PEARSON EDEXCEL INTERNATIONAL A LEVEL

CHEMISTRY

Student Book 2

Cliff Curtis
Jason Murgatroyd
with David Scott

Published by Pearson Education Limited, 80 Strand, London, WC2R 0RL.

www.pearsonglobalschools.com

Copies of official specifications for all Edexcel qualifications may be found on the website: https://qualifications.pearson.com

Designed by Tech-Set Ltd, Gateshead, UK
Typeset by Tech-Set Ltd, Gateshead, UK
Edited by Gerard Delaney, Sharon Jordan and Sarah Wright

Cover images: Front: **Getty Images:** David Malin/Science Faction
Inside front cover: **Shutterstock.com**/Dmitry Lobanov

First published 2019

22 21 20 19
10 9 8 7 6 5 4 3 2 1

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library
ISBN 978 1 2922 4472 3

Printed in Slovakia by Neografia

Acknowledgements
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ABOUT THIS BOOK

This book is written for students following the Pearson Edexcel International Advanced Level (IAL) Chemistry specification. This book covers the full International Advanced Subsidiary (IAS) course and the first year of the International A Level (IAL) course.

The book contains full coverage of IAL units (or exam papers) 4 and 5. Each unit has five Topic areas that match the titles and order of those in the specification. You can refer to the Assessment Overview on pages xii–xiii for further information. Students can prepare for the written Practical Paper by using the IAL Chemistry Lab Book (see pages x–xi of this book).

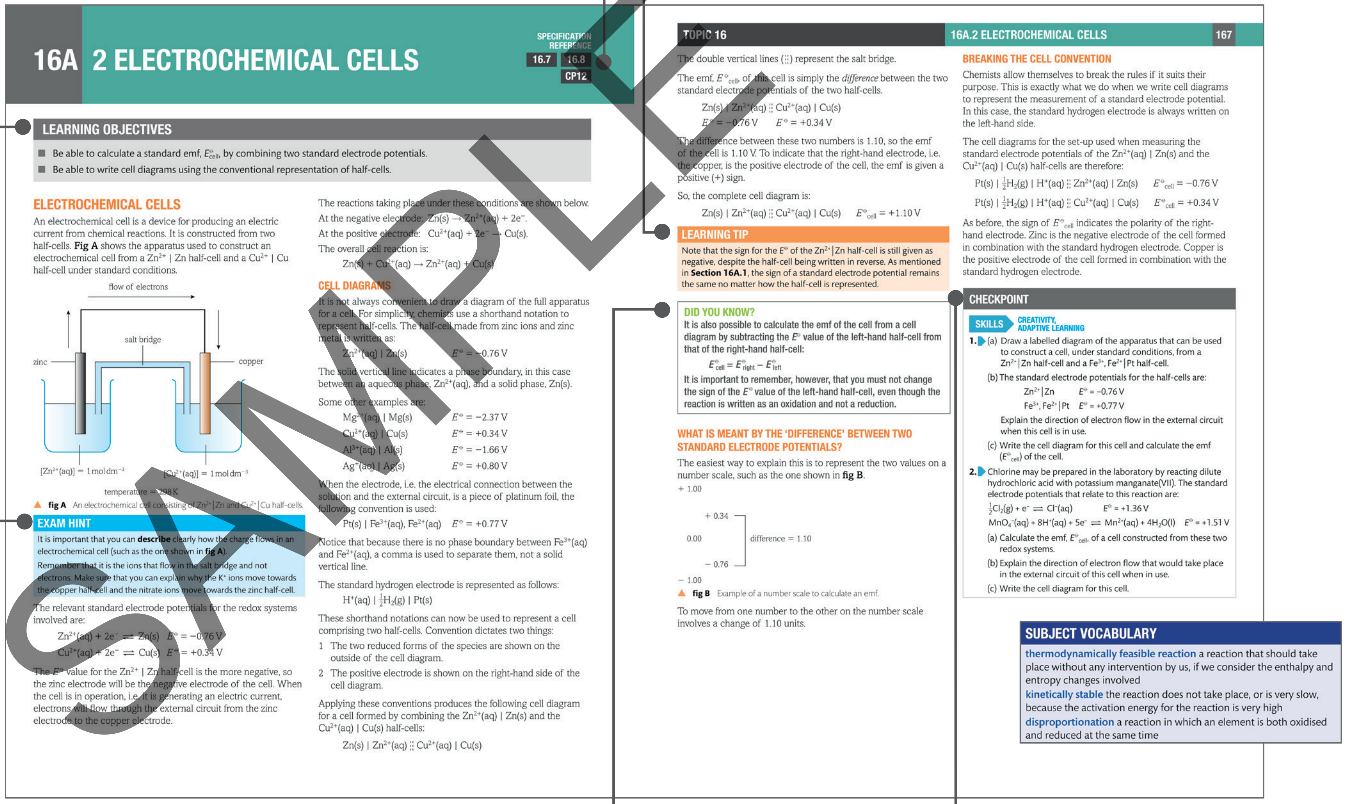
Each Topic is divided into chapters and sections to break the content down into manageable chunks. Each section features a mix of learning and activities supported by the features explained below.

Learning objectives
Each chapter starts with a list of key learning objectives.

Specification reference
The exact specification points covered in the section are provided.

Learning tips
These help you focus your learning and avoid common errors. **Cross references** to previous or following Student Book content help you to navigate course content.

Worked examples
Worked examples show you how to work through questions, and set out calculations.



16A 2 ELECTROCHEMICAL CELLS

SPECIFICATION REFERENCE 16.7 16.8 CP12

LEARNING OBJECTIVES

- Be able to calculate a standard emf, $E^{\ominus}_{cell}$, by combining two standard electrode potentials.
- Be able to write cell diagrams using the conventional representation of half-cells.

ELECTROCHEMICAL CELLS

An electrochemical cell is a device for producing an electric current from chemical reactions. It is constructed from two half-cells. **Fig A** shows the apparatus used to construct an electrochemical cell from a Zn^{2+} | Zn half-cell and a Cu^{2+} | Cu half-cell under standard conditions.

fig A An electrochemical cell consisting of $Zn^{2+}|Zn$ and $Cu^{2+}|Cu$ half-cells.

EXAM HINT

It is important that you can **describe** clearly how the charge flows in an electrochemical cell (such as the one shown in **fig A**).

Remember that it is the ions that flow in the salt bridge and not electrons. Make sure that you can explain why the K^+ ions move towards the copper half-cell and the nitrate ions move towards the zinc half-cell.

The relevant standard electrode potentials for the redox systems involved are:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^{\ominus} = -0.76\,V$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^{\ominus} = +0.34\,V$

The $E^{\ominus}$ value for the Zn^{2+} | Zn half-cell is the more negative, so the zinc electrode will be the negative electrode of the cell. When the cell is in operation, i.e. it is generating an electric current, electrons will flow through the external circuit from the zinc electrode to the copper electrode.

The reactions taking place under these conditions are shown below.

At the negative electrode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$.

At the positive electrode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.

The overall cell reaction is:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

CELL DIAGRAMS

It is not always convenient to draw a diagram of the full apparatus for a cell. For simplicity, chemists use a shorthand notation to represent half-cells. The half-cell made from zinc ions and zinc metal is written as:

$Zn^{2+}(aq) \mid Zn(s) \qquad E^{\ominus} = -0.76\,V$

The solid vertical line indicates a phase boundary, in this case between an aqueous phase, $Zn^{2+}(aq)$, and a solid phase, Zn(s).

Some other examples are:

$Mg^{2+}(aq) \mid Mg(s) \qquad E^{\ominus} = -2.37\,V$

$Cu^{2+}(aq) \mid Cu(s) \qquad E^{\ominus} = +0.34\,V$

$Al^{3+}(aq) \mid Al(s) \qquad E^{\ominus} = -1.66\,V$

$Ag^{+}(aq) \mid Ag(s) \qquad E^{\ominus} = +0.80\,V$

When the electrode, i.e. the electrical connection between the solution and the external circuit, is a piece of platinum foil, the following convention is used:

$Pt(s) \mid Fe^{3+}(aq), Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V$

Notice that because there is no phase boundary between $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$, a comma is used to separate them, not a solid vertical line.

The standard hydrogen electrode is represented as follows:

$H^+(aq) \mid \frac{1}{2}H_2(g) \mid Pt(s)$

These shorthand notations can now be used to represent a cell comprising two half-cells. Convention dictates two things:

1 The two reduced forms of the species are shown on the outside of the cell diagram.
2 The positive electrode is shown on the right-hand side of the cell diagram.

Applying these conventions produces the following cell diagram for a cell formed by combining the $Zn^{2+}(aq) \mid Zn(s)$ and the $Cu^{2+}(aq) \mid Cu(s)$ half-cells:

$Zn(s) \mid Zn^{2+}(aq) \,⁞⁞\, Cu^{2+}(aq) \mid Cu(s)$

TOPIC 16

The double vertical lines (⁞⁞) represent the salt bridge.

The emf, $E^{\ominus}_{cell}$, of this cell is simply the *difference* between the two standard electrode potentials of the two half-cells.

$Zn(s) \mid Zn^{2+}(aq) \,⁞⁞\, Cu^{2+}(aq) \mid Cu(s)$

$E^{\ominus} = -0.76\,V \qquad E^{\ominus} = +0.34\,V$

The difference between these two numbers is 1.10, so the emf of the cell is 1.10 V. To indicate that the right-hand electrode, i.e. the copper, is the positive electrode of the cell, the emf is given a positive (+) sign.

So, the complete cell diagram is:

$Zn(s) \mid Zn^{2+}(aq) \,⁞⁞\, Cu^{2+}(aq) \mid Cu(s) \qquad E^{\ominus}_{cell} = +1.10\,V$

LEARNING TIP

Note that the sign for the $E^{\ominus}$ of the $Zn^{2+}|Zn$ half-cell is still given as negative, despite the half-cell being written in reverse. As mentioned in **Section 16A.1**, the sign of a standard electrode potential remains the same no matter how the half-cell is represented.

DID YOU KNOW?

It is also possible to calculate the emf of the cell from a cell diagram by subtracting the $E^{\ominus}$ value of the left-hand half-cell from that of the right-hand half-cell:

$E^{\ominus}_{cell} = E^{\ominus}_{right} - E^{\ominus}_{left}$

It is important to remember, however, that you must not change the sign of the $E^{\ominus}$ value of the left-hand half-cell, even though the reaction is written as an oxidation and not a reduction.

WHAT IS MEANT BY THE ‘DIFFERENCE’ BETWEEN TWO STANDARD ELECTRODE POTENTIALS?

The easiest way to explain this is to represent the two values on a number scale, such as the one shown in **fig B**.

fig B Example of a number scale to calculate an emf.

To move from one number to the other on the number scale involves a change of 1.10 units.

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BREAKING THE CELL CONVENTION

Chemists allow themselves to break the rules if it suits their purpose. This is exactly what we do when we write cell diagrams to represent the measurement of a standard electrode potential. In this case, the standard hydrogen electrode is always written on the left-hand side.

The cell diagrams for the set-up used when measuring the standard electrode potentials of the $Zn^{2+}(aq) \mid Zn(s)$ and the $Cu^{2+}(aq) \mid Cu(s)$ half-cells are therefore:

$Pt(s) \mid \frac{1}{2}H_2(g) \mid H^+(aq) \,⁞⁞\, Zn^{2+}(aq) \mid Zn(s) \qquad E^{\ominus}_{cell} = -0.76\,V$

$Pt(s) \mid \frac{1}{2}H_2(g) \mid H^+(aq) \,⁞⁞\, Cu^{2+}(aq) \mid Cu(s) \qquad E^{\ominus}_{cell} = +0.34\,V$

As before, the sign of $E^{\ominus}_{cell}$ indicates the polarity of the right-hand electrode. Zinc is the negative electrode of the cell formed in combination with the standard hydrogen electrode. Copper is the positive electrode of the cell formed in combination with the standard hydrogen electrode.

CHECKPOINT

SKILLS CREATIVITY, ADAPTIVE LEARNING

1. (a) Draw a labelled diagram of the apparatus that can be used to construct a cell, under standard conditions, from a $Zn^{2+}|Zn$ half-cell and a $Fe^{3+}, Fe^{2+}|Pt$ half-cell.
   (b) The standard electrode potentials for the half-cells are:
   $Zn^{2+}|Zn \qquad E^{\ominus} = -0.76\,V$
   $Fe^{3+}, Fe^{2+}|Pt \qquad E^{\ominus} = +0.77\,V$
   Explain the direction of electron flow in the external circuit when this cell is in use.
   (c) Write the cell diagram for this cell and calculate the emf ($E^{\ominus}_{cell}$) of the cell.
2. Chlorine may be prepared in the laboratory by reacting dilute hydrochloric acid with potassium manganate(VII). The standard electrode potentials that relate to this reaction are:
   $\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq) \qquad E^{\ominus} = +1.36\,V$
   $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^{\ominus} = +1.51\,V$
   (a) Calculate the emf, $E^{\ominus}_{cell}$, of a cell constructed from these two redox systems.
   (b) Explain the direction of electron flow that would take place in the external circuit of this cell when in use.
   (c) Write the cell diagram for this cell.

SUBJECT VOCABULARY

thermodynamically feasible reaction a reaction that should take place without any intervention by us, if we consider the enthalpy and entropy changes involved
kinetically stable the reaction does not take place, or is very slow, because the activation energy for the reaction is very high
disproportionation a reaction in which an element is both oxidised and reduced at the same time

Exam hints
Tips on how to answer exam-style questions and guidance for exam preparation, including requirements indicated by particular **command words**.

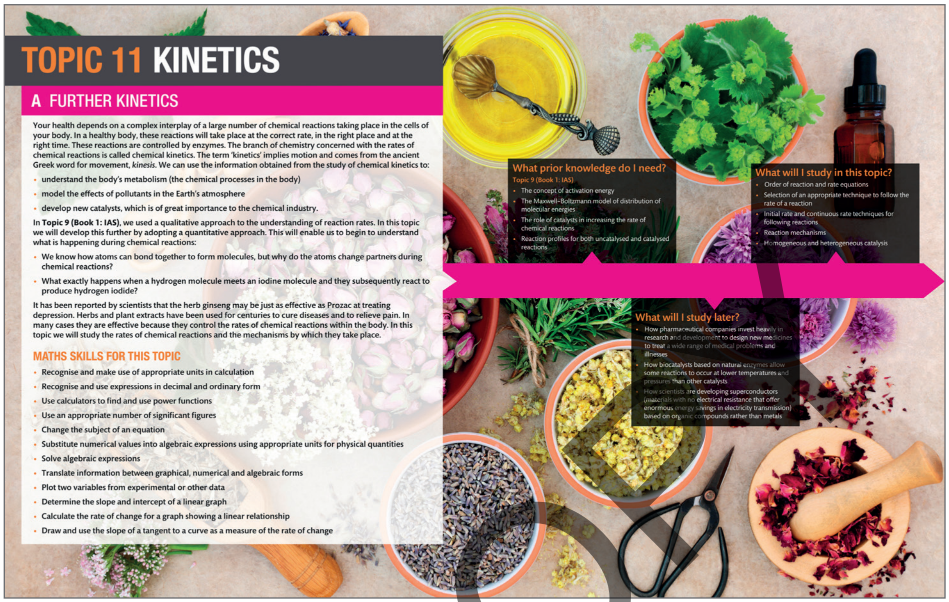
Did you know?
Interesting facts help you remember the key concepts.

Checkpoint
Questions at the end of each section check understanding of the key learning points in each chapter. Certain questions allow you to develop **skills** that will be valuable for further study and in the workplace.

Subject Vocabulary
Key terms are highlighted in blue in the text. Clear definitions are provided at the end of each section for easy reference, and are also collated in a **glossary** at the back of the book.

You should be able to put every stage of your learning in context, chapter by chapter.

- Links to other areas of Chemistry include previous knowledge that is built on in the topic, and future areas of knowledge and application that you will cover later in your course.
- Maths knowledge required is detailed in a handy checklist. If you need to practise the maths you need, you can use the **Maths Skills** reference at the back of the book as a starting point.



TOPIC 11 KINETICS

A FURTHER KINETICS

Your health depends on a complex interplay of a large number of chemical reactions taking place in the cells of your body. In a healthy body, these reactions will take place at the correct rate, in the right place and at the right time. These reactions are controlled by enzymes. The branch of chemistry concerned with the rates of chemical reactions is called chemical kinetics. The term 'kinetics' implies motion and comes from the ancient Greek word for movement, *kinesis*. We can use the information obtained from the study of chemical kinetics to:

- understand the body's metabolism (the chemical processes in the body)
- model the effects of pollutants in the Earth's atmosphere
- develop new catalysts, which is of great importance to the chemical industry.

In **Topic 9 (Book 1: IAS)**, we used a qualitative approach to the understanding of reaction rates. In this topic we will develop this further by adopting a quantitative approach. This will enable us to begin to understand what is happening during chemical reactions:

- We know how atoms can bond together to form molecules, but why do the atoms change partners during chemical reactions?
- What exactly happens when a hydrogen molecule meets an iodine molecule and they subsequently react to produce hydrogen iodide?

It has been reported by scientists that the herb ginseng may be just as effective as Prozac at treating depression. Herbs and plant extracts have been used for centuries to cure diseases and to relieve pain. In many cases they are effective because they control the rates of chemical reactions within the body. In this topic we will study the rates of chemical reactions and the mechanisms by which they take place.

MATHS SKILLS FOR THIS TOPIC

- Recognise and make use of appropriate units in calculation
- Recognise and use expressions in decimal and ordinary form
- Use calculators to find and use power functions
- Use an appropriate number of significant figures
- Change the subject of an equation
- Substitute numerical values into algebraic expressions using appropriate units for physical quantities
- Solve algebraic expressions
- Translate information between graphical, numerical and algebraic forms
- Plot two variables from experimental or other data
- Determine the slope and intercept of a linear graph
- Calculate the rate of change for a graph showing a linear relationship
- Draw and use the slope of a tangent to a curve as a measure of the rate of change

What prior knowledge do I need?

Topic 9 (Book 1: IAS)

- The concept of activation energy
- The Maxwell-Boltzmann model of distribution of molecular energies
- The role of catalysts in increasing the rate of chemical reactions
- Reaction profiles for both uncatalysed and catalysed reactions

What will I study in this topic?

- Order of reaction and rate equations
- Selection of an appropriate technique to follow the rate of a reaction
- Initial rate and continuous rate techniques for following reactions
- Reaction mechanisms
- Homogeneous and heterogeneous catalysis

What will I study later?

- How pharmaceutical companies invest heavily in research and development to design new medicines to treat a wide range of medical problems and illnesses
- How biocatalysts based on natural enzymes allow some reactions to occur at lower temperatures and pressures than other catalysts
- How scientists are developing superconductors (materials with no electrical resistance that offer enormous energy savings in electricity transmission) based on organic compounds rather than metals

13 THINKING BIGGER

CATASTROPHE FOR CORAL?

SKILLS CRITICAL THINKING, INTERPRETATION

You should know about the impact of rising carbon dioxide levels on the Earth's atmosphere. The following extract describes the impact on life in our oceans.

OCEANS ABSORB HUMAN CARBON POLLUTION

As humans burn fossil fuels and release greenhouse gases, those gases enter the atmosphere where they cause increases in global temperatures and climate consequences such as more frequent and severe heat waves, droughts, changes to rainfall patterns, and rising seas. But for many years scientists have known that not all of the carbon dioxide we emit ends up in the atmosphere. About 40% actually gets absorbed in the ocean waters.

I like to use an analogy from everyday experience: the ocean is a little like a soda. When we shake soda, it fizzes. That fizz is the carbon dioxide coming out of the liquid (that is why sodas are called "carbonated beverages"). We're doing the reverse process in the climate. Our carbon dioxide is actually going into the oceans.

The process of absorption is not simple – the amount of carbon dioxide that the ocean can hold depends on the ocean temperatures. Colder waters can absorb more carbon dioxide; warmer waters can absorb less. Scientists believe that as the oceans warm, they will become less and less capable of taking up carbon dioxide. As a result, more of our carbon pollution will stay in the atmosphere, worsening global warming. But it's clear that, at least for now, the oceans are doing us a great favour by absorbing large amounts of carbon pollution.

▲ **fig A** Coral bleaching near Christmas Island, Australia. This is an example of the effect of global warming in our oceans.

Knowing the rate at which the oceans absorb carbon dioxide is key to understanding how fast climate change will occur. This is an active area of research. In particular, scientists are closely watching the oceans to see if their ability to absorb is changing over time.

From an article in The Guardian, 'Scientists Study Ocean Absorption of Human Carbon Pollution' by John Abraham, 16 February 2017, https://www.theguardian.com/environment/climate-consensus-97-per-cent/2017/feb/16/scientists-study-ocean-absorption-of-human-carbon-pollution

TOPIC 13 THINKING BIGGER 75

SCIENCE COMMUNICATION

1 You may have heard people say that "a picture is worth a thousand words". Carry out an Internet search to find five images (e.g. photos or diagrams) that powerfully show the main issues in climate change. Add a short caption to each of the images you choose.

CHEMISTRY IN DETAIL

2 The equilibrium between gaseous carbon dioxide and dissolved carbon dioxide can be represented by the equation:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

Suggest the impact that an increasing concentration of atmospheric carbon dioxide will have on the concentration of dissolved carbon dioxide in the oceans.

3 Once dissolved, carbon dioxide reacts with water as follows:

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

(a) Write an expression for the equilibrium constant (K_c) for this reaction (remember that H_2O is not included in the expression for K_c).

(b) A sample of seawater is shown to have 0.07 g of CO_2 per dm^3 dissolved in it. Calculate the concentration of this solution in mol dm^{-3}.

(c) Assuming that the value for K_c in (a) is 4.5×10^{-7} mol dm^{-3}, calculate the pH of this solution. State any assumptions you have made.

THINKING BIGGER TIP

The material covered in Topic 13 is developed further in Topic 14. You may prefer to wait until you have studied Topic 14 before answering questions 2 and 3.

CHEMISTRY TIP

The hydrogen carbonate ion (HCO_3^-) is sometimes referred to as the bicarbonate ion.

DID YOU KNOW

The UK's Met Office has predicted that CO_2 levels will rise to a record 415 ppm in 2019.

ACTIVITY

The evidence for anthropogenic climate change is now very strong. Using the Internet (including the useful website https://climate.nasa.gov), carry out research to answer the following questions:

(i) What is meant by anthropogenic climate change?

(ii) Are there any other gases responsible for climate change? If so, what are they and how are they produced?

(iii) Some scientists now call the current geological time period the Anthropocene. What does this term mean and why do you think scientists are using it?

You can present your answers in a PowerPoint presentation or as a poster.

Thinking Bigger

At the end of each topic there is an opportunity to read and work with real-life research and writing about science.

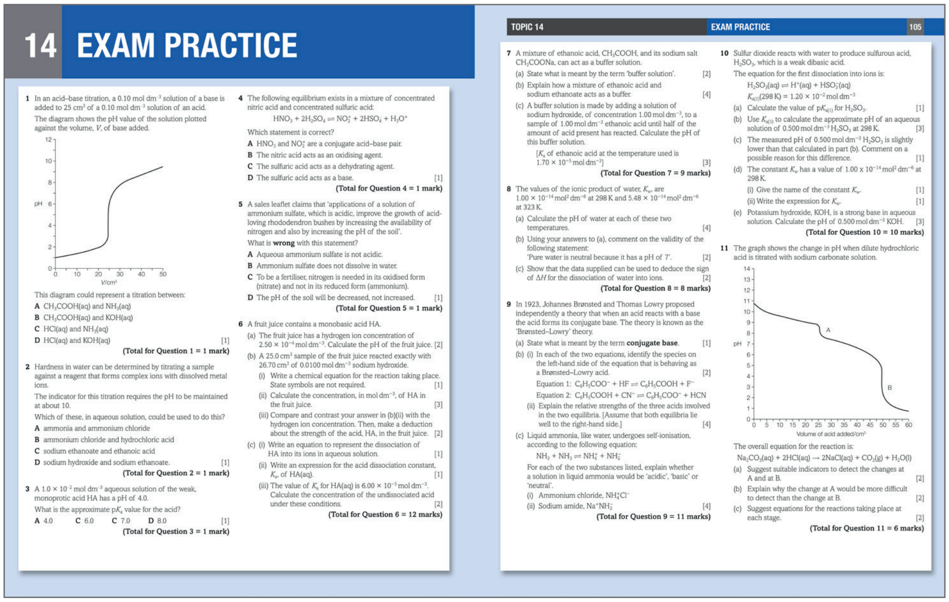
The activities help you to read real-life material that's relevant to your course, analyse how scientists write, think critically and consider how different aspects of your learning piece together.

These Thinking Bigger activities focus on key transferable skills, which are an important basis for key academic qualities.

Exam Practice

Exam-style questions at the end of each chapter are tailored to the Pearson Edexcel specification to allow for practice and development of exam writing technique. They also allow for practice responding to the command words used in the exams (see the **command words glossary** at the back of this book).

You can also refer to the **Preparing for Your Exams** section at the back of the book, for sample exam answers with commentary.



14 EXAM PRACTICE

1 In an acid–base titration, a 0.10 mol dm^{-3} solution of a base is added to 25 cm^3 of a 0.10 mol dm^{-3} solution of an acid.

The diagram shows the pH value of the solution plotted against the volume, *V*, of base added.

This diagram could represent a titration between:

A $CH_3COOH(aq)$ and $NH_3(aq)$

B $CH_3COOH(aq)$ and $KOH(aq)$

C $HCl(aq)$ and $NH_3(aq)$

D $HCl(aq)$ and $KOH(aq)$ [1]

(Total for Question 1 = 1 mark)

2 Hardness in water can be determined by titrating a sample against a reagent that forms complex ions with dissolved metal ions.

The indicator for this titration requires the pH to be maintained at about 10.

Which of these, in aqueous solution, could be used to do this?

A ammonia and ammonium chloride

B ammonium chloride and hydrochloric acid

C sodium ethanoate and ethanoic acid

D sodium hydroxide and sodium ethanoate. [1]

(Total for Question 2 = 1 mark)

3 A 1.0×10^{-2} mol dm^{-3} aqueous solution of the weak, monoprotic acid HA has a pH of 4.0.

What is the approximate pK_a value for the acid?

A 4.0 C 6.0 C 7.0 D 8.0 [1]

(Total for Question 3 = 1 mark)

4 The following equilibrium exists in a mixture of concentrated nitric acid and concentrated sulfuric acid:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$$

Which statement is correct?

A HNO_3 and NO_2^+ are a conjugate acid–base pair.

B The nitric acid acts as an oxidising agent.

C The sulfuric acid acts as a dehydrating agent.

D The sulfuric acid acts as a base. [1]

(Total for Question 4 = 1 mark)

5 A sales leaflet claims that 'applications of a solution of ammonium sulfate, which is acidic, improve the growth of acid-loving rhododendron bushes by increasing the availability of nitrogen and also by increasing the pH of the soil'.

What is **wrong** with this statement?

A Aqueous ammonium sulfate is not acidic.

B Ammonium sulfate does not dissolve in water.

C To be a fertiliser, nitrogen is needed in its oxidised form (nitrate) and not in its reduced form (ammonium).

D The pH of the soil will be decreased, not increased. [1]

(Total for Question 5 = 1 mark)

6 A fruit juice contains a monobasic acid HA.

(a) The fruit juice has a hydrogen ion concentration of 2.50×10^{-4} mol dm^{-3}. Calculate the pH of the fruit juice. [2]

(b) A 25.0 cm^3 sample of the fruit juice reacted exactly with 26.70 cm^3 of 0.0100 mol dm^{-3} sodium hydroxide.

(i) Write a chemical equation for the reaction taking place. State symbols are not required. [1]

(ii) Calculate the concentration, in mol dm^{-3}, of HA in the fruit juice. [3]

(iii) Compare and contrast your answer in (b)(ii) with the hydrogen ion concentration. Then, make a deduction about the strength of the acid, HA, in the fruit juice. [2]

(c) (i) Write an equation to represent the dissociation of HA into its ions in aqueous solution. [1]

(ii) Write an expression for the acid dissociation constant, K_a, of HA(aq). [1]

(iii) The value of K_a for HA(aq) is 6.00×10^{-5} mol dm^{-3}. Calculate the concentration of the undissociated acid under these conditions. [2]

(Total for Question 6 = 12 marks)

TOPIC 14 EXAM PRACTICE 105

7 A mixture of ethanoic acid, CH_3COOH, and its sodium salt CH_3COONa, can act as a buffer solution.

(a) State what is meant by the term 'buffer solution'. [2]

(b) Explain how a mixture of ethanoic acid and sodium ethanoate acts as a buffer. [4]

(c) A buffer solution is made by adding a solution of sodium hydroxide, of concentration 1.00 mol dm^{-3}, to a sample of 1.00 mol dm^{-3} ethanoic acid until half of the amount of acid present has reacted. Calculate the pH of this buffer solution.

[K_a of ethanoic acid at the temperature used is 1.70×10^{-5} mol dm^{-3}] [3]

(Total for Question 7 = 9 marks)

8 The values of the ionic product of water, K_w, are 1.00×10^{-14} mol² dm^{-6} at 298 K and 5.48×10^{-14} mol² dm^{-6} at 323 K.

(a) Calculate the pH of water at each of these two temperatures. [4]

(b) Using your answers to (a), comment on the validity of the following statement:

'Pure water is neutral because it has a pH of 7'. [2]

(c) Show that the data supplied can be used to deduce the sign of ΔH for the dissociation of water into ions. [2]

(Total for Question 8 = 8 marks)

9 In 1923, Johannes Brønsted and Thomas Lowry proposed independently a theory that when an acid reacts with a base the acid forms its conjugate base. The theory is known as the 'Brønsted–Lowry' theory.

(a) State what is meant by the term **conjugate base**. [1]

(b) (i) In each of the two equations, identify the species on the left-hand side of the equation that is behaving as a Brønsted–Lowry acid. [2]

Equation 1: $C_6H_5COO^- + HF \rightleftharpoons C_6H_5COOH + F^-$

Equation 2: $C_6H_5COOH + CN^- \rightleftharpoons C_6H_5COO^- + HCN$

(ii) Explain the relative strengths of the three acids involved in the two equilibria. [Assume that both equilibria lie well to the right-hand side.] [4]

(c) Liquid ammonia, like water, undergoes self-ionisation, according to the following equation:

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

For each of the two substances listed, explain whether a solution in liquid ammonia would be 'acidic', 'basic' or 'neutral'.

(i) Ammonium chloride, $NH_4^+Cl^-$

(ii) Sodium amide, $Na^+NH_2^-$ [4]

(Total for Question 9 = 11 marks)

10 Sulfur dioxide reacts with water to produce sulfurous acid, H_2SO_3, which is a weak dibasic acid.

The equation for the first dissociation into ions is:

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$$

$$K_{a(1)}(298\,K) = 1.20 \times 10^{-2}\ mol\ dm^{-3}$$

(a) Calculate the value of $pK_{a(1)}$ for H_2SO_3. [1]

(b) Use $K_{a(1)}$ to calculate the approximate pH of an aqueous solution of 0.500 mol dm^{-3} H_2SO_3 at 298 K. [3]

(c) The measured pH of 0.500 mol dm^{-3} H_2SO_3 is slightly lower than that calculated in part (b). Comment on a possible reason for this difference. [1]

(d) The constant K_w has a value of 1.00×10^{-14} mol² dm^{-6} at 298 K.

(i) Give the name of the constant K_w. [1]

(ii) Write the expression for K_w. [1]

(e) Potassium hydroxide, KOH, is a strong base in aqueous solution. Calculate the pH of 0.500 mol dm^{-3} KOH. [3]

(Total for Question 10 = 10 marks)

11 The graph shows the change in pH when dilute hydrochloric acid is titrated with sodium carbonate solution.

The overall equation for the reaction is:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

(a) Suggest suitable indicators to detect the changes at A and at B. [2]

(b) Explain why the change at A would be more difficult to detect than the change at B. [2]

(c) Suggest equations for the reactions taking place at each stage. [2]

(Total for Question 11 = 6 marks)

PRACTICAL SKILLS

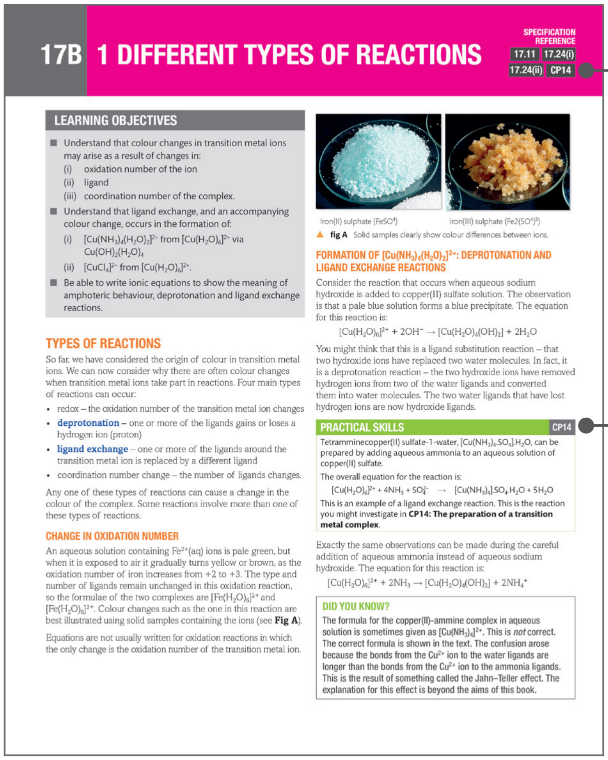
Practical work is central to the study of chemistry. The second year of the Pearson Edexcel International Advanced Level (IAL) Chemistry course includes eight Core Practicals that link theoretical knowledge and understanding to practical scenarios.

Your knowledge and understanding of practical skills and activities will be assessed in all examination papers for the IAL Chemistry qualification.

- Papers 4 and 5 will include questions based on practical activities, including novel scenarios.
- Paper 6 will test your ability to plan practical work, including risk management and selection of apparatus.

In order to develop practical skills, you should carry out a range of practical experiments related to the topics covered in your course. Further suggestions in addition to the Core Practicals are included in the specification, which is available online.

STUDENT BOOK TOPIC	IAL CORE PRACTICALS	
TOPIC 11 KINETICS	**CP9a**	Following the rate of the iodine–propanone reaction by a titrimetric method
	CP9b	Investigating a ‘clock reaction’ (Harcourt–Esson, iodine clock)
	CP10	Finding the activation energy of a reaction
TOPIC 14 ACID–BASE EQUILIBRIA	**CP11**	Finding the K_a value for a weak acid
TOPIC 16 REDOX EQUILIBRIA	**CP12**	Investigating some electrochemical cells
	CP13a	Redox titrations with iron(II) ions and potassium manganate(VII)
	CP13b	Redox titrations with sodium thiosulfate and iodine
TOPIC 17 TRANSITION METALS AND THEIR CHEMISTRY	**CP14**	Preparation of a transition metal complex
TOPIC 19 ORGANIC NITROGEN COMPOUNDS: AMINES, AMIDES, AMINO ACIDS AND PROTEINS	**CP15**	Analysis of some inorganic and organic unknowns
TOPIC 20 ORGANIC SYNTHESIS	**CP16**	Preparation of aspirin



17B 1 DIFFERENT TYPES OF REACTIONS

SPECIFICATION REFERENCE
17.11 17.24(i)
17.24(ii) CP14

LEARNING OBJECTIVES

- Understand that colour changes in transition metal ions may arise as a result of changes in:
  - (i) oxidation number of the ion
  - (ii) ligand
  - (iii) coordination number of the complex.
- Understand that ligand exchange, and an accompanying colour change, occurs in the formation of:
  - (i) $[Cu(NH_3)_4(H_2O)_2]^{2+}$ from $[Cu(H_2O)_6]^{2+}$ via $Cu(OH)_2(H_2O)_4$
  - (ii) $[CuCl_4]^{2-}$ from $[Cu(H_2O)_6]^{2+}$.
- Be able to write ionic equations to show the meaning of amphoteric behaviour, deprotonation and ligand exchange reactions.

TYPES OF REACTIONS

So far, we have considered the origin of colour in transition metal ions. We can now consider why there are often colour changes when transition metal ions take part in reactions. Four main types of reactions can occur:

- redox – the oxidation number of the transition metal ion changes
- **deprotonation** – one or more of the ligands gains or loses a hydrogen ion (proton)
- **ligand exchange** – one or more of the ligands around the transition metal ion is replaced by a different ligand
- coordination number change – the number of ligands changes.

Any one of these types of reactions can cause a change in the colour of the complex. Some reactions involve more than one of these types of reactions.

CHANGE IN OXIDATION NUMBER

An aqueous solution containing $Fe^{2+}(aq)$ ions is pale green, but when it is exposed to air it gradually turns yellow or brown, as the oxidation number of iron increases from +2 to +3. The type and number of ligands remain unchanged in this oxidation reaction, so the formulae of the two complexes are $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$. Colour changes such as the one in this reaction are best illustrated using solid samples containing the ions (see **Fig A**).

Equations are not usually written for oxidation reactions in which the only change is the oxidation number of the transition metal ion.

Iron(II) sulphate ($FeSO^4$) Iron(III) sulphate ($Fe2(SO^4)^3$)

▲ **fig A** Solid samples clearly show colour differences between ions.

FORMATION OF $[Cu(NH_3)_4(H_2O)_2]^{2+}$: DEPROTONATION AND LIGAND EXCHANGE REACTIONS

Consider the reaction that occurs when aqueous sodium hydroxide is added to copper(II) sulfate solution. The observation is that a pale blue solution forms a blue precipitate. The equation for this reaction is:

$$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$$

You might think that this is a ligand substitution reaction – that two hydroxide ions have replaced two water molecules. In fact, it is a deprotonation reaction – the two hydroxide ions have removed hydrogen ions from two of the water ligands and converted them into water molecules. The two water ligands that have lost hydrogen ions are now hydroxide ligands.

PRACTICAL SKILLS CP14

Tetramminecopper(II) sulfate-1-water, $[Cu(NH_3)_4.SO_4].H_2O$, can be prepared by adding aqueous ammonia to an aqueous solution of copper(II) sulfate.

The overall equation for the reaction is:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 + SO_4^{2-} \rightarrow [Cu(NH_3)_4].SO_4.H_2O + 5H_2O$$

This is an example of a ligand exchange reaction. This is the reaction you might investigate in **CP14: The preparation of a transition metal complex**.

Exactly the same observations can be made during the careful addition of aqueous ammonia instead of aqueous sodium hydroxide. The equation for this reaction is:

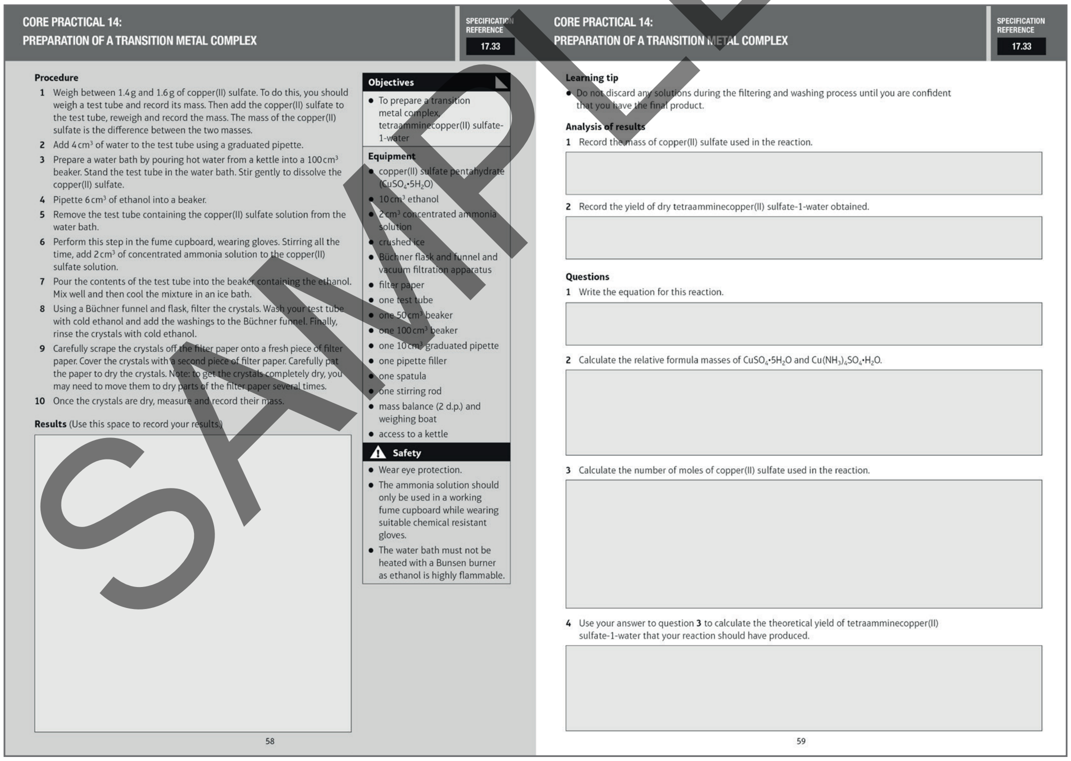
$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

DID YOU KNOW?

The formula for the copper(II)-ammine complex in aqueous solution is sometimes given as $[Cu(NH_3)_4]^{2+}$. This is *not* correct. The correct formula is shown in the text. The confusion arose because the bonds from the Cu^{2+} ion to the water ligands are longer than the bonds from the Cu^{2+} ion to the ammonia ligands. This is the result of something called the Jahn–Teller effect. The explanation for this effect is beyond the aims of this book.

In the **Student Book**, the Core Practical specifications are supplied in the relevant sections.

Practical Skills
Practical skills boxes explain techniques used in the Core Practicals, and also detail useful skills and knowledge gained in other related investigations.



CORE PRACTICAL 14:
PREPARATION OF A TRANSITION METAL COMPLEX

SPECIFICATION REFERENCE
17.33

Procedure

1. Weigh between 1.4 g and 1.6 g of copper(II) sulfate. To do this, you should weigh a test tube and record its mass. Then add the copper(II) sulfate to the test tube, reweigh and record the mass. The mass of the copper(II) sulfate is the difference between the two masses.
2. Add 4 cm³ of water to the test tube using a graduated pipette.
3. Prepare a water bath by pouring hot water from a kettle into a 100 cm³ beaker. Stand the test tube in the water bath. Stir gently to dissolve the copper(II) sulfate.
4. Pipette 6 cm³ of ethanol into a beaker.
5. Remove the test tube containing the copper(II) sulfate solution from the water bath.
6. Perform this step in the fume cupboard, wearing gloves. Stirring all the time, add 2 cm³ of concentrated ammonia solution to the copper(II) sulfate solution.
7. Pour the contents of the test tube into the beaker containing the ethanol. Mix well and then cool the mixture in an ice bath.
8. Using a Büchner funnel and flask, filter the crystals. Wash your test tube with cold ethanol and add the washings to the Büchner funnel. Finally, rinse the crystals with cold ethanol.
9. Carefully scrape the crystals off the filter paper onto a fresh piece of filter paper. Cover the crystals with a second piece of filter paper. Carefully pat the paper to dry the crystals. Note: to get the crystals completely dry, you may need to move them to dry parts of the filter paper several times.
10. Once the crystals are dry, measure and record their mass.

Results (Use this space to record your results.)

Objectives

- To prepare a transition metal complex, tetraamminecopper(II) sulfate-1-water

Equipment

- copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$)
- 10 cm³ ethanol
- 2 cm³ concentrated ammonia solution
- crushed ice
- Büchner flask and funnel and vacuum filtration apparatus
- filter paper
- one test tube
- one 50 cm³ beaker
- one 100 cm³ beaker
- one 10 cm³ graduated pipette
- one pipette filler
- one spatula
- one stirring rod
- mass balance (2 d.p.) and weighing boat
- access to a kettle

Safety

- Wear eye protection.
- The ammonia solution should only be used in a working fume cupboard while wearing suitable chemical resistant gloves.
- The water bath must not be heated with a Bunsen burner as ethanol is highly flammable.

CORE PRACTICAL 14:
PREPARATION OF A TRANSITION METAL COMPLEX

SPECIFICATION REFERENCE
17.33

Learning tip

- Do not discard any solutions during the filtering and washing process until you are confident that you have the final product.

Analysis of results

1 Record the mass of copper(II) sulfate used in the reaction.

2 Record the yield of dry tetraamminecopper(II) sulfate-1-water obtained.

Questions

1 Write the equation for this reaction.

2 Calculate the relative formula masses of $CuSO_4 \cdot 5H_2O$ and $Cu(NH_3)_4SO_4 \cdot H_2O$.

3 Calculate the number of moles of copper(II) sulfate used in the reaction.

4 Use your answer to question **3** to calculate the theoretical yield of tetraamminecopper(II) sulfate-1-water that your reaction should have produced.

This Student Book is accompanied by a **Lab Book**, which includes instructions and writing frames for the Core Practicals for you to record your results and reflect on your work. Practical skills practice questions and answers are also provided. The Lab Book records can be used as preparation for the Practical Skills Paper.

ASSESSMENT OVERVIEW

The following tables give an overview of the assessment for Pearson Edexcel International Advanced Level course in Chemistry. You should study this information closely to help ensure that you are fully prepared for this course and know exactly what to expect in each part of the examinations. More information about this qualification, and about the question types in the different papers, can be found in *Preparing for your exams* on page 286 of this book.

PAPER / UNIT 4	PERCENTAGE OF IA2	PERCENTAGE OF IAL	MARK	TIME	AVAILABILITY
RATES, EQUILIBRIA AND FURTHER ORGANIC CHEMISTRY Written exam paper Paper code WCH14/01 Externally set and marked by Pearson Edexcel Single tier of entry	40%	20%	90	1 hour 45 minutes	January, June and October First assessment: January 2020

PAPER / UNIT 5	PERCENTAGE OF IA2	PERCENTAGE OF IAL	MARK	TIME	AVAILABILITY
TRANSITION METALS AND ORGANIC NITROGEN CHEMISTRY Written exam paper Paper code WCH15/01 Externally set and marked by Pearson Edexcel Single tier of entry	40%	20%	90	1 hour 45 minutes	January, June and October First assessment: June 2020

PAPER / UNIT 6	PERCENTAGE OF IA2	PERCENTAGE OF IAL	MARK	TIME	AVAILABILITY
PRACTICAL SKILLS IN CHEMISTRY II Written exam paper Paper / Unit code WCH16/01 Externally set and marked by Pearson Edexcel Single tier of entry	20%	10%	50	1 hour 20 minutes	January, June and October First assessment: June 2020

ASSESSMENT OBJECTIVES AND WEIGHTINGS

ASSESSMENT OBJECTIVE	DESCRIPTION	% IN IAS	% IN IA2	% IN IAL
A01	Demonstrate knowledge and understanding of science.	34–36	29–31	32–34
A02	(a) Application of knowledge and understanding of science in familiar and unfamiliar contexts.	34–36	33–36	33–36
	(b) Analysis and evaluation of scientific information to make judgements and reach conclusions.	9–11	14–16	11–14
A03	Experimental skills in science, including analysis and evaluation of data and methods.	20	20	20

RELATIONSHIP OF ASSESSMENT OBJECTIVES TO UNITS

UNIT NUMBER	ASSESSMENT OBJECTIVE (%)			
	A01	**A02 (A)**	**A02 (B)**	**A03**
UNIT 1	17–18	17–18	4.5–5.5	0.0
UNIT 2	17–18	17–18	4.5–5.5	0.0
UNIT 3	0.0	0.0	0.0	20
TOTAL FOR INTERNATIONAL ADVANCED SUBSIDIARY	**33–36**	**34–36**	**9–11**	**20**

UNIT NUMBER	ASSESSMENT OBJECTIVE (%)			
	A01	**A02 (A)**	**A02 (B)**	**A03**
UNIT 1	8.5–9.0	8.5–9.0	2.2–2.8	0.0
UNIT 2	8.5–9.0	8.5–9.0	2.2–2.8	0.0
UNIT 3	0.0	0.0	0.0	10
UNIT 4	7.3–7.8	8.4–8.9	3.6–4.0	0.0
UNIT 5	7.3–7.8	8.4–8.9	3.6–4.0	0.0
UNIT 6	0.0	0.0	0.0	10
TOTAL FOR INTERNATIONAL ADVANCED LEVEL	**32–34**	**33–36**	**11–14**	**20**

TOPIC 11 KINETICS

A FURTHER KINETICS

Your health depends on a complex interplay of a large number of chemical reactions taking place in the cells of your body. In a healthy body, these reactions will take place at the correct rate, in the right place and at the right time. These reactions are controlled by enzymes. The branch of chemistry concerned with the rates of chemical reactions is called chemical kinetics. The term 'kinetics' implies motion and comes from the ancient Greek word for movement, *kinesis*. We can use the information obtained from the study of chemical kinetics to:

- understand the body's metabolism (the chemical processes in the body)
- model the effects of pollutants in the Earth's atmosphere
- develop new catalysts, which is of great importance to the chemical industry.

In **Topic 9 (Book 1: IAS)**, we used a qualitative approach to the understanding of reaction rates. In this topic we will develop this further by adopting a quantitative approach. This will enable us to begin to understand what is happening during chemical reactions:

- We know how atoms can bond together to form molecules, but why do the atoms change partners during chemical reactions?
- What exactly happens when a hydrogen molecule meets an iodine molecule and they subsequently react to produce hydrogen iodide?

It has been reported by scientists that the herb ginseng may be just as effective as Prozac at treating depression. Herbs and plant extracts have been used for centuries to cure diseases and to relieve pain. In many cases they are effective because they control the rates of chemical reactions within the body. In this topic we will study the rates of chemical reactions and the mechanisms by which they take place.

MATHS SKILLS FOR THIS TOPIC

- Recognise and make use of appropriate units in calculation
- Recognise and use expressions in decimal and ordinary form
- Use calculators to find and use power functions
- Use an appropriate number of significant figures
- Change the subject of an equation
- Substitute numerical values into algebraic expressions using appropriate units for physical quantities
- Solve algebraic expressions
- Translate information between graphical, numerical and algebraic forms
- Plot two variables from experimental or other data
- Determine the slope and intercept of a linear graph
- Calculate the rate of change for a graph showing a linear relationship
- Draw and use the slope of a tangent to a curve as a measure of the rate of change

What prior knowledge do I need?

Topic 9 (Book 1: IAS)

- The concept of activation energy
- The Maxwell–Boltzmann model of distribution of molecular energies
- The role of catalysts in increasing the rate of chemical reactions
- Reaction profiles for both uncatalysed and catalysed reactions

What will I study in this topic?

- Order of reaction and rate equations
- Selection of an appropriate technique to follow the rate of a reaction
- Initial rate and continuous rate techniques for following reactions
- Reaction mechanisms
- Homogeneous and heterogeneous catalysis

What will I study later?

- How pharmaceutical companies invest heavily in research and development to design new medicines to treat a wide range of medical problems and illnesses
- How biocatalysts based on natural enzymes allow some reactions to occur at lower temperatures and pressures than other catalysts
- How scientists are developing superconductors (materials with no electrical resistance that offer enormous energy savings in electricity transmission) based on organic compounds rather than metals

11A 1 TECHNIQUES FOR MEASURING THE RATE OF REACTION

SPECIFICATION REFERENCE

11.1(i) 11.3(i) 11.3(ii)
11.3(iii) 11.3(iv) 11.3(v)

LEARNING OBJECTIVES

- Understand the term 'rate of reaction'.
- Select and justify a suitable experimental technique to obtain rate data for a given reaction, including:
  - (i) titration
  - (ii) colorimetry
  - (iii) mass change
  - (iv) volume of gas evolved
  - (v) other suitable technique(s) for a given reaction.

RATE OF REACTION

The **rate of a reaction** can be expressed in two ways:

(1) How the concentration of a product *increases* with time.

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

(2) How the concentration of a reactant *decreases* with time.

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

The negative sign in the second expression shows that the concentration of the reactant is decreasing and therefore gives a positive value for the rate.

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

The expressions in calculus notation are:

$$\text{rate} = \frac{d[\text{product}]}{dt}$$

$$\text{rate} = -\frac{d[\text{reactant}]}{dt}$$

This **rate of reaction** is sometimes called the 'overall rate of reaction'.

TECHNIQUES FOR MEASURING THE RATE OF REACTION

Before investigating the rate of a particular reaction, it is necessary to know the overall equation, including state symbols, for the reaction so that we can decide what technique to use to follow the reaction.

There are various techniques available to use, such as:

1 measuring the volume of a gas evolved
2 measuring the change in mass of a reaction mixture
3 monitoring the change in intensity of colour of a reaction mixture (colorimetry)
4 measuring the change in concentration of a reactant or product using titration
5 measuring the change in pH of a solution
6 measuring the change in electrical conductivity of a reaction mixture.

The technique chosen to follow the reaction will depend on the nature of the reactants and products, as well as the conditions under which the reaction is carried out.

For example, the reaction between calcium carbonate and dilute hydrochloric acid,

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

could conveniently be followed by measuring the volume of gas (technique 1) given off at regular time intervals, or by measuring the change in mass of the reaction mixture with time (technique 2).

However, the reaction between propanone and iodine in aqueous solution,

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

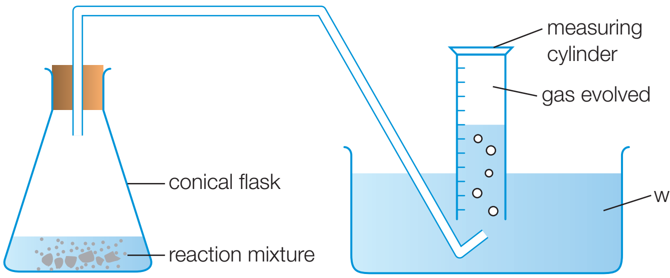
could not be followed by measuring the change in mass because all products of the reaction remain in solution. It would be possible, however, to follow the reaction by monitoring the decrease in intensity of colour of the reaction mixture, since $I_2(aq)$ is the only coloured **species** present (technique 3).

TECHNIQUE 1: MEASURING THE VOLUME OF A GAS EVOLVED

The two most common techniques for collecting and measuring the volume of a gas evolved during a reaction are:

1 collection over water into a measuring cylinder (**fig A**), and
2 collection using a gas syringe (**fig B**).

The technique chosen will depend partly on the level of precision required. The gas syringe has a greater degree of precision, but if a large volume of gas is being measured, the difference in the degree of measurement uncertainty becomes so small that either instrument is sufficiently precise.



▲ **fig A** Collecting a gas over water.

EXAM HINT

Reactions producing gases that are very soluble in water, such as sulfur dioxide, cannot use the gas collection over water technique.

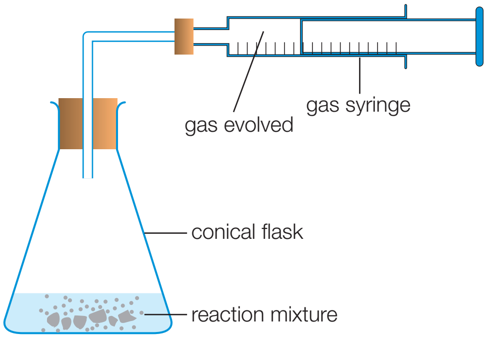


fig B Collecting a gas in a gas syringe.

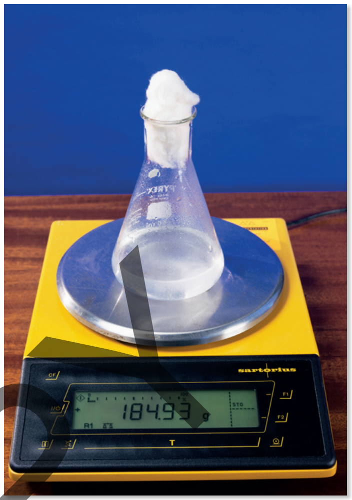


fig C Cotton wool is placed in the neck of the flask to prevent the loss of liquid spray.

TECHNIQUE 2: MEASURING THE CHANGE IN MASS OF A REACTION MIXTURE

This is another technique applicable to reactions in which a gas is evolved.

The reaction flask and contents are placed on a digital balance and the decrease in mass is measured as the reaction proceeds (**fig C**).

This technique is most precise when the gas given off has a relatively high density, such as with carbon dioxide. With a low-density (i.e. low relative molecular mass) gas such as hydrogen, the mass changes are so small that the measurement uncertainties become significant.

TECHNIQUE 3: MONITORING A COLOUR CHANGE (COLORIMETRY)

Colour change can sometimes be monitored using observation only. However, using a colorimeter gives more precise results (**fig D**). A colorimeter can detect far more subtle changes than the human eye can observe, and provides a quantitative (rather than a subjective) measurement.

fig D A colorimeter.

TECHNIQUE 4: ANALYSIS BY TITRATION

This technique involves using a pipette to remove small samples (aliquots) from a reaction mixture at regular intervals. The reaction in the aliquot can either be stopped by adding another substance to it or slowed down to almost zero by immersing it in an ice bath. The aliquot is then titrated to determine the concentration of a reactant or product species.

The process of stopping or slowing down the reaction in an aliquot is known as ‘quenching’.

For example, if the reaction involves an acid, the aliquot, after quenching, could be titrated against a standard solution of sodium hydroxide to determine the concentration of the acid. This technique is used to investigate the reaction between iodine and propanone, which is catalysed by acid. Sodium hydrogen carbonate is added to the aliquot to remove the acid catalyst and, as a result, effectively stops the reaction. The remaining iodine is then titrated against a standard solution of sodium thiosulfate (**fig E**).

fig E Titrating iodine against sodium thiosulfate.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

TECHNIQUE 5: MEASURING THE ELECTRICAL CONDUCTIVITY

If the total number, or type, of ions in solution changes during a reaction, it might be possible to follow the reaction by measuring changes in the electrical conductivity of the solution using a conductivity meter. For example, it could be used to follow this reaction:

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

TECHNIQUE 6: MEASURING ANY OTHER PHYSICAL PROPERTY THAT SHOWS A SIGNIFICANT CHANGE

Possible physical properties that have not already been mentioned include changes in the volume of liquid (‘dilatometry’), chirality and refractive index.

CHECKPOINT

1. State suitable techniques to collect rate data for each of the following reactions.

(a) Magnesium with dilute sulfuric acid:

$$Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$$

(b) Ethyl ethanoate with sodium hydroxide:

$$CH_3COOCH_2CH_3(l) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + CH_3CH_2OH(aq)$$

(c) Hydrogen gas with iodine gas:

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

SKILLS CREATIVITY

2. ▶ Why would the technique of measuring the change in mass of a reaction vessel and contents not work well in the reaction between magnesium and dilute sulfuric acid?

3. ▶ The reaction between calcium carbonate and dilute hydrochloric acid can be followed by collecting and measuring the volume of gas produced. The gas could be collected over water in a measuring cylinder or in a gas syringe. Which technique would be the more suitable for this reaction? Explain your answer.

SUBJECT VOCABULARY

(overall) **rate of reaction** the change in concentration of a species divided by the time it takes for the change to occur. All reaction rates are positive

(chemical) **species** an atom, a molecule or an ion that is taking part in a chemical reaction

11A 2 RATE EQUATIONS, RATE CONSTANTS AND ORDERS OF REACTION

SPECIFICATION REFERENCE
11.1(ii) 11.1(iii) 11.1(iv) 11.1(v) 11.1(vii)

LEARNING OBJECTIVES

- Understand the terms:
  (i) rate equation, rate = $k[A]^m[B]^n$, where m and n are 0, 1 or 2
  (ii) order with respect to a substance in a rate equation
  (iii) overall order of a reaction
  (iv) rate constant
  (v) rate-determining step.

RATE EQUATION

WHAT IS A RATE EQUATION?

The usual relationship between the rate of reaction and the concentration of a reactant is that the rate of reaction is directly proportional to the concentration. In other words, as the concentration is doubled, the rate of reaction doubles.

Unfortunately, this is not always the case. Sometimes the rate will double, but sometimes it will increase by a factor of four. In some cases, the rate of reaction does not increase at all, or it increases in an unexpected way.

Let us consider the simple relationship where the rate is directly proportional to the concentration of a reactant, say A. We can represent this by the expression:

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

or:

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

where k is the proportionality constant.

This is called the *first order* **rate equation**. The constant k is called the *rate constant*.

- Every reaction has its own particular rate equation and its own rate constant.
- Rate constants will only change their value with a change in temperature.

Other common rate equations with respect to an individual reactant are:

second order rate equation: rate = $k[A]^2$

zero order rate equation: rate = $k[A]^0$ or rate = k

Zero order reactions do not occur very often, and it might be difficult at this stage for you to imagine why they should occur at all. However, you will find out shortly why they can occur.

If two or more reactants are involved, then it is possible to have a third order rate equation:

third order rate equation: rate = $k[A]^2[B]$

THE UNITS OF RATE CONSTANTS

Table A shows the units for rate constants, using mol dm^{-3} as the unit of concentration and seconds as the unit of time. You find the units by rearranging the rate equation.

ORDER	UNIT
Zero	mol dm^{-3} s^{-1}
First	s^{-1}
Second	dm^3 mol^{-1} s^{-1}
Third	dm^6 mol^{-2} s^{-1}

table A

EXAM HINT

The values for orders of reaction in rate equations will only ever be 0, 1 or 2 at International A Level.

The units are obtained by rearranging the rate equation. For example, for a second order reaction:

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

Inserting the units we obtain:

$$\frac{\text{mol dm}^{-3}\,\text{s}^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$$

This cancels down to:

$$\frac{\text{s}^{-1}}{\text{mol dm}^{-3}}$$

which equates to $\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$.

The majority of reactions involve two or more reactants. If we call the reactants A, B and C, then the reaction may be first **order** with respect to A, first order with respect to B and second order with respect to C. The *overall* rate equation will be:

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

and the **overall order** of the reaction is four (1 + 1 + 2). Note that you are adding the powers.

For a general reaction in which the orders are m, n and p, we have:

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

The overall order of the reaction is $m + n + p$.

REACTION MECHANISMS

Many reactions can be represented by a stoichiometric equation containing many reactant particles. For example, the reaction between manganate(VII) ions and iron(II) ions in acidic solution can be represented by:

$$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 5\text{Fe}^{3+}(\text{aq})$$

If this reaction actually proceeded in a single step, then the reaction would be very slow indeed. The probability of 14 particles simultaneously colliding, all with the correct orientation and energy, is so small that we can say it is effectively zero. The reaction is, however, very fast indeed even at room temperature. It must, therefore, proceed via a series of steps, all of which follow on quickly from one another. It is important to recognise that a reaction involving simultaneous collision of more than two particles is very rare.

The orders of reaction of the individual reactants can help us to suggest a possible mechanism for a reaction. The mechanism cannot be inferred from the stoichiometric equation, because the mathematical relationship between the rate of reaction and the concentration of reactants (i.e. the orders of reaction) can only be determined *through experiments*.

Consider the reaction:

$$\text{A} + \text{B} + \text{C} \rightarrow \text{D} + \text{E}$$

for which the experimentally determined rate equation is:

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

This could mean that C was present in such a large excess that changes in its concentration were negligible and therefore had no measurable effect on the rate of reaction.

If, however, this is not the case, and changes in [C] really do not have any effect on the overall rate of reaction, then a different explanation must be sought for why [C] does not appear in the rate equation.

In this case, there must be a step involving a reaction between A and B that has an effect on the rate of reaction. There must also be another step in which C reacts, but this reaction has *no effect* on the overall rate of reaction. This could be explained by assuming that the reaction between A and B takes place *before* C has a chance to react, and that the reaction between A and B is significantly *slower* than the reaction involving C. If this were the case, then the mechanism for the reaction could be:

Step 1:	$\text{A} + \text{B} \rightarrow \text{Z}$	SLOW
Step 2:	$\text{Z} + \text{C} \rightarrow \text{D} + \text{E}$	FAST

Since only Step 1 is **rate-determining**, then only changes in [A] and [B] will affect the overall rate of reaction. Changes in the rate at which Step 2 occurs, owing to changes in [C], will be negligible.

Important points to remember are that:

- *The slowest step in a reaction determines the overall rate of the reaction.*
- The slowest step is known as the *rate-determining step* of the reaction.

We will return to the concept of reaction mechanisms, and consider them in much more detail, in **Section 11A.4**.

WORKED EXAMPLE

A useful way of visualising the idea of a rate-determining step is to imagine that three students are arranging some sheets of notes into sets (**fig A**).

Step 1: the notes are arranged into ten piles and the first student collects a sheet from each of the piles.

Step 2: the second student takes the set of ten papers and shuffles them so that they are tidy and ready for stapling.

Step 3: the third student staples the set of notes together.

The overall rate of this process (i.e. the rate at which the final sets of notes are prepared) depends on the rate of Step 1, the collecting of the sheets of notes, since this is by far the slowest step.

It does not matter, within reason, how quickly the tidying up for stapling is done. For most of the time the second and third students will be doing nothing while they wait for the first student to collect the sheets. The mechanism of the process is therefore:

Step 1:	Student 1 collects sheets	SLOW
Step 2:	Student 2 tidies set of sheets	FAST
Step 3:	Student 3 staples set of sheets	FAST

▲ **fig A** Analogy for rate-determining step.

LEARNING TIP

All reactant species involved either in, or before, the rate-determining step have an effect on the rate of the reaction and will appear in the rate equation.

CHECKPOINT

1. The rate equation for the reaction between peroxydisulfate ions and iodide ions is:

rate = $k[S_2O_8^{2-}][I^-]$

(a) What is the order of reaction with respect to (i) peroxydisulfate ions and (ii) iodide ions?

(b) What is the overall order of reaction?

2. The rate equation for the reaction between P and Q is:

rate = $k[P][Q]^2$

What will be the increase in rate if:

(a) [P] is doubled, while [Q] is kept constant?

(b) [Q] is doubled, while [P] is kept constant?

(c) [P] and [Q] are both doubled?

3. In the reaction between R, S and T:

- when the concentration of R is doubled, the rate increases by four times
- when the concentration of S is doubled, the rate does not change
- when the concentration of T is doubled, the rate doubles.

SKILLS PROBLEM-SOLVING

(a) Deduce the orders of reaction with respect to R, S and T.

(b) Write the rate equation for the reaction.

(c) What is the overall order of reaction?

SUBJECT VOCABULARY

rate equation an equation expressing the mathematical relationship between the rate of reaction and the concentrations of the reactants

order (of a reactant species) the power to which the concentration of the species is raised in the rate equation

overall order (of a reaction) the sum of all the individual orders

rate-determining step (of a reaction) the slowest step in the mechanism for the reaction

11A 3 DETERMINING ORDERS OF REACTION

SPECIFICATION REFERENCE

11.1(ii) 11.1(vi) 11.2 11.4(i)
11.4(ii) 11.5(i) 11.5(ii) 11.5(iii)

LEARNING OBJECTIVES

- Understand the terms:
  - (i) rate equation, rate = $k[A]^m[B]^n$, where m and n are 0, 1 or 2
  - (ii) half-life.
- Be able to calculate the half-life of a reaction, using data from a suitable graph, and identify a reaction with a constant half-life as being first order.
- Understand experiments that can be used to investigate reaction rates by:
  - (i) an initial-rate method
  - (ii) a continuous monitoring method.
- Be able to deduce the order (0, 1 or 2) with respect to a substance in a rate equation, using data from:
  - (i) a concentration–time graph
  - (ii) a rate–concentration graph
  - (iii) an initial-rate method.

HOW CAN WE DETERMINE THE RATE EQUATION?

This question can equally be phrased 'How can we determine the order of reaction with respect to each reactant?'

There are two methods for determining orders of reaction. They are both experimental. Indeed, orders of reaction can only be determined by experiment.

The first is sometimes called the 'continuous method'.

The second is sometimes called the 'initial-rate method'.

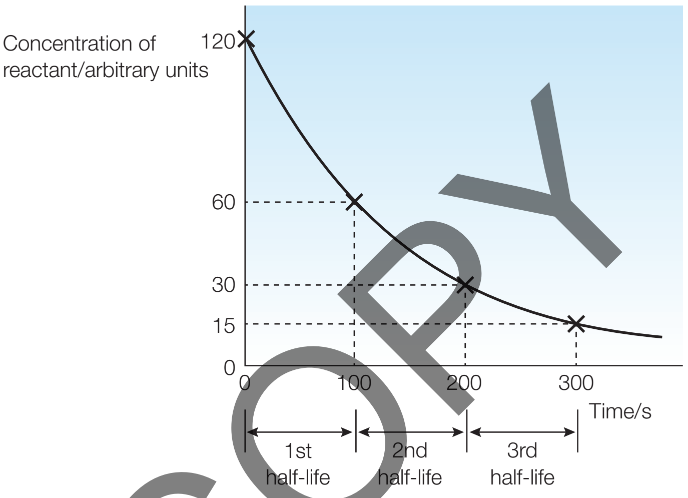
THE CONTINUOUS METHOD

In this method, *one* reaction mixture is made up and samples of the reaction mixture are withdrawn at regular time intervals. The reaction in the sample is stopped, if necessary, by quenching. The concentration of the reactant is then determined by an appropriate experimental technique, such as titration.

- The first step is to draw a 'concentration–time' graph.
- The second step is to find out the **half-life** for the reaction at different concentrations.

If the half-life has a constant value, then the reaction is first order with respect to the reactant.

The 1st half-life, for the change in concentration from 120 to 60 units, is 100 s (**fig A**).



▲ **fig A** A graph of concentration of reactant against time for a first order reaction.

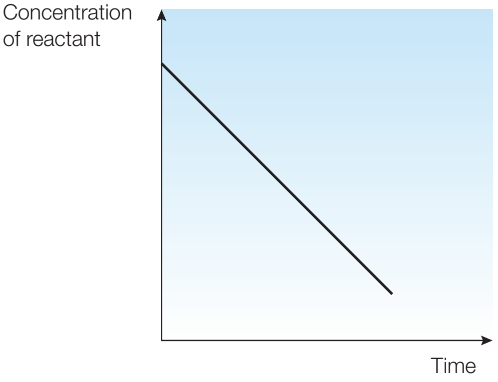
The 2nd half-life, for the change in concentration from 60 to 30 units, is 100 s.

The 3rd half-life, for the change in concentration from 30 to 15 units, is 100 s.

Since all three half-lives are the same, the reaction is first order with respect to the concentration of the reactant plotted.

If the half-life doubles as the reaction proceeds, then the reaction is second order.

If the graph is a straight line with a negative gradient, then the rate of reaction is constant no matter what the concentration of the reactant (**fig B**). In other words, the reaction is zero order with respect to the reactant.



▲ **fig B** A graph of concentration against time for a zero order reaction.

A typical set of results is shown in **table A** for the reaction:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

TIME/min	0	10	20	30	40	50	60	70	80	90
$[N_2O_5]/10^{-3}$ mol dm^{-3}	22.90	16.27	12.29	9.35	6.89	4.88	3.68	2.74	2.16	1.85

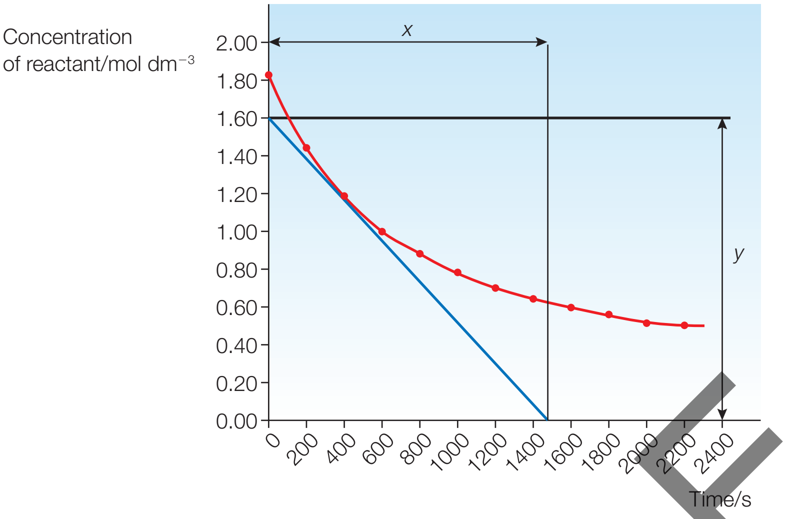
table A

If you plot a graph of $[N_2O_5]$ against time using the above data, you will find that the line is curved and the half-life is constant; as a result, the reaction is first order with respect to N_2O_5.

CALCULATING RATE FROM A CONCENTRATION–TIME GRAPH

The rate of reaction at any given time can be determined from a concentration–time or volume–time graph by drawing a tangent to the curve at the given time and calculating the gradient of the tangent.

Fig C shows the change in concentration of a reactant with time.



▲ **fig C** Determining an instantaneous rate of reaction from a graph of concentration of reactant against time.

A tangent to the curve has been drawn at time = 400 s.

To find the rate at this time point, draw as large a triangle as possible and then measure *x* and *y*.

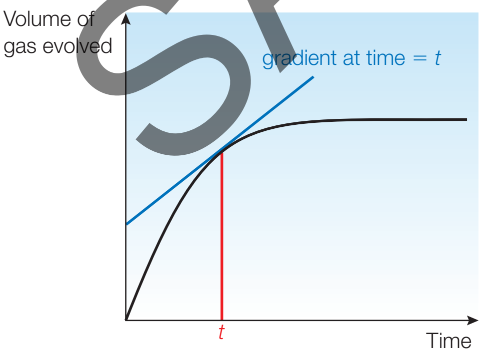
$x = 1470$ s and $y = -1.60$ mol dm^{-3}.

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

$$= -\frac{-1.60\ \text{mol dm}^{-3}}{1470\ \text{s}} = 1.09 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

CALCULATING RATE FROM A VOLUME–TIME GRAPH

The procedure is exactly the same for a volume–time graph for a gas evolved (**Section 11A.1**). This time the curve will slope upwards not downwards (**fig D**).



▲ **fig D** Determining an instantaneous rate of reaction from a graph of volume of gas evolved against time.

The rate of reaction obtained in this way is sometimes called the **instantaneous reaction rate**.

THE INITIAL-RATE METHOD FOR DETERMINING THE RATE EQUATION

In this method, *several* reaction mixtures are made up and the initial rate (i.e. the time taken for a fixed amount of reactant to be used up or for a fixed amount of product to be formed) is measured. From these times, it is then possible to calculate the mathematical relationship between the rate of the reaction and the concentration of the reactant.

A typical set of results is shown in **table B** for the reaction:

$$A + B \rightarrow C$$

EXPERIMENT	[A]/mol dm^{-3}	[B]/mol dm^{-3}	INITIAL RATE OF FORMATION OF C/mol dm^{-3} s^{-1}
1	0.1	0.1	0.02
2	0.1	0.2	0.04
3	0.2	0.1	0.04
4	0.2	0.2	0.08

table B

If we now look at experiments 1 and 3, we can see that [A] has doubled while [B] has remained constant. The rate of reaction has also doubled. This indicates that the reaction is first order with respect to A and, as a result, we can write:

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

If we now look at experiments 1 and 2, or experiments 3 and 4, we can see that [B] has doubled while [A] has remained constant. The initial rate of reaction has also doubled. This indicates that the rate of reaction is directly proportional to [B]. That is, the reaction is first order with respect to B. As a result, we can write:

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

The overall order of the reaction is two, and the complete rate law (rate equation) is:

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

Note that the numbers in **table B** were deliberately kept simple to illustrate a point. Real experimental results rarely fit such an exact pattern, and you may have to look for the nearest whole numbers to obtain orders.

DETERMINING ORDER FROM A RATE–CONCENTRATION GRAPH

The method described above to determine initial rates, with changing concentrations, results in only approximate values for the initial rates. However, since most orders of reaction with respect to individual reactants have integer values, this approximation is usually acceptable.

In an initial rates experiment, the time measured is that for a fixed amount of product to be formed, or that for a fixed amount of reactant to be used up. Since the amount of product formed, or reactant used up, is kept constant, the initial rate of reaction is proportional to the reciprocal of the time, t, measured. That is:

$$\text{rate} \propto \frac{1}{t}$$

This assumes that the rate is constant for the whole time period, t. However, this is not true because as soon as the reaction starts the rate begins to decrease. The rate calculated from the expression is, therefore, the *mean (average)* rate over time, t, and not the *true* initial rate of reaction. The approximation becomes poorer with larger values of t. However, the approximation is good enough to determine integer order.

It might be possible to determine orders of reaction from just a few measurements. However, it is usual to record a range of results and plot a graph of $\frac{1}{t}$ against concentration of reactant.

The shape of the graph in **table C** indicates the order of reaction.

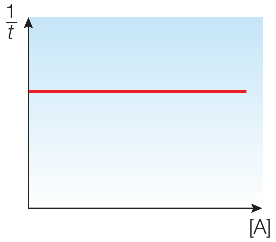
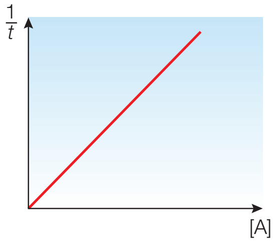
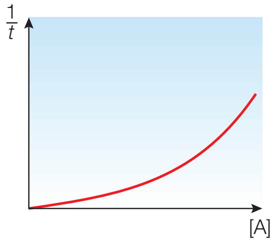
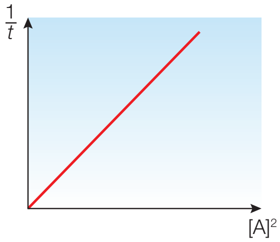
ZERO ORDER WITH RESPECT TO A $1/t\ (\propto \text{RATE}) = k[A]^0$	FIRST ORDER WITH RESPECT TO A $1/t\ (\propto \text{RATE}) = k[A]^1$	SECOND ORDER WITH RESPECT TO A $1/t\ (\propto \text{RATE}) = k[A]^2$
		

table C

EXAM HINT

Be careful to check the units on the axes of graphs. Graphs with the same shape will have different meanings if there are different units on the axes!

It is impossible to determine directly by sight from a rate–concentration graph that the reaction is second order. If the graph is a curve as shown, then it is necessary to then plot $\frac{1}{t}$ against $[A]^2$. If this produces a straight line passing through the origin, then the reaction is second order with respect to A.

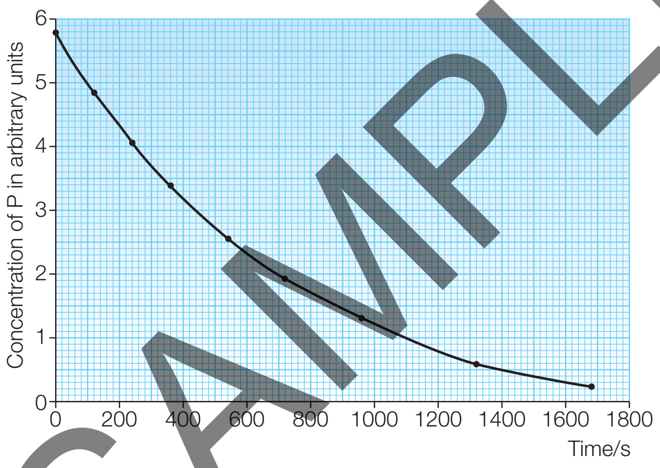


▲ **fig E** A graph of $\frac{1}{t}$ against the square of the concentration of a reactant for a second order reaction.

CHECKPOINT

SKILLS INTERPRETATION

1. A compound P decomposes when heated. The graph shows the change in concentration when a sample of P is heated.



(a) State what is meant by the term *half-life of reaction*.

(b) Use the graph to show that the decomposition of P is a first order reaction.

(c) Explain the effect on the half-life of doubling the initial concentration of P.

(d) Calculate the rate constant, *k*, for this reaction using the following expression:

$$k = \frac{0.693}{\text{half-life}}$$

Include units in your answer.

(e) Write the rate equation for this reaction.

(f) (i) Use the graph to determine the concentration of P at 800 s.

(ii) Use the rate equation from (e) and your answers to (d) and (f)(i) to calculate the rate of reaction at 800 s. Include units in your answer.

(g) Describe how could you determine the reaction rate at 800 s directly from the graph.

SKILLS INTERPRETATION

2. The equation for the reaction between bromide ions and bromate(V) ions in acidified aqueous solution is:

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

The table shows the results of four experiments carried out using different concentrations of the three reactants.

EXPERIMENT	$[Br^-(aq)]$/ mol dm^{-3}	$[BrO_3^-(aq)]$/ mol dm^{-3}	$[H^+(aq)]$/ mol dm^{-3}	INITIAL RATE/ mol dm^{-3} s^{-1}
1	0.10	0.10	0.10	1.2×10^{-3}
2	0.10	0.20	0.10	2.4×10^{-3}
3	0.30	0.10	0.10	3.6×10^{-3}
4	0.10	0.20	0.20	9.6×10^{-3}

(a) Deduce the order of reaction with respect to:

(i) Br^-

(ii) BrO_3^-

(iii) H^+

(b) Write the rate equation for the reaction.

(c) Using the results from experiment 1, calculate the rate constant, *k*, for the reaction. Include units in your answer.

SUBJECT VOCABULARY

half-life (of a reaction) the time taken for the concentration of the reactant to fall to one-half of its initial value

instantaneous reaction rate the gradient of a tangent drawn to the line of the graph of concentration against time. The instantaneous rate varies as the reaction proceeds (except for a zero order reaction)

11A 4 RATE EQUATIONS AND MECHANISMS

SPECIFICATION REFERENCE

11.6 11.7 11.8 11.9 CP9A CP9B

LEARNING OBJECTIVES

- Deduce the rate-determining step from a rate equation and vice versa.
- Deduce a reaction mechanism, using knowledge of the rate equation and the stoichiometric equation for a reaction.
- Understand that knowledge of the rate equations for the hydrolysis of halogenoalkanes can be used to provide evidence for S_N1 or S_N2 mechanisms for tertiary and primary halogenoalkane hydrolysis.
- Understand how to:
  - (i) obtain data to calculate the order with respect to the reactants (and the hydrogen ion) in the acid-catalysed iodination of propanone
  - (ii) use these data to make predictions about species involved in the rate-determining step
  - (iii) deduce a possible mechanism for the reaction.

REACTION MECHANISMS

You will remember from **Book 1** that the basic view as to how a reaction takes place at a particulate level is that particles (atoms, molecules, ions or radicals) first have to collide in the correct orientation and with sufficient energy for products to be formed.

For the following reaction:

$$P + Q \rightarrow \text{products}$$

we expect the rate law to be:

$$\text{rate} = k[P][Q]$$

In other words, we might expect the reaction to be first order with respect to each reactant and second order overall.

ELEMENTARY REACTIONS

A reaction taking place in this manner (a single collision between the two reactant particles) is described as being *elementary*.

If we know that a reaction is elementary, then we can deduce the rate law directly from the stoichiometric equation. For example, the following reaction is known to be elementary:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

so the rate equation is:

$$\text{rate} = k[NO][O_3]$$

The reaction takes place when a molecule of NO collides with a molecule of O_3.

If the reaction is not elementary, it is *not* possible to deduce the rate equation by simply looking at the stoichiometric equation for the reaction.

For example, the decomposition of dinitrogen pentoxide into nitrogen dioxide and oxygen is first order with respect to dinitrogen pentoxide, not second.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The experimentally determined rate equation is:

$$\text{rate} = k[N_2O_5]$$

A reaction that is not elementary takes place via a series of interconnected elementary reactions that are collectively called the *mechanism* for the reaction. You will have already come across a number of such mechanisms in your study of organic chemistry. For example, the radical substitution reaction between methane and chlorine to form chloromethane (CH_3Cl) is thought to have the following mechanism:

Step 1: $Cl_2 \rightarrow 2Cl\bullet$

Step 2: $Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3$

Step 3: $Cl_2 + \bullet CH_3 \rightarrow Cl\bullet + CH_3Cl$

The overall stoichiometric equation for the reaction is:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

The species $Cl\bullet$ and $\bullet CH_3$ are called *intermediates*. They do not appear in the overall equation for the reaction, but are involved in reactions that ultimately result in the reactants being converted into the products.

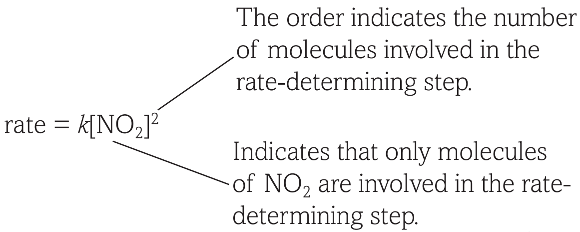
If the experimentally determined rate equation does not match the overall stoichiometry, then it is almost certain that the reaction is not elementary. For example, the rate equation for the following reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

is:

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

This suggests that only molecules of NO_2 are involved in the rate-determining step, and that *two* molecules of NO_2 are involved in this step.


rate = $k[NO_2]^2$

The order indicates the number of molecules involved in the rate-determining step.

Indicates that only molecules of NO_2 are involved in the rate-determining step.

fig A Molecules involved in the rate-determining step.

Using our knowledge of molecules that do exist, two possible rate-determining steps are:

1 $NO_2 + NO_2 \rightarrow N_2O_4$, or

2 $NO_2 + NO_2 \rightarrow 2NO + O_2$

Both of these reactions are equally valid, and we have no way of knowing, without carrying out further investigations, which is the more likely to be taking place.

We also have no way of knowing what is involved in the remaining steps, but we do know that the sum of all the steps must add up to the overall stoichiometric equation.

Using the second of the two possible rate-determining steps, the following mechanism is consistent with the data:

$NO_2 + NO_2 \rightarrow 2NO + O_2$ SLOW

$CO + O_2 \rightarrow CO_2 + O$ FAST

$NO + O \rightarrow NO_2$ FAST

This shows how the particles in the proposed mechanism cancel to produce the overall equation:

$$\begin{array}{rcl} NO_2 + \cancel{NO_2} & \rightarrow & \cancel{NO} + NO + \cancel{O_2} \\ CO + \cancel{O_2} & \rightarrow & CO_2 + \cancel{O} \\ \cancel{NO} + \cancel{O} & \rightarrow & \cancel{NO_2} \\ \hline NO_2 + CO & \rightarrow & NO + CO_2 \end{array}$$

As it happens, further investigations into this reaction have identified the mechanism as:

$NO_2 + NO_2 \rightarrow NO_3 + NO$ SLOW

$NO_3 + CO \rightarrow NO_2 + CO_2$ FAST

This is not what we would immediately suspect as the mechanism because the existence of NO_3 is not something with which we would be familiar.

Even if the experimentally determined rate equation is simple, it does not necessarily follow that the reaction proceeds in a single elementary step. For example, the rate expression for the following gas-phase reaction:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

is:

$$\text{rate} = k[N_2O_5]$$

Yet, the reaction is thought to involve several steps and a number of intermediates.

ALKALINE HYDROLYSIS OF HALOGENOALKANES

The hydrolysis of halogenoalkanes by hydroxide ions is a reaction we introduced in **Topic 10 (Book 1: IAS)**. The hydroxide ion acts as a nucleophile and replaces the halogen in the halogenoalkanes. The reaction, therefore, can also be described as *nucleophilic substitution*.

HYDROLYSIS OF A TERTIARY HALOGENOALKANE

The equation for the alkaline hydrolysis of 2-chloromethylpropane is:

$$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$$

The experimentally determined rate equation for this reaction is:

$$\text{rate} = k[(CH_3)_3CCl]$$

The reaction is first order with respect to 2-chloromethylpropane, but zero order with respect to the hydroxide ion.

The sensible conclusion to reach is that the 2-chloromethylpropane undergoes slow ionisation as the rate-determining step. This is then followed by a very fast step involving attack by the hydroxide ion on the carbocation formed in Step 1.

Step 1: $(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$ SLOW

Step 2: $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ FAST

This type of mechanism is named S_N1, i.e. *S*ubstitution *N*ucleophilic *uni*molecular.

The rate-determining step is said to be *uni*molecular because there is only *one* reactant particle present, $(CH_3)_3CCl$.

The carbocation, $(CH_3)_3C^+$, formed in Step 1 is an *intermediate* (see **Section 11A.6**).

HYDROLYSIS OF A PRIMARY HALOGENOALKANE

The equation for the alkaline hydrolysis of 1-chlorobutane is:

$$CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Cl^-$$

The experimentally determined rate equation for this reaction is:

$$\text{rate} = k[CH_3CH_2CH_2CH_2Cl][OH^-]$$

This time the reaction is first order with respect to each reactant, so it is reasonable to suggest that one particle of each reactant is present in the rate-determining step of the mechanism.

The accepted mechanism for the reaction is:

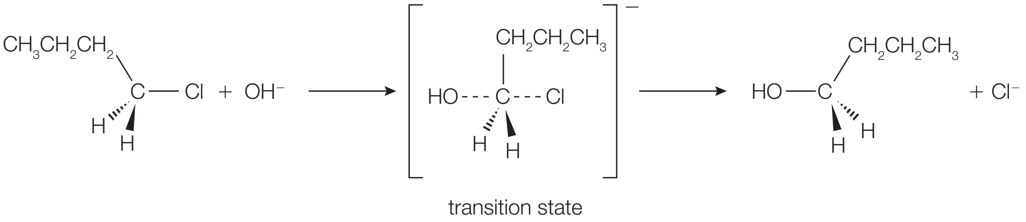


fig B S_N2 mechanism of the alkaline hydrolysis of 1-chlorobutane.

This type of mechanism is named S_N2, i.e. *S*ubstitution *N*ucleophilic *bi*molecular.

The rate-determining step is *bi*molecular because there are *two* reactant particles present.

It is a continuous single one-step reaction. The complex shown in square brackets is not an intermediate (like the carbocation formed in the S_N1 mechanism), but is a *transition state* (see **Section 11A.6**).

PRACTICAL SKILLS CP9A

A study of the acid-catalysed iodination of propanone

The reaction between propanone and iodine in aqueous solution may be acid catalysed:

$$I_2(aq) + CH_3COCH_3(aq) + H^+(aq) \rightarrow CH_3COCH_2I(aq) + 2H^+(aq) + I^-(aq)$$

The influence of the iodine on the reaction rate may be studied if the concentrations of propanone and hydrogen ions effectively remain constant during the reaction. This is achieved by using a *large excess* of both propanone and acid in the original reaction mixture. You will investigate this in **CP9A Following the rate of iodine–propanone reaction by a titrimetric method**.

Procedure

1 Mix 25 cm^3 of 1 mol dm^{-3} aqueous propanone with 25 cm^3 of 1 mol dm^{-3} sulfuric acid.

2 Start the stop clock *the moment you add* 50 cm^3 of 0.02 mol dm^{-3} iodine solution. Shake well.

3 Using a pipette, withdraw a 10 cm^3 sample and place it in a conical flask. Stop the reaction by adding a 'spatula-measure' of sodium hydrogen carbonate. Note the exact time at which the sodium hydrogen carbonate is added.

4 Titrate the remaining iodine present in the sample with 0.01 mol dm^{-3} sodium thiosulfate(VI) solution, using starch indicator.

5 Withdraw further 10 cm^3 samples at suitable time intervals (approx. 5 to 7 minutes) and treat them similarly, always noting the exact time at which the sodium hydrogen carbonate is added. Waste should be contained in a fume cupboard.

Treatment of results

The Lab Book can give additional guidance in the treatment and analysis of results.

- Plot a graph of titre against time. (The titre is proportional to the concentration of iodine.)
- Deduce from the graph the order of reaction with respect to iodine.

Analysis of results

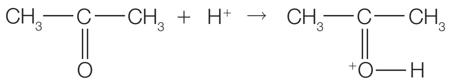
The graph produced shows that the reaction is zero order with respect to iodine.

Similar experiments show that the reaction is first order with respect to both propanone and hydrogen ions.

This gives us the following rate equation:

$$\text{rate} = k[CH_3COCH_3][H^+]$$

This would suggest the following reaction as the first step of the reaction:



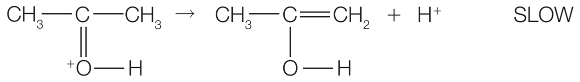
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H^+ \rightarrow CH_3-\underset{\underset{^+O-H}{\|}}{C}-CH_3$$

Similar reactions in other mechanisms are very fast, so this reaction is unlikely to be the rate-determining step of this reaction.

EXAM HINT

Examiners may ask you to **evaluate** different methods for investigating rates of reaction. One limitation of the method described here is the time delay between withdrawing a reaction sample by pipette and quenching it with sodium hydrogen carbonate.

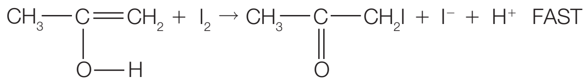
The second step probably controls the rate of the reaction and produces H^+ that, being a catalyst, is not used up in the reaction:



$$CH_3-C(=O^+H)-CH_3 \rightarrow CH_3-C(OH)=CH_2 + H^+ \quad \text{SLOW}$$

This rearrangement is likely to be very slow and hence is probably the rate-determining step of the reaction.

Iodine can now react in a fast step as follows:



$$CH_3-C(OH)=CH_2 + I_2 \rightarrow CH_3-C(=O)-CH_2I + I^- + H^+ \quad \text{FAST}$$

Testing the mechanism

We have a proposed mechanism for the reaction that is consistent with the kinetic data obtained from experiment. This is not the same as saying that the mechanism is the correct one, or indeed the most likely one.

We now need to carry out further experiments to confirm, or deny, our proposed mechanism. Here are three techniques that can be employed in this case.

- *Use a wider range of concentrations*

  The experimentally determined rate equation may hold over only a limited range of concentrations. For example, the mechanism we have proposed for the iodination of propanone predicts that, at very low concentrations of iodine, the order of reaction with respect to iodine will change from zero to first. This is because the rate of the final step in the mechanism is given by the expression:

  Rate = $k[I_2][CH_3C(OH){=}CH_2]$

  and so the rate of the step will decrease as $[I_2]$ decreases. This has been shown to be the case, so supports the proposed mechanism.
- *Use instrumental analysis*

  This may be able to detect the presence of intermediates that have been proposed. Nuclear magnetic resonance can be used to show that acidified propanone contains about one molecule in a million in the form $CH_3C(OH){=}CH_2$. This is an intermediate stated in the proposed mechanism.
- *Carry out the reaction with deuterated propanone, CD_3COCD_3*

  Deuterium $^{2}_{1}H$ (or simply D) behaves slightly differently to hydrogen $^{1}_{1}H$ (or simply H).

  A C–D bond is slightly stronger, and therefore harder to break, than a C–H bond. If this is the bond that breaks in the rate-determining step, as suggested by our proposed mechanism, then the iodination of CD_3COCD_3 will be slower than that of CH_3COCH_3. This is found to be the case.

CHECKPOINT

1. The equation for the reaction between ethanal, CH_3CHO, and hydrogen cyanide, HCN, is:

$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

Two mechanisms that have been proposed for this reaction are:

Mechanism 1

Step 1: $CH_3CHO + H^+ \rightarrow [CH_3CHOH]^+$
Step 2: $[CH_3CHOH]^+ + CN^- \rightarrow CH_3CH(OH)CN$

Mechanism 2

Step 1: $CH_3CHO + CN^- \rightarrow [CH_3CHOCN]^-$
Step 2: $[CH_3CHOCN]^- + H^+ \rightarrow CH_3CH(OH)CN$

The rate equation for the reaction is:

rate = $k[CH_3CHO][CN^-][H^+]^0$

(a) Explain which of the two mechanisms is consistent with the rate equation.

(b) Which step in this mechanism is the rate-determining step?

2. The equation for the reaction between hydrogen and nitrogen monoxide is:

$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$

The rate equation for the reaction is:

rate = $k[H_2][NO]^2$

A proposed mechanism for this reaction is:

Step 1: $2NO(g) \rightarrow N_2O_2(g)$ FAST
Step 2: $N_2O_2(g) + H_2(g) \rightarrow H_2O(g) + N_2O(g)$ SLOW
Step 3: $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ FAST

Is this mechanism consistent with the rate equation? Explain your answer.

3. Assume the following proposed reaction mechanism is correct:

$Cl_2 \rightarrow 2Cl\bullet$ SLOW
$H_2 + Cl\bullet \rightarrow HCl + H\bullet$ FAST
$H\bullet + Cl\bullet \rightarrow HCl$ FAST

(a) Write the overall equation for the reaction.

(b) Write a rate equation for the reaction that is consistent with the mechanism.

(c) What would be the effect on the rate of reaction of doubling the concentration of Cl_2?

(d) What would be the effect on the rate of reaction of doubling the concentration of H_2?

4. The nucleophilic substitution reaction between equimolar quantities of CH_3Cl and OH^- is second order overall. However, if the reaction is carried out using a large excess of OH^-, the reaction becomes first order overall. Suggest an explanation for these observations.

5. Bromine can be formed by the oxidation of hydrogen bromide with oxygen.

A proposed mechanism for this reaction is:

Step 1: $HBr + O_2 \rightarrow HBrO_2$
Step 2: $HBrO_2 + HBr \rightarrow 2HBrO$
Step 3: $HBrO + HBr \rightarrow Br_2 + H_2O$
Step 4: $HBrO + HBr \rightarrow Br_2 + H_2O$ (a repeat of Step 3)

The rate equation for this reaction is:

rate = $k[HBr][O_2]$

(a) Explain which of the above four steps is the rate-determing step for this reaction.

(b) Write the overall equation for the reaction.

11A 5 ACTIVATION ENERGY AND CATALYSIS

SPECIFICATION REFERENCE

11.1(viii) 11.1(ix)
11.11 CP10

LEARNING OBJECTIVES

- Understand the terms:
    (i) activation energy
    (ii) heterogeneous and homogeneous catalyst
    (iii) autocatalysis.
- Understand the use of a solid (heterogeneous) catalyst for industrial reactions, in the gas phase, in terms of providing a surface for the reaction.

ACTIVATION ENERGY, E_a

In **Topic 9** (**Book 1: IAS**), we defined activation energy, E_a, as the minimum energy that colliding particles must possess for a reaction to occur.

The activation energy represents the energy that the colliding particles must obtain in order to reach the energy level of the *transition state* (see **Section 11A.6** for more details). Once the energy level of the transition state has been reached, the particles can react to form the products and release energy as they do so. The energy profile diagram for an exothermic reaction is shown in **fig A**.

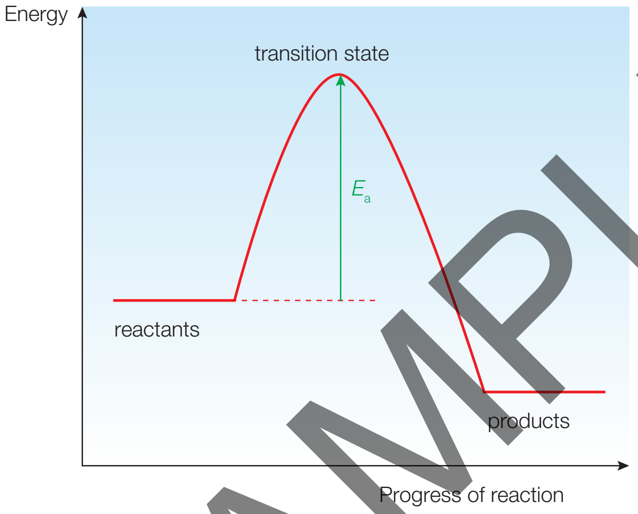


fig A A reaction profile for an elementary exothermic reaction.

CATALYSTS

In **Topic 9** (**Book 1: IAS**), we defined a catalyst as a substance that increases the rate of a chemical reaction but is chemically unchanged at the end of the reaction.

We then went on to explain that a catalyst works by providing an alternative route for the reaction, and that this alternative route has a lower activation energy than the original route. Although the original route is still available for the reactants, most collisions resulting in reaction will occur by the alternative route, since the fraction of particles possessing this lower activation energy will be greater.

Catalysts can be divided into two groups:

- homogeneous catalysts
- heterogeneous catalysts.

HOMOGENEOUS CATALYSTS

A *homogeneous catalyst* is in the same phase (solid, liquid, solution or gas) as the reactants.

Many reactions in aqueous solution are catalysed by the hydrogen ion, $H^+(aq)$. An example is the iodination of propanone, a reaction we discussed in detail in **Section 11A.4**:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The production of chlorine radicals from chlorofluorocarbons (CFCs) is responsible for the destruction of ozone in the upper atmosphere. Ultraviolet radiation from the Sun produces chlorine radicals, Cl•, from CFCs such as dichlorodifluoromethane, CCl_2F_2:

$$CCl_2F_2(g) \xrightarrow{\text{ultraviolet radiation}} \bullet CClF_2(g) + Cl\bullet(g)$$

The chlorine radicals then take part in a chain reaction with ozone:

$$Cl\bullet(g) + O_3(g) \rightarrow ClO\bullet(g) + O_2(g)$$

$$ClO\bullet(g) + O_3(g) \rightarrow 2O_2(g) + Cl\bullet(g)$$

The chlorine radical is regenerated and so is acting as a catalyst. Since the catalyst is in the same phase, i.e. the gas phase, as the reacting species, it is classified as a homogeneous catalyst.

The overall reaction is:

$$2O_3(g) \rightarrow 3O_2(g)$$

Another reaction involving a homogeneous catalyst is the one between peroxydisulfate ions and iodide ions in aqueous solution:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

This reaction is catalysed by either $Fe^{2+}(aq)$ or $Fe^{3+}(aq)$.

With $Fe^{2+}(aq)$, the reaction mechanism is:

Step 1: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

Step 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

With $Fe^{3+}(aq)$ as the catalyst, Steps 1 and 2 occur in the reverse order

LEARNING TIP

The action of $Fe^{2+}(aq)$ or $Fe^{3+}(aq)$ as a catalyst in the reaction between $S_2O_8^{2-}(aq)$ and $I^-(aq)$ is sometimes explained in terms of standard electrode potentials ($E^\ominus$ values).

However, it is important to note that standard electrode potentials can predict only the thermodynamic feasibility of a reaction, and not the kinetics. The reason why the reactions are faster in the presence of either Fe^{2+} or Fe^{3+} is that the activation energies for both Steps 1 and 2 are lower than the activation energy for the overall reaction.

HETEROGENEOUS CATALYSTS

A *heterogeneous* catalyst is in a different phase to that of the reactants.

Two important uses of heterogeneous catalysts in industry are in the Haber process and the Contact process. The use of solid vanadium(V) oxide (V_2O_5), in which the vanadium changes its oxidation number, in the Contact process is described in the section on transition elements (**Topic 17**).

We will now describe the action of solid iron as a catalyst in the reaction between nitrogen gas and hydrogen gas to form ammonia gas in the Haber process.

The equation for the formation of ammonia in the Haber process is:

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

Iron is able to act as a catalyst because it can form an *interstitial hydride* with hydrogen molecules. In this hydride, hydrogen atoms are held in spaces between the metal ions in the lattice. The atoms are then able to react with nitrogen molecules that are adsorbed onto the metal surface nearby. There are three stages in catalysis involving surface **adsorption**. These are:

1. *Adsorption* – the reactants are first adsorbed onto the surface of the catalyst.
2. *Reaction* – the reactant molecules are held in positions that enable them to react together.
3. *Desorption* – the product molecules leave the surface.

The rate of reaction is controlled by how fast the reactants are adsorbed and how fast the products are desorbed. As mentioned in **Topic 9** (**Book 1: IAS**), once the surface of the iron is covered with molecules, there is no further increase in reaction rate even if the pressure of the reactants is increased.

DID YOU KNOW?

The efficiency of a heterogeneous catalyst depends on the surface of the catalyst. In particular, the efficiency of the catalyst can be affected significantly by poisoning and by the use of promoters.

POISONING

Many catalysts are made ineffective by trace impurities. For example, catalysts used in hydrogenation reactions are poisoned by sulfur impurities. This is one reason why nickel is preferred to platinum as a catalyst in the hydrogenation of alkenes. Nickel is relatively inexpensive, so a large quantity can be used. If some of it is deactivated by poisoning, enough will remain for it still to be effective. On the other hand, platinum is expensive, and so small quantities would have to be used. In this case, it is possible for all of the catalyst to become poisoned.

PROMOTERS

The spacing on the surface of the catalyst is important. For example, only some surfaces of the iron crystals act as effective catalysts in the Haber process. The addition of traces of potassium oxide and aluminium oxide act as promoters by producing *active sites* where the reaction takes place most readily.

DID YOU KNOW?

An interstitial hydride, sometimes called a metallic hydride, is not strictly a compound. It is more like an alloy than a compound. The hydrogen absorbs into the metal and can exist in the form of either atoms or diatomic molecules. For example, palladium absorbs up to 900 times its own volume of hydrogen at room temperature, and forms palladium hydride. This material has been considered as a method to carry hydrogen in fuel cells for use in vehicles (see **Section 14.2.1**).

A heterogeneous catalyst is used in a three-way catalytic converter, which is employed in the exhaust of cars. This converts unburned hydrocarbons into water and carbon dioxide, and carbon and carbon monoxide into carbon dioxide. It also converts oxides of nitrogen into oxygen and nitrogen. The reactions involved are discussed in more detail in **Topic 17**.

DID YOU KNOW?

The electrophilic addition reaction between ethene and bromine vapour (**Topic 5 (Book 1: IAS)**) was once thought to be entirely a homogeneous process in which the molecules collided in the gas phase and reacted.

It is now known that the reaction takes place almost entirely on the surface of the walls of the reaction vessel. The reaction takes place very quickly on a glass surface and even more quickly when the surface of the vessel is covered with a polar substance such as cetyl alcohol (hexadecan-1-ol, $CH_3(CH_2)_{15}OH$). It takes place even more quickly still on a surface of stearic acid (octadecanoic acid, $CH_3(CH_2)_{16}COOH$), presumably because stearic acid molecules are more polar than molecules of cetyl alcohol.

However, if the walls of the reaction vessel are coated with a non-polar substance such as paraffin wax, very little reaction, if any, occurs. So, a process once thought to be a homogeneous gas phase reaction is now known to be heterogeneously catalysed.

It is sometimes stated that a catalyst does not change the products of a reaction, but only increases the rate at which the reaction takes place. This is not entirely true, as demonstrated by the different products obtained when hot ethanol vapour is passed over different solid catalysts.

With copper or nickel as the catalyst, at 400 °C, a dehydrogenation reaction takes place in which the products are ethanal and hydrogen:

$$CH_3CH_2OH(g) \longrightarrow CH_3CHO(g) + H_2(g)$$

If, at the same temperature, aluminium oxide is used as the catalyst, the more familiar dehydration reaction into ethene and water takes place:

$$CH_3CH_2OH(g) \longrightarrow CH_2{=}CH_2(g) + H_2O(g)$$

It is interesting to note that the dehydrogenation catalysts, copper and nickel, adsorb hydrogen very strongly, whereas the dehydration catalyst, aluminium oxide, adsorbs water in preference.

These two examples illustrate that there is a lot more to heterogeneous catalysis than is mentioned at International A Level. This might encourage you to do your own research into the topic and learn even more about it.

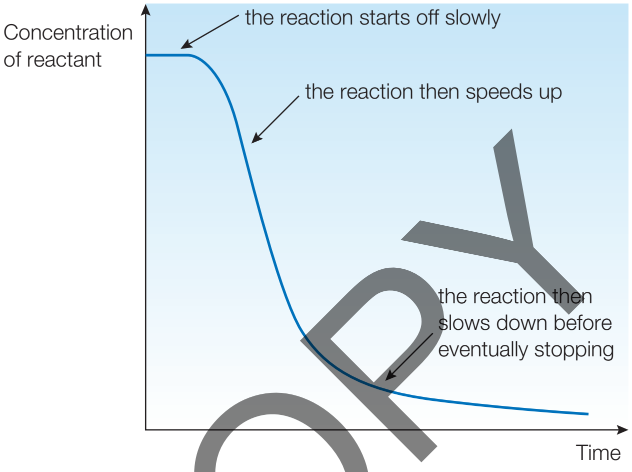
OXIDATION OF ETHANEDIOIC ACID BY MANGANATE(VII) IONS

In **autocatalysis**, the reaction is catalysed by one of its products. One of the simplest examples of this is the oxidation of ethanedioic acid by acidified potassium manganate(VII). The equation for the reaction is:

$$5(COOH)_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

The reaction is very slow at room temperature, but is catalysed by manganese(II) ions, Mn^{2+}. The Mn^{2+} ions are not present initially, so the reaction starts off extremely slowly at room temperature. However, Mn^{2+} is a product of the reaction. As soon as it is produced in a catalytic amount, the reaction rate increases.

You can show this effect by plotting the concentration of one of the reactants against time. The graph obtained is unlike the normal rate curve for a reaction.



▲ **fig B** A graph of concentration against time for an autocatalysed reaction.

In **fig B** you can see the slow (uncatalysed) reaction at the beginning. As catalyst begins to be formed in the mixture, the reaction speeds up – it gets faster and faster as more and more catalyst is formed. Eventually, the rate decreases in the normal way as the concentrations of the reactants decrease.

LEARNING TIP

Do not assume that a rate curve similar to the curve in **fig B** always shows an example of autocatalysis. There are other effects that might produce a similar graph.

For example, if the reaction involves a solid reacting with a liquid, liquid might have to penetrate a substance on the surface of the solid before the expected reaction can happen.

Another possibility is that the reaction is strongly exothermic and the temperature is not being controlled. The heat evolved during the reaction speeds up the reaction.

CHECKPOINT

1. Explain why only a small quantity of a homogeneous catalyst is required in order for it to be effective.

2. Cars in some parts of the world still run on leaded petrol. Leaded petrol contains a compound called tetraethyl lead, $(CH_3CH_2)_4Pb$. Tetraethyl lead reacts in the engine with oxygen and forms lead and lead(II) oxide. These substances remove radical intermediates in the combustion reactions, thus increasing the octane rating of the petrol. Excess lead and lead(II) oxide is removed by adding 1,2-dibromoethane. This forms volatile lead(II) bromide that escapes through the exhaust.

Suggest why a catalytic converter could not be used in a car running on leaded petrol.

SUBJECT VOCABULARY

adsorption the adhesion of atoms, molecules or ions to the surface of a solid
autocatalysis when a reaction product acts as a catalyst for the reaction

11A 6 EFFECT OF TEMPERATURE ON THE RATE CONSTANT

SPECIFICATION REFERENCE
11.10

LEARNING OBJECTIVES

- Use the Arrhenius equation to explain the effect of temperature on the rate constant of a reaction.
- Use calculations and graphical methods to find the activation energy for a reaction from experimental data.

RELATIONSHIP BETWEEN TEMPERATURE AND RATE OF REACTION

In **Book 1** we discussed qualitatively why an increase in temperature increased the rate of a reaction. There are two reasons for this:

- an increase in the fraction of molecules with energy equal to or greater than the activation energy for the reaction
- an overall increase in the frequency of collisions between the reacting molecules.

The second effect is considerably less significant than the first and means that we can effectively ignore the overall increase in the frequency of collisions.

THE ARRHENIUS EQUATION

In 1889, Svante Arrhenius, a Swedish chemist, proposed a quantitative relationship between temperature and the rate constant, k, for a reaction. This is described by the *Arrhenius equation* and is usually expressed in the form:

$$k = Ae^{\left(-\frac{E_a}{RT}\right)}$$

EXAM HINT

You will always be given the Arrhenius equation if it is needed in an exam question.

where:

- A is a constant known as the pre-exponential factor, which is a measure of the rate at which collisions occur irrespective of their energy. It also includes other factors, the most important of which is that reactions can only occur when the molecules are correctly orientated at the time of collision.
- E_a is the activation energy of the reaction.
- R is the gas constant.
- T is the absolute temperature (i.e. the temperature in kelvin).

If we take natural logarithms (i.e. logarithms to the base ‘e’) of the Arrhenius equation. we obtain:

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

If a graph of $\ln k$ is plotted against $\frac{1}{T}$, a straight line is obtained with a gradient of $-\frac{E_a}{R}$

This provides an experimental method for determining the activation energy of a reaction.

The intercept with the vertical axis gives $\ln A$.

WORKED EXAMPLE

Table A shows some data related to the reaction between peroxydisulfate and iodide ions in aqueous solution:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

TEMPERATURE/K	MAGNITUDE OF RATE CONSTANT, k	$\ln k$	$1/T$/K^{-1}
300	0.00513	−5.27	0.00333
310	0.00833	−4.79	0.00323
320	0.0128	−4.36	0.00313
330	0.0201	−3.91	0.00303
340	0.0301	−3.50	0.00294

table A

Fig A shows ln*k* plotted against $\frac{1}{T}$.

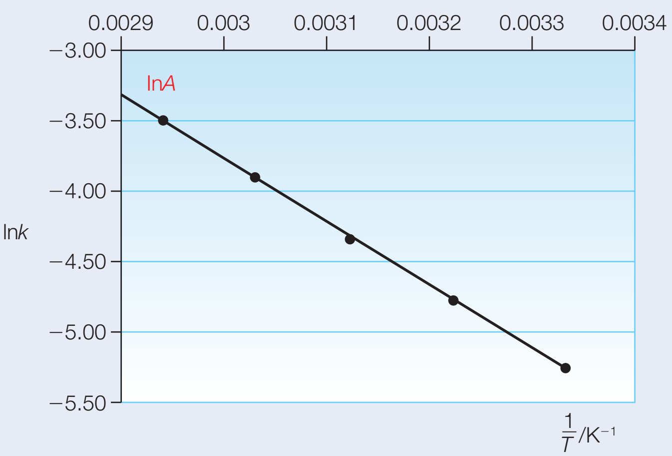


fig A A graph of ln*k* against 1/*T*.

The gradient of the line, $-\frac{E_a}{R}$

$$= -\frac{(-3.50 - -5.27)}{(0.00333 - 0.00294)}$$

$$= -4538$$

[$R = 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$]

$E_a = -(-4538 \times 8.31) = 37\,700\ \text{J mol}^{-1} = +37.7\ \text{kJ mol}^{-1}$ (to 3 s.f.)

DID YOU KNOW?

When we state that the relationship between ln*k* and $-\frac{1}{T}$ is linear, we have assumed that both E_a and *A* remain constant over a range of temperatures. This is not strictly true. However, the change in the values of E_a and *A* with temperature are insignificant compared with the effect of temperature on the rate constant, and so can be ignored.

DID YOU KNOW?

The significance of the factor $e^{-\frac{E_a}{RT}}$

The factor $e^{-\frac{E_a}{RT}}$ represents the fraction of collisions that have energy equal to or greater than the activation energy, E_a. For example, a reaction with an E_a of 60 kJ mol^{-1} gives a fraction, at 298 K, of:

$$e^{-(60\,000/8.31 \times 298)} = 3 \times 10^{-11}$$

So, only one collision in 3×10^{11} has sufficient energy to react.

It is often assumed that the fraction of collisions with energy equal to or greater than E_a is the same as the fraction of molecules with this energy. This is not strictly true, but the difference is insignificant at high energies, where the fraction is very small.

It is, therefore, reasonable to draw the molecular energy distribution curve, instead of the collision frequency curve, when demonstrating the effect of temperature on collision frequency. (See **Topic 9** (**Book 1: IAS**).

LEARNING TIP

The effect of E_a on reaction rate:

- reactions with a large E_a are slow, but the rate increases rapidly with an increase in temperature
- reactions with a small E_a are fast, but the rate does not increase as rapidly with an increase in temperature
- catalysed reactions have small values of E_a.

DID YOU KNOW?

Reaction profiles

When drawing reaction profile diagrams for multi-step reactions, it is important to distinguish between an *intermediate* and a *transition state*:

- an intermediate has an energy minimum
- a transition state occurs at the top of the energy curve and therefore has an energy maximum.

An intermediate is a definite chemical species that exists for a finite length of time. By comparison, a transition state has no significant permanent lifetime of its own: it exists for a period of the order of 10^{-15} seconds, when the molecules are in contact with one another. Even a very reactive intermediate, with a lifetime of only 10^{-6} seconds, has a long lifetime in comparison with the period that colliding molecules are in contact with one another.

A simple one-step reaction, such as the S_N2 hydrolysis of a primary halogenoalkane, has a single maximum energy. The reaction profile for the hydrolysis of a primary halogenoalkane, represented as RHal, is therefore:

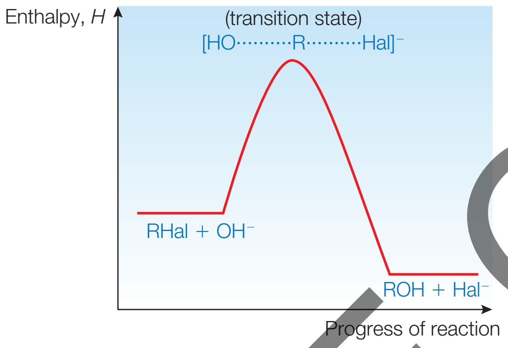


fig B The reaction profile diagram for the hydrolysis of a primary halogenoalkane.

The reaction profile for the S_N1 hydrolysis of a tertiary halogenoalkane, R_3CHal, which is a two-step reaction involving the intermediate R_3C^+, is:

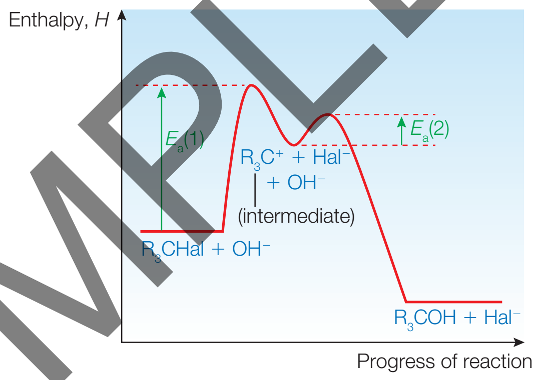


fig C The reaction profile diagram for the hydrolysis of a tertiary halogenoalkane.

LEARNING TIP

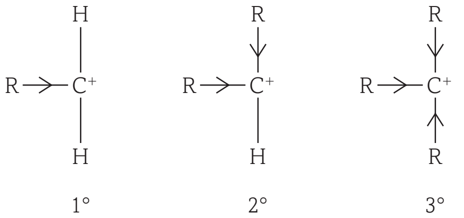
In the S_N1 hydrolysis of a tertiary halogenoalkane, the first step of the mechanism is the rate-determining step of the reaction, and it therefore has the higher activation energy. That is, $E_a(1) > E_a(2)$.

If the second step in a reaction mechanism is rate-determining, $E_a(1) < E_a(2)$.

DID YOU KNOW?

The relative rates of S_N1 and S_N2 reactions depend on structure

You learned in **Book 1** that alkyl groups donate electrons by the inductive effect. This means that the stability of carbocations increases in the order 1° < 2° < 3°, as the number of alkyl groups donating electrons towards the positive carbon atom increases.



As the stability of the carbocation increases, the activation energy for the reaction leading to its formation also decreases.

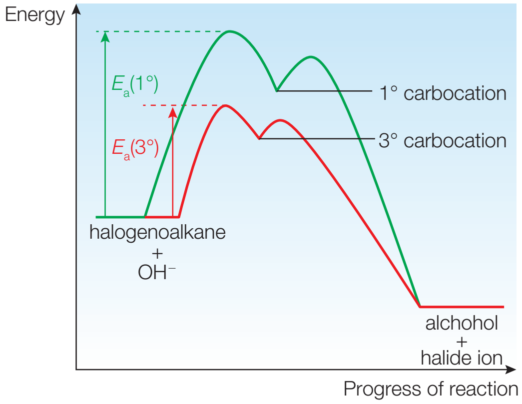


fig D Reaction profiles for the S_N1 hydrolysis of primary and tertiary halogenoalkanes.

We therefore expect the rate of the S_N1 reaction to increase in the order 1° < 2° < 3°.

No carbocations are formed during the S_N2 reaction. In an S_N2 reaction, the transition state has five groups arranged around the central carbon atom. It is therefore more crowded than either the starting halogenoalkane or the alcohol product, each of which have only four groups around the central carbon atom.

Alkyl groups are much larger than hydrogen atoms. Therefore, the more alkyl groups around the central carbon atom, the more crowded will be the transition state, and the higher the activation energy for its formation.

We therefore expect the rate of the S_N2 reaction to increase in the order 3° < 2° < 1°.

The two effects reinforce one another. The S_N1 reaction is fastest with tertiary halides and slowest with primary halides, while the S_N2 reaction is fastest with primary halides and slowest with tertiary halides. Overall, primary halides react predominantly via the S_N2 mechanism and tertiary halides react predominantly via the S_N1 mechanism. Secondary halides tend to react via a mixture of the two mechanisms.

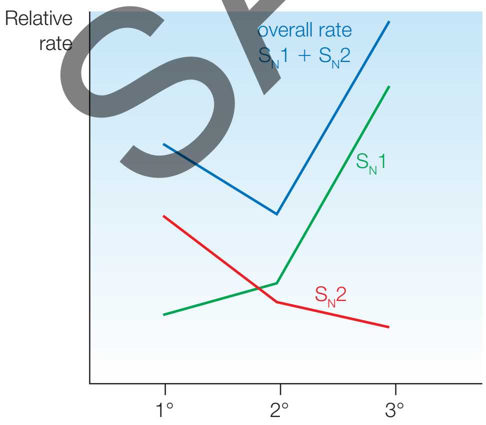


fig E S_N1 and S_N2 hydrolysis reactions for primary, secondary and tertiary halogenoalkanes.

CHECKPOINT

SKILLS CREATIVITY

1. Use the Arrhenius equation to explain why an increase in temperature results in an increase in the rate of reaction.
2. The rate constant, k, for a reaction increases from $10.0\ s^{-1}$ to $100.0\ s^{-1}$ when the temperature is increased from 300 K to 400 K.

   Calculate the activation energy, E_a, for this reaction. [$R = 8.31\ J\ mol^{-1}\ K^{-1}$].

CATALYST CRAFT

SKILLS CREATIVITY

In this article you will look at an example of how an engineered metalloenzyme can improve both the kinetics and specificity of a reaction. The extract is from *Chemistry World*, the print and online magazine of the Royal Society of Chemistry.

ENGINEERED METALLOENZYME CATALYSES FRIEDEL–CRAFTS REACTION

Reprogramming the genetic code of bacteria to include an unnatural amino acid has allowed scientists in the Netherlands to create a new metalloenzyme capable of catalysing an enantioselective reaction.

‘Nature is extremely good at catalysing reactions with very high rate accelerations and very high selectivity. But it does so, from our perspective, with a relatively limited set of reactions,’ explains Gerard Roelfes from the University of Groningen in the Netherlands, who led the study. His group is looking at existing reactions that use traditional catalysts, but fail to achieve the same rate acceleration and selectivity as enzyme catalysed reactions.

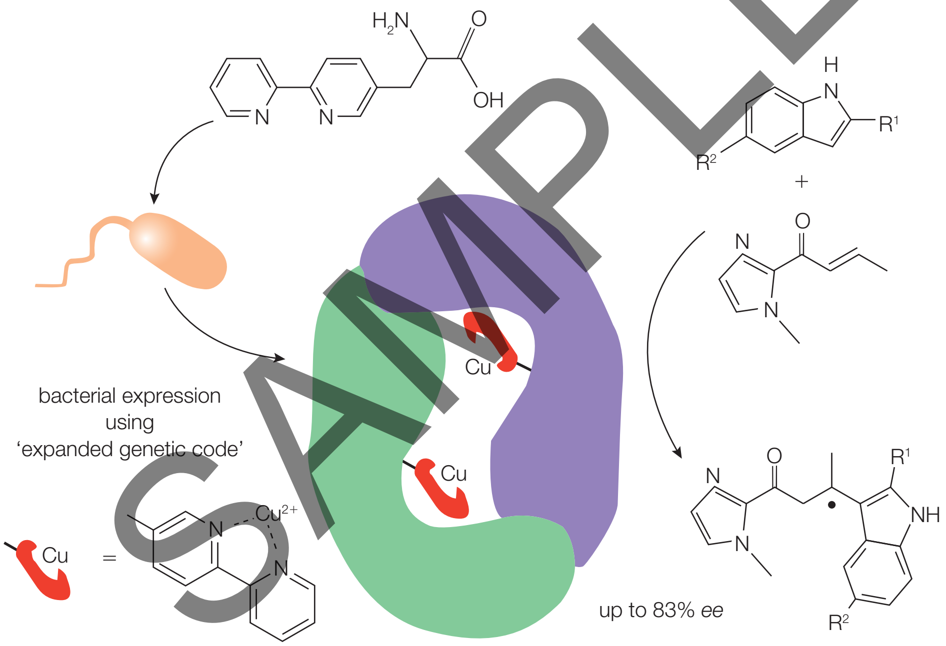


fig A The artificial metalloenzymes were applied in a catalytic asymmetric Friedel–Crafts alkylation reaction.

Metalloenzymes combine the flexibility of metal catalysts with the high activity and selectivity of enzymes. Artificial metalloenzymes are produced by inserting a catalytically active transition metal complex into a biomolecular scaffold, like a protein.

Roelfes’ team engineered *Escherichia coli* cells to include a copper-binding amino acid into one of its proteins. This method requires no further chemical modification or purification steps, giving it an advantage over existing methods. The resulting metalloenzyme was tested on a catalytic asymmetric Friedel–Crafts alkylation reaction, achieving an enantiomeric excess of up to 83%.

Takafumi Ueno, who researches the mechanisms of chemical reactions in living cells at the Tokyo Institute of Technology in Japan, is impressed by the work. ‘It could be applied not only for rapid screening of artificial metalloenzymes but also for in vivo use of them to govern cell fate in future’.

The group are now looking to develop new artificial metalloenzymes with the capability to perform chemistry that traditional transition metal catalysts cannot. Ultimately, they hope to integrate these enzymes into biosynthetic pathways.

Adapted (with permission) from ‘Engineered Metalloenzyme Catalyses Friedal–Crafts Reaction’ by Debbie Houghton, *Chemistry World*, 3 November 2014

SCIENCE COMMUNICATION

1 (a) After reading the article for the first time, write a one-paragraph summary of what you think the article is about.

(b) Now write down a list of any words from the article of which you do not know the meaning. Do some research into what they mean. Is there anything about your summary from (a) that you would change?

INTERPRETATION NOTE

You may find that it is easier than you think to get an overall understanding of what a detailed scientific article is about. You do not need to understand every single word to learn something new and interesting!

CHEMISTRY IN DETAIL

2 Assuming the reaction is exothermic, sketch an energy profile for the catalysed reaction showing:

(a) the overall reaction enthalpy change

(b) the activation energy for the formation of the enzyme—substrate complex.

3 Under certain conditions the rate equation for an enzyme–catalysed reaction takes the form: Rate = $k[E]^n$, where [E] is the enzyme concentration and *k* and *n* are experimentally determined constants. What does this rate equation suggest about the reaction mechanism under these conditions?

4 Name the type of bond that is formed between the copper ion and the unusual amino acid in the metalloenzyme shown in **fig A**.

5 Suggest why the use of a metalloenzyme of this type might be a better alternative than the traditional Friedel–Crafts methods for alkylation.

6 Suggest why this method might be expected to increase the enantioselectivity of this reaction.

7 Suggest why the Zn^{2+} ion may not be a suitable replacement for the Cu^{2+} ion in this enzyme.

THINKING BIGGER TIP

When you are asked to draw something, make sure you use a sharp HB pencil so that your drawing is clear, and use a ruler if you are drawing straight lines.

ACTIVITY

Although the metalloenzyme detailed above is genetically engineered, there are many naturally occurring metalloenzymes that carry out a range of reactions in organisms. Most of these can be found in a freely accessible online database called the PDB (alternatively, the PDBe).

Choose one of the following metals: Fe, Zn, Cu, Mo, Co.

- Find a protein that contains the metal.
- Find out what the protein does.
- Find out how much of the metal is present in a typical healthy adult.

Give a five-minute presentation on your chosen metal, featuring no more than five slides. You will have the opportunity to display your chosen molecules using some of the freely available software packages such as Jmol.

DID YOU KNOW?

Although a typical adult has only about 1.5 mg of copper per kg of body mass, an inability to regulate copper has disastrous effects. For example, the inability to excrete excess copper from the body (Wilson's disease) can be fatal if left untreated. Menkes' syndrome manifests itself if the body is unable to retain (hold on to) copper. Although not fatal, it can lead to developmental delay and neurological problems.

11 EXAM PRACTICE

1 An experiment is set up to measure the rate of hydrolysis of methyl ethanoate, CH_3COOCH_3.

$$CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$$

The hydrolysis is very slow in neutral aqueous solution. When dilute hydrochloric acid is added, the reaction is faster.

What is the function of the hydrochloric acid?

A to increase the reaction rate by acting as a catalyst

B to make sure that the reaction reaches equilibrium

C to maintain a constant pH during the reaction

D to dissolve the methyl ethanoate [1]

(Total for Question 1 = 1 mark)

2 For the gaseous reaction $2X(g) + Y(g) \rightarrow Z(g)$, the rate equation is

$$\text{rate} = k[X]^2[Y]^0$$

If the pressure in the reaction vessel is doubled but the temperature remains constant, by what factor does the rate of reaction increase?

A 2 **B** 3 **C** 4 **D** 8 [1]

(Total for Question 2 = 1 mark)

3 The alkaline hydrolysis of RBr, where RBr = $(CH_3)_3Br$, takes place in two steps:

$RBr \rightarrow R^+ + Br^-$ SLOW

$R^+ + OH^- \rightarrow ROH$ FAST

Which of the following rate equations is consistent with this scheme?

A rate = $k[OH^-]$

B rate = $k[RBr]$

C rate = $k[RBr][OH^-]$

D rate = $k[R^+][OH^-]$ [1]

(Total for Question 3 = 1 mark)

4 The table gives data for the reaction between X and Y at constant temperature.

Experiment	[X] / mol dm^{-3}	[Y] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.3	0.2	4.0×10^{-4}
2	0.6	0.4	1.6×10^{-3}
3	0.6	0.8	6.4×10^{-3}

What is the rate equation for the reaction?

A rate = $k[X][Y]^2$

B rate = $k[X]^2[Y]$

C rate = $k[X]^2$

D rate = $k[Y]^2$ [1]

(Total for Question 4 = 1 mark)

5 The reaction of acidified aqueous potassium iodide with aqueous hydrogen peroxide

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

is thought to involve three steps:

$H_2O_2 + I^- \rightarrow H_2O + OI^-$ SLOW

$OI^- + H^+ \rightarrow HOI$ FAST

$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ FAST

Which of the following conclusions **cannot** be deduced from this information?

A The acid is a catalyst.

B The reaction is first order with respect to the iodide ion.

C The rate determining step is $H_2O_2 + I^- \rightarrow H_2O + OI^-$

D The rate equation for the reaction is: rate = $k[H_2O_2][I^-]$ [1]

(Total for Question 5 = 1 mark)

6 Propanone and iodine react in aqueous acidic solution according to the following overall equation:

$$CH_3COCH_3 + I_2 + H^+ \rightarrow CH_3COCH_2I + 2H^+ + I^-$$

The experimentally determined rate equation for this reaction is:

$$\text{rate} = k[CH_3COCH_3][H^+]$$

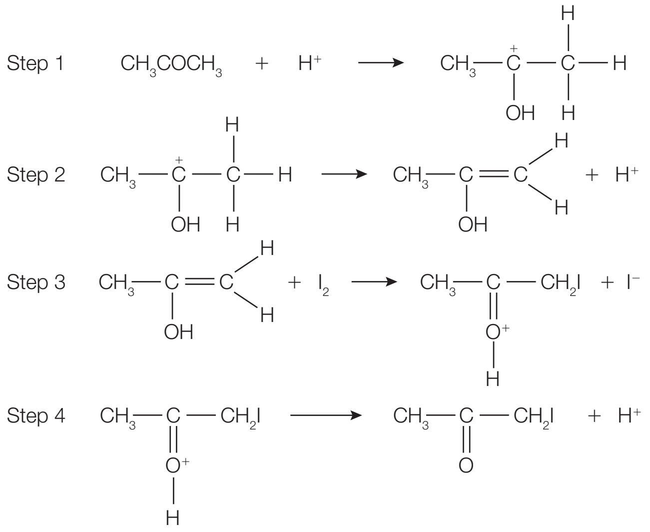
(a) With initial concentrations as shown, the initial rate of reaction was 1.43×10^{-6} mol dm^{-3} s^{-1}.

	Initial concentration/mol dm^{-3}
CH_3COCH_3	0.400
H^+	0.200
I_2	4.00×10^{-4}

Calculate a value for the rate constant, k, for the reaction. [3]

(b) Explain the effect on the rate of reaction of doubling the concentration of iodine, but keeping the concentrations of propanone and hydrogen ions constant. [2]

(c) The proposed mechanism for the overall reaction is:



Explain which of the four steps could be the rate-determing step. [3]

(Total for Question 6 = 8 marks)

7 Most chemical reactions involve two or more steps. The experimentally determined rate equation indicates which species are involved either before or in the rate-determining step.

(a) State what is meant by the term **rate-determining step**. [1]

(b) Hydrogen reacts with iodine monochloride in a two-step mechanism according to the following overall equation:

$$H_2(g) + 2ICl(g) \rightarrow 2HCl(g) + I_2(g)$$

The experimentally determined rate equation for this reaction is:

$$\text{rate} = k\,[H_2(g)][ICl(g)]$$

The rate-determining step is the first step in the mechanism for the reaction.

(i) Write an equation for the rate-determining step. [1]

(ii) Write an equation for the second step. [1]

(c) A series of experiments were carried out on the reaction A + B + C → products. The results are shown in the table.

Experiment	**Initial concentrations/ mol dm^{-3}**			**Initial rate/ mol dm^{-3} s^{-1}**
	[A]	**[B]**	**[C]**	
1	0.100	0.100	0.100	6.20×10^{-4}
2	0.100	0.200	0.100	6.20×10^{-4}
3	0.100	0.100	0.200	2.48×10^{-3}
4	0.200	0.100	0.100	1.24×10^{-3}

(i) Determine the order of reaction with respect to A, B and C. Show how you obtain your answers. [3]

(ii) Write the rate equation for the reaction. [1]

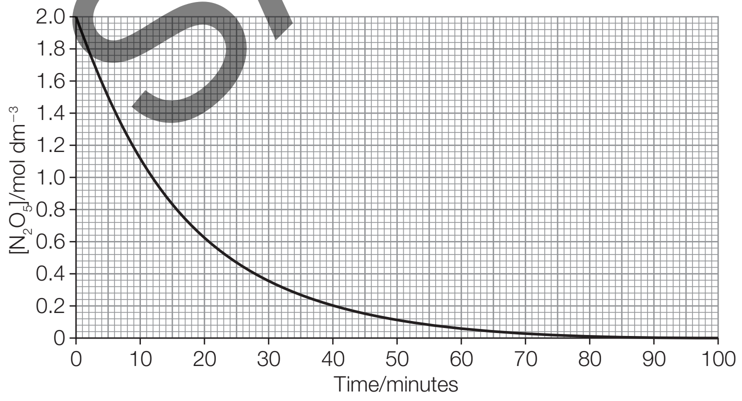
(iii) Which reactant is unlikely to be in the rate determining step? [1]

(Total for Question 7 = 8 marks)

8 Nitrogen pentoxide decomposes on heating to form nitrogen tetroxide and oxygen. The equation for the reaction is:

$$N_2O_5(g) \rightarrow N_2O_4(g) + \tfrac{1}{2}O_2(g)$$

The progress of the reaction can be followed by measuring the concentration of N_2O_5 present. The graph shows the results obtained in an experiment conducted at constant temperature.



(a) (i) Use the graph to predict the rate of reaction after 20 minutes and after 90 minutes. [3]

(ii) Deduce the rate of production of oxygen after 20 minutes? [1]

(b) (i) Plot on the graph two successive half-lives for this reaction. [2]

(ii) Deduce the order of reaction with respect to N_2O_5. Justify your answer. [2]

(iii) Write a rate equation for the reaction. [1]

(c) (i) Calculate a value for the rate constant, *k*, for this reaction. [3]

(ii) Deduce the initial rate of reaction when the initial concentration of N_2O_5 is 1.50 mol dm^{-3}. Assume the reaction is carried out under the same conditions of temperature and pressure. [2]

(Total for Question 8 = 14 marks)

9 Nitrogen dioxide, NO_2, is decomposed on heating into nitrogen monoxide, NO, and oxygen. The proposed mechanism for this reaction is:

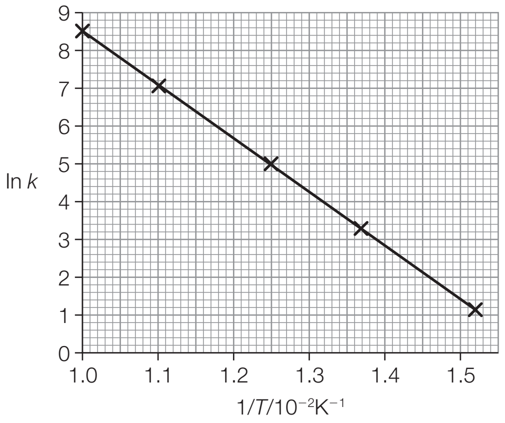
$NO_2 + NO_2 \rightarrow NO_3 + NO$ SLOW

$NO_3 \rightarrow NO + O_2$ FAST

(a) (i) Write an overall equation for the decomposition of nitrogen dioxide. [1]

(ii) Write a rate equation for the reaction. [1]

(b) The rate constant, *k*, for the decomposition was determined at several different temperatures. The results obtained were used to plot the graph shown below.



(i) Use the graph and the expression

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

to calculate the activation energy, E_a, for the thermal decomposition of nitrogen dioxide. Give your answer to an appropriate number of significant figures. [4]

(ii) A vessel of volume 2.00 dm^3 is filled with 4.00 mol of ntitrogen dioxide at a temperature of 650 K. The initial rate of reaction was found to be 12.64 mol dm^{-3} s^{-1}.

Calculate a value for the rate constant, *k*, at this temperature. [3]

(Total for Question 9 = 9 marks)