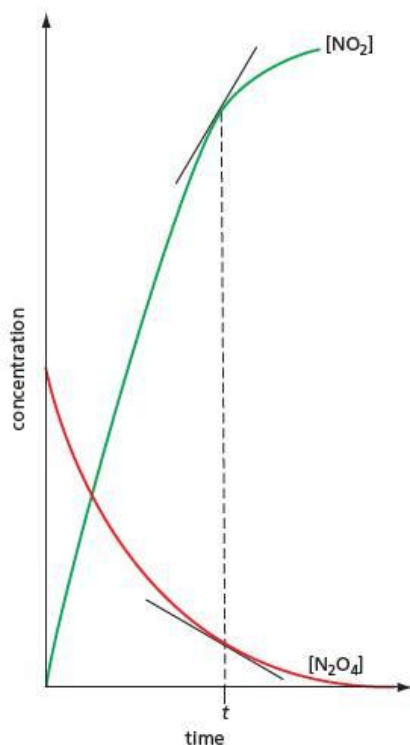


Figure 21.1 The rate of the reaction at time t is the gradient of the concentration–time graph at that point. The rate is either $-d[N_2O_4]/dt$ or $+\frac{1}{2}d[NO_2]/dt$.

So in this case:

$$\text{rate} = \frac{-d[N_2O_4]}{dt} = \frac{1}{2} \frac{d[NO_2]}{dt}$$

Figure 21.1 illustrates this point.

As we mentioned in Topic 8, although chemical analysis can be used to follow how the amount of one substance changes in a reaction, physical methods are usually preferred. For the reaction above, for example, we could follow the change in volume if we were carrying out the reaction in the gas phase, because the number of moles of gas is changing. Alternatively, if we carried out the reaction in solution, we could follow the change in colour (dinitrogen tetroxide is pale yellow, while nitrogen dioxide is dark brown).

The esterification reaction is difficult to follow using a physical method because there is no obvious change in a physical property as the reaction proceeds. Here we would have to use a chemical method of analysis. Samples of the reaction mixture are extracted at measured time intervals and the amount of ethanoic acid remaining is found by titration with alkali. One problem with this method is that the reaction continues to take place in the sample until the titration is complete, so that the concentration of ethanoic acid at time t is difficult to measure accurately. This reaction is carried out using an acid catalyst, and the reaction in the samples can be effectively stopped by immediately adding the exact amount of alkali needed to neutralise the acid catalyst which was added to the reaction mixture at the start of the reaction. Other reactions can be stopped by appropriate methods, such as rapid cooling of the samples.

Factors affecting the rate of a reaction – a quantitative approach

In Topic 8, we looked at the various factors that determine the rate of a reaction. In this topic, we examine quantitatively how some of these factors affect the rate. This quantitative data often gives information about how the reaction takes place, that is, about the **mechanism** of the reaction. This allows us to study chemical reactions at the most fundamental level.

We have already discussed qualitatively how the following factors affect the rate of a reaction:

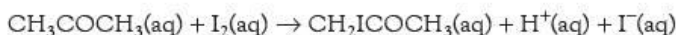
- concentration (or pressure for gas reactions)
- temperature
- catalysts
- state of division
- nature of the solvent
- light.

For convenience, when we carry out kinetics experiments in the laboratory, we usually study homogeneous reactions in aqueous solution. The principal factors that we can study under these conditions are the effects of concentration, temperature and homogeneous catalysts. These will now be considered in some detail.

21.2 The effect of concentration

In this section we shall study a single reaction – the iodination of propanone – but the principles established can be applied to many other reactions.

In acid solution, iodine reacts with propanone as follows:



It would be tempting to predict that the rate of the reaction depends on the concentration of both the iodine and the propanone but, as we shall see, this is not the case. Information about the kinetics of a reaction can be found only by experiment, and does not always agree with what might be expected from the stoichiometric equation.

- The stoichiometric equation *cannot* be used to predict how concentration affects the rate of a reaction.
- Kinetic data must be found by experiment.

The stoichiometric equation is used to decide which substance we are going to follow during the reaction in order to measure the rate. In this case, the concentration of iodine is most easily measured, either using a colorimeter (see section 8.2) or by titration with sodium thiosulfate (see section 7.4). It is much more difficult to follow the change in concentration of either propanone or the products of the reaction.

Because we are investigating the effect of concentration on the rate of the reaction, all other factors that might affect the rate should be kept constant. Accurate control of temperature is essential. The reaction should be carried out in a water bath whose temperature is controlled to within 1 K. For very accurate work, thermostatic water baths whose temperature varies by less than 0.1 K are available (see Figure 21.2). Once the reaction has started, the reactants are shaken well in order to mix them thoroughly.

Figure 21.2 A thermostatic water bath keeps the temperature of the reaction constant, removing one factor that might affect the rate.



Initial investigations show that the reaction is not affected by light, but that it is affected by $\text{H}^+(\text{aq})$ ions, which act as a catalyst. As this is a homogeneous catalyst, we shall treat $\text{H}^+(\text{aq})$ ions in the same way as we treat the other two reactants. We now have three substances whose concentration may affect the rate: $\text{I}_2(\text{aq})$, $\text{CH}_3\text{COCH}_3(\text{aq})$ and $\text{H}^+(\text{aq})$. In order to find out how each of them affects the rate of the reaction, we must vary each in turn while keeping the other two constant. There are two main ways of designing experiments to achieve this:

- keeping all reactants in excess except the one being studied
- the initial-rates method.

Keeping all reactants in excess except one

If the concentrations of propanone and hydrogen ions are chosen to be much higher than that of iodine, then during the course of the reaction, their concentrations vary so little that they may be taken as constant. Table 21.1 illustrates why this is the case.

Table 21.1 A typical set of concentrations used to study the iodination of propanone. The concentration of hydrogen ions increases because as well as being a catalyst, it is also being produced by the reaction.

Reactant	Concentration at start/ mol dm^{-3}	Concentration at end/ mol dm^{-3}
I_2	0.01	0.0
CH_3COCH_3	1.00	0.99
H^+	0.50	0.51

A mixture of propanone and sulfuric acid is placed in a thermostatically controlled water bath. The solution of iodine is also placed in the bath in a separate container. At the start of the experiment, the two solutions are mixed, shaken well and a stop-clock started. At regular times, the concentration of iodine is found, and a graph is plotted of iodine concentration against time (see Figure 21.3).

The graph is a straight line. This shows that the rate, given by the negative gradient of the graph, is constant. The rate does not change as the iodine concentration falls – the rate is independent of the iodine concentration.

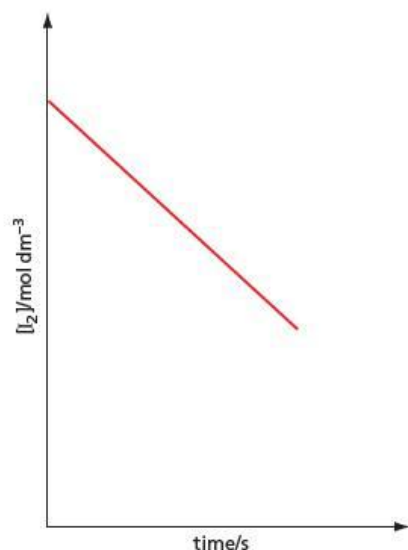


Figure 21.3 Graph of iodine concentration against time for the iodination of propanone

Figure 21.4 The three most common types of concentration–time graphs: **a** zero order, **b** first order, **c** second order. $[R]_0$ is the concentration at time $t = 0$.

Analysing the results – the order of the reaction with respect to each reactant

The **order of reaction** with respect to a reactant, X, tells us to what extent the concentration of that reactant has an effect on the reaction rate. In this case, since the rate of the reaction is independent of the iodine concentration, we can write:

$$\text{rate} = \frac{-d[I_2]}{dt} = k, \text{ a constant}$$

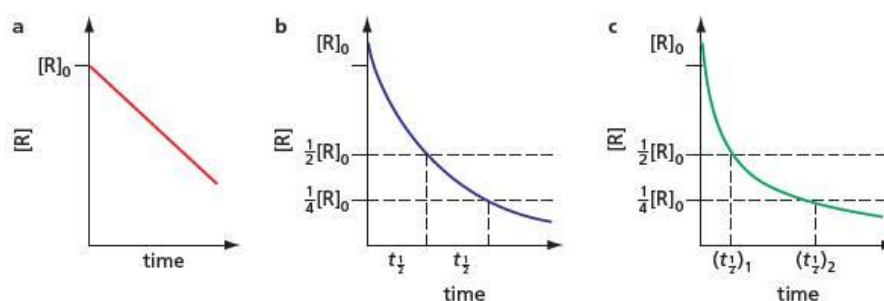
We can indicate the fact that the rate is not affected by the iodine concentration by writing:

$$\text{rate} = k[I_2]^0$$

Any term raised to the power of zero is equal to 1, so the term could be omitted altogether. We include it to emphasise that the effect of iodine concentration on the rate has been studied and found to be **zero order**. This result may seem surprising, and emphasises the point that we cannot predict which reactants determine the reaction rate by looking at the stoichiometric equation.

Of course, the rate is not independent of *all* the reactants, and the concentration of at least one of them must affect the rate.

The order with respect to each reactant can be found by studying concentration–time graphs like the one obtained for iodine. The three common types of rate dependence are shown in Figure 21.4.



The first example, Figure 21.4a, is like Figure 21.3 for iodine. The graph is a straight line and the rate is constant. This shows that the rate is zero order with respect to that reactant, so that $\text{rate} = k[R]^0$. (Since $[R]^0 = 1$, $\text{rate} = k$.)

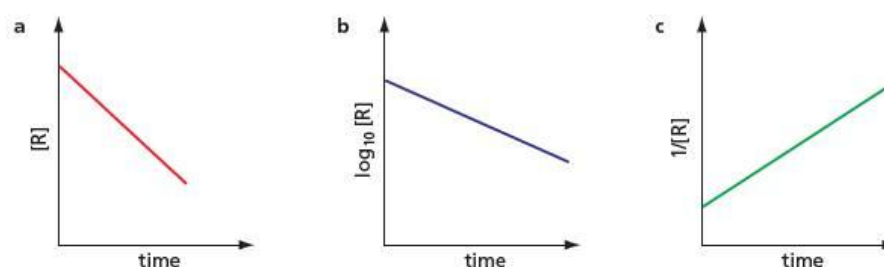
In the second example, Figure 21.4b, the curve is an exponential, and has a constant half-life, $t_{1/2}$. By ‘constant half-life’ we mean that the successive half-lives are the same. That is, the time taken for the concentration of the reactant to decrease from $[R]_0$ to $\frac{1}{2}[R]_0$ is the same as the time taken for the concentration to decrease from $\frac{1}{2}[R]_0$ to $\frac{1}{4}[R]_0$, and so on.

In the third example, Figure 21.4c, successive half-lives become longer. This indicates an order greater than 1. Since orders higher than 2 are most unusual, the rate is likely to be second order, that is, $\text{rate} = k[R]^2$.

In order to confirm that the reaction is of the order suggested by the concentration–time graph, the results can be used to plot a graph that is a straight line. For a zero-order reaction, the graph of $[R]$ against time is a straight line, a first-order reaction gives a straight line for a graph of $\log_{10}[R]$ against time, and a second-order reaction gives a straight-line graph when $1/[R]$ is plotted against time (see Figure 21.5).

Figure 21.5 Straight-line graphs are obtained for the following plots:

- a** zero order: $[R]$ against time
- b** first order: $\log_{10}[R]$ against time
- c** second order: $1/[R]$ against time.



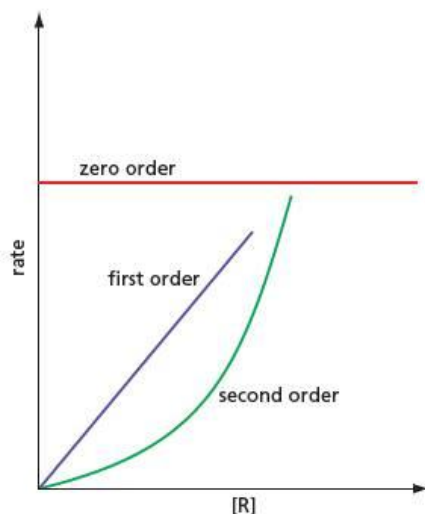


Figure 21.6 Rate-concentration graphs can be used to distinguish between zero-order, first-order and second-order reactions. The zero-order graph is a straight line parallel to the x-axis. The first-order graph is a straight line passing through the origin. The second-order graph is a parabola starting at the origin.

Another, less reliable, way to check the order is to measure the gradient of the concentration-time graph at various times in order to find the rates. These rates can then be plotted against concentration: Figure 21.6 shows how this distinguishes between the three possible orders.

- If it is found by experiment that

$$\text{rate} = k[X]^1$$

then the order with respect to X is 1.

- If it is found that

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

then the order with respect to X is 2.

- There are some reactions where changing the concentration of a reactant has *no* effect on the rate. In this case we can write

$$\text{rate} = k[X]^0$$

and we say that the order with respect to X is zero. (Note that $n^0 = 1$, a constant, no matter what the value of n .)

The initial-rates method

Analysing the effect of concentration of a reactant on the rate of a reaction by the method of keeping all reactants except one in excess has the advantage that a large amount of data can be collected from each experiment. The results may be plotted so that a straight-line graph is obtained, possibly up to the point when the reaction is 90% completed. If this is the case, we can be confident that the order suggested by the results is the one that should be taken as correct.

Sometimes, however, it is not possible for all the reactants to be in excess. In the iodination of propanone experiment, for example, the iodine concentration must always be small, as this is the reactant whose concentration we are following during the course of the reaction. Another method is therefore needed to find the order of reaction with respect to the propanone and with respect to the acid.

This is done by carrying out a series of experiments in which the initial concentration of all the reactants is kept the same except for the one under investigation, whose concentration is varied. At the start of each experiment, the **initial rate** is found from the gradient of the concentration-time graph (see Figure 21.7). By studying how the initial rate changes when the concentration of this one reactant is varied, we can find the order with respect to that reactant.

The **initial rate** of a reaction is the slope (tangent) of the concentration-time graph at the start of the reaction, when $t = 0$.

Figure 21.7 The initial rate is found from the gradient at the start of the reaction, that is, when $t = 0$.

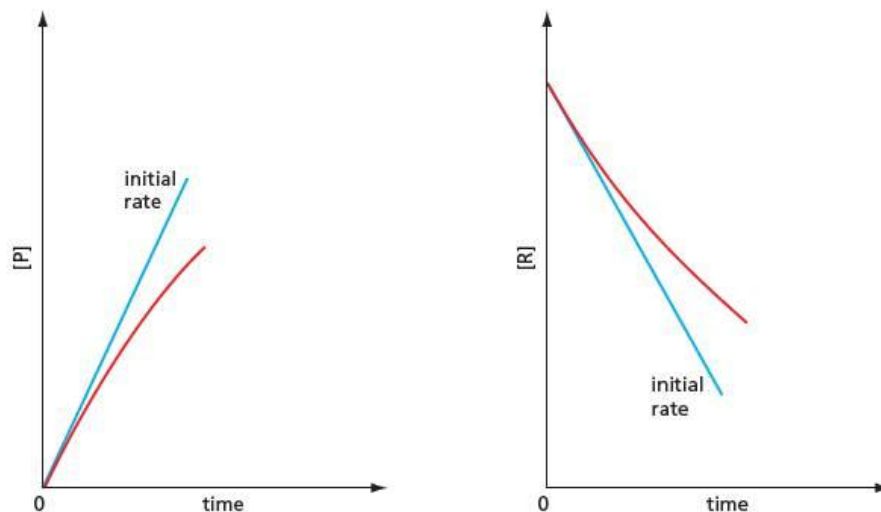


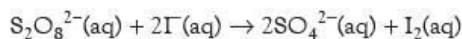
Table 21.2 A typical set of results for the iodination of propanone. Initial rates were calculated from the iodine concentration–time graph. Because the order of the reaction with respect to iodine has already been found, it is not necessary to vary $[I_2]$. $[I_2]$ is kept smaller than the concentrations of the other reactants because the change in $[I_2]$ is being used to monitor the reaction rate. Note that at the start of the reaction, when the initial rate is measured, $[I_2]$ is constant at $0.002 \text{ mol dm}^{-3}$.

Experiment	$[H^+]/\text{mol dm}^{-3}$	$[I_2]/\text{mol dm}^{-3}$	$[CH_3COCH_3]/\text{mol dm}^{-3}$	Initial rate/ $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.50	0.002	0.50	2.0×10^{-5}
2	0.30	0.002	0.50	1.2×10^{-5}
3	0.10	0.002	0.50	4.0×10^{-6}
4	0.50	0.002	0.30	1.2×10^{-5}
5	0.50	0.002	0.10	4.0×10^{-6}

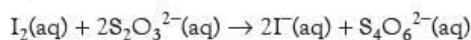
From experiments 1, 4 and 5, as $[CH_3COCH_3]$ is reduced in the ratio 5:3:1, so the rate again decreases in the ratio 5:3:1. Therefore, the reaction is also first order with respect to $[CH_3COCH_3]$.

In the case of the iodination of propanone experiment, it is easy to obtain an accurate value for the initial rate because the graph of $[I_2]$ against t is a straight line. This is not usually the case, and then the determination of the initial rate, found from the gradient when $t = 0$, is much more difficult.

Sometimes the initial rate may be found by a 'clock' method. The initial rate of the reaction between peroxodisulfate(VI) ions and iodide ions:



can be found by adding a known small amount of thiosulfate ions and a little starch. Initially the iodine produced reacts with the thiosulfate ions:

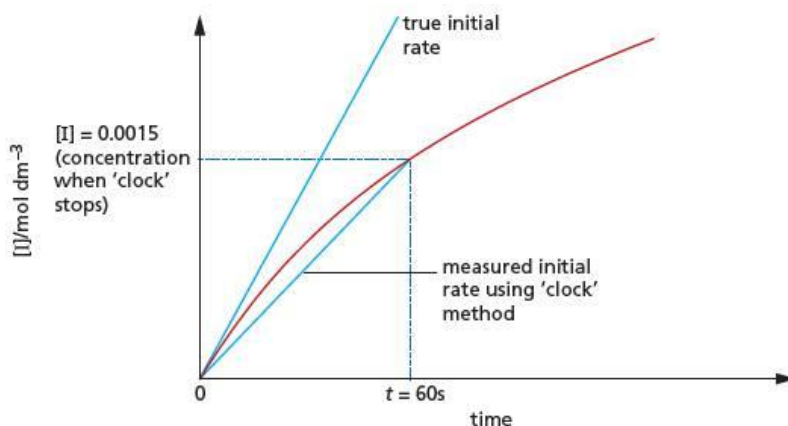


but, as we saw in section 8.2, after the thiosulfate ions have been used up, the iodine reacts with the starch to give a blue colour. The time taken, t , for this colour to appear may be used as an approximate measure of the initial rate. If, for example, $[S_2O_3^{2-}] = 0.0030 \text{ mol dm}^{-3}$, the equation shows that this will be used up when $[I_2] = 0.0015 \text{ mol dm}^{-3}$. Suppose that the time taken, t , is 60 s. Then:

$$\begin{aligned} \text{initial rate of reaction} &= \frac{-\Delta[I_2]}{\Delta t} = \frac{0.0015}{60} \\ &= 2.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1} \end{aligned}$$

This is only an approximate value because it assumes that the concentration–time graph is a straight line not only near the origin, but up to the point when the blue colour appeared (see Figure 21.8). The approximation is reasonable provided the reaction is only a small way towards completion.

Figure 21.8 A 'clock' method gives a value for the initial rate that is lower than the true value, because it assumes that the concentration–time graph is a straight line until the 'clock' stops.



21.3 The rate equation

Arriving at the rate equation

When the order of a reaction with respect to each reactant has been found, the results are combined together in the form of a **rate equation**. For the iodination of propanone, we have the following results:

$$\text{rate} \propto [\text{I}_2]^0 \quad \text{rate} \propto [\text{H}^+]^1 \quad \text{rate} \propto [\text{CH}_3\text{COCH}_3]^1$$

These may be combined to give the following equation:

$$\text{rate} = k[\text{I}_2]^0[\text{H}^+]^1[\text{CH}_3\text{COCH}_3]^1$$

The constant k is known as the **rate constant**. Strictly speaking, it is not necessary to include the $[\text{I}_2]^0$ term (which is equal to 1), and the exponent '1' after $[\text{H}^+]$ and $[\text{CH}_3\text{COCH}_3]$ could be omitted. It is, however, sometimes useful to include these terms in the rate equation as they emphasise the effect of varying the concentration of each reactant.

The reaction is now described as follows. It is:

- zero order with respect to $[\text{I}_2]$
- first order with respect to $[\text{H}^+]$
- first order with respect to $[\text{CH}_3\text{COCH}_3]$
- of total order 2, or **second order overall**.

The total order is the sum of the exponents from the rate equation. In this case, the total order is:

$$0 + 1 + 1 = 2$$

Finding the rate constant

In order to work out a value for the rate constant, k , we can use a set of readings such as those in Table 21.2. For example, if we use the figures in experiment 1, including the units:

$$\begin{aligned} \text{rate} &= k[\text{I}_2]^0[\text{H}^+]^1[\text{CH}_3\text{COCH}_3]^1 \\ 2.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1} &= k \times 1 \text{ (no units)} \times 0.50 \text{ mol dm}^{-3} \times 0.50 \text{ mol dm}^{-3} \\ k &= \frac{2.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}}{1 \times 0.50 \times 0.50 \text{ mol}^2 \text{ dm}^{-6}} \\ &= 8.0 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \end{aligned}$$

The units for the rate constant depend on the total order of the reaction.

Units of k

- overall first-order reaction: s^{-1}
- overall second-order reaction: $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
- overall third-order reaction: $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

The first-order case is interesting because k has no units of concentration. This means that it can be determined directly from a change in a physical property such as volume or colour. As long as it is known that this property is proportional to the concentration, it is not necessary to use the actual concentration. For example, the rate of decomposition of hydrogen peroxide may be studied by measuring the volume of oxygen evolved, and the rate of bromination of methanoic acid by measuring the decrease in absorbance of the bromine. One key reading must be determined as accurately as possible; this is the final reading, when the reaction is complete. This enables us to construct a graph of how the concentration of a reactant (or the volume of gas, or the absorbance) decreases with time, which finishes at zero. Such a graph can be used to evaluate the rate constant for a first-order reaction (see Figures 21.9 and 21.10).

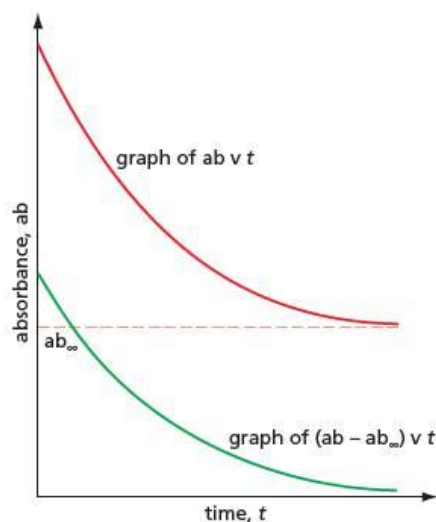


Figure 21.9 Graph showing how a property of a reactant, such as the absorbance, changes with time for a first-order reaction. The final reading ab_∞ may not be zero, so this value has to be subtracted from all the readings. An example is using a colorimeter to measure the decrease in absorbance of bromine as it reacts with methanoic acid.

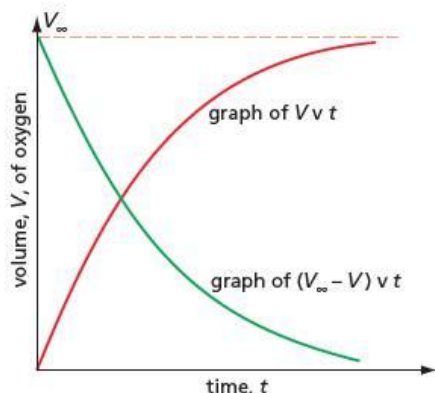


Figure 21.10 Graph showing how a property of a product, such as the volume of a gas, changes with time for a first-order reaction. The volume readings are each subtracted from the final volume to produce the required exponential curve. An example is the volume of oxygen produced during the decomposition of hydrogen peroxide.

These exponential 'concentration'–time graphs for first-order reactions can be used to find the half-life of the reaction, which is related to the rate constant by the following equation:

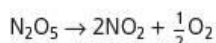
$$k = \frac{2.30 \log_{10} 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

The rate equation shows how the rate changes with the concentration of the reactants (and the concentration of a homogeneous catalyst, if one is present). The rate constant is unaffected by changes in these concentrations. That is why it is called a rate *constant*. If we exclude heterogeneous catalysts and light, the only factor that changes the value of a rate constant is temperature.

- The **rate constant** is the constant of proportionality in a rate equation.
- It is unaffected by changes in concentration.
- It changes with temperature.

Worked example

In tetrachloromethane at 45°C, dinitrogen pentaoxide, N_2O_5 , decomposes as follows:



The rate of the reaction was measured at different times. The results are shown in Table 21.3.

Table 21.3 Rates and reactant concentrations at different times. $1 \mu\text{mol} = 10^{-6} \text{ mol}$.

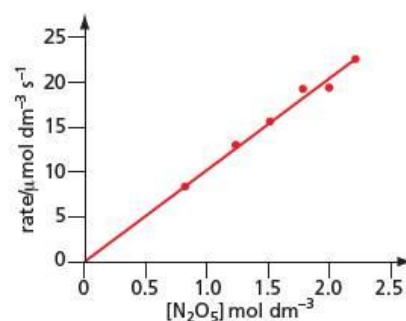
$[\text{N}_2\text{O}_5]/\text{mol dm}^{-3}$	2.21	2.00	1.79	1.51	1.23	0.82
Rate/ $\mu\text{mol dm}^{-3} \text{ s}^{-1}$	22.7	21.0	19.3	15.7	13.0	8.3

- Suggest a method of following the reaction.
- Plot a graph of rate against $[\text{N}_2\text{O}_5]$.
- Use your graph to find the order of the reaction with respect to N_2O_5 .
- Calculate the rate constant, giving its units.
- What will be the shape of the graph of $[\text{N}_2\text{O}_5]$ against time?

Answer

- Either measure the volume of oxygen given off, or measure the absorbance, since nitrogen dioxide is coloured.
- See Figure 21.11.

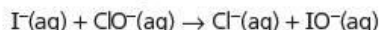
Figure 21.11



- The graph is a straight line passing through the origin, so the reaction is first order.
- Rate = $k[\text{N}_2\text{O}_5]$ so $k = \frac{\text{rate}}{[\text{N}_2\text{O}_5]}$ = gradient of graph = $1.0 \times 10^{-5} \text{ s}^{-1}$
- The graph will show an exponential decay with a constant half-life.

Now try this

In alkaline solution, iodide ions react with chlorate(I) ions as follows:



The reaction can be followed by measuring the absorbance of $\text{IO}^-(\text{aq})$ ions at 400 nm in a colorimeter. Table 21.4 shows a series of measured initial rates.

Table 21.4

Experiment number	$[\text{I}^-(\text{aq})]/\text{mol dm}^{-3}$	$[\text{ClO}^-(\text{aq})]/\text{mol dm}^{-3}$	Initial rate/ $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.0010	0.00073	4.5×10^{-5}
2	0.0010	0.0010	6.2×10^{-5}
3	0.0010	0.0014	8.7×10^{-5}
4	0.00073	0.0010	4.6×10^{-5}
5	0.0014	0.0010	8.6×10^{-5}

- 1 Calculate the order of the reaction with respect to $\text{I}^-(\text{aq})$ ions and $\text{ClO}^-(\text{aq})$ ions. Explain your answer.
- 2 Write a rate equation for the reaction.
- 3 Calculate the rate constant, stating the units.

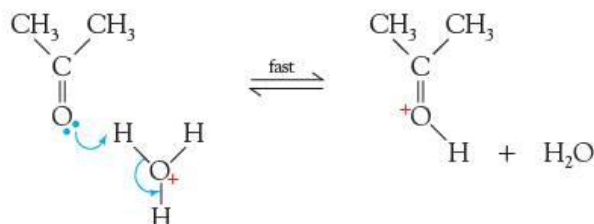
21.4 Reaction mechanisms

Proposing a mechanism

The rate equation is often used as a basis for suggesting a likely mechanism for the reaction. Most reactions can be broken down into a number of steps, one of which has a high activation energy that determines the overall rate of the reaction. This step is called the **rate-determining step**. An analogy is a group of people buying a paper at the local newsagent. If one person arrives, it takes them 1 second to pick up the paper, 10 seconds to pay for it and 1 second to leave the shop. If ten people arrive at the same time, it takes 10 seconds for them all to pick up their paper and 100 seconds for them all to pay, but they still take only 1 second each to leave the shop. There will be a queue to pick up the paper and at the checkout, but not on the way out of the shop. Any step that takes place after the rate-determining step has no effect on the overall rate. In the rate equation for the iodination of propanone,

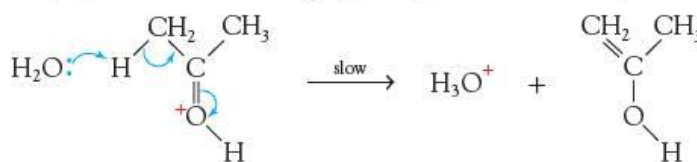
$$\text{rate} = k[\text{I}_2]^0[\text{H}^+]^1[\text{CH}_3\text{COCH}_3]^1$$

iodine does not appear in the rate equation, so any step involving iodine must come after the rate-determining step. It is also reasonable to conclude that the first step is the reaction of a proton with propanone, as both H^+ and CH_3COCH_3 appear as first-order terms in the rate equation. This reaction is an acid–base reaction. Such reactions are usually fast and reversible (H^+ exists as H_3O^+ in aqueous solution). So we write:

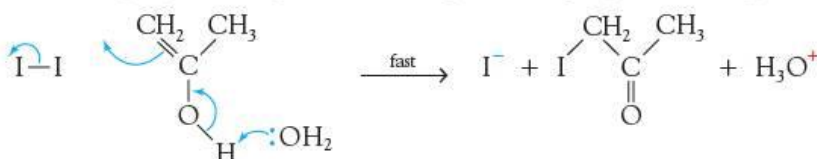


The second step, involving the breaking of a C—H bond, probably controls the rate of the reaction: C—H bond breaking is known to be much slower than O—H bond breaking. In this step, a water molecule could act as a base, taking a proton off the

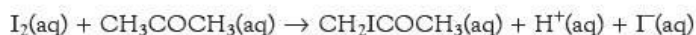
protonated propanone and re-forming H_3O^+ . A possible second step is therefore:



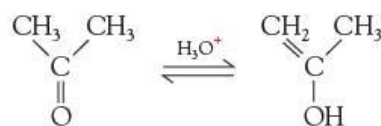
Iodine reacts rapidly with compounds containing the $\text{C}=\text{C}$ group, so a fast step follows:



Adding up all the individual steps in the mechanism, we arrive at the overall stoichiometric equation:

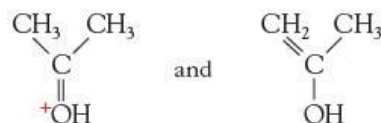


Mechanistically we can define a homogeneous catalyst as a substance that appears in the rate equation but not in the stoichiometric equation. If we consider just the first two steps, of which the second is the rate-determining step, H_3O^+ is a **homogeneous catalyst**.



Note, however, that the last of the three steps described above produces $\text{H}^+(\text{aq})$, which, as we have seen, is the catalyst for the first two steps. A reaction which produces its own catalyst like this is called **autocatalytic reaction**.

Substances such as:



are known as **intermediates**, because they are produced during the reaction but are not part of the final products.

Testing the mechanism

We have now put forward a *possible* mechanism for the reaction, which is consistent with the kinetic data. We do not yet know if this mechanism is the *most likely* one and so we need to carry out further experiments to confirm the mechanism. Some of the techniques used are listed below.

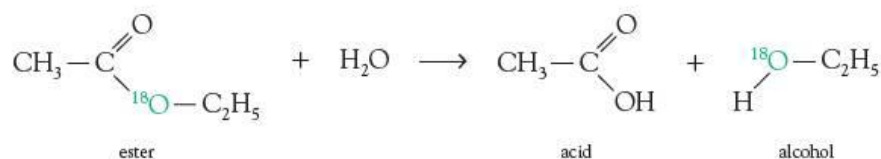
- **Use a wider range of concentrations** – the experimentally determined rate equation may hold over only a limited range of concentrations. For example, the proposed mechanism for the iodination of propanone predicts that at very low concentrations of iodine, the zero-order dependence of the iodine changes to first-order dependence. This is because the rate of the last reaction will be given by the expression:

$$\text{rate} = k'[\text{I}_2][\text{CH}_2=\text{C}(\text{OH})\text{CH}_3]$$

where k' is the rate constant for the third step shown above, and so this rate will decrease as $[\text{I}_2]$ decreases. At very low concentrations of iodine, the third step could

become so slow that it effectively becomes the rate-determining step. This has been shown to be the case, which fits in with the mechanism we have suggested above.

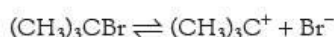
- **Use sophisticated analytic techniques** – these may be able to detect the presence of the suggested intermediates. The use of nuclear magnetic resonance (see Topic 29) shows that acidified propanone contains about one molecule in 10^6 of the enol form, $\text{CH}_2=\text{C}(\text{OH})\text{CH}_3$, an intermediate proposed by the mechanism.
- **Do experiments on the intermediates** – some intermediates are stable enough for experiments to be carried out on them. For example, some organic halides form tertiary carbocations (see section 14.3) that can be isolated.
- **Use isotopic labelling** – if an atom is labelled with an isotope (not necessarily a radioactive one), the label may indicate which bond has been broken in a reaction. For example, when some esters labelled with ^{18}O are hydrolysed, the ^{18}O appears in the alcohol and not in the acid group. This shows that the acyl oxygen bond, and not the alkyl oxygen bond, is the one that is broken:



- **Kinetic isotope effect** – deuterium behaves slightly differently from hydrogen; for example, the C—D bond is slightly harder to break than the C—H bond. This means that if this bond is broken during the rate-determining step, a compound containing C—D bonds reacts between 5 and 10 times as slowly as one with C—H bonds. This is the case with the iodination of propanone: CD_3COCD_3 reacts considerably more slowly than CH_3COCH_3 .

On the other hand, the fact that C_6H_6 and C_6D_6 nitrate at the same rate shows that the rate-determining step is the initial attack by the NO_2^+ ion (see section 25.3), and not the elimination of the proton.

- **Change the solvent** – the rate of ionic reactions changes with the polarity of the solvent. For example, the rate of hydrolysis of 2-bromo-2-methylpropane is raised by the addition of sodium chloride. The sodium chloride increases the polarity of the solvent and increases the ionisation of the bromide:



On the other hand, the addition of sodium bromide reduces the overall rate. This is because the ionisation of $(\text{CH}_3)_3\text{CBr}$ is suppressed by the high concentration of Br^- ions (Le Chatelier's Principle), and this can be larger than the positive effect caused by the increased polarity of the solvent.

No amount of experimental work can ever prove that the proposed mechanism is the correct one. In particular, the role of the solvent is always uncertain, as there is no way in which its concentration can be varied without changing the overall polarity.

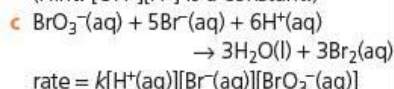
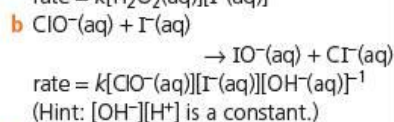
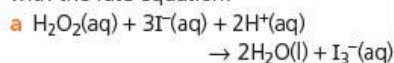
Order and molecularity

Some complex reactions have orders that are negative or fractional. Other reactions have an order that changes with concentration, and only a detailed mathematical treatment shows why this is so.

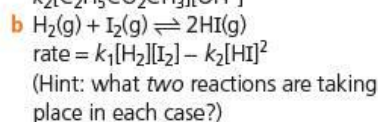
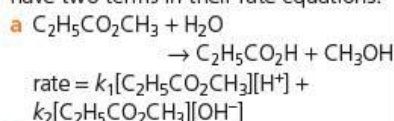
While the order of reaction may be non-integral, the molecularity of a reaction is integral. The **molecularity** is the number of species in the rate-determining step. This must be integral, probably 1 or 2. For many reactions, the order and molecularity are the same, and this can cause confusion between them.

Now try this

- 1 For each of the following reactions, suggest a mechanism that is compatible with the rate equation.



- 2 Suggest why the following reactions have two terms in their rate equations.



Worked example

Hydrogen cyanide, HCN, adds on to ethanal, CH_3CHO , to give CH_3CHOHCN . Two mechanisms have been proposed for this reaction:



or



The rate equation is $\text{rate} = k[\text{CN}^-][\text{CH}_3\text{CHO}][\text{H}^+]^0$.

- a Which mechanism is consistent with the rate equation? Explain your answer.
 b Which step in this mechanism is the rate-determining step?

Answer

- a Mechanism (1) is excluded because $[\text{H}^+]$ is in the first equation and so would appear in the rate equation. Mechanism (2) is consistent with the rate equation because the step involving H^+ appears after the rate-determining step.
 b The first step is the rate-determining step.

21.5 Reaction profiles

Intermediates and transition states

If we draw the reaction profile for a multi-step reaction such as that outlined in section 21.4, it is important to distinguish an **intermediate** (symbol **I**), which has an energy minimum, from a **transition state** (symbol **TS[‡]**), at the top of the energy curve, which has an energy maximum. An intermediate is a definite chemical species that exists for a finite length of time. A transition state has no permanent lifetime of its own – it exists for just a few femtoseconds (10^{-15}s) when the molecules are in contact with each other. Even a reactive intermediate, with a lifetime of only a microsecond, has a long lifetime in comparison with the time that colliding molecules are in contact.

A simple one-step reaction, for example the $\text{S}_{\text{N}}2$ hydrolysis of a primary halogenoalkane (see section 15.2), has a single energy maximum (see Figure 21.12).

Figure 21.12 The reaction profile for a one-step reaction. There is a single transition state at the energy maximum.

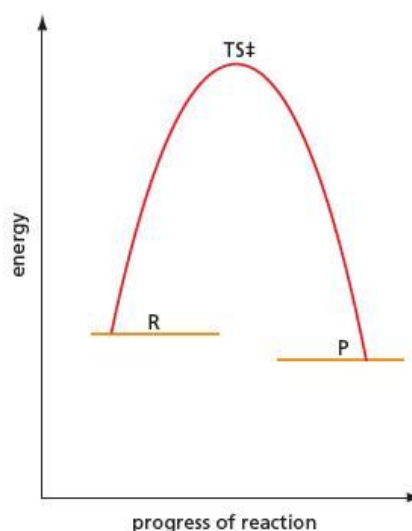
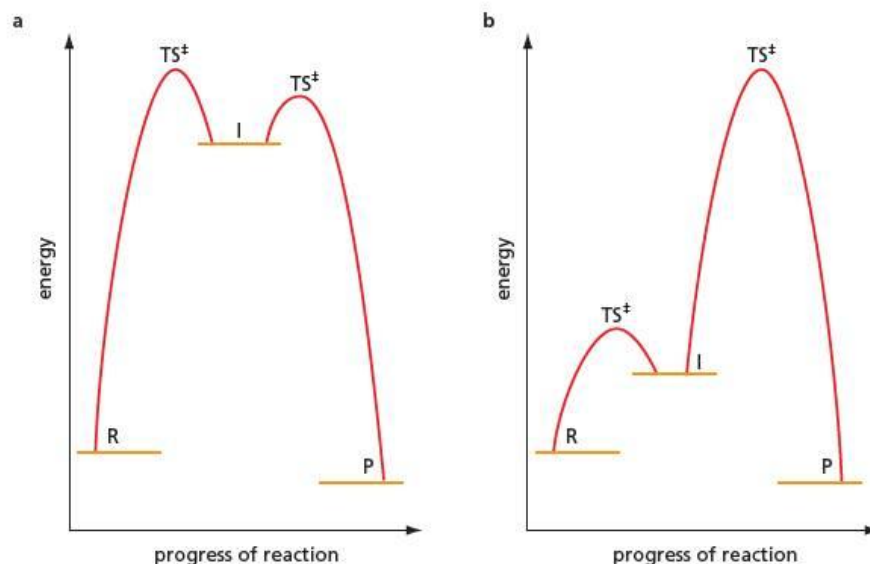


Figure 21.13 The reaction profile for a two-step reaction. There is an intermediate I and also two transition states. In **a**, the first step is rate determining; in **b**, the second step is rate determining.



If the reaction has two steps, on the other hand, there is an intermediate, I, and two transition states. An example is the hydrolysis of 2-bromo-2-methylpropane, which is an S_N1 reaction (see section 15.2). The first step is rate determining and so has the higher activation energy (see Figure 21.13a).

The structure of the transition state

It is possible to guess the structure of the transition state using **Hammond's postulate**. This states that the structure of the transition state will resemble that of the intermediate nearest to it in energy. In Figure 21.13a, the structures of the two transition states resemble that of the intermediate, I. In Figure 21.13b, the structure of the first transition state resembles that of the intermediate, while that of the second will be somewhere between that of the intermediate and the product.

While it is not possible to find the exact energy of the transition state except by experiment, some common-sense rules can be followed. For example, if the stage involves bond breaking, the activation energy is high, but if the stage is a reaction between ions of opposite charge, the activation energy is low.

Steps with high activation energy:

- between two neutral molecules
- between ions of similar charge
- if a bond breaks to form free radicals.

Steps with low activation energy:

- between two free radicals
- between ions of opposite charge
- acid–base reactions.

21.6 Some examples of catalysis

The Haber process

The Haber process produces ammonia by combining hydrogen gas with nitrogen gas. The temperature and pressure required to bring about the reaction are discussed in section 10.5, but it is also essential to use a catalyst. The catalyst is made of iron that has traces of potassium oxide and aluminium oxide in it. These impurities improve

the efficiency of the catalyst and are called **promoters**. Because the iron is a solid and is in a different phase from the reactants, which are gases, it is a **heterogeneous catalyst**. Because the reaction takes place on the surface of the catalyst, it is essential that the iron is finely divided so as to make the surface area as large as possible. This can be achieved by reducing powdered iron oxide with hydrogen to make the iron catalyst.

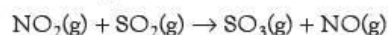
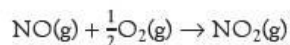
The way the catalyst works is not completely understood. It is thought that the hydrogen and nitrogen are adsorbed onto the surface of the iron, where the interatomic bonds are weakened sufficiently for the hydrogen atoms to add onto the nitrogen atoms in three steps. Breaking the nitrogen–nitrogen triple bond needs a lot of energy and is thought to be the rate-determining step.

The three-way catalytic converter

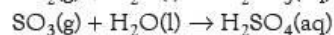
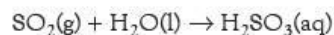
This has been covered in section 8.6, page 166.

Oxidation of sulfur dioxide: the formation of 'acid rain'

A mixture of sulfur dioxide and air is very slowly converted into sulfur trioxide. In the presence of oxides of nitrogen, the reaction proceeds rapidly, the nitrogen monoxide acting as a homogeneous catalyst by the following mechanism:



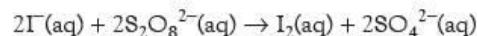
Sulfur dioxide dissolves in water to give sulfurous acid, which is a weak acid, but sulfur trioxide forms sulfuric acid, which is a strong acid:



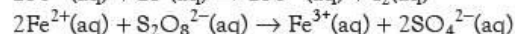
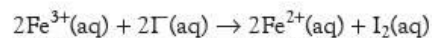
Being a strong acid, sulfuric acid attacks buildings much more rapidly than sulfurous acid. It is also much more damaging to plants because it makes the soil very acidic.

The iodide–peroxydisulfate(VI) reaction

Iodide reacts slowly with aqueous peroxydisulfate(VI) ions to produce iodine and sulfate ions:



The reaction is catalysed by the addition of some transition metal cations, for example $\text{Fe}^{3+}\text{(aq)}$:



Now try this

Considering ionic attractions and repulsions, explain why Fe^{3+} or Fe^{2+} speed up the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$, whereas VO_3^- , ClO^- and NO_3^- are not effective catalysts.

Summary

- The **rate** of a reaction is given by the following expressions:
 $\text{rate} = \frac{\Delta[\text{P}]}{\Delta t}$ or $\text{rate} = -\frac{\Delta[\text{R}]}{\Delta t}$
- The units of rate are $\text{mol dm}^{-3} \text{s}^{-1}$.
- The **order** of the reaction with respect to a reactant shows how the concentration of that reactant affects the rate of the reaction. The order for each reactant is found by experiment, and these orders are combined together in a **rate equation**.
- The proportionality constant in the rate equation is called the **rate constant**. The rate constant does not vary with concentration but it does vary with temperature.
- A **homogeneous catalyst** does not appear in the overall stoichiometric equation, but its concentration does appear in the rate equation.
- If the reactants and their coefficients in the rate equation are the same as those in the stoichiometric equation, the reaction may take place in a single step.
- If the reactants and their coefficients in the rate equation differ from those in the stoichiometric equation, the reaction takes place in more than one step.
- The step with the highest activation energy is the **rate-determining step**. The number of species that take part in the rate-determining step is known as the **molecularity** of the reaction.
- Reactants whose concentrations appear in the rate equation react before or at the rate-determining step. Reactants whose concentrations do not appear in the rate equation but do appear in the stoichiometric equation react after the rate-determining step.
- Transition states** are at the maxima in the energy profile of a reaction.
- Intermediates** are at the minima in the energy profile of a reaction.
- A **heterogeneous catalyst** is one that is in a different phase from the reactants. Heterogeneous catalysts are important in many well-known industrial reactions.

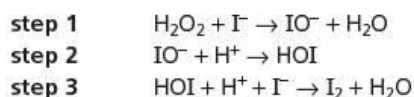
Examination practice questions

Please see the data section of the CD for any A_r values you may need.

- 1 In the late 19th century the two pioneers of the study of reaction kinetics, Vernon Harcourt and William Esson, studied the rate of the reaction between hydrogen peroxide and iodide ions in acidic solution.



This reaction is considered to go by the following steps.



The general form of the rate equation is as follows.

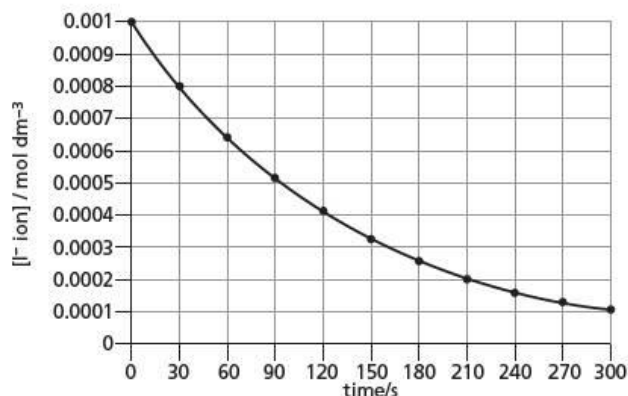
$$\text{rate} = k[\text{H}_2\text{O}_2]^a[\text{I}^-]^b[\text{H}^+]^c$$

- a Suggest how the appearance of the solution might change as the reaction takes place. [1]
 b Suggest values for the orders a , b and c in the rate equation for each of the following cases.

Case	Numerical value		
	a	b	c
step 1 is the slowest overall			
step 2 is the slowest overall			
step 3 is the slowest overall			

[3]

A study was carried out in which both $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$ were kept constant at 0.05 mol dm^{-3} , and $[\text{I}^-]$ was plotted against time. The following curve was obtained.



If you are aiming for a top-level grade you will need to draw relevant construction lines on the graph to show your working. Draw them using a pencil and ruler.

- c Calculate the initial rate of this reaction and state its units. [2]
 d Use half-life data calculated from the graph to show that the reaction is first order with respect to $[\text{I}^-]$. [2]

- e Use the following data to deduce the orders with respect to $[H_2O_2]$ and $[H^+]$, explaining your reasoning. [2]

$[H_2O_2]/\text{mol dm}^{-3}$	$[H^+]/\text{mol dm}^{-3}$	Relative rate
0.05	0.05	1.0
0.07	0.05	1.4
0.09	0.07	1.8

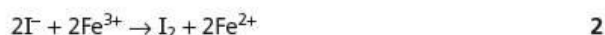
- f From your results, deduce which of the three steps is the slowest (rate-determining) step. [1]

[Cambridge International AS & A Level Chemistry 9701, Paper 4 Q2 November 2008]

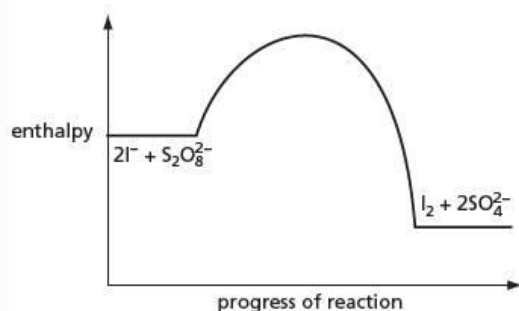
- 2 a The reaction between iodide ions and persulfate ions, $S_2O_8^{2-}$, is slow.



The reaction can be speeded up by adding a small amount of Fe^{2+} or Fe^{3+} ions. The following two reactions then take place.



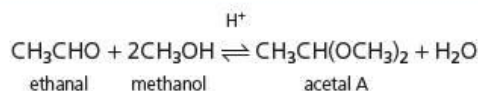
- What type of catalysis is occurring here?
- The rates of reactions 2 and 3 are both faster than that of reaction 1. By considering the species involved in these reactions, suggest a reason for this.
- The following reaction pathway diagram shows the enthalpy profile of reaction 1.



Use the same axes to draw the enthalpy profiles of reaction 2 followed by reaction 3 starting reaction 2 at the same enthalpy level as reaction 1. [4]

- b The oxidation of SO_2 to SO_3 in the atmosphere is speeded up by the presence of nitrogen oxides.
- Describe the environmental significance of this reaction.
 - Describe a major source of SO_2 in the atmosphere.
 - By means of suitable equations, show how nitrogen oxides speed up this reaction. [4]
- [Cambridge International AS & A Level Chemistry 9701, Paper 4 Q4 June 2009]

- 3 Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.



- a When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

Experiment number	$[CH_3CHO]/\text{mol dm}^{-3}$	$[CH_3OH]/\text{mol dm}^{-3}$	$[H^+]/\text{mol dm}^{-3}$	Relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.16	0.05	2.00
4	0.20	0.16	0.10	3.20

- Use the data in the table to determine the order with respect to each reactant.
- Use your results from part i to write the rate equation for the reaction.
- State the units of the rate constant in the rate equation.
- Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3} . [6]

- b The concentration of the acetal product was measured when experiment number 1 was allowed to reach equilibrium. The result is included in the following table.

	$[CH_3CHO]/\text{mol dm}^{-3}$	$[CH_3OH]/\text{mol dm}^{-3}$	$[H^+]/\text{mol dm}^{-3}$	[acetal A]/ mol dm^{-3}	$[H_2O]/\text{mol dm}^{-3}$
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	$(0.20 - x)$			x	
at equilibrium				0.025	

- Copy and complete the second row of the table in terms of x, the concentration of acetal A at equilibrium. You may wish to consult the chemical equation above.
 - Using the [acetal A] as given, $0.025 \text{ mol dm}^{-3}$, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table.
 - Write the expression for the equilibrium constant for this reaction, K_c , stating its units.
 - Use your values in the third row of the table to calculate the value of K_c . [9]
- [Cambridge International AS & A Level Chemistry 9701, Paper 41 Q2 November 2011]

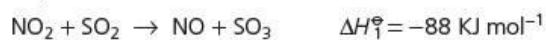
- 4 a Catalysts can be described as homogeneous or heterogeneous.

- What is meant by the terms *homogeneous* and *heterogeneous*?
- By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysis.

Choose **one** example of each type, and for **each** example you should

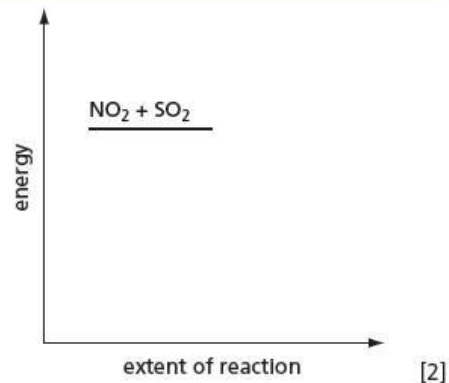
- state what the catalyst is, and whether it is acting as a homogeneous or a heterogeneous catalyst,
- write a balanced equation for the reaction,
- outline how the catalyst you have chosen works to decrease the activation energy. [8]

b The reaction between SO_2 , NO_2 and O_2 occurs in two steps.



The activation energy of the first reaction, E_{a1} , is higher than that of the second reaction, E_{a2} .

Construct a fully-labelled reaction pathway diagram for this reaction, labelling E_{a1} , E_{a2} , ΔH_1^\ominus and ΔH_2^\ominus .



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