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# Chemistry A

Second Edition

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# Contents

How to use this book

## Module 5 Physical chemistry and transition elements

### 5.1 Rates, equilibrium and pH

- 5.1.1 Orders, rate equations and rate constants
- 5.1.2 Concentration–time graphs
- 5.1.3 Rate–concentration graphs
- 5.1.4 Rate-determining step
- 5.1.5 The effect of temperature on rate constants
- 5.1.6 Equilibrium
- 5.1.7 Equilibrium and  $K_p$
- 5.1.8 Equilibrium constants and their significance
- 5.1.9 Brønsted–Lowry acids and bases
- 5.1.10 Acid–base reactions and  $K_a$
- 5.1.11 Calculating pH of strong and weak acids
- 5.1.12 The ionisation of water and  $K_w$
- 5.1.13 Buffers
- 5.1.14 Neutralisation – titration curves

**Thinking Bigger: Ocean acidification**

**Practice questions**

6	<b>5.2 Energy</b>	52
	5.2.1 Lattice enthalpy	54
	5.2.2 Born–Haber cycle calculations	58
	5.2.3 Further Born–Haber cycle calculations	60
	5.2.4 Enthalpy change of solution and hydration	62
	5.2.5 Entropy	66
8	5.2.6 Free energy	69
10	5.2.7 Redox	71
14	5.2.8 Redox titrations	73
16	5.2.9 Standard electrode potentials	77
19	5.2.10 Standard cell potentials	80
21	<b>Thinking Bigger: Hydrogen fuel cells</b>	84
23	<b>Practice questions</b>	86
26		
28	<b>5.3 Transition metals</b>	88
31	5.3.1 Transition metals	90
33	5.3.2 Transition metal compounds	93
36	5.3.3 Transition metals and complex ions	97
39	5.3.4 Stereoisomerism in complex ions	100
42	5.3.5 Ligand substitution in complexes	104
45	5.3.6 Ligand substitution and precipitation reactions	106
48	5.3.7 Redox reactions	109
50	5.3.8 Testing for ions	114
	<b>Thinking Bigger: Octopus adaptations</b>	116
	<b>Practice questions</b>	118

# Module 6

## Organic chemistry and analysis

<b>6.1 Aromatic compounds, carbonyls and acids</b>	<b>120</b>	<b>6.3 Analysis</b>	<b>182</b>
6.1.1 Benzene and its structure	122	6.3.1 Chromatography	184
6.1.2 Naming aromatic compounds	124	6.3.2 Tests for organic functional groups	186
6.1.3 Electrophilic substitution	126	6.3.3 Introduction to nuclear magnetic resonance	187
6.1.4 Halogenation and Friedel–Crafts	128	6.3.4 Carbon-13 NMR spectroscopy	189
6.1.5 Phenols	130	6.3.5 Proton NMR spectroscopy	193
6.1.6 Electrophilic substitution in aromatic compounds	132	6.3.6 NMR spectra of –OH and –NH protons	197
6.1.7 Reactions of carbonyl compounds	134	6.3.7 Combined techniques	199
6.1.8 Characteristic tests for carbonyl compounds	136	Thinking Bigger: Making pain history	202
6.1.9 Carboxylic acids	138	Practice questions	204
6.1.10 Esters	140	Maths skills	206
6.1.11 Acyl chlorides	142	Preparing for your exams	210
Thinking Bigger: The impact of pesticides	144	Glossary	218
Practice questions	146	Periodic Table	221
		Index	222
<b>6.2 Nitrogen compounds, polymers and synthesis</b>	<b>148</b>		
6.2.1 Basicity and the preparation of amines	150		
6.2.2 Reactions of amino acids	154		
6.2.3 Amides	156		
6.2.4 Chirality	158		
6.2.5 Condensation polymers	160		
6.2.6 Hydrolysis of polymers	164		
6.2.7 Extending carbon chain length	166		
6.2.8 Reactions of nitriles	168		
6.2.9 Substitution reactions in aromatic compounds	170		
6.2.10 Practical skills for organic synthesis	172		
6.2.11 Synthetic routes in organic synthesis	174		
Thinking Bigger: Chart toppers	178		
Practice questions	180		

# How to use this book

**5** Physical chemistry and transition elements

**CHAPTER 5.1** RATES, EQUILIBRIUM AND pH

**Introduction**

Why are reaction rates, equilibrium constants and pH important? How do these factors affect the rate of a reaction? How do these factors affect the position of equilibrium? How do these factors affect the concentration of H<sup>+</sup> ions in a solution? How do these factors affect the colour of a solution? How do these factors affect the pH of a solution? How do these factors affect the rate of a reaction? How do these factors affect the position of equilibrium? How do these factors affect the concentration of H<sup>+</sup> ions in a solution? How do these factors affect the colour of a solution? How do these factors affect the pH of a solution?

**What have I studied before?**

- Rate equations and the order of reaction
- Chemical equilibrium and Le Chatelier's principle
- Acid-base reactions and pH
- Half-life and exponential decay
- Temperature and equilibrium constants
- Reaction rate and rate-determining step
- Collision theory and activation energy

**What will I study later?**

- Reaction rate and rate-determining step
- Chemical equilibrium and Le Chatelier's principle
- Acid-base reactions and pH
- Half-life and exponential decay
- Temperature and equilibrium constants
- Reaction rate and rate-determining step
- Collision theory and activation energy

**What will I study in this chapter?**

- Reaction rate and rate-determining step
- Chemical equilibrium and Le Chatelier's principle
- Acid-base reactions and pH
- Half-life and exponential decay
- Temperature and equilibrium constants
- Reaction rate and rate-determining step
- Collision theory and activation energy

**All the maths you need**

To understand this chapter you should know the following maths:

- Graphical work and the use of logarithmic scales
- Exponential functions and the use of the natural logarithm
- Algebraic manipulation of fractions and the use of the quadratic formula
- Use of the quadratic formula to solve quadratic equations
- Use of the quadratic formula to solve quadratic equations
- Use of the quadratic formula to solve quadratic equations
- Use of the quadratic formula to solve quadratic equations

Welcome to your OCR A level Chemistry A student book. In this book you will find a number of features designed to support your learning.

## Chapter openers

Each chapter starts by setting the context for that chapter's learning.

- Links to other areas of Chemistry are shown, including previous knowledge that is built on in the chapter and future learning that you will cover later in your course.
- The **All the maths you need** checklist helps you to know what maths skills will be required.

**6.1** Benzene and its structure

By the end of this topic, you should be able to demonstrate and apply your knowledge and understanding of:

- the structure of benzene in terms of hybridisation, delocalisation and resonance
- the experimental evidence for a delocalised, rather than Kekulé, model for benzene in terms of bond lengths, enthalpy change of hydrogenation and resistance to reaction

**Problems with the Kekulé model**

Although the Kekulé model is still used today to describe benzene, the structure is not actually correct. There are three pieces of experimental evidence that do not support the Kekulé model:

- Coupling constants, benzene is resistant to addition reactions
- Enthalpy of hydrogenation of benzene does not match that predicted
- All carbon-carbon bonds are the same length

**Delocalised structure of benzene**

It is now thought that benzene has a delocalised electron system. The delocalised model can explain all three pieces of experimental evidence. The delocalised model is represented by two structures known as resonance structures. These structures are shown in Figure 6.1.1. The delocalised model is represented by two structures known as resonance structures. These structures are shown in Figure 6.1.1. The delocalised model is represented by two structures known as resonance structures. These structures are shown in Figure 6.1.1.

**Resonance structures**

The delocalised model of benzene is represented by two structures known as resonance structures. These structures are shown in Figure 6.1.1. The delocalised model is represented by two structures known as resonance structures. These structures are shown in Figure 6.1.1.

## Main content

The main part of the chapter covers all of the points from the specification you need to learn. The text is supported by diagrams and photos that will help you understand the concepts.

Within each topic, you will find the following features:

- Learning objectives** at the beginning of each topic highlight what you need to know and understand.
- Key terms** are shown in bold and defined within the relevant topic for easy reference.
- Worked examples** show you how to work through questions, and how your calculations should be set out.
- Investigations** provide a summary of practical experiments that explore key concepts.
- Learning tips** help you focus your learning and avoid common errors.
- Did you know?** boxes feature interesting facts to help you remember the key concepts.

At the end of each topic, you will find **questions** that cover what you have just learned. You can use these questions to help you check whether you have understood what you have just read, and to identify anything that you need to look at again. Answers to all questions in this student book are available at <http://www.pearsonschoolsandfecolleges.co.uk/Secondary/Science/16Biology/OCR-A-level-Science-2015/FreeResources/FreeResources.aspx>.

**6.1** Characteristic tests for carbonyl compounds

By the end of this topic, you should be able to demonstrate and apply your knowledge and understanding of:

- use of 2,4-dinitrophenylhydrazine to:
  - confirm the presence of a carbonyl group in an organic compound
  - identify a carbonyl compound from the melting point of the derivative
- use of Tollens' reagent to determine:
  - the presence of an aldehyde group
  - the structure of a carbonyl compound, in terms of the oxidation of aldehydes to carboxylic acids and reduction of ketones to alcohols

**Identifying a specific aldehyde or ketone**

After a positive Beilstein test, further processing of the precipitate allows the specific aldehyde or ketone to be identified. The 2,4-dinitrophenylhydrazine derivative precipitate can be used to identify aldehydes and ketones by its melting point. The melting point of the derivative can be used to identify aldehydes and ketones. The melting point of the derivative can be used to identify aldehydes and ketones.

Compound	mp, °C	Melting point of parent, °C
Propan-2-one	175	42
Propanal	170	48
Butan-2-one	146	82
Butanal	177	82

**2,4-dinitrophenylhydrazine**

Testing for a carbonyl functional group

2,4-dinitrophenylhydrazine (2,4-DNPH) is a yellow crystalline solid. It is used to identify carbonyl compounds. It is used to identify carbonyl compounds. It is used to identify carbonyl compounds.

## Thinking Bigger

At the end of each chapter there is an opportunity to read and work with real-life research and writing about science. These sections will help you to expand your knowledge and develop your own research and writing techniques. The questions and tasks will help you to apply your knowledge to new contexts and to bring together different aspects of your learning from across the whole course. The timeline at the bottom of the spread highlights which other chapters of your book the material relates to.

These spreads will give you opportunities to:

- read real-life material that's relevant to your course
- analyse how scientists write
- think critically and consider relevant issues
- develop your own writing
- understand how different aspects of your learning piece together.

### THINKING BIGGER

#### CHART TOPPERS

The original plot of the fragrance industry is presented in every 10th issue of the 2014 and is published in issue 40 before 2020. For copyrighting, a new fragrance can be something of a 'classic' option. It can be in the following section we will look at the history of some of the most important molecules in the industry.

#### MOLECULES OF FRAGRANCE AND TASTE

In order to create fragrances, new molecules are often synthesized from scratch. For each fragrance, a complex mixture of molecules is used. The molecules are often synthesized from simple starting materials. The molecules are often synthesized from simple starting materials. The molecules are often synthesized from simple starting materials.

The molecules are often synthesized from simple starting materials. The molecules are often synthesized from simple starting materials. The molecules are often synthesized from simple starting materials.

Let us start by considering the nature of the writing in the article.

This article is written for a specialist audience and this reflects the nature of the writing. The article is written for a specialist audience and this reflects the nature of the writing. The article is written for a specialist audience and this reflects the nature of the writing.

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Book 1

5.1

5.2

5.3

6.1

6.2

6.3

Figure 1: The chromatogram shows the abundance of molecules over time. The x-axis is labeled 'Retention time (min)' and the y-axis is labeled 'Abundance'. There are several distinct peaks, with the most prominent one around 10 minutes.

## Practice questions

At the end of each chapter, there are practice questions to test how fully you have understood the learning.

Answers to all questions in this student book are available at <http://www.pearsonschoolsandfecolleges.co.uk/Secondary/Science/16Biology/OCR-A-level-Science-2015/FreeResources/FreeResources.aspx>.

## Maths Skills

At the end of the book there is a **Maths Skills** section that focuses on key mathematical concepts to provide greater depth of explanation and enhance your understanding through worked examples.

## Preparing for your exams

The book concludes with a section that offers some practical advice about preparing for your exams, including sample questions and answers that allow you to see where common mistakes are made and how you can improve your responses.

## Getting the most from your ActiveBook

Your ActiveBook is the perfect way to personalise your learning as you progress through your OCR A level Chemistry course. You can:

- access your content online, anytime, anywhere
- use the inbuilt highlighting and annotation tools to personalise the content and make it really relevant to you
- search the content quickly.

## Highlight tool

Use this to pick out key terms or topics so you are ready and prepared for revision.

## Annotations tool

Use this to add your own notes, for example, links to your wider reading, such as websites or other files. Or make a note to remind yourself about work that you need to do.

### 6.3 Practice questions

1. Compound C is a saturated liquid. It forms an orange precipitate with 2,4-DNP but does not react with Tollens' reagent. Predict the IR and explain these results. What would its  $^1\text{H}$  NMR spectrum look like?

2. A molecule of compound B ( $\text{C}_6\text{H}_{10}\text{O}_2$ ) is a cyclic ester. It is a saturated liquid. It forms an orange precipitate with 2,4-DNP but does not react with Tollens' reagent. Predict the IR and explain these results. What would its  $^1\text{H}$  NMR spectrum look like?

3. Compound A, shown below, is a structural isomer of propanoic acid.

4. Compound B is an organic compound that is a saturated liquid. It forms an orange precipitate with 2,4-DNP but does not react with Tollens' reagent. Predict the IR and explain these results. What would its  $^1\text{H}$  NMR spectrum look like?

5. The chromatogram shows the abundance of molecules over time. The x-axis is labeled 'Retention time (min)' and the y-axis is labeled 'Abundance'. There are several distinct peaks, with the most prominent one around 10 minutes.

6. The chromatogram shows the abundance of molecules over time. The x-axis is labeled 'Retention time (min)' and the y-axis is labeled 'Abundance'. There are several distinct peaks, with the most prominent one around 10 minutes.

MODULE **5**

## Physical chemistry and transition elements

CHAPTER **5.1**

# RATES, EQUILIBRIUM AND pH

## Introduction

Why do some reactions happen quickly and others slowly? How do we find out which reactants will change the speed of a reaction? How do we know how many steps are involved in a chemical reaction? Why are some acids weak and others strong? Do all reactions go to completion, and can we affect this?

If we can find out exactly how a reaction occurs and what factors affect it, we can manipulate it to make it as effective and efficient as possible. This is why chemists study reaction kinetics, including rates and equilibrium.

Acids and bases have been known about for many years, but it has taken a lot of research to find out exactly what it is that makes an acid an acid and a base a base. Acid and base reactions are some of the most important processes in many chemical and biological systems, so it is helpful to study these reactions in some detail.

In this chapter, you will learn about rates of reactions and the ways in which reactions are influenced by temperature. You will also learn about the information (about reactants and reaction mechanisms) that can be obtained from rate equations, rate constants and rate graphs.

You will learn about how to use an equilibrium expression to determine the extent of an equilibrium reaction, and you will find out about the role of the equilibrium constant in controlling the position of equilibrium. You will also learn what acids and bases are, how to calculate their pH and why their strength all comes down to equilibrium.

## All the maths you need

To unlock the puzzles of this chapter you need the following maths:

- Recognise and make use of appropriate units in calculations (*e.g. determining the units for equilibrium constants*)
- Recognise and use expressions in decimal and ordinary form (*e.g. quoting equilibrium amounts*)
- Use an appropriate number of significant figures (*e.g. quoting pH values*)
- Change the subject of an equation (*e.g. finding equilibrium amounts using equilibrium constants*)
- Use exponential and logarithm functions (*e.g. calculating pH*)
- Use logarithmic scales (*e.g. calculating  $pK_a$  values*)
- Plot and translate graphical information, including gradients, intercepts, and tangents (*e.g. rate graphs*)



### What have I studied before?

- How collision theory can be used to predict how changes in conditions influence rates of reactions
- How to calculate a rate using a graph of a physical quantity changing over time
- The effect of catalysts on rates of reactions and how catalysts lower the activation barrier
- Dynamic equilibrium
- How an equilibrium expression is written
- What the magnitude of  $K_c$  can tell you about the position of equilibrium
- Acids and bases
- Le Chatelier's principle

### What will I study later?

- How titrations and indicators can be used to determine concentrations of ions such as  $\text{Fe}^{2+}$
- The acidic behaviour of some organic compounds, including phenol and carboxylic acids
- The basic behaviour of amines
- The acid–base behaviour of amino acids

### What will I study in this chapter?

- Orders of reactions: what they are and how they are determined
- How to interpret rate graphs, including how to determine the rate constant for first order reactions
- What a rate-determining step is, and how to predict rate equations that are consistent with the rate-determining step
- How to calculate further rate constants, including  $K_p$ ,  $K_a$  and  $K_w$
- Equilibrium and equilibrium constants
- Acids and bases, including how to determine their pH
- Titration curves and how they can be used to choose suitable indicators

# Orders, rate equations and rate constants

By the end of this topic, you should be able to demonstrate and apply your knowledge and understanding of:

- \* use of the terms: *rate of reaction*, *order*, *overall order*, *rate constant*
- \* explanation and deduction of:
  - (i) orders from experimental data
  - (ii) a rate equation from orders of the form:  $\text{rate} = k[\text{A}]^m[\text{B}]^n$ , where  $m$  and  $n$  are 0, 1 or 2
- \* calculation of the rate constant,  $k$ , and related quantities, from a rate equation including determination of units

## KEY DEFINITIONS

**Rate of reaction** is the change in concentration of a reactant or a product per unit time.

The **order** with respect to a reactant is the power to which the concentration of the reactant is raised in the rate equation.

The **rate constant**,  $k$ , is the constant that links the rate of reaction with the concentrations of the reactants raised to the powers of their orders in the rate equation.

The **rate equation** for a reaction  $\text{A} + \text{B} \rightarrow \text{C}$  is given by:  $\text{rate} = k[\text{A}]^m[\text{B}]^n$

where  $m$  is the order of reaction with respect to A and  $n$  is the order of reaction with respect to B.

The **overall order** of a reaction is the sum of the individual orders,  $m + n$

You learnt about collision theory in Book 1, topic 3.2.7. You will recall that reactions only proceed when successful collisions occur – that is, particles must collide with the correct orientation and with enough energy to overcome the activation barrier (i.e. the activation energy). How frequently these successful collisions occur will determine the rate of a reaction.

## Rate of reaction

The amount of reactant that is used up, or the amount of product that is made, over a given time is known as the **rate of reaction**.

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

Rates are usually measured in  $\text{mol dm}^{-3} \text{s}^{-1}$  (mol per  $\text{dm}^3$  per s), but other units may sometimes be more appropriate. If a reaction is very slow, a larger timescale (such as minutes) may be used. In this case, the units would be  $\text{mol dm}^{-3} \text{min}^{-1}$ . If it is difficult to measure the concentration, you may use another measurement which allows you to monitor the amount of a product or reactant. For example, if a gas is produced in a reaction, you could measure the volume of gas produced over a time period. In this case, the units would be  $\text{cm}^3 \text{s}^{-1}$ .

## Orders of reactions

If more than one reactant is involved in a reaction, each reactant can affect the rate of the reaction differently. The effect of the individual reactants is described by stating an **order** with respect to each reactant.

Consider a reactant, A. Its concentration affects the rate of a reaction. This can be expressed mathematically as:

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

**LEARNING TIP**

Square brackets are used to show a concentration.

The  $x$  denotes any power to which the concentration of A is raised.

$\propto$  means 'is proportional to'.

You would read the expression  $\text{rate} \propto [\text{A}]^x$  as 'rate is proportional to the concentration of A, raised to the power  $x$ '.

The order is always specific to each of the reactants present. There are three main types of order.

**Zero order**

If the order is 0 with respect to a reactant A, then:  $\text{rate} \propto [\text{A}]^0$

- The rate is unaffected by changing the concentration of A.
- Note that any number to the power 0 is equal to 1.

**First order**

If the order is 1 with respect to a reactant B, then:  $\text{rate} \propto [\text{B}]^1$

The rate is directly proportional to the concentration.

- If [B] increases by 2 times, the rate also increases by 2 times.
- If [B] increases by 3 times, the rate also increases by 3 times.

**Second order**

If the order is 2 with respect to a reactant C, then:  $\text{rate} \propto [\text{C}]^2$

The change in rate will be equal to the change in concentration squared.

- If [C] increases by 2 times, the rate increases by  $2^2 = 4$  times.
- If [C] increases by 3 times, the rate increases by  $3^2 = 9$  times.

**Rate reactions and overall orders**

Chemists use rate equations to mathematically express the influence each reactant has on a reaction.

Take the reaction  $\text{A} + \text{B} + \text{C} \rightarrow \text{products}$

If the orders for A, B and C were  $x$ ,  $y$  and  $z$  respectively, you could write the following expression for the rate:

$$\text{rate} \propto [\text{A}]^x[\text{B}]^y[\text{C}]^z$$

The sign for proportional can be removed if a constant is added into the equation. Chemists use the **rate constant**,  $k$ . The rate constant links the concentrations and orders of reactants to the rate. The expression then becomes a **rate equation**:

$$\text{rate} = k[\text{A}]^x[\text{B}]^y[\text{C}]^z$$

**LEARNING TIP**

You do not need to explain why  $k$  can be used to replace the sign for proportional in the rate equation.

Notice that the rate constant is a lower-case  $k$ . Do not use an upper-case  $K$ , as this is a different constant that you will encounter later in the course.  $K$  is also the chemical symbol for potassium, so if potassium appears in a chemical equation, the use of a capital  $K$  for the rate constant would generate confusion.

If any reactant is zero order then it will not appear in the rate equation. This is because it does not affect the rate. For instance, in our example above, where the orders are 0, 1 and 2 with respect to A, B and C, the rate equation would be:

$$\text{rate} = k[\text{A}]^0[\text{B}]^1[\text{C}]^2$$

However, because any number raised to the power zero = 1, that reactant can be removed. Powers of 1 can also be omitted from outside the brackets. Do not remove the reactant from the rate equation though! Therefore this rate equation would become:

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

### Overall order

The **overall order** of a reaction is the sum of the individual orders.

In the example above,  $\text{rate} = k[\text{B}]^1[\text{C}]^2$  and the overall order is  $1 + 2$ , which is 3.

The rate equation can be determined only from experimental results. Note that the orders are not the same as the numbers used to balance an equation.

#### LEARNING TIP

Remember,  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$  is the same as  $\text{dm}^3/\text{mol/s}$  or  $\text{dm}^3$  per mol per second. This is because if a quantity  $x$  is divided by a quantity  $y$ , the division  $x/y$ , can be replaced by multiplying  $x$  by  $y$  raised to the power  $-1$ :  $x y^{-1}$ .

### Calculating the value and units for rate constants

The rate constant is calculated by substituting values for concentration and rates into the rate equation and rearranging to find  $k$ .

The units of  $k$  depend on the overall order of the rate reaction. The units of  $k$  are determined by substituting units for rate and concentration into the rate equation.

$$\text{Zero order, rate} = k[\text{A}]^0 = k \quad k = \frac{\text{rate}}{1} \quad \text{units of } k = \text{mol dm}^{-3} \text{s}^{-1} = \text{mol dm}^{-3} \text{s}^{-1}$$

$$\text{First order, rate} = k[\text{A}] \quad k = \frac{\text{rate}}{[\text{A}]} \quad \text{units of } k = \frac{(\text{mol dm}^{-3} \text{s}^{-1})}{(\text{mol dm}^{-3})} = \text{s}^{-1}$$

$$\text{Second order, rate} = k[\text{A}]^2 \quad k = \frac{\text{rate}}{[\text{A}]^2} \quad \text{units of } k = \frac{(\text{mol dm}^{-3} \text{s}^{-1})}{(\text{mol dm}^{-3})^2} = \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$$

$$\text{Third order, rate} = k[\text{A}]^2[\text{B}] \quad k = \frac{\text{rate}}{[\text{A}]^2 [\text{B}]} \quad \text{units of } k = \frac{(\text{mol dm}^{-3} \text{s}^{-1})}{(\text{mol dm}^{-3})^2 (\text{mol dm}^{-3})} = \text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$$

#### WORKED EXAMPLE 1

The following experimental results were obtained for the reaction  $\text{A} + \text{B} + \text{C} \rightarrow \text{products}$

Experiment number	Concentration of reactants/mol dm <sup>-3</sup>			Rate/mol dm <sup>-3</sup> s <sup>-1</sup>
	A	B	C	
1	$1.0 \times 10^2$	$1.0 \times 10^2$	$1.0 \times 10^2$	$3.0 \times 10^4$
2	$2.0 \times 10^2$	$1.0 \times 10^2$	$1.0 \times 10^2$	$6.0 \times 10^4$
3	$1.0 \times 10^2$	$2.0 \times 10^2$	$1.0 \times 10^2$	$3.0 \times 10^4$
4	$1.0 \times 10^2$	$1.0 \times 10^2$	$2.0 \times 10^2$	$12.0 \times 10^4$

Use these results to determine the order with respect to each reactant and the overall order.

Write a rate equation for the reaction.

- Between experiment 1 and experiment 2, the concentration of A has doubled. The rate has also doubled. The order with respect to reactant A is **first order**.
- Between experiment 1 and experiment 3, the concentration of B has doubled. The rate has remained unchanged. The order with respect to reactant B is **zero order**.
- Between experiment 1 and experiment 4, the concentration of C has doubled. The rate has increased by 4, i.e.  $2^2$ . This is equal to the change in concentration squared. The order with respect to C is **second order**.

The rate equation can be written as:

$$\text{rate} = k [\text{A}]^1 [\text{B}]^0 [\text{C}]^2$$

This can be simplified to:

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

The overall order of the reaction is **third order** as  $1 + 2 = 3$ .