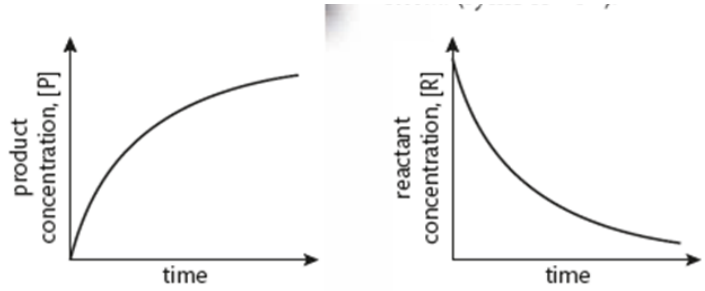
Topic 6 - kinetics

6.1 Collision theory and rates of reaction

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

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:

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



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

On a graph plotting [X] against time, we can calculate the rate by calculating the gradient of the tangent at the point we are considering. The graph below shows the changing concentration of a reactant, R, over time.

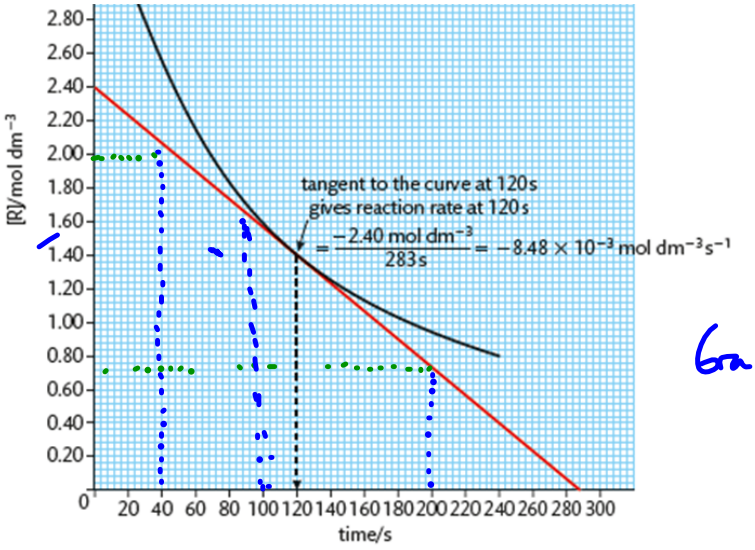


Figure 6.4 Measuring the gradient of the tangent to the curve at time t = 120 seconds. The measured rate of the reaction is 8.48 × 10^{-3} mol dm^{-3} s^{-1} at this time.

$$\text{Gradient} = \frac{\text{Up}}{\text{Across}} = \frac{\Delta y}{\Delta x}$$

Why is the rate greater at the beginning and then progressively decreases?

Note: Rates of reaction can only be calculated using experimental data.

Measuring rates of reaction uses different techniques depending on the reaction

1 Change in volume of gas produced

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

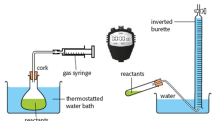
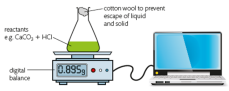


Figure 6.6 Experiments to measure rate of reaction by following change in volume against time.

2 Change in mass

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

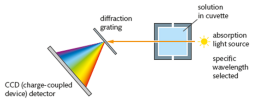


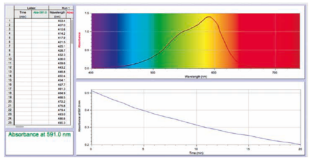
Why might this method be a poor choice if the gas released is hydrogen?

3 Change in transmission of light: colorimetry/spectrophotometry

This method can be used for reactions in which a reactant or product is coloured and therefore absorbs light in the visible part of the spectrum. As the concentration of this compound decreases or increases, the absorbance will decrease or increase.

We can monitor this absorbance continually using a spectrophotometer and plot it against time to give us a rate curve.





4 Change in concentration measured using titration

For example, the reaction between H_2O_2 and acidified KI yields I_2, which can be titrated against sodium thiosulfate, $Na_2S_2O_3$ to determine its concentration. Sodium carbonate, Na_2CO_3, is used to quench the reaction by neutralising the added acid.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

What does quenching mean?

Is simply the process of stopping a reaction at a fixed time.

5 Change in concentration measured using conductivity

For example, in the reaction:

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

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.

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

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

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

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

$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(aq) + H_2O(l) + S(s)$

Exercises

1 Consider the following reaction:

$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

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

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

A mol dm^{-3} time **B** mol^{-1} dm^3 time^{-1} **C** mol dm^{-3} time^{-1} **D** mol time^{-1}

3 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.

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

(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.

4 The following data were collected for the reaction

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ at 390 °C

$[H_2O_2]$ / mol dm^{-3}	Time / s	$[H_2O_2]$ / 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		

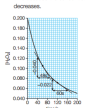
Draw a graph of concentration against time and determine the reaction rate after 60 s and after 120 s.

$\times 10^{-3}$ mol dm^{-3} $[H_2O_2]$ Time

2 C

3 **(a)** (i) Measure the decrease in the mass of flask + contents.
(ii) Measure the increase in pH of the reaction mixture.
(iii) Measure the increase in volume of gas collected.
(b) The rate of the reaction decreases with time because the concentration of the acid decreases.

4



At 60 s, rate = 8.3 × 10^{-4} mol dm^{-3} s^{-1}
At 120 s, rate = 3.7 × 10^{-4} mol dm^{-3} s^{-1}

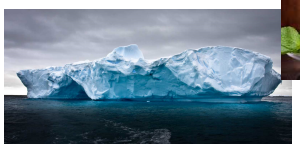
Collision theory

Kinetic energy and temperature

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

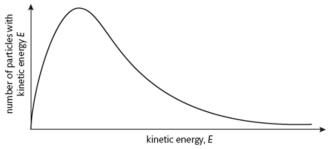
Which of these has the most heat and which has the highest temeprature?

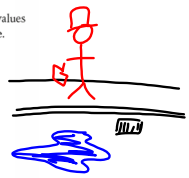
temperature



The Maxwell–Boltzmann distribution curve

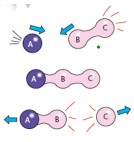
The fact that particles in a gas at a particular temperature show a range in their values of kinetic energy is expressed by the **Maxwell–Boltzmann distribution curve.**





How reactions happen

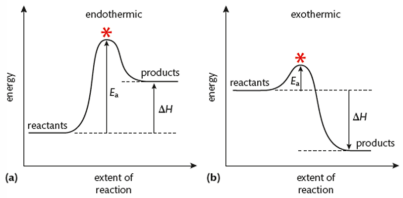
When reactants are placed together, the kinetic energy that their particles possess causes them to collide with each other. The energy of these collisions may result in some bonds between the reactants being broken, and some new bonds forming. As a result, products form and the reaction 'happens'.



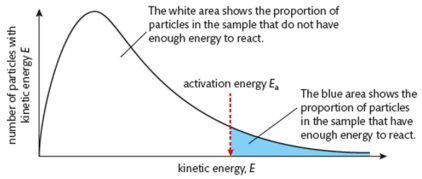
- energy of collision and
- geometry of collision.

i Energy of collision

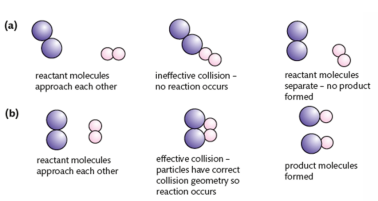
Activation energy (E_a) is defined as the minimum value of kinetic energy which particles must have before they are able to react.



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.



ii Geometry of collision



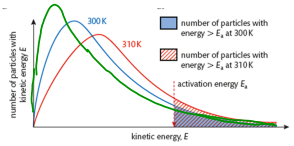
NATURE OF SCIENCE

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.

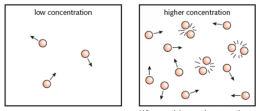
Factors affecting rate of reaction

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.

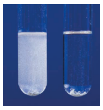
1 Temperature



2 Concentration



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



3 Particle size

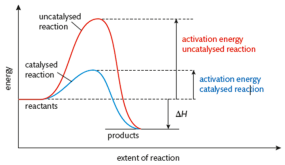
This effect of particle size on reaction rate can be quite dramatic. It has been responsible for many industrial accidents involving explosions of flammable dust powders – for example coal dust in mines and flour in mills.

https://www.youtube.com/watch?v=XM2TbddOhN0

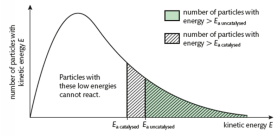
4 Pressure

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.

5 Catalyst



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



12 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. $2CO + 2NO \xrightarrow{Pt} 2CO_2 + N_2$

(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? ↑ surface area

(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.

Exercises

8 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.

9 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

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

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

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

11 A sugar cube cannot be ignited with a match, but a sugar cube coated in ashes will ignite. Suggest a reason for this observation.