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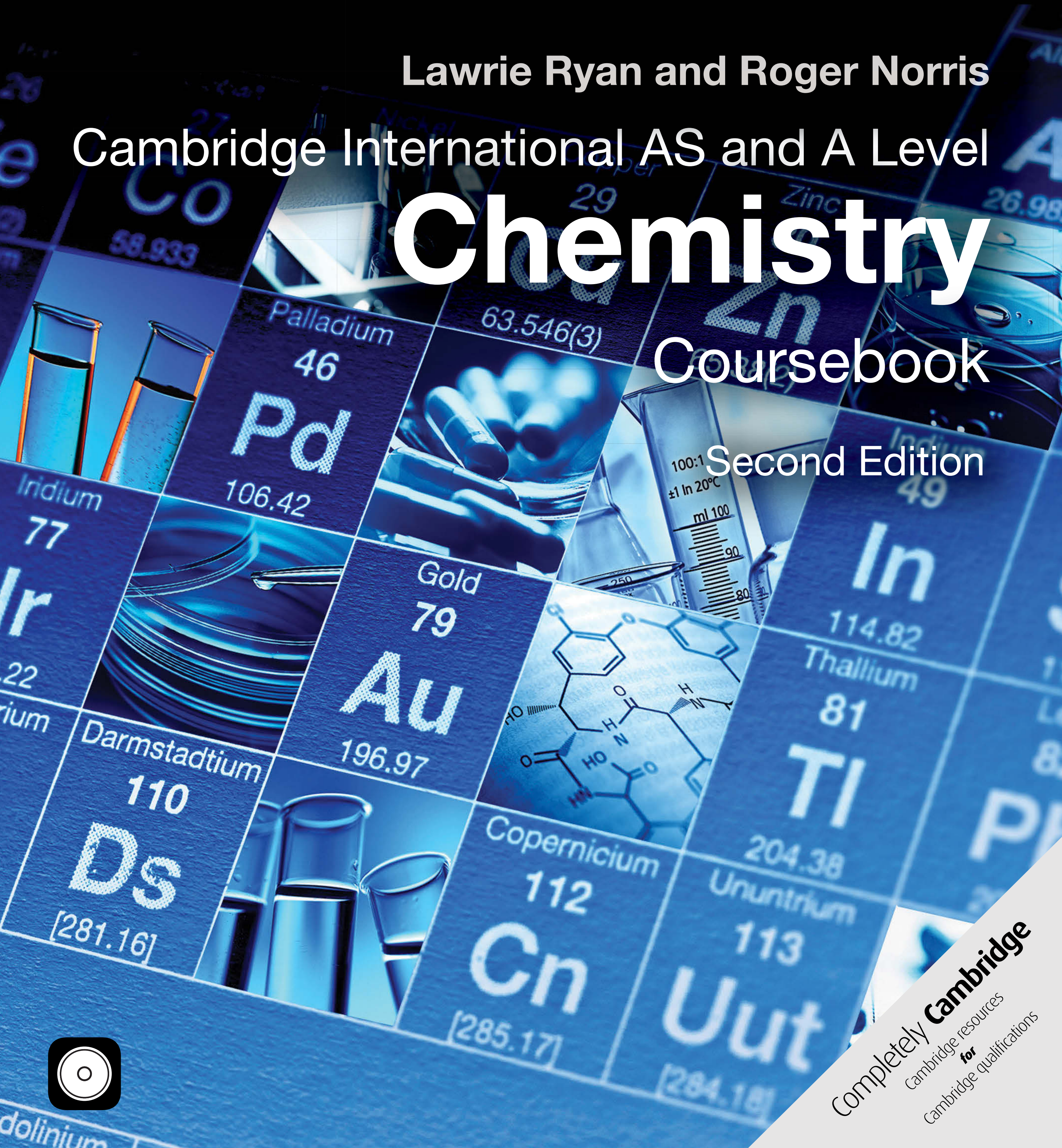
Cambridge International AS and A Level
Chemistry
Coursebook
Second Edition


Co
58.933
29
63.546(3)
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Zn
26.98
Palladium
46
Pd
106.42
Iridium
77
Ir
Gold
79
Au
196.97
Indium
49
In
114.82
Thallium
81
Tl
204.38
Darmstadtium
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Ds
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Copernicium
112
Cn
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Ununtrium
113
Uut
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250

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Lawrie Ryan and Roger Norris

Cambridge International AS and A Level
Chemistry
Coursebook

Second Edition

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Example answers and all other end-of-chapter questions were written by the authors.

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Advice on how to revise for and approach examinations CD4
Answers to end-of-chapter questions CD10
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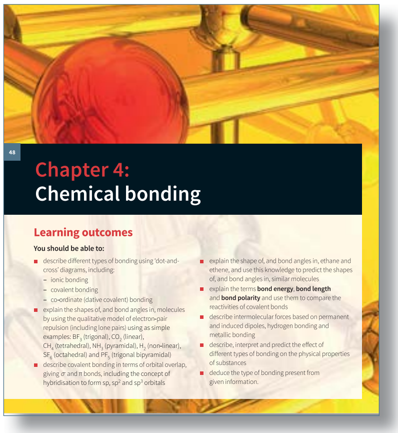
How to use this book

Each chapter begins with a short list of the facts and concepts that are explained in it.



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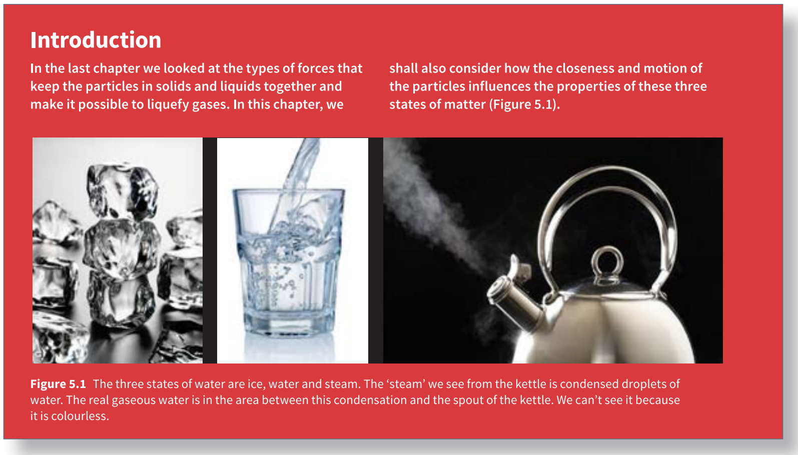
Chapter 4:
Chemical bonding

Learning outcomes

You should be able to:

- describe different types of bonding using 'dot-and-cross' diagrams, including:
  - ionic bonding
  - covalent bonding
  - co-ordinate (dative covalent) bonding
- explain the shapes of, and bond angles in, molecules by using the qualitative model of electron-pair repulsion (including lone pairs) using as simple examples: BF_3 (trigonal), CO_2 (linear), CH_4 (tetrahedral), NH_3 (pyramidal), H_2 (non-linear), SF_6 (octahedral) and PF_5 (trigonal bipyramidal)
- describe covalent bonding in terms of orbital overlap, giving σ and π bonds, including the concept of hybridisation to form sp, sp^2 and sp^3 orbitals
- explain the shape of, and bond angles in, ethane and ethene, and use this knowledge to predict the shapes of, and bond angles in, similar molecules
- explain the terms **bond energy**, **bond length** and **bond polarity** and use them to compare the reactivities of covalent bonds
- describe intermolecular forces based on permanent and induced dipoles, hydrogen bonding and metallic bonding
- describe, interpret and predict the effect of different types of bonding on the physical properties of substances
- deduce the type of bonding present from given information.

There is a short context at the beginning of each chapter, containing an example of how the material covered in the chapter relates to the 'real world'.



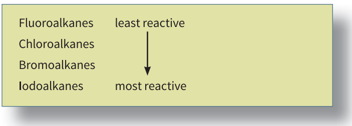
Introduction

In the last chapter we looked at the types of forces that keep the particles in solids and liquids together and make it possible to liquefy gases. In this chapter, we shall also consider how the closeness and motion of the particles influences the properties of these three states of matter (Figure 5.1).

Figure 5.1 The three states of water are ice, water and steam. The 'steam' we see from the kettle is condensed droplets of water. The real gaseous water is in the area between this condensation and the spout of the kettle. We can't see it because it is colourless.

This book does not contain detailed instructions for doing particular experiments, but you will find background information about the practical work you need to do in these boxes. There are also two chapters, P1 and P2, which provide detailed information about the practical skills you need to develop during the course.

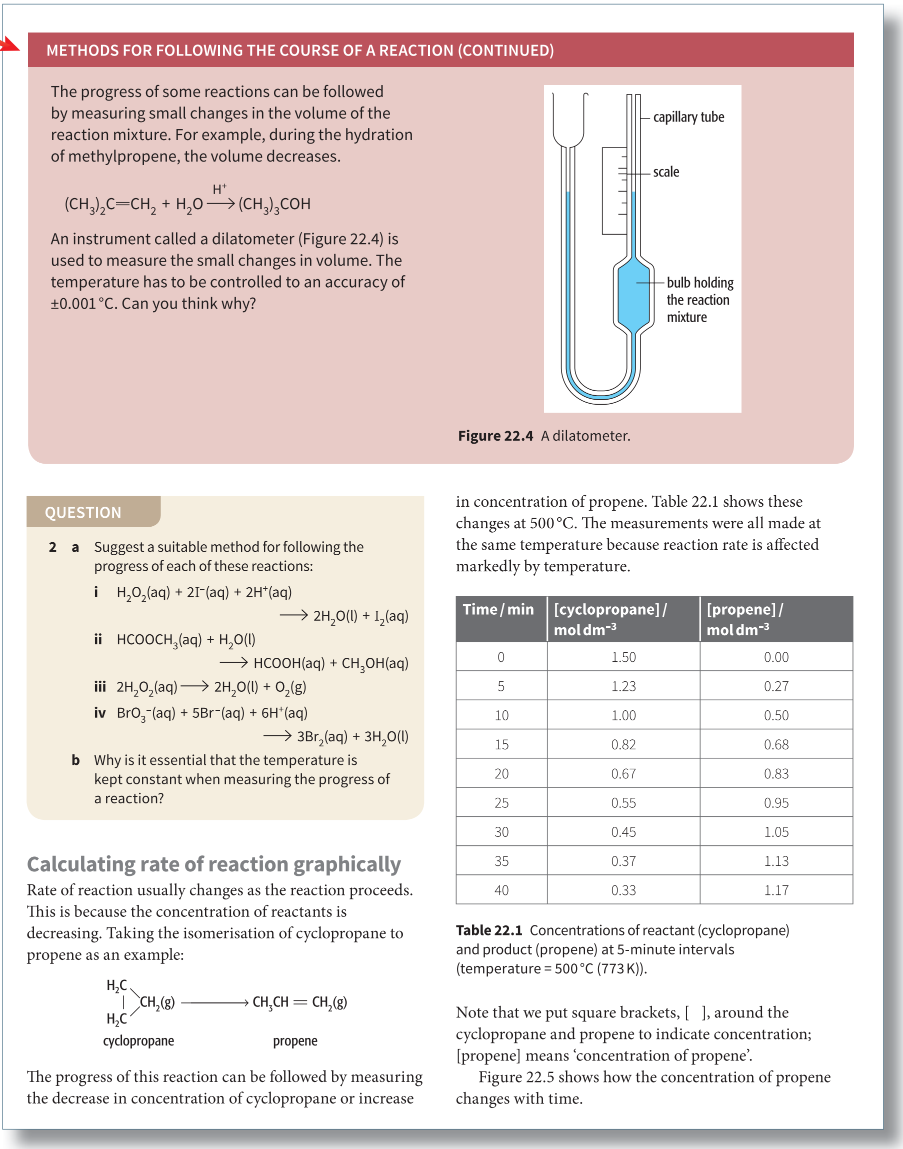
Important equations and other facts are shown in highlight boxes.



Fluoroalkanes	least reactive
Chloroalkanes	↓
Bromoalkanes	
Iodoalkanes	most reactive

Questions throughout the text give you a chance to check that you have understood the topic you have just read about. You can find the answers to these questions on the CD-ROM.

The text and illustrations describe and explain all of the facts and concepts that you need to know. The chapters, and often the content within them as well, are arranged in the same sequence as in your syllabus.



METHODS FOR FOLLOWING THE COURSE OF A REACTION (CONTINUED)

The progress of some reactions can be followed by measuring small changes in the volume of the reaction mixture. For example, during the hydration of methylpropene, the volume decreases.

$$(CH_3)_2C{=}CH_2 + H_2O \xrightarrow{H^+} (CH_3)_3COH$$

An instrument called a dilatometer (Figure 22.4) is used to measure the small changes in volume. The temperature has to be controlled to an accuracy of ±0.001 °C. Can you think why?

Figure 22.4 A dilatometer.

QUESTION

2 a Suggest a suitable method for following the progress of each of these reactions:

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

ii $HCOOCH_3(aq) + H_2O(l) \longrightarrow HCOOH(aq) + CH_3OH(aq)$

iii $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

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

b Why is it essential that the temperature is kept constant when measuring the progress of a reaction?

Calculating rate of reaction graphically

Rate of reaction usually changes as the reaction proceeds. This is because the concentration of reactants is decreasing. Taking the isomerisation of cyclopropane to propene as an example:

$$\underset{\text{cyclopropane}}{H_2C\text{–}CH_2(g)\text{–}CH_2} \longrightarrow \underset{\text{propene}}{CH_3CH{=}CH_2(g)}$$

The progress of this reaction can be followed by measuring the decrease in concentration of cyclopropane or increase in concentration of propene. Table 22.1 shows these changes at 500 °C. The measurements were all made at the same temperature because reaction rate is affected markedly by temperature.

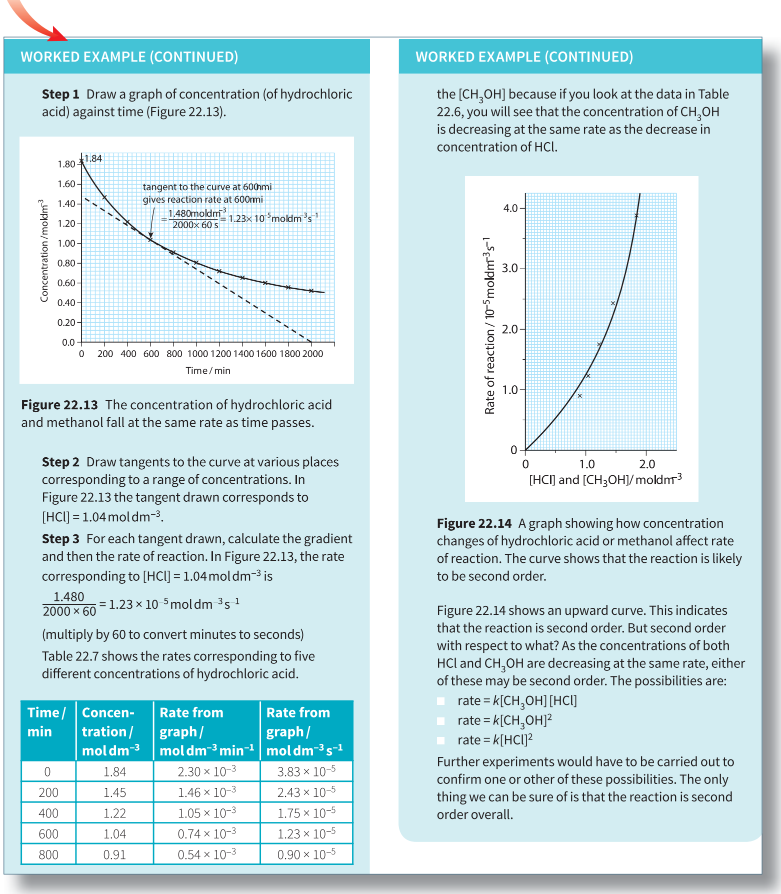
Time / min	[cyclopropane] / mol dm^{-3}	[propene] / mol dm^{-3}
0	1.50	0.00
5	1.23	0.27
10	1.00	0.50
15	0.82	0.68
20	0.67	0.83
25	0.55	0.95
30	0.45	1.05
35	0.37	1.13
40	0.33	1.17

Table 22.1 Concentrations of reactant (cyclopropane) and product (propene) at 5-minute intervals (temperature = 500 °C (773 K)).

Note that we put square brackets, [ ], around the cyclopropane and propene to indicate concentration; [propene] means 'concentration of propene'.

Figure 22.5 shows how the concentration of propene changes with time.

Wherever you need to know how to use a formula to carry out a calculation, there are worked example boses to show you how to do this.



WORKED EXAMPLE (CONTINUED)

Step 1 Draw a graph of concentration (of hydrochloric acid) against time (Figure 22.13).

1.84
tangent to the curve at 600mi
gives reaction rate at 600mi
$= \frac{1.480\,\text{moldm}^{-3}}{2000 \times 60\ \text{s}} = 1.23 \times 10^{-5}\,\text{moldm}^{-3}\text{s}^{-1}$
Concentration / moldm^{-3}
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Time / min

Figure 22.13 The concentration of hydrochloric acid and methanol fall at the same rate as time passes.

Step 2 Draw tangents to the curve at various places corresponding to a range of concentrations. In Figure 22.13 the tangent drawn corresponds to [HCl] = 1.04 mol dm^{-3}.

Step 3 For each tangent drawn, calculate the gradient and then the rate of reaction. In Figure 22.13, the rate corresponding to [HCl] = 1.04 mol dm^{-3} is

$$\frac{1.480}{2000 \times 60} = 1.23 \times 10^{-5}\,\text{mol dm}^{-3}\,\text{s}^{-1}$$

(multiply by 60 to convert minutes to seconds)

Table 22.7 shows the rates corresponding to five different concentrations of hydrochloric acid.

Time / min	**Concentration / mol dm^{-3}**	**Rate from graph / mol dm^{-3} min^{-1}**	**Rate from graph / mol dm^{-3} s^{-1}**
0	1.84	2.30×10^{-3}	3.83×10^{-5}
200	1.45	1.46×10^{-3}	2.43×10^{-5}
400	1.22	1.05×10^{-3}	1.75×10^{-5}
600	1.04	0.74×10^{-3}	1.23×10^{-5}
800	0.91	0.54×10^{-3}	0.90×10^{-5}

WORKED EXAMPLE (CONTINUED)

the [CH_3OH] because if you look at the data in Table 22.6, you will see that the concentration of CH_3OH is decreasing at the same rate as the decrease in concentration of HCl.

Rate of reaction / 10^{-5} moldm^{-3}s^{-1}
4.0
3.0
2.0
1.0
0
0
1.0
2.0
[HCl] and [CH_3OH]/ moldm^{-3}

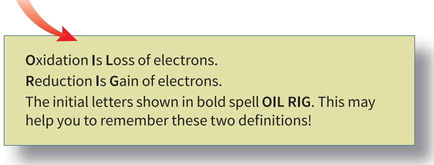
Figure 22.14 A graph showing how concentration changes of hydrochloric acid or methanol affect rate of reaction. The curve shows that the reaction is likely to be second order.

Figure 22.14 shows an upward curve. This indicates that the reaction is second order. But second order with respect to what? As the concentrations of both HCl and CH_3OH are decreasing at the same rate, either of these may be second order. The possibilities are:

- rate = $k[CH_3OH][HCl]$
- rate = $k[CH_3OH]^2$
- rate = $k[HCl]^2$

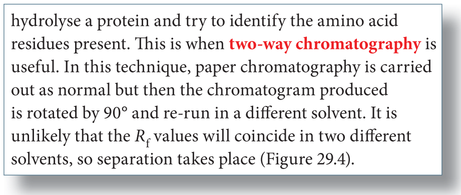
Further experiments would have to be carried out to confirm one or other of these possibilities. The only thing we can be sure of is that the reaction is second order overall.

Definitions that are required by the syllabus are shown in highlight boxes.



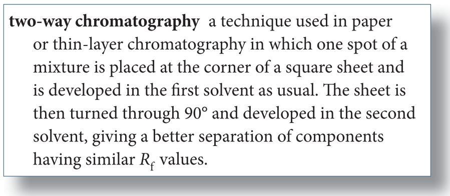
Oxidation **I**s **L**oss of electrons.
Reduction **I**s **G**ain of electrons.
The initial letters shown in bold spell **OIL RIG**. This may help you to remember these two definitions!

Key words are highlighted in the text when they are first introduced.



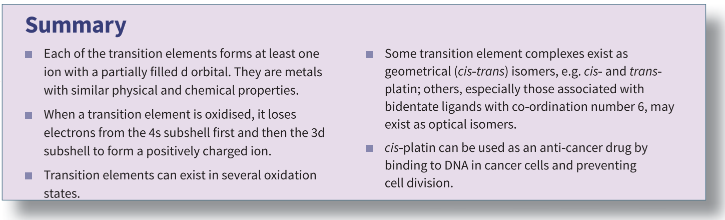
hydrolyse a protein and try to identify the amino acid residues present. This is when **two-way chromatography** is useful. In this technique, paper chromatography is carried out as normal but then the chromatogram produced is rotated by 90° and re-run in a different solvent. It is unlikely that the R_f values will coincide in two different solvents, so separation takes place (Figure 29.4).

You will also find definitions of these words in the Glossary.



two-way chromatography a technique used in paper or thin-layer chromatography in which one spot of a mixture is placed at the corner of a square sheet and is developed in the first solvent as usual. The sheet is then turned through 90° and developed in the second solvent, giving a better separation of components having similar R_f values.

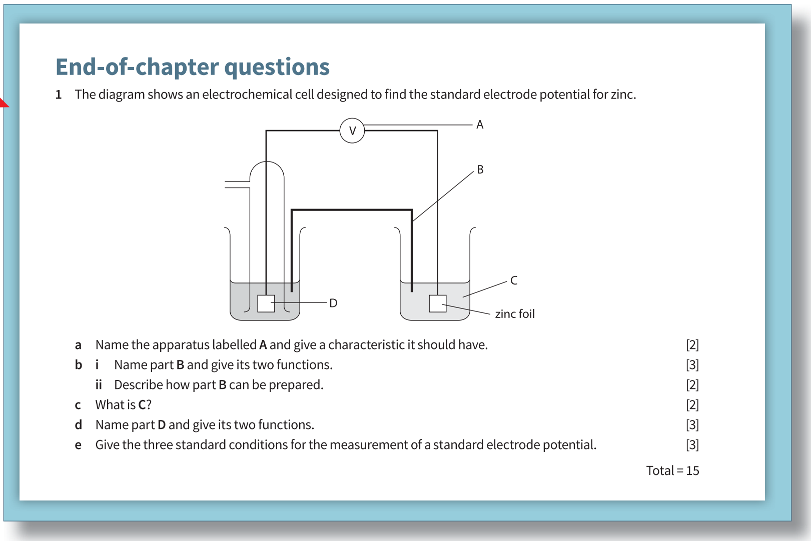
There is a summary of key points at the end of each chapter. You might find this helpful when you are revising.



Summary

- Each of the transition elements forms at least one ion with a partially filled d orbital. They are metals with similar physical and chemical properties.
- When a transition element is oxidised, it loses electrons from the 4s subshell first and then the 3d subshell to form a positively charged ion.
- Transition elements can exist in several oxidation states.
- Some transition element complexes exist as geometrical (*cis-trans*) isomers, e.g. *cis*- and *trans*-platin; others, especially those associated with bidentate ligands with co-ordination number 6, may exist as optical isomers.
- *cis*-platin can be used as an anti-cancer drug by binding to DNA in cancer cells and preventing cell division.

Questions at the end of each chapter are more demanding exam-style questions, some of which may require use of knowledge from previous chapters. Answers to these questions can be found on the CD-ROM.



End-of-chapter questions

1 The diagram shows an electrochemical cell designed to find the standard electrode potential for zinc.

a Name the apparatus labelled **A** and give a characteristic it should have. [2]
b i Name part **B** and give its two functions. [3]
ii Describe how part **B** can be prepared. [2]
c What is **C**? [2]
d Name part **D** and give its two functions. [3]
e Give the three standard conditions for the measurement of a standard electrode potential. [3]

Total = 15

Chapter 1:
Moles and equations

Learning outcomes

You should be able to:

- define and use the terms:
  - **relative atomic mass**, **isotopic mass** and **formula mass** based on the ^{12}C scale
  - **empirical formula** and **molecular formula**
  - the **mole** in terms of the Avogadro constant
- analyse and use mass spectra to calculate the relative atomic mass of an element
- calculate empirical and molecular formulae using combustion data or composition by mass
- write and construct balanced equations
- perform calculations, including use of the mole concept involving:
  - reacting masses (from formulae and equations)
  - volumes of gases (e.g. in the burning of hydrocarbons)
  - volumes and concentrations of solutions
- deduce stoichiometric relationships from calculations involving reacting masses, volumes of gases and volumes and concentrations of solutions.

Introduction

For thousands of years, people have heated rocks and distilled plant juices to extract materials. Over the past two centuries, chemists have learnt more and more about how to get materials from rocks, from the air and the sea, and from plants. They have also found out the right conditions to allow these materials to react together to make new substances, such as dyes, plastics and medicines. When we make a new substance it is important to mix the reactants in the correct proportions to ensure that none is wasted. In order to do this we need to know about the relative masses of atoms and molecules and how these are used in chemical calculations.

Figure 1.1 A titration is a method used to find the amount of a particular substance in a solution.

Masses of atoms and molecules

Relative atomic mass, A_r

Atoms of different elements have different masses. When we perform chemical calculations, we need to know how heavy one atom is compared with another. The mass of a single atom is so small that it is impossible to weigh it directly. To overcome this problem, we have to weigh a lot of atoms. We then compare this mass with the mass of the same number of 'standard' atoms. Scientists have chosen to use the isotope carbon-12 as the standard. This has been given a mass of exactly 12 units. The mass of other atoms is found by comparing their mass with the mass of carbon-12 atoms. This is called the **relative atomic mass**, A_r.

The relative atomic mass is the weighted average mass of naturally occurring atoms of an element on a scale where an atom of carbon-12 has a mass of exactly 12 units.

From this it follows that:

$$A_r\ [\text{element } Y] = \frac{\text{average mass of one atom of element } Y \times 12}{\text{mass of one atom of carbon-12}}$$

We use the average mass of the atom of a particular element because most elements are mixtures of isotopes. For example, the exact A_r of hydrogen is 1.0079. This is very close to 1 and most periodic tables give the A_r of hydrogen as 1.0. However, some elements in the Periodic Table have values that are not whole numbers. For example, the A_r for chlorine is 35.5. This is because chlorine has two isotopes. In a sample of chlorine, chlorine-35 makes up about three-quarters of the chlorine atoms and chlorine-37 makes up about a quarter.

Relative isotopic mass

Isotopes are atoms that have the same number of protons but different numbers of neutrons (see page 28). We represent the **nucleon number** (the total number of neutrons plus protons in an atom) by a number written at the top left-hand corner of the atom's symbol, e.g. ^{20}Ne, or by a number written after the atom's name or symbol, e.g. neon-20 or Ne-20.

We use the term **relative isotopic mass** for the mass of a particular isotope of an element on a scale where an atom of carbon-12 has a mass of exactly 12 units. For example, the relative isotopic mass of carbon-13 is 13.00. If we know both the natural abundance of every isotope of an element and their isotopic masses, we can calculate the relative atomic mass of the element very accurately. To find the necessary data we use an instrument called a mass spectrometer (see box on mass spectrometry).

Relative molecular mass, M_r

The **relative molecular mass** of a **compound** (M_r) is the relative mass of one molecule of the compound on a scale where the carbon-12 isotope has a mass of exactly 12 units. We find the relative molecular mass by adding up the relative atomic masses of all the atoms present in the molecule.

For example, for methane:

formula	CH_4
atoms present	1 × C; 4 × H
add A_r values	$(1 \times A_r[C]) + (4 \times A_r[H])$
M_r of methane	$= (1 \times 12.0) + (4 \times 1.0)$
	$= 16.0$

Relative formula mass

For compounds containing ions we use the term **relative formula mass**. This is calculated in the same way as for relative molecular mass. It is also given the same symbol, M_r. For example, for magnesium hydroxide:

formula	$Mg(OH)_2$
ions present	$1 \times Mg^{2+}$; $2 \times (OH^-)$
add A_r values	$(1 \times A_r[Mg]) + (2 \times (A_r[O] + A_r[H]))$
M_r of magnesium hydroxide	$= (1 \times 24.3) + (2 \times (16.0 + 1.0))$
	$= 58.3$

QUESTION

1 Use the Periodic Table on page 473 to calculate the relative formula masses of the following:

a calcium chloride, $CaCl_2$

b copper(II) sulfate, $CuSO_4$

c ammonium sulfate, $(NH_4)_2SO_4$

d magnesium nitrate-6-water, $Mg(NO_3)_2.6H_2O$

Hint: for part **d** you need to calculate the mass of water separately and then add it to the M_r of $Mg(NO_3)_2$.

Accurate relative atomic masses

MASS SPECTROMETRY

A mass spectrometer (Figure 1.2) can be used to measure the mass of each isotope present in an element. It also compares how much of each isotope is present – the relative abundance (isotopic abundance). A simplified diagram of a mass spectrometer is shown in Figure 1.3. You will not be expected to know the details of how a mass spectrometer works, but it is useful to understand how the results are obtained.

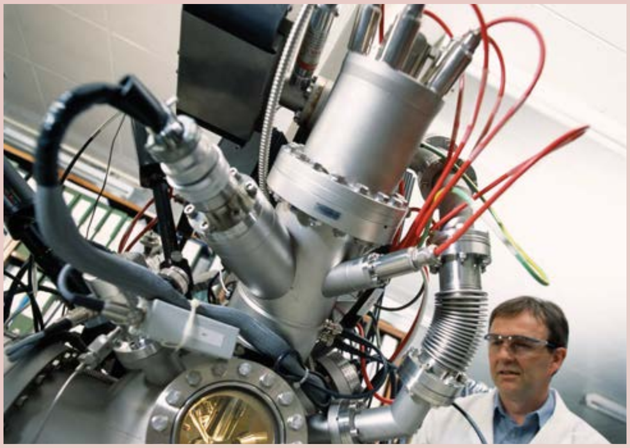


Figure 1.2 A mass spectrometer is a large and complex instrument.

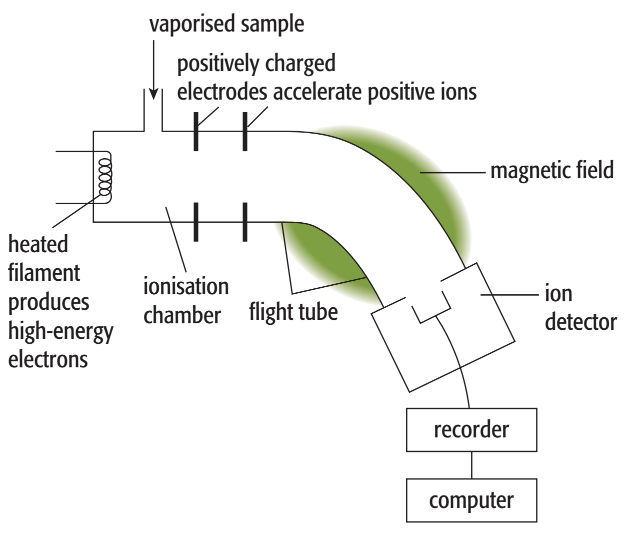

vaporised sample
positively charged electrodes accelerate positive ions
magnetic field
heated filament produces high-energy electrons
ionisation chamber
flight tube
ion detector
recorder
computer

Figure 1.3 Simplified diagram of a mass spectrometer.

MASS SPECTROMETRY (CONTINUED)

The atoms of the element in the vaporised sample are converted into ions. The stream of ions is brought to a detector after being deflected (bent) by a strong magnetic field. As the magnetic field is increased, the ions of heavier and heavier isotopes are brought to the detector. The detector is connected to a computer, which displays the mass spectrum.

The mass spectrum produced shows the relative abundance (isotopic abundance) on the vertical axis and the mass to ion charge ratio (*m*/*e*) on the horizontal axis. Figure 1.4 shows a typical mass spectrum for a sample of lead. Table 1.1 shows how the data is interpreted.

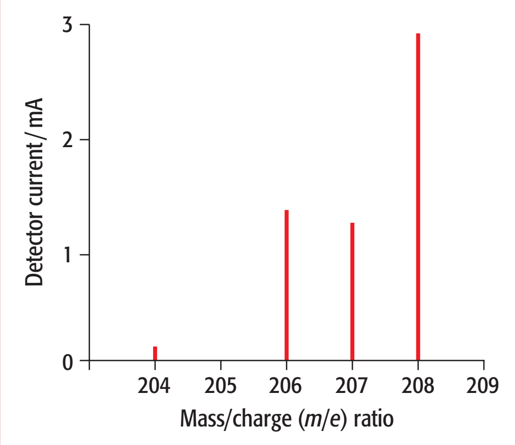


Figure 1.4 The mass spectrum of a sample of lead.

For singly positively charged ions the *m*/*e* values give the nucleon number of the isotopes detected. In the case of lead, Table 1.1 shows that 52% of the lead is the isotope with an isotopic mass of 208. The rest is lead-204 (2%), lead-206 (24%) and lead-207 (22%).

Isotopic mass	Relative abundance / %
204	2
206	24
207	22
208	52
total	100

Table 1.1 The data from Figure 1.4.

Determination of A_r from mass spectra

We can use the data obtained from a mass spectrometer to calculate the relative atomic mass of an element very accurately. To calculate the relative atomic mass we follow this method:

- multiply each isotopic mass by its percentage abundance
- add the figures together
- divide by 100.

We can use this method to calculate the relative atomic mass of neon from its mass spectrum, shown in Figure 1.5.

The mass spectrum of neon has three peaks:

^{20}Ne (90.9%), ^{21}Ne (0.3%) and ^{22}Ne (8.8%).

$$A_r \text{ of neon} = \frac{(20 \times 90.9) + (21.0 \times 0.3) + (22 \times 8.8)}{100} = 20.2$$

Note that this answer is given to 3 significant figures, which is consistent with the data given.

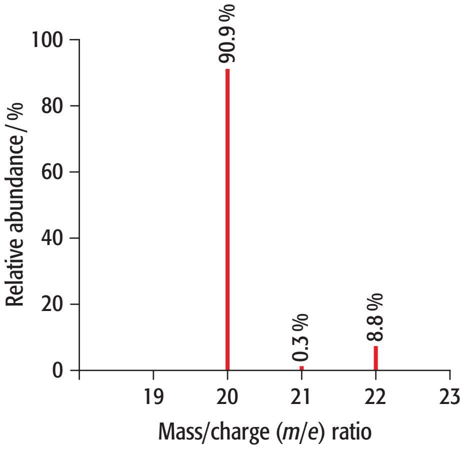


Figure 1.5 The mass spectrum of neon, Ne.

A high-resolution mass spectrometer can give very accurate relative isotopic masses. For example ^{16}O = 15.995 and ^{32}S = 31.972. Because of this, chemists can distinguish between molecules such as SO_2 and S_2, which appear to have the same relative molecular mass.

QUESTION

2 Look at the mass spectrum of germanium, Ge.

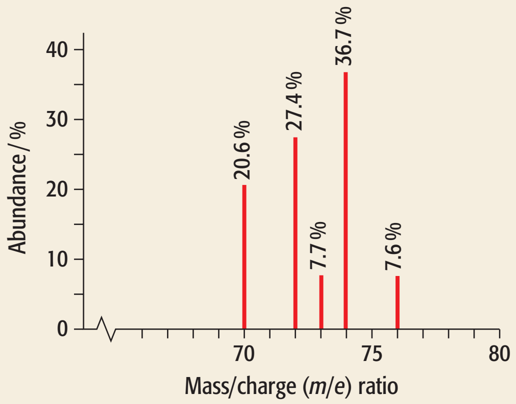


Figure 1.6 The mass spectrum of germanium.

a Write the isotopic formula for the heaviest isotope of germanium.

b Use the % abundance of each isotope to calculate the relative atomic mass of germanium.

Amount of substance

The mole and the Avogadro constant

The formula of a compound shows us the number of atoms of each element present in one formula unit or one molecule of the compound. In water we know that two atoms of hydrogen ($A_r = 1.0$) combine with one atom of oxygen ($A_r = 16.0$). So the ratio of mass of hydrogen atoms to oxygen atoms in a water molecule is 2 : 16. No matter how many molecules of water we have, this ratio will always be the same. But the mass of even 1000 atoms is far too small to be weighed. We have to scale up much more than this to get an amount of substance that is easy to weigh.

The relative atomic mass or relative molecular mass of a substance in grams is called a **mole** of the substance. So a mole of sodium ($A_r = 23.0$) weighs 23.0 g. The abbreviation for a mole is mol. We define the mole in terms of the standard carbon-12 isotope (see page 28).

One mole of a substance is the amount of that substance that has the same number of specific particles (atoms, molecules or ions) as there are atoms in exactly 12 g of the carbon-12 isotope.

We often refer to the mass of a mole of substance as its **molar mass** (abbreviation M). The units of molar mass are $\mathrm{g\,mol^{-1}}$.

The number of atoms in a mole of atoms is very large: 6.02×10^{23} atoms. This number is called the **Avogadro constant** (or Avogadro number). The symbol for the Avogadro constant is L (the symbol N_A may also be used). The Avogadro constant applies to atoms, molecules, ions and electrons. So in 1 mole of sodium there are 6.02×10^{23} sodium atoms and in 1 mole of sodium chloride (NaCl) there are 6.02×10^{23} sodium ions and 6.02×10^{23} chloride ions.

It is important to make clear what type of particles we are referring to. If we just state 'moles of chlorine', it is not clear whether we are thinking about chlorine atoms or chlorine molecules. A mole of chlorine molecules, Cl_2, contains 6.02×10^{23} chlorine molecules but twice as many chlorine atoms, as there are two chlorine atoms in every chlorine molecule.

Figure 1.7 Amedeo Avogadro (1776–1856) was an Italian scientist who first deduced that equal volumes of gases contain equal numbers of molecules. Although the Avogadro constant is named after him, it was left to other scientists to calculate the number of particles in a mole.

Moles and mass

The Système International (SI) base unit for mass is the kilogram. But this is a rather large mass to use for general laboratory work in chemistry. So chemists prefer to use the relative molecular mass or formula mass in grams (1000 g = 1 kg). You can find the number of moles of a substance by using the mass of substance and the relative atomic mass (A_r) or relative molecular mass (M_r).

$$\text{number of moles (mol)} = \frac{\text{mass of substance in grams (g)}}{\text{molar mass } (\mathrm{g\,mol^{-1}})}$$