IONIC COMPOUNDS ——— *tools for enthalpy calculations* ——— Born–Haber cycle

enthalpy change of solution (ΔH_{sol}): heat given out or taken in when one mole of a solute is dissolved into excess solvent to form a solution of infinite dilution

types of enthalpy change

Standard enthalpy change of atomisation (ΔH_{at}) is the enthalpy change when one mole of gaseous atoms is formed from an element under standard conditions.

1st electron affinity: heat given out when one electron is added to each atom in one mole of gaseous atoms

1st ionisation energy: heat taken in when one electron is removed from each atom in one mole of gaseous atoms

$\Delta H_{sol}(XY) = \Delta H_{latt} + \Delta H_{hyd}(X^+) + \Delta H_{hyd}(Y^-)$

lattice enthalpy (ΔH_{latt}): heat taken in when one mole of an ionic compound is broken apart into its constituent gaseous ions

is the result of electrostatic interactions between the ions

higher charge/smaller ions – higher lattice enthalpy

ΔH_{hyd} is more exothermic for more highly charged ions and smaller ions

ENTROPY, S ——— depends on the number of ways the available energy can be distributed among the particles ——— units: $J K^{-1} mol^{-1}$

gas > liquid > solid

$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

– if number of gas molecules increases: ΔS is +ve
– if number of gas molecules decreases: ΔS is −ve

SPONTANEOUS REACTIONS ——— occur without any outside influence

$\Delta G^{\ominus}$ is negative

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

If ΔS is positive, the reaction becomes more spontaneous as T increases.

If ΔS is negative, the reaction becomes less spontaneous as T increases.

ΔG = Gibbs free energy change ——— The value of ΔG is related to the position of equilibrium.
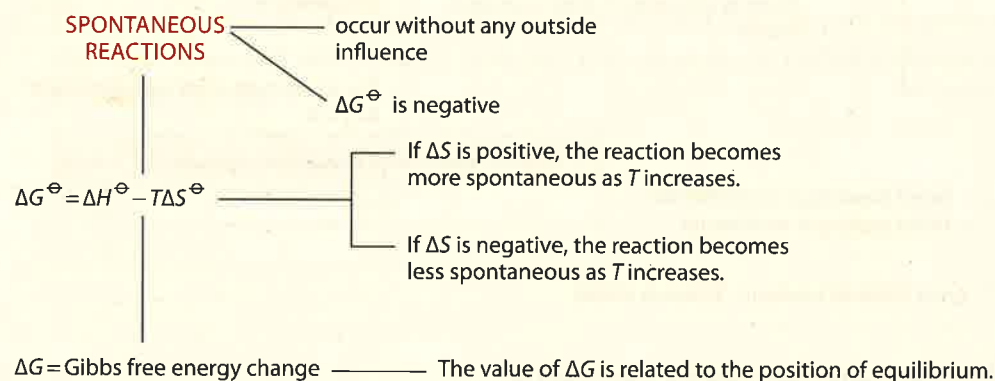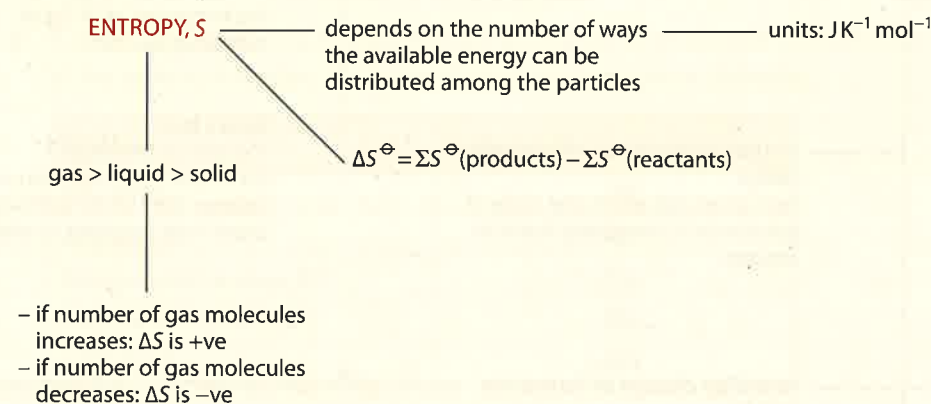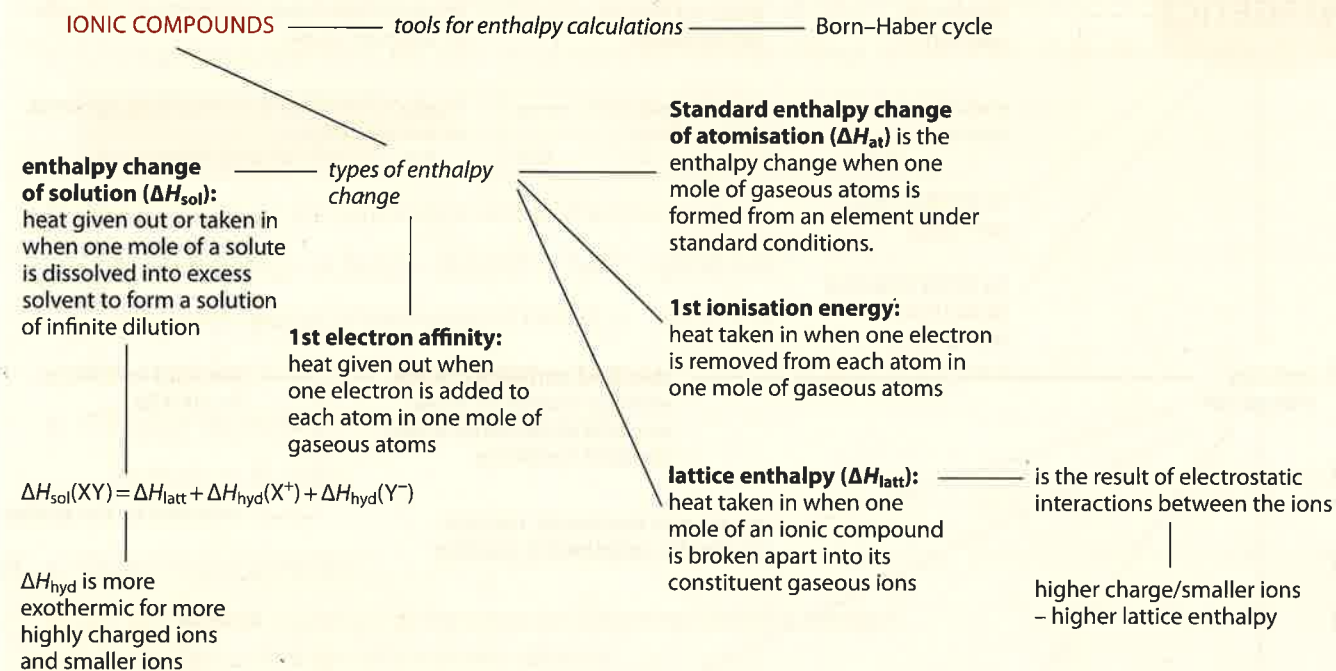
Chemical kinetics 6

6.1 Collision theory and rate of reaction

6.1.1 What is 'rate of reaction'?

When we consider the rate of a chemical reaction what we are looking at is how fast or slow the reaction is (Figures **6.1** and **6.2**). This can be thought of in terms of how quickly the reactants are used up or how quickly the products are formed.

> **Rate of reaction** is the speed at which reactants are used up or products are formed.

Experiments to measure the rate of reaction

Consider the reaction between calcium carbonate and hydrochloric acid:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

The rate of this reaction can be measured in various ways, two of which will be considered for this experiment:

1. measurement of the rate at which CO_2 is produced
2. measurement of the rate at which the mass decreases.

Measurement of the rate at which CO₂ is produced

The apparatus is set up as shown in Figure **6.3** without the calcium carbonate. The bung in the conical flask (Erlenmeyer flask) is removed, the calcium carbonate added, the bung quickly replaced and the timer started. This experiment can be used to generate a graph of volume of carbon dioxide produced against time by noting the volume on the measuring cylinder every ten seconds and then plotting the data. Sample data for this experiment are shown in Table **6.1**.
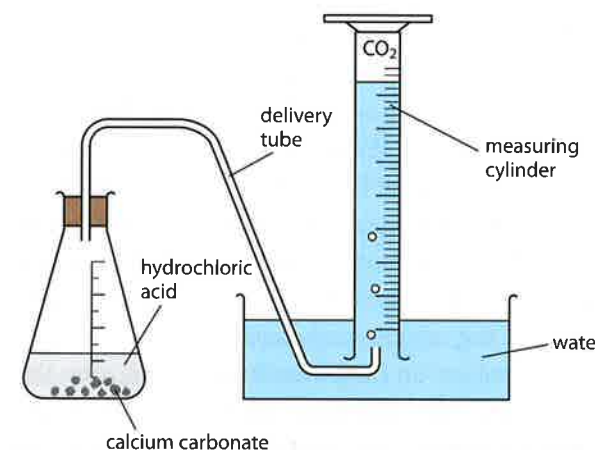

Figure 6.3 An experiment to measure rate of CO_2 production.

Learning objectives

- Understand what is meant by and define the rate of a chemical reaction
- Describe experimental methods for measuring the rates of various types of chemical reactions
- Analyse numerical and graphical data from rate experiments

Figure 6.1 Rusting is a very slow chemical reaction but one that costs economies billions of dollars each year.
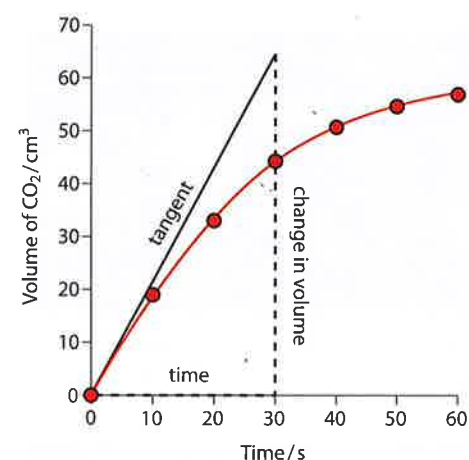

Figure 6.2 An explosion is a very fast reaction – gases and a great deal of heat are generated very quickly.

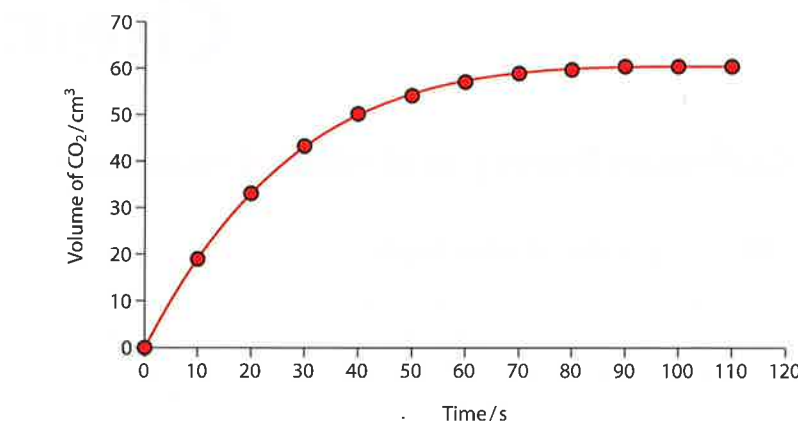> Instead of a measuring cylinder, a gas burette or a gas syringe could be used.

Time / s	Volume of CO_2 / cm^3
0	0.0
10	19.0
20	33.0
30	44.0
40	50.0
50	54.0
60	56.5
70	58.5
80	59.5
90	60.0
100	60.0
110	60.0

Table 6.1 Sample data for the experiment shown in Figure **6.3**.

Figure 6.4 Change in volume with time.

The reaction appears to finish at 90 s (Figure **6.4**) because no more gas is produced after that. The average rate of reaction during the first 90 s can then be worked out as:

$$\text{average rate} = \frac{\text{change in volume}}{\text{time}} = \frac{60.0}{90} = 0.67 \, cm^3 \, s^{-1}$$

The rate at any particular time is given by the slope (gradient) of the graph at that time. This can be worked out by drawing a tangent to the curve at that point (Figure **6.5**).

The gradient of the tangent is given by:

$$\text{gradient} = \frac{\text{change in volume}}{\text{time}} = \frac{64}{30} = 2.1 \, cm^3 \, s^{-1}$$

Therefore the initial rate of reaction is $2.1 \, cm^3 \, s^{-1}$, which means that, initially, the gas is being produced at a rate of $2.1 \, cm^3$ per second.

It can be seen from the graph in Figure **6.4** that the gradient decreases as time goes on – in other words, the rate is fastest at the beginning and gets slower. At 90 s, the reaction has stopped and the gradient of the graph is zero.

The volume of carbon dioxide produced can be used to calculate the concentration of hydrochloric acid in the flask at any time. The more gas that has been produced, the lower the concentration of the remaining hydrochloric acid. The actual concentration of acid at any time could be worked out using a moles calculation, assuming that the initial volume and concentration of the acid are known. These data could, then be used to plot a graph of concentration of hydrochloric acid against time.

Possible problems with experiments like this include the fact that some gas is likely to escape before the bung is put on the flask (resulting in all values for the volume of carbon dioxide being lower than expected) and variations in the sizes of the calcium carbonate pieces.

The same experimental set-up can be used for investigating the rate of reaction between magnesium and hydrochloric acid. This reaction is strongly exothermic and the reaction mixture becomes hotter during the experiment. This will cause the rate to be higher than expected.

Figure 6.5 The tangent is drawn at the initial point to determine the initial rate.

Measurement of the rate at which the mass decreases

The rate of this reaction can also be determined by measuring the speed at which the mass decreases. The experimental set-up for this is shown in Figure **6.6**. The mass decreases as carbon dioxide is given off. The data for this experiment are shown in Table **6.2**, along with the resulting graph in Figure **6.7**.
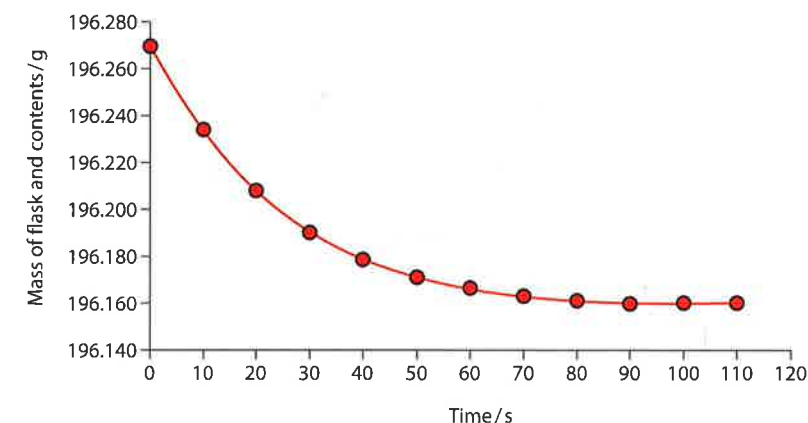
Figure 6.7 Change in mass with time.
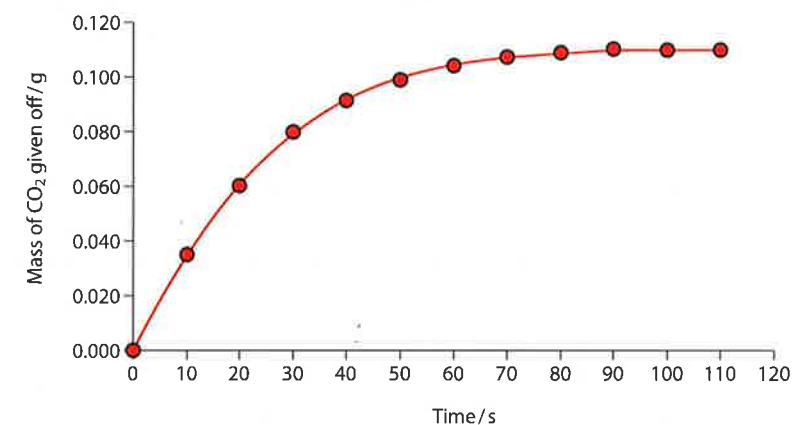

Figure 6.8 Loss in mass with time.

Alternatively, the mass of carbon dioxide lost can be worked out (196.270 − mass at any time, see Table **6.3**), and this can be plotted as shown in Figure **6.8**.

The average rate of reaction and initial rate of reaction can be worked out from either graph, using the same techniques as above. In this case we get:

$$\text{average rate} = \frac{\text{change in mass}}{\text{time}} = \frac{0.110}{90} = 1.22 \times 10^{-3} \, g \, s^{-1}$$

The initial rate is given by drawing a tangent at the initial point and in this case the initial rate is $4.0 \times 10^{-3} \, g \, s^{-1}$.

As above, the mass of carbon dioxide produced can be related to the concentrations of the hydrochloric acid or calcium chloride in the flask at any time and a graph of concentration against time could be plotted.
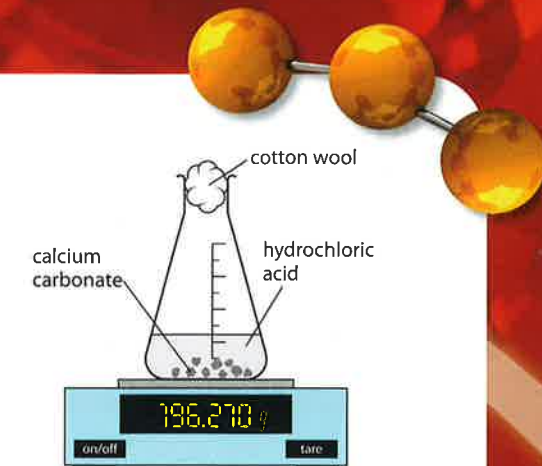
Figure 6.6 The cotton wool allows the gas to escape but stops mass being lost as a result of splashes.

Time / s	Mass of flask / g
0	196.270
10	196.235
20	196.210
30	196.189
40	196.178
50	196.171
60	196.166
70	196.163
80	196.161
90	196.160
100	196.160
110	196.160

Table 6.2 Sample data for the experiment shown in Figure **6.6**.

Time / s	Mass lost / g
0	0.000
10	0.035
20	0.060
30	0.081
40	0.092
50	0.099
60	0.104
70	0.107
80	0.109
90	0.110
100	0.110
110	0.110

Table 6.3 Calculating the carbon dioxide lost.

Rate of reaction defined

Although the above reactions were followed by looking at changes in volume and mass, rates are most often considered in terms of changing concentrations. We can define the rate of reaction:

Rate of reaction is the change in concentration of reactants or products per unit time.

Units for rate of reaction are therefore $mol\,dm^{-3}\,s^{-1}$, $mol\,dm^{-3}\,min^{-1}$, etc.

The average rate over a period of time can be worked out as:

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

For the reaction $A + B \rightarrow C$, the rate at which the reactants are used up is equal to the rate at which the products are produced, i.e. if the rate of reaction with respect to A is $0.12\,mol\,dm^{-3}\,s^{-1}$, the rate of reaction with respect to C will also be $0.12\,mol\,dm^{-3}\,s^{-1}$.

However, for the reaction $A \rightarrow 2D$, the rate at which D is produced will be twice the rate at which A is used up, because one mole of A will produce two moles of D. Therefore, if the rate of reaction with respect to A is $0.16\,mol\,dm^{-3}\,s^{-1}$, the rate of reaction with respect to D will be $0.32\,mol\,dm^{-3}\,s^{-1}$.

The rate of reaction at any time can be found from a graph of concentration against time by drawing a tangent at the particular time and finding the gradient (slope) of the tangent, in a similar way to that shown for a volume against time graph in Figure **6.5**.

Figure **6.9a** shows the how the concentration of A varies in the reaction $A \rightarrow 2D$. The initial rate of reaction can be determined from the gradient of the tangent shown ($\frac{2}{24} = 0.083\,mol\,dm^{-3}\,s^{-1}$). The graph in Figure **6.9b** shows how the concentration of the product, D, changes in the same reaction. The rate at 40 s can be determined from the graph using the tangent shown ($\frac{2}{76} = 0.026\,mol\,dm^{-3}\,s^{-1}$).

Unit time could be 1 s, 1 min, etc.
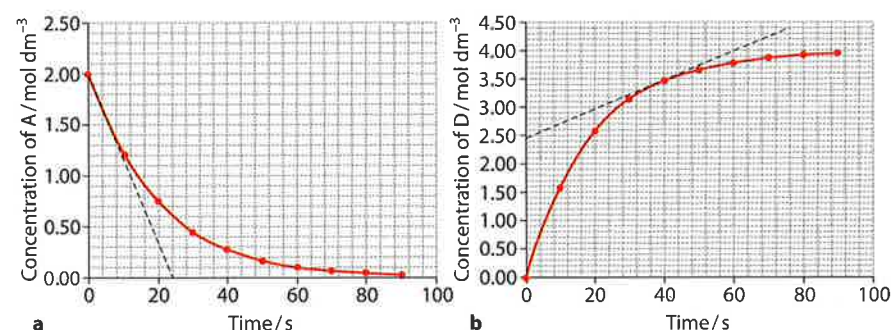
Figure 6.9 Graphs showing how the concentrations of **a** the reactant and **b** the product vary for the reaction $A \rightarrow 2D$.
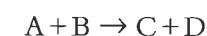
### Following the rate of a chemical reaction using changes in colour

The iodination of propanone in the presence of an acid catalyst can be followed conveniently using a colorimeter (Figure **6.10**) to monitor the changes in colour that occur as iodine is used up.

$$\underset{\text{propanone}}{CH_3COCH_3(aq)} + I_2(aq) \xrightarrow{H^+} \underset{\text{iodopropanone}}{CH_3COCH_2I(aq)} + H^+(aq) + I^-(aq)$$
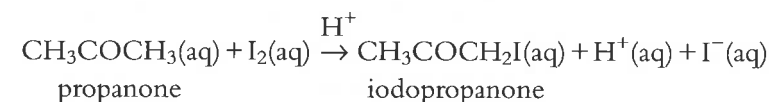
The iodine is brown and all the other species are colourless. The reaction mixture fades from brown to colourless as iodine is used up in the reaction and the decrease in the absorption of light can be measured using the colorimeter (Figure **6.11**).
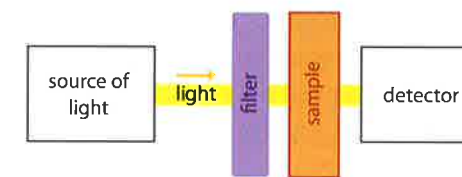
Figure 6.10 A colorimeter can be used to measure the amount of light absorbed at a particular wavelength – the darker the colour of the sample, the more light is absorbed.
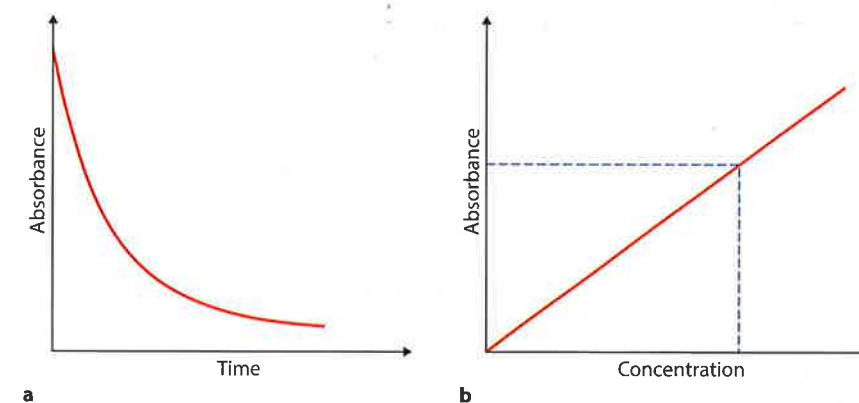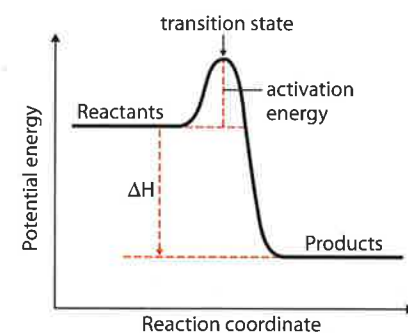
Figure 6.11 a The absorbance falls with time as iodine is used up. **b** A calibration curve is used to convert the absorbance of iodine to a concentration. It can be constructed by measuring the absorbance of several solutions of known iodine concentration.

Learning objectives

- Describe and explain the collision theory
- Define the activation energy of a reaction
- Understand the effects of surface area of solid reactants, temperature, catalysts, concentration and pressure on rate of reaction
- Understand that the average energy of particles in a gas is proportional to its temperature in kelvin
- Sketch the Maxwell–Boltzmann distribution and use it to explain the effect of a change in temperature on the rate of a reaction and how a catalyst speeds up a reaction

6.1.2 Collision theory

Particles must collide to react

Reaction rates are generally discussed in terms of **collision theory**. This states that for a reaction to occur particles must collide; however, for these collisions to result in a reaction, two conditions must be fulfilled:

- a collision must involve more than a certain **minimum amount of energy**
- molecules must collide with the **correct orientations**.

Note: not all collisions result in a reaction.

The collision must involve more than a certain minimum amount of energy

Particles must collide with sufficient energy in order to react. The minimum amount of energy that colliding particles must possess to result in a reaction is called the **activation energy (E_a)**. If two particles with less than the activation energy collide, they will just bounce off each other and no reaction will result; however, if the particles have energy greater than or equal to the activation energy then, assuming the orientation of the collision is also correct, the particles will react. A collision that results in a reaction is called a **successful** or **effective** collision.

Activation energy is the energy needed to overcome repulsions, to start breaking bonds, to deform molecules and to allow rearrangement of atoms, electrons etc.

The activation energy for an exothermic reaction is shown on the potential energy profile in Figure **6.12**.

Imagine the reaction between two particles, A and BC:

$$A + B-C \rightarrow A-B + C$$
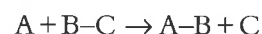
As the two particles approach, repulsion between the atoms (internuclear and between electrons) causes an increase in the potential energy. The B–C bond begins to break and the A–B bond begins to form. The highest point along the curve is called the **transition state** (activated complex) and all three atoms are joined together by partial bonds (A···B···C). As the A–B bond continues to form, the potential energy falls (remember, bond-making releases energy).

Figure 6.12 A potential energy profile, showing the activation energy for an exothermic reaction.

Molecules must collide with the correct orientation

If molecules do not collide with the correct orientation they will not react (Figure **6.13**).

Not every collision with energy greater than the activation energy results in a reaction.
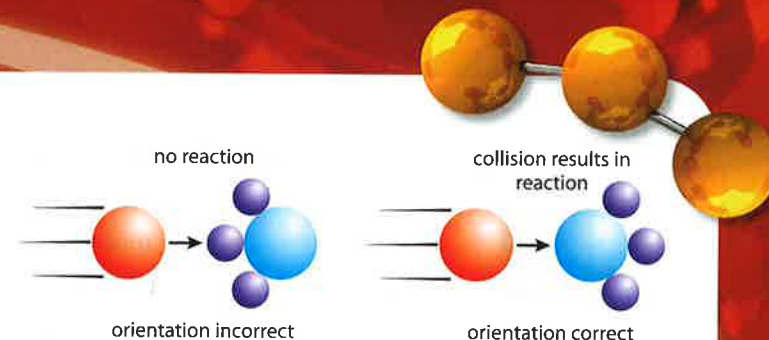
Figure 6.13 Orientation is important.

Factors affecting reaction rate

The main factors that affect the rate of a chemical reaction are:

- concentration of reactants
- pressure for (reactions involving gases)
- surface area of solid reactants
- temperature
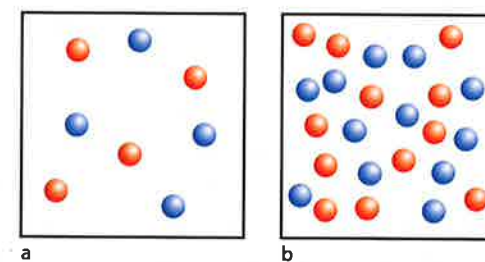- catalysis.

These will be considered in turn.

The effect of concentration on the reaction rate

With more particles in a certain volume, the particles collide more often (the collision frequency is higher) and therefore there is greater chance of a successful collision (i.e. one that results in a reaction) occurring in a certain time (Figure **6.14**).

The effect of pressure on the reaction rate

The effect of increasing the pressure is essentially the same as that of increasing the concentration of gaseous reactants. As the pressure is increased, the collision frequency increases (Figure **6.15**).

Only reactions involving gases are significantly affected by changing the pressure.

Exam tip

We are dealing here with how quickly a reaction occurs and you must therefore have the idea of **time** in your explanation – it is not correct here to say that 'the particles collide more' you must write something like 'the particles collide more often/more frequently' or 'there are more collisions in a certain time'.
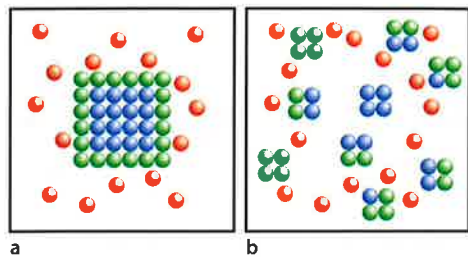
Figure 6.14 a Lower concentration – the particles are further apart and collide less frequently; **b** higher concentration – the particles are closer together and collide more frequently.
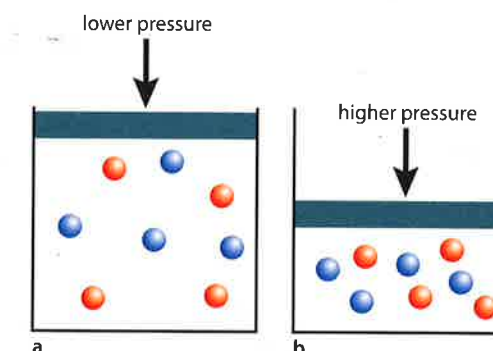
Figure 6.15 a Lower pressure – the particles are further apart and collide less frequently; **b** higher pressure – the particles are closer together and collide more frequently.

Figure 6.16 **a** Low surface area – only the particles coloured green are exposed on the surface and able to collide with the red particles; **b** high surface area – particles coloured both green and blue are exposed and are able to collide with the red particles.

Was temperature invented or discovered?

At the same temperature lighter particles travel faster than heavier ones.

kinetic energy $= \frac{1}{2}mv^2$
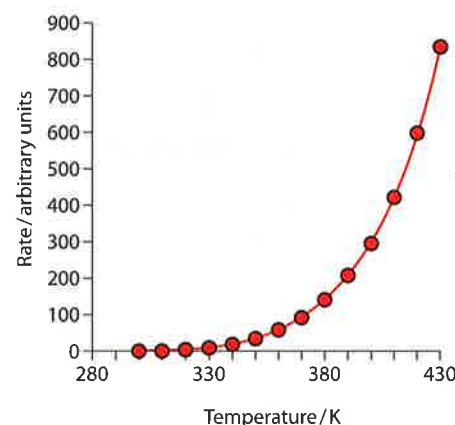
Figure 6.17 The rate of a reaction increases exponentially as the temperature rises.

The effect of surface area of solid reactants

Reactions generally only occur at the surface of a solid. Making a solid more finely divided increases the surface area and therefore the number of particles exposed at the surface. The effective concentration of the particles of the solid has thus been increased and there is a greater chance of a particle of the other reactant colliding with a particle on the surface and reaction occurring (Figure **6.16**).

The relationship between temperature and the energy of particles in a gas

Before we can understand the effect of temperature on the rate of a chemical reaction, we must look at how changing the temperature affects how the particles in a gas move.

For an ideal gas:

The average kinetic energy of the particles in a gas is proportional to its temperature in kelvin.

Therefore if a sample of oxygen is heated from 300 K to 600 K, the **average** energy of the particles is doubled.

This relationship does not depend on the identity of the gas. So the average kinetic energy of the particles in a sample of helium at 300 K is the same as the average kinetic energy of the particles in oxygen at 300 K. However, because the mass of an O_2 molecule is eight times the mass of a helium atom, the helium atoms will be travelling substantially faster at the same temperature.

A consequence of this relationship between temperature and kinetic energy is that a large increase in temperature is required for a significant increase in the average speed of the particles and hence in the collision frequency – you will see the importance of this in the next section.

The effect of temperature on rate of reaction

Increasing the temperature has a major effect on the rate of the reaction. As the temperature increases, the rate of reaction increases exponentially (Figure **6.17**).

It is often said that, as a rough rule of thumb, a rise in temperature of 10 K causes the reaction rate to be approximately doubled.
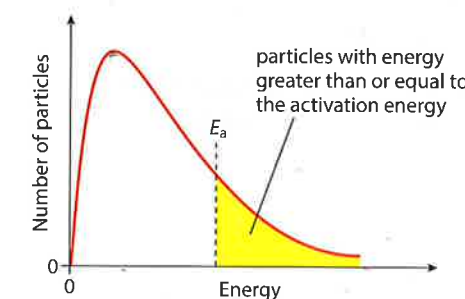
As the temperature increases, the molecules have more energy and therefore move faster. This means that the collision frequency increases, i.e. the particles collide more often. This is, however, only a minor effect and can explain only a small increase in rate (approximately 2% for a 10 K rise in temperature) as the temperature increases. The major cause of the increase in rate as the temperature increases is that, not only do the particles collide more often, but they also collide harder, that is, with more energy, so that there is greater chance that a collision will result in reaction.

Let us consider a sample of gas – the molecules are constantly colliding with each other and, therefore, do not all have the same speed and hence energy. This is shown in Figure **6.18**, which represents the **Maxwell–Boltzmann distribution** of molecular kinetic energies at a particular temperature. It can be seen that there are only a few particles with high energy and only a few with very low energy. Most particles have energy around the average.

Features to note on Figure **6.18**:

- it is **not** symmetrical
- no molecules have zero kinetic energy
- at higher energy the line does not reach the energy axis
- the area under the curve represents the total number of particles and will not change as the temperature changes.
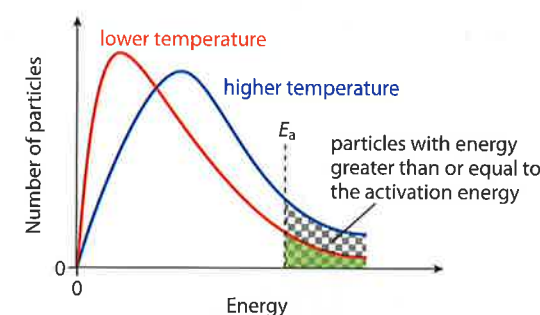
The vertical axis could be labelled as 'number of particles with a certain amount of energy' or 'proportion of particles with a certain amount of energy'.

The main reason that the rate of reaction increases with temperature is an increase in the number of particles with energy greater than or equal to the activation energy.

As the temperature is increased, this distribution of energies changes (Figure **6.19**). At higher temperatures the curve is flatter and the maximum has moved to the right. So there are fewer particles with lower energy and more particles with higher energy. With more particles having energy greater than or equal to the activation energy (E_a) at the higher temperature, a greater proportion of collisions will be successful, and therefore the rate of reaction will increase. The areas underneath the curves are the same because the number of particles (amount of substance) does not change if the temperature is increased.

Figure 6.18 The Maxwell–Boltzmann distribution of the energy of the particles in a sample of gas. The shaded area represents the particles that have sufficient energy to react when they collide.

Extension

The graph in Figure **6.19** is actually a histogram, where each bar in the histogram represents the number of molecules in a certain narrow range of kinetic energies.

Figure 6.19 The shaded area represents the number of particles with energy greater than or equal to the activation energy at the lower temperature. The checked area represents the number of particles with energy greater than or equal to the activation energy (E_a) at the higher temperature.

How do we know when we encounter a new reaction that the rate will increase when we increase the temperature? This comes from the idea of inductive reasoning – inductive reasoning is a fundamental tool of scientists, and to a certain extent chemistry would not exist in the form it does without inductive reasoning. Inductive reasoning allows us to generalise from the specific – for instance, if we carry out a series of experiments and each one gives us the result that increasing the temperature increases the rate of reaction, then we postulate a general law that the rate of reaction increases with temperature. How is it possible to do this when we have not studied every single chemical reaction? Indeed, a philosopher would say that this is not rational and there is no logical basis for being able to do this – this is the problem with induction. Common sense, however, would tell us that the rate of reaction for every simple reaction should increase as temperature increases – we rely on the uniformity of nature and we cannot imagine a situation in which it would not be true. But can we know this, or only believe it to be true? Is there a difference between a scientist having faith in induction and religious faith?

Catalysis

> A **catalyst** is a substance that increases the rate of a chemical reaction without itself being used up in the reaction.
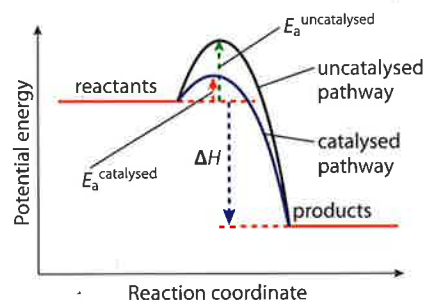
An example of a catalyst is manganese(IV) oxide in the decomposition of hydrogen peroxide solution:
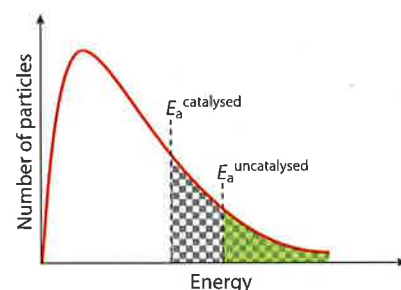
$$2H_2O_2(aq) \xrightarrow{MnO_2} 2H_2O(l) + O_2(g)$$
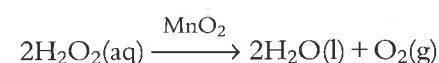
Without the catalyst the reaction occurs very slowly, but it is very rapid once the catalyst has been added.

> A **catalyst acts by allowing the reaction to proceed by an alternative pathway of lower activation energy.**

This is shown on the potential energy profile in Figure **6.20**.
If we look at the Maxwell–Boltzmann distribution we can understand why a lower activation energy results in a faster reaction (Figure **6.21**).

The catalyst is often written above the reaction arrow and does not appear in the chemical equation because it does not change in the reaction.

Catalysts are important in many industrial processes.

Higher Level only: the mechanism is different for a catalysed reaction (see page **264**).

Figure 6.20 Effect of a catalyst on the activation energy of a reaction.


Figure 6.21 The shaded area represents the number of particles with energy greater than or equal to the activation energy for the uncatalysed reaction. The checked area represents the number of particles with energy greater than or equal to the activation energy for the catalysed reaction. A larger number of particles have energy greater than the activation energy; therefore a greater proportion of collisions results in reaction and the reaction rate increases.

Nature of science

Although collision theory is consistent with experimental results, this does not prove that the theory is correct. The mark of a scientific theory, and what distinguishes it from a non-scientific one, is the idea of falsifiability – so far, collision theory has been supported by experimental evidence, but if new experimental data are produced that cannot be explained using the current collision theory, then the theory will have to be modified or dismissed in favour of a new theory that does explain all the available experimental data. Collision theory is the best explanation (at this level) of the experimental data produced so far. Other explanations may be possible, but this interpretation of the results is widely accepted at the moment, and the theory is used to make predictions and explain phenomena.

? Test yourself

1 A series of experiments was carried out to measure the volume of gas produced when magnesium reacts with dilute hydrochloric acid. The equation for the reaction is:

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$
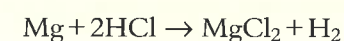
In the first experiment, $0.10\,g$ of Mg ribbon was reacted with $30\,cm^3$ of $0.50\,mol\,dm^{-3}$ HCl. The data for this experiment are recorded in the table. The reaction was carried out at $20\,°C$.

a Draw a graph of these data and state and explain, in terms of the collision theory, how the rate of reaction changes with time.

b Use your graph to calculate the initial rate of the reaction with units.

c Calculate the average rate for the first $120\,s$.

d The experiment was repeated under the same conditions, except that $0.10\,g$ of powdered Mg were used. On the same set of axes you used in part **a**, sketch the graph that would be obtained. Label this graph **X**.

e The original experiment was repeated, except that $0.05\,g$ of Mg ribbon was used. On the same axes sketch the graph that would be obtained. Label this graph **Y**.

f The original experiment was repeated at $10\,°C$. On the same axes sketch the graph that would be obtained. Label this graph **Z**.

g Sketch the Maxwell–Boltzmann distribution for the original experiment and the experiment at $10\,°C$ and use this to explain the effect of a change in temperature on the rate of this reaction.

Time / s	Volume of gas / cm³
0	0.0
15	18.6
30	32.3
45	44.3
60	54.8
75	62.7
90	68.4
105	72.6
120	74.9
135	75.4
150	75.6
165	75.6
180	75.6

Learning objectives

- Explain the terms rate constant and order of reaction
- Work out the rate expression (rate equation) from numerical data and solve problems related to it
- Sketch and explain graphs of concentration against time and rate against time for zero-, first- and second-order reactions
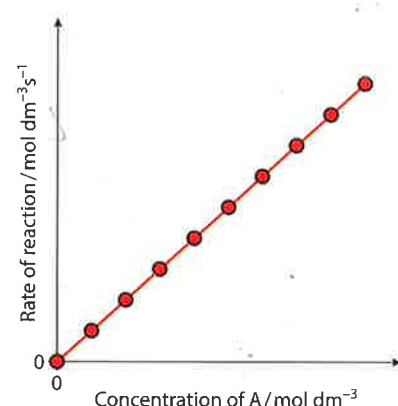

Figure 6.22 Possible rate-concentration graph for a reaction A → B.

A rate equation is also called a rate law.

Note: small k – not capital.

6.2 Rate expression and reaction mechanism (HL)

6.2.1 The rate equation/rate expression

In this section, we will consider the quantitative effect of changes in conditions on the rate of reaction.

A rate of reaction is usually affected by a change in concentration of the reactants. Consider the reaction A → B. If a series of experiments is carried out in which the concentration of A is varied and the rate of reaction measured, a graph like the one in Figure **6.22** might be plotted.

From this graph it can be seen that the rate of reaction is directly proportional to the concentration of A. For this reaction we can write:

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

where [A] is the concentration of A. By adding a constant of proportionality, we can write:

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

This equation is called a **rate equation** or **rate expression** – k is called the **rate constant**.

> The rate equation is an **experimentally determined** equation that relates rate of reaction to the concentrations of substances in the reaction mixture.

We can write a rate equation for any reaction. For example, for the reaction:

$$W + X \rightarrow Y + Z$$
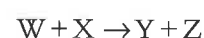
we can write:

> $$\text{rate} = k[W]^m[X]^n$$

> The **rate constant** is a constant of proportionality relating the concentrations in the experimentally determined rate equation to the rate of a chemical reaction.

The rate constant is only a constant for a particular reaction at a particular temperature.

> The **order of a reaction** with respect to a particular reactant is the power of the reactant's concentration in the experimentally determined rate equation.

In the rate equation above, the order with respect to W is m and the order with respect to X is n. The overall order is $m + n$.

If we consider our original rate equation, rate = $k[A]$, again: this reaction is **first order with respect to A** (the power of [A] is 1) and first order overall.

A rate equation can be determined only from experimental data – that is, from a series of experiments in which the effect of changing the concentration of the reactants on the rate of reaction is investigated. The important thing to realise is that there is no connection between the chemical (stoichiometric) equation for a reaction and the rate equation – i.e. we can not simply look at an equation such as $2A + B \rightarrow C + D$ and deduce that the order with respect to A is two and that with respect to B is one. The reason for this is that the reaction may not occur in one single step – this will be considered in more detail below.

The order of a reaction with respect to a particular reactant or overall order may have an integral or fractional value. Fractional orders are only found in complex reactions, for instance the pyrolysis of ethane to ethene and hydrogen:

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

involves a complex chain reaction and has a rate equation of the form: rate = $k[C_2H_6]^{\frac{1}{2}}$

Experimental determination of a rate equation

Consider the reaction A + B → C. The dependence of the reaction rate on the concentrations of A and B can be determined by conducting the following set of experiments.

First, a series of experiments is carried out using a fixed amount of B and changing the concentration of A each time. Each experiment should yield a graph of concentration of A against time. The initial rates can be worked out from these graphs by drawing tangents at the initial points. From these data the order of the reaction with respect to A can be determined by plotting a graph of initial rate against concentration of A.

Next, the experiments are repeated using a fixed amount of A and varying the concentration of B. This allows the order of reaction with respect to B to be calculated.

When the orders with respect to A and B are known, the rate equation, and hence a value for the rate constant, can be worked out.

6.2.2 Determining the order of reaction and the rate expression from experimental data

Example

Consider the data for the reaction 2A → B, given in Table **6.4**. We want to determine:

> An **overall order of reaction** is the sum of the powers of the concentration terms in the experimentally determined rate equation.

Exam tip
Remember that the rate equation can be determined only from experimental data and not from the chemical (stoichiometric) equation.

The initial rate is taken because this is the only point at which we know the concentration of A and concentration of B – none has been used up.

Experiment	[A]/ mol dm^{-3}	Rate/ mol dm^{-3} s^{-1}
1	1.0	0.60
2	2.0	1.2
3	5.0	3.0

Table 6.4 Experimental data for the reaction $2A \rightarrow B$.

Because the order with respect to A is 1, the order is omitted from the rate equation.

This could also have been worked out by realising that the reaction is first order with respect to A, and that 1.3 mol dm^{-3} is 1.3 times the concentration of A in experiment 1, and therefore the rate of reaction is 1.3^1 times the rate of reaction in experiment 1.

1 the order with respect to A
2 the rate equation
3 the value of the rate constant (with units)
4 the rate of reaction when $[A] = 1.3$ mol dm^{-3}.

1 If we consider experiments 1 and 2, we can see that as the concentration of A is doubled from 1.0 mol dm^{-3} to 2.0 mol dm^{-3}, the rate of reaction also doubles from 0.60 mol dm^{-3} s^{-1} to 1.2 mol dm^{-3} s^{-1}. So concentration is multiplied by a factor of two and the rate goes up by a factor of 2^1. This means that the order with respect to A is one – in other words, the reaction is first order with respect to A. This can be summarised:

The fact that the order of reaction with respect to A is 1 can be further confirmed by looking at experiments 1 and 3. As the concentration of A is multiplied by a factor of five, the rate of reaction is multiplied by a factor of 5^1.

2 The reaction is first order with respect to A, so the rate equation is:
rate $= k[A]$

3 To find the value of k, we substitute the values from any of the experiments into the rate equation. If this is done using the values from experiment 1, we get:

$$0.60 = k \times 1.0$$

This can be rearranged to give $k = 0.60$.

k has units, and these can be worked out by substituting units into the rate equation:

$$\text{rate} = k[A] \quad \rightarrow \quad \text{mol dm}^{-3}\,\text{s}^{-1} = k \times \text{mol dm}^{-3}$$

'mol dm^{-3}' can be cancelled from each side:

$$\cancel{\text{mol dm}^{-3}}\,\text{s}^{-1} = k \times \cancel{\text{mol dm}^{-3}}, \text{ so } \text{s}^{-1} = k$$

Therefore the units of k are s^{-1} in this case, and the rate constant is $0.60\,\text{s}^{-1}$.

4 The rate of reaction when $[A] = 1.3$ mol dm^{-3} can be worked out by substituting this value into the rate equation along with the value of k:

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

$$\text{rate} = 0.60 \times 1.3$$

The rate of reaction is 0.78 mol dm^{-3} s^{-1}.

Worked examples

Experiment	[A]/mol dm^{-3}	[B]/mol dm^{-3}	Rate/mol dm^{-3} h^{-1}
1	0.10	0.10	0.50
2	0.30	0.10	4.50
3	0.30	0.20	4.50

6.1 Given these data for the reaction $3A + B \rightarrow C + D$ determine:

a the order with respect to A

b the order with respect to B

c the overall order of the reaction

d the rate equation

e the value of the rate constant (with units)

f the rate of reaction when $[A] = 1.60$ mol dm^{-3} and $[B] = 0.30$ mol dm^{-3}

a To find the order with respect to A, we must consider experiments 1 and 2, because the only thing that changes in these two experiments is the concentration of A (the concentration of B remains constant). From experiment 1 to experiment 2, the concentration of A is multiplied by a factor of three and the rate goes up by a factor of nine, which is 3^2. This means that the order with respect to A is two – the reaction is second order with respect to A.

b To find the order with respect to B, we must consider experiments 2 and 3, because the only thing that changes in these two experiments is the concentration of B (the concentration of A remains constant). From experiment 2 to experiment 3, the concentration of B is multiplied by a factor of two and the rate does not change, i.e. it is multiplied by a factor of 2^0. This means that the order with respect to B is zero – the reaction is zero order with respect to B.

Any number to the power zero is one.

c The overall order of reaction is the sum of the orders with respect to A and B – in this case $2 + 0$. Therefore the overall order is 2.

d The rate equation is: rate $= k[A]^2[B]^0$, which is usually just written as: rate $= k[A]^2$.

e The value of the rate constant can be calculated by substituting values from any experiment into the rate equation. It doesn't matter which experiment is taken, but values must not be taken from different experiments. If we use the data from experiment 2:

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

$$4.50 = k \times 0.30^2$$

$$k = 50$$

To work out the units for k, the units of concentration and rate are substituted into the rate equation:

$$\text{mol dm}^{-3}\text{h}^{-1} = k(\text{mol dm}^{-3})^2$$

mol dm^{-3} can be cancelled from each side:

$$\cancel{\text{mol dm}}^{-3}\text{h}^{-1} = k(\text{mol dm}^{-3})^{\cancel{2}}$$

$$\text{h}^{-1} = k \, \text{mol dm}^{-3}$$

This can be rearranged to give:

$$\frac{\text{h}^{-1}}{\text{mol dm}^{-3}} = k$$

i.e. $k = \text{mol}^{-1}\text{dm}^3\text{h}^{-1}$

> Alternatively, at this stage it can be seen that the units of k must include $\text{mol}^{-1}\text{dm}^3$ for the powers of mol and dm to be zero on both sides.

> When a quantity with a power is brought from the bottom to the top of an expression, the sign of the power changes, i.e. $\frac{1}{x^2}$ is equivalent to x^{-2}.

Therefore the value of the rate constant, k, is $50 \, \text{mol}^{-1}\text{dm}^3\text{h}^{-1}$.

> It is good practice to write any positive powers first, so this is better written as $50 \, \text{dm}^3\text{mol}^{-1}\text{h}^{-1}$.

f The rate of reaction when $[A] = 1.60 \, \text{mol dm}^{-3}$ and $[B] = 0.30 \, \text{mol dm}^{-3}$ can be worked out by substituting these values together with the value of k into the rate equation:

$$\text{rate} = k[A]^2 = 50 \times 1.60^2 = 128 \, \text{mol dm}^{-3}\text{h}^{-1}.$$

6.2 Given these data for the reaction $2P + Q \rightarrow R + S$ determine:

Experiment	[P]/mol dm⁻³	[Q]/mol dm⁻³	Rate/mol dm⁻³ s⁻¹
1	1.20	2.00	5.00×10^3
2	2.40	2.00	1.00×10^{-2}
3	6.00	8.00	0.100

a the order with respect to P
b the order with respect to Q
c the overall order of the reaction
d the rate equation
e the value of the rate constant (with units)

a To find the order with respect to P, we must consider experiments 1 and 2, because the only thing that changes in these two experiments is the concentration of P (the concentration of Q remains constant). From experiment 1 to experiment 2, the concentration of P is multiplied by a factor of two and the rate goes up by a factor of two, i.e. 2^1. This means that the order with respect to P is one – the reaction is first order with respect to P.

b It is a more difficult problem to find the order with respect to Q because there are no two experiments in which the concentration of P remains constant, and so we cannot easily see how just changing [Q] affects the rate. One way of getting around this is to add another row to the table:

Experiment	[P]/mol dm⁻³	[Q]/mol dm⁻³	Rate/mol dm⁻³ s⁻¹
1	1.20	2.00	5.00×10^{-3}
2	2.40	2.00	1.00×10^{-2}
2A			
3	6.00	8.00	0.100

We can fill in the values in this new row by realising that the order with respect to P is one. If the concentration of P in experiment 2A is five times that in experiment 1, and because [Q] is the same in both experiments, the rate in experiment 2A will be $5 \times 5.00 \times 10^{-3}$ i.e. $2.50 \times 10^{-2} \, \text{mol dm}^{-3}\text{s}^{-1}$.

Experiment	[P]/mol dm⁻³	[Q]/mol dm⁻³	Rate/mol dm⁻³ s⁻¹
1	1.20	2.00	5.00×10^{-3}
2	2.40	2.00	1.00×10^{-2}
2A	**6.00**	**2.00**	**2.50×10^{-2}**
3	6.00	8.00	0.100

> The concentration of P has been chosen to be the same as that in experiment 3.

We can now consider experiments 2A and 3 and see the effect of just changing the concentration of Q on the rate of reaction. From experiment 2A to experiment 3, the concentration of Q is multiplied by a factor of four and the rate changes by a factor of 4^1. This means that the order with respect to Q is one.

Another way to approach this, without adding another row to the table, is to just consider experiments 1 and 3.

Experiment	[P]/mol dm⁻³	[Q]/mol dm⁻³	Rate/mol dm⁻³ s⁻¹
1	1.20	2.00	5.00×10^{-3}
2	2.40	2.00	1.00×10^{-2}
3	6.00	8.00	0.100

We know that going from experiment 1 to experiment 3 the concentration of P has increased by a factor of five. Because the reaction is first order with respect to P, the result of this will be to multiply the rate of reaction by a factor of 5^1. If this were done without any change in the concentration of Q, the rate of reaction would be $5 \times 5.00 \times 10^{-3}$, i.e. $2.50 \times 10^{-2} \, \text{mol dm}^{-3}\text{s}^{-1}$. However, the rate of reaction in experiment 3 is 0.100, which is four times 2.50×10^{-2}. Thus the effect of multiplying the concentration of Q by four is that the rate of reaction is multiplied by 4^1; therefore the order with respect to Q is one. This approach is, of course, equivalent to adding an extra row to the table.

c The order with respect to P is 1 and the order with respect to Q is 1, so the overall order is $1 + 1$, i.e. 2.

d The rate equation is: $\text{rate} = k[P]^1[Q]^1$, which is usually just written: $\text{rate} = k[P][Q]$.

e The value of the rate constant can be calculated by substituting values from any one experiment into the rate equation. If we use the data from experiment 3:

$$0.100 = k \times 6.00 \times 8.00$$

$$0.100 = k \times 48.0$$

$$k = 2.08 \times 10^{-3}$$

To work out the units for k, the units of concentration and rate must be substituted into the rate equation:

$$\text{mol dm}^{-3}\text{s}^{-1} = k \times \text{mol dm}^{-3} \times \text{mol dm}^{-3}$$

mol dm^{-3} can be cancelled from each side:

$$\cancel{\text{mol dm}}^{-3}\text{s}^{-1} = k \times \text{mol dm}^{-3} \times \cancel{\text{mol dm}}^{-3}$$

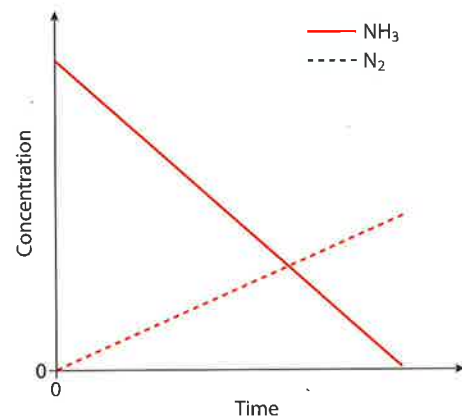So $\text{s}^{-1} = k \times \text{mol dm}^{-3}$.

This can be rearranged to give:

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

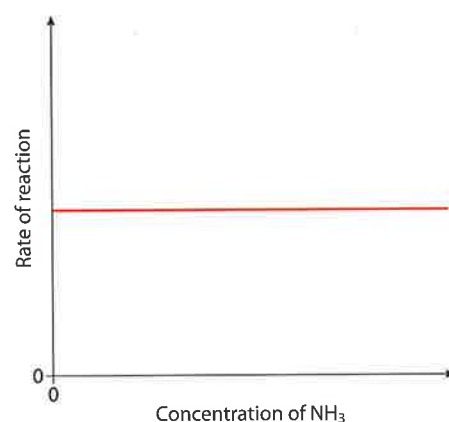$$k = mol^{-1}\,dm^3\,s^{-1}$$

Therefore the rate constant, k, is $2.08 \times 10^{-3}\,mol^{-1}\,dm^3\,s^{-1}$.

Figure 6.23 Concentration of reactant and product against time for a zero-order reaction.

> The rate is independent of the concentration.

Figure 6.24 Rate against concentration for a zero-order reaction.

Zero-order reactions

Consider a zero-order reaction – the decomposition of ammonia on a tungsten surface:

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

The concentration of ammonia decreases at a constant rate in this reaction. The constant rate is indicated by the graph of concentration against time being a straight line (Figure 6.23). A straight line has a constant gradient (slope) and indicates that the rate does not change as the concentration of NH_3 changes.

The concentration of the nitrogen increases at a constant rate, indicated by the straight dashed line in Figure 6.23.

The two graphs of concentration against time were drawn to the same scale, and it can be seen that the magnitude of the gradient of the line for N_2 is half that for NH_3. This is because in the chemical equation for this reaction the coefficient of NH_3 is 2 but that of N_2 is 1 – so N_2 is produced at half the rate at which NH_3 is used up.

Changing the concentration of ammonia has no effect on the rate of the reaction (Figure 6.24).

The rate equation is rate $= k$, which shows that the rate is constant. The units of the rate constant are the same as the rate – i.e. concentration $\times$ time^{-1}. A set of units for the rate constant could therefore be $mol\,dm^{-3}\,s^{-1}$.

> The rate equation for this reaction is rate $= k$.
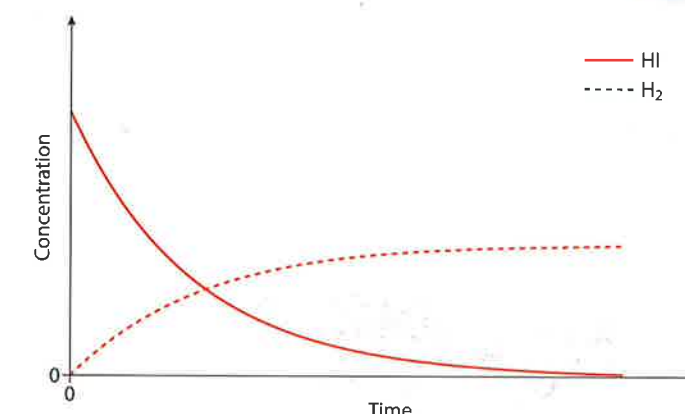> The units of k are concentration $\times$ time^{-1} (i.e. units could be $mol\,dm^{-3}\,s^{-1}$ or $mol\,dm^{-3}\,h^{-1}$ etc.)

First-order reactions

Let us consider a first-order reaction – the decomposition of hydrogen iodide on a platinum surface:

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$
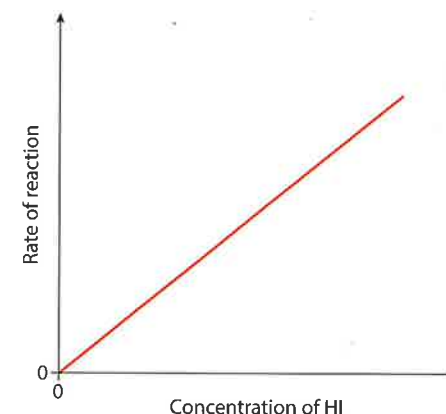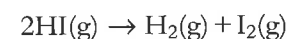
Figure 6.25 Rate against concentration for a first-order reaction.

Figure 6.26 Concentration of reactant and product against time for a first-order reaction.

The rate of this reaction is directly proportional to the concentration of HI, as shown by the straight line through the origin in Figure 6.25.

The graph in Figure 6.26 shows how the concentration of HI decreases with time. This shows an exponential decay and a constant **half-life**. The time taken for the concentration to drop by half does not depend on concentration in a first-order reaction – the time taken for the concentration to fall from $0.1\,mol\,dm^{-3}$ to $0.05\,mol\,dm^{-3}$ is the same as the time taken for the concentration to fall from $0.08\,mol\,dm^{-3}$ to $0.04\,mol\,dm^{-3}$.

The dashed line in Figure 6.26 shows the increase in concentration of one of the products (H_2) with time. The rate of production of H_2 is half the rate at which HI is used up, which can be seen from the coefficients in the chemical equation:

$$2HI \rightarrow H_2 + I_2$$
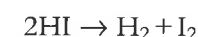
Second-order reactions

Consider a second-order reaction – the decomposition of hydrogen iodide without a catalyst:
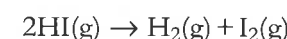
$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

Figure 6.27 shows how the rate of the reaction varies with the concentration of hydrogen iodide.

It can be proved that a reaction is second order (rather than third order, etc.) by plotting a graph of rate against concentration of HI squared (Figure 6.28). As the rate is proportional to $[HI]^2$, this graph is a straight line through the origin.
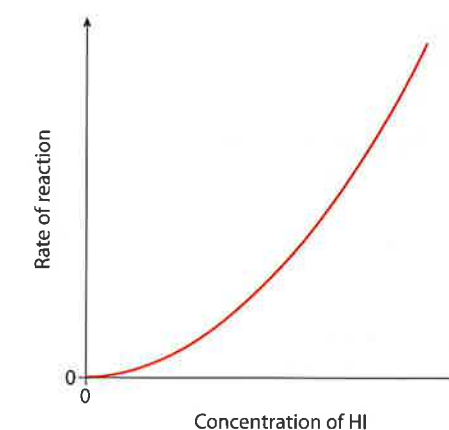
> The rate of reaction is proportional to concentration squared.

> The rate is directly proportional to the concentration.

> The rate equation for this reaction is: rate $= k[HI]$. The units of k are time^{-1}.

> The half-life is related to the rate constant by the equation
> $$\text{rate constant} = \frac{\ln 2}{\text{half-life}}$$

Figure 6.27 Rate against concentration for a second-order reaction.

The rate equation for this reaction is rate $= k[HI]^2$. The units of the rate constant are concentration^{-1} time^{-1} (i.e. units could be mol^{-1} dm^3 s^{-1}).
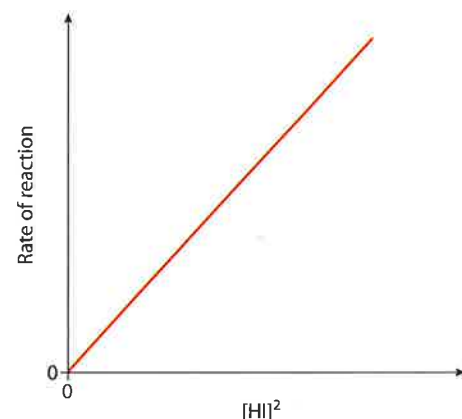

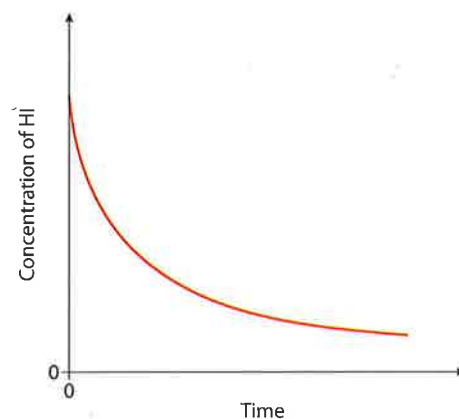Figure 6.28 Rate against concentration^2 for a second-order reaction.

Figure 6.29 Concentration of reactant against time for a second-order reaction.

Figure **6.29** shows how the concentration of HI changes with time. This is not an exponential relationship and does not have a constant half-life.

The units of the rate constant

It can be seen from the treatment above that the units of the rate constant are related to the overall order of the reaction. This is summarised in Table **6.5**.

| Overall order	Units of k	Example of units
0	concentration time^{-1}	mol dm^{-3} s^{-1}
1	time^{-1}	s^{-1}
2	concentration^{-1} time^{-1}	mol^{-1} dm^3 s^{-1}
3	concentration^{-2} time^{-1}	mol^{-2} dm^6 s^{-1}

Table 6.5 The relationship between overall order of the reaction and the units of the rate constant.

For a zero-order reaction, the units of k are the same as that of the rate. Each time the overall order increases by 1 the units of k are divided by concentration.

Generally the units of k are concentration$^{(1-\text{overall order})}$ time^{-1}.

? Test yourself

2 Consider the following data for the reaction:

$A + 2B \rightarrow C + D$
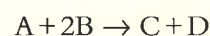
a Deduce the order of reaction with respect to A and with respect to B.
b What is the overall order of reaction?
c Work out a value for the rate constant of this reaction with units.
d What will be the rate of reaction when the concentration of A is 0.100 mol dm^{-3} and that of B is 0.0500 mol dm^{-3}?

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.200	0.100	0.0200
2	0.400	0.100	0.0400
3	0.400	0.200	0.160

3 Consider the following data for the reaction:

$2X + 4Y \rightarrow Q + 2R$
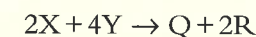
a Write the rate equation for this reaction.
b Calculate a value for the rate constant from these data.
c What are the units of the rate constant?

Experiment	[X] / mol dm^{-3}	[Y] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	1.50×10^{-2}	3.00×10^{-2}	1.78×10^{-3}
2	4.50×10^{-2}	3.00×10^{-2}	5.34×10^{-3}
3	4.50×10^{-2}	1.20×10^{-1}	2.14×10^{-2}
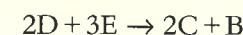
4 A reaction is zero order with respect to P and second order with respect to Q. What would be the effect of doubling the concentration of P and the concentration of Q on the overall rate of reaction?

5 Consider the following data for the reaction:

$2D + 3E \rightarrow 2C + B$

a Work out the order of reaction with respect to D.
b Work out the order of reaction with respect to E.
c What is the rate equation for the reaction?
d Work out a value, with units, for k, the rate constant for this reaction.
e What is the rate of reaction when the concentration of D is 0.0600 mol dm^{-3} and that of E is 0.0300 mol dm^{-3}?

Experiment	[D] / mol dm^{-3}	[E] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	2.50×10^{-3}	5.00×10^{-3}	4.28×10^{-4}
2	1.00×10^{-2}	5.00×10^{-3}	1.71×10^{-3}
3	4.00×10^{-2}	2.00×10^{-2}	6.84×10^{-3}

6.2.3 Mechanisms of reactions

In this section we consider why a rate equation cannot be derived directly from the chemical equation for a reaction. Consider the reaction:

$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$
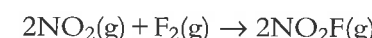
If this reaction were to occur in one single step, all three molecules must collide together at exactly the same time, and we would expect that doubling the concentration of any one of the three reactant molecules would double the chance of a collision and therefore the rate of the reaction. The rate of reaction in this case would therefore depend on $[NO_2]^2$ and $[F_2]$, and the rate equation would be:

$\text{rate} = k[NO_2]^2[F_2]$

The actual rate equation obtained from experiment is, however,

$\text{rate} = k[NO_2][F_2]$

The fact that these two equations are different suggests that the reaction does not occur in just one step in which all three molecules collide and break apart to form the products. This was always going to be unlikely because the chance of three gas molecules all colliding at exactly the same time is extremely small. This reaction must occur in a series of steps, and it is most likely that each step involves just two molecules colliding. A mechanism that has been proposed for this reaction is:

Learning objectives

- Understand what is meant by the mechanism of a reaction and the rate–determining step
- Work out reaction mechanisms from experimental data and relate a given mechanism to the experimental data

$[NO_2]^2$ because there are two NO_2 molecules and doubling the concentration of each will cause the rate to double.
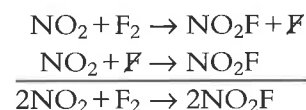
A **reaction mechanism** consists of a series of steps that make up a more complex reaction. Each simple step involves a maximum of two molecules colliding.
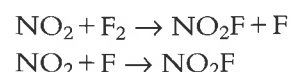
$$NO_2 + F_2 \rightarrow NO_2F + F \qquad \text{step 1}$$
$$NO_2 + F \rightarrow NO_2F \qquad \text{step 2}$$

The first thing that must be checked with the mechanism is that it agrees with the overall chemical equation. In order to do this, species that are the same on both sides of the equations are cancelled and then the two equations are added together:
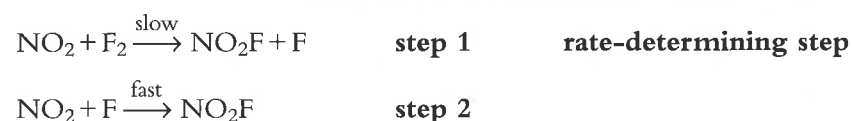
$$NO_2 + F_2 \rightarrow NO_2F + \cancel{F} \qquad \text{step 1}$$
$$\underline{NO_2 + \cancel{F} \rightarrow NO_2F} \qquad \text{step 2}$$
$$2NO_2 + F_2 \rightarrow 2NO_2F \qquad \text{overall equation}$$

F is produced in step 1 and used up again in step 2. F is an intermediate.

Now we need to see whether or not this mechanism agrees with the experimental rate equation. Each step involves just two species colliding, and therefore we can derive the rate equation for each step directly from its chemical equation:

Step 1: rate $= k_1[NO_2][F_2]$

Step 2: rate $= k_2[NO_2][F]$
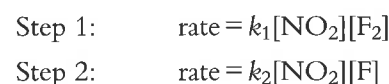
It can be seen that the rate equation for step 1 is the same as the experimental rate equation, and so it would seem that this step governs the overall rate of reaction and that the second step has no apparent effect on the rate. Step 1 is called the **rate-determining step** of the mechanism and occurs significantly more slowly than step 2.

$$NO_2 + F_2 \xrightarrow{\text{slow}} NO_2F + F \qquad \text{step 1} \qquad \textbf{rate-determining step}$$

$$NO_2 + F \xrightarrow{\text{fast}} NO_2F \qquad \text{step 2}$$

Step 2 is fast compared with the rate-determining step and has, effectively, no influence on the overall rate of reaction. This means that changing the concentrations of the species present in this step does not affect the rate of the reaction to any great extent, so the concentrations of these species do not occur in the rate equation.

The potential energy profile for this reaction is shown in Figure **6.30** and it can be seen that the rate-determining step (step 1) has a much higher activation energy than the other step.
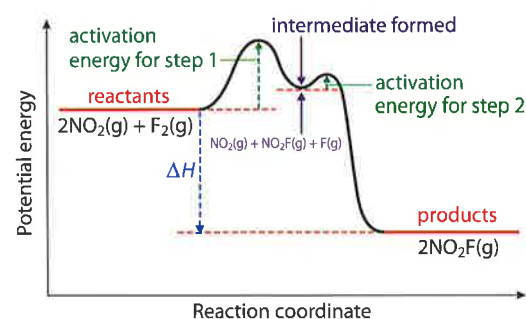

Figure 6.30 Potential energy profile for a two-step reaction. The formation of an intermediate is shown by the potential energy well in the profile.

The mechanism must be consistent with the overall chemical equation.

k_1 is the rate constant for step 1.

**The slowest step in a reaction mechanism is called the rate-determining step.**

The idea of a rate-determining step can be seen by analogy with a football stadium. The owners of the football club Rapid Kinetics have considered various options for speeding up the process of getting the spectators to their seats. They have broken down the process of getting to the seats into three separate steps:

1 getting to the stadium by road

2 getting into the stadium

3 getting to your seat once you are in the stadium.

It was suggested that the owners of the club could apply to the local council to improve the roads and the traffic flow leading to the stadium, and someone else suggested that they could install lifts and escalators to improve the process of getting around the stadium, but then some bright spark noticed the main problem – there was only one gate to get into the stadium! Improving the roads around the stadium and installing lots of lifts and escalators would have very little effect on the rate of the overall process of people getting to their seats because the rate-determining step is getting people through the one turnstile into the stadium. They need to work on improving the rate of the rate-determining step, and it could be expected that doubling the number of gates to get into the stadium would double the speed of the overall process.

Let us consider another mechanism, this time for the reaction $A + 2B \rightarrow C$:

$$B + B \rightarrow Q \qquad \text{step 1} \qquad \textbf{rate-determining step}$$
$$Q + A \rightarrow C \qquad \text{step 2} \qquad \textbf{fast}$$
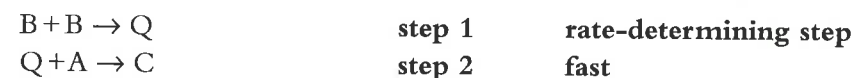
Q is an intermediate.

Let us first check that the mechanism agrees with the chemical equation:

$$B + B \rightarrow \cancel{Q} \qquad \text{step 1}$$
$$\underline{\cancel{Q} + A \rightarrow C} \qquad \text{step 2}$$
$$2B + A \rightarrow C \qquad \text{overall equation}$$

Step 1 is the rate-determining step, so the concentrations of the reactants involved in this affect the rate of the overall reaction and occur in the rate equation. Step 2 is a fast step that occurs after the rate-determining step, and therefore the species involved do not affect the rate of reaction or occur in the rate equation. This means that B occurs twice in the rate equation and A not at all. The rate equation consistent with this mechanism is:

rate $= k[B]^2$

In both examples we have considered, the rate-determining step is the first step. Now consider a mechanism in which the rate-determining step is the second step.

For the same overall equation, $A + 2B \rightarrow C$, another possible mechanism could be:

$$B + B \rightleftharpoons Q \qquad \text{step 1} \qquad \textbf{fast}$$
$$Q + A \rightarrow C \qquad \text{step 2} \qquad \textbf{rate-determining step}$$
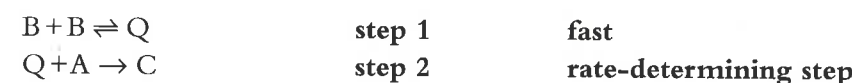
Step 1 is an equilibrium reaction. At equilibrium, the rate of the forward reaction is the same as the rate of the reverse reaction, i.e.

rate of forward reaction $= k_f[B]^2$

rate of reverse reaction $= k_r[Q]$

$k_f[B]^2 = k_r[Q]$

which can be rearranged to give:

$$[Q] = \frac{k_f[B]^2}{k_r}$$

So concentration of Q is proportional to the concentration of B squared.

S is an intermediate.

Intermediates do not appear in a rate equation.

This is basically the same as the previous mechanism, except that the second step is the rate-determining step. The species in step 2 influence the rate of the reaction and we can write the rate equation as:

rate $= k[Q][A]$

However, Q is produced by the reaction between two molecules of B, and we can replace [Q] with $[B]^2$ in the rate equation. Therefore the rate equation consistent with this mechanism would be:

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

Which of the two above mechanisms is more likely to be the actual mechanism can be worked out by experimentally determining the rate equation for the reaction.

From the treatment above we can see that:

The rate equation contains concentrations of reactants involved up to and including the rate-determining step.

This can be further seen with another possible mechanism for this reaction:

$A + B \rightleftharpoons S$	**step 1**	**fast**
$S + B \rightarrow C$	**step 2**	**rate-determining step**
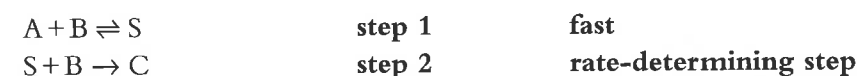
The reactants involved up to and including the rate-determining step are A once and B twice, so the rate equation would also be:

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

There is no simple way of distinguishing between the two above mechanisms experimentally.

Reactions involving a catalyst

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

This reaction is acid (H^+) catalysed.
The experimental rate equation is:

rate $= k[CH_3COCH_3][H^+]$

The rate equation does not include I_2, so this must be involved only after the rate-determining step.
At a simple level, the mechanism could be proposed as:

X is an intermediate.

H^+ will cancel out when the equations are added together.

|	
$CH_3COCH_3 + \mathbf{H^+} \rightarrow X$	**rate-determining step**
$X + I_2 \rightarrow CH_3COCH_2I + HI + \mathbf{H^+}$	**fast**

The catalyst is involved in the rate-determining step but is regenerated in the second step and therefore does not appear in the overall chemical equation.

Catalysts change a reaction mechanism, allowing the reaction to occur via an alternative pathway that has a lower activation energy. A homogeneous catalyst (in the same phase as the reactants) usually works by forming an intermediate with one or other of the reactant molecules – this requires a lower activation energy than the original reaction.

Consider the reaction $A \rightarrow X + Y$, which occurs in a single step. If a catalyst (C) is introduced, the reaction will happen by a different mechanism involving two steps:

$A + C \rightarrow A{-}C$	**rate-determining step** (activation energy E_2)
$A{-}C \rightarrow X + Y + C$	**fast** (activation energy E_3)

The rate equation for the original reaction would be rate $= k[A]$ and that for the catalysed reaction would be rate $= k[A][C]$. It can be seen that the catalyst appears in the rate equation. The potential energy profile for this reaction is shown in Figure **6.31**.
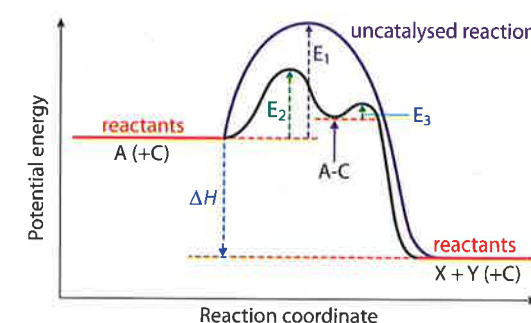

Figure 6.31 The effect of a catalyst on activation energy. E_1 is the activation energy for the uncatalysed reaction, E_2 is the activation energy for the first step of the catalysed reaction (the rate-determining step) and E_3 is the activation energy for the second step (fast) of the catalysed reaction.

S_N1 versus S_N2 mechanisms

In this section, we will consider the kinetics of the reactions that will be studied further in Subtopic **10.3.1**.
Consider the reaction:

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$
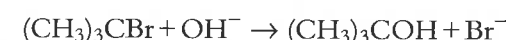
This is a nucleophilic substitution reaction of 2–bromo–2–methylpropane. The experimentally determined rate equation for this reaction is:

rate $= k[(CH_3)_3CBr]$

OH^- does not occur in the rate equation and therefore can be involved only in a fast step after the rate-determining step. The mechanism for this reaction has been suggested as:

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$	**rate-determining step**
$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$	**fast**

Molecularity is the number of 'molecules' that react in a particular step (usually the rate-determining step).

The reaction is described as an S_N1 mechanism, where S stands for substitution, N for nucleophilic (the attacking species is a nucleophile in this case) and 1 is the molecularity of the rate-determining step – the molecularity is 1 because **one** molecule reacts in the rate-determining step.

$CH_3CH_2CH_2Br$ (1-bromopropane) also undergoes a nucleophilic substitution reaction:

$$CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$$
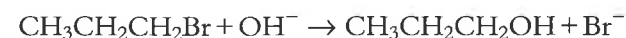
The rate equation is different:

$$rate = k[CH_3CH_2CH_2Br][OH^-]$$

With both reactants from the original equation appearing once only in the rate equation, this suggests that this reaction occurs in just one step and the mechanism is simply:

$$CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$$
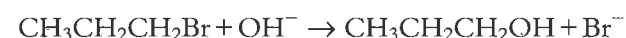
Because there is only one step it is, of course, also the rate-determining step. This reaction mechanism is described as S_N2, where the 2 refers to the molecularity of the single step.

Summary of 'rules' for writing mechanisms

1 The mechanism must agree with the overall stoichiometric equation.
2 A maximum of two particles can react in any one step.
3 All species in the rate equation must appear in the mechanism in or before the rate-determining step.
4 The power of a particular reactant's concentration in the rate equation indicates the number of times it appears in the mechanism up to and including the rate-determining step.

A mechanism being consistent with the experimental rate equation does not mean that the mechanism is correct. It can never be proved that a mechanism is correct, only that it is incorrect. A mechanism is accepted so long as it agrees with the experimental data, but if new experimental data are produced that are not consistent with the mechanism, the mechanism is disproved and a new mechanism must be developed that agrees with these and other experimental data.

Nature of science

The principle of Occam's (Ockham's) razor is often used in science to decide between different theories. It involves the idea that if there are two theories that give equally acceptable explanations of experimental data, the simpler one should be adopted. This is often used to decide between different reaction mechanisms. Consider the reaction $A + 2B \rightarrow X + Y$, which has the rate equation: $rate = k[A][B]$.

A mechanism that is consistent with the rate equation and the stoichiometric equation is:

|	
$A + B \rightarrow Q$	rate-determining step
$B + Q \rightarrow X + Y$	fast
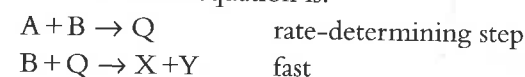
However, it is possible to come up with lots of other possible mechanisms (an infinite number if we are just dealing with random letters and not actual chemicals!), such as:

$A + B \rightarrow Q$	rate-determining step
$Q \rightarrow R + S$	fast
$S + B \rightarrow Z$	fast
$Z + R \rightarrow X + Y$	fast
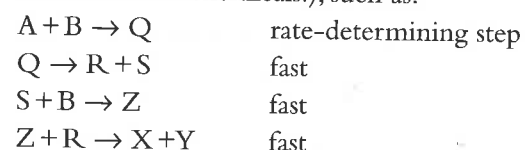
This mechanism also fits the experimental data, but unless there is experimental evidence for the transient existence of, for instance S, in the reaction mixture, this mechanism will be rejected in favour of the first one – the extra steps are not needed to fit the experimental data. It is important when using Occam's razor to realise that it works only when both theories provide a full explanation of the data – if there were extra data that suggested the formation of S in the reaction mixture then the first mechanism must be rejected because it does not account for this. In that case, we should seek the simplest possible mechanism that includes the formation of S as an intermediate.
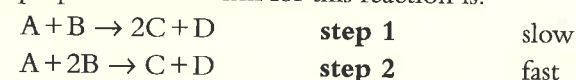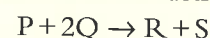
? Test yourself
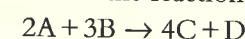
6 Consider the reaction:
$$2A + 3B \rightarrow 4C + D$$
The rate equation is: $rate = k[B]^2$.
A proposed mechanism for this reaction is:

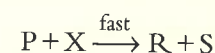|		
$A + B \rightarrow 2C + D$	**step 1**	slow
$A + 2B \rightarrow C + D$	**step 2**	fast

Suggest **three** reasons why this is not a suitable mechanism for this reaction.
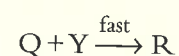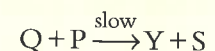
7 Consider the reaction:
$$P + 2Q \rightarrow R + S$$
A student has suggested some possible two-step mechanisms for this reaction:

Mechanism 1
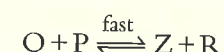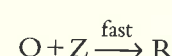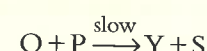
$Q + Q \xrightarrow{slow} X$

$P + X \xrightarrow{fast} R + S$

Mechanism 2

$Q + P \underset{}{\overset{fast}{\rightleftharpoons}} Z + R$

$Q + Z \xrightarrow{slow} S$

Mechanism 3

$Q + P \xrightarrow{slow} Y + S$

$Q + Y \xrightarrow{fast} R$

Mechanism 4
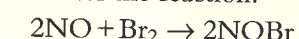
$Q + P \xrightarrow{slow} Y + S$

$Q + Z \xrightarrow{fast} R$
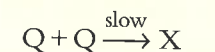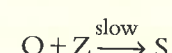
a Write the rate equation that would be consistent with Mechanism 1.
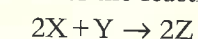b Explain why Mechanism 4 cannot be the mechanism for this reaction.
c The experimentally determined rate equation for this reaction is: $rate = k[P][Q]$. Which mechanism is consistent with the experimental data?

8 Consider the reaction:
$$2NO + Br_2 \rightarrow 2NOBr$$
The rate equation is $rate = k[NO]^2[Br_2]$. Suggest two different mechanisms that are consistent with this rate equation.

9 Consider the reaction:
$$2X + Y \rightarrow 2Z$$
The rate equation for this reaction is: $rate = k[X][Y]$. Suggest a mechanism for this reaction.

Learning objectives

- Understand that increasing the temperature causes the rate constant to increase
- Work out values of activation energy and the frequency factor (pre-exponential factor) using the Arrhenius equation

6.3 Activation energy (HL)

The Arrhenius equation

In a rate equation such as rate = k[A][B], the effect of temperature variation is accounted for by a change in the value of the rate constant.

> **As the temperature increases, the rate constant increases exponentially.**

The **Arrhenius equation** can be used to model the variation of the rate constant with temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

$e^{\frac{-E_a}{RT}}$ represents the fraction of collisions that have $E \geq E_a$. However, not all collisions with $E \geq E_a$ result in reaction. The molecules must collide in the correct orientation, and A contains a factor that allows for this.

A is called the frequency factor (also called the pre-exponential factor or A-factor) and takes account of the **frequency** of collisions and the **orientation** of the collisions. A can be regarded as the product of two terms – one representing the frequency of molecular collisions and the other taking account of the fact that not all collisions with $E \geq E_a$ result in reaction because the molecules must collide with the correct orientation. A can be regarded as a **constant** (it actually varies very slightly with temperature).

The Arrhenius equation may also be written in the form:

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

R is the gas constant, i.e. $8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

T is the temperature in kelvin.

The Arrhenius equation in this form can be used to work out a value for the activation energy for a reaction. In order to do this, the following procedure must be followed:

1 Conduct a series of experiments at a range of temperatures.
2 Calculate a rate constant (k) for each temperature.
3 Plot a graph of $\ln k$ (y-axis) against $\frac{1}{T}$ (x-axis), where T is the absolute temperature (in kelvin). This graph should be a straight line. The gradient of the graph is $\frac{-E_a}{R}$, where R is the gas constant.
4 The intercept of the graph on the $\ln k$ axis (y-axis) is $\ln A$.

After we have carried out the series of experiments, we could have data such as those listed in the first two columns of Table **6.6**. $\frac{1}{T}$ and $\ln k$ are then calculated.

T/K	k/s⁻¹	$\frac{1}{T}$/K⁻¹	ln k
300	0.00088	0.003 33	−7.03
350	0.0037	0.002 86	−5.60
400	0.0108	0.002 50	−4.53
450	0.0250	0.002 22	−3.69
500	0.0487	0.002 00	−3.02
550	0.0842	0.001 82	−2.47
600	0.133	0.001 67	−2.02
650	0.195	0.001 54	−1.63
700	0.272	0.001 43	−1.30

Table 6.6 Sample experimental data and derived values.

A graph of $\ln k$ (y-axis) against $\frac{1}{T}$ (x-axis) produces a straight-line graph (Figure **6.32**).
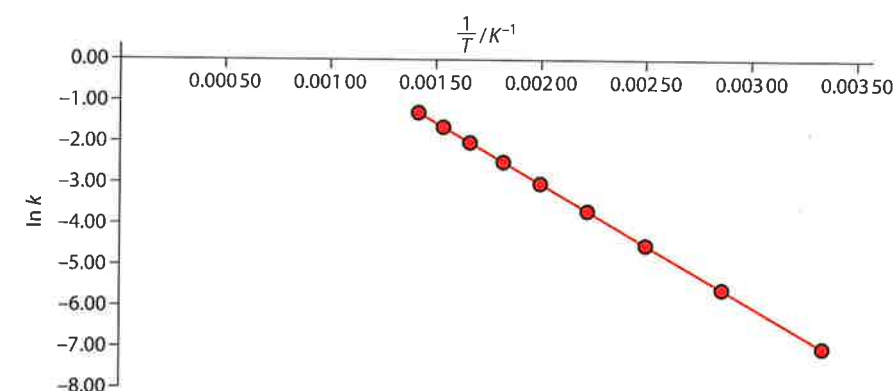

Figure 6.32 $\ln k$ (y-axis) against $\frac{1}{T}$ (x-axis).

We can understand why a straight-line graph is produced by comparing the Arrhenius equation with the equation of a straight line ($y = mx + c$, where m is the gradient and b is the intercept on the y-axis):

$$\underbrace{\ln k}_{y} = \underbrace{\frac{-E_a}{R}}_{m} \times \underbrace{\frac{1}{T}}_{x} + \underbrace{\ln A}_{c}$$

Extension

The Arrhenius equation is a mathematical model that works well to explain variation of the rate of most reactions over a limited temperature range. There are actually a few reactions that get slower as temperature increases, which would correspond to a negative activation energy using this equation.

So, the Arrhenius equation is the equation of a straight line, where $\ln k$ is y and $\frac{1}{T}$ is x. From this equation we can see that the gradient of this straight line is $\frac{-E_a}{R}$. From the graph in Figure **6.32** we can work out the gradient of the straight line:

$$\text{gradient} = \frac{(-1.3) - (-7.0)}{0.001\,43 - 0.003\,33}$$

i.e. the gradient $= -3000\,K$.

The gradient of the line is equal to $\frac{-E_a}{R}$, so:

$$\frac{-E_a}{R} = -3000$$

$$E_a = 3000 \times R$$

$$E_a = 3000 \times 8.31 = 24\,900\,J\,mol^{-1}$$

i.e. the activation energy $= 24.9\,kJ\,mol^{-1}$.

From the equation of a straight line above it can be seen that the intercept on the $\ln k$ axis (y-axis) is $\ln A$. The intercept occurs at 3.00 and therefore $\ln A = 3.00$. The value of A can be obtained by raising each side as a power of e (e^x is the inverse function of $\ln x$).

Therefore $A = e^{3.00}$ – i.e. $A = 20.1\,s^{-1}$.

The units of A will be the same as the unit of k.

The values of E_a and A can also be worked out without using a graph if the values of the rate constant are known at two different temperatures. For example, if the values are:

$$T_1 = 300\,K \qquad k_1 = 8.80 \times 10^{-4}\,s^{-1}$$

$$T_2 = 550\,K \qquad k_2 = 8.42 \times 10^{-2}\,s^{-1}$$

and:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Subtracting the first equation from the second we get:

$$\ln k_2 - \ln k_1 = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

In our example:

$$\ln k_1 = -7.03 \text{ and } \ln k_2 = -2.47$$

$$\frac{1}{T_1} = 3.33 \times 10^{-3}\,K^{-1} \text{ and } \frac{1}{T_2} = 1.82 \times 10^{-3}\,K^{-1}$$

Substituting the numbers in to the above equation gives:

$$-2.47 + 7.03 = -\frac{E_a}{8.31}(1.82 \times 10^{-3} - 3.33 \times 10^{-3})$$

Rearranging this gives $E_a = 25\,100\,J\,mol^{-1}$ or $25.1\,kJ\,mol^{-1}$.

The value of A is obtained by substituting the values of k_1, T_1 and E_a (in $J\,mol^{-1}$) into $\ln k_1 = -\frac{E_a}{RT_1} - \ln A$. This gives $A = 20.8\,s^{-1}$.

The values calculated here are different from those worked out using a graphical method because only two points have been used from the graph and there is no guarantee that they lie exactly on the line of best fit. Also, working out gradients and intercepts by hand from a graph introduces more uncertainties.

Interpretation of activation energy and frequency factor values

In general, all other things being equal, the higher the activation energy for a reaction the slower it will be. $e^{-E_a/RT}$ can be rewritten as $\frac{1}{e^{E_a/RT}}$ – so if E_a is larger, $e^{E_a/RT}$ will be larger and $\frac{1}{e^{E_a/RT}}$ will be smaller and k will be smaller.

All other things being equal, the value of the frequency factor A will be smaller for reactions between more complicated molecules because these can collide in many different ways and only a small proportion of collisions will be in the correct orientation for reaction. However, if two atoms collide virtually all the collisions will be in the correct orientation.

The effect of a catalyst on the value of the rate constant

The effect of a catalyst on the rate equation, rate $= k[A][B]$, is to **increase the value of the rate constant**.

A catalyst provides an alternative pathway of lower activation energy. E_a is smaller and, because e is raised to a negative power, this makes the value of $e^{-E_a/RT}$ bigger and hence k is bigger.

Nature of science

Scientific theories must explain experimental data. The first process in developing a theory of the effect of temperature on reaction rate would involve collecting data. Many different systems would have to be studied to make sure that a general law could be established. At the simplest level these data would suggest the law: increasing the temperature increases reaction rate. A simple theory based on the idea of particles colliding more often could explain this law. However, as more quantitative data are collected a more mathematical description of the effect of temperature could be developed. Mathematical analysis of the effect of temperature on collision rate would indicate problems with the theory and require development of a more sophisticated model based on the Arrhenius equation.

? Test yourself

The value of the gas constant is $8.31\,JK^{-1}mol^{-1}$.

10 Use the following data to calculate values for the activation energy and frequency factor for the second-order reaction $P + Q \rightarrow Z$

| $\dfrac{1}{T}$/K^{-1}	ln k
0.00250	2.27
0.00222	4.14
0.00200	5.64
0.00182	6.86
0.00167	7.88
0.00154	8.75
0.00143	9.49
0.00133	10.1
0.00125	10.7

11 Use the following data to calculate values for the activation energy and frequency factor for the reaction $A + B \rightarrow C$

Temperature/K	k/mol^{-1}dm^{3}s^{-1}
400	1.74×10^{-2}
450	3.53×10^{-1}
500	3.92
550	28.1
600	145
650	581
700	1.91×10^3
750	5.35×10^3
800	1.32×10^4

Exam-style questions

1 Which of the following best explains why an increase in temperature causes the rate of a reaction to increase?

- **A** the particles collide more
- **B** the particles collide more frequently
- **C** more particles have energy greater than the activation energy
- **D** the activation energy is lower at higher temperature

2 An experiment was carried out to measure the rate of decomposition of hydrogen peroxide according to the equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$
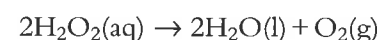
56.0 cm^3 of gas was produced in 30.0 s. The average rate of reaction during this time was:

- **A** 1.87 cm^{3}s^{-1}
- **B** 28.0 cm^{3}min^{-1}
- **C** 0.536 s cm^{-3}
- **D** 112 min cm^{-3}

3 Which of the following will **not** increase the rate of the reaction between magnesium and hydrochloric acid?

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$
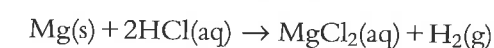
- **A** increasing the surface area of the magnesium
- **B** increasing the volume of hydrochloric acid used
- **C** increasing the concentration of the hydrochloric acid
- **D** increasing the temperature

4 In the decomposition of hydrogen peroxide, manganese(IV) oxide is a catalyst. Which of the following best describes the function of a catalyst and its mode of action?

- **A** it speeds up the reaction by increasing the activation energy
- **B** it slows down the reaction by decreasing the collision frequency of particles
- **C** it speeds up the reaction by allowing the reaction to occur by an alternative pathway of lower activation energy
- **D** it speeds up the reaction by increasing the average energy of the particles

5 In the reaction between 1.00 g marble chips (calcium carbonate) and 25.0 cm^3 hydrochloric acid, which of the following sets of conditions should give the fastest rate of reaction?

- **A** 0.50 mol dm^{-3} HCl(aq) and small marble chips at 20 °C
- **B** 0.10 mol dm^{-3} HCl(aq) and small marble chips at 30 °C
- **C** 0.30 mol dm^{-3} HCl(aq) and small marble chips at 70 °C
- **D** 0.50 mol dm^{-3} HCl(aq) and large marble chips at 30 °C

HL 6 The rate equation for the reaction $CO + NO_2 \rightarrow CO_2 + NO$ is: rate $= k[NO_2]^2$. When the concentration of CO is increased by a factor of 2 and the concentration of NO_2 is increased by a factor of 3, the rate of reaction is increased by a factor of:

- **A** 3
- **B** 6
- **C** 9
- **D** 18

HL 7 Consider the following experimental data for this reaction:

$$2NO + Br_2 \rightarrow 2NOBr$$
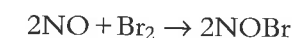
[NO]/mol dm^{-3}	[Br$_2$]/mol dm^{-3}	Rate/mol dm^{-3}s^{-1}
0.10	0.10	0.010
0.20	0.10	0.040
0.20	0.30	0.12

The rate equation for this reaction is:

- **A** rate $= k[NO]^2[Br_2]$
- **B** rate $= k[NO_2] + [Br_2]$
- **C** rate $= k[NO_2]^2[Br_2]^3$
- **D** rate $= k[NO_2][Br_2]$

HL 8 The activation energy for a reaction can be calculated from a graph of:

- **A** ln k vs T
- **B** $\frac{1}{k}$ vs ln T
- **C** ln k vs $\frac{1}{T}$
- **D** ln k vs ln T

9 Consider the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
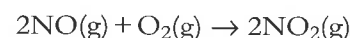
Some possible mechanisms for this reaction are:

I	$NO(g) + NO(g) \rightleftharpoons N_2O_2(g)$	fast	**III**	$NO(g) + O_2(g) \rightleftharpoons NO_3(g)$	fast
	$N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$	slow		$NO_3(g) + NO(g) \rightarrow 2NO_2(g)$	slow
II	$NO(g) + NO(g) \rightarrow N_2O_2(g)$	slow	**IV**	$NO(g) + O_2(g) \rightarrow NO_3(g)$	slow
	$N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$	fast		$NO_3(g) + NO(g) \rightarrow 2NO_2(g)$	fast

The rate equation for this reaction is: rate $= k[NO]^2[O_2]$. Which of these mechanisms is/are consistent with this rate equation?

    A **I** only   **C** **II** and **III** only

    B **I** and **IV** only   **D** **I** and **III** only

10 The units of k for a reaction with rate equation rate $= k[A]^2$ could be:

    A $mol\,dm^{-3}\,s^{-1}$ **C** $mol^2\,dm^{-6}\,s^{-1}$

    B $mol^{-1}\,dm^3\,h^{-1}$ **D** $mol^{-2}\,dm^6\,h^{-1}$

11 Explain by reference to the Maxwell–Boltzmann distribution why the rate of a reaction in the gas phase increases as temperature increases. **[4]**

12 The data in the table refer to the reaction:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Time / s	Volume of CO_2 produced / cm^3
0	0.0
10	16.0
20	30.0
30	41.0
40	47.0
50	51.0
60	53.5
70	55.5
80	56.5
90	57.0
100	57.0
110	57.0

a Explain, with the aid of a diagram, how these data could be obtained experimentally. **[3]**

b Plot these data on graph paper and label the line **A**. **[2]**

c Use the graph that you have plotted in part **b** to state and explain where the rate of reaction is fastest. **[2]**

d The original data were collected for an experiment using 1.00 g of calcium carbonate and 20.0 cm³ of 0.300 mol dm⁻³ hydrochloric acid at 20 °C. The experiment was then repeated using exactly the same conditions, except that the temperature of the HCl(aq) was 30 °C.

Sketch, on the same axes as your graph in part **b**, the curve that would be obtained. Label this graph **B**. **[2]**

e **i** Calculate the maximum volume of carbon dioxide (in cm³) that should have been collected in the original experiment if 1.00 mol CO_2 occupies 24.0 dm³ under these conditions. **[3]**

    ii Explain why the volume of gas collected is less than you predicted in part **i**. **[1]**

13 The following data refer to the reaction:

$$X + 2Y \rightarrow Z$$

Experiment	Concentration of X / mol dm⁻³	Concentration of Y / mol dm⁻³	Rate of reaction / mol dm⁻³ s⁻¹
1	0.500	0.500	3.20×10^{-3}
2	0.250	0.500	1.60×10^{-3}
3	0.250	0.250	8.00×10^{-4}

a Explain what is meant by the term 'order of reaction'. **[2]**

b Deduce the rate equation for this reaction. **[4]**

c Calculate the rate constant with units for this reaction. **[2]**

d What is the rate of reaction when the concentrations of X and Y are both 0.100 mol dm⁻³? **[2]**

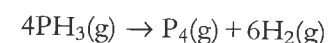**e** State and explain how the value of the rate constant for this reaction will change as the temperature increases. **[2]**

14 Under certain conditions the decomposition of phosphine, PH_3, is zero order. The equation for the reaction is:
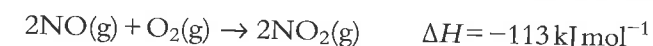
$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

a Sketch a graph showing how the concentration of phosphine varies with time. **[2]**

b Sketch a graph showing how the rate of decomposition of phosphine varies as the concentration of phosphine changes. **[2]**

15 Consider the gas-phase reaction between nitrogen(II) oxide and oxygen:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H = -113\,kJ\,mol^{-1}$$

The rate equation for the reaction is: rate $= k[NO]^2$.

a Explain, by reference to this reaction, why the rate equation cannot be derived from the stoichiometric equation. **[2]**

b Explain what is meant by the 'rate-determining step' in a chemical reaction. **[1]**

c Suggest a two-step mechanism for this reaction and state the molecularity of the rate-determining step. **[4]**

d If the total volume of the reaction container is doubled at constant temperature, state and explain the effect on the rate of this reaction. **[2]**

e Sketch, on the same axes, a potential energy profile for this reaction with and without a catalyst. Clearly label the curves and the activation energies of the catalysed and uncatalysed reactions. **[4]**

Summary

RATES OF REACTION ── change in concentration of reactants or products per unit time
- units: concentration time^{-1}, e.g. mol dm^{-3} s^{-1}
- average rate $= \dfrac{\text{change in concentration}}{\text{time}}$

collision theory: particles must collide in order to react ── two conditions:
- collision must involve more than the **activation energy, E_a**
- molecules must collide in the correct orientation

To RATE EQUATION on next page

influencing factors

- concentration of reactants ── Increased concentration causes higher collision frequency.
- pressure ── Increased pressure causes higher collision frequency for gases.
- surface area of solid reactants ── Increased surface area means increased number of particles exposed, therefore collision frequency is higher.
- temperature ── Increased temperature means increased speed of particles.
  - average kinetic energy $\propto$ temperature
  - Maxwell–Boltzmann distribution
  - At higher temperature there are more particles with energy $\geq E_a$.
  - more collisions (minor effect)
  - collisions are more energetic (main effect)
- catalysis ── This allows an alternative reaction pathway with a lower activation energy.
  - A catalyst speeds up a reaction but is not used up.

RATE EQUATION $\text{rate} = k[A]^m[B]^n$ ── can only be experimentally determined

$k =$ **rate constant** ── constant of proportionality relating concentrations in the rate equation to rate of reaction
- units: concentration$^{(1-\text{overall order})}$ time^{-1}

increases with increasing temperature ── **Arrhenius equation:** $\ln k = Ae^{-E_a/RT}$
- A is a factor that depends on the frequency of collisions and orientation of collisions
- On a plot of $\ln k$ versus $1/T$, the gradient is $-E_a/R$ and the y-intercept is $\ln A$.

order of reaction
- Order of reaction with respect to a reactant is the power of the reactant's concentration in the rate equation.
- Overall order of reaction is the sum of the powers of the concentrations in the rate equation.
- zero order: rate independent of concentration
- first order: rate proportional to concentration
- second order: rate proportional to concentration squared

mechanism: series of steps that make up a more complex reaction
- must agree with the overall chemical equation
- maximum of two particles react in any one step

slowest step is the **rate-determining step** ── The rate equation contains the concentrations of the reactants involved up to and including the rate-determining step.
- has highest activation energy