

REACTIVITY

2.2

How fast? The rate of chemical change



◀ The launch of the first Bangladeshi geostationary communications and broadcast satellite, *Bandabanghu-1*, on a Falcon 9 rocket from Cape Canaveral, Florida, in 2018. To produce enough thrust to launch a rocket, an extremely high rate of reaction between a fuel (in this case kerosene) and an oxidizing agent (liquid oxygen) is required to produce a rapid flow of exhaust gases out of the combustion chamber. The ability to control and influence the rate of a chemical reaction is an essential feature of all industrial chemical processes.

Guiding question

How can the rate of a reaction be controlled?

The **rate**, or kinetics, of a chemical reaction refers to the speed at which reactants are converted into products during a chemical process. We will all have some familiarity with this concept in everyday life. Imagine, for example, you are cooking in the kitchen. As you drop an egg into hot oil in the pan, it immediately changes to a white solid; meanwhile, a container of milk that was left out of the refrigerator is slowly turning sour. We observe a similarly wide variation in the rate of reactions that we study in the laboratory, and these data can be very useful.

Studies of rates of reaction are of prime importance in industry because they give information on how quickly products form and on the conditions that give the most efficient and economic yield. They can also be useful in situations where we want to slow reactions down – for example, the reactions that cause the destruction of ozone in the stratosphere, or the reactions where pollutants in the air combine to produce smog. At other times, it is important to know for how long a certain reaction will continue – for example, the radioactive effect from radioactive waste.

This chapter begins with a study of reaction rates and a consideration of how these are measured in different cases. Through the explanation of **collision theory**, we will come to understand why different factors affect the rate of reactions. These factors will include pressure, concentration, surface area, temperature and presence of a catalyst..

Reactivity 2.2.1 – Rate of reaction

Reactivity 2.2.1 – The rate of reaction is expressed as the change in concentration of a particular reactant or product per unit time.

Determine rates of reaction.

Calculation of reaction rates from tangents of graphs of concentration, volume or mass against time should be covered.

Tool 1, 3, Inquiry 2 – Concentration changes in reactions are not usually measured directly. What methods are used to provide data to determine the rate of reactions?

Tool 1 – What experiments measuring reaction rates might use time as (i) a dependent variable or (ii) an independent variable?

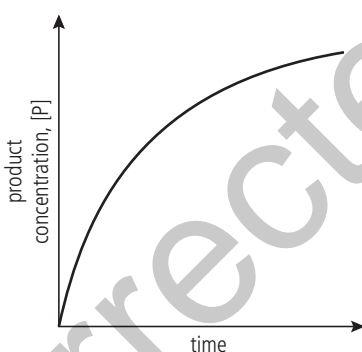
Rate of reaction is defined as the rate of change in concentration

When we are interested in how quickly something happens, the factor that we usually measure is **time**. For example, in a sports race, the competitors are judged by the time it takes them to reach the finishing line. However, if we want to compare their performance in different races over different distances, we would need to express this as a **rate** – in other words how they performed **per unit time**.

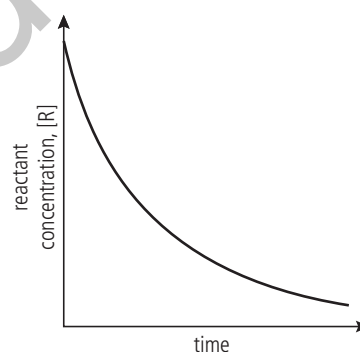
Rate takes the reciprocal value of time, so is expressed *per unit time* or, in SI units, *per second* (symbol = s^{-1}).

$$\text{rate} = \frac{1}{\text{time}} = \frac{1}{s} = s^{-1}$$

In the study of chemical reactions, we use the concept of **rate of reaction** to describe how quickly a reaction happens. As the reaction proceeds, reactants are converted into products, and so the concentration of reactants decreases as the concentration of products increases. The graphs in Figures 1 and 2 show sketches of typical data from reactions.



R2.2 Figure 1 Concentration of product against time.



R2.2 Figure 2 Concentration of reactant against time.

The rate of a reaction depends on how quickly the concentration of either reactant or product changes with respect to time. It can be defined as follows:

$$\text{rate of reaction} = \frac{\text{increase in product concentration}}{\text{time taken}} \quad \text{or} \quad \frac{\text{decrease in reactant concentration}}{\text{time taken}}$$

Using Δ to represent 'change in', $[R]$ for concentration of reactant, and $[P]$ for concentration of product, we can express this as

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

It is worth noting that, by convention, rate should be expressed as a positive value. For this reason, a negative sign has been placed in front of the reactant expression which would otherwise produce a negative value due to $[R]$ decreasing over time.

As rate = change in concentration per time, its units are **$\text{mol dm}^{-3} \text{s}^{-1}$** .

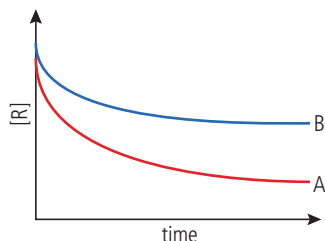
Note that because time and rate are reciprocal values, as one decreases, the other increases. So in the example above, the racer with the *shortest time* wins the race, because they had the *fastest rate*.



The rate of a chemical reaction is the increase in concentration of products, or the decrease in concentration of reactants, per unit time.



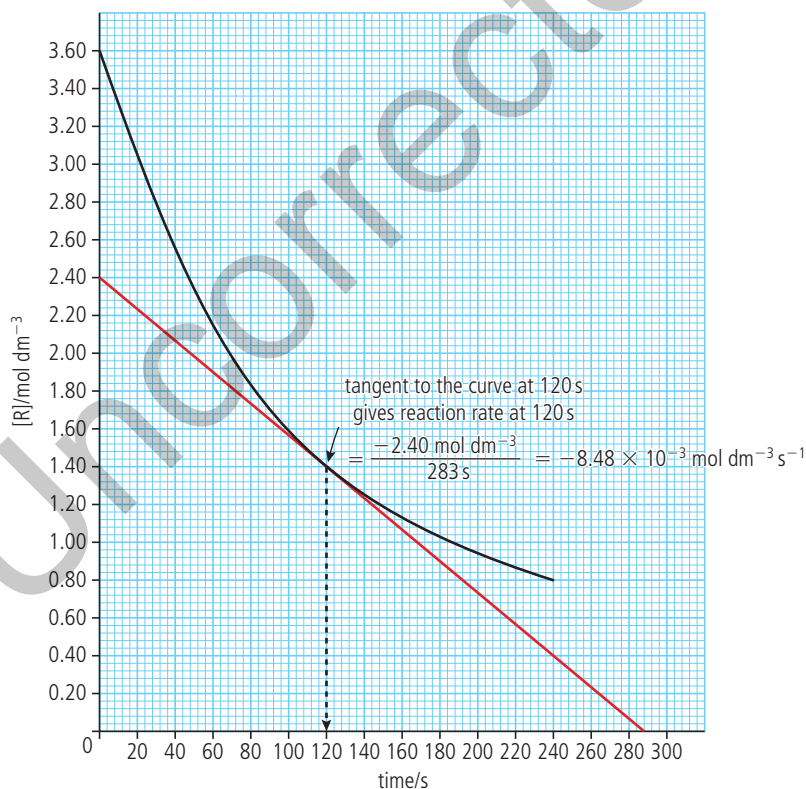
Figure 3 presents graphs of two different reactions showing the change in concentration of reactant against time.



R2.2 Figure 3 Reactant concentration against time for two different reactions, A and B.

We can see that the concentration of reactants is decreasing more quickly in reaction A than in reaction B – the curve is steeper. The steepness, or gradient, of the curve is a measure of the change in concentration per unit time, in other words, the rate of the reaction.

Because the graphs are curves and not straight lines, the gradient is not constant and so can only be given for a particular value of time. We can measure this by drawing a tangent to the curve at the specified time point and measuring its gradient. This is shown in Figure 4 for the time at 120 seconds. Note that the gradient of this graph is negative as the reactant concentration is decreasing, but rate is expressed as a positive value.

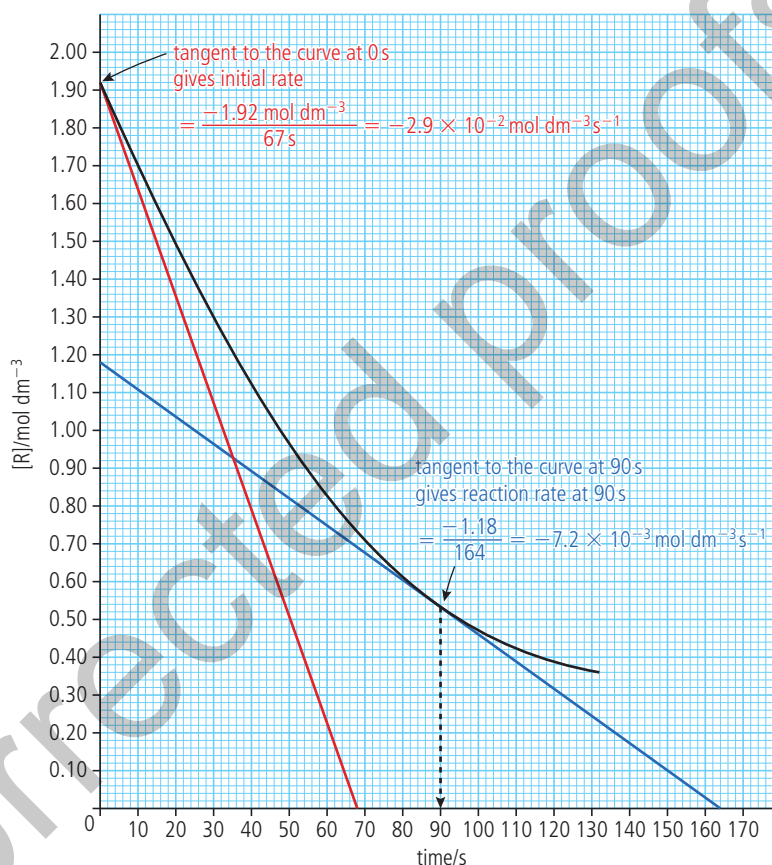


R2.2 Figure 4 Measuring the gradient of the tangent to the curve at time $t = 120$ seconds. The measured rate of the reaction is $8.48 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ at this time. Note that, by convention, rate is always expressed as a positive value.

The shape of the curve indicates that the rate of the reaction is not constant during the reaction, but is greatest at the start and slows down as the reaction proceeds. This is illustrated in Figure 5, which shows the calculation of reaction rate at two different times during a reaction.

$$t = 0 \text{ s; rate} = 2.9 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$t = 90 \text{ s; rate} = 7.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$



R2.2 Figure 5 Measuring the gradient of the tangent to the curve at two different times during a reaction. The rate decreases as the reaction proceeds.

The rate is greatest at the start because this is when the reactant concentration is highest. The effect of concentration on reaction rate is discussed later in this chapter. Because of this variation in rate as a reaction proceeds, in order to compare the rates of reactions under different conditions, it is common to compare the **initial rate** of each reaction by taking the tangent to the curve at $t = 0$. As we will see later in this chapter, initial rate data is very useful in analyzing the effect of concentration on rate.

The rate of a reaction is not constant during a reaction, but is greatest at the start and decreases as the reaction proceeds.

You will get a more accurate value for the slope of the tangent if you draw it as long as you reasonably can, so that the 'y' value (concentration) and the 'x' value (time) are as large as possible.

Note the difference between the two instructions 'draw a graph' and 'sketch a graph'. *Drawing* is based on actual data so scales must be chosen appropriately and data points and units clearly marked; *sketching* is a way of showing a trend in the variables, without reference to specific data. Note that in both cases, the axes must be clearly labelled with the dependent variable on the y-axis and the independent variable on the x-axis.

Measuring rates of reaction uses different techniques depending on the reaction

Choosing whether to measure the change in concentration of reactants or products, and the technique with which to measure that change, really depends on what is the most convenient for a particular reaction. This is different for different reactions. In most cases the concentration is not measured directly, but is measured by means of a signal that is related to the changing concentration. If, for example, a reaction forms a coloured precipitate as product, the change in colour could be measured. If a reaction gives off a gas, then the change in volume or change in mass could be measured. The raw data collected using these 'signals' will be in a variety of units, rather than as concentrations measured in mol dm^{-3} directly. This is generally not a problem, as it still enables us to determine the rate of the reaction. Many of the experiments used here can be carried out using data-logging devices. Some examples of common techniques in relation to specific reactions are discussed below.

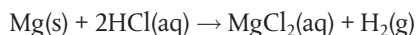


Nature of Science

Although the chemical reactions between individual molecules cannot be observed directly, there are many indirect methods for investigating these processes in order to develop explanations for what is happening. As with all of chemistry, the validity of these theories is dependent on the extent to which they are supported by experimental data and their ability to make accurate predictions.

Change in volume of gas produced

This is a convenient method if one of the products is a gas. Collecting the gas and measuring the change in volume at regular time intervals enables a graph to be plotted of volume against time. A **gas syringe** can be used for this purpose. It consists of a ground glass barrel and plunger. The plunger moves outwards as the gas collects and the barrel is calibrated to record the volume directly. Alternatively, the gas can be collected by displacement of water from an inverted burette. Note though that the displacement method can only be used if the gas collected has low solubility in water. Data loggers are also available for continuous monitoring of volume change against time. The rate of reaction of a metal with dilute acid to release hydrogen gas can be followed in this way.



Challenge yourself

1. Most gases are less soluble in warm water than in cold water, so using warm water may help to reduce a source of error when collecting a gas by displacement of water. But what new error might this create?



Tool 1, 3, Inquiry 2 - Concentration changes in reactions are not usually measured directly. What methods are used to provide data to determine the rate of reactions?

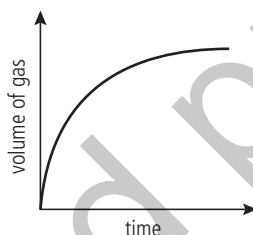
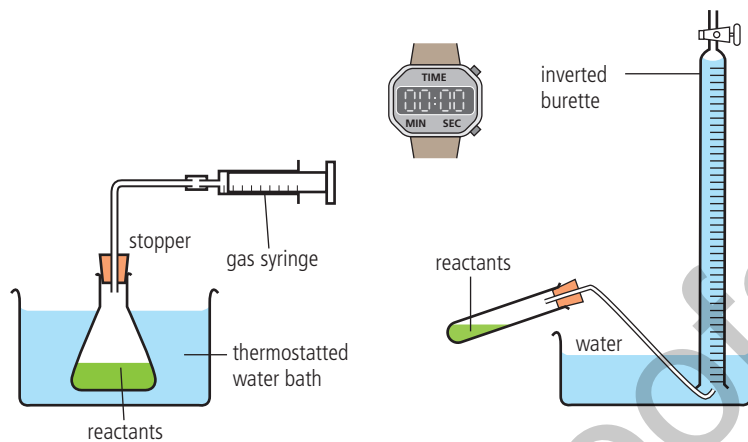


Note that the balanced equation of a reaction gives us no information about its rate. We can obtain this information only from experimental (empirical) data. Is there a fundamental difference between knowledge claims based on conclusions from theoretical data and those based on experimental data?

Experiments to measure rate of reaction by following change in volume against time.

When you take a glass of cold water from the refrigerator and leave it by your bed overnight, you may notice bubbles of gas have formed by morning. This is because the gas (mostly dissolved oxygen) has become less soluble as the temperature of the water has increased.

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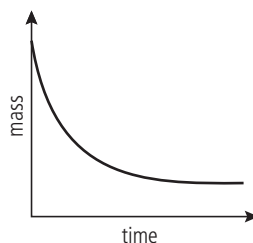
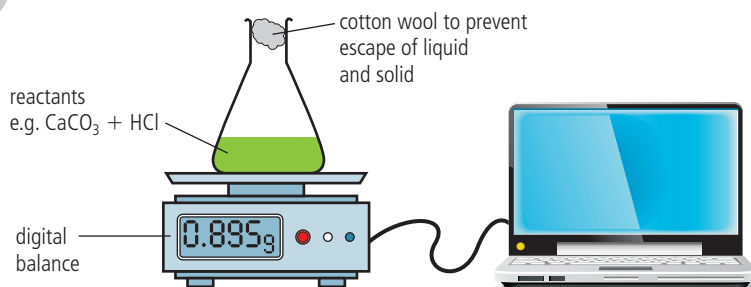
Volume of gas against time. The reaction has ended when the curve reaches a plateau.

Change in mass

Many reactions involve a change in mass, and it may be convenient to measure this directly. If the reaction is giving off a gas, the corresponding decrease in mass can be measured by standing the reaction mixture directly on a balance. This method is unlikely to work well where the evolved gas is hydrogen, as it is too light to give significant changes in mass. The method allows for continuous readings, so a graph can be plotted directly of mass against time. For example, the release of carbon dioxide from the reaction between a carbonate and dilute acid can be followed in this way.



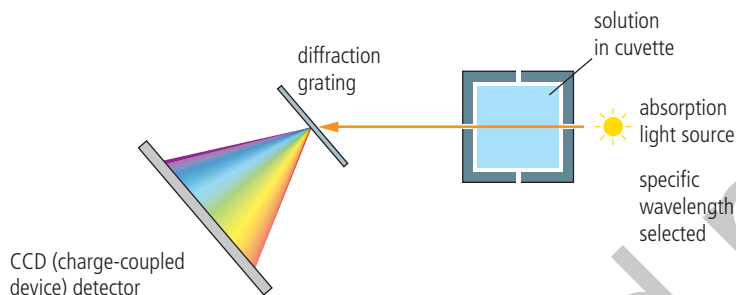
Experiment to measure rate of reaction by following change in mass against time.



Mass against time. The reaction has ended when the curve reaches a plateau.

Change in transmission of light: colorimetry/spectrophotometry

This technique can be used if one of the reactants or products is coloured and so gives characteristic absorption in the visible region (wavelengths about 320–800 nm). Sometimes an indicator can be added to generate a coloured compound that can then be followed in the reaction. A colorimeter or spectrophotometer works by passing light of a selected wavelength through the solution being studied and measuring the intensity of the light transmitted by the reaction components. As the concentration of the coloured compound increases, it absorbs proportionally more light, so less is transmitted. A photocell generates an electric current according to the amount of light transmitted and this is recorded on a meter or connected to a computer.

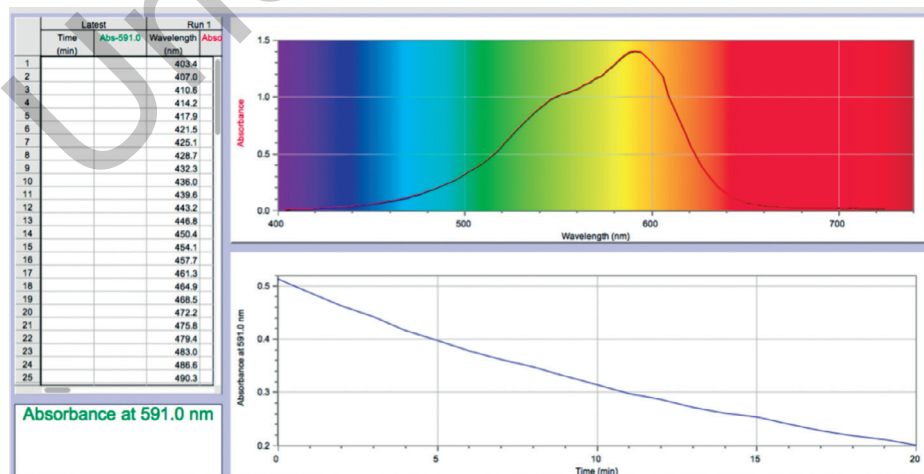


The method allows for continuous readings to be made, so a graph of absorbance against time can be plotted directly. It is possible to convert the absorbance values into concentrations using a standard curve based on readings of known concentration. Often, however, it is sufficient to record absorbance itself (or transmittance, which is inversely proportional to absorbance) as a function against time.

For example, the reaction between the dye crystal violet and sodium hydroxide solution can be written in an abbreviated form as follows:



The initial crystal violet solution (CV^+) is coloured but this slowly changes to a colourless solution as the product (CVOH) is formed. So we can determine the rate of product formation by measuring the *decrease in absorbance* that occurs as the coloured reactant is depleted. The figure shows data from this reaction, with absorbance at 591 nm measured against time.



A spectrophotometer measures absorbance, which directly relates to concentration. Light of a specific wavelength is selected from an internal source and passed through the solution placed in the cuvette. The transmitted light passes through a diffraction grating, then the diffracted light is collected and changed into a digital signal by the charge-coupled device (CCD) detector.

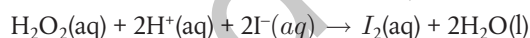
Results of an experiment to determine the rate of reaction by following change in absorbance against time using a digital spectrophotometer.

An example of the use of a calibration curve to determine concentration from absorbance data is outlined in Structure 3.1.10.

Change in concentration measured using titration

In some reactions it may be possible to measure the concentration of one of the reactants or products by titrating it against a known 'standard' (see Structure 1.4). However, because this technique involves chemically changing the reaction mixture, it cannot be done continuously as the reaction proceeds. Instead, samples must be withdrawn from the reaction mixture at regular time intervals and then analyzed by titration. A problem here is that the process of titration takes time, during which the reaction mixture in the sample will continue to react. To overcome this, a technique known as **quenching** can be used, where a substance is introduced which effectively stops the reaction in the sample at the moment it is withdrawn. It is rather like obtaining a 'freeze frame' shot of the reaction at a particular interval of time. In order to see how concentration changes as the reaction proceeds, it is necessary to repeat this process at several intervals of time.

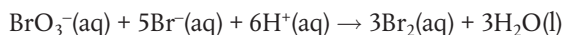
For example, the reaction between H_2O_2 and acidified KI yields I_2 , which can be titrated against sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, to determine its concentration. Sodium carbonate, Na_2CO_3 , is used to quench the reaction by neutralizing the added acid.



Change in concentration measured using conductivity

The total electrical conductivity of a solution depends on the total concentration of its ions and on their charges. If this changes when reactants are converted to products, it can provide a convenient method to follow the progress of the reaction. Conductivity can be measured directly using a conductivity meter which involves immersing inert electrodes in the solution. As with colorimetry, the apparatus can be calibrated using solutions of known concentration so that the readings can be converted into the concentrations of the ions present.

For example, in the reaction



the sharp decrease in the concentration of ions (12 on the reactants side and 0 on the products side) will give a corresponding decrease in the electrical conductivity of the solution as the reaction proceeds.

Non-continuous methods of detecting change during a reaction: 'clock reactions'

Sometimes it is difficult to record the continuous change in the rate of a reaction. In these cases, it may be more convenient to measure the time it takes for a reaction to reach a certain chosen fixed point – that is, something observable which can be used as an arbitrary 'end point' by which to stop the clock. The time taken to reach this point for the same reaction under different conditions can then be compared and used as a means of judging the different rates of the reaction. So in contrast to the first five techniques of measuring rate of reaction where time is the independent variable, detecting a change in a clock reaction uses time as a dependent variable.

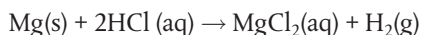
Tool 1 - What experiments measuring reaction rates might use time as (i) a dependent variable or (ii) an independent variable?



Note that the limitation of this method is that the data obtained gives only an average rate over the time interval.

For example, the following can be measured:

- the time taken for a certain size piece of magnesium ribbon to react completely with dilute acid, until it is no longer visible



- the time taken for a solution of sodium thiosulfate titrated with dilute acid to become opaque by the precipitation of sulfur, so that a cross viewed through paper is no longer visible



SKILLS

Rates of reaction. Full details of how to carry out this experiment with a worksheet are available in the eBook.



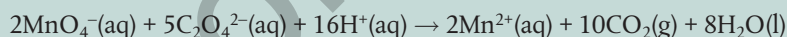
Recording the increase in opacity during a reaction. Sodium thiosulfate (left) is a clear liquid, which reacts with hydrochloric acid (upper centre) to form an opaque solution (right). A cross (left) drawn onto paper is placed under the reaction beaker to allow the end-point to be confirmed. The experiment is timed from when the reactants are mixed until the cross disappears from sight.



In all these reactions, the goal is to measure change in concentration against time. This allows a comparison of reaction rates under different conditions. But because the rate is dependent on temperature, it is essential to control the temperature throughout these experiments. It is sometimes suitable to carry out the reactions in a thermostatically controlled water bath.

Exercise

Q1. Consider the following reaction.



Describe three different ways in which you could measure the rate of this reaction.

Q2. Which units are used to express the rate of a reaction?

A $\text{mol dm}^{-3} \text{ time}$

B $\text{mol}^{-1} \text{ dm}^3 \text{ time}^{-1}$

C $\text{mol dm}^{-3} \text{ time}^{-1}$

D mol time^{-1}

Q3. The reaction between calcium carbonate and hydrochloric acid is carried out in an open flask. Measurements are made to determine the rate of the reaction.



(a) Suggest three different types of data that could be collected to measure the rate of this reaction.

(b) Explain how you would expect the rate of the reaction to change with time and why.

Q4. The following data were collected for the reaction
 $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ at 390°C .

$[\text{H}_2\text{O}_2] / \text{mol dm}^{-3}$	Time / s	$[\text{H}_2\text{O}_2] / \text{mol dm}^{-3}$	Time / s
0.200	0	0.070	120
0.153	20	0.063	140
0.124	40	0.058	160
0.104	60	0.053	180
0.090	80	0.049	200
0.079	100		

Draw a graph of concentration against time and determine the reaction rate after 60s and after 120s.

Collisions in the court.
 Full details of how to carry out this activity with a worksheet are available in the eBook.

SKILLS



Reactivity 2.2.2 – Collision theory

Reactivity 2.2.2 – Species react as a result of collisions of sufficient energy and proper orientation.

Explain the relationship between the kinetic energy of the particles and the temperature in kelvin, and the role of collision geometry.

Structure 1.1 – What is the relationship between the kinetic molecular theory and collision theory?

TOK

The Kelvin scale of temperature gives a natural measure of the average kinetic energy of molecules in a gas, whereas the Celsius scale is based on the properties of water. Are physical properties such as temperature invented or discovered?

Species react as a result of collisions

Kinetic energy and temperature

Since the early 18th century, scientists have developed theories to explain the fact that gases exert a pressure. These theories developed alongside a growing understanding of the atomic and molecular nature of matter, and were extended to include the behaviour of particles in all states of matter. Today they are summarized as the **kinetic molecular theory of matter** (see Structure 1.1).

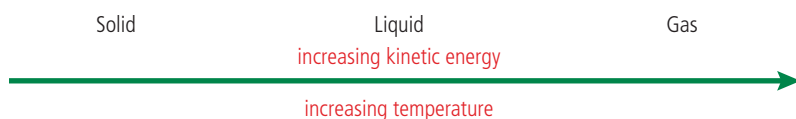
The essence of kinetic molecular theory is that particles in a substance move randomly as a result of the **kinetic energy** that they possess. Because of the random nature of these movements and collisions, not all particles in a substance at any one time have the same values of kinetic energy, but will instead have a range of values. A convenient way to describe the kinetic energy of a substance is therefore to take the *average* of these values, and this is directly related to its **absolute temperature** – that is, its temperature measured in kelvin.

Increasing temperature therefore means an increase in the average kinetic energy of the particles of a substance. As we supply a substance with extra energy through heating it, we raise the average kinetic energy of the particles and so also raise its temperature. When we compare the behaviour of the particles in the three states of matter from solid, through liquid, to gas, the differences are a result of this increase in the average kinetic energy of the particles.



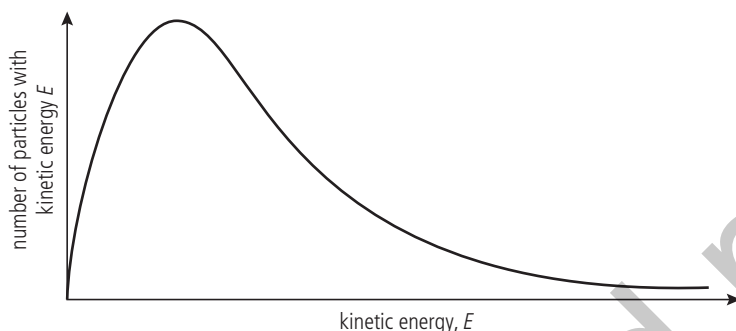
▲ A puddle of water evaporates, even on a cold day, because a small proportion of molecules on the surface have enough kinetic energy to vaporize. This demonstrates that the particles in a substance must have a range of values of kinetic energy as described by kinetic molecular theory.

For a given substance this can be summarized as follows:



The Maxwell-Boltzmann energy distribution curve

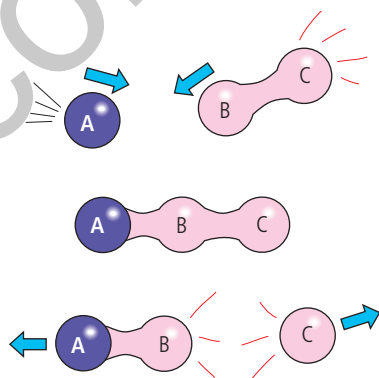
The fact that particles in a gas at a specific temperature show a range in their values of kinetic energy is expressed by the **Maxwell-Boltzmann energy distribution curve**.



Like other distribution curves, this shows the number of particles having a specific value of kinetic energy (or the probability of that value occurring) plotted against the values for kinetic energy. The area under the curve represents the total number of particles in the sample.

The nature of collisions between particles

When reactants are placed together, the kinetic energy that their particles possess causes them to collide with each other. The energy of these collisions may result in some bonds within the reactants being broken, and some new bonds forming. As a result, products form and the reaction 'happens'. This explanation of chemical reactions is known as **collision theory**



It follows that the rate of the reaction will depend on the number of collisions between particles that are 'successful', that is, which lead to the formation of products. But a very important point is that *not all collisions will be successful*. There are two main factors that influence this:

- energy of collision and
- geometry of collision.



Temperature in Kelvin (K) is proportional to the average kinetic energy of the particles in a substance.

The Maxwell-Boltzmann energy distribution curve.



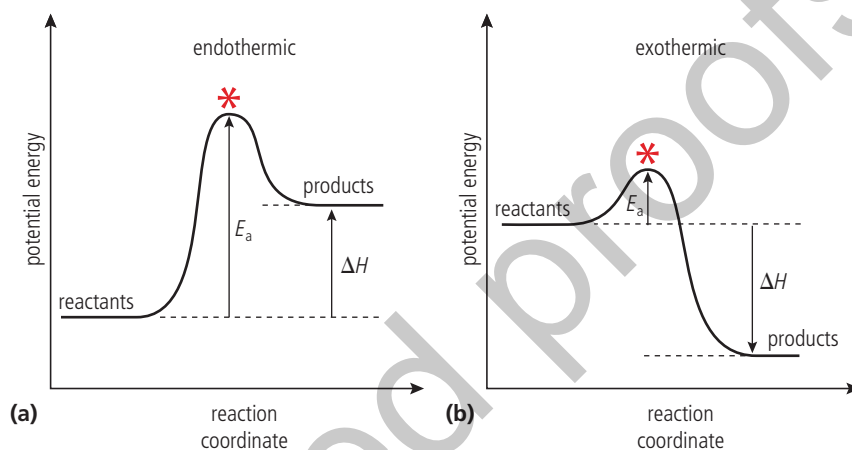
Although their names are linked in the famous energy distribution curve discussed here, James Clerk Maxwell and Ludwig Boltzmann had very different outlooks on life. Maxwell was a Scottish physicist, known for his curiosity and humour. His wife worked alongside him in many of his experiments. Boltzmann, an Austrian, was prone to depression and took his own life, seemingly believing that his work was not valued. Nonetheless, as peers during the 19th century, they refined and developed each other's ideas, culminating in the distribution curve that bears their two names.

Particles react by colliding with sufficient kinetic energy and in the correct orientation.

Energy of collision

In order for a collision to lead to a reaction, the particles must have a certain minimum value for their kinetic energy, known as the **activation energy**, E_a . This energy is necessary for overcoming repulsion between molecules, and often for breaking some bonds in the reactants before they can react. When this energy is supplied, the reactants achieve the **transition state** from which products can form. The activation energy therefore represents an energy barrier for the reaction, and it has a different value in different reactions.

Energy path of a reaction with the activation energy for (a) endothermic and (b) exothermic reactions. * represents the transition state



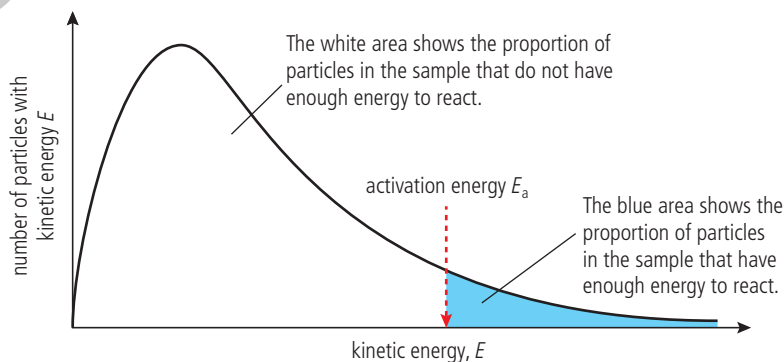
Activation energy (E_a) is defined as the minimum value of kinetic energy that particles must have before they are able to react.



We can think of the activation energy as a 'threshold value' – a bit like a pass mark in an examination: values greater than this mark achieve a pass, lower values do not achieve a pass. The activation energy threshold similarly determines which particles react and which do not. So only particles that have a kinetic energy value greater than the activation energy will have successful collisions. Note that particles with lower values of kinetic energy may still collide, but these collisions will not be 'successful' in the sense of causing a reaction.

It therefore follows that the rate of the reaction depends on the proportion of particles that have values for kinetic energy greater than the activation energy.

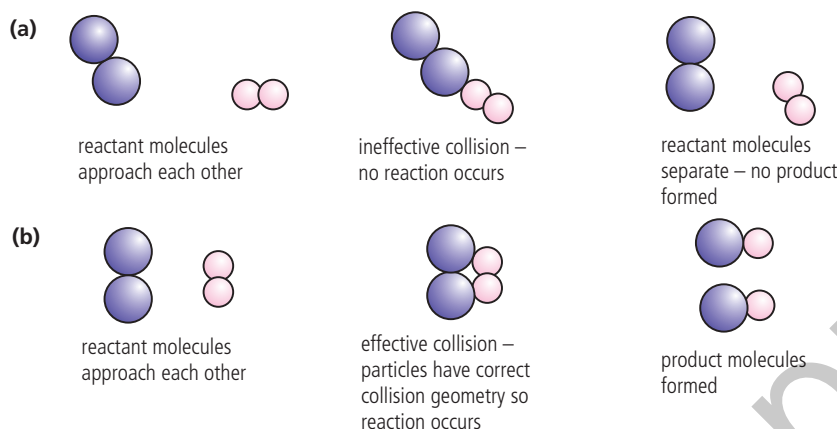
Maxwell-Boltzmann energy distribution curve showing how the activation energy, E_a , distinguishes between particles that have greater or lesser values of kinetic energy



The magnitude of the activation energy varies greatly from one reaction to another, and it is an important factor in determining the overall rate of the reaction. In general, reactions with high activation energy proceed more slowly than those with low activation energy as fewer particles will have the required energy for a successful collision.

Geometry of collision

Because collisions between particles are random, they are likely to occur with the particles in many different orientations. In some reactions, this can be crucial in determining whether or not the collisions will be successful, and therefore what proportion of collisions will lead to a reaction.



We can now summarize the collision theory as follows. The rate of a reaction depends on the frequency of collisions that occur between particles possessing both:

- values of kinetic energy greater than the activation energy and
- appropriate collision geometry.

Understanding this theory will help us to investigate and explain the factors that increase the rate of reaction.

Nature of Science

The collision between a small number of reacting species resulting in chemical change has not been observed directly. Instead, collision theory is based on an application of kinetic molecular theory and theory of how chemical reactions occur through bond-breaking and bond-making. In science, theories generally accommodate the assumptions and premises of other theories in this way. The fact that collision theory helps to explain the observed effects of factors influencing the rate of reactions adds to its validity. The theory enables chemists to make predictions about the impact of different factors on the rates of specific reactions, which has important applications in many branches of chemistry such as industry, biochemistry and environmental chemistry.

Exercise

- Q5. Which statement is correct for a collision between reactant particles that leads to reaction?
- A Colliding particles must have different energy.
 - B Colliding particles must have the same energy.
 - C Colliding particles must have kinetic energy greater than the average kinetic energy.
 - D Colliding particles must have kinetic energy greater than the activation energy.

The effect of collision geometry. In (a) the particles do not have the correct collision geometry and no reaction occurs. In (b) the particles collide with the correct geometry, enabling products to form.

In order to react, particles must collide with kinetic energy greater than the activation energy and have the correct collision geometry.

Structure 1.1 – What is the relationship between the kinetic molecular theory and collision theory?

- Q6.** Which of the following determine whether a reaction will occur?
- I. the orientation of the molecules
 - II. the energy of the molecules
 - III. the volume of the container
- A** I and II **B** I and III **C** II only **D** I, II, and III
- Q7.** If we compare two reactions, one which requires the simultaneous collision of three molecules and the other which requires a collision between two molecules, which reaction would you expect to be faster? Explain why.

Reactivity 2.2.3, 2.2.4 and 2.2.5 – Factors that influence the rate of reaction

Reactivity 2.2.3 – Factors that influence the rate of a reaction include pressure, concentration, surface area, temperature and the presence of a catalyst.

Predict and explain the effects of changing conditions on the rate of a reaction.

Tool 1 – What variables must be controlled in studying the effect of a factor on the rate of a reaction?

Nature of Science, Tool 3, Inquiry 3 – How can graphs provide evidence of systematic and random error?

Reactivity 2.2.4 – Activation energy, E_a , is the minimum energy that colliding particles need for a successful collision leading to a reaction.

Construct Maxwell–Boltzmann energy distribution curves to explain the effect of temperature on the probability of successful collisions.

Reactivity 2.2.5 – Catalysts increase the rate of reaction by providing an alternative reaction pathway with lower E_a .

Sketch and explain energy profiles with and without catalysts for endothermic and exothermic reactions.

Construct Maxwell–Boltzmann energy distribution curves to explain the effect of different values for E_a on the probability of successful collisions.

Biological catalysts are called enzymes.

The different mechanisms of homogeneous and heterogeneous catalysts will not be assessed.

Reactivity 2.3 – What is the relative effect of a catalyst on the rate of the forward and backward reactions?

Be careful not to confuse the question of 'how fast?' a reaction goes with the question of 'how far?' it goes. We are discussing only the first question here. The question of how far a reaction goes, which influences the *yield* of the reaction, will be discussed in Reactivity 2.3.

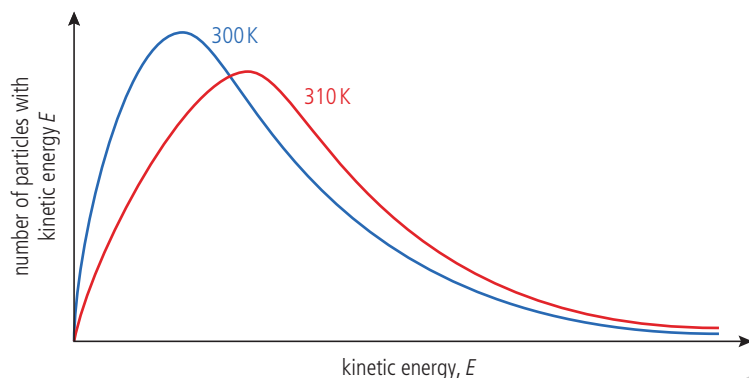


Temperature, concentration, pressure, surface area and the use of a catalyst can influence the rate of reaction

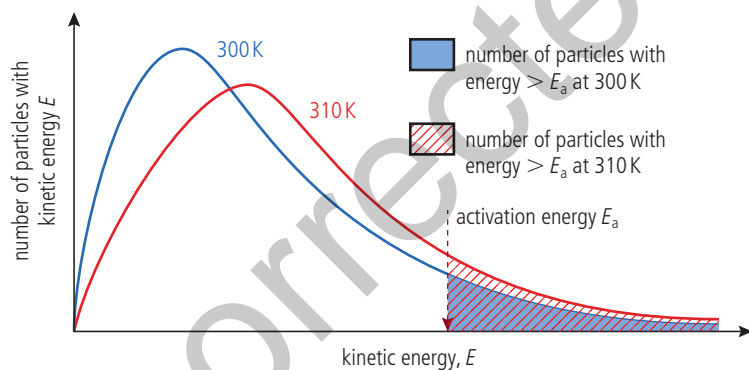
From the collision theory, we know that any factor which increases the number of successful collisions will increase the rate of the reaction. We will investigate five such factors here.

Temperature

Increasing the **temperature** causes an increase in the average kinetic energy of the particles. We can see this by comparing Maxwell–Boltzmann energy distribution curves of the same sample of particles at two different temperatures.



The area under the two curves is equal as this represents the total number of particles in the sample. But at the higher temperature, more of the particles have higher values for kinetic energy and the peak of the curve shifts to the right. In Figure 6, we can see how this shift increases the proportion of particles that have values for kinetic energy greater than that of the activation energy.



So, as temperature increases, there is an increase in collision frequency due to the higher kinetic energy, but more importantly there is an increase in the number of collisions involving particles with the necessary activation energy to overcome the activation energy barrier. Consequently, there is an increase in the frequency of *successful* collisions and so an increase in the rate of reaction. Many reactions approximately double their reaction rate for every 10°C increase in temperature.

Concentration

Increasing the **concentration** of reactants increases the rate of reaction. This is because as concentration increases, the frequency of collisions between reactant particles increases, as shown in Figure 7. The frequency of successful collisions therefore increases too.

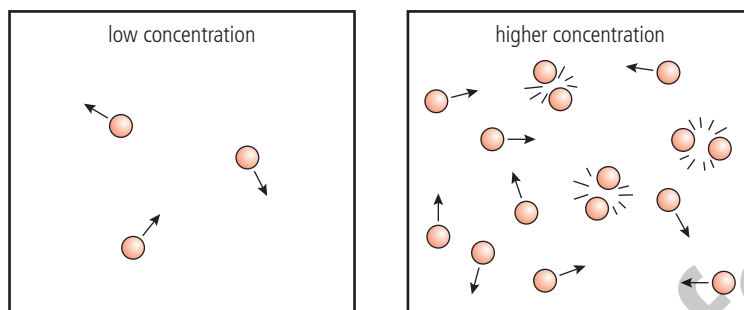
Maxwell–Boltzmann distribution curves for a sample of gas at 300 K and 310 K. At the higher temperature, the curve has shifted to the right and become broader, showing a larger number of particles with higher values for kinetic energy.

R2.2 Figure 6 Maxwell–Boltzmann energy distribution curves for a sample of gas at two different temperatures, showing the higher proportion of particles with kinetic energy greater than the activation energy at the higher temperature.

i

Specimens of the extinct mammal the mammoth, dated as 10 000 years old, have been found perfectly preserved in the Arctic ice, whereas for individual specimens of a similar age found in California, only bones remain. This is an illustration of the effect of the cold temperature in the Arctic decreasing the rate of the reactions of decay. The same concept is used in the process of refrigerating or freezing food to preserve it.

R2.2 Figure 7 Effect of concentration on collision frequency.



When particles are closer together they have a greater chance of reacting.

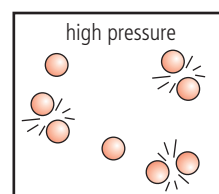
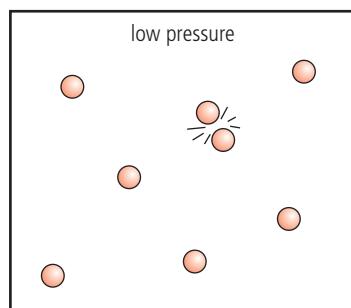
We can see the effect of concentration by following the rate of a reaction as it progresses. As reactants are used up, their concentration falls and the rate of the reaction decreases, giving the typical rate curves we saw in Figures 1 and 2.

The effect of concentration on the rate of reaction between zinc and sulfuric acid. The tube on the left has a more concentrated solution of the acid, the tube on the right has a more dilute solution. The product, hydrogen gas, is seen collecting much more quickly in the presence of the more concentrated acid.



Pressure

For reactions involving gases, increasing **pressure** increases the rate of reaction. This is because the higher pressure compresses the gas, effectively increasing its concentration. This will increase the frequency of collisions.



In this example, the pressure has been increased by decreasing the size of the container

At the same temperature, the box on the right has a higher pressure and a greater collision frequency.

Surface area

Increasing the **surface area** of reactants increases the rate of reaction. This is important in heterogeneous reactions where the reactants are in different phases, such as a solid reacting with a solution. Subdividing a large particle into smaller parts increases the total surface area and therefore allows more contact and a higher probability of collisions between the reactants. You may know, for example, how much easier it is to start a fire using small pieces of wood, rather than a large log – it is because with the small pieces there is more contact between the wood and the oxygen with which it is reacting. In reactions involving solids in solutions, stirring may help to increase the surface area of the solid by ensuring individual particles are spread throughout the solution and do not aggregate at the bottom of the container. This increases the rate of reaction.

The effect of particle size can be demonstrated in the reaction between marble (CaCO_3) and hydrochloric acid. When marble chips are replaced with powder, the effervescence caused by carbon dioxide release is much more vigorous.

This effect of particle size on reaction rate can be quite dramatic. It has been responsible for many industrial accidents involving explosions of flammable dust powders – for example, coal dust in mines and flour in mills.

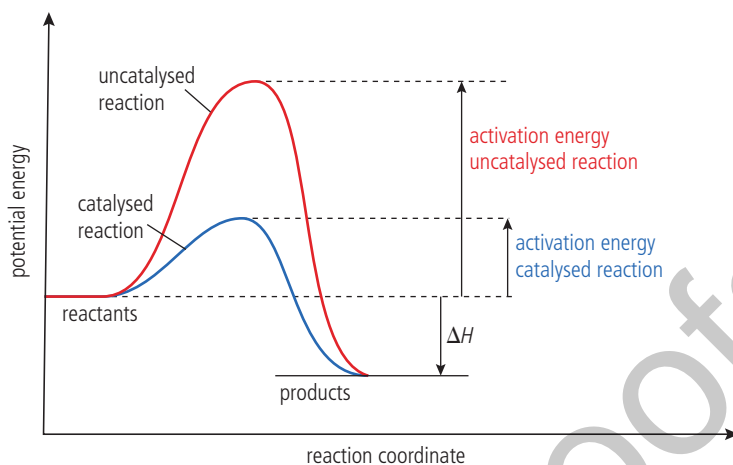


◀ Coal dust explosion experiment at Altofts Colliery, Yorkshire, UK. Health and safety research in the UK started with investigations in the early 20th century into safety in mines. Experiments were carried out at locations such as Altofts Colliery, helping to determine that coal dust was explosive under certain circumstances.

Catalyst

A **catalyst** is a substance that increases the rate of a chemical reaction without itself undergoing chemical change. Most catalysts work by providing an alternative route for the reaction that has a lower activation energy.

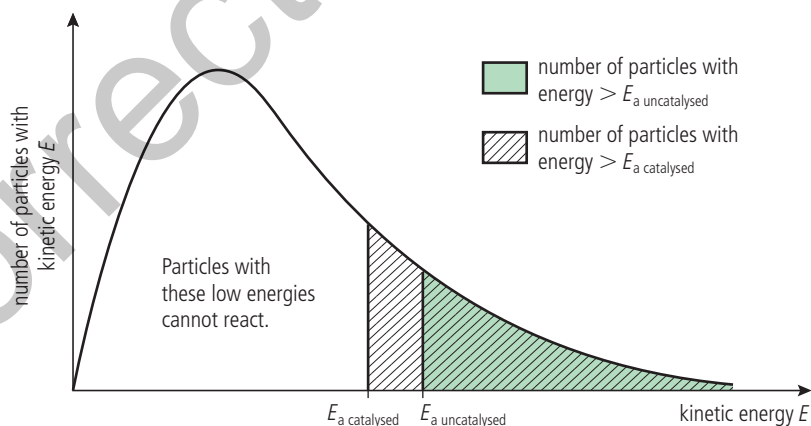
Effect of a catalyst on lowering the activation energy of a reaction.



This means that without increasing the temperature, a larger number of particles will now have values of kinetic energy greater than the activation energy, and so will be able to undergo successful collisions. Think again of activation energy as being like the pass mark in an examination: the effect of the catalyst is like lowering the pass mark. This means that with the same work in the tests, a higher number of people would be able to achieve a pass!

Figure 8 uses the Maxwell–Boltzmann distribution to show how a catalyst increases the proportion of particles having values of kinetic energy greater than the activation energy.

R2.2 Figure 8 Effect of catalyst on increasing the proportion of particles able to react.



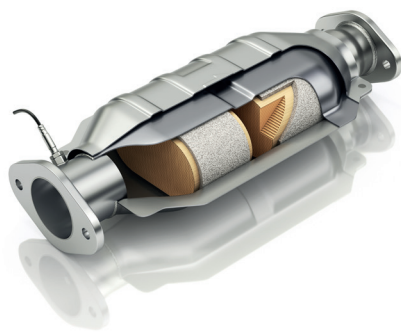
A catalyst is a substance that increases the rate of a chemical reaction without itself undergoing permanent chemical change.



Catalysts bring about an equal reduction in the activation energy of both the forward and the reverse reactions, so they do not change the position of equilibrium or the yield (seen in Reactivity 2.3). However, because of their ability to increase the *rate* of reactions, they influence the rate of formation of product and so play an essential role in the efficiency of many industrial processes. Without catalysts, many reactions would proceed too slowly, or would have to be conducted at such high temperatures that they would simply not be worthwhile. This is why the discovery of the ‘best’ catalyst for a particular reaction is a very active area of research, and often the exact specification of a catalyst used in an industrial process is a matter of secrecy.

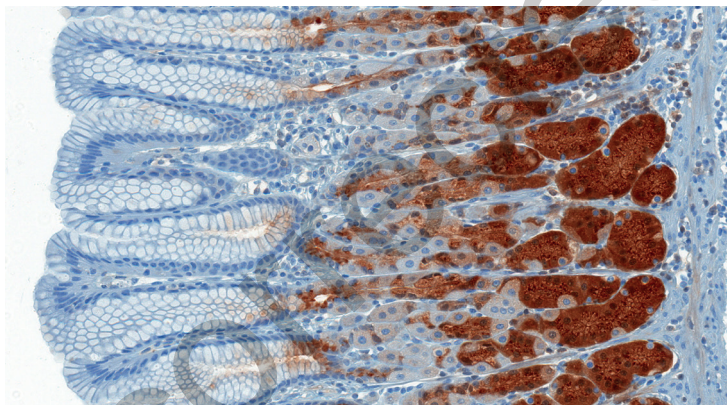
Reactivity 2.3 – What is the relative effect of a catalyst on the rate of the forward and backward reactions?





▲ A catalytic converter containing transition metal catalysts such as platinum, palladium and rhodium. This device catalyzes reactions that convert the toxic emissions from an internal combustion engine into less harmful ones. It is estimated that catalytic converters can reduce pollution emission by 90% without loss of engine performance or fuel economy.

Every *biological* reaction is controlled by a catalyst, known as an **enzyme**. Thousands of different enzymes exist as they are each specific for a particular biochemical reaction. Enzymes are finding increasingly widespread uses in many domestic and industrial processes, from biological detergents to acting as 'biosensors' in medical studies. Some of these applications, such as cheese making, are centuries old, but others are developing rapidly, constituting the field known as **biotechnology**.



Catalysis is also an important aspect of Green Chemistry, which seeks to reduce the negative impact of chemical processes on the environment. Catalysts can replace stoichiometric reagents, and can greatly enhance the selectivity of processes. As they are effective in very small quantities and can frequently be reused, catalysts do not contribute to the chemical waste, and so they increase the atom economy.

Challenge yourself

2. Catalysts can be categorized as 'homogeneous' or 'heterogeneous'. A homogeneous catalyst is in the same phase as the reactants. For example, gaseous chlorine radicals catalyze the breakdown of ozone in the stratosphere. A heterogeneous catalyst, such as solid vanadium(V) oxide in the reaction between gaseous sulfur dioxide and oxygen, is in a different phase to the reactants. Can you identify which type of catalyst might be more difficult to recover after a reaction and suggest a possible approach for doing so?



Catalytic reforming is the process by which linear hydrocarbons are converted into branched or cyclic molecules that burn more smoothly. The development of this process is thought to have played a major role in the Second World War. Aircraft fuel using such hydrocarbons increased the performance of the European allies' planes to the point where they were able to gain victory in the skies.



Biological catalysts are called enzymes.



A microscopic cross-section of glands found in the stomach. The pepsinogen digestive enzyme is shown in brown. It is converted by gastric acid into the active enzyme pepsin which catalyzes the breakdown of proteins into small units of amino acids called peptides.

SKILLS



Effect of a catalyst. Full details of how to carry out this experiment with a worksheet are available in the eBook.



Nature of Science

Depletion of the protective ozone layer in the stratosphere has been caused largely by the catalytic effects of CFCs and nitrogen oxides. These chemicals are produced from a variety of sources and often have their most destructive effect far from the country of their origin. International action and cooperation have played an important part in reducing the effects of ozone depletion, and continuing adherence by all countries to international treaties is essential.

Inquiry-based skills for investigating rate of reaction

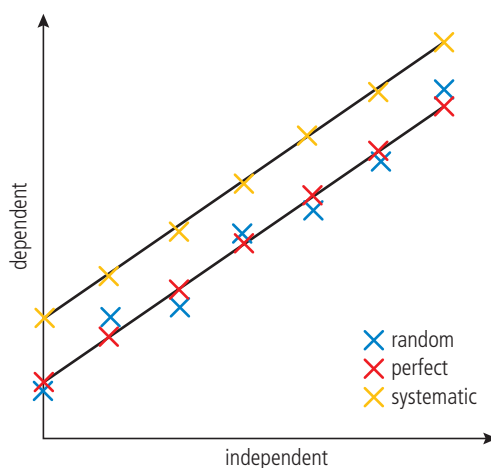
Identification of controlled variables

Given the range of factors that can affect the rate of reaction, we must be careful to identify the relevant controlled variables when planning an investigation. For example, when investigating the effect of temperature on the reaction between hydrochloric acid, $\text{HCl}(\text{aq})$, and magnesium, $\text{Mg}(\text{s})$, we would need to ensure that the same concentration of acid is used in each trial as well as using the same sized magnesium strip to control the surface area.

When you are identifying variables to be controlled, it can be helpful to first consider the factors that affect rate of reaction, such as concentration, surface area and temperature, and then the specific details of your measurement technique. For example, when using a light sensor to measure the rate of formation of a precipitate in a reaction, you would need to ensure that the position of the sensor and light source are the same during all trials. This approach is crucial in obtaining valid data from an investigation.

Evidence for systematic and random error in graphs

As well as identifying the effect of a given variable on the rate of reaction, graphs can also be used to provide evidence of systematic and random error.



In a perfect data set, all data points would be positioned on the trend line. A systematic error produces a displaced straight line above or below the expected position. Random errors lead to points on both sides of the trend line.

Tool 1 – What variables must be controlled in studying the effect of a factor on the rate of a reaction?



We can evaluate the fit of a trend line or curve by applying the coefficient of determination, R^2 (pronounced 'R squared'). An R^2 value will fall between 0 and 1, where 1 indicates that the trend line or curve passes perfectly through all data points. This value can be calculated automatically on most graph plotting software.



Systematic errors occur when all measurements are higher, or all measurements are lower, than the expected value. This leads to inaccuracy in the final results. Random errors occur in individual measurements due to limitations in measurement equipment (uncertainty), changes in the surroundings, misinterpreted measurements or an insufficient number of repeat trials. These can lead to imprecision in collected data.

Exercise

- Q8.** Which of the following statements is correct?
- A** A catalyst increases the rate of the forward reaction only.
 - B** A catalyst increases the rate of the forward and backward reactions.
 - C** A catalyst increases the yield of product formed.
 - D** A catalyst increases the activation energy of a reaction.
- Q9.** Which statements are correct for the effects of catalyst and temperature on the rate of reaction?

	Adding a catalyst	Increasing the temperature
A	collision frequency increases	collision frequency increases
B	activation energy decreases	collision frequency increases
C	collision frequency increases	activation energy increases
D	activation energy increases	activation energy decreases

- Q10.** In the reaction between marble (calcium carbonate) and hydrochloric acid, which set of conditions would give the highest rate of reaction?



- A** marble chips and 1.0 mol dm^{-3} HCl
 - B** marble powder and 1.0 mol dm^{-3} HCl
 - C** marble chips and 0.1 mol dm^{-3} HCl
 - D** marble powder and 0.1 mol dm^{-3} HCl
- Q11.** A sugar cube cannot be ignited with a match, but a sugar cube coated in ashes will ignite. Suggest a reason for this observation.
- Q12.** Catalytic converters are now used in most cars to convert some components of exhaust gases into less environmentally damaging molecules. One of these reactions converts carbon monoxide and nitrogen monoxide into carbon dioxide and nitrogen. The catalyst usually consists of metals such as platinum or rhodium.
- (a)** Write an equation for this reaction.
 - (b)** Explain why it is important to reduce the concentrations of carbon monoxide and nitrogen monoxide released into the atmosphere.
 - (c)** Why do you think the converter sometimes consists of small ceramic beads coated with the catalyst?
 - (d)** Suggest why the converter usually does not work effectively until the car engine has warmed up.
 - (e)** Discuss whether the use of catalytic converters in cars solves the problem of car pollution.



Guiding question revisited

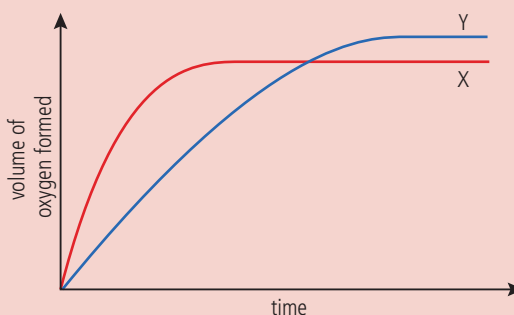
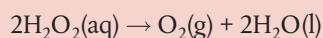
How can the rate of a reaction be controlled?

In this chapter we have explored collision theory and investigative techniques to show:

- The rate of reaction is expressed as the change in concentration of a particular reactant or product per unit time. It has units of $\text{mol dm}^{-3} \text{s}^{-1}$.
- Rate of reaction can be measured indirectly using different experimental techniques. The choice of technique will depend on the changes that occur during a specific reaction such as the production of a gas, the formation of a precipitate, or changes in the colour or electrical conductivity of a solution.
- The rate at a specific point in a reaction can be calculated from the gradient of a tangent on a graph of concentration, volume, absorbance or mass against time.
- For a reaction to occur, species must collide with sufficient kinetic energy and proper orientation. These collisions are known as 'successful' collisions.
- The minimum energy required for a successful collision is called the activation energy, E_a .
- The use of a catalyst and increases in pressure, concentration, surface area and temperature lead to an increase in the frequency of successful collisions per unit time and so increase the rate of a reaction.
- Catalysts increase rate of reaction by providing an alternative reaction pathway with a lower E_a . This effect can be represented in a reaction energy profile.
- Maxwell-Boltzmann distribution curves can be used to explain the effect of changing temperature and the use of a catalyst on the probability of successful collisions occurring.

Practice questions

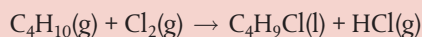
1. Curve X on the graph shows the volume of oxygen formed during the catalytic decomposition of a 1.0 mol dm^{-3} solution of hydrogen peroxide:



Which change would produce curve Y?

- A adding water
- B adding some 0.1 mol dm^{-3} hydrogen peroxide solution
- C using a different catalyst
- D lowering the temperature

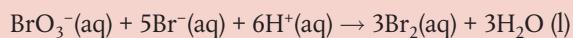
2. Which changes increase the rate of the reaction below?



- I. increase of pressure
- II. increase of temperature
- III. removal of $\text{HCl}(\text{g})$

- A** I and II only **B** I and III only
C II and III only **D** I, II, and III

3. Which experimental procedure could be used to determine the rate for the following reaction?



- A** measure the change in electrical conductivity in a given time
- B** measure the change in mass in a given time
- C** record the time taken for the formation of a precipitate
- D** measure the change in volume of gas produced in a given time

4. The catalyst manganese(IV) oxide, $\text{MnO}_2(\text{s})$, increases the rate of the decomposition reaction of hydrogen peroxide, $\text{H}_2\text{O}_2(\text{aq})$. Which statements about MnO_2 are correct?

- I. The rate is independent of the particle size of MnO_2 .
- II. MnO_2 provides an alternative reaction pathway for the decomposition with a lower activation energy.
- III. All the MnO_2 is present after the decomposition of the hydrogen peroxide is complete.

- A** I and II only **B** I and III only
C II and III only **D** I, II, and III

5. Which of the following statements is incorrect?

- A** The rate of a chemical reaction depends on the temperature.
- B** Rate and time are directly proportional.
- C** The rate of most chemical reactions decreases with time.
- D** A catalyst for a reaction increases the rate of both its forward and backward reactions.

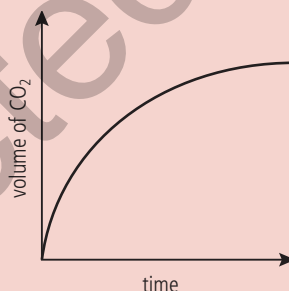
6. A student measures the rate of a reaction by timing the appearance of a precipitate that forms in aqueous solution. Which of the following factors would increase the time required for the precipitate to form?

- A** raising the temperature
- B** adding a catalyst
- C** diluting the solution
- D** stirring the reaction mixture

Questions 7–9 refer to the reaction between magnesium carbonate and hydrochloric acid, which is as follows:



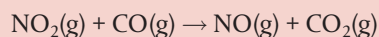
7. Which of the conditions described below will produce the fastest rate of reaction?
- A 2.0 mol dm⁻³ HCl and MgCO₃ lumps
 - B 1.0 mol dm⁻³ HCl and MgCO₃ powder
 - C 2.0 mol dm⁻³ HCl and MgCO₃ powder
 - D 1.0 mol dm⁻³ HCl and MgCO₃ lumps
8. Which of the following measurements would not be a suitable means to follow the rate of this reaction?
- A increase in mass of reaction mixture
 - B increase in volume of gas produced at constant pressure
 - C increase in pH of reaction mixture
 - D increase in pressure of gas produced at constant volume
9. The sketch graph below represents the result of an experiment to measure the rate of this reaction.



Which of the following is the best explanation for the shape of the graph?

- A The rate of reaction increases with time because the acid becomes more dilute.
 - B The rate of reaction increases with time because the calcium carbonate pieces become smaller.
 - C The rate of reaction decreases with time because the acid becomes more dilute.
 - D The rate of reaction decreases with time because the calcium carbonate pieces become smaller.
10. Collision theory states that collisions between reactant molecules do not always lead to the formation of product. Which of the following is the best explanation for this statement?
- A The reactant molecules are at too low a concentration.
 - B The reaction is at equilibrium.
 - C The reaction needs a catalyst in order to occur.
 - D The reactant molecules do not have sufficient energy.

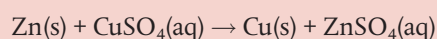
11. It is found that in the reaction:



an increase in temperature increases the rate of reaction. Which of the statements below is the main reason for this?

- A The molecules collide more frequently.
- B The proportion of molecules with energy greater than the activation energy increases.
- C The pressure exerted by the molecules increases.
- D The proportion of molecules with the correct collision geometry increases.

12. Zinc metal reacts with copper(II) sulfate solution as follows:



Which of the following factors will increase the rate of reaction?

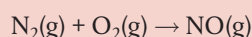
- I. increasing the concentration of $\text{CuSO}_4(\text{aq})$
- II. decreasing the size of the zinc pieces
- III. carrying out the reaction at a higher temperature

- A I and II
- B I and III
- C II only
- D I, II and III

13. Which of the following units could not be used to express the rate of a reaction?

- A $\text{mol dm}^{-3} \text{s}$
- B $\text{g cm}^{-3} \text{s}^{-1}$
- C $\text{mol dm}^{-3} \text{s}^{-1}$
- D $\text{g dm}^{-3} \text{s}^{-1}$

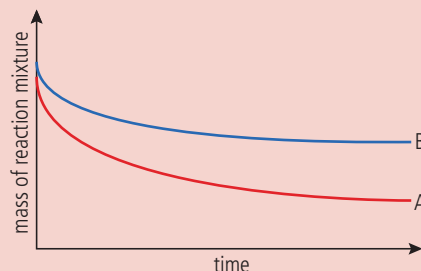
14. The atmosphere consists mostly of the gases nitrogen, N_2 , and oxygen, O_2 . Under normal conditions these two gases react together to form nitrogen monoxide, NO , extremely slowly.



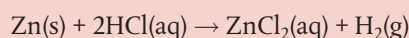
Which statement below is the best explanation for the low rate of this reaction?

- A The atmosphere does not contain a catalyst for this reaction.
- B The reaction between nitrogen and oxygen has a very high activation energy.
- C Oxygen molecules are more likely to collide with themselves than with nitrogen molecules.
- D The simultaneous collision of three molecules is unlikely.

15. The graph below was obtained when zinc carbonate reacted with dilute hydrochloric acid under two different conditions, denoted as experiments A and B.



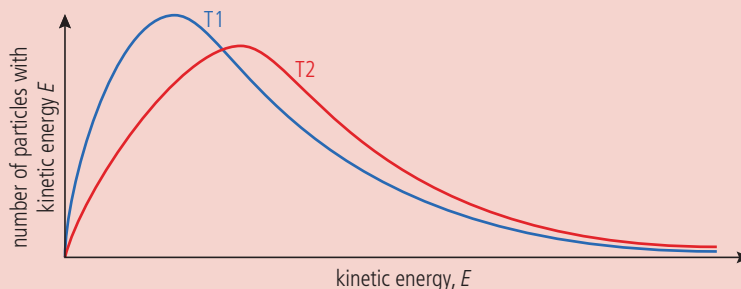
- Write an equation including state symbols for the reaction occurring. (2)
- Explain why the mass of the reaction mixture decreases in both cases. (1)
- Make reference to collision theory to explain the shape of curve A. (3)
- Describe the measurements that could be made from the graph to compare the initial rates of the reactions in A and B. Comment on the results expected. (3)
- The concentration of hydrochloric acid used in experiments A and B was the same. Suggest three possible differences in the conditions of experiments A and B. (3)
- For each of the conditions given in (e), explain why it would affect the rate of the reaction. (6)
- The experiment was repeated using zinc metal in place of zinc carbonate. (3)



Describe the differences you would expect in the results, and evaluate whether this is likely to be a satisfactory method for following the rate of reaction.

(Total 20 marks)

16. The figure below shows a Maxwell-Boltzmann distribution curve for a sample of a gas at two different temperatures, T1 and T2.



- Deduce the relative values of T1 and T2. (1)
- Make reference to your answer to (a) to explain the differences in the shape of the two graphs. (2)
- 'A catalyst provides a reaction route with a lower activation energy, and so increases the rate of reaction.'

Justify this statement by means of a suitably labelled Maxwell-Boltzmann distribution curve, showing the proportion of reacting particles with and without a catalyst. (4)

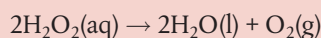
(d) Explain why catalysts increase the rate of reaction but have no effect on:

(i) the enthalpy change

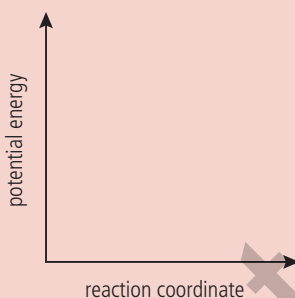
(ii) the stoichiometric yield of a product (4)

(Total 11 marks)

17. The decomposition of hydrogen peroxide, H_2O_2 , into water and oxygen gas is an exothermic reaction.



(a) On the axes below, sketch an energy profile for an exothermic reaction and annotate the key features. (3)



(b) The enzyme 'catalase' can be used to increase the rate of decomposition of hydrogen peroxide.

(i) Outline how the energy profile would change if catalase was added to the reaction mixture. (1)

(ii) Explain why the addition of catalase would have no effect on the enthalpy change of the reaction. (2)

(Total 6 marks)