Name ______________________________

Second edition

Continuing Chemistry

NCEA Level 3

Anne Wignall • Terry Wales

PEARSON
Longman

Preface

Continuing Chemistry combines the convenience of a write-on workbook with the content of a text book and the interactivity of the electronic age.

It takes time to put together a project as complex as *Continuing Chemistry*. The first edition, published in 2006, included the notes, *Revision* activities, *Exam papers* and *PowerPoints*. For this edition we have added the *Practicals*, the *Encounters*, the *Quiz* file for teachers, the latest *Exam papers*, some new *Revision* activities plus made minor changes to the text.

The printed book contains short, readable theory notes and step-by-step methods for common calculations, followed by formative *Test yourself* questions which are intended for classroom use or for homework. At the end of each chapter are a summary of *Key learning outcomes* for that chapter, followed by exam-style *Review questions* which include A, M, E grades to indicate the depth of answer expected. Fully-worked *Answers* to all these questions (with judgement statements for the *Review questions*) are at the end of the book. The *Practicals* that follow the theory notes include all the common reactions done at this level. Model answers for the practicals, including sample results, are on the CD.

The companion CD contains *PowerPoint*™ shows of important practicals and worked examples for the typical calculation questions; 18 *Encounters* covering chemistry and chemists outside the classroom; sets of *Examination questions* for each chapter plus five *Practice examination papers* for each external Achievement Standard; and a wide variety of on-screen *Revision* activities to help students memorise the key facts and develop the skills needed at this level; and a teachers' password-protected *Quiz* file for classroom use. Margin graphics in the printed text direct students (and teachers) to the CD content. They become hot-links in the full-colour *PDF version* of the text also on the CD.

Together the text and CD comprise a resource that can be used in-class and at home, caters for times when students (or teachers) are absent from class, uses simple language (ideal for ESOL students) and provides a wide range of activities to suit a range of student abilities and learning styles.

Acknowledgements

Although our names are on the cover of this book, we did not work alone. We are grateful for the generous assistance provided by Rudi Jansen, Alan Happer, Richard Hartshorn, Alastair Lightfoot, and Graeme Tinkler. Particular thanks go to those people who were willing to have their personal stories told for the Encounters section, and the dozen of other people, not mentioned, who answered questions about the aspects of chemistry in New Zealand.

Thanks to NZQA who consented to the reproduction of the Bursary and NCEA examination questions. NZQA retain the copyright on these questions.

And, as always, our thanks to Betty and Sylvia: their support and encouragement is the vital ingredient in our continuing partnership.

Anne and Terry

www.pearsoned.co.nz

Your comments on this book are welcome at
feedback@pearsoned.co.nz

Pearson Education New Zealand a division of Pearson New Zealand Ltd
67 Apollo Drive, Mairangi Bay, Auckland, New Zealand

(c) Pearson Education New Zealand 1994, 1998, 1999, 2004, 2006, 2007
First published as *Longman Write-on Notes Chemistry 7* by Longman Paul 1994
Reprinted 1994, 1995, 1996 (twice)
Second edition published by Addison Wesley Longman New Zealand Limited 1998
Reprinted 1999
Third edition published as *Longman Write-on Notes Chemistry 13* by Pearson Education New Zealand 1999
Reprinted 2000, 2001, 2002 (twice), 2003
Fourth edition published by Pearson Education New Zealand 2004
Reprinted 2004
Fifth edition published as *Continuing Chemistry* by Pearson Education New Zealand 2006
Reprinted 2006
This edition published 2007

ISBN 978 0 7339 9257 5

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior permission of the publisher.

We use paper from sustainable forestry

Produced by Pearson Education New Zealand
Designers: Marie Low and Allan Hawes
Page layout and photographs: Anne Wignall
Printed in Malaysia

Contents

Using the book

This book contains notes covering the important concepts in Level 3 Chemistry and including numerous *Worked examples*, followed by *Test yourself* and *Review questions* to develop and test your understanding, and *Key learning outcomes* for each chapter to guide your study. Fully worked *Answers* to all the questions in the notes are included at the back of the book.

To do well in chemistry you need to learn actively. Highlight key points in the text; write reminders to yourself in the margins; write in the answers to each question, *then* mark them (you won't be able to copy out answers in the exams). **You should aim to complete every question in this book.**

The practical section covers all the key reactions and techniques required at this level. A technician's guide, listing the reagents required for each practical, is included in the Teachers folder on the CD.

The final three sheets of this book should be pulled out and folded to make a *Key Facts* booklet which you could keep in the CD pocket on the inside front cover of your book. Use it for quick revision before each class test or exam.

Using the CD

The CD which accompanies this book contains a large number of additional resources to reinforce and develop your understanding of chemistry. If you have the space on your computer, we recommend you copy the contents of the CD onto your hard drive. This will make loading the files faster, and you won't need to find the CD each time you want to do some chemistry.

PDF file of the printed text

The heart of the CD is a PDF file, in full colour, of the printed text. All margin links from the text become clickable hot links to the other material on the CD. Bookmarks at the side of the page will take you straight to each chapter, or you can click on the contents pages to jump directly to the section you need.

Revision tasks

152 revision tasks provide a wide variety of on-screen activities to help you memorise the facts you need to know, and to develop specific skills required at this level. Do each task as often as necessary to score at least 85%. Then redo it several times over the next weeks and months to help you to retain that knowledge.

In the Teachers folder on this CD is a set of Quizzes for use in class. Most of these quizzes parallel the revision tasks and are intended to test your knowledge of this material. A password – available from Pearson Education – is required to open this file.

Examination questions

By answering questions from recent examination papers, you become familiar with the questioning styles and language used by a variety of examiners. The CD contains both Bursary and NCEA papers from 2000–2006. The Bursary questions have been modified to fit the NCEA style of questions. Fully-worked model answers for all questions are supplied, along with the AME judgement statements.

Practice exam questions

For each chapter of the book we have included a set of examination questions to show you the kinds of questions you can expect in the exam. You should answer these questions before attempting any of the practice exam papers. A, M, E grades have been shown on all questions to guide your answers.

Sample examination papers

Two practice exam papers made up from Bursary questions, plus NCEA papers from 2004–6 are provided for each of the four external Achievement Standards. We recommend that you save them for use prior to your school exams, and in the month or so before the real exam in November.

Encounters

Chemistry is more than just passing exams! Click on the Encounters links in the pdf file to read about how the chemistry you are learning is useful in the world outside the classroom. You will also meet people – some from history, but most living – who use chemistry in their work. We think you will find their stories interesting.

Legal stuff

Students: permission is given for you to make a copy of the CD onto your hard drive for personal use, but you may not make multiple copies of the CD or its contents for all your friends!

Teachers: please read the legal notice on the CD itself for further conditions regarding the use of this material in schools.

Software requirements

Adobe Reader® is required to open the pdf file of the text, plus the exam files. *Microsoft PowerPoint*™ *2003*, *PowerPoint Viewer*™ or alternative is required to open the PowerPoint files. Movies open in *Windows Media Player* or other media programs. The revision tasks will open in any Javascript capable web browser.

The CD contains further software information and copies of *Adobe Reader* and *PowerPoint Viewer* for Windows machines. Equivalent files are also available on the web for users of Macintosh computers.

PowerPoint™ shows

The CD contains 54 PowerPoint™ shows. Many review practicals you should have done in class, while we have also included some practicals which can be difficult to do in a classroom setting. Other shows take you through the various types of calculations you need to master.

The camera icon below indicates those shows which contain photographs of practical work.

Teachers' notes, listing the reagents required for each of the practicals done here are provided in the Teachers folder on this CD.

Oxidation and reduction

Calculating and using oxidation numbers

Chemical tests for redox species

Permanganate with neutral and acidified H_2O_2

Bromate and sulfur dioxide

Reactions involving I_2(aq) and I^-(aq)

$CuSO_4$(aq) and I^-(aq)

Permanganate with alkaline hydrogen sulfite

Lead dioxide and conc HCl

Hydrogen sulfide gas and iodine solution

Standardising potassium permanganate solution

Oxalic acid and permanganate titration

Ethanol and dichromate calculation

Standardising thiosulfate (iodimetry)

Practical electrochemical cells

Electrode potentials and predicting reactions

The lead-acid cell

Particles and thermochemistry

Particle theory

Determining enthalpy experimentally

Hess's law calculations

Bond energy calculations

Transition metal compounds

Drawing Lewis diagrams

Shapes and polarity of molecules

Solids (revision)

Conductivity in solids

Organic chemistry

Properties of optically-active compounds

Hydrocarbons (revision)

Reactions of alcohols

Preparation of a haloalkane

Properties of haloalkanes

Properties of amines

Preparation of an aldehyde

Distinguishing between aldehydes and ketones

Properties of acyl chlorides

Preparation of an ester

Making soap (revision)

Preparation of nylon

Acids and bases

K_s from solubility

Solubility from K_s

Ionic product calculations

The common ion effect

Strong and weak acids (revision)

Acidic, basic and neutral salts

pH of strong acids and bases

pH of weak acids and bases

Aqueous solutions

Buffer solutions

Buffer calculations

Titration curves

Drawing titration curves

Extended practical

Back titrations

Colorimetric analysis

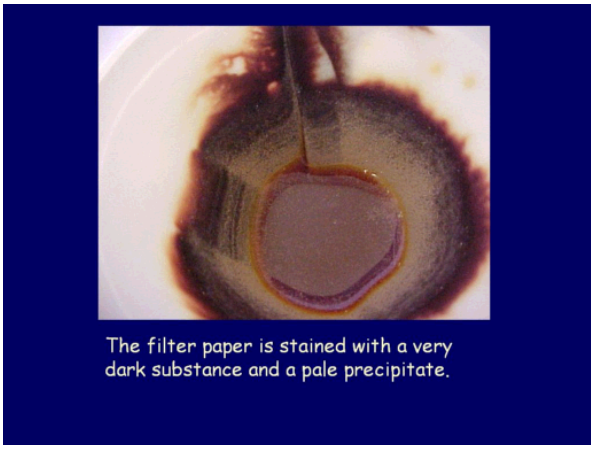
Understanding concentration

Excellent investigations

Section 1

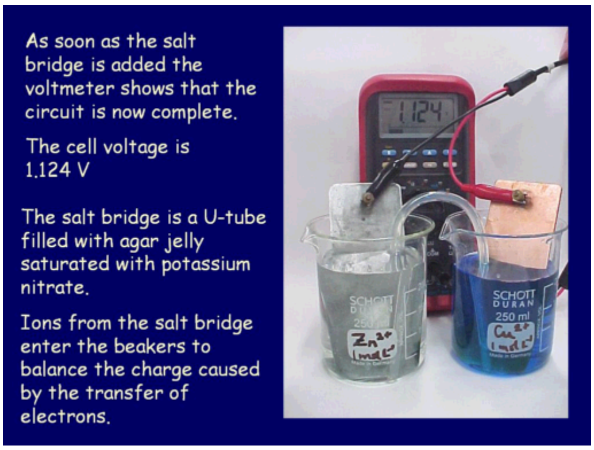
Oxidation and reduction

Chemistry 3.2 2 credits	AS90695 Internal	Determine the concentration of an oxidant or reductant by titration
Chemistry 3.3 3 credits	AS90696 External	Describe oxidation-reduction processes



1 Principles of oxidation and reduction

2 Volumetric analysis



3 Electrochemistry

1

Principles of oxidation and reduction

Oxidation and reduction

Definitions

You should remember the following from your Year 12 work.

- An **oxidation-reduction** (redox) reaction is any reaction involving a *transfer of electrons*.
- In all redox reactions, oxidation and reduction occur at the same time.
- **Oxidation** is a *loss* of electrons.
- **Reduction** is a *gain* of electrons.
- **Oxidising agents** (oxidants) are themselves reduced, **reducing agents** (reductants) are themselves oxidised.

REVISION

1A 1 Oxidation-reduction key facts

Quiz 1A 1

Oxidation numbers

Oxidation numbers are a form of electronic book-keeping. They are particularly useful when working with reactions involving elements which can exist in a number of different oxidation states, such as sulfur, nitrogen and the transition elements.

Rules for assigning oxidation numbers

1 The oxidation number of any free, uncombined element is zero. This includes polyatomic molecules of elements such as H_2, O_3 and S_8.

2 The charge on a simple (monatomic) ion is the oxidation number of the element in that ion. In a polyatomic ion, the sum of the oxidation numbers of the atoms in that ion is equal to the charge on the ion.

3 In compounds (whether ionic or covalent), the sum of the oxidation numbers of all atoms in the compound is zero.

4 The oxidation number of oxygen is –2, except in the case of peroxides where it is –1.

5 The oxidation number of hydrogen is +1, except in the case of metallic hydrides where it is –1.

Example 1.1 **Oxidation numbers**

Write the oxidation numbers for each of the underlined atoms:

a $\underline{Pb}O_2$ **b** $\underline{Br}O_3^-$ **c** $[\underline{Fe}SCN]^{2+}$

a PbO_2 is a compound, so the sum of the oxidation numbers (ON) will be zero (rule 3), and the oxygen has an ON of –2 (rule 4), so we can calculate the ON of the Pb by simple algebra:

$$\begin{aligned} Pb + 2O &= 0 \\ Pb + (2 \times -2) &= 0 \\ Pb - 4 &= 0 \\ Pb &= +4 \end{aligned}$$

POWERPOINT

1A 1 Calculating and using oxidation numbers

b BrO_3^- is an ion, so the sum of its ON will be –1 (rule 2). The oxygen atoms will again have ON of –2 (rule 4), so:

$$\begin{aligned} Br + 3O &= -1 \\ Br + (3 \times -2) &= -1 \\ Br - 6 &= -1 \\ Br &= -1 + 6 \\ Br &= +5 \end{aligned}$$

c $[FeSCN]^{2+}$ is a complex ion, containing the SCN^- ion. It is not necessary to work out the ON for the S, C and N atoms, since we know that their sum will be –1 (rule 2).

$$\begin{aligned} Fe + SCN &= +2 \\ Fe - 1 &= +2 \\ Fe &= +3 \end{aligned}$$

Identifying redox equations

Oxidation numbers can be used to identify what has been oxidised or reduced in an equation.

- If its oxidation number increases, the element has been oxidised.
- If its oxidation number decreases, the element has been reduced.

Example 1.2 Using oxidation numbers

Use oxidation numbers to determine whether the following reaction is a redox reaction, and if so, which element has been oxidised, and which reduced.

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(l)$$

It is simplest to write the oxidation numbers above each element:

$$4\overset{-3}{N}\overset{+1}{H_3}(g) + 3\overset{0}{O_2}(g) \longrightarrow 2\overset{0}{N_2}(g) + 6\overset{+1}{H_2}\overset{-2}{O}(l)$$

The oxidation numbers of N and O have changed: it is a redox reaction.

The oxidation number of N has gone from –3 to 0: it has been oxidised.

The oxidation number of O has gone from 0 to –2: it has been reduced.

REVISION

1A 2 Oxidation number

Quiz 1A 2

Test yourself 1A Electron transfer reactions

1 Define the terms *oxidation* and *reduction* in terms of electron transfer.

2 Determine the oxidation numbers of the underlined atoms:

a $\underline{Cl}O^-$ **b** $\underline{Cr}O_4^{2-}$ **c** $\underline{C}O_2$ **d** $\underline{S}O_3^{2-}$ **e** $H_2\underline{S}$

3 Use oxidation numbers to determine whether the following reactions are redox reactions. For those that are, identify the element oxidised, and the element reduced.

a $HgCl_2(aq) + 2KI(aq) \longrightarrow HgI_2(s) + 2KCl(aq)$

b $3HCl(aq) + HNO_3(aq) \longrightarrow Cl_2(g) + NOCl(g) + 2H_2O(l)$

c $ICl(s) + H_2O(l) \longrightarrow HCl(aq) + HOI(aq)$

d $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

e $2MnO_4^-(aq) + HSO_3^-(aq) + 3OH^-(aq) \longrightarrow 2MnO_4^{2-}(aq) + SO_4^{2-}(aq) + 2H_2O(l)$

4 Put circles around the oxidants, and squares around the reductants, in the following equations:

a $CuO + H_2 \longrightarrow Cu + H_2O$

b $Ag^+(aq) + Fe^{2+}(aq) \longrightarrow Ag(s) + Fe^{3+}(aq)$

c $5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$

Laboratory redox

Identifying species in redox reactions

For many redox reactions there are visible changes in the appearance of one or both of the reacting species. For example, when acidified potassium permanganate is added to hydrogen peroxide solution the purple colour disappears as MnO_4^- is reduced to Mn^{2+}. In other reactions no colour change is visible, so we have to add another reagent if we wish to detect the reaction. You should remember the following tests from Year 12 chemistry:

I_2: turns blue/black with starch solution
SO_4^{2-}: forms a white precipitate with acidified barium chloride solution
Fe^{3+}: forms a blood-red solution with potassium thiocyanate solution
Cl_2: turns damp starch-iodide paper blue/black.

You should be familiar with the following redox reagents from Year 12 chemistry.

Reduced form		**Oxidised form**	
Formula	**Appearance**	**Formula**	**Appearance**
Cu	brown solid	Cu^{2+}	blue ion
SO_2	colourless gas	SO_4^{2-}	colourless ion
Mn^{2+}	colourless ion	H^+/MnO_4^-	purple ion
H_2O_2	colourless liquid	O_2	colourless gas
H_2O	colourless liquid	H_2O_2	colourless liquid
Cr^{3+}	blue/green ion	$Cr_2O_7^{2-}$	orange ion
Fe^{2+}	pale green ion	Fe^{3+}	orange ion
Cl^-	colourless ion	Cl_2	pale green gas
Br^-	colourless ion	Br_2	red/orange liquid
H_2	colourless gas	H^+	colourless ion

You also need to learn the colours and formulae of the following reagents, which will be probably be new to you this year.

POWERPOINT

1B 1 Chemical tests for redox species

Use coloured pencils or pens to show the colour of each species in this table.

REVISION

1B 1 Formula practice

1B 2 Redox colours

Quizzes 1B 1, 1B 2a, 1B 2b

PRACTICAL

1.1 P 149 Redox reactions: some examples

POWERPOINT

1B 2 Permanganate with neutral and acidified H_2O_2

1B 3 Bromate and sulfur dioxide

1B 4 Reactions involving I_2 and I^-

1B 5 $CuSO_4(aq)$ and $I_2(aq)$

REVISION

1B 3a Testing for redox species

1B 3b–3g Learning redox pairs

1B 4a–4b Studying redox reactions

Quizzes 1B 3, 1B 4a, 1B 4b

Reduced form		Oxidised form	
Formula	**Appearance**	**Formula**	**Appearance**
MnO_2	brown precipitate	H_2O/MnO_4^-	purple ion
MnO_4^{2-}	green ion	OH^-/MnO_4^-	purple ion
I^-	colourless ion	I_2 (in $I^- = I_3^-$)	brown solution
I_2 (in $I^- = I_3^-$)	brown solution	IO_3^-	colourless ion
H_2S	colourless gas	S	yellow/white solid
Pb^{2+}	colourless ion	PbO_2	brown solid
NO_2	brown gas	NO_3^-	colourless ion
$C_2O_4^{2-}$	colourless ion	CO_2	colourless gas
$S_2O_3^{2-}$	colourless ion	$S_4O_6^{2-}$	colourless ion
Br_2	red-orange liquid	BrO_3^-	colourless ion

Use coloured pencils or pens to show the colour of each species in this table.

Important oxidising agents are MnO_4^- (in acid, neutral or alkaline conditions), $H^+/Cr_2O_7^{2-}$, H_2O_2, Cl_2 and IO_3^- or BrO_3^-.

Important reducing agents are SO_2 (or HSO_3^-), $S_2O_3^{2-}$ (thiosulfate), Fe^{2+}, and $C_2O_4^{2-}$ (oxalate—from oxalic acid).

You will meet other redox reagents as well, but those listed above are the important ones.

Test yourself 1B Laboratory redox

1 Describe what you would see when:

a $Cr_2O_7^{2-}$ is reduced ______________________________

b Br^- is oxidised ______________________________

c IO_3^- is reduced ______________________________

d H_2O_2 is oxidised ______________________________

2 Describe what you would see when:

a Iodine solution, to which a few drops of starch have been added, is reduced to I^- by thiosulfate solution. The thiosulfate is oxidised to $S_4O_6^{2-}$.

____

____

b Oxalic acid reduces H^+/MnO_4^- to Mn^{2+}. The oxalic acid is oxidised to CO_2.

____

____

c Zinc metal is oxidised to Zn^{2+} by dilute sulfuric acid. The H^+ is reduced.

____

____

Balancing redox equations

When writing equations for redox reactions, we normally write two half-equations (for the oxidation and the reduction processes), then add them together. Usually we keep things simple by leaving out the spectator ions.

Balancing redox equations in acidic or neutral conditions

For each half-equation:

1 Balance the atoms that are not O or H.
2 Balance the O by adding water.
3 Balance the H by adding H^+.
4 Balance the charge by adding electrons to the more positive side.

To put the half-equations together:

5 Multiply the half-equations by the factors needed to make the number of electrons transferred in each half-equation the same.
6 Add the two equations together, cancelling out the electrons and any other duplicated species.

Example 1.3 Balancing a redox equation in acid conditions

Acidified potassium permanganate is decolourised by iron(II) sulfate solution. Write an ionic equation for this reaction.

Break the reaction into two half-equations. The Fe^{2+} will be oxidised to Fe^{3+}. The ion-electron half-equation is simple:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

The MnO_4^- will be reduced to Mn^{2+}. Follow the steps above to write the ion-electron half-equation:

$$MnO_4^- \longrightarrow Mn^{2+}$$
$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$
$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

In combining the two half-equations, multiply the Fe^{2+} equation by 5, since there are $5e^-$ in the MnO_4^- equation:

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^-$$

Finally, add the two equations together:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Balancing redox equations in alkaline conditions

The method shown above is used for all reactions done in acidic or neutral conditions. To balance reactions done in strongly alkaline conditions we modify step **3** of the above method.

3 Balance the H by adding H^+, then add an equal amount of OH^- to both sides of the equation (which changes the H^+ into H_2O).

Example 1.4 Balancing a redox equation in alkaline conditions

Write an ion-electron half-equation for the reduction of MnO_4^- to MnO_2 in alkaline conditions.

$$MnO_4^- \longrightarrow MnO_2$$

Balance the atoms that aren't O or H.

$$MnO_4^- \longrightarrow MnO_2$$

Balance the O by adding H_2O.

$$MnO_4^- \longrightarrow MnO_2 + 2H_2O$$

Balance the H by adding H^+.

$$MnO_4^- + 4H^+ \longrightarrow MnO_2 + 2H_2O$$

Cancel out the H^+ by adding OH^-.

$$MnO_4^- + 4H^+ + 4OH^- \longrightarrow MnO_2 + 2H_2O + 4OH^-$$
$$MnO_4^- + 4H_2O \longrightarrow MnO_2 + 2H_2O + 4OH^-$$

Cancel out extra waters, etc.

$$MnO_4^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$$

Balance the charge by adding electrons.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

PRACTICAL

1.2 P 152 Redox reactions involving the halogens

ENCOUNTER

1A Sodium percarbonate — a modern bleach

POWERPOINT

1C 1 Permanganate with alkaline hydrogen sulfite
1C 2 Lead dioxide and conc HCl
1C 3 Hydrogen sulfide gas and iodine solution
Quizzes 1C 1a, 1C 1b, 1C 1c

To check whether you have balanced a complex redox half-equation correctly: the change in oxidation number should equal the number of electrons transferred. In this equation the ON has changed from +7 to +4 and there are 3 electrons transferred.

Test yourself 1C Redox equations

Write ion-electron half-equations, and hence the full ionic equations, for the following redox reactions.

1 Sodium thiosulfate solution decolourises iodine solution.

2 Oxalic acid decolourises acidified potassium permanganate solution.

3 A brown solution forms when potassium bromate is added to acidified potassium iodide solution.

4 To balance this equation under alkaline conditions, first divide it into two half-equations.

$$TeO_3^{2-} + V^{4+} \longrightarrow Te + V^{5+}$$

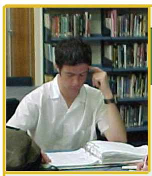
Key learning outcomes for Chapter 1

By now you should be able to:

1. Determine the oxidation number of any atom in a compound or ion and use oxidation numbers to identify the oxidised and reduced species in a given reaction.
2. Recall common oxidising and reducing agents, state the colours of the reagents and their products, and recall any other observations or conditions characteristic of their use.
3. Write ion-electron equations for oxidation and reduction half-reactions and combine the half-equations to give a balanced ionic equation.

EXAM QUESTIONS

Practice questions



Review questions for Chapter 1

1 For each of the following oxidation-reduction reactions, write the oxidation number for each element above its symbol, identify the oxidising agent and reducing agent, and state what you would observe during the reaction. A M

a $Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$

b $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

c $2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

2 Match the reagents below with the colours listed (colours may be used more than once, or not at all). A

red *orange* *brown* *yellow* *green* *blue* *purple* *colourless*

a $NO_2(g)$ b $I_2(aq)$ (in I^-) c $MnO_2(s)$

d $Cr_2O_7^{2-}(aq)$ e $S_4O_6^{2-}(aq)$ f $Cu^{2+}(aq)$

g $Cr^{3+}(aq)$ h $MnO_4^{2-}(aq)$ i $IO_3^-(aq)$

3 What substances are commonly detected using these reagents? A

a starch-iodide paper b potassium thiocyanate solution

c Ba^{2+} solution d starch solution

4 Write ion-electron half-equations, and hence the full ionic equations, for the following reactions.

a A sharp-smelling gas is evolved when concentrated hydrochloric acid is added to lead dioxide (PbO_2). A M E

b Copper sulfate solution is decolourised by iron wool. A M E

c A white precipitate of copper(I) iodide forms when copper sulfate solution reacts with potassium iodide solution. A M E

d Chlorine gas is bubbled through potassium bromide solution. **A M E**

e Potassium permanganate is added to alkaline sodium thiosulfate solution. **A M E**

5 A test for the nitrate ion is to mix the unknown sample with sodium hydroxide solution, add powdered aluminium metal, heat, and hold damp, red litmus paper above the test tube. The aluminium metal reacts with any nitrate present, producing ammonia gas which turns the litmus paper blue.

a Is aluminium acting as an oxidising or reducing agent in this reaction? Why? **A M**

b Complete these two redox half-equations *in alkaline conditions*, then combine them to make the complete ionic equation for this reaction: **M E**

NO_3^- $\longrightarrow$ NH_3

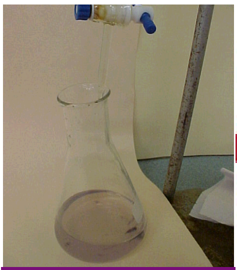
Al $\longrightarrow$ $[Al(OH)_4]^-$

6 What would you expect to *see* if: **A M**

a Chlorine gas was bubbled through a solution of potassium iodide (oxidising the iodide to iodine)?

b A copper electrode was left overnight in a beaker of silver nitrate solution?

c Filter paper soaked in acidified potassium dichromate solution was held in a stream of sulfur dioxide gas?



2

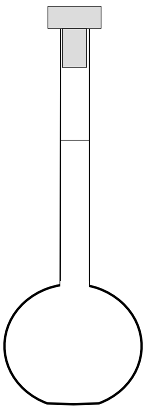
Volumetric analysis

Volumetric analysis

Volumetric analysis involves determining the volume of a solution of unknown concentration that is required to react completely with a known volume of a solution whose concentration is accurately known. From this result the concentration of the unknown solution is calculated. The process is also known as a **titration**.

Titrations

The equipment used for titrations is shown below.

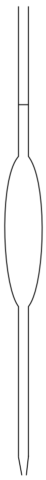


Volumetric flask

(Also called a standard flask.)
Used when making accurate concentrations of solutions.

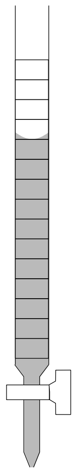
Each flask measures one volume accurately.

Volumetric flasks should be rinsed with distilled water before use.



Pipette

Used to measure accurate volumes of liquid. They come in sizes ranging from 1.0 mL to 100.0 mL, but 10.0 mL, 20.0 mL and 25.0 mL are the most common.
Liquid is drawn up past the mark and allowed to run back to the mark. It is then emptied into the reaction vessel.
The last drop of liquid is pulled out by touching the tip of the pipette to the wall of the vessel.
Pipettes should be rinsed before use with the solution they will contain.



Burette

Used to measure varying volumes of liquid.

Liquid level is measured before and after delivery and the volume used is calculated by subtraction.

Burettes should be rinsed before use with the solution they will contain.

Titration terms

- A **standard** solution is one whose concentration is accurately known.
- To **standardise** a solution is to do a titration to find out its concentration accurately.
- A **titre** is the volume of solution required for the reaction.
- The **equivalence point** is the point when the titration is over—when all of the compound in the conical flask has reacted.
- **Concordant** titres are those which ‘agree’—ideally those within 0.1 mL of each other.

Titration techniques

The reaction vessel for titrations is normally a conical flask (sometimes called an Erlenmeyer flask) which is easy to swirl. It may first be rinsed with distilled water. The first titre may be a trial run to find out approximately how much to use, while the following titres should be more accurate. You should aim to get three titres within 0.1 mL of each other. Make sure you swirl the flask as you run in liquid from the burette. Use a wash-bottle filled with distilled water to rinse any reagents off the sides of the flask. A white tile (or sheet of paper) under the flask will make it easier to see the end-point.

When calculating the average volume required, average *only your concordant titres* (i. e. your best three titres).

Concentration

There are three common ways the concentration of a solution is expressed: grams per litre (g L^{-1}), percentage (g/100 g or %) and moles per litre (mol L^{-1}). The first two are often used in a laboratory, and the third is important in chemical calculations. You need to be able to convert from one to the other. Use the relationships:

$$n = cV \quad \text{and} \quad n = \frac{m}{M}$$

where n = *amount* in moles, c = *concentration* in moles per litre, m = *mass* in grams, M = *molar mass* in grams per mole and V = *volume* in litres.

If the volume is quoted in millilitres, you will need to convert from mL into L. It is simplest to simply rewrite q mL as $q \times 10^{-3}$ L.

A word about calculations

During titration calculations there are usually two and sometimes three different reagents involved. It is very important that you indicate at all times which substance is meant when you calculate its amount or concentration or quote a volume. Likewise, always show the formula being used: it helps your teacher follow your calculation, and it also makes it far less likely that you will make a mistake. Finally, always include the *units* of any quantity you calculate.

Example 2.1 **Concentration of a solution (1)**

Calculate the concentration of a solution of sodium carbonate made by dissolving 1.47 g of Na_2CO_3 in distilled water and making the volume up to 250.0 mL.

$m(Na_2CO_3)$ = 1.47 g $\quad$ $M(Na_2CO_3)$ = 106 g mol^{-1}

$V(Na_2CO_3)$ = 250.0 mL or 250.0 × 10^{-3} L

$$n = \frac{m}{M}$$

$$n(Na_2CO_3) = \frac{1.47\ \text{g}}{106\ \text{g mol}^{-1}} = 0.013\,87\ \text{mol}$$

$$c = \frac{n}{V}$$

$$c(Na_2CO_3) = \frac{0.013\,87\ \text{mol}}{250.0 \times 10^{-3}\ \text{L}} = 0.0555\ \text{mol L}^{-1}$$

Example 2.2 **Concentration of a solution (2)**

What is the concentration, in g L^{-1}, of a 0.0200 mol L^{-1} $KMnO_4$ solution?

$n(KMnO_4)$ = 0.0200 mol L^{-1} $\quad$ $M(KMnO_4)$ = 158 g mol^{-1}

$V(KMnO_4)$ = 1.00 L

.

$$
\begin{aligned}
n &= cV \\
n(KMnO_4) &= 0.0200 \text{ mol L}^{-1} \times 1.00 \text{ L} \\
&= 0.0200 \text{ mol} \\
m &= nM \\
m(KMnO_4) &= 0.0200 \text{ mol} \times 158 \text{ g mol}^{-1} \\
&= 3.16 \text{ g}
\end{aligned}
$$

The concentration of the solution is 3.16 g L^{-1}

Primary standards

In a titration, a solution of known concentration is used to determine the concentration of an unknown solution. The first or **primary** standard solution must be made up by accurately weighing out powder, adding it to a volumetric flask, and making it up to volume with distilled water. The concentration of the solution can then be calculated accurately.

For our calculation to be accurate, it is necessary that we know *exactly* what goes into the flask. Compounds suitable as primary standards must:

- be pure
- not lose water of crystallisation on storage
- be stable in air and not pick up water or CO_2 on standing
- have a relatively large M so that weighing errors are minimal
- react quickly to completion.

Very few compounds have all of these properties. The ones we use are:

- oxalic acid, $(COOH)_2.2H_2O$, for acid-base and redox titrations
- anhydrous Na_2CO_3 for acid-base work
- $KBrO_3$ and KIO_3 for redox work.

Substances which are not suitable are:

- H_2SO_4 (absorbs water from the air)
- NaOH (absorbs water and CO_2 from the air)
- I_2, HCl and HNO_3 (volatile)
- $Na_2S_2O_3$ and hydrated Na_2CO_3 (lose water of crystallisation on storage)
- $KMnO_4$ (reduced by contaminants in the air and cannot be obtained pure enough)
- Fe^{2+} compounds (oxidised by the air).

PRACTICAL

2.1 P 155 — Preparation of standard iron(II) ammonium sulfate solution

REVISION

2A 1a — Volumetric analysis equipment
2A 1b — Titration techniques
2A 1c — Volumetric analysis key facts
2A 2 — Significant figures
Quizzes 2A 1, 2A 2

Test yourself 2A About titrations

1 Albert wanted to standardise some hydrochloric acid. He prepared a standard solution of sodium hydroxide by weighing out 4.000 g of solid NaOH into a conical flask, which he had rinsed with distilled water. He then added distilled water to the 100 mL mark and mixed well. He rinsed a burette with distilled water, added indicator and filled it with the sodium hydroxide solution. Then he rinsed another conical flask and a pipette with the hydrochloric acid solution and pipetted in 20.0 mL of hydrochloric acid. Then he did the titration.

Underline the mistakes Albert made, and explain what he should have done.

2 Convert 1.000 g L^{-1} Na_2CO_3 into mol L^{-1}. ______

______

3 What mass of KIO_3 should be dissolved in 250.0 mL to form a 0.200 mol L^{-1} solution?

______

______

4 Convert 1.80 mol L^{-1} H_2O_2 solution into g/100 mL (%). ______

______

5 It is important that you know how to use your calculator correctly.

a Write these calculator displays in standard form (eg 3.65×10^{-2}):

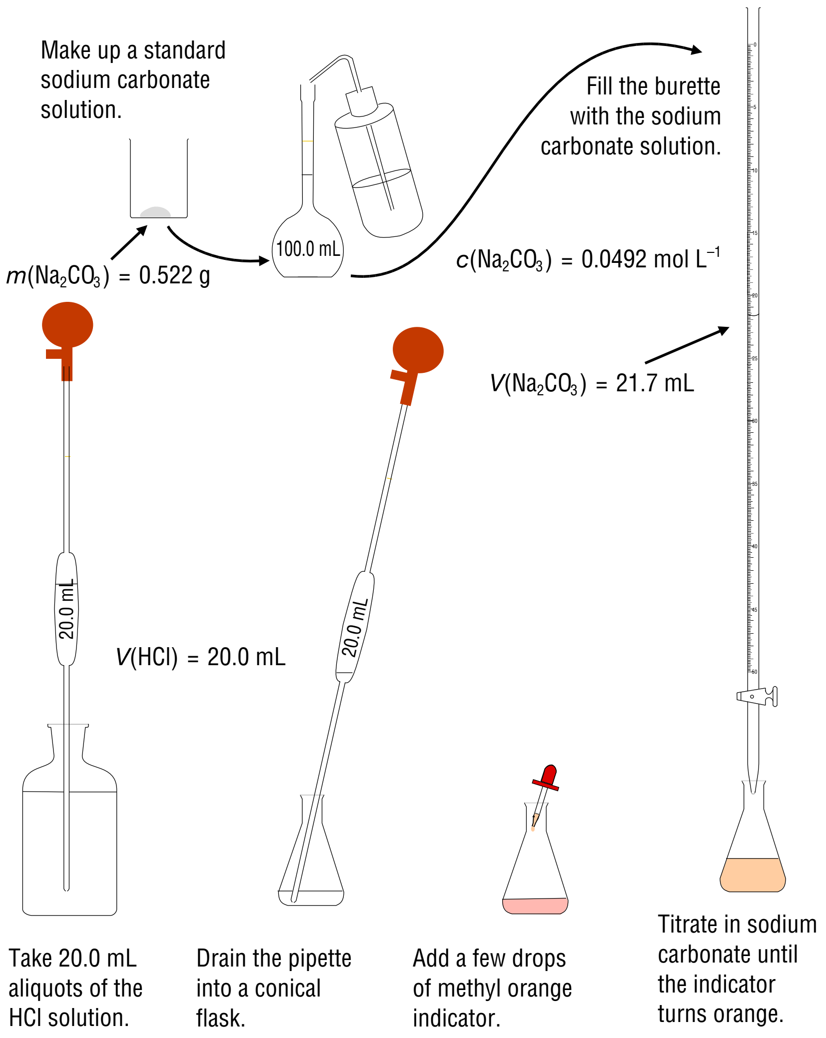
i 5.167 ^{08} ______ **ii** 1.7 $^{-04}$ ______ **iii** 0.084 $^{-15}$ ______

b Do these calculations on your calculator, quoting your answers in standard form to 3 significant figures.

i $\dfrac{39.14 \times 10^5}{7.02}$ = ______ **ii** $\dfrac{8.48 \times 10^{-4}}{37.4 \times 10^6}$ = ______

iii $\dfrac{(1.11 \times 10^{-2})^2}{(0.0278)^3}$ = ______ **iv** $\dfrac{42.7 \times 10^{-3}}{1.40 \times 10^{-4} \times 5.00 \times 10^7}$ = ______

An acid-base titration



Steps in titration calculations

In a titration we take a known amount of one reagent and find out how much of the other reagent it reacts with. The aim is to find the concentration or mass of that second reagent. The key to this calculation is the balanced equation for the reaction.

Known reagent → *n*(known) $\xrightarrow[\text{balanced equation}]{\text{Mole ratio from}}$ *n*(unknown) → Unknown reagent

The steps in titration calculations are:

1 Write a balanced equation for the reaction which occurs.
2 Calculate the amount, in moles, of the *known* substance.
3 Use the balanced equation to calculate the amount, in moles, of the *unknown* substance.
4 Calculate the concentration (or mass) of the unknown substance.

Mole ratios

Many students have difficulty working out the mole ratios for the reagents. The balanced equation for the reaction above is:

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

Na_2CO_3 is the *known* reagent, since we know both its concentration and the volume used. HCl is the *unknown* reagent. We need to write *n*(HCl) in terms of $n(Na_2CO_3)$:

$$n(\mathrm{HCl}) = ? \times n(\mathrm{Na_2CO_3})$$

To write the mole ratio:

1 Express the amount in moles as a mathematical expression as shown:

unknown on top
known at the bottom

$$\frac{n(\mathrm{HCl})}{n(\mathrm{Na_2CO_3})} = \frac{2}{1}$$

Numbers from balanced equation

2 Rearrange this expression, solving for the unknown:

$$n(\mathrm{HCl}) = 2 \times n(\mathrm{Na_2CO_3})$$

REVISION

2B 1 Mole ratios for titrations
2B 2 Concentration problems

Quizzes 2B 1, 2b 2a, 2B 2b

Example 2.3 A simple titration calculation

Calculate the concentration of hydrochloric acid if 20.0 mL of acid reacts with 21.7 mL of 0.0492 mol L^{-1} sodium carbonate solution.

It is helpful to summarise the key data first of all:

$V(\mathrm{HCl}) = 20.0$ mL $= 20.0 \times 10^{-3}$ L

$V(\mathrm{Na_2CO_3}) = 21.7$ mL $= 21.7 \times 10^{-3}$ L

$c(\mathrm{HCl}) = ?$

$c(\mathrm{Na_2CO_3}) = 0.0492$ mol L^{-1}

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

Data is accurate to 3 sig. fig.

$$\begin{aligned} n(\mathrm{Na_2CO_3}) &= cV \\ &= 0.0492 \text{ mol L}^{-1} \times 21.7 \times 10^{-3} \text{ L} \\ &= 1.068 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\mathrm{HCl}) &= 2 \times n(\mathrm{Na_2CO_3}) \\ &= 2 \times 1.068 \times 10^{-3} \text{ mol} \\ &= 2.136 \times 10^{-3} \text{ mol} \end{aligned}$$

Write down one more sig. fig. than the data provides, but leave all the numbers on the calculator.

$$\begin{aligned} c(\mathrm{HCl}) &= \frac{n}{V} \\ &= \frac{2.136 \times 10^{-3} \text{ mol}}{20.0 \times 10^{-3} \text{ L}} \\ &= 0.107 \text{ mol L}^{-1} \end{aligned}$$

Quote the final answer to the same accuracy as the data.

PRACTICAL

2.2 P 156 Standardising potassium permanganate solution

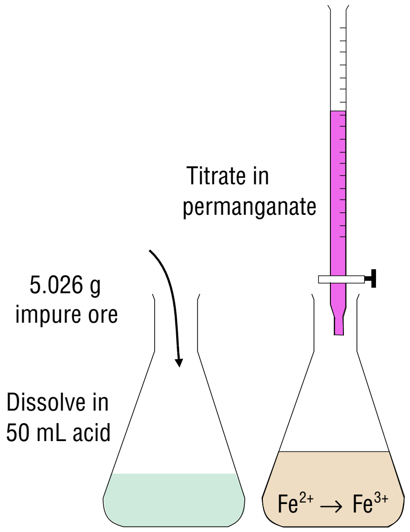
2.3 P 157 Standardising potassium permanganate solution with oxalic acid

Accuracy

Volumetric analysis is all about accuracy. Make sure you don't throw away the accuracy of the 4-figure balance, volumetric flask, pipette and burette by excessive rounding of your answers.

The accuracy of the data can also be helpful in helping to sort out which numbers are important and which ones are not. In the example below, the acid used to dissolve the iron is measured roughly (probably in a measuring cylinder) while the permanganate solution is added by burette. It may also help to sketch a diagram of the method.

Example 2.4 A more complex titration problem



A 5.026 g sample of an ore of iron was dissolved in 50 mL of dilute sulfuric acid. The iron was converted to Fe^{2+}(aq). The resulting solution was titrated against 0.064 02 mol L^{-1} $KMnO_4$ solution and required 30.68 mL to oxidise all the iron. Calculate the mass of iron in the ore and hence the percentage of iron in the ore.

The mass of the ore has been given accurately, but the ore is impure, so we won't need that number until the end of the problem. The key reaction is that between Fe^{2+} and MnO_4^-. It is done under acid conditions, so the MnO_4^- will be reduced to Mn^{2+}. We need to work out the amount of Fe^{2+} which reacted, first in moles, and then in grams.

$c(MnO_4^-)$ = 0.064 02 mol L^{-1} $\quad$ $n(Fe^{2+})$ = ?

$V(MnO_4^-)$ = 30.68 mL $\quad$ M(Fe) = 55.85 g mol^{-1}

= 30.68 × 10^{-3} L $\quad$ m(ore) = 5.026 g

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

$$\begin{aligned} n(MnO_4^-) &= cV \\ &= 0.064\,02 \text{ mol L}^{-1} \times 30.68 \times 10^{-3} \text{ L} \\ &= 1.9641 \times 10^{-3} \text{ mol} \end{aligned}$$

Known

Unknown on top

$$\frac{n(Fe^{2+})}{n(MnO_4^-)} = \frac{5}{1}$$

Known below

$$\begin{aligned} n(Fe^{2+}) &= 5 \times n(MnO_4^-) \\ &= 5 \times 1.9641 \times 10^{-3} \text{ mol} \\ &= 9.8207 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} m(\text{Fe}) &= nM \\ &= 9.8207 \times 10^{-3} \text{ mol} \times 55.85 \text{ g mol}^{-1} \\ &= 0.548\,48 \text{ g} \end{aligned}$$

$$\begin{aligned} \%(\text{Fe in ore}) &= \frac{\text{mass iron found}}{\text{mass of ore}} \times 100 \\ &= \frac{0.548\,48 \text{ g}}{5.026 \text{ g}} \times 100 \\ &= 10.91\% \end{aligned}$$

Titrations with two reactions

It is quite common with redox titrations to do two reactions. The most common involves an oxidising agent such as IO_3^- or OCl^- oxidising iodide to iodine, which is then reacted with sodium thiosulfate in a separate reaction. For these questions the relevant redox equations are usually supplied.

The hardest part of these calculations is working out what the mole ratio is when there are two equations to combine.

Example 2.5 A titration problem with two equations

A student prepared a 0.016 36 mol L^{-1} solution of $KBrO_3$, then took 25.0 mL samples of this solution, added 1 g of KI crystals and 15 mL dilute sulfuric acid, and titrated the liberated iodine against sodium thiosulfate solution. An average of 27.32 mL of thiosulfate were required. What is the concentration of the thiosulfate solution?

$$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3H_2O + 3I_2$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

$c(KBrO_3) = 0.016\ 36$ mol L^{-1} $\quad c(S_2O_3^{2-}) = ?$

$V(KBrO_3) = 25.0$ mL $= 25.0 \times 10^{-3}$ L $\quad V(S_2O_3^{2-}) = 27.32$ mL $= 27.32 \times 10^{-3}$ L

$$n(BrO_3^-) = cV = 0.016\ 36 \text{ mol L}^{-1} \times 25.0 \times 10^{-3} \text{ L} = 4.0900 \times 10^{-4} \text{ mol}$$

Unknown on top

$$\frac{n(S_2O_3^{2-})}{\cancel{n(I_2)}} \times \frac{\cancel{n(I_2)}}{n(BrO_3^-)} = \frac{2}{1} \times \frac{3}{1}$$

Numbers from balanced equation.

Known below

$$n(S_2O_3^{2-}) = 6 \times n(BrO_3^-) = 6 \times 4.090 \times 10^{-4} \text{ mol} = 2.454 \times 10^{-3} \text{ mol}$$

$$c(S_2O_3^{2-}) = \frac{n}{V} = \frac{2.454 \times 10^{-3} \text{ mol}}{27.32 \times 10^{-3} \text{ L}} = 0.0898 \text{ mol L}^{-1}$$

POWERPOINT

- 2B 1 Standardising potassium permanganate solution
- 2B 2 Oxalic acid and permanganate titration
- 2B 3 Ethanol and dichromate calculation
- 2B 4 Standardising thiosulfate (iodimetry)

Quizzes 2B 3a, 2B 3b

PRACTICAL

- 2.4 P 158 Standardising sodium thiosulfate solution
- 2.5 P 159 Standardising sodium thiosulfate using potassium iodate
- 2.6 P 160 Analysis of copper

Test yourself 2B Titration calculations

1 Oxalic acid can be used to standardise potassium permanganate solution. A student reacted 20.0 mL of 0.172 mol L^{-1} oxalic acid with potassium permanganate solution and obtained titres of 22.74 mL, 22.42 mL, 22.38 mL, 22.46 mL and 22.34 mL.

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

a What special conditions does this reaction require? ______

b Calculate the average volume of MnO_4^- required for the titration.

______

c Calculate the amount, in moles, of oxalic acid used.

______

______

______

d Calculate the amount, in moles, of potassium permanganate that reacted.

e Calculate the concentration of the potassium permanganate solution.

2 A *Consumer* scientist took 25.0 mL of household bleach and diluted it to 250.0 mL in a volumetric flask. She took 25.0 mL samples of this solution, added 1 g of potassium iodide powder and 15 mL of dilute sulfuric acid, then titrated the iodine liberated with 0.0964 mol L^{-1} sodium thiosulfate solution. An average of 25.3 mL of thiosulfate were required.

$$OCl^- + 2H^+ + 2I^- \longrightarrow I_2 + Cl^- + H_2O$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

a How would the endpoint of this titration be detected?

b Calculate the amount, in moles, of thiosulfate used in the reaction.

c Use the equations to calculate the amount, in moles, of OCl^- reacting.

d Calculate the concentration of OCl^- in the diluted sample, and hence in the original bleach.

e Express the concentration of OCl^- in the bleach as percentage of NaOCl (weight per volume).

Key learning outcomes for Chapter 2

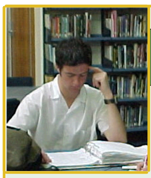
By now you should be able to:

1. State the characteristics of reagents suitable for use as primary standards in volumetric analysis.
2. Describe in detail these particular redox titrations, including any special conditions and how the end-point is detected:
   a. acidified permanganate with oxalic acid or with iron(II)
   b. acidified iodate (or bromate) with iodine
   c. thiosulfate with iodine
   d. copper(II) with iodine.
3. Carry out redox titrations with precision and accuracy.
4. Perform calculations based on titration data.

EXAM QUESTIONS

Practice questions

Sample examination papers



Review questions for Chapter 2

1 Calculate the mass of Na_2CO_3 required to make up 250.0 mL of a 0.0500 mol L^{-1} solution.
$M(Na_2CO_3) = 106$ g mol^{-1}. **A M**

2 A student weighed 0.714 g of impure sodium carbonate into a flask, dissolved it in water, added methyl orange indicator and titrated it against 0.107 mol L^{-1} hydrochloric acid. 41.3 mL of acid were required. Calculate the percentage purity of the sodium carbonate.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

A M E

3 A student was given 14.8 g of impure iron(II) sulfate, $FeSO_4.7H_2O$. He dissolved it in distilled water and made it up to 250.0 mL in a volumetric flask. He diluted this solution by taking 25.0 mL and making it up to 250.0 mL with water. Then he took 25.0 mL samples of this diluted solution, added 20 mL dilute sulfuric acid and then titrated it against 0.0100 mol L^{-1} potassium permanganate solution. An average of 8.7 mL of permanganate were required.

a How would the end-point of this titration be determined? **A**

b Write two ion-electron half-equations, and hence the balanced ionic equation, for this reaction. **A M**

c Calculate the concentration of Fe^{2+} in the diluted solution. **A M**

d Calculate the percentage purity of the iron(II) sulfate sample. **A M**

4 A hospital technician was checking the concentration of a hydrogen peroxide solution. She acidified 20.0 mL portions of the solution and titrated them against 0.104 mol L^{-1} potassium permanganate solution. An average of 13.2 mL were required.

$$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

a Calculate the amount, in moles, of $KMnO_4$ which reacted.

b Use the equation to calculate the amount, in moles, of H_2O_2 in the sample.

c Calculate the concentration of H_2O_2 in mol L^{-1} and in g L^{-1}. **A M (for a to c)**

5 Calculate the concentration of a sodium thiosulfate solution given the following information. **A M E**

$c(KIO_3) = 0.0153$ mol L^{-1} $V(KIO_3) = 20.0$ mL $V(S_2O_3^{2-}) = 17.8$ mL

$$IO_3^- + 6I^- + 6H^+ \longrightarrow I^- + 3H_2O + 3I_2$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

6 Brass is an alloy of copper. The percentage of copper in brass can be determined using the following method.

The brass is dissolved in concentrated nitric acid, which oxidises the Cu to Cu^{2+}. The solution is then made up to 250.0 mL with distilled water. 25.0 mL aliquots of this solution are pipetted into conical flasks. The excess acid is neutralised with sodium carbonate solution, and any excess carbonate removed with ethanoic acid. Excess potassium iodide solution is added:

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI(s) + I_2$$

and the iodine liberated is titrated with sodium thiosulfate solution:

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

In an analysis of brass following this method, Corina obtained the following results:

Mass of brass = 2.916 g, $c(S_2O_3^{2-}) = 0.115$ mol L^{-1}, titres (mL) = 25.54, 25.36, 24.90, 25.02, 24.88.

a Choose the most appropriate titres to use, and calculate the average $V(S_2O_3^{2-})$.

b Calculate the concentration of copper in the 250.0 mL solution.

c Calculate the mass of copper in the 250.0 mL solution, and hence the percentage of copper in the brass sample. $M(Cu) = 63.55$ g mol^{-1}. **A M E (for a to c)**

3 Electrochemistry

Electrochemistry

Electrochemistry is the chemistry of reactions that involve electron transfer.

In **spontaneous** reactions, electrons are released with energy that can be used in **electrochemical cells**. In **non-spontaneous** reactions, electrons have to be supplied with energy in order to produce chemicals that are wanted in **electrolytic cells** or **electrolysis.**

In both electrochemical and electrolytic cells the terms *anode* and *cathode* have the following meanings:

Anode: The electrode where **oxidation** is occurring.

Cathode: The electrode where **reduction** is occurring.

Anode and **oxidation** both start with vowels.
Cathode and **reduction** both start with consonants.

Electrochemical cells

If zinc powder is put into copper nitrate solution, a redox reaction occurs:

$$Zn(s) + Cu(NO_3)_2(aq) \longrightarrow Zn(NO_3)_2(aq) + Cu(s)$$

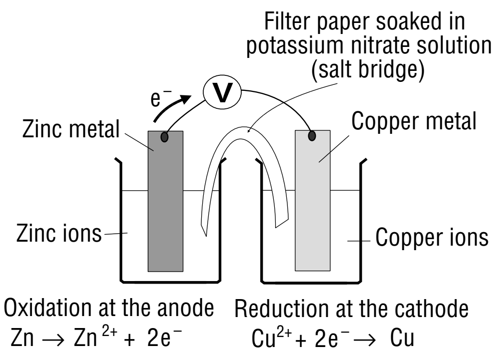
Energy is lost in the form of heat.

Since this is a redox reaction we can write it as two half-equations:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

These two half-equations can occur in separate beakers, provided there is a path for the electrons to travel (a wire), and a path for the ions to travel (a salt bridge).

REVISION
3A 1 Electrochemical cells key facts
Quiz 3A 1



A zinc electrode is placed in a beaker containing zinc nitrate solution. Beside it is a beaker containing a copper electrode in copper nitrate solution. A piece of filter paper soaked in potassium nitrate solution connects the beakers. Before the two electrodes are connected by wire, the metal atoms are in equilibrium with the metal ions in their respective beakers. The position of each equilibrium will depend on the temperature and concentration of each solution. When the wire connects the electrodes, electrons can flow from the zinc to the copper (shown by the voltmeter), leaving behind Zn^{2+} ions in the zinc beaker, and forming Cu atoms in the copper beaker. Potassium ions enter the copper beaker and nitrate ions enter the zinc beaker to keep the system electrically neutral.

The flow of electrons in the wire is an electric current. We call each beaker a **half-cell**. 200 years ago Humphry Davy did the first electrolysis experiments using electricity generated by piles of zinc and silver discs, separated by filter paper soaked in sulfuric acid. A series of cells connected together is called a **battery**.

PRACTICAL
3.1 P 161 Electrochemical cells 1

ENCOUNTER
3A John Frederic Daniell

Standard electrode potentials

The voltage produced by a given combination of half-cells depends on the willingness for one cell to lose electrons (be oxidised) and the other cell to gain electrons (be reduced). When two half-cells are connected with a voltmeter, chemists say they are measuring the **electromotive force** (**emf** or ***E***) of the cell. We can therefore use emf figures to compare the strength of oxidising and reducing agents.

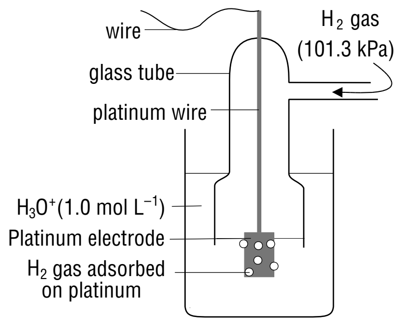
The equilibrium reaction in each half-cell is affected by concentration, so clearly the actual emf of a given combination of half-cells is affected by both the redox power of the reagents and the concentrations of their solutions. If we want to compare the strengths of oxidising and reducing agents we must test them under the same conditions of concentration, temperature and pressure.

POWERPOINT

3A Practical electrochemical cells

The standard half-cell

Oxidation will not occur without reduction, so it is impossible to find the emf of a single half-cell (eg Cl_2/Cl^-). If each half-cell is to have a meaningful number, we must measure the emf of that half-cell relative to a common half-cell. The **standard half-cell** is the H^+/H_2 half-cell—chosen because about half the redox reagents oxidise it, and the other half reduce it. This cell is defined as having an emf of zero. The standard hydrogen half-cell is shown on the left.



The standard hydrogen electrode.

Standard conditions for emf measurements are:

- All elements are in pure form
- Temperature 25 °C or 298 K
- All concentrations 1.0 mol L^{-1}
- Pressure of gases 1.0 atm or 101.3 kPa

For half-cells such as this one that have no solid conducting reagent that can act as an electrode, an electrode must be added. In this case platinum is chosen, but graphite is also used as an inert electrode for many half-cells.

Standard electrode potentials ($E°$) for each substance are found by putting the hydrogen half-cell on the right-hand side and connecting the positive terminal of the voltmeter to that cell. They are also called **standard reduction potentials**.

Cell diagrams

When an electrochemical cell is set up, and the voltage measured, the voltmeter will give a positive or negative value, depending on which way round the terminals of the voltmeter are connected. Obviously, if we are going to use the cell emf readings we have to know which way round the readings were taken. One way would be to draw a picture of the set-ups shown above, but that would be far too time-consuming and take up too much space. Instead, a special IUPAC convention (a set of agreed rules) is used to write a 'cell diagram' of the cell.

In the zinc/copper cell opposite, the zinc half-cell is on the left, and the copper half-cell is on the right. The cell diagram of this system is as follows:

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

It does not matter initially which electrode system is chosen for the left-hand or right-hand side but this convention is agreed to:

- a double line (//) represents the salt bridge or other device separating the two cells
- a single line (/) represents a change of phase, with the two phases in direct contact
- if two species are both present in a single solution, we separate them with a comma
- write the left-hand electrode first
- write the left-hand cell as oxidation (ie, write the reduced form first, then the oxidised form)
- write the right-hand side as reduction (ie, write the oxidised form first, then the reduced form)
- write the right-hand electrode last.

Reduction on the **R**ight
(both begin with **R**)
Oxidation on the Left

REVISION

3A 2a Assemble cell diagrams (1–2)

3A 2b Assemble cell reactions (1–2)

By writing the cell in this manner the direction of flow of electrons is from left to right.

The symbols (aq) and (s) meaning aqueous or solid phase are often omitted.

In cells where an inert electrode is used (eg H_2/H^+) we would have:

$$Pt(s) / H_2(g) / H^+(aq) // Ag^+(aq) / Ag(s)$$

Where two reagents are together in the same container a comma is used:

$$C(s) / MnO_4^-(aq), Mn^{2+}(aq) // Cl^-(aq) / Cl_2(g) / Pt(s)$$

Test yourself 3A Electrochemical cells

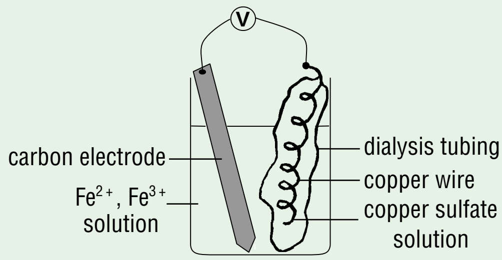
1 Draw a picture showing how to measure the electromotive force between the Fe/Fe^{2+} and Cu/Cu^{2+} half-cells.

2 What is the purpose of a salt bridge in electrochemical cells?

3 List the standard conditions for emf measurements.

4 Write the IUPAC cell diagram for the cell you drew in **1**.

5 Dialysis tubing is a semi-permeable membrane that allows the passage of ions in the same way as a salt bridge. The diagram on the right shows how dialysis tubing can be used to make an electrochemical cell. Draw the cell diagram for the system shown.



6 In the cell represented by the following cell diagram, oxidation occurs in the left-hand cell, and reduction in the right-hand cell.

$$Pt(s) / Cl^-(aq) / Cl_2(g) // MnO_4^-(aq), Mn^{2+}(aq) / C(s)$$

Write half-equations, and hence the full ionic equation, for the cell reaction represented by this cell.

Electromotive force of a cell

Standard electrode potentials ($E°$) can be used to calculate the emf for a given cell. The agreed convention is:

$$E°(\text{cell}) = E°(\text{RHE}) - E°(\text{LHE})$$

Note: Use the $E°$ values as printed in the tables—don't change the sign for the left-hand electrode just because the cell diagram has it written as oxidation.

If the electrodes are swapped round, so that the right-hand cell becomes the left-hand cell, then the voltage of the cell will remain the same, but its sign will be reversed (ie positive becomes negative).

If the $E°$(cell) for a given cell is *positive* then the reaction will occur as written in the cell diagram—with the cell on the left experiencing oxidation and the one on the right experiencing reduction. If the $E°$(cell) is *negative* then the opposite reactions will occur—oxidation on the right and reduction on the left.

Chemists say that when the E°(cell) is positive the reaction is spontaneous.

PRACTICAL

3.2 P 162 Electrochemical cells 2

Example 3.1 Calculating $E°$(cell)

Calculate the $E°$(cell) for the following cell, then write the overall cell equation.

$$Zn / Zn^{2+}//Cu^{2+} / Cu$$

$$E°(Zn^{2+} / Zn) = -0.76\ V \qquad E°(Cu^{2+} / Cu) = +0.34\ V$$

$$\begin{aligned} E°(\text{cell}) &= E°(\text{RHE}) - E°(\text{LHE}) \\ &= +0.34\ V - (-0.76\ V) \\ &= +1.10\ V \end{aligned}$$

Since the $E°$(cell) is positive, oxidation will occur on the left and reduction on the right.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Overall equation:

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

Predicting reactions

$E°$ values are often used to predict whether a reaction will occur spontaneously or not. We might want to do this because we want to build a new battery. More likely, we want to find a suitable oxidising or reducing agent for a chemical reaction (or simply get answers right in examinations!). There are several different ways to solve these problems.

A Write the cell diagram, then use
$$E°(\text{cell}) = E°(\text{RHE}) - E°(\text{LHE}).$$

B Write the two proposed half-equations together with their appropriate $E°$ values (remembering to reverse the sign of the $E°$ for the oxidation equation), then add the two equations together.

C Use the equation
$$E°(\text{cell}) = E°(\text{Red}) - E°(\text{Ox}).$$
Do *not* change the sign of the oxidation $E°$ — that's taken care of by the subtraction sign in the equation.

D Follow the patterns: the half-cell with the most negative $E°$ will be oxidised (oxidation number goes up), while the half-cell with the most positive $E°$ will be reduced (oxidation number goes down).

Method A is useful if you are faced with a cell diagram or beakers and salt bridges. Methods B and C are best when you are trying to decide whether a particular reaction will occur. Use method B if you are not confident in your ability to remember the formula correctly or to decide which reaction is oxidation and which reduction. Method C is faster if you can use it correctly. Method D is most useful when faced with a list of many potential half-cells.

POWERPOINT

3B Electrode potentials and predicting reactions

REVISION

3B 1 Calculating E(cell) from cell diagrams

3B 2 Predict cell reactions (1–4)

Quizzes 3B 1a, 3B 1b, 3B 2a, 3B 2b

Example 3.2 Predicting reactions using $E°$

$E°\ (Cu^{2+} / Cu) = +0.34\ V$ $E°\ (Fe^{3+}, Fe^{2+}) = +0.77\ V$

Will iron(III) (Fe^{3+}) ions be reduced by copper?

Using method B:

Fe^{3+} is to be reduced, so write the reduction equation and use the provided $E°$:

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E° = +0.77\ V$$

The other reactant is copper, which must be oxidised, so write the oxidation half-equation and reverse the $E°$:

$$Cu \longrightarrow Cu^{2+} + 2e^- \qquad E° = –0.34\ V$$

Add the two equations together

$$2Fe^{3+} + Cu \longrightarrow Cu^{2+} + 2Fe^{2+} \qquad E° = +0.43\ V$$

(Notice that we need $2Fe^{3+}$, but **do not** double the $E°$ value.)

Since the $E°$ is positive, the reaction is spontaneous and Fe^{3+} will be reduced by copper.

Using method C:

Reduction is to occur in the Fe^{3+}, Fe^{2+} cell, so oxidation occurs in the Cu^{2+}/Cu cell.

$$E°(cell) = E°(Red) – E°(Ox)$$
$$E°(cell) = +0.77\ V – 0.34\ V$$
$$= +0.43\ V$$

Since the $E°$ is positive, the reaction is spontaneous and Fe^{3+} will be reduced by copper.

Standard reduction potentials $E°$

MnO_4^-, Mn^{2+}	=	+1.51V
Au^{3+} / Au	=	+1.50 V
Cl_2 / Cl^-	=	+1.40 V
Cu^{2+} / CuI	=	+0.86 V
Fe^{3+} / Fe^{2+}	=	+0.77 V
I_2 / I^-	=	+0.54 V
Cu^{2+}/Cu	=	+0.34 V
Zn^{2+} / Zn	=	–0.76V
Fe^{2+}/Fe	=	–0.47 V
Al^{3+} / Al	=	–1.66 V
Mg^{2+} / Mg	=	–2.36 V
Na^+ / Na	=	–2.71 V

REVISION

3B 3 Reduction potential lists (1–2)

Quiz 3B 3

Example 3.3 Strongest and weakest

Use the standard reduction potentials in the margin to find:

a the strongest reductant

b the cation that is the strongest oxidant

c the element that is the weakest oxidant

The reduction potentials are written with the oxidants on the left and the reductants on the right.

a The strongest reductant is the species on the right with the most negative $E°$, which is Na.

b The strongest oxidant is the species on the left with the most positive $E°$. The cation on the left with the most positive $E°$ is Au^{3+}.

c The weakest oxidant will be the species on the left with the most negative $E°$. The element on the left with the most negative $E°$ is I_2.

Test yourself 3B Calculating $E°$(cell) and predicting reactions

1 Calculate the $E°$(cell) for the following cells using the standard reduction potentials in the margin above.

a $Mg / Mg^{2+} // Cu^{2+} / Cu$ **b** $Au / Au^{3+}//Al^{3+} / Al$ **c** $Pt / Fe^{2+}, Fe^{3+} // MnO_4^-, Mn^{2+} /C$

2 Write equations for the spontaneous reactions that occur in **1**.

3 Use the standard reduction potentials above to decide whether these reactions will take place.

a Will Cl^- ions reduce Al^{3+} to Al?

b Will Au^{3+} oxidise Cl^- to Cl_2?

c Will MnO_4^- oxidise I^- to I_2?

4 Use the standard reduction potentials opposite to find:

a the element that is the weakest reductant

b the strongest oxidant

c the anion that is the strongest reductant

d the element that is the strongest oxidant

e the cation that is the strongest reductant

f the weakest oxidant

Practical electrochemical cells

The lead-acid battery

The common car battery is a set of six electrochemical cells, each generating about 2 volts, connected in series. Each cell consists of alternating plates of lead and lead dioxide immersed in an aqueous solution of sulfuric acid which acts as the electrolyte. When the cell is supplying current, the lead metal is oxidised to Pb^{2+} and the PbO_2 is reduced to Pb^{2+}:

Anode (negative electrode):

$$Pb(s) - 2e^- \longrightarrow Pb^{2+}(aq)$$

Cathode (positive electrode):

$$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$$

The $Pb^{2+}(aq)$ produced reacts with the sulfuric acid to form a precipitate of lead sulfate which builds up on the plates:

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

The concentration of sulfuric acid in the cells decreases as the cell goes flat. Since the density of concentrated sulfuric acid is almost twice that of water (1.98 g/mL), a density measurement on the acid will give a good indication of how flat the battery is.

The feature which distinguishes the lead-acid battery from most other commercially available electrochemical cells is that the above reactions

PRACTICAL
3.3 P 164 The lead-acid cell

POWERPOINT
3C The lead-acid cell

ENCOUNTER

3C Vanadium flow battery

can be reversed. By passing an electric current back through the cell, the Pb^{2+} can be converted to Pb and PbO_2:

$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$$

A car battery provides the energy needed to start the engine. Once it is running the engine turns the alternator which generates electricity to recharge the battery. After many repeated charge-discharge cycles, some of the $PbSO_4$ falls to the bottom of the container and the H_2SO_4 concentration remains correspondingly low. The battery can no longer be recharged fully. It should be traded in for a new one, and the lead recovered and reused to make new batteries.

The dry cell (Leclanché cell)

The common dry cell or torch battery (non-rechargeable) consists of:

- a zinc case, which is the negative electrode
- a central graphite electrode, which is the positive electrode
- black manganese dioxide powder held around the central electrode in a paste
- an electrolyte paste of NH_4Cl, $ZnCl_2$ and water
- a physical separator between the electrodes, such as paper or muslin.

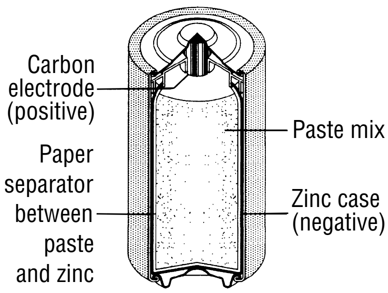
When the cell is generating electricity, the zinc is oxidised to $Zn^{2+}(aq)$ and the MnO_2 is reduced to the Mn(III) compound $Mn(OH)_3$.

Anode (negative electrode):

$$Zn(s) - 2e^- \longrightarrow Zn^{2+}(aq)$$

Cathode (positive electrode):

$$MnO_2(s) + NH_4^+(aq) + H_2O + e^- \longrightarrow Mn(OH)_3(s) + NH_3(aq)$$



The traditional 'zinc-carbon' cell has a central carbon electrode (+); a paste mix containing the $NH_4Cl/ZnCl_2$ electrolyte and the MnO_2 oxidising agent; a paper separator and a zinc case which acts as the negative electrode.

It is not possible to use acid as the electrolyte because the acid would dissolve the zinc. Instead acidic salts are used, which provide sufficient $H^+(aq)$ for the reduction of MnO_2 without dissolving the case. The ammonia that is produced forms a complex with the Zn^{2+}.

Alkaline dry cells are similar to ordinary dry cells, except that the electrolyte is alkaline because it contains KOH instead of NH_4Cl and the inner surface of the zinc case is roughened to give a larger surface area.

The cathode reaction is different:

$$2MnO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$$

Quiz 3C 1

The voltage of an alkaline dry cell is slightly lower than the standard cell (1.4 V rather than 1.5 V), but the voltage stays constant for the life of the cell, instead of gradually decreasing like the Leclanché cell.

Test yourself 3C Practical electrochemical cells

1 In the lead-acid battery, during discharge:

a what species is oxidised?__________ **b** what species is reduced?__________

2 Why does the density of the acid solution in a lead-acid battery decrease as the battery discharges?

____

____

3 In the common dry cell (Leclanché cell):

a what species is oxidised?__________ **b** what species is reduced?__________

c what is the function of the carbon?____________________

4 The silver-zinc cell is a rechargable cell in which the following (discharge) reactions occur:

$$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$$
$$Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$$

a Write the cell diagram for this cell.

b Write the overall equation for the reaction which occurs while the cell is charging.

Key learning outcomes for Chapter 3

By now you should be able to:

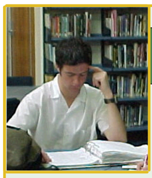
1 Show how any redox reaction can be separated into oxidation and reduction half-reactions.
2 Describe how a cell can be constructed using a redox reaction in which half-reactions are contained in half-cells joined by a salt bridge or separated by a porous partition.
3 Explain standard electrode potentials as the conventional voltage of a cell with a standard hydrogen electrode and recall standard conditions for a cell when standard electrode potentials are measured.
4 Describe and use the IUPAC convention for standard reduction potentials.
5 Use standard electrode potentials to compare the strengths of oxidising and reducing agents.
6 Calculate cell emf and predict any spontaneous redox reaction.
7 Realise that prediction of such a reaction does not extend to prediction of its rate of reaction.
8 Apply the principles of electrochemistry to practical electrochemical cells (details of specific electrochemical cells will be supplied).

REVISION

- Chemistry 3.2 and 3.3 key facts crossword
- Chemistry 3.2 and 3.3 key facts flip cards

EXAM QUESTIONS

- Practice questions
- Sample examination papers



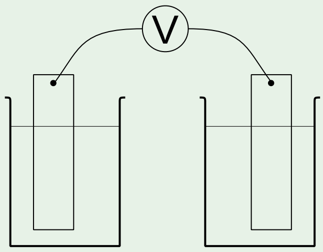
Review questions for Chapter 3

1 Students placed various metal electrodes in solutions of their metal ions, and measured the actual emf for different combinations of half-cells. They found their measured voltages were different from those calculated using book $E°$ values for those same half-cells. Suggest a reason for this difference. **A M**

2 An electrochemical cell with the following cell diagram is set up:

$$Cu / Cu^{2+} // Fe^{2+} / Fe$$

The voltage generated by this cell is –0.81 V. **A M E**



a Complete and label the drawing on the right.
b Show on the diagram the direction of electron flow.
c What would you observe in each beaker if this cell was left operating for a long time? Justify your answer.

3 Use the $E°$ values below to answer the following questions. Show working to support your answers

$E°(Cl_2 / Cl^-) = +1.36$ V $E°(S / H_2S) = +0.14$ V $E°(Fe^{3+}, Fe^{2+}) = +0.77$ V

$E°(MnO_4^-, Mn^{2+}) = +1.52$ V $E°(Cr_2O_7^{2-}, Cr^{3+}) = +1.33$ V **A M E**

a Is it likely that acidified potassium permanganate will oxidise sodium chloride solution to chlorine?

b Is it likely that an acidified iron(II) sulfate solution will reduce a suspension of sulfur to hydrogen sulfide?

c Will acidified potassium dichromate oxidise chloride ions to chlorine gas?

4 Use the $E°$ values on the right to answer the following questions.

$E°(Ag^+ / Ag)$	=	+0.80 V
$E°(Cr^{3+}, Cr^{2+})$	=	–0.41 V
$E°(Cu^{2+} / Cu)$	=	+0.34 V
$E°(Pb^{2+} / Pb)$	=	–0.13 V
$E°(Sn^{4+}, Sn^{2+})$	=	+0.15 V

a What species is the strongest oxidising agent? **A** ______

b What species is the strongest reducing agent? **A** ______

c Which metal is the weakest reducing agent? **A** ______

d The Cu^{2+} / Cu and Sn^{4+}, Sn^{2+} half-cells are connected by electrodes, wires and a salt bridge (copper on the left).

i Write the cell diagram for this set-up. **A M**

ii Calculate the emf for the cell. **A M**

iii Write half-equations for the reaction which occurs in each cell and hence write the overall cell equation. **A M**

5 A cell made from the I_2, I^- and Fe^{3+}, Fe^{2+} half-cells has the iodine half-cell on the left and includes electrodes made of platinum.

a Complete this cell diagram for the cell. **A M**

/ // /

b Explain the symbols used in the cell diagram you completed above. **A M**

c Explain why platinum electrodes are used with this cell. **A M**

6 Although potassium iodide is a white crystalline solid, many laboratory samples have a faint orange-yellow colour due to trace amounts of iodine, formed when iodide is oxidised by oxygen from the air. Use the data below to work out whether this reaction occurs in acidic or alkaline conditions. **A M E**

$$I_2 + 2e^- \longrightarrow 2I^- \qquad E° = +0.54\ V$$
$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad E° = +1.23\ V$$
$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad E° = +0.40\ V$$

7 The following reactions are relevant in a standard dry cell:

$$[Zn(NH_3)_4]^{2+}(aq) + 2e^- \longrightarrow Zn(s) + 4NH_3(aq) \qquad E° = -1.03\ V$$
$$NH_4^+(aq) + MnO_2(s) + H_2O(l) + e^- \longrightarrow Mn(OH)_3(aq) + NH_3(aq) \qquad E° = +1.00\ V$$

a Write a balanced equation for the overall cell reaction. **A M**

b Calculate the theoretical emf for this cell. **A M**

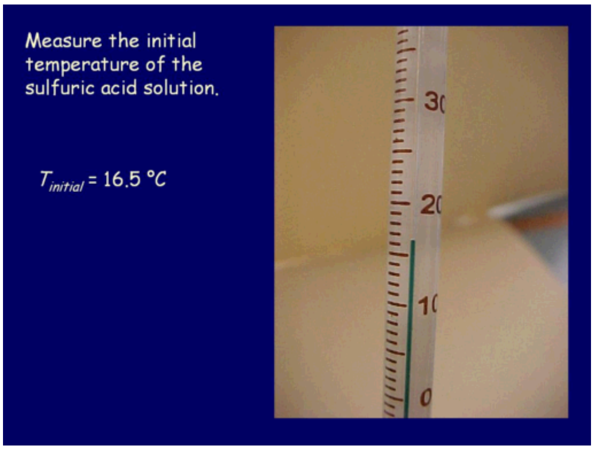
c The actual cell emf is 1.5 V because the cell is not operating under standard conditions. What are *standard conditions*? **A**

Section 2

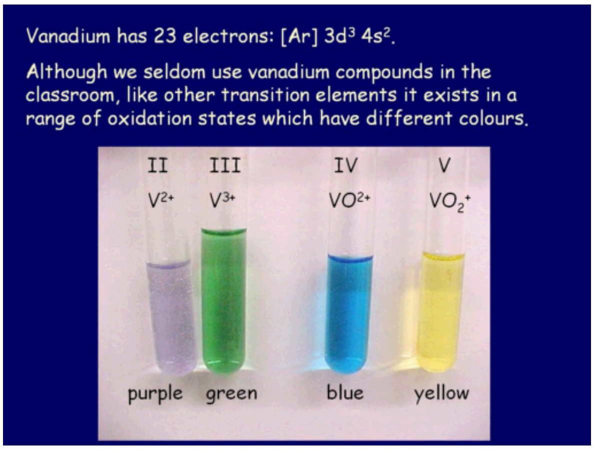
Particles and thermochemistry

Chemistry 3.4
5 credits

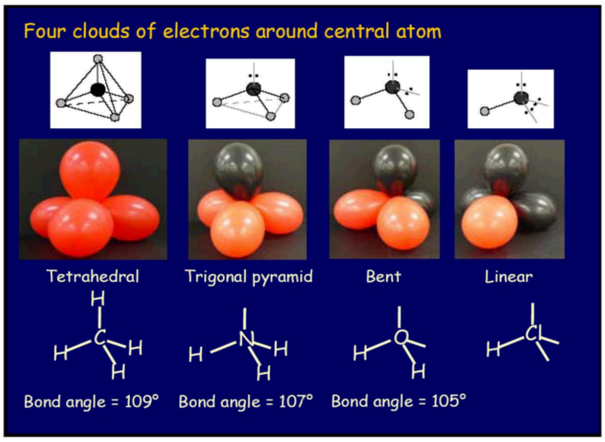
AS60780 External — Describe properties of particles and thermochemical principles



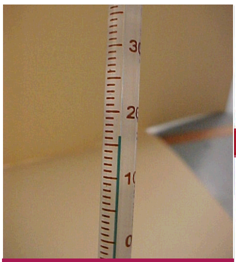
4 Thermochemistry



5 Atoms



6 Molecules and intermolecular forces



4

Thermochemistry

Thermochemistry

Exo- and endo-

A large number of chemical reactions produce heat during the reaction—the test tube gets hot. These reactions are described as **exothermic** reactions. A few reactions take in heat—the test tube gets colder. Such reactions are called **endothermic**.

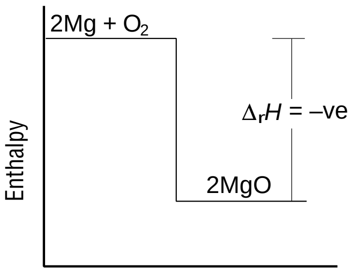
Exothermic: heat is given out
Endothermic: heat is taken in.

Remember ***en***ter/***en***dothermic = go in ***ex***it/***ex***othermic = go out.

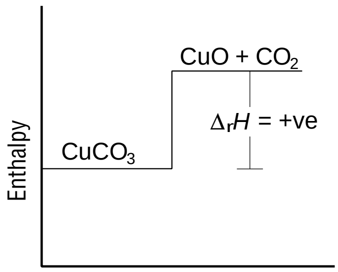
Enthalpy

When heat is produced or absorbed during reactions, the heat content or **enthalpy** (think 'entHalpy' for Heat) of the reactants and products must be different. Scientists use the symbol Δ ('delta') to mean *change in*, so ΔH means *change in enthalpy*, and $\Delta_r H$ means *change in enthalpy of reaction*.

$\Delta_r H$ *= enthalpy of products – enthalpy of reactants*



Exothermic reaction: reactants have more energy than products, $\Delta_r H$ is negative.



Endothermic reaction: reactants have less energy than products, $\Delta_r H$ is positive.

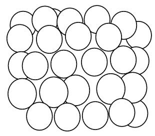
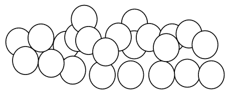
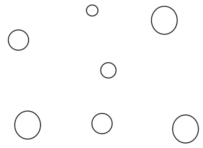
Heat is a form of energy, and the amount of energy released or absorbed depends on the amount of the reagents involved, so the unit of enthalpy is kJ mol^{-1}.

Enthalpy changes are particularly important in industrial chemistry. If a reaction is endothermic, the chemist needs to know how much fuel must be burnt (and paid for) for a given quantity of product formed. With exothermic reactions, enthalpy change is even more important because the rate of reactions increase with temperature, so exothermic reactions can speed up and become explosive if the temperature is not carefully controlled with suitable cooling systems.

Phases and phase changes

States of matter

One of the first things we learn about the world is the differences between solids, liquids and gases. Your Year 9 science notes probably contain this summary of the structure of matter:

Solid	Liquid	Gas
		
Particles are close together and held in fixed positions.	Particles are fairly close together but able to move freely throughout the liquid.	Particles are far apart and moving rapidly in all directions.

POWERPOINT
4A Particle theory

It doesn't matter whether the 'particles' are atoms, ions or molecules, the particles in solids are always in a fixed pattern, while in liquids they are free to move, and in gases they are far apart and moving quickly.

Effect of heat on matter

Heat versus temperature

Also in your junior science classes you will have discovered that hot water has a greater volume than cold water, that solids and gases also expand when heated and contract when cooled and that dye spreads throughout hot water much more rapidly than through cold water. From investigations like these we conclude that particles move more rapidly when heated.

It is important not to confuse *heat* with *temperature*.

- ***Heat is the sum of the kinetic energies of all the particles in a sample.***
- ***Temperature is proportional to the average kinetic energy of the particles.***

The particles in a spark may have a high average kinetic energy (ie a high temperature), but since there are few particles the heat doesn't burn you.

Specific heat capacity

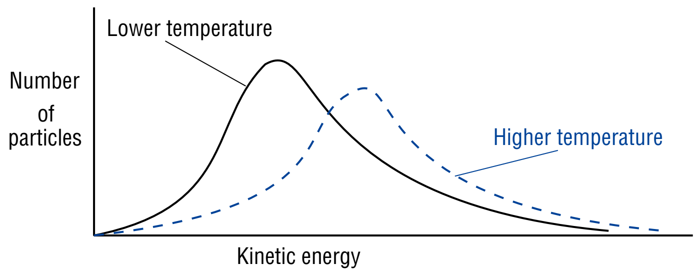
When you go to the beach on a hot, sunny day, the sand can be very hot while the water in a rock pool is only warm. It takes much more energy to raise the temperature of water than to heat the same mass of sand. We say water has a high **specific heat capacity**.

A substance's specific heat capacity, c, is the amount of heat energy required to raise the temperature of 1.00 g of the substance by 1.00 K (= 1.00 °C).

Water has an unusually high specific heat capacity of 4.18 J g^{-1} K^{-1}. Most metals have specific heat capacities of between 0.3 and 1.0 J g^{-1} K^{-1}. Published data normally relates to heating the substance from room temperature, since specific heat capacity changes slightly with temperature and relates only to temperature changes within a phase (eg heating a solid).

Boltzmann and absolute temperature

A physicist called Ludwig Boltzmann studied the kinetic energy of particles in more detail. He showed that not all particles in a sample at a particular temperature have the same kinetic energy.

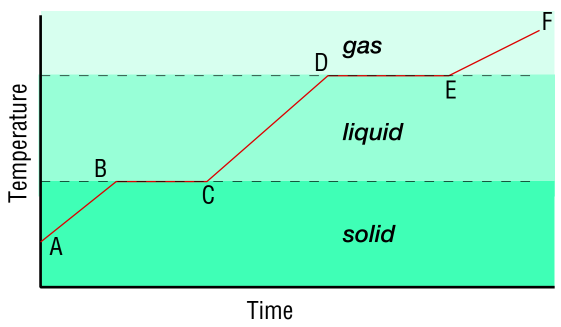


The **absolute temperature** is temperature on the Kelvin scale. 0 °C = 273 K. A doubling of the absolute temperature from 200 K to 400 K (–73 °C to 127 °C), will double the kinetic energy of the particles. Going from 10 °C to 20 °C will *not* double the kinetic energy of the particles.

A consequence of Boltzmann's discovery is that at absolute zero (0 K), the kinetic energy of the particles is zero.

Heating or cooling curves

Any pure substance, on heating, undergoes a characteristic pattern of periods of constant temperature and temperature increase. This can be observed by melting ice, boiling water, or heating naphthalene. If the temperature changes are plotted against time for a constant rate of heating, any pure solid will produce the following graph.



- Regions of the graph where the temperature increases (A to B, C to D and E to F) represent periods when the *kinetic* energy of the particles is increasing. The particles in the solid vibrate more quickly, and the particles in the liquid and gas move around more quickly.
- Where the temperature remains constant (B to C and D to E) the chemical *potential* energy of the particles is increasing. During this time the substance is changing phase—from solid to liquid at B to C, and from liquid to gas at D to E. The energy increase allows the particles to partially (as the solid melts) or fully (when the liquid boils) overcome the attractive forces between them.

REVISION
4A 1a Interpreting a data table

ENCOUNTER
4A Using phase change materials

Fusion and vaporisation

Molar heat of fusion

The energy required to change one mole of a substance from a solid to a liquid at the melting point is called the **molar heat of fusion ($\Delta_{fus}H$)**.

H_2O(solid at 0 °C) $\longrightarrow$ H_2O(liquid at 0 °C) $\Delta_{fus}H = 6.0$ kJ mol^{-1}

The molar heat of fusion provides a measure of the strength of the force holding the particles together in the solid phase.

PRACTICAL
4.1 P 165 Heat and phase changes

Molar heat of vaporisation

The energy required to change one mole of a substance from a liquid to a gas at the boiling point is called the **molar heat of vaporisation ($\Delta_{vap}H$)**.

H_2O(liquid at 100 °C) $\longrightarrow$ H_2O(gas at 100 °C) $\Delta_{vap}H = 41.0$ kJ mol^{-1}

Molar heat of vaporisation indicates the strength of the force between particles in the liquid phase.

REVISION

4A 1b Boiling points: elements

4A 1c Boiling points: compounds

4A 1d Phase change key facts

Quizzes 4A 1, 4A 2

Relationships between $\Delta_{vap}H$, $\Delta_{fus}H$, melting and boiling points

$\Delta_{vap}H$ is always greater than $\Delta_{fus}H$ because it takes more energy to completely overcome the attractive forces between the particles (to allow them to go anywhere, as in a gas) than to partially overcome those forces (as in liquids, in which the particles are still held close together). The greater the $\Delta_{fus}H$, the higher the melting point, since when particles are held together more firmly they will require greater kinetic energy before they can begin to overcome the attractive forces between them. Similarly, the greater the $\Delta_{vap}H$, the higher the boiling point. Hence

the melting and boiling points of a substance indicate the strength of the forces between the particles in the solid or liquid phase.

Test yourself 4A Thermochemical principles and phase changes

1 How can you tell the difference between exothermic and endothermic reactions from:

a the temperature of the mixture before and after the reaction? ______

b the enthalpies of the reactants and product? ______

______

c the $\Delta_r H$? ______

2 What evidence have you that the particles in solids are much closer together than those in gases?

______

______

3 Describe an experiment which shows that particles in a liquid move more rapidly when heated than when cold.

______

______

4 Why does a drink stay cold while it contains ice cubes? ______

______

5 **a** Calculate the energy released by a hot water bottle containing 1.5 L (1500 g) of water at 90 °C as it cools down to 25 °C. Specific heat capacity of water = 4.18 J g^{-1} $°C^{-1}$.

______

______

______

b 30.0 g of water are placed in one beaker, and 30.0 g of ethanol in another, identical, beaker. Both liquids start at 20.0 °C and are heated on the same hotplate for 3 minutes. The water reaches a temperature of 42.0 °C. What is the final temperature of the ethanol? Specific heat capacity of ethanol = 2.46 J g^{-1} $°C^{-1}$.

______

______

______

______

______

______

6 Define the term *molar heat of fusion*.

7 $\Delta_{vap}H(NH_3)$ = 5.65 kJ mol^{-1} and its boiling point is –33 °C. Write a thermodynamic equation for this data.

8 Another quantity, symbolised $\Delta_{sub}H$, can be estimated by adding the $\Delta_{fus}H$ and $\Delta_{vap}H$ together. What is $\Delta_{sub}H$? Give a reason for your answer.

9 Use your knowledge of the properties of these substances to place them in order of $\Delta_{vap}H$ (lowest to highest):

Br_2 C $C_6H_{12}O_6$ CO_2 Fe Hg I_2 MgO N_2 Na NaCl

Data book enthalpies

We can't measure enthalpies of specific reactants or products directly: all we can measure are enthalpy changes. Rather than list the enthalpy change for every possible chemical reaction, data books list the standard enthalpy of combustion and/or the standard enthalpy of formation for compounds. These figures can be used to calculate the enthalpy change for other reactions.

$\Delta_c H°$—Standard enthalpy (heat) of combustion

The standard enthalpy of combustion is the enthalpy change when one mole of the substance is completely burnt, with all reactants and products in their standard states.

Standard states are the states at room temperature (25° C) and pressure—that is, oxygen is O_2(g) and water is H_2O(l) (even though the water forms as a gas first). Since we must start with one mole of the reactant, the equation may end up with fractional co-efficients (numbers) when it is balanced:

$C_2H_6(g) + 3½O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta_c H° = -1557$ kJ mol^{-1}

Heats of combustion are *always* exothermic.

$\Delta_f H°$—Standard enthalpy (heat) of formation

The standard enthalpy of formation of a compound is the enthalpy change when one mole of the substance is formed from its elements, with all reactants and products in their standard states.

Sometimes the equations for enthalpies of formation look rather strange—no-one would really make ethanol by shaking carbon, hydrogen and oxygen together in a test tube!

$2C(s) + 3H_2(g) + ½O_2(g) \longrightarrow C_2H_5OH(l) \quad \Delta_f H° = -278$ kJ mol^{-1}

Data tables list heats of formation for compounds, but not for elements. Can you see why, by looking at the definition again? If we wanted the heat of formation for oxygen—O_2(g), we'd have to start with O_2(g), so the enthalpy change would be zero.

The standard enthalpy of formation for all elements is zero.

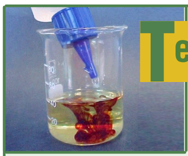
Heats of formation may be exothermic or endothermic, depending on the compound.

REVISION

4B 1a Assemble heat of combustion

4B 1b Assemble heat of formation

Quiz 4B 1



Test yourself 4B Data book enthalpies

1 Define the term *standard enthalpy of combustion*.

2 State why it is very important to include state symbols in all thermochemical equations.

3 Write equations for the enthalpies of combustion of:

a ethanol (C_2H_5OH)

b hydrogen

4 Define the term *standard enthalpy of formation*.

5 Write equations for the enthalpy of formation of:

a sodium chloride

b $CH_3OH(l)$

6 When would $\Delta_f H$ for an element not be zero? Explain your answer.

POWERPOINT

4C Determining enthalpy experimentally

PRACTICAL

4.2 P 166 Heats of combustion

4.3 P 168 Finding the enthalpy change for redox reactions

Calculating enthalpy

1 From experimental data

Determining the enthalpy change for test tube reactions is a relatively simple process, provided the system is closed (so that no heat is lost). Sometimes the reaction is done in a container which is surrounded by water. More usually at school, one of the reagents is a dilute aqueous solution, and we measure the temperature change of this solution which is assumed to have the same specific heat capacity as pure water. Remember that at room temperature 1.0 mL of water has a mass of 1.0 g, so for dilute aqueous solutions you can assume that 100 mL of solution has the same specific heat capacity as 100 g of water.

The method is:

1 Measure the temperature change for a known mass of water.

2 Calculate the energy absorbed by the water, using the specific heat capacity of water (4.18 J $°C^{-1}$ g^{-1}).

3 Calculate the energy absorbed or released per mole of reactants.

Example 4.1 Calculating enthalpy from experimental data

When 50.0 mL of 2.0 mol L^{-1} sodium hydroxide solution neutralised 50.0 mL of 2.0 mol L^{-1} hydrochloric acid solution, the temperature of the solution rose from 21 °C to 35 °C. Calculate the heat of the reaction assuming 1.0 mL of the combined solution required 4.2 J of energy to raise its temperature by 1 °C.

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Calculate the temperature change.

$$\text{Temperature change} = 35\ °C - 21\ °C = 14\ °C.$$

Calculate the energy change.

$$m(\text{water}) = 100.0\ \text{g} \quad \Delta T = 14\ °C \quad s = 4.2\ \text{J g}^{-1}\ °C^{-1}$$

$$\begin{aligned}\Delta E &= m(\text{water}) \times \Delta T \times s\\ &= 100\ \text{g} \times 14\ °C \times 4.2\ \text{J g}^{-1}\ °C^{-1}\\ &= 5880\ \text{J}\\ &= 5.9\ \text{kJ (2 sig fig)}\end{aligned}$$

Calculate the enthalpy change in kJ mol^{-1}

$V(\text{NaOH}) = 50.0$ mL $\quad c(\text{NaOH}) = 2.0$ mol L^{-1} $\quad n(\text{NaOH}) = ?$

$$\begin{aligned}n(\text{NaOH}) &= \frac{c\,V}{1000}\\ &= \frac{2.0\ \text{mol L}^{-1} \times 50.0\ \text{mL}}{1000}\\ &= 0.1\ \text{mol}\end{aligned}$$

$$\begin{aligned}\Delta H(\text{reaction}) &= \frac{\Delta E}{n}\\ &= \frac{5.9\ \text{kJ}}{0.1\ \text{mol}}\\ &= 59\ \text{kJ mol}^{-1}\end{aligned}$$

Write the thermochemical equation, including the appropriate sign for the ΔH.

The temperature *increased* (by 14 °C) so the ΔH is *negative*.

$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) \quad \Delta H = -59$ kJ mol^{-1}

- Many students make the mistake of trying to calculate the energy change by using the mass of one of the reagents, rather than the mass of water (or aqueous solution) absorbing the energy.

2 Calculating enthalpy from heats of formation

If we know the standard enthalpies of formation for all the compounds in a given reaction, we can calculate the enthalpy of reaction using the following formula:

$$\Delta_r H° = \Sigma\Delta_f H°(\text{products}) - \Sigma\Delta_f H°(\text{reactants})$$

(the symbol Σ means ‘sum of’).

These calculations are relatively straight-forward, providing you remember the following:

- the formula only works if the heats of *formation* for all the compounds are used.
- set your work out very carefully, paying close attention to the + and – signs.

If you have time during a test or exam, it is probably a good idea to repeat the calculation just to make sure you haven’t made an arithmetical error.

If you don't like using this formula for calculating enthalpies of reaction from heats of formation, you can use the Hess's law method on the next page instead.

Example 4.2 $\Delta_r H°$ from $\Delta_f H°$

Calculate $\Delta_r H°$ for the highly exothermic 'thermite' reaction

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr(s) + Al_2O_3(s)$$

Given $\Delta_f H°$ (Cr_2O_3) = –1128.4 kJ mol^{-1}

$\Delta_f H°$ (Al_2O_3) = –1669.3 kJ mol^{-1}

$\Delta_f H°(Al)$ and $\Delta_f H°(Cr)$ are both zero because they are elements in their standard states so:

$$\begin{aligned}\Delta_r H° &= \Sigma\Delta_f H°(\text{products}) - \Sigma\Delta_f H°(\text{reactants})\\ &= [2\Delta_f H°(Cr) + \Delta_f H°(Al_2O_3)] - [\Delta_f H°(Cr_2O_3) + 2\Delta_f H°(Al)]\\ &= [0 + (-1669.3 \text{ kJ mol}^{-1})] - [(-1128.4 \text{ kJ mol}^{-1}) + 0]\\ &= -540.9 \text{ kJ mol}^{-1}\end{aligned}$$

Test yourself 4C Thermochemical calculations (1)

1 Calculate the $\Delta_r H$ for the exothermic reaction between zinc powder and excess silver nitrate solution given the following data.

$m(Zn)$ = 0.250 g $M(Zn)$ = 65.4 g mol^{-1} $V(AgNO_3)$ = 100.0 mL ΔT = 18.0 °C s = 4.18 J g^{-1} °C^{-1}

$$Zn(s) + 2AgNO_3(aq) \longrightarrow 2Ag(s) + Zn(NO_3)_2(aq)$$

2 Calculate the enthalpy of the reactions below using the enthalpies of formation provided.

a $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

$\Delta_f H°$ $(CaCO_3(s))$ = –1207 kJ mol^{-1} $\Delta_f H°$ $(CaO(s))$ = –635.5 kJ mol^{-1} $\Delta_f H°$ $(CO_2(g))$ = –393 kJ mol^{-1}

b $4NH_3(g) + 5O_2(g) \longrightarrow 6H_2O(g) + 4NO(g)$

$\Delta_f H°$ $(NH_3(g))$ = –46.11 kJ mol^{-1} $\Delta_f H°$ $(NO(g))$ = 90.25 kJ mol^{-1}

$\Delta_f H°$ $(H_2O(g))$ = –241.8 kJ mol^{-1}

3 Janine was investigating the reaction between zinc powder and copper sulfate solution:

$$Zn(s) + CuSO_4(aq) \longrightarrow Cu(s) + ZnSO_4(aq)$$

She wasn't quite sure how to do the calculation, so she recorded the following data:

$M(Zn)$ = 65.4 g mol^{-1}	$M(CuSO_4.5H_2O)$ = 249.5 g mol^{-1}	Room temperature = 17.5 °C
$m(Zn)$ = 3.17 g	$c(CuSO_4)$ = 0.125 mol L^{-1}	$T_{initial}$ = 16.0 °C
	$V(CuSO_4)$ = 100.0 mL	T_{final} = 20.5 °C

She noticed that after the reaction the liquid in the styrofoam cup was colourless, and that as well as the copper precipitate there was unreacted zinc in the cup.

Her teacher told her that the heat capacity of the liquid would be 4.18 J g^{-1} °C^{-1}.

a For which reagent (Zn or $CuSO_4$) do you know the exact amount (in moles) which reacted? Give a reason for your answer.

b Calculate the ΔH for the reaction between zinc and copper sulfate in kJ mol^{-1}.

3 Hess's law

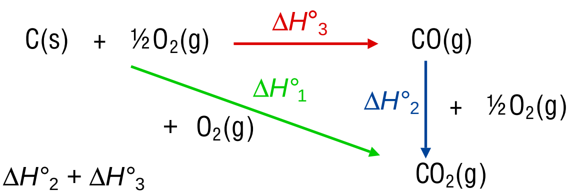
The distance between your home and school is the same, no matter what route you use to get there. Likewise, the enthalpy change for a given chemical reaction is independent of the steps taken between reactants and products. This principle is called Hess's law. More formally it states that:

the enthalpy change for a reaction is independent of the way in which a reaction proceeds and depends only on the initial conditions of the reactants and the final conditions of the products.

PRACTICAL

4.4 P 170 Hess's law: the law of heat summation

Hess's law can be illustrated with the following:



$\Delta H°_1 = \Delta H°_2 + \Delta H°_3$

In practice, it is impossible to measure the value of $\Delta H°_3$ (the heat of formation of CO(g)) directly as some CO_2(g) is always formed as a by-product. However we can calculate it using the principle of Hess's law.

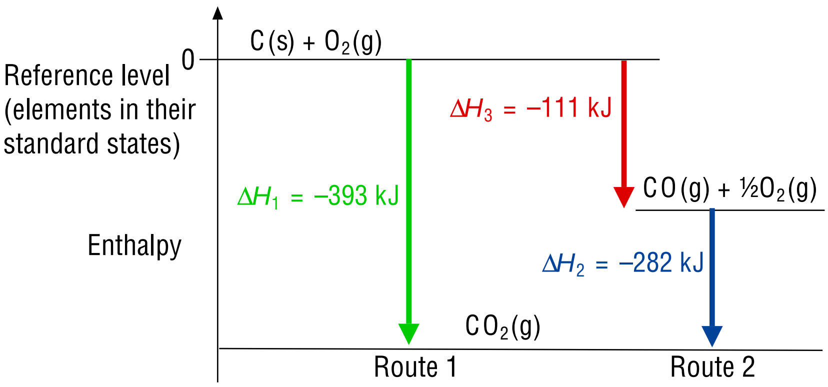
Given $\Delta H°_1 = -393$ kJ mol^{-1} and $\Delta H°_2 = -282$ kJ mol^{-1}

$\Delta H°_3 = \Delta H°_1 - \Delta H°_2$

$\Delta H°_3 = -393 - (-282)$

$= -111$ kJ mol^{-1}

This relationship can also be seen on the following diagram.



As a result of this principle of conservation of energy,

chemical reactions and their corresponding ΔH values can be added, subtracted and multiplied as if they were algebraic equations.

Solving problems using Hess's Law

1 Write the data in the form of equations.
2 Rewrite the equations to give the desired species on the correct side of the equation. If the reaction must be reversed (perhaps because we require a species to be a reactant and not a product), then the sign of the ΔH must also be reversed.
3 Add the equations, and the ΔH, together.

Example 4.3 Hess's law calculation

Calculate the heat of formation of $CS_2(l)$ given that the heats of combustion of carbon, sulfur and carbon disulfide are –393, –297 and –1007 kJ mol^{-1} respectively. (Sulfur burns to SO_2 in oxygen.)

Write the data given in the form of equations.

(1) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393$ kJ mol^{-1}
(2) $S(s) + O_2(g) \longrightarrow SO_2(g) \quad \Delta H = -297$ kJ mol^{-1}
(3) $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \quad \Delta H = -1007$ kJ mol^{-1}

The equation we are looking for is:

$$C(s) + 2S(s) \longrightarrow CS_2(l)$$

Rewrite the equations to give the desired species on the correct side of the equation.

(1) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393$ kJ mol^{-1}
(2) $2S(s) + 2O_2(g) \longrightarrow 2SO_2(g) \quad \Delta H = 2 \times -297$ kJ mol^{-1}
(3) $CO_2(g) + 2SO_2(g) \longrightarrow CS_2(l) + 3O_2(g) \quad \Delta H = +1007$ kJ mol^{-1}

Add the equations, and the ΔH, together:

(1) $C(s) + \cancel{O_2(g)} \longrightarrow \cancel{CO_2(g)} \quad \Delta H = -393$ kJ mol^{-1}
(2) $2S(s) + \cancel{2O_2(g)} \longrightarrow \cancel{2SO_2(g)} \quad \Delta H = 2 \times -297$ kJ mol^{-1}
(3) $\cancel{CO_2(g)} + \cancel{2SO_2(g)} \longrightarrow CS_2(l) + \cancel{3O_2(g)} \quad \Delta H = +1007$ kJ mol^{-1}

$$C(s) + 2S(s) \longrightarrow CS_2(l) \quad \Delta H = +20 \text{ kJ mol}^{-1}$$

Thus the $\Delta_f H°$ ($CS_2(l)$) is +20 kJ mol^{-1}

POWERPOINT

4D 1 Hess's law calculations

Quizzes 4D 1a, 4D 1b

If you <u>don't</u> find that all the extra parts of the equations cancel out, leaving you with only those bits you need, then you've made a mistake. Go back and find it.

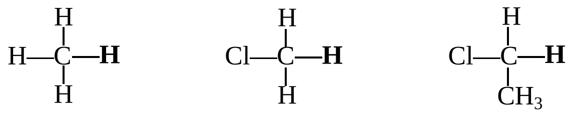
4 Bond energies

Bond energy is a measure of intra-molecular bond strength in a covalent molecule.

$$AB(g) \longrightarrow A(g) + B(g)$$

Bond energy is the energy required to break one mole of a particular bond ***when the reactants and products are in the gaseous state***. Since bonds are being broken, ΔH for the reaction is always positive.

The exact value of the C—H bond depends on the environment it is in:



so the bond energies given in data books are **average** bond energies.

Notice that the bond energy equations have all species present as gases. This is different from most other enthalpy data in which species are in their standard states.

Also note that the products are atoms, not ions.

ENCOUNTER

4D Atomic hydrogen welding

Bond energy calculations

A chemical reaction is a series of bond breaking processes (ΔH positive) and bond making processes (ΔH negative). We can estimate the enthalpy of a chemical reaction by adding the positive bond energies for those bonds which are broken to the negative bond energies for those bonds which are made.

Example 4.4 Enthalpy calculation using bond energies

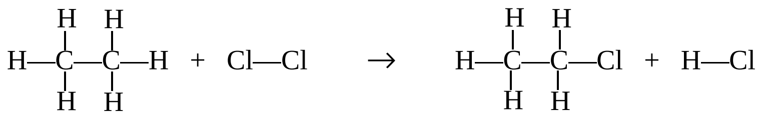
Calculate the heat of reaction for the following:

$$C_2H_6(g) + Cl_2(g) \longrightarrow C_2H_5Cl(g) + HCl(g)$$

given the following bond energies:

C—H	413 kJ mol^{-1}	Cl—Cl	242 kJ mol^{-1}
C—Cl	339 kJ mol^{-1}	H—Cl	431 kJ mol^{-1}

This kind of problem is simple once you write out the equation using graphic formulae, with every bond shown.



Bond breaking (ΔH +)		Bond making (ΔH –)	
C—H	+413 kJ mol^{-1}	C—Cl	–339 kJ mol^{-1}
Cl—Cl	+242 kJ mol^{-1}	H—Cl	–431 kJ mol^{-1}

$$\Delta H = +413 + 242 - 339 - 431$$
$$= -115 \text{ kJ mol}^{-1}$$

Note: In multiple bonds such as O=O we do not double the bond energy for the single bond (O—O). The double bond is a different kind of bond from the single bond.

POWERPOINT

4D 2 Bond energy calculations

Quiz 4D 2

REVISION

4D 3a Thermochemical processes

4D 3b Thermochemical definitions hangman

Test yourself 4D Thermochemical calculations (2)

1 From the following equations and $\Delta H°$ values,

$H_2(g) + Br_2(l) \longrightarrow 2HBr(g) \quad \Delta H° = -72.8$ kJ mol^{-1}

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \quad \Delta H° = -483.7$ kJ mol^{-1}

calculate the $\Delta_r H°$ for the following reaction: $4HBr(g) + O_2(g) \longrightarrow 2Br_2(l) + 2H_2O(g)$

2 Calculate the heat of reaction for the water gas reaction: $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

$\Delta_f H°\ (CO_2(g)) = -394$ kJ mol^{-1} $\quad \Delta_f H°\ (H_2O(g)) = -242$ kJ mol^{-1} $\quad \Delta_c H°\ (CO(g)) = -282$ kJ mol^{-1}

3 If the bond energy for H—Cl is 431 kJ mol^{-1}, write the thermodynamic equation for the dissociation of HCl(g).

4 Use the bond energy data given to predict the enthalpy of reaction for the equations below.

Bond energies in kJ mol^{-1}					
Br—Br	192	H—O	464	C = C	598
C—O	352	C—C	346	O = O	494
H—C	414	C—Br	276	C = O	724

a $CH_2{=}CH_2(g) + Br_2(g) \longrightarrow CH_2BrCH_2Br(g)$

b $CH_2CH_2(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$

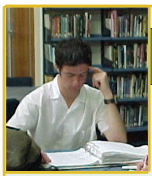
Key learning outcomes for Chapter 4

By now you should be able to:

1. Identify exothermic and endothermic reactions from experimental data or the $\Delta_r H$.
2. Describe the changes that take place at melting points and boiling points in terms of the changing kinetic and potential energy of particles.
3. Recall the relationship between absolute temperature and the average kinetic energy of particles.
4. Define enthalpies of fusion and vaporisation for a pure substance, eg water.
5. Recognise the significance of the state of each species in thermochemical equations.
6. Define enthalpies of formation and combustion.
7. Use standard enthalpies of formation to calculate the enthalpy change for a reaction.
8. Calculate enthalpy changes from experimental data.
9. Use Hess's law to calculate enthalpy changes for reactions.
10. Recall that bond breaking is endothermic and bond making is exothermic.
11. Calculate the enthalpy change for a reaction using bond energies and recognise the approximate nature of these calculations.

EXAM QUESTIONS

Practice questions



Review questions for Chapter 4

1 The table on the right lists values of $\Delta_{fus}H$ and $\Delta_{vap}H$ for some compounds. By referring to these values answer the following questions.

	$\Delta_{fus}H$ kJ mol^{-1}	$\Delta_{vap}H$ kJ mol^{-1}
MgO	77	528
H_2O	6.0	44
CH_4	0.84	9.2
Na	3	106

a $\Delta_{vap}H(CH_4)$ = 9.2 kJ mol^{-1}. Explain fully what this statement means. **A M**

b Which solid in the table has the strongest forces between its particles? Why? **A M**

c For all compounds, the $\Delta_{vap}H$ values are much higher than the $\Delta_{fus}H$ values. By referring to the inter-particle forces give an explanation for this. **A M**

2 $\Delta_f H°$ (Al_2O_3(s)) = –1676 kJ mol^{-1}. Calculate $\Delta_c H°$ (Al(s)). **A**

3 Calculate the enthalpy change of the reaction below using the heats of formations from the table on the right. **A M**

$$2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(g) + 2SO_2(g)$$

Compound	$\Delta_f H°$ (kJ mol^{-1})
H_2S(g)	–20.6
H_2O(g)	–241.8
SO_2(g)	–296.8

4 Calculate the $\Delta_f H°$ for methane CH_4(g) given the heats of combustion for carbon, hydrogen and methane are –393, –285 and –888 kJ mol^{-1} respectively. **A M E**

5 $H_2O_2(l) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$ $\Delta H = -52\ \text{kJ mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -286\ \text{kJ mol}^{-1}$

Calculate the enthalpy of formation of hydrogen peroxide (H_2O_2). **A M**

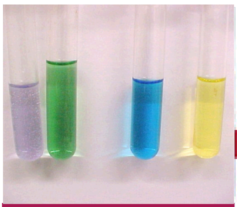
6 Calculate the enthalpy of the reaction below, given the bond energies in kJ mol^{-1} on the right.

$H_2(g) + I_2(g) \longrightarrow 2HI(g)$ **A M**

H—H = 436
I—I = 151
H—I = 299

7 Use bond energy data to suggest why eight sulfur atoms tend to form one S_8 molecule whereas eight oxygen atoms form four O_2 molecules.

Bond energies (kJ mol^{-1}): O=O = 494 O—O = 146 S=S = 352 S—S = 226 **A M E**



5 Atoms

Introduction

Many properties of atoms are *periodic* — as atomic number increases, the property goes up and down, making a wave-like pattern rather than a typical line graph. That's why we call the chart showing the elements the *periodic* table, because it arranges the elements according to the periodic properties they display.

Chemists studying the periodic properties of atoms have been able to draw conclusions about the internal structure of the different elements. By understanding the patterns it is possible to predict the properties of different elements without having to memorise large lists of numbers.

Atomic and ionic radii

One of the most obvious questions about an atom is 'how big is it' — in other words, 'what is its radius'? Since an atom consists of a very dense nucleus, surrounded by a cloud of electrons, what we really want to know is, 'where is the edge of the electron cloud'?

It is impossible to measure the atomic radius of an individual atom, but it is possible to measure the distances between adjacent nuclei of various substances. In metals the radius is defined as half the distance between adjacent nuclei in the metal. In non-metals we look at covalent bonds, and define the covalent radii as half the distance between nuclei of like atoms covalently bound together in a molecule. It is not possible to measure the radii of noble gases because they do not form bonds.

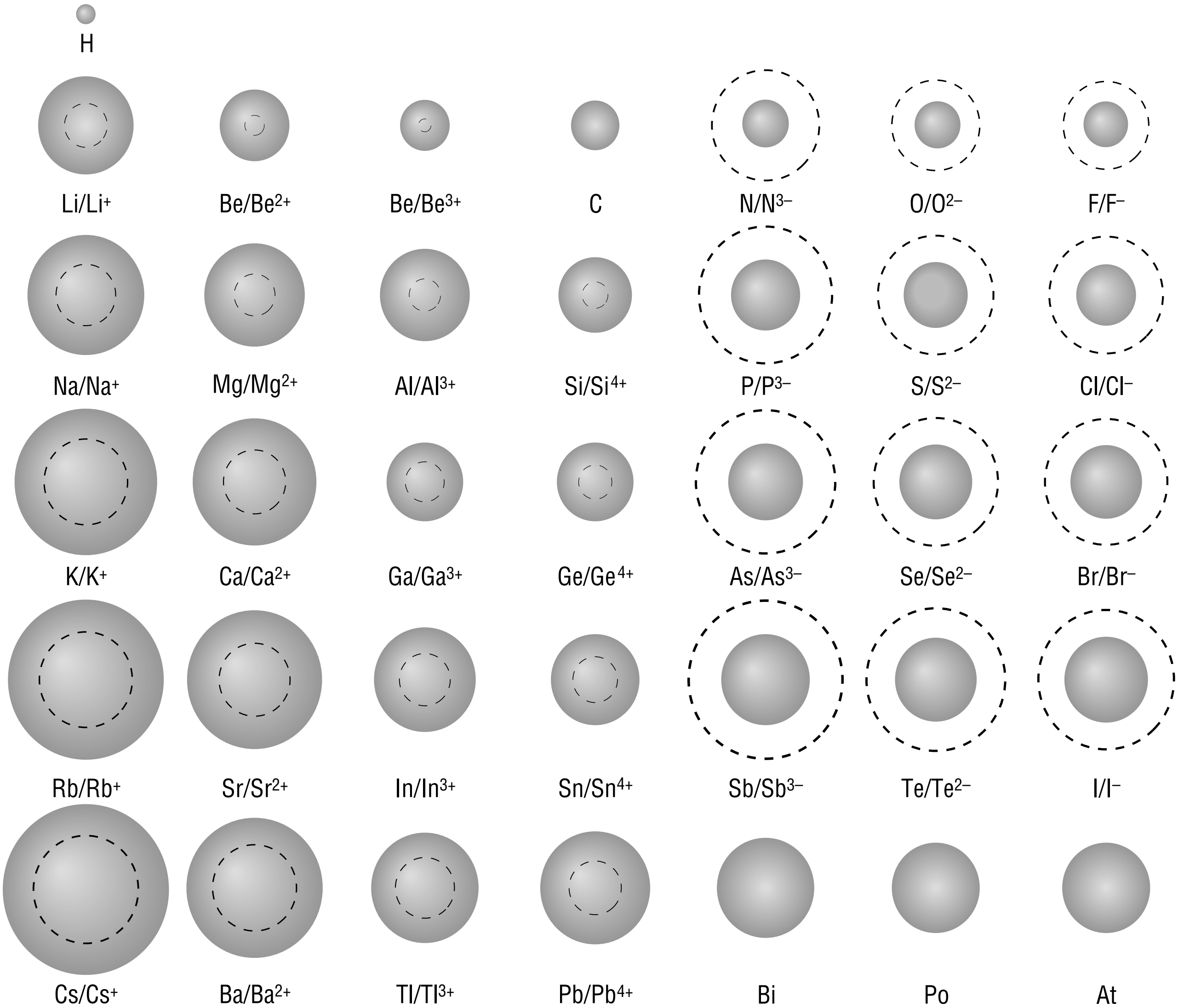
Trends in atomic radii

Atomic and ionic radii for the non-transition elements are shown on page 46.

We find the *radii decrease going across a period*. As we move across a period the electron shells are pulled closer into the nucleus. Why?

Moving across a period, the number of electrons in the outer shell increases, which increases the electron-electron repulsive forces. At the same time, the number of protons in the nucleus increases, which increases the attractive forces between the nucleus and the valence electrons. Since we see that that the atomic radii decrease going across the period, the effect of the increased nuclear charge must be greater than effect of electron repulsion.

We find that the *radii increase going down a group*. Each atom in the group has the same number of valence electrons, and the same effective nuclear charge, but there are more electron shells as we move down a group. (The effective nuclear charge is the nuclear charge felt by the valence electrons. Since the valence layer is protected or *shielded* from the nucleus by the inner electrons, the effective nuclear charge is the same as



Pictorial representation of the atomic and ionic radii of the non-transition elements. The dashed lines represent the relative circumference of the ions named.

the number of valence electrons.) The valence shells end up further away from the nucleus, and therefore the electrostatic force between the nucleus and the valence electrons decreases.

Understanding ionic radii

The ionic radius of a positive ion is smaller than the corresponding atom because the entire valence shell has been removed. The more positive the ion (in the same period) the smaller it is — for the same reason the atoms are smaller going across the period. The ionic radius of a negative ion is greater than the corresponding atom. As more electrons are added to the valence shell they repel each other more. The effective nuclear charge remains the same, so the ionic radius increases. The greater the negative charge on the ion, the more the repulsion and the larger the radius.

Electronegativity

Chemists use the term **electronegativity** to measure the tendency of each atom in a molecule to attract bonding electrons. Since the noble gases do not readily form bonds, their electronegativities have not been calculated.

Electronegativities of the elements

H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
Fr 0.7	Ra 0.9	Ac 1.1															

Fluorine has the highest electronegativity, followed by oxygen and nitrogen. These three elements, when bonded to a hydrogen atom, cause *hydrogen bonding* (see page 65). Notice that although the electronegativities of the heavier group 1 and 2 elements are low, *no atom has an electronegativity of zero*.

Using electronegativity to predict bond type

When two atoms of identical electronegativity form a bond, that bond will be a pure covalent bond: the electrons will be shared exactly equally between the atoms. We normally say that a bond is polar covalent when the electronegativity difference is between about 0.5 and 1.6, and ionic when the difference is greater than 1.6. These cut-off points are somewhat arbitrary, though: many compounds have bonding with some ionic and some covalent characteristics.

REVISION

5A 1 Atoms multichoice

Quizzes 5A 1a, 5A 1b

Test yourself 5A Atomic and ionic radii and electronegativity

1 What is the trend in atomic radii across a period? Explain this trend.

2 Circle the larger of each of these pairs:

a Mg / Al **b** O / S **c** Na / Na^+ **d** K^+ / Na^+

e P^{3-} / P **f** N^{3-} / O^{2-} **g** Mg / Ca **h** K^+ / Ca^{2+}

3 Explain why the fluoride ion is so much larger than the fluorine atom.

4 What is the trend in electronegativity

a across a period? **b** down a group?

5 Predict the bonding between the following elements.

a C, H **d** H, Br

b Mg, Cl **e** Al, Cl

c S, O **f** K, S

Ionisation energy

Ionisation energies always relate to the loss of electrons to form **positive** ions — even for those elements such as chlorine that normally gain electrons.

Ionisation energy is defined as

the energy required to remove the least tightly bound electron from each atom of one mole of gaseous atoms or ions.

It is measured in kJ mol^{-1} (or sometimes in electron-volts). The first ionisation energy of an atom is the energy required to remove the first electron from the atom, the second ionisation energy removes the second electron from the ion, etc. (If the phrase 'ionisation energy' is used without specifying first, second, etc, assume it means the first ionisation energy.)

$$Ne(g) \longrightarrow Ne^{+}(g) + e^{-} \qquad \Delta H = +2087\ \text{kJ mol}^{-1}$$
$$Ne^{+}(g) \longrightarrow Ne^{2+}(g) + e^{-} \qquad \Delta H = +6128\ \text{kJ mol}^{-1}$$

Notice **the second ionisation energy is greater than the first.** This will *always* be the case since you are removing electrons from a positive ion. Also notice that ionisation energies are *endothermic* (ΔH is positive). It takes energy to remove electrons from an atom or ion.

REVISION

5B 1 Arrange ionisation energy
5B 2a Match thermochemical equations
5B 2b Thermochemical true-false
5B 2c Thermochemical definitions

Quizzes 5B 1, 5B 2

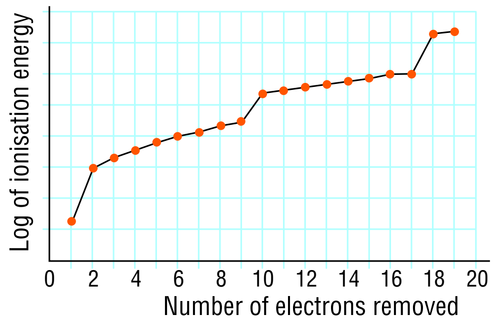
Using ionisation energies

If we remove all the electrons from an atom, we can deduce its electron structure. We see from the graph on the left that the first electron is easy to remove from a potassium atom, but then there is a jump to the next 8 electrons, another jump to the next 8, and finally a jump to the last 2 electrons.

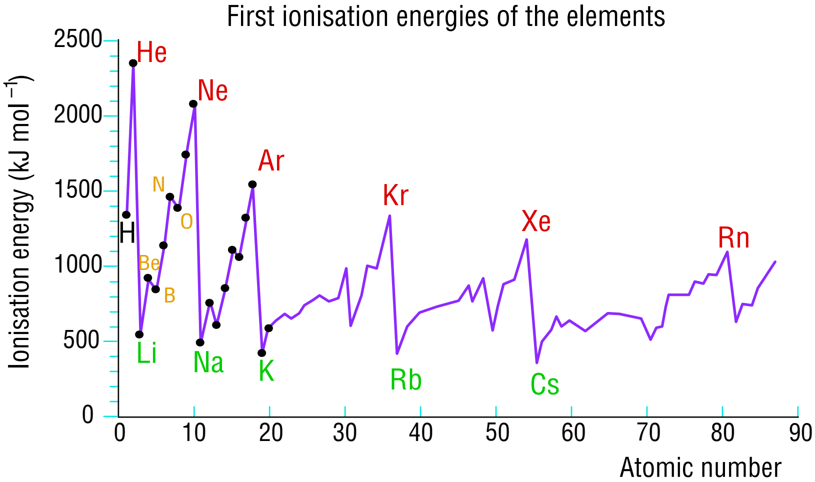
It seems the electrons are arranged (for taking-off purposes) 1.8.8.2. Since we normally write **electron configurations** from the nucleus out, we say that the electron configuration of potassium is 2.8.8.1.

In studying a graph of the first ionisation energies with atomic number we notice definite periodic trends.

Successive ionisation energies for potassium



First ionisation energies of the elements



- Highlighting atoms in the same group (such as the noble gases or the alkali metals), first ionisation energies go *down*. In other words, the further away from the nucleus an electron is, the easier it is to remove.
- The general trend across a period is of increasing ionisation energies (eg from Na to Ar) due to the increasing effective nuclear charge.
- The zig-zag shape of the graph indicates that some electron numbers are less stable than others. B and O seem to be less stable (ie easier to remove electrons from) than Be and N.

REVISION

5B 3 Atoms key facts

Quiz 5B 3

Electron configuration

Careful studies of ionisation energies and of line spectra (produced when electrons drop from higher to lower energy levels) provided evidence for the existence of the following orbitals, in order of increasing energy or distance from the nucleus:

1s 2s 2p 3s 3p 4s 3d 4p

(The letters s, p, d and f refer to spectral lines that are Sharp, Principal, Diffuse and Faint—f orbitals are beyond the Y13 syllabus.)

Notice that the 4s orbitals have a lower energy than the 3d orbitals. On the periodic table the elements with partially filled d orbitals are called

transition elements and are found in the middle section of the table.

- Each level contains one s orbital holding one pair of electrons.
- From the second level there are 3 p orbitals per level, holding a total of 6 electrons.
- From the third level there are 5 d orbitals per level, holding a total of 10 electrons. (And from the fourth level the 7 f orbitals hold a total of 14 electrons.)

ENCOUNTER

5B Linus Carl Pauling

Rules for filling sublevels and orbitals

These rules are used to write electron configurations using the sublevel and orbital symbols *s*, *p*, *d*, and *f*.

1 All orbitals hold a maximum of 2 electrons. An orbital containing 2 electrons is called a *filled orbital*.

2 Electrons occupying the same orbital must have *opposite spin***,** indicated with arrows: ↑ and ↓.

3 Electrons fill up orbitals at the lowest energy sublevels first.

4 The lowest or most stable arrangement of electrons in a sublevel is the one with the *greatest number of parallel spins*. (This is **Hund's rule**.) This means when orbitals of the same energy are available, electrons will avoid pairing if possible, by entering separate sub-orbitals.

Configuration of the first 20 elements

Applying these rules to the period Li to Ne we get:

	1s	2s	2p			Configuration
Li	↑↓	↑				$1s^2\ 2s^1$
Be	↑↓	↑↓				$1s^2\ 2s^2$
B	↑↓	↑↓	↑			$1s^2\ 2s^2\ 2p^1$
C	↑↓	↑↓	↑	↑		$1s^2\ 2s^2\ 2p^2$
N	↑↓	↑↓	↑	↑	↑	$1s^2\ 2s^2\ 2p^3$
O	↑↓	↑↓	↑↓	↑	↑	$1s^2\ 2s^2\ 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2\ 2s^2\ 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2\ 2s^2\ 2p^6$

Explaining ionisation energies

The general trend in ionisation energies is for an increase across each period due to the increased effective nuclear charge on the valence electrons. However, we need to explain those first ionisation energies that do not follow this trend.

B and Be

B has a lower first ionisation energy than Be. The 2*p* orbital is slightly further from the nucleus than the 2*s*, and this greater distance out-weighs the increased effective nuclear charge on the valence electrons. Thus less energy is required to remove boron's least tightly held electron.

O and N

The explanation for oxygen's lower than expected first ionisation energy is different. Just as there is greater electron-electron repulsion in the valence shell when it contains more electrons, so when a sub-orbital contains paired electrons, it is easier to remove one of them than if it were in that sub-orbital by itself. This greater electron-electron repulsion out-weighs the increase in effective nuclear charge from N to O, so less energy is required to remove the paired electron from O.

Why isn't Be lower than Li? It has paired electrons in its 2*s* orbital. In this case, the increase in effective nuclear charge is the over-riding factor.

REVISION

5B 4a Atomic explanations 1
5B 4b Atomic explanations 2

Quizzes 5B 4a, 5B 4b

Third row elements

The elements from sodium to argon follow the same pattern as from Li to Ne, using the 3s and 3p orbitals for the valence elections.

Electron configurations of elements beyond argon

The 4s orbital has a slightly lower energy than the 3d orbitals, so the 4s orbital is filled before the 3d orbitals:

		3d	4s	Configuration
K	[Ar]		↑	[Ar] $4s^1$
Ca	[Ar]		↑↓	[Ar] $4s^2$

The 10 elements beyond calcium all have 2 electrons in the 4s orbital, plus electrons in the 3d orbitals. Notice the unusual electron configurations of chromium and copper:

		3d					4s	Configuration
Sc	[Ar]	↑					↑↓	[Ar] $3d^1\ 4s^2$
Ti	[Ar]	↑	↑				↑↓	[Ar] $3d^2\ 4s^2$
V	[Ar]	↑	↑	↑			↑↓	[Ar] $3d^3\ 4s^2$
Cr	[Ar]	↑	↑	↑	↑	↑	↑	[Ar] $3d^5\ 4s^1$ (max. spin)
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓	[Ar] $3d^5\ 4s^2$
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓	[Ar] $3d^6\ 4s^2$
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓	[Ar] $3d^7\ 4s^2$
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓	[Ar] $3d^8\ 4s^2$
Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑	[Ar] $3d^{10}\ 4s^1$
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	[Ar] $3d^{10}\ 4s^2$

You'll just have to learn copper's electron arrangement. Having 10 electrons in the 3d orbitals makes the 3rd shell completely full, which is clearly a more stable arrangement – otherwise copper wouldn't do it. But we can give no convincing reason for why it is more stable. It just is.

These elements are commonly known as the *transition elements*. They are found in the middle block of the periodic table.

When transition elements form positive ions, the first electrons lost are those from the outer-most shell—from the 4s orbital. Don't be tricked into thinking that the 3d electrons are lost before the 4s just because they are at a higher energy level. So the electron configuration of iron(II) and iron(III) ions are:

Fe^{2+}	[Ar]	3d	↑↓	↑	↑	↑	↑	4s	____	[Ar] $3d^6$
Fe^{3+}	[Ar]	3d	↑	↑	↑	↑	↑	4s	____	[Ar] $3d^5$

The electron configurations of the elements Ga–Kr carry on filling the 4p orbitals. You may be required to write electron configurations of any atom or ion up to Kr.

Electron configuration of excited atoms

If energy is applied to isolated atoms, the electrons may move into higher energy levels, for example, a 4s electron may go into the 5s orbital (even though there are unfilled 4p orbitals). The electron remains in this higher orbital for only a fraction of a second, before dropping back down—either directly, 5s → 4s, or in steps, 5s → 4p → 4s. At each step it releases its excess energy in the form of a photon. If this photon has the energy corresponding to visible light we see this as a colour. This is where flame emission spectra come from.

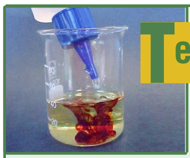
You can recognise the electron configuration of excited atoms because the electrons are in the 'wrong' place:

Na*: $1s^2\ 2s^2\ 2p^5\ 3s^1\ 3p^1$
Cl*: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4\ 3d^1$

REVISION

5B 5a Assemble electron configurations (1–12)
5B 5b Match electron configurations

Quiz 5B 5



Test yourself 5B Ionisation energy and electron configurations

1 The first ionisation energy of aluminium is 578 kJ mol^{-1}. Write the thermodynamic equation for this data.

2 Explain why the first ionisation energy of:

a argon is lower than that of neon

b lithium is lower than that of neon

3 Write electron configurations for the following species using s p d notation:

a $_{7}N^{3-}$

b $_{33}As$

c $_{28}Ni^{2+}$

d $_{24}Cr$

e $_{35}Br^{-}$

f $_{12}Mg^{2+}$

A closer look at transition elements

The *d*-block elements, in the middle section of the periodic table, are often known as the transition elements. Technically, only those elements that contain partially-filled *d*-orbitals are transition elements (so that eliminates zinc), but most of the time we ignore this distinction.

Having partially-filled *d*-orbitals gives the transition elements some unusual characteristics.

- **Transition elements can have a number of different oxidation states by holding on to, or losing, varying numbers of *d* electrons.** Iron, for example, forms Fe^{2+} and Fe^{3+} compounds. You will have met the +3 and +6 states of chromium in Year 12, along with Mn^{2+}, MnO_2 (+4) and MnO_4^- (+7). This year you will have also met (or will meet) MnO_4^{2-} (+6). Copper forms Cu^+ and Cu^{2+}, and vanadium also exists in +2, +3, +4 and +5 forms. By contrast, the non-transition elements, sodium, magnesium, aluminium and zinc each form only a single ion: Na^+, Mg^{2+}, Al^{3+} and Zn^{2+}. Scandium, too, normally only forms Sc^{3+}, which is why some chemists do not call scandium a transition element.
- **The compounds and complexes of transition elements are almost always coloured.** We see objects as coloured because they absorb some wavelengths of light and not others. Transition element compounds absorb light in the visible region of the spectrum when electrons move between different *d* orbitals.

  Colours you need to remember:

  V^{2+} = purple, V^{3+} = green, VO^{2+} = blue, VO_2^+ = yellow
  Cr^{3+} = blue/green, CrO_4^{2-} = yellow, $Cr_2O_7^{2-}$ = orange
  Mn^{2+} = pale pink/colourless, MnO_2 = dark brown/black,
  MnO_4^{2-} = green, MnO_4^- = purple
  Fe^{2+} = green, Fe^{3+} = orange
  CuI = white, Cu_2O = brick red, $Cu^{2+}(aq)$ = blue, CuO = black

POWERPOINT

5C Transition metal ions

PRACTICAL

5.1 P 172 Transition metal chemistry 1: Manganese

5.2 P 173 Transition metal chemistry 2: Vanadium

REVISION

5C 1a Characteristics of transition elements
5C 1b Colours of transition metal ions
5C 1c Complexes
5C 1d Why do transition metals have coloured compounds?
Quizzes 5C 1, 5C 2

All compounds of zinc are white and, if soluble, form colourless solutions. However, solid zinc oxide will turn bright yellow when heated strongly. It returns to white when cooled again.

- **Many catalysts are transition elements or their compounds.** This is often because they can be oxidised at one stage of the reaction, then reduced in another stage. You probably saw the catalytic effect of MnO_2 on hydrogen peroxide in Year 9. V_2O_5 is the catalyst used to convert SO_2 into SO_3 during the manufacture of sulfuric acid, while Fe_2O_3 is the catalyst in the Haber process for ammonia and copper metal catalyses the oxidation of methanol to methanal.

Test yourself 5C Transition elements

1 V_2O_5 is the catalyst used in the manufacture of sulfuric acid.

a What is the oxidation number of vanadium in V_2O_5? ____ **b** Predict the colour of V_2O_5 ____________

2 Use electron configurations to show why:

a Almost all transition elements form compounds with the +2 oxidation state.

____

____

b The only stable oxidation state for scandium is +3. ______________________________

____

____

c Copper is able to form compounds in the +1 state. ______________________________

____

3 Write the formulae of two transition ions or compounds with each of these colours:

a green: ____________ **d** orange: ____________

b yellow: ____________ **e** purple: ____________

c blue: ____________ **f** black: ____________

4 Why are zinc compounds white rather than coloured? ______________________________

____

____

Key learning outcomes for Chapter 5

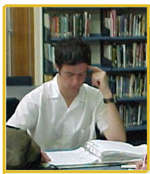
By now you should be able to:

1 Describe and discuss periodic trends in covalent radii of atoms and the ionic radii of ions.
2 Describe periodic trends in electronegativity of the elements.
3 Use electronegativity differences to predict bond type.
4 Define ionisation energy and write thermochemical equations for a given ionisation energy of an element.
5 Describe trends in ionisation energies for atoms in rows and columns of the periodic table.

6 Write *s*, *p*, *d* electron configurations for atoms and ions up to Kr.
7 Interpret differences in the first ionisation energies of atoms in terms of their electron structure.
8 Recognise the characteristic properties of transition metals and their compounds which are related to their electron structure.
9 Recall the formulae and colours of some important compounds or ions of the elements V, Cr, Mn, Fe, Cu and Zn.

EXAM QUESTIONS

Practice questions



Review questions for Chapter 5

1 The first four ionisation energies for element Q (in kJ mol^{-1}) are: 589 1144 4905 6464

a How many valence electrons does element Q have? Justify your answer. A M

b Write a thermodynamic equation for the second ionisation energy of element Q. A M

2 Write atomic symbols and charge for the following species. A M

a [Ar] $3d^{10}\ 4s^2\ 4p^1$ charge = 0

b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ charge = –2

c [Ar] $3d^9\ 4s^2$ charge = 0

d [Ar] $3d^5$ charge = +2

3 Write the electron configuration for the following species using s p d notation. (Ca* is an excited atom.) A M

a $_{14}Si$

b $_{34}Se^{2-}$

c $_{13}Al^{3+}$

d $_{23}V$

e $_{20}Ca^*$

f $_{26}Fe^{2+}$

4 Ionisation energies provide important information about the electron structure of atoms.

a Describe and account for the trend in first ionisation energies of the elements moving down a group of the periodic table. A M

b Nitrogen has a higher first ionisation energy than oxygen. Discuss. A M E

5 A student took a sample of brass (an alloy of copper), dissolved it in concentrated nitric acid then added water to form a solution of copper nitrate. She took samples of this solution, added potassium iodide solution and titrated the iodine liberated with sodium thiosulfate solution. Describe the observations (especially colour changes) during this analysis. **A M**

6 When yellow potassium chromate is acidified it turns orange.

a Complete and balance this equation for this transformation: **A**

$$CrO_4^{2-}(aq) + H^+ \rightleftharpoons$$

b What should be added to turn the orange solution yellow again? **A**

7 Write electron configurations for: **A**

a $_{24}Cr$

b $_{28}Ni$

c $_{23}V^{3+}$

d $_{26}Fe^{3+}$

8 Transition metals have many oxidation states. For the oxidation states listed below, give an example of a common transition metal compound with that oxidation state, and state the colour of the compound you have named. **A**

I

II

III

IV

V

VI

VII

9 Sodium and magnesium are typical non-transition metals, while iron and copper are typical transition metals. Using these examples, show how transition metals differ from the non-transition metals. **A M E**

10 Explain why the sodium atom is larger than the chlorine atom, yet the sodium ion is much smaller than the chloride ion. **A M**

6

Molecules and intermolecular forces

Bonding

All forces between particles are electrostatic. They are a combination of the attraction between oppositely charged particles and the repulsion between like charges. If particles are to hold together, then the attractive forces must be stronger than the repulsive forces.

- Metals are composed of positively-charged ions surrounded by delocalised electrons. The ***metallic bond*** is caused by the attraction of the positive metal ions for the negative electrons.
- Ionic solids are composed of a lattice (regular arrangement) of positive and negative ions. The ***ionic bond*** is created by the attractive force between these oppositely-charged ions.
- In covalent molecules, atoms share electrons. The ***covalent bond*** is formed when two positively-charged nuclei are attracted to the same cloud of electrons. A single molecule may contain many covalent bonds.

The location of the electron clouds around each atom determines the position of the atoms, and thus the shape of the molecule and many of its properties. The first step to working out where those electron clouds will be is to draw a Lewis diagram.

Lewis diagrams

Lewis diagrams, also called **electron dot** diagrams, help us predict the bonding and shapes of many molecules and ions.

Steps to drawing Lewis diagrams

1 Calculate the total number of valence electrons of all the atoms in the compound. (If you are drawing the Lewis diagram of an ion, add one electron for each negative charge, and subtract an electron for each positive charge.)

2 Write the symbols for the atoms in the compound in their approximate positions. The central atom is normally the most electropositive element. (For an ion, put the whole structure inside square brackets and write the charge of the ion on the outside of the brackets.)

3 Place one pair of electrons in each bond location.

4 Arrange the other electrons around the outer atoms first, and then the central atom, until all electrons are distributed.

5 Count electrons around each atom. If any atom does not have

a a full outer shell of electrons or

b all its valence electrons paired

then shift pairs of electrons from a non-bonding space to a bonding space (to make multiple bonds) until these conditions are satisfied.

POWERPOINT

6A Drawing Lewis diagrams

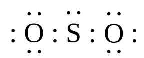
Example 6.1 Drawing Lewis diagrams (1)

Draw the Lewis diagram for SO_2.

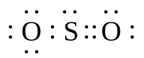
1 Sulfur has 6 valence electrons, oxygen has 6 valence electrons.
Total = 18 electrons.

2 O S O

3 O : S : O

4 

5 Each oxygen is surrounded by 8 electrons, but the sulfur only has 6 electrons, which is not acceptable. Move one pair of electrons to make a double bond.

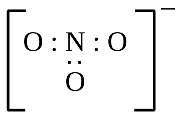
6 

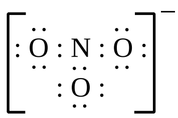
This final structure shows that SO_2 contains one double bond, one single bond and one pair of non-bonding electrons.

Example 6.2 Drawing Lewis diagrams (2)

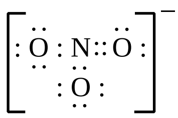
Draw the Lewis diagram for the NO_3^- ion.

Nitrogen has 5 valence electrons and oxygen 6, so the total number of valence electrons is 5 + (3 × 6) + 1 = 24.





Nitrogen is only surrounded by 6 electrons.



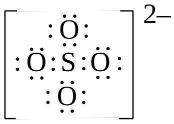
Moving one electron pair forms a double bond.

In these examples it appears that SO_2 and NO_3^- contain single and double bonds, but studies of the bond lengths of these species reveal that all the S—O or N—O bonds are identical. In reality, the bonds are part-way between single and double bonds. We could show this by drawing two (or three) diagrams, with the double bonds in different places, or by writing *all* S—O (etc) *bonds are equivalent.*

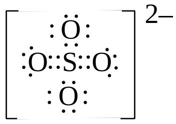
Unusual Lewis structures

Chemists can use X-ray diffraction data to work out whether atoms are joined by single, double or triple bonds. That's how we know that the bonds in SO_2 are both the same, even though the Lewis diagram shows one single and one double bond.

A simple Lewis diagram for the sulfate ion can be drawn, in which all the bonds are single bonds, and the sulfur atom is surrounded by 8 electrons. X-ray analysis reveals the bond lengths to be part-way between single and double bonds, suggesting the sulfur atom is surrounded by 12 electrons. That would mean all 6 of sulfur's valence electrons are paired. Such an electron arrangement is also consistent with the oxidation number of +6 for sulfur.



A valid Lewis diagram with all S–O bonds as single bonds — but not what happens.



This is the correct Lewis diagram, showing two single S–O bonds and two S = O double bonds; however all four S–O bonds are equivalent.

Other ions which have unexpected Lewis structures are the phosphate ion (PO_4^{3-}) and the chlorate ion (ClO_4^-). These ions are iso-electronic with the sulfate ion (ie they have the same number of electrons as the sulfate ion). In PO_4^{3-} the phosphorus atom is surrounded by 10 electrons, and in ClO_4^- the chlorine atom is surrounded by 14 electrons.

Quizzes 6A 1

Learn the correct structure for the sulfate ion.

Test yourself 6A Lewis diagrams

1 Draw the Lewis diagrams for the following molecules.

a H_2S **b** PCl_3 **c** CCl_4

d SO_3 **e** CO

2 Draw the Lewis diagrams for the following ions.

a NH_4^+ **b** CO_3^{2-} **c** OH^-

d H_3O^+ **e** OCl^-

3 Draw the Lewis diagrams for these molecules and ions in which the central atom is not surrounded by 8 electrons.

a PCl_5 **b** BeF_2 **c** I_3^-

d NO **e** BCl_3

4 Draw the Lewis structures for

a SiO_4^{4-} **b** PO_4^{3-} **c** ClO_4^{-}

Shapes of molecules

After the Lewis diagram has been drawn you will normally be asked to state the shape of the atom or ion. Use the table on the next page to help you.

Points to keep in mind:

- Electron clouds repel each other.
- Although we draw in two dimensions, the space around each atom is three dimensional.
- The shape of the molecule or ion is defined by the location of the *atoms*—the non-bonding electron clouds take up space but cannot be seen.
- Multiple bonds act as a single electron cloud.

POWERPOINT

6B Shapes and polarity of molecules

Example 6.3 **Shapes**

What are the shapes of the SO_2 molecule and the NO_3^- ion?

SO_2: The Lewis diagram shows that the central sulfur atom is surrounded by three clouds of electrons (one lone pair, a single bond and a double bond). The arrangement of these clouds will be trigonal planar, and the shape formed by the atoms will be **bent**.

NO_3^-: The Lewis diagram shows that the central nitrogen atom is surrounded by three clouds of electrons (two single bonds and a double bond). The arrangement of these clouds will be trigonal planar, and the shape formed by the atoms will be **trigonal planar**.

REVISION

6B 1 Naming shapes

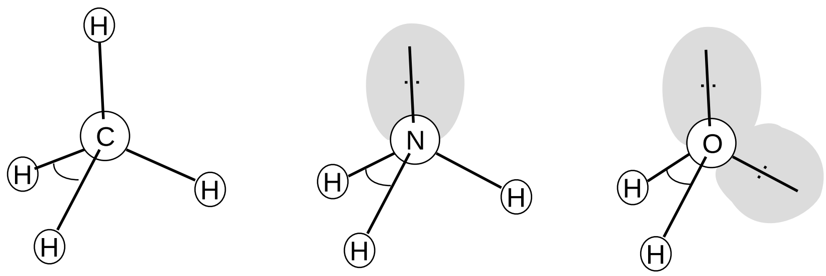
6B 2a–c Shapes from Lewis diagrams ((1–3)

6B 3 Bond angles

Quizzes 6B 1, 6B 2, 6B 3

Lone pair repulsion

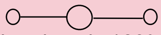
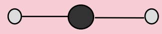
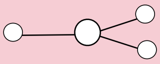
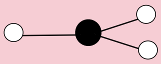
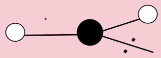
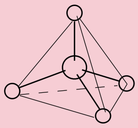
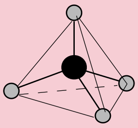
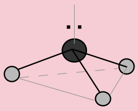
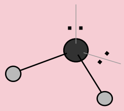
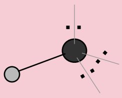
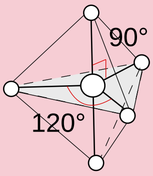
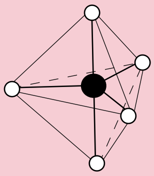
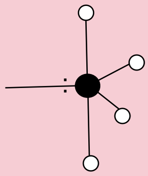
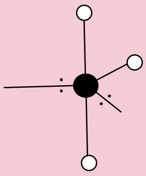
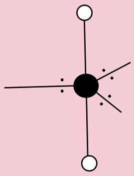
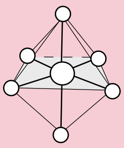
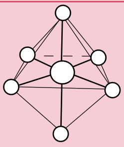
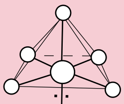
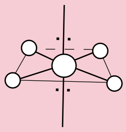
In water, the four electron clouds around the central atom are arranged tetrahedrally, and the tetrahedral angle is 109.5°, yet the actual angle between hydrogen atoms is only 104.5°. The reason is that the two lone pairs are closer to the oxygen atom, and take up more than their ‘fair’ share of the space, and so they repel the bonding pairs more, pushing them closer together. All lone pairs will push bonding pairs closer together, and double bonds will also take up more room than single bonds.



Methane, CH_4
No lone pairs
109.5°

Ammonia, NH_3
One lone pair
107.3°

Water, H_2O
Two lone pairs
104.5°

Shapes of molecules				
Number of electron clouds around central atom	**Arrangement of electron clouds around central atom**	**Possible shapes of final molecule**		**Example**
2	 bond angle 180°	 linear		CO_2
3	 bond angle 120°	 trigonal planar	 angular (bent)	BF_3 $SnCl_2$
4	 bond angle 109°	 tetrahedral	 trigonal pyramidal	CCl_4 NH_3
		 angular (bent)	 linear	H_2O HCl
5	 bond angles 90° and 120°	 trigonal bipyramidal	 seesaw	PCl_5 SF_4
		 T-shaped	 linear	ClF_3 I_3^-
6	 bond angle 90°	 octahedral	 square-based pyramid	SF_6 IF_5
		 square planar		XeF_4

Predicting polar molecules

A covalent bond will be *polar* if the electrons are not evenly shared between the two atoms. Uneven sharing will occur when the electronegativities differ significantly (ie a difference in electronegativity of between 0.5 and 1.6: if the difference is greater than 1.6 we say the bond is ionic). Apart from the C—H bond, almost every bond you meet that is between two different elements will be a polar bond.

A molecule will be polar if there is an uneven distribution of electrons throughout the molecule. Molecules containing polar bonds will be non-polar if the dipoles on those bonds balance out. So the CO_2 molecule

REVISION

6B 4a Polarity from Lewis diagrams

6B 4b Polarity from shapes

Quiz 6B 4

(which is linear) is non-polar because the two polar C=O bonds are at 180° to each other and so the net dipole on the molecule is zero. The water molecule is polar because the two H—O bonds add together, rather than cancelling out.

Test yourself 6B Shapes and polarity of molecules

Use the Lewis diagrams drawn for **Test yourself 6A** to answer these questions.

1 State the shape of the following molecules.

a H_2S ______ **b** PCl_3 ______ **c** CCl_4 ______

d SO_3 ______ **e** CO ______

2 Decide whether each of the molecules in **1** are polar or non-polar and give a reason for your answer in each case.

a ______

b ______

c ______

d ______

e ______

3 State the shape of the following ions.

a NH_4^+ ______ **b** CO_3^{2-} ______ **c** OH^- ______

d H_3O^+ ______ **e** OCl^- ______

4 State the shape of the following molecules or ions.

a PCl_5 ______ **b** BeF_2 ______ **c** I_3^- ______

d NO ______ **e** BCl_3 ______ **f** SO_4^{2-} ______

5 Which of the molecules in **4** are polar? ______

6 Predict which of the following angles is closest to the angle between the atoms in the molecules below.
60° 90° 109° 120° 180°

a : Ö :: C :: Ö : ______

b H : C :: C : H ______
H H

c : F : B : F : ______
: F :

d H : N : H ______
H

7 A stream of water (such as from a tap or burette) will bend towards a charged rod because water molecules are polar. Explain why water is polar. You should first explain why the bonds within the molecule are polar, and then explain why the molecule itself is also polar.

______

______

______

______

______

______

______

Solids

Types of solids

You should remember the characteristics of the four different types of solids from your Year 12 work:

Solid type	Examples	Melting point	Electrical conductivity	Charge carriers
Metallic	Cu, Na, Fe, Al	moderate	solid: yes molten: yes	mobile electrons
Ionic	NaCl, Al_2O_3, KBr, $PbCl_2$	high	solid: no molten or solution: yes	ions
Covalent network	C (diamond), C (graphite), Si, SiC, SiO_2 (silica)	very high	solid: no molten: no Exception: graphite conducts electricity in the solid phase	none mobile electrons in graphite
Molecular	I_2, CO_2, H_2O, S_8, C_2H_5OH	low	solid: no molten or solution*: no	none

POWERPOINT

6C 1 Solids revision

6C 2 Conductivity in solids

*Note: some covalent molecular substances, such as HCl(g), react with water (in hydrolysis reactions) to form ions. These solutions conduct electricity, but the charge-carriers are the ions, not the molecules.

Metals are found on the left hand side of the periodic table.
Ionic compounds usually contain metal and non-metal atoms.
Covalent network substances are rare: learn the five on the table above.
Covalent molecular substances are normally composed entirely of non-metal atoms.

A closer look at metals

Metals are composed of **positively charged ions** surrounded by a cloud or 'sea' of **delocalised electrons**. It is these freely moving electrons which allow the metal to conduct electricity. The **metallic bond** is formed by the attraction of the positive metal ions for the negatively charged electrons. It is non-directional, which is why it is possible to hammer the solid into different shapes without breaking the bonds. The strength of the metallic bond varies according to the size and charge of the metal ions.

A closer look at ionic compounds

Ionic compounds are composed of **positive and negative ions** held together by electrostatic forces called **ionic bonds.** Ionic solids have high melting points, which tells us that ionic bonds are strong. The ions are fixed in place in the solid, but are free to move in the liquid, which is why molten ionic compounds, or their aqueous solutions, conduct electricity. Crystals are brittle because when the arrangement of ions is deformed sufficiently then like charges are pushed close enough together for repulsion to occur.

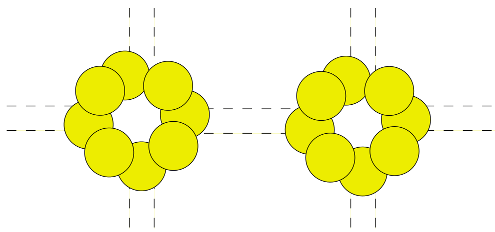
A closer look at covalent networks

Covalent network solids are composed of **atoms**, held together by **covalent bonds** that are clearly very strong since these substances have extremely high melting points. Diamond is the simplest example: each carbon atom is bonded to four other atoms in a tetrahedral arrangement that continues for the whole crystal. In effect, a diamond crystal is a single molecule. Graphite is also composed of carbon atoms, but in graphite each carbon atom is bonded to three others in flat, hexagonal sheets. Delocalised electrons within the sheets conduct electricity, while weak van der Waals' forces between them allow the sheets to slide over each other, making graphite slippery. Silicon, silicon carbide (SiC) and silica (SiO_2) are the other covalent network solids you should know. They have structures similar to diamond.

A closer look at covalent molecular substances

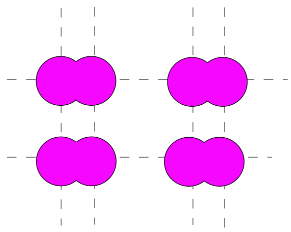
Covalent molecular substances have low melting and boiling points so the forces between the particles are weak. However, when those particles separate in the liquid and gas phases, we see that the particles are **molecules**—not atoms. (Water vapour, formed when water boils, is composed of H_2O molecules, not separate hydrogen and oxygen atoms. In fact, even at 2000 °C only 2% of water molecules are broken up into separate atoms.) That tells us that the between-molecule *inter-molecular* forces in covalent molecular substances are weak, but the within-molecule *covalent bonds* are strong. The weak inter-molecular forces are called **van der Waals' forces.**

Sulfur S_8



Eight sulfur atoms are joined by covalent bonds in a ring. The molecules are held together by van der Waals' forces.

Iodine I_2



Diatomic molecules held together by van der Waals' forces.

REVISION

6C 1a — Kinds of solids

6C 1b–c — Explaining the properties of solids (1–2)

Test yourself 6C Solids

1 What *kind* of substances are these?

a Cl_2 ____ **b** SiO_2 ____ **c** MgO ____

d Ca ____ **e** P_4 ____ **f** graphite ____

g Si ____ **h** KCl ____ **i** SO_2 ____

2 What evidence do you have that water is composed of separate molecules?

3 Identify the *kind* of substance described below.

a This substance is composed of neutral particles held together by very strong, highly directional bonds.

b This substance has a low melting point and does not conduct electricity when solid or liquid.

c This substance is composed of neutral particles held together by weak forces.

d These substances have relatively high melting points because the electrostatic attractions between oppositely charged particles are strong.

e Some of these substances have high melting points because the forces between the particles are strong, but these forces are also non-directional so the substances are easy to shape.

f The forces between the particles in these substances can be due to instantaneous dipole-induced dipole interactions.

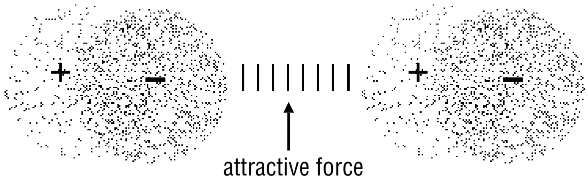
Inter-molecular forces

Van der Waals' forces

Covalent molecules are neutral because the number of positive and negative charges (ie protons and electrons) within the molecule are equal: there is no net charge on the molecule. However, it is still possible for parts of the molecule to have positive or negative charges. If there are more electrons around one part of the molecule, and fewer somewhere else, then the first part of the molecule will have a slight negative charge and the second part a slight positive charge. We say the molecule has an electrostatic **dipole**.

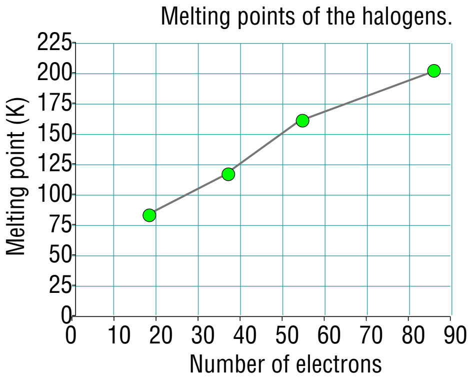
Polar molecules have a **permanent dipole**, which means one part of the molecule will always be slightly negative, and another part always slightly positive. Each molecule is like an 'electrostatic magnet', and just as magnets will align themselves and hold together, so polar molecules orientate themselves so that the positive part of one molecule is close to the negative part of the next molecule. There are thus small electrostatic attractive forces between these molecules which hold the molecules together. These forces are named after the Dutch physicist who investigated them: **van der Waals' forces**.

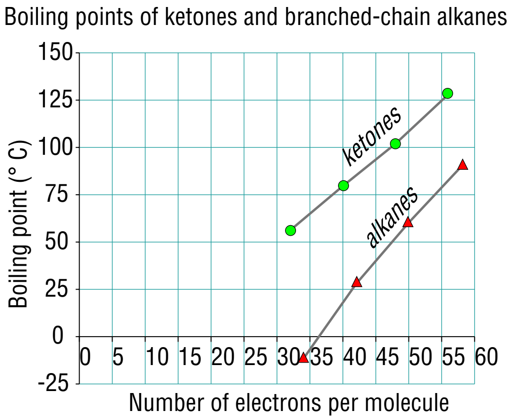
Electrons are constantly moving, so even in **non-polar** molecules **instantaneous dipoles** form when, for an instant, there are more electrons in one part of the molecule and fewer in another. That dipole will cause **induced dipoles** in nearby molecules, as their electrons are attracted or repelled by the charges in the first molecule. The attractive force between the molecules holds them together. Of course, the electrons keep moving, so these interactions are very short, but replacement centres for attraction keep on popping up. Even though the van der Waals' forces holding non-polar molecules together are very weak, they are still sufficient to allow non-polar substances such as iodine and sulfur to be solid at room temperature.



Instantaneous dipole-induced dipole forces are sometimes known as *London forces* or *dispersion forces*. They exist between all molecular substances, not just between non-polar ones.

Relative strength of van der Waals' forces





Noble gases like helium and neon exist as separate atoms. The van der Waals' forces between these atoms are due to uneven distribution of electrons around the nucleus of each atom. The boiling points of the noble gases increase with the number of electrons in the atom. A similar trend is seen in the boiling points of the halogens and alkanes:

the greater the number of electrons, the stronger the van der Waals' force between the molecules.

The shape of molecules also makes a difference: *cis* alkenes tend to have lower melting points than their *trans* isomers because the *C*-shaped kink in the *cis* molecules makes it difficult for the molecules to fit close together in the solid state. Similarly, straight-chain alkanes have higher melting points than their branched-chain isomers.

the more closely molecules can fit together, the stronger the van der Waals' forces between the molecules.

Polar substances—such as ketones—have higher boiling points than similarly sized and shaped non-polar compounds, since the polar compound has a permanent dipole:

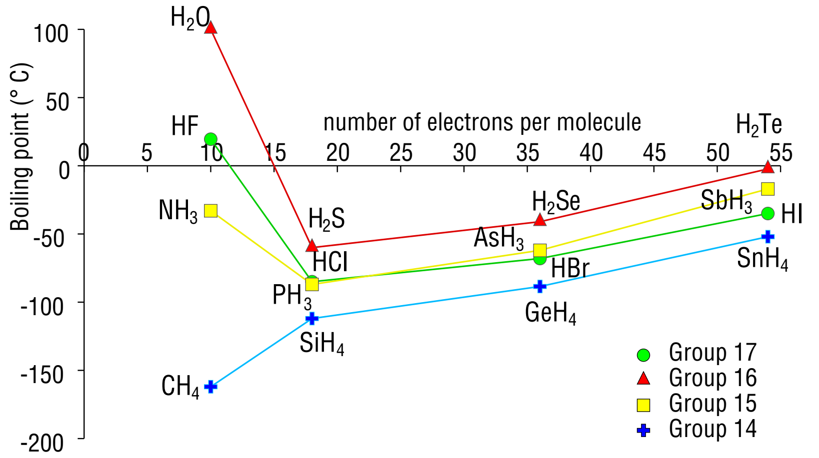
polar compounds have stronger van der Waals' forces than comparable non-polar compounds.

In situations where both shape and polarity differ (such as between *cis* and *trans* dichloro alkenes), shape has the greater affect on melting point, while polarity has the greater affect on boiling point. (*Cis* 1, 2-dichloroethene: MP = –80.5 °C, BP = 60.3 °C, *trans* 1, 2-dichloroethene: MP = –50 °C, BP = 47.5 °C.)

Hydrogen bonding

Most trends in melting and boiling points of molecular substances can be explained by the strength of the van der Waals' forces between the molecules. However, certain compounds have intermolecular forces which are much stronger than ordinary van der Waals' forces. The graph alongside shows how some of these compounds break the pattern.

Many organic compounds, such as alcohols, amine and carboxylic acids, also have unexpectedly high melting and boiling points.



The hydrogen compounds of group 14 show the expected trend of increasing boiling point as the number of electrons increase. This trend is also shown in groups 15, 16 and 17 hydrides, apart from NH_3, H_2O and HF which have unexpectedly high boiling points. The melting points of the hydrides show a similar pattern.

Compounds containing a hydrogen atom bonded to a fluorine, nitrogen or oxygen atom will have unusually high melting and boiling points.

F, N and O are the most electronegative of all the elements. When any of these atoms are bonded to a hydrogen atom, the electrons spend so much time with the F, N or O that their end of the molecule has quite a 'large' δ–, with a correspondingly 'large' δ+ on the hydrogen. But a positively charged hydrogen atom is simply a proton. This naked proton is attracted to a lone pair of electrons on the negatively charged F, N or O of the next-door molecule. In other words, the hydrogen atom is shared between two molecules. This joint custody of a proton is called a **hydrogen bond**.

Hydrogen bonds have a strength about 10% of a covalent bond.

They link molecules together via the lone pairs in the F, N or O atoms.

Hydrogen bonding accounts for the unusually high melting and boiling points of water, ammonia and hydrogen fluoride. It also explains why ice is less dense than water. In ice, the water molecules are arranged in a hexagonal arrangement which is more open than the random mix occurring in liquid water. When the ice melts only some of the hydrogen bonds are broken. The remaining hydrogen bonds are responsible for the unusually high heat capacity of liquid water and the unusual difference between the melting and boiling points of water. Hydrogen bonds are very important in natural fibres such as paper and wool. They hold protein molecules in their characteristic shapes, cause honey to be sticky and give water its high surface tension (which in turn causes soap bubbles to hold together).

Solubility

A solute will dissolve in a solvent if the forces between the solute and solvent are stronger than the forces within the solute or the solvent. In other words, salt dissolves in water because Na^+ ions are more strongly attracted to water molecules than they are to Cl^- ions, and because water molecules are more strongly attracted to the Na^+ and Cl^- than to other water molecules.

Non-polar substances like I_2 and alkanes are not soluble in water because water molecules are strongly attracted to other water molecules (through hydrogen bonding), while there is little attraction between the non-polar molecules and water.

Polar organic molecules, such as haloalkanes, are not soluble in water either, because even a permanent dipole is no match for hydrogen bonding.

PRACTICAL

6.1 P 174 — Hydrogen bonding

There are no hydrogen bonds in hydrogen gas! Hydrogen bonds only occur when a hydrogen atom is bonded to an oxygen, nitrogen or fluorine atom.

REVISION

6D 1 — Intermolecular forces key facts

6D 2 — Understanding intermolecular forces

6D 3a — Predicting patterns in melting and boiling points

6D 3b — Intermolecular forces true-false

Quizzes 6D 1, 6D 2

ENCOUNTER

6D1 — Building bones

6D2 — Antarctic sea ice

Low mass alcohols, carboxylic acids and amines form hydrogen bonds and are soluble in water. Low mass ketones and aldehydes are also soluble, because although they do not form hydrogen bonds themselves, the C=O has two lone pairs which can interact with the hydrogen atoms in water molecules.

Non-polar solvents, such as cyclohexane, dissolve non-polar substances such as iodine, because the forces within the solvent and within the solute are no stronger than the forces between solvent and solute.

Test yourself 6D Intermolecular forces

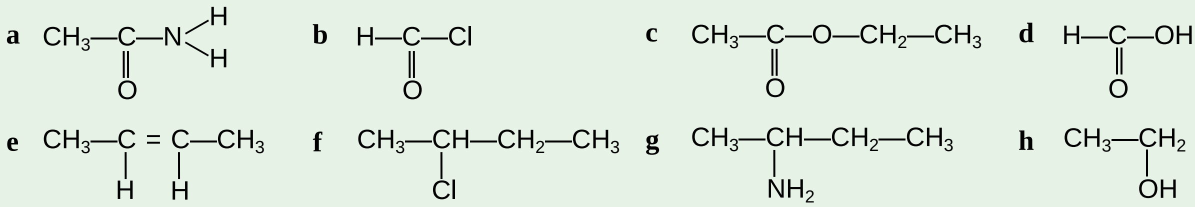
1 Name the attractive force that must be overcome when each of the following solids is melted:

a neon ____________ **b** sodium chloride ____________

c ice ____________ **d** sulfur ____________

e copper ____________ **f** propanone (acetone) ____________

2 Circle the compounds below which you would expect to show hydrogen bonding.



3 Arrange the following materials in order of increasing boiling point:

propane ethanol chloroethane butane propanone

____

4 The melting points of the hydrogen halides from HCl to HI increase with increasing molecular mass, but HF has a higher melting point than HCl. Explain these observations.

____

Key learning outcomes for Chapter 6

By now you should be able to:

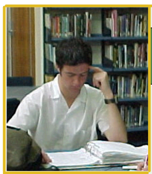
1. Draw the Lewis diagrams (electron dot diagrams) of polyatomic molecules and ions with up to 6 electron pairs around the central atom, including those involving multiple bonds.
2. Predict the shapes of molecule and ions with up to 6 electron pairs around the central atom and estimate the bond angles within such molecules or ions.
3. Predict the polarity of molecules from their shapes and the electronegativities of the elements involved.
4. Recognise that Lewis diagrams and the octet rule are unable to represent some molecules and ions accurately, eg nitrate, sulfate.
5. Explain properties of solids by discussing the nature of their particles and the forces between them.
6. Predict and discuss trends in melting and boiling points in covalent molecular compounds of different molecular mass, polarity and shape.
7. Show, using the melting and boiling points of volatile compounds of hydrogen, the existence of hydrogen bonds.
8. Identify compounds where hydrogen bonding will occur.
9. Relate appropriate physical properties of compounds to the presence of hydrogen bonding in those compounds.

REVISION

- Chemistry 3.4 key facts crossword
- Chemistry 3.4 key facts flip cards

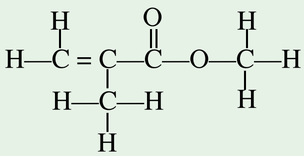
EXAM QUESTIONS

- Practice questions
- Sample examination papers



Review questions for Chapter 6

1 Bond angles of approximately 180°, 120°, 109° and 90° are commonly found in molecular substances. The diagram alongside shows the bonding in methyl methacrylate—the monomer used to make perspex. Mark on it one example of each type of bond angle found in this molecule. **A M**



methyl methacrylate

2 Draw Lewis diagrams for the following substances, and below each one, state its shape and polarity. **A M E**

a CS_2 **b** H_2S **c** C_2H_2

d BrF_3 **e** O_3

3 **a** Draw the Lewis structure for NO_2.

b Use your answer to **a** to draw the Lewis structure for the N_2O_4 dimer.

c Why is N_2O_4 more stable at low temperatures than NO_2?

A M E

4 Use diagrams to explain why CO_2 is non-polar, yet SO_2 is polar. A M

5 **a** Draw the Lewis diagram for SF_6 and use it to predict **b** the shape and **c** the polarity of SF_6. A M

6 The Lewis diagram for methanal is shown on the right.

H : C : H
: :
: O :

a What is the shape of this molecule? A

b Predict whether the HCH bond angle is greater than, equal to, or less than the HCO angle and explain why. A M

7 Discuss the variation in the boiling points of the compounds below in terms of the forces between the molecules in the liquid state.

water, H_2O BP 100 °C dimethyl ether, CH_3OCH_3 BP –23 °C oxygen, O_2 BP –183 °C A M E

8 Discuss why hydrogenating polyunsaturated vegetable oils (which contain predominantly *cis* double bonds) causes the melting point of the substance to rise—turning a liquid oil into a solid fat. A M E

9 Salt (NaCl) and sugar ($C_{12}H_{22}O_{11}$) are common white crystalline solids. Discuss what happens when each one is melted in terms of the forces between the particles. A M

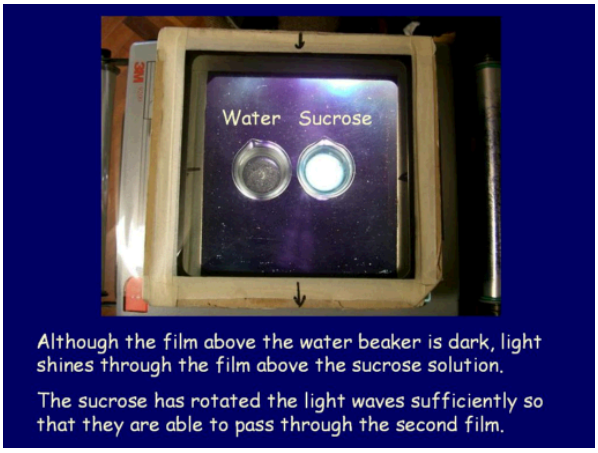
10 BCl_3 has a molar mass of 117.2 g mol^{-1} and BP of 12 °C. NCl_3 has a molar mass of 120.4 g mol^{-1} and BP of 71 °C.
Account for the large difference in boiling points of these two substances. A M E

Section 3

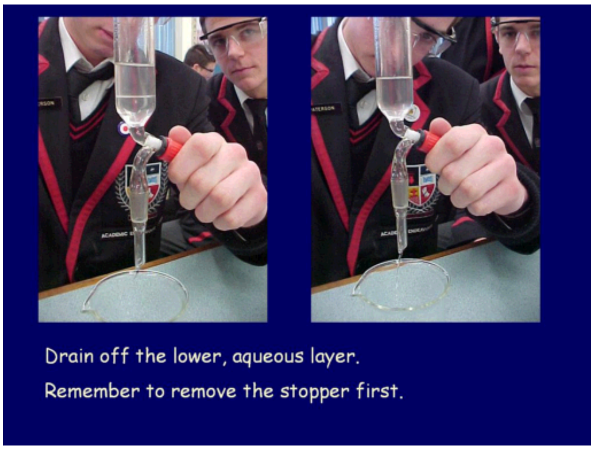
Organic chemistry

Chemistry 3.5
5 credits

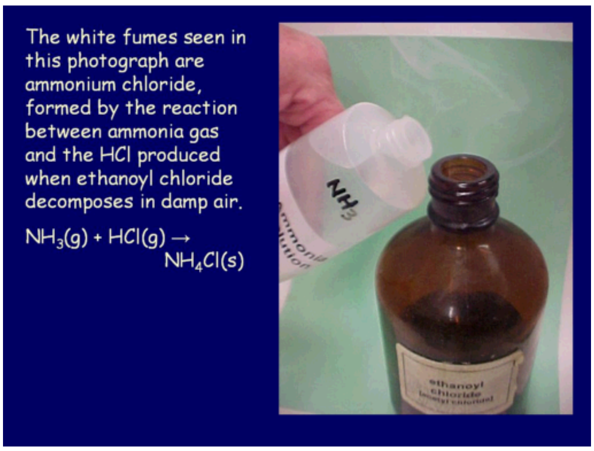
AS60698 Describe principles of organic chemistry
External



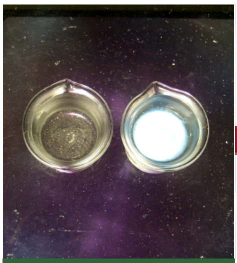
7 Organic chemistry: the basics



8 Alcohols and their derivatives



9 Carboxylic acid derivatives and polymers



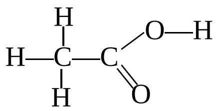
7

Organic chemistry: the basics

The basics

Structural and condensed formulae

Chemists were completely mystified by organic chemistry until Kekulé started drawing pictures of organic compounds in 1856. He used the valence of each atom to tell him how many bonds each one must have: carbon always has 4 bonds, hydrogen 1, oxygen 2, nitrogen 3 and the halogens 1 each. Today Kekulé's pictures are called **structural formulae**.



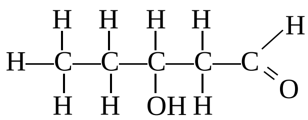
The structural formula for ethanoic (acetic) acid

Structural formulae are the easiest to understand, but they take up a lot of space, and are fiddly to draw. Chemists frequently use **condensed structural** formulae instead. The condensed structural formula for ethanoic acid is CH_3COOH. You need to be able to read condensed formulae, even if you choose to draw structural formulae most of the time.

Every carbon atom will form 4 bonds

The atoms immediately after each carbon are bonded to it.

$CH_3CH_2CHOHCH_2CHO$ =



In the example above, we know that there is a double bond between the final carbon and oxygen atoms because otherwise that carbon atom would only have three bonds, not four.

In some formulae you will see an X, which represents a halogen atom (usually Cl or Br, sometimes I, and occasionally F). The symbols R and R´ can also used in formulae. R stands for any carbon chain—you can think of it as the **R**est of the molecule. Sometimes R can be a single H atom. R´ stands for another carbon chain, which may be the same as the first, or different.

REVISION

7A 1 Introduction to organic chemistry

PRACTICAL

7.1 P 175 Structures of organic molecules

Functional groups

The functional groups in an organic compound are the parts which give it its characteristic properties. Complicated formulae may have several different functional groups, each one reacting in characteristic ways. You will be expected to recognise and name those functional groups listed at the top of page 72.

Once the functional groups have been identified, you can name the compound using the IUPAC system. The important rules to remember are:

- ***name the compound using the longest possible carbon chain,***
- ***number that chain so that the functional groups are on the lowest possible number carbon.***

Group	Group name	Homologous series	Group	Group name	Homologous series
C = C	double bond	alkenes	–C(=O)–	carbonyl group	ketones
–OH	hydroxyl group	alcohols	–C(=O)–H	aldehyde group	aldehydes
–C(=O)–OH	carboxyl group	carboxylic acids	$-NH_2$	amino group	amines
–O–C(=O)–	ester	esters	–C(=O)–Cl	acyl chloride	acyl chlorides
–Cl	chloro group	chloroalkanes	$-C(=O)-NH_2$	amide	amides

The IUPAC system for naming carbon chains

Number of carbons	Prefix	Side chain
1	meth-	methyl
2	eth-	ethyl
3	prop-	propyl
4	but-	butyl
5	pent-	pentyl
6	hex-	hexyl
7	hept-	heptyl
8	oct-	octyl
9	non-	nonyl
10	dec-	decyl

The table below summarises the naming rules for the organic compounds you will be expected to name this year. (Use the table on the left if you have forgotten how to name carbon chains.)

Homologous series	Suffix	
Alkenes	-ene	indicate position of C=C
Alcohols	-anol	indicate position of –OH
Haloalkanes	-ane	indicate position of halogens
Aldehydes	-anal	
Ketones	-anone	indicate position of C=O
Carboxylic acids	-anoic acid	
Amines	-ane	indicate position of NH_2 group
Esters	-anoate	eg propyl ethanoate (see page 97)
Acyl chlorides	-anoyl chloride	
Amides	-anamide	

REVISION

7A 2a Recognising organic families memory

7A 2b Classify organic compounds

7A 3 Name organic compounds

Quizzes 7A 2a, 7A 2b, 7A 3

Example 7.1 Naming organic compounds

Name these compounds.

a $CH_3CH_2COCH_2CH_3$ **b** $CH_3CH_2CH_2COCl$

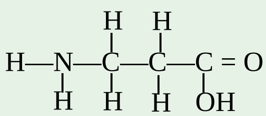
a The compound has a 5-carbon chain with a C=O group off the third carbon: it is pentan-3-one.

b This is a 4-carbon acyl chloride: butanoyl chloride.

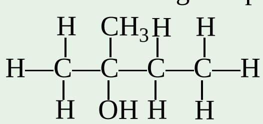
Test yourself 7A Organic compounds and functional groups

1 Write condensed structural formulae for the following compounds.

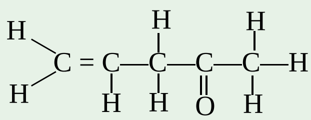
a



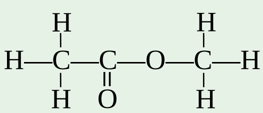
b



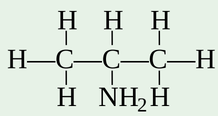
c



d



e

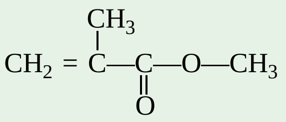


2 Write structural formulae for these compounds.

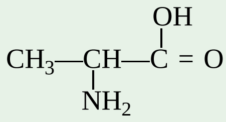
a $CH_2ClCH_2CH_2CH(OH)CH_3$ **b** $HCOOCH_2CH_3$ **c** CH_3CH_2COCl

3 Circle and name two functional groups in each of these compounds.

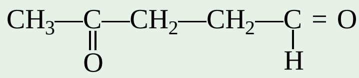
a



b



c



4 Name these compounds.

a $CH_3CH_2COCH_3$

b $CH_3CH_2CONH_2$

c $CH_2{=}CClCH_3$

d $CH_3COH(CH_3)CH_3$

e CH_3COOCH_3

f CH_3COCl

5 Write condensed structural formulae for these compounds.

a 3-chloropropanoic acid

b 3-methylbut-1-ene

c 2-bromopropan-1-ol

d propanal

e 2-chloro, 2-aminopropane

f ethyl propanoate

Isomers

Isomers are different arrangements of the same atoms. They have the same molecular formula, but different structural formulae.

Structural isomers

Structural isomers have atoms arranged in different orders. Some structural isomers are from different groups of compounds, such as ethanoic acid, CH_3COOH, and methyl methanoate, $HCOOCH_3$. Cyclic alkanes are isomers of their corresponding straight-chain alkenes. Aldehydes and ketones with the same number of carbon atoms will be isomers. And, of course, there are the isomers produced by moving a side-chain to another carbon atom, or shifting a double bond (eg propan-1-ol and propan-2-ol).

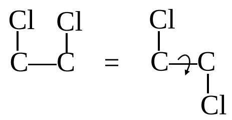
Structural isomers will have different physical and chemical properties.

Stereoisomers

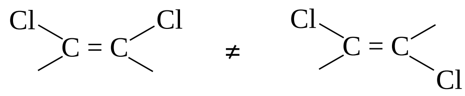
Stereoisomers have atoms arranged in the same order, but in different positions in space. Their condensed structural formulae will be the same, but their structural formulae will be different. There are two forms of stereoisomerism: geometric, and optical.

Geometric isomers

Geometric isomers, also called ***cis-trans* isomers**, are caused by the rigidity of the double bond. While the C—C bond will rotate freely, the C=C bond does not rotate.

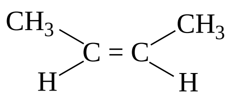


The C—C bond will rotate easily: one compound.

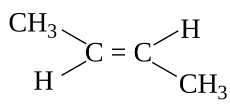


The C=C bond does not rotate, so these two compounds are different.

Cis isomers have the matching groups on the same side of the double bond, while in *trans* isomers the groups are on opposite sides of the double bond:

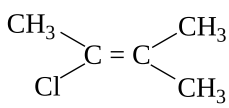


cis-but-2-ene

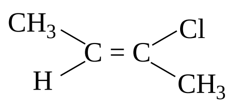


trans-but-2-ene

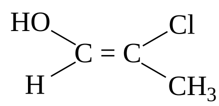
We often have to decide whether a given compound has *cis-trans* isomers or not. To decide, look at *each* carbon in the double bond *separately*. Are the two groups attached to *each* carbon different? If not, the compound doesn't have *cis-trans* isomers. If they are different, then the compound will have *cis* and *trans* versions.



no



yes



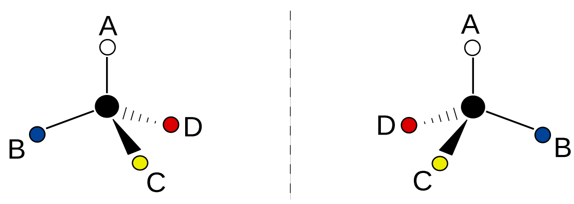
yes

Geometric isomers have the same chemical properties, but their physical properties will differ. Why?

The 'C' shaped kink in *cis* isomers makes it more difficult for them to pack closely together than the 'Z' shaped *trans* forms, causing *cis* isomers to have lower melting points than their *trans* twins. However, *cis* forms are sometimes polar, and thus they have stronger inter-molecular forces than *trans* forms, causing them to have higher boiling points.

Optical isomers

Whenever four different groups are attached to a single carbon atom, they can be attached in two different ways which are mirror images of each other:



Attach four different groups to a central atom. Two different structures, which are mirror images of each other, can be formed.

A carbon atom with four different groups off it is sometimes called a **chiral** carbon, and sometimes called an **asymmetric** carbon. The four different groups can be as simple as an H, a CH_3, a CH_2CH_3, and a $CH_2CH_2CH_3$.

Drawing molecules in three dimensions

Organic chemists use specific symbols to show molecules in three dimensions.

- A 'staircase' going down represents a bond which goes down into the page.
- A wedge represents a bond coming out of the page towards you (the thick end is closer to you).
- A plain line represents a bond which is in the plane of the page itself.

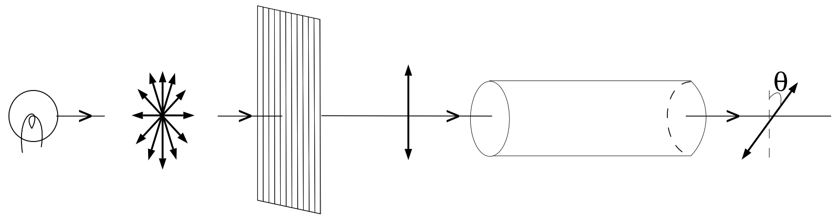
Your hands are mirror images of each other. You cannot *superimpose* your right hand on top of your left hand (say with both palms down and the thumbs on the same side). Similarly, you cannot superimpose these two mirror image isomers.

The isomers created by a chiral carbon have identical chemical properties, and their physical properties are also the same, except for one:

the two isomers will rotate plane-polarised light in opposite directions**.**

For this reason they are known as **optical isomers**.

Huh? Well, you could just memorise the phrase and be ready to write it in the exam, but it would help to understand it first!



Light is a wave. A light source (lamp) makes lots of waves. All the waves come outwards from the lamp, but they vibrate in lots of planes (directions): some of them up and down, others side to side and at all the other angles. A polarising filter is like a sheet with many fine slits in it. Only light vibrating in one plane is able to pass through the filter. We call light vibrating in only one plane *plane-polarised*.

An optically active solution rotates plane-polarised light—it turns the wave so that it vibrates in a different plane. One optical isomer of a particular substance will rotate the wave to the left, and the other to the right. The angle of rotation depends on the compound involved, its concentration, and the length of the light path.

A large number of organic compounds have optical isomers, including many of the hormones and enzymes found in living things. In biochemical reactions, the shape of the molecule is of critical importance, and just as a left hand and a right hand cannot shake hands, so the mirror image of an enzyme will not work properly in the body. In nature, most of the biologically active compounds rotate light to the left. The 'right-handed' form of adrenalin, for example, has no effect on the human body.

Optical isomers have identical chemical and physical properties except that they rotate plane-polarised light in opposite directions. They may perform differently in biochemical systems.

POWERPOINT

7B Properties of optically active compounds

ENCOUNTER

7B1 Louis Pasteur

7B2 Optically active compounds

Only those waves which vibrate in the right plane are able to pass through the polarising filter.

REVISION

7B 1 Isomers

7B 2 Optical isomers key facts

7B 3 Understanding optical isomers

Quizzes 7B 1a, 7B 1b, 7B 2, 7B 3

Test yourself 7B Isomers

1 Draw and name all the isomers of C_4H_8

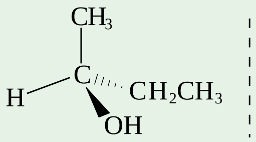
2 **a** Which of the following compounds exhibit *cis-trans* isomerism?

i CH_2=CHBr ________ **ii** CHCl=CClCH_3 ________

iii CH_2=CCl_2 ________ **iv** CH_3CH_2CH=CHCH_3 ________

b Draw and name the *cis-trans* isomers of those compounds in **a** which have *cis-trans* isomers.

3 Draw the optical isomer of this compound.



4 Which of these compounds will have optical isomers?

a CH_3CH(OH)COOH ________ **b** $(CH_3)_2$CHOCH_3 ________

c NH_2CH_2COOH ________ **d** NH_2CH(CH_3)COOH ________

5 **a** What are the physical differences between optical isomers? ________________________________

____

b How do optical isomers differ in biochemical systems? ________________________________

____

Reaction types

You'll probably be asked to classify certain reactions by their type.

You should remember the following types of reactions from your Level 2 Chemistry.

Substitution reactions

In a **substitution** reaction, one atom is exchanged for another. There are two products. You should remember that alkanes undergo a slow substitution reaction with bromine in the light:

$$CH_3CH_3 + Br_2 \xrightarrow{\text{UV light}} CH_3CH_2Br + HBr$$

You will meet some more substitution reactions in Chapter 8.

Addition reactions

In **addition** reactions, a double bond is broken and atoms are added into the molecule. Addition reactions are normally rapid and have only one product.

$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

When the addition reagent (eg Br_2) is symmetrical—as Br_2 is— there will be only one product. Each carbon of the double bond will bond with a Br atom. But when the addition reagent is unsymmetrical (eg HBr or H_2O), the two carbon atoms will bond with different atoms. Often that results in two different compounds.

$$CH_3CH{=}CH_2 + HBr \longrightarrow CH_3CHBrCH_3 + CH_3CH_2CH_2Br$$

If the two carbon atoms of the double bond are bonded to different numbers of hydrogen atoms, then **Markovnikov's rule** applies:

POWERPOINT

7C Hydrocarbons (revision)

the hydrogen atom of the addition reagent tends to go to the carbon atom (of the double bond) attached to the greatest number of hydrogen atoms.
It's easier to remember the summary: ***the rich get richer***.

$$\underset{\text{poor}}{CH_3CH} = \underset{\text{rich}}{CH_2} + HBr \longrightarrow \underset{\text{major product}}{CH_3CHBrCH_3} + \underset{\text{minor product}}{CH_3CH_2CH_2Br}$$

A major product is the one you get most of; the minor product is produced in smaller amounts.

Condensation reactions

In **condensation** reactions, two large(ish) molecules combine, discarding a small one—often water or HCl. The formation of an ester from an alcohol and an acid is a condensation reaction:

$$HCOOH + CH_3CH_2OH \xrightarrow{\text{conc } H_2SO_4} HCOOCH_2CH_3 + H_2O$$

When amino acids combine to make protein they do so in a series of condensation reactions.

Elimination reactions

Elimination reactions are the reverse of addition reactions. They form double bonds. You have already met the formation of an alkene by dehydration of an alcohol:

$$CH_2CH_3OH \xrightarrow{\text{conc } H_2SO_4} CH_2 = CH_2 + H_2O$$

Saytzeff's rule (a reverse of Markovnikov's rule) applies:

the hydrogen tends to be eliminated from that carbon atom joined to the least number of hydrogen atoms.

In other words ***the poor get poorer***.

$$\underset{\text{poor}}{CH_3}\text{—}CH_2\text{—}\underset{\substack{|\\ OH}}{CH}\text{—}\underset{\text{rich}}{CH_3} \xrightarrow{\text{conc } H_2SO_4} \begin{array}{c} \underset{\text{major product}}{CH_3\text{—}CH = CH\text{—}CH_3} \\ \underset{\text{minor product}}{CH_3\text{—}CH_2\text{—}CH = CH_2} \end{array} + H_2O$$

Remember that whenever there is a choice of products, both will form — it's just that you may get more of one than the other. If you're told to write the major product, do so. Likewise, write the major product where there is only one option possible. Otherwise, write both products and indicate which is the major product.

Oxidation-reduction reactions

Oxidising agents such as H^+/MnO_4^-, $H^+/Cr_2O_7^{2-}$ and even Cu^{2+} are an important part of organic chemistry. The oxidation of a primary alcohol produces an aldehyde, followed by a carboxylic acid.

$$CH_3CH_2OH \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3CHO \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3COOH$$

You will meet some other important oxidation reactions in Chapter 8.

REVISION

7C 1 Hydrocarbon key facts
7C 2a Completing organic reactions 1
7C 2b Classifying reactions
7C 2c Organic choices

Quizzes 7C 1, 7C 2a, 7C 2b

Test yourself 7C Types of reactions

1–4 Complete these reactions and state the reaction type in each case. Where relevant, write only the *major* organic products.

1 $CH_3CH = C(CH_3)CH_2CH_3 + HBr \longrightarrow$ ____________

2 $CH_3CH_2CH_2OH + HCOOH \xrightarrow{\text{conc } H_2SO_4}$ ____________

3 $CH_3CH_3 + Br_2 \xrightarrow{\text{UV light}}$ ____________

4 $CH_3\text{—}CH_2\text{—}\underset{\substack{|\\ OH}}{CH}\text{—}\underset{\substack{|\\ CH_3}}{CH}\text{—}CH_3 \xrightarrow{\text{conc } H_2SO_4}$

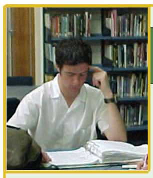
Key learning outcomes for Chapter 7

By now you should be able to:

1. Draw condensed structural formulae for, and name, organic compounds with up to 8 carbons in the series studied.
2. Identify the functional groups present in given organic compounds.
3. Identify examples of structural, geometric and optical isomers.
4. Identify the major and minor products of reactions involving alkenes.
5. Recognise substitution, addition, condensation, elimination and oxidation-reduction reactions.

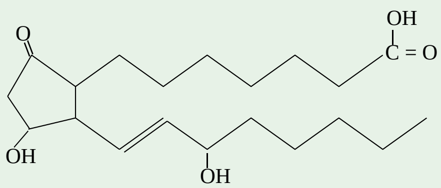
EXAM QUESTIONS

Practice questions



Review questions for Chapter 7

1 Circle and name each functional group on this structure for the hormone prostaglandin. **A**



2 Name these compounds. **A**

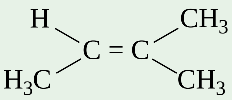
a CH_3CHO ____________________

b $CH_3CCl_2CH{=}CH_2$ ____________________

c $CH_3CHNH_2CH(CH_3)_2$ ____________________

d CH_3CH_2COCl ____________________

e



____

3 Draw condensed structural or structural formulae for these compounds. **A**

a ethanamide **b** pentan-2-one **c** methanoyl chloride

4 2, 3-dichlorobut-2-ene has two isomers: one polar, the other non-polar.

a Draw and name both isomers. **A**

b Which isomer would you expect to have the lower boiling point? **A** ____________________

c How many isomers of 2. 3 dichlorobut-1-ene would you expect, and why? **A M** ____________________

____

____

5 Amino acids, the building-block molecules of proteins, contain both an amino (NH_2) group and an acid (COOH) group. Most amino acids have optical isomers.

a Draw the structural formulae for both isomers of the simplest amino acid to have optical isomers. **A**

b Discuss the similarities and differences between these two compounds. **A M E**

6 Write equations, using condensed formulae, for the following reactions: **A M E**

a the addition reaction between hydrogen chloride and but-2-ene (major products only)

b the formation of ethyl butanoate from an acid and an alcohol

c the oxidation of butan-1-ol by $H^+/Cr_2O_7^{2-}$ (organic product only)

d the hydrolysis of but-1-ene (identify major and minor products)

e the oxidation of pentanal (organic product only)

7 Draw structural formulae to show the dehydration of 3-methylpenan-2-ol. Show and name all possible products. **A M E**

8

Alcohols and their derivatives

Alcohols

Alcohols contain the –OH group (called the hydroxy group).

Naming

The name of an alcohol ends in -anol. You can either put the number (indicating where the -OH group is) next to the -ol, or at the beginning of that section of the name.

$$CH_3CHOHCH_3 = \text{propan-2-ol or 2-propanol}$$

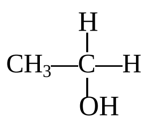
Normally we are concerned about compounds with only one –OH group; however the following should also be learnt.

ethan-1, 2-diol (ethylene glycol) found in antifreeze

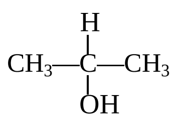
propan-1, 2, 3-triol (glycerol) found in moisturisers

Primary, secondary and tertiary alcohols

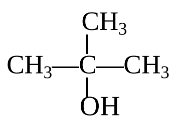
Alcohols are classified as *primary* (1°), *secondary* (2°) or *tertiary* (3°) according to the number of carbon atoms bonded to the carbon with the hydroxyl group. The different classes of alcohols have different chemical properties.



primary alcohol



secondary alcohol



tertiary alcohol

Methanol, with no carbons attached to the carbon attached to the –OH, is considered to be a primary alcohol.

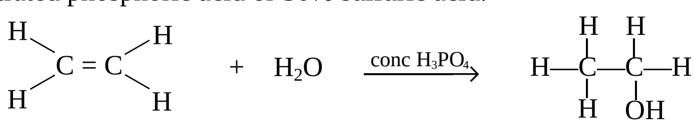
Preparation of alcohols

Ethanol can be made by fermentation of sugar.

Methanol can be made by destructive distillation of wood (the old name for methanol was wood alcohol) or from synthesis gas (recall the synthetic petrol process).

$$CO + 2H_2 \longrightarrow CH_3OH$$

All alcohols can be made by hydration of alkenes using a catalyst of concentrated phosphoric acid or 50% sulfuric acid.



Remember that Markovnikov's rule will apply (see page 77).

Alcohols can also be made from haloalkanes (see page 84).

Physical properties

An alcohol has physical properties that depend on its similarity to water or to an alkane. The lower alcohols are colourless, water-soluble liquids but as the size of the carbon chain increases, the solubility rapidly decreases so that the higher alcohols are waxy solids. The –OH group makes that part of the molecule *polar* and allows for hydrogen bonding to adjacent molecules and to water. Hydrogen bonding also causes alcohols to have much higher melting and boiling points than their corresponding alkanes.

Alkane	Boiling point	Alcohol	Boiling point
methane	–162 °C	methanol	64 °C
ethane	–89 °C	ethanol	78 °C
propane	–42 °C	propan-1-ol	98 °C

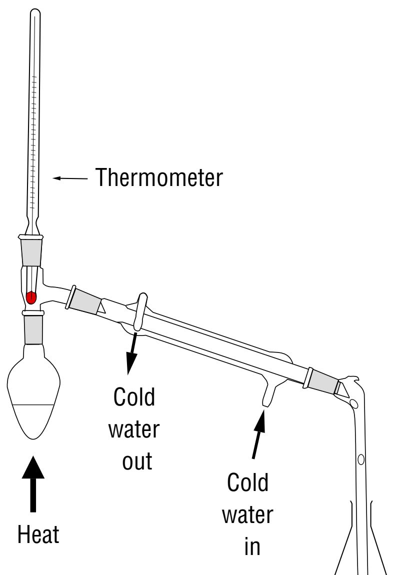
Chemical properties

Combustion

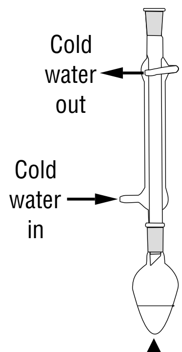
Alcohols burn readily with a non-smoky flame to form CO_2 and H_2O.

PRACTICALS

8.1 P 177 Oxidation of alcohols



Distillation—to collect a volatile product.



Refluxing—to prevent loss by evaporation.

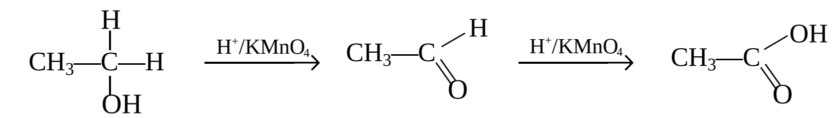
Oxidation

The reactions of alcohols with oxidising agents like dichromate and permanganate depend upon the structure.

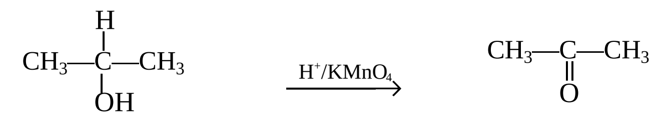
- Primary alcohols are oxidised first to the aldehyde, and then to the carboxylic acid.

  If the aldehyde is the desired product, use a mild oxidising agent ($K_2Cr_2O_7$ rather than $KMnO_4$) and distil off the product quickly. Aldehydes have a lower boiling point than their corresponding alcohols because they do not hydrogen bond, so the aldehyde readily distils off.

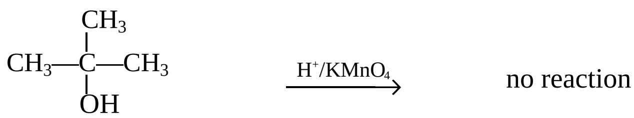
  If the carboxylic acid is required, do the reaction under reflux, returning the aldehyde to the reaction vessel for further oxidation.
- Secondary alcohols are oxidised to the ketone.
- Tertiary alcohols are not oxidised by common oxidising agents (but will still burn).



primary alcohol aldehyde carboxylic acid



secondary alcohol ketone



tertiary alcohol

Dehydration by concentrated sulfuric acid (elimination)

Concentrated sulfuric acid is a powerful dehydrating agent which will rip water molecules out of compounds containing H and OH, including alcohols. The product is an alkene. Saytzeff's rule may apply.

$$CH_3CH_2OH \xrightarrow{\text{conc } H_2SO_4} CH_2 = CH_2 + H_2O$$

Substitution by chlorine (chlorination)

Chloroalkanes are important reagents in the formation of other organic compounds. Alcohols can form chloroalkanes with three different reagents:

- ***with phosphorous pentachloride PCl_5***

  $$ROH(l) + PCl_5(s) \longrightarrow RCl(l) + POCl_3(l) + HCl(g)$$

  Phosphorus trichloride (PCl_3) reacts in exactly the same way, forming POCl as the middle product.

- ***with thionyl chloride $SOCl_2$***

  $$ROH(l) + SOCl_2(l) \longrightarrow RCl(l) + SO_2(g) + HCl(g)$$

  Thionyl chloride is a particularly useful reagent because the other two products of this reaction are gases and bubble off, leaving RCl as the only product.

- ***with $HCl/ZnCl_2$ (Lucas reagent)***

  A mixture of conc HCl and anhydrous zinc chloride crystals (which act as a catalyst) will react with alcohols to form chloroalkanes.

  $$R\text{—}OH + HCl \xrightarrow{ZnCl_2} R\text{—}Cl + H_2O$$

POWERPOINT

8A Reactions of alcohols

Distinguishing alcohols using the Lucas test

The Lucas test can be used to distinguish between water-soluble alcohols. 3° alcohols go cloudy immediately due to the formation of the chloroalkane which is immiscible in water, while the 2° alcohols go cloudy after a few minutes when warmed. No reaction after 10 minutes should indicate a 1° alcohol. (1° alcohols will eventually react with $HCl/ZnCl_2$, given enough time.) The identification of the alcohol can be confirmed by testing with an oxidising reagent. Remember, 1° alcohols are oxidised to form aldehydes and acids, 2° form ketones, and 3° won't react at all.

PRACTICALS

8.2 P 178 Reactions of alcohols with Lucas reagent

Condensation reactions with carboxylic acids

Alcohols react with carboxylic acids to form esters. An acid catalyst is needed. Concentrated sulfuric acid is usually used because it also removes the water produced and helps drive the equilibrium reaction to the right.

$$R\text{—}OH + R'COOH \rightleftharpoons R'COOR + H_2O$$

Esters are discussed in more detail on pages 97–99 .

Alcohols also form esters with acyl chlorides (see page 96).

REVISION

8A 1a Oxidation of alcohols

8A 1b Completing organic reactions 2

Quiz 8A 1

Test yourself 8A Alcohols

1 Write the condensed structural formulae and systematic names for ethylene glycol and glycerol.

2 Write the condensed structural formulae and systematic names for the 5-carbon:

a primary alcohol **b** secondary alcohol **c** tertiary alcohol

3 How do primary, secondary and tertiary alcohols differ in their reactions with $Cr_2O_7^{2-}/H^+$?

4 How do the three classes of alcohols differ in their rate of reaction with the Lucas reagent?

5 Write equations for the following reactions:

a 2-methylpropan-1-ol with H^+/MnO_4^- (under distillation)

b methanol with H^+/MnO_4^- (under reflux)

c pentan-2-ol with $H^+/Cr_2O_7^{2-}$

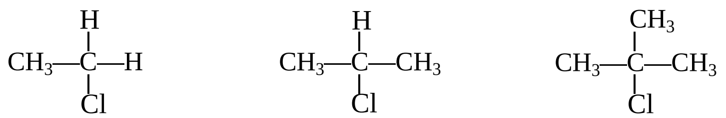
d 2-methylpropan-2-ol with $HCl/ZnCl_2$

e butan-1-ol and PCl_5

f ethanol and $SOCl_2$

Haloalkanes (alkyl halides)

Haloalkanes are alkanes in which one (or more) hydrogen atoms have been replaced by halogen atoms. Like alcohols, haloalkanes are classified as primary, secondary or tertiary, according to the number of carbon atoms bonded to the carbon atom bonded to the halogen.



primary chloroalkane   secondary chloroalkane   tertiary chloroalkane

Naming

Haloalkanes are normally named as the halogen side-group of an alkane, eg CH_3CH_2Cl chloroethane $CH_2BrCH_2CH_2Br$ 1, 3-dibromopropane.

Physical properties

Fluoroalkanes are relatively unreactive (due to the strong C—F bond) and are usually considered separately as fluorocarbons.

Chloromethane, bromomethane and chloroethane are colourless gases at room temperature and pressure. Other low-mass haloalkanes are colourless, pleasant-smelling liquids, often volatile. Higher molar masses are solids.

Although polar, haloalkanes are only slightly soluble in water because no hydrogen bonding can occur. Their polarity does cause their boiling points to be higher than their corresponding alkanes.

POWERPOINT

8B 1 Preparation of a haloalkane

8B 2 Properties of haloalkanes

PRACTICALS

8.3 P 179 Preparation of 2-chloro 2-methylpropane

8.4 P 180 Hydrolysis of haloalkanes

Preparation

Haloalkanes can be formed by:

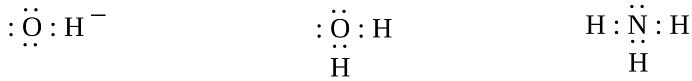
- substitution of a halogen with an alkane (in light)
- addition of HX to an alkene (remember Markovnikov's rule)
- chlorination of an alcohol with $HCl/ZnCl_2$, PCl_5 or $SOCl_2$.

Chemical reactions

Short-chain haloalkanes do not burn readily or react with oxidising agents, but they do react with metals, especially sodium and magnesium, and they do undergo very important substitution reactions and elimination reactions.

Nucleophilic substitution

A **nucleophile** is any species which 'loves' nuclei—that is, anything attracted to a positive charge. Nucleophiles are therefore species carrying a negative charge or a lone pair of electrons, in particular $OH^-(aq)$, H_2O and $NH_3(alc)$.



The C—X bond in haloalkanes is polar, and therefore the C has a slight positive charge. Some of the molecules may have already ionised into R^+ and X^-. Either way, the positive centre is vulnerable to attack by any passing nucleophile. Thus:

$$R\text{—}X(l) + OH^-(aq) \longrightarrow R\text{—}OH + X^-(aq)$$

$$\text{(Tertiary only) } R\text{—}X(l) + H_2O(l) \longrightarrow R\text{—}OH + HX(aq)$$

For NH_3 to act as a nucleophile it must be dissolved in alcohol, not in H_2O (which would produce NH_4^+ and OH^-: NH_4^+ has no lone pairs, and the OH^- would react with the R—X instead of the NH_3).

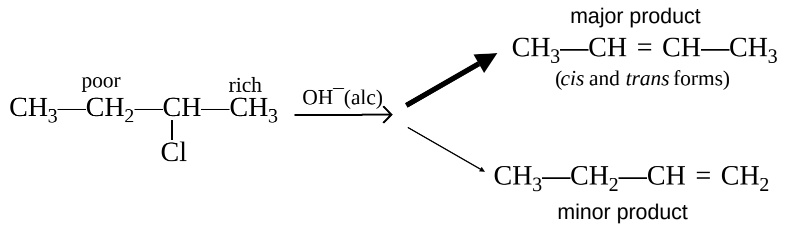
$$R\text{—}X(l) + NH_3(alc) \longrightarrow \underset{\text{amine}}{R\text{—}NH_2} + HX(alc)$$

Elimination reactions

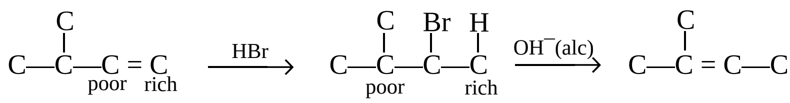
Just as alkenes form haloalkanes, so the reaction can be reversed:

$$R\text{—}X \xrightarrow{OH^-(alc)} R=C + HX$$

The KOH or NaOH is dissolved in alcohol to prevent nucleophilic substitution—also the ethanol forms an intermediate step in the formation of the double bond. Tertiary haloalkanes undergo elimination the fastest while primary haloalkanes are very difficult to turn into alkenes. Remember that the reverse of Markovnikov's rule applies: the poor get poorer.



But notice what happens here:



(At each step there are, of course, major and minor products.)

This sequence of reactions can be used to shift a double bond from one position to another.

Haloalkanes you may have met

- Teflon is a fluorocarbon used to make paint and non-stick frying pans.
- Chloroform is $CHCl_3$. Used primarily as a solvent, it is also found in cough mixtures and in gangster movies as an anaesthetic.
- 'Carbon tet' is tetrachloromethane, CCl_4. It is an excellent solvent and was used in fire extinguishers and extensively in dry-cleaning fluids until it was discovered to cause liver damage. Other dry-cleaning fluids and solvents used in paint strippers are also haloalkanes (and all such fluids should be used sparingly and with good ventilation).

REVISION

8B 3a General reactions of alcohols and haloalkanes
8B 3b Completing organic reactions 3
Quizzes 8B 2, 8B 3a, 8B 3b

Test yourself 8B Haloalkanes

1 Write the condensed structural formula for and name a 5-carbon:
 a primary chloroalkane **b** secondary bromoalkane **c** tertiary chloroalkane

2 Compare the physical properties of haloalkanes with their corresponding alkanes and alcohols.

3 What is a nucleophile? Give two examples.

4 **a** Write a balanced equation for the reaction between bromoethane and aqueous potassium hydroxide.

 b Write a balanced equation for the reaction of 2-iodobutane and alcoholic ammonia.

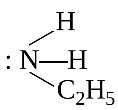
5 **a** Write an equation for the reaction between 2-methylbutan-2-ol and alcoholic potassium hydroxide.

 b What kind of reaction takes place in **a** above?

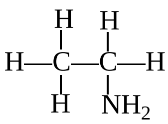
Amines

Amines contain the amino group, $–NH_2$. They can be viewed in two ways:

1 as an ammonia molecule with one (or more) hydrogens replaced by alkyl groups.



2 as an alkane with a hydrogen atom replaced by an amino group.



Naming

The naming of amines is derived from the structure.

If the amine is thought of as a variation on ammonia (ie structure **1** above) then the name is as an **alkyl** derivative of ammonia, eg ethylamine, $NH_2C_2H_5$.

If the amine is thought of as a variation on an alkane then the name is as an **amino** derivative of an alkane, eg $CH_3CH_2NH_2$, aminoethane. The standard IUPAC name is aminoethane, but ethylamine is used on reagent bottles, so you really do need to understand both methods of naming.

Types of amines

There are *primary*, *secondary*, and *tertiary* amines depending on the number of carbon atoms the nitrogen is bonded to. CH_3NHCH_3 is a secondary amine because the nitrogen atom is bonded to two carbon atoms.

CH_3—$\underset{\mid}{CH}$—CH_3 OH	CH_3—$\underset{\mid}{CH}$—CH_3 Br	CH_3—$\underset{\mid}{CH}$—CH_3 NH_2
secondary alcohol	secondary haloalkane	primary amine

In this course we are mainly concerned with primary amines.

Preparation

Primary amines can be prepared by the nucleophilic substitution of an haloalkane by *alcoholic* ammonia.

$$CH_3CH_2CH_2Cl(l) + NH_3(alc) \longrightarrow CH_3CH_2CH_2NH_2(l) + HCl(alc)$$

Physical properties

Primary and secondary amines can hydrogen bond with each other and with water. (Remember that hydrogen bonding occurs in compounds where a hydrogen atom is bonded to a N, O or F atom: in tertiary amines the N is bonded to three carbon atoms, so hydrogen bonding cannot occur.) This hydrogen bonding is stronger in primary amines than secondary, but not as strong as the hydrogen bonding in alcohols. Thus, methyl amine and ethyl amine are gases at 20 °C; other low-mass amines are volatile liquids with a characteristically fishy smell. Amines with more than 5 carbons are usually solid. Low molar mass amines are soluble in water, higher amines are not.

POWERPOINT

8C Properties of amines

PRACTICAL

8.5 P 181 Properties of amines

Chemical properties

Behaviour in water

Amines are *bases*—like ammonia. They turn damp litmus paper and universal indicator solution blue. The lone pair of electrons on the nitrogen atom makes the molecule a nucleophile and causes it to accept a proton from water (ie it shares a pair of electrons with a proton—the hydrogen ion in water).

$$R—NH_2 + H_2O \rightleftharpoons R—NH_3^+ + OH^-$$
$$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$$

Amines of low molar mass are ***stronger bases than ammonia*** because the alkyl radical does not hold on to its electrons as strongly as hydrogen atoms do. So the partial negative charge on the nitrogen atom of an amine is greater than that on the nitrogen atom of ammonia.

Reaction with HCl

As bases, amines react with acids such as HCl to form salts just as ammonia does.

$$NH_3(g) + HCl(g) \longrightarrow NH_4^+Cl^-(s)$$

eg $$\underset{\text{aminomethane}}{CH_3NH_2(g)} + HCl(g) \longrightarrow \underset{\text{methyl ammonium chloride}}{CH_3NH_3^+Cl^-(s)}$$

The amine shares the lone pair in the nitrogen atom with a proton from the acid, to form a salt. All amines, even the larger ones that don't dissolve in water, react with acids to form salts. These salts are colourless, crystalline solids, soluble in water (as all ammonium salts are soluble) and have no smell. The citric acid in lemon juice and the acetic acid in vinegar react readily with the amines found in seafood, forming non-smelly salts. That's one reason lemons and vinegar are often served with fish.

Reaction with copper sulfate

Just as copper sulfate reacts with ammonia to give first a pale blue precipitate of $Cu(OH)_2$ and then the deep blue solution of $[Cu(NH_3)_4]^{2+}$ (tetrammine copper(II) complex), so amines also react with Cu^{2+} solutions to give deep blue complexes which are soluble in water.

eg $Cu^{2+}(aq) + 4C_2H_5NH_2(aq) \longrightarrow [Cu(C_2H_5NH_2)_4]^{2+}(aq)$

Uses of amines

It is rare to find free amines in nature but they are produced by the decomposition of proteins. Amines are not in frequent use, but some are used in detergents, antiseptic powders and in some drugs.

ENCOUNTER

8C Vital amines

REVISION

8C 1 Alcohols, haloalkanes and amines key facts

8C 3 Completing organic reactions 3

Quizzes 8C 1, 8C 2, 8C 3a, 8C 3b

Test yourself 8C Amines

1 Write the structural formulae for a 5-carbon
a primary amine **b** secondary amine **c** tertiary amine

2 How would you confirm that a colourless organic liquid was an amine?

3 Write equations for the following reactions, naming the organic product for **a** and **b**.
a aminomethane with water

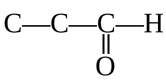
b aminoethane with HCl

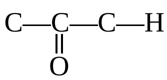
c 1-aminopropane with $Cu^{2+}(aq)$

Aldehydes and ketones

Aldehydes and ketones are generally treated together because they both contain the **carbonyl** group, C=O.

Aldehydes and ketones with the same number of carbons are structural isomers.


propanal

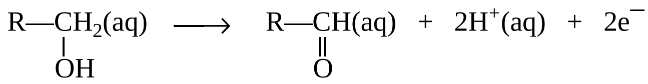

propanone

Naming

Aldehydes have the C=O on the end (terminal) carbon. The name ends in –anal.
Ketones have the C=O on a middle (non-terminal) carbon. The name ends in –anone. If the ketone has more than 4 carbons the position of the carbonyl group must be specified, eg pentan-3-one.

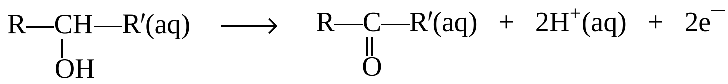
Preparation

Aldehydes are produced by the oxidation of *primary* alcohols. The mixture must be distilled to prevent the oxidation continuing on to produce the carboxylic acid.



primary alcohol aldehyde

Ketones are produced by the oxidation of *secondary* alcohols.



secondary alcohol ketone

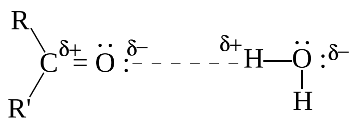
POWERPOINT
8D1 Preparation of an aldehyde

Physical properties

Except for methanal (formaldehyde), which is a gas (BP –21 °C), the lower aldehydes and ketones are all colourless liquids at room temperature. The aldehydes possess rather unpleasant, pungent smells, whereas the ketones have pleasant, sweet odours.

Inter-molecular attractions between both series of polar compounds cause them to have higher boiling points than alkanes of similar mass, but since the molecules cannot form hydrogen bonds with each other they are considerably more volatile than the corresponding alcohol and carboxylic acid.

The low-mass aldehydes and ketones are appreciably soluble in water due to their ability to form hydrogen bonds *with water*:



Low-mass aldehydes and ketones can hydrogen-bond with water.

Aldehydes or ketones containing more than five carbons are virtually insoluble in water.

All carbonyl compounds in these series are miscible with most of the usual oxygen-containing organic solvents and the simpler ones, notably propanone (acetone), are themselves useful solvents.

Chemical reactions

PRACTICAL
8.6 P 182 Reactions of aldehydes and ketones

This year we are mostly concerned with distinguishing between aldehydes and ketones. All these reactions depend on the fact that aldehydes can be oxidised to carboxylic acids but that ketones do not oxidise further (except by combustion).

Three classic (ie popular with examiners) redox tests need to be learnt.

1 Acidified potassium dichromate/permanganate (warm)

These oxidising agents oxidise both alcohols (1° and 2°) and aldehydes. The reactions are very slow at room temperature, so it is best to warm the mixture in a water bath. Dichromate must be acidified first, and changes from orange to colourless. If permanganate is acidified it will change from purple to colourless, otherwise it forms a brown precipitate.

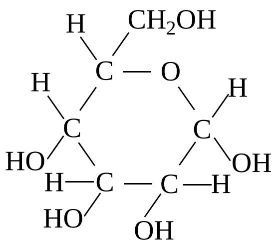
2 Tollens reagent (warm)

Tollens reagent is the diammine silver complex $[Ag(NH_3)_2]^+$, made by adding a drop of sodium hydroxide solution to 1 mL of silver nitrate solution, then dissolving the precipitate that forms in a minimum of ammonia solution. It is a mild oxidising agent that will oxidise aldehydes but not alcohols. When aldehyde is added to Tollens reagent and warmed (in hot water) the aldehyde is oxidised to carboxylic acid and the diammine silver is reduced to silver metal. The metallic silver is seen as either a fine black precipitate or as a 'silver mirror' on the inside of the clean test tube. Tollens reagent does not react with ketones.

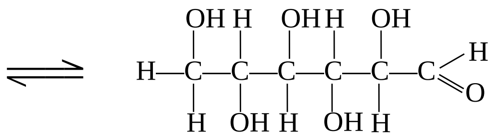
3 Benedict / Fehling's solution (boil)

Benedict (or Fehling's) solution contains Cu^{2+} ions in the form of a complex. Blue Cu^{2+} is a mild oxidising agent which can be reduced by an aldehyde to form copper(I) oxide (Cu_2O), which is a red-brown precipitate. Ketones and alcohols do not react with Cu^{2+}.

The Benedict test for aldehydes will be recognised as the test for a reducing sugar (eg glucose). The test is the same because the straight-chain form of glucose (as opposed to the ring form) is an aldehyde.



Ring form of glucose



Aldehyde form of glucose

POWERPOINT

8D 2 Distinguishing between aldehydes and ketones

Uses of aldehydes and ketones

- Formalin is a 40% solution of methanal (a gas) dissolved in water. It is used as a disinfectant and a preservative.
- Acetone is used as a solvent (nail-polish remover) and to dissolve acetylene gas for welding, while butanone is the solvent in model aeroplane glue.
- Many aldehydes are used as starting materials for making other compounds.

REVISION

8D 1 Aldehyde and ketone key facts

8D 2a Choosing the product (1)

8D 2b Completing organic reactions 5

Quizzes 8D 1, 8D 2a, 8D 2b

Test yourself 8D Aldehydes and ketones

1 Compare the physical and chemical properties of aldehydes and primary alcohols.

2 What is Tollens reagent, and how is it used?

3 A few drops of Benedict solution are heated with glucose solution in a water bath.

a What would you observe?

b Identify the two coloured species in this reaction.

4 What is the relationship between aldehydes and ketones with the same number of carbon atoms?

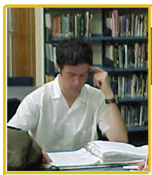
Key learning outcomes for Chapter 8

By now you should be able to:

1. Name and draw condensed structural formulae for given alcohols.
2. Give the structure of ethylene glycol (a diol) and glycerol (a triol).
3. Describe alcohols as primary, secondary or tertiary by referring to their structure or their chemical properties.
4. Describe the action on alcohols of:
   - oxidising agents such as $H^+/Cr_2O_7^{2-}$ or H^+/MnO_4^-
   - concentrated sulfuric acid
   - $ZnCl_2/HCl$ (Lucas reagent)
   - PCl_3 or PCl_5
   - $SOCl_2$ (thionyl chloride)
   - carboxylic acids or acyl chlorides
5. Name and draw condensed structural formulae for a variety of haloalkanes.
6. Describe, using equations, the nucleophilic substitution of haloalkanes with:
   - aqueous hydroxide ion (or water)
   - alcoholic ammonia.
7. Describe, using equations, the elimination of haloalkanes with alcoholic hydroxide ion to give alkenes as a competing reaction with substitution.
8. Name and draw condensed structural formulae for given primary amines.
9. Recognise primary, secondary and tertiary amines from their structures.
10. Describe the main properties of primary amines, showing their similarity to ammonia:
    - characteristic smell
    - hydrolysis with water
    - salt formation with acids
    - complex formation with copper sulfate solution.
11. Name and draw condensed structural formulae for given aldehydes and ketones, noting the common carbonyl group.
12. Describe the use of a mild oxidising agent (Tollens or Benedict reagents) to distinguish between aldehydes and ketones.
13. Explain why it is necessary to distill the reaction mixture of primary alcohol and oxidising agent to obtain the aldehyde.

EXAM QUESTIONS

Practice questions



Review questions for Chapter 8

$2CH_3H_6(g) + 2H_2(g) + 2CO(g)$

$\downarrow$

compound A + compound B ______

$CH_3CH_2CH_2CHO(l)$

$\downarrow$ $\downarrow$

butan-1-ol alcohol C

1 Part of a reaction sequence between synthesis gas and propene is shown on the right.
Compound A has the formula $CH_3CH_2CH_2CHO$. Compound B is an isomer of A and belongs to the same class of organic compound.

a Which series of organic compounds do A and B belong to? **A**

b Draw the condensed structural formula of B and name it. **M**

c What reagent would be used in place of propene if hexan-1-ol was to be produced instead of butan-1-ol? **A**

d Will alcohol C be primary, secondary or tertiary? **A** ______

e Draw the condensed structural formula of the organic product formed when butan-1-ol reacts with ethanoic acid in the presence of concentrated sulfuric acid. **A**

2 Write the formulae for the (major) organic products of these reactions and name the compounds formed. **A M**

a $CH_3CH_2OH + SOCl_2 \longrightarrow$ ______

b $CH_3CH_2NH_2 + HCl \longrightarrow$ ______

c $CH_3CHBrCH_3 + NH_3(alc) \longrightarrow$ ______

d $CH_3CHOHCH_3 + H^+/MnO_4^- \longrightarrow$ ______

e $CH_3CHBrCH_2CH_3 + OH^-(alc) \longrightarrow$ ______

3 Write equations (organic reagents only) for the reactions between **A M E**

a the Lucas reagent and 3-methylpentan-3-ol

b aqueous sodium hydroxide and chloromethane

c the oxidation of butanal by acidified potassium dichromate (under distillation)

d the hydration of but-1-ene

e Tollens reagent and pentanal

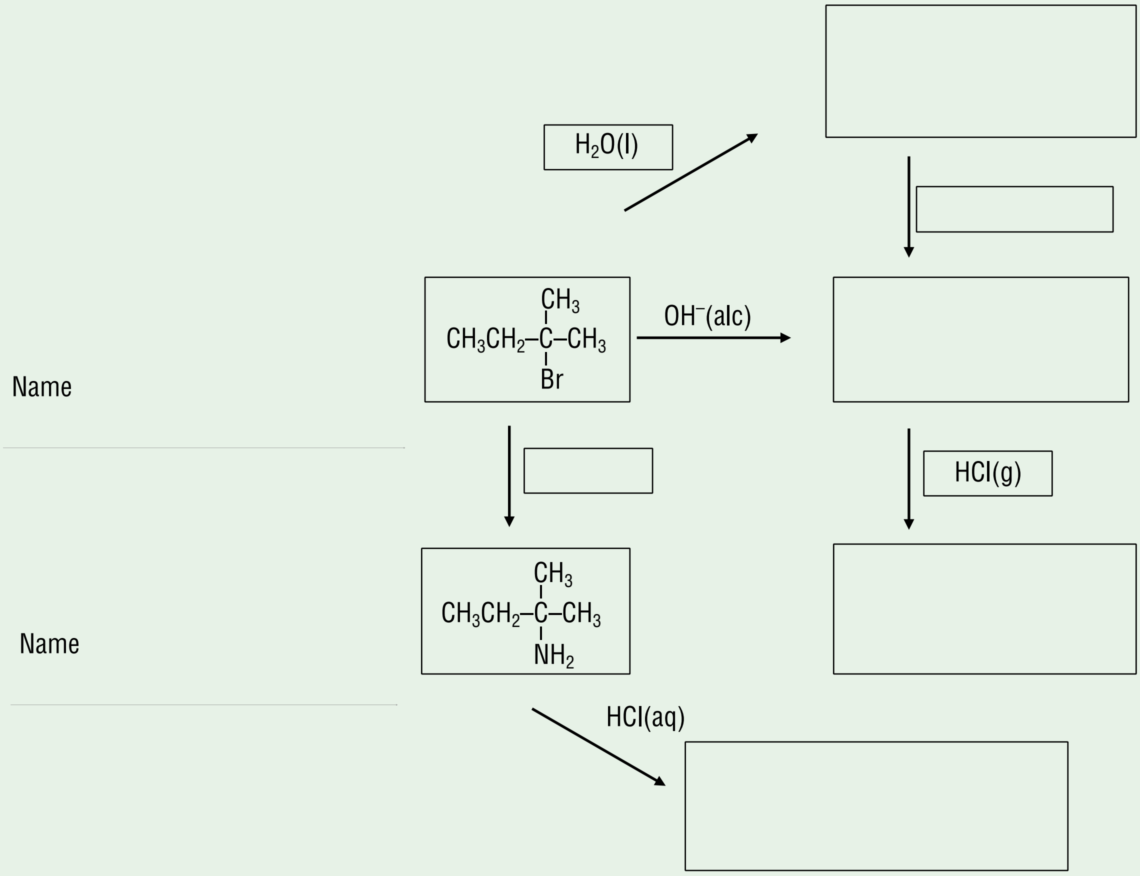
4 Give a chemical test (say what you would do and see in each case) which would distinguish between **A M**

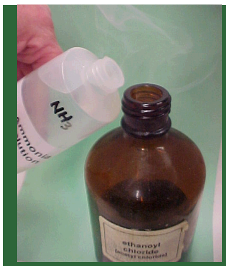
a 2-aminobutane and 2-chlorobutane

b propanal and propan-1-ol

c butan-1-ol and butan-2-ol

5 Complete the diagram below, writing the structural formulae of the *major* products where applicable, and naming those compounds indicated. **A M E**



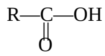


9

Carboxylic acid derivatives and polymers

Carboxylic acids

Carboxylic acids have the general formula RCOOH.


carboxylic acid

Naming

The names of carboxylic acids end in –anoic acid, eg ethanoic acid CH_3COOH.

Since the –COOH is always on the end carbon there is no need to number the functional group.

Preparation and natural sources

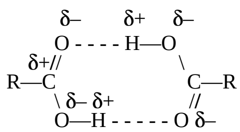
Formic (methanoic) acid is found in ant stings and nettles. Ethanoic (acetic) acid is the active ingredient in vinegar and is made by the oxidation of ethanol. Citric acid, ascorbic acid (vitamin C) and acetyl salicylic acid (aspirin) are also very common.

In the laboratory carboxylic acids are made by the oxidation of primary alcohols and aldehydes.

Physical properties

All the simple, straight-chain carboxylic acids up to C_{10} are liquids at room temperature, although pure ethanoic acid freezes to an ‘ice-like’ solid below 17 °C and is commonly known as *glacial* acetic acid. The liquids have sharp, pungent odours and all have high boiling points (100–250 °C). Smaller molecules (< C_4) are completely miscible in water due to the formation of hydrogen bonds with water. Above C_4 the hydrocarbon chain lowers the solubility. All carboxylic acids can be dissolved in suitable organic solvents.

The highly polar carboxylic acid molecules dimerise in the liquid phase and in non-aqueous solvents (eg CCl_4) forming two hydrogen bonds between each pair of molecules.


Hydrogen bonding in carboxylic acids.

This extra degree of hydrogen bonding causes carboxylic acids to have boiling points about 20 °C higher than their corresponding alcohols. The dimers dissociate in aqueous solution.

Chemical reactions

Carboxylic acids react by donating a hydrogen in typically acidic reactions, or in losing the –OH in ‘organic’ reactions.

Hydrolysis with water

Carboxylic acids are *acids*: they react with water to form H_3O^+:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

They are *weak* acids, so only a small percentage of acid molecules react.

Neutralisation to make salts

In chemical reactions with metals, bases and carbonates, organic acids react in exactly the same way as inorganic acids:

$$\begin{array}{lclcl} \text{acid} & + \text{ metal} & \longrightarrow & \text{salt} & + \text{ hydrogen} \\ 2CH_3CH_2COOH & + \text{ } Mg & \longrightarrow & (CH_3CH_2COO)_2Mg & + \text{ } H_2 \\ \text{propanoic acid} & & & \text{magnesium propanoate} & \end{array}$$

$$\begin{array}{lclccc} \text{acid} & + \text{ carbonate} & \longrightarrow & \text{salt} & + \text{ carbon dioxide} & + \text{ water} \\ 2CH_3COOH & + \text{ } (NH_4)_2CO_3 & \longrightarrow & 2CH_3COONH_4 & + \text{ } CO_2 & + \text{ } H_2O \\ \text{ethanoic acid} & & & \text{ammonium ethanoate} & & \end{array}$$

$$\begin{array}{lclcl} \text{acid} & + \text{ base} & \longrightarrow & \text{salt} & + \text{ water} \\ HCOOH & + \text{ } NaOH & \longrightarrow & HCOONa & + \text{ } H_2O \\ \text{methanoic acid} & & & \text{sodium methanoate} & \end{array}$$

The *rates* of these reactions are slow, due to the low concentrations of H_3O^+ present.

Condensation with alcohols to make esters

When carboxylic acids react with alcohols to form esters, the acid loses an –OH and the alcohol loses an H:

$$\underset{\text{methanoic acid}}{\underset{\displaystyle O}{\overset{\|}{HC}}\text{—}OH} \;+\; \underset{\text{ethanol}}{H\text{—}O\text{—}CH_2CH_3} \;\rightleftharpoons\; \underset{\text{ethyl methanoate}}{\underset{\displaystyle O}{\overset{\|}{HC}}\text{—}O\text{—}CH_2CH_3} \;+\; H_2O$$

The reaction is slow and is catalysed by the presence of H^+. If we use conc H_2SO_4 we can increase the yield of ester as the concentrated sulfuric acid removes H_2O as it is formed. The rate of reaction is also increased by doing the reaction in a beaker of hot water.

Nucleophilic substitution

Carboxylic acids react to form acyl chlorides by nucleophilic substitution with PCl_3 or PCl_5 or $SOCl_2$. (These reagents also form chloroalkanes with alcohols, but notice that the third way of forming chloroalkanes—with $ZnCl_2$/HCl—is not possible with carboxylic acids because it would require the acid to accept a proton on the way to losing the –OH group and gaining the Cl.)

$$\underset{\text{carboxylic acid}}{R\text{—}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}\text{—}OH} \;+\; PCl_5 \;\longrightarrow\; \underset{\text{acyl chloride}}{R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}Cl} \;+\; POCl_3 \;+\; HCl$$

$$\underset{\text{carboxylic acid}}{R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}OH} \;+\; SOCl_2 \;\longrightarrow\; \underset{\text{acyl chloride}}{R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}Cl} \;+\; SO_2 \;+\; HCl$$

REVISION

9A 1 Completing organic reactions 6

Quizzes 9A 1a, 9A 1b

Test yourself 9A Carboxylic acids

1 Compare the physical and chemical properties of carboxylic acids with their corresponding alcohols.

2 Compare the properties of organic acids with those of hydrochloric acid.

3 Write balanced equations, and name the organic products, for these reactions.

a methanoic acid and calcium carbonate

b butanoic acid and potassium hydroxide

c ethanoic acid and sodium

d methanoic acid and ethanol (in the presence of conc H_2SO_4)

e propanoic acid and thionyl chloride

4 Many carboxylic acids have strong, unpleasant smells—butanoic acid smells like vomit! Explain why the smell of spilt butanoic acid can be removed with a solution of baking soda.

Acyl chlorides

Acyl chlorides (also known as acid chlorides) are carboxylic acids with the –OH group replaced by a chlorine atom.

Naming

The names of acyl chlorides end in –anoyl chloride, eg ethanoyl chloride, CH_3COCl.

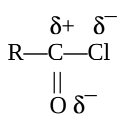
Preparation

Acyl chlorides are not found in nature because they are highly reactive. They are normally formed by nucleophilic substitution of carboxylic acids by PCl_3, PCl_5 and $SOCl_2$.

Properties and uses

The lower acyl chlorides are mobile, colourless liquids with pungent odours. They react with the water vapour in moist air to produce HCl(g). Methanoyl chloride decomposes at room temperature to form CO and HCl. Acyl chlorides have moderately low melting points since the molecules are polar but there is no hydrogen bonding. They do not dissolve in water, but the lower acyl chlorides are decomposed by water.

Acyl chlorides are very reactive and are an important source of a number of other organic compounds. Their reactivity is due to the polarity of the –COCl group as shown in the diagram alongside. As with



Charge distribution in acyl chlorides.

haloalkanes, acyl chlorides contain a positively charged carbon atom. Both the chlorine and oxygen atoms bonded to the end carbon tend to pull shared electrons away from it, leaving this carbon with a net positive charge. Nucleophiles (positive seekers) are strongly attracted to the positive carbon and will bond to it, replacing the chlorine atom (similar to the nucleophilic substitution of haloalkanes).

Acyl chlorides are used to prepare esters, amides, secondary amides and carboxylic acids.

All acyl chloride reactions are highly exothermic and give high yields of product. HCl gas is produced in every acyl chloride reaction you need to learn.

POWERPOINT

9B Properties of acyl chlorides

PRACTICAL

9.1 P 183 Reactions of acyl chlorides (demo)

Chemical reactions

Hydrolysis with water

Water is a nucleophile. Acyl chlorides react vigorously with water to produce HCl gas and a carboxylic acid:

$$\underset{\text{acyl chloride}}{R{-}\underset{\underset{\displaystyle O}{\Vert}}{C}{-}Cl} + \underset{\text{water}}{H{-}OH} \longrightarrow \underset{\text{carboxylic acid}}{R{-}\underset{\underset{\displaystyle O}{\Vert}}{C}{-}OH} + HCl$$

$$\underset{\text{ethanoyl chloride}}{CH_3COCl} + H_2O \longrightarrow \underset{\text{ethanoic acid}}{CH_3COOH} + HCl$$

The HCl gas formed by the reaction is extremely soluble in water, and in moist air it forms droplets of hydrochloric acid HCl(aq). The reaction is called hydrolysis. If open bottles of an acyl chloride and concentrated ammonia solution are held close together, you will see a white ‘smoke’ as HCl(g) combines with $NH_3(g)$ to produce $NH_4Cl(s)$.

Condensation with alcohol to form esters

Acyl chlorides react with alcohols in a similar reaction to that with water. A vigorous reaction occurs to form an ester and HCl gas. This reaction is a more efficient method of preparing esters since the evolution of HCl gas drives the reaction to completion.

$$\underset{\text{acyl chloride}}{R{-}\underset{\underset{\displaystyle O}{\Vert}}{C}{-}Cl} + \underset{\text{alcohol}}{H{-}O{-}R'} \longrightarrow \underset{\text{ester}}{R{-}\underset{\underset{\displaystyle O}{\Vert}}{C}{-}O{-}R'} + HCl$$

$$\underset{\text{ethanoyl chloride}}{CH_3COCl} + \underset{\text{ethanol}}{CH_3CH_2OH} \longrightarrow \underset{\text{ethyl ethanoate}}{CH_3COOCH_2CH_3} + HCl$$

A condensation reaction is one in which two ‘large’ molecules combine, ejecting a small molecule. In this case the small molecule is HCl, rather than the H_2O you may be more familiar with.

Amide formation

Ammonia is another nucleophile. It reacts with acyl chlorides to form amides:

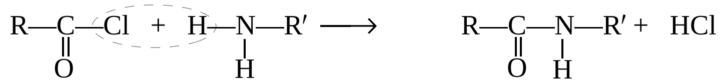
$$\underset{\text{acyl chloride}}{R{-}\underset{\underset{\displaystyle O}{\Vert}}{C}{-}Cl} + \underset{\text{ammonia (alc)}}{H{-}NH_2} \longrightarrow \underset{\text{amide}}{R{-}\underset{\underset{\displaystyle O}{\Vert}}{C}{-}NH_2} + HCl$$

$$\underset{\text{propanoyl chloride}}{CH_3CH_2COCl} + NH_3 \longrightarrow \underset{\text{propanamide}}{CH_3CH_2CONH_2} + HCl$$

We must use ammonia dissolved in alcohol—if aqueous ammonia was used the acyl chloride would react with the water instead.

Amides are discussed on page 100. They should not be confused with amines (which have no ‘O’ in them).

Amines ($R\text{-}NH_2$) also contain the nucleophile NH_2 and so react with acyl chlorides, this time to form secondary amides:



acyl chloride   amine   secondary amide

The R and R' alkyl groups need not be the same.

$CH_3COCl + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + HCl$

You do not need to be able to name secondary amides.

REVISION

9B 1 Completing organic reactions 1

Quizzes 9B 1a, 9B 1b

Test yourself 9B Acyl chlorides

1 Write a balanced equation for the preparation of propanoyl chloride using PCl_5.

2 Why does a bottle of propanoyl chloride fume when it is opened to the air?

3 Write equations for the reactions between

a ethanoyl chloride and ammonia

b butanoyl chloride and methanol

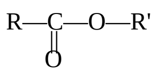
c methanoyl chloride and aminoethane

d propanoyl chloride and water

Esters

Esters are responsible for the characteristic odours of many fruits and perfumes. They are used as solvents and plasticisers as well as for their fragrance. Fats, waxes and vegetable oils are types of esters called **triglycerides**.

Esters have the general formula RCOOR'.



ester

Naming

Esters are named after the acid and alcohol from which they were formed. When writing the formula for an ester, the part derived from the acid is usually written first, but when naming the compound the alcohol part comes first.

$CH_3CH_2COO—CH_2CH_3$

propanoate   ethyl   =   ethyl propanoate

To name esters:

1 divide the ester into two groups by drawing a line after the COO

2 name the group that comes after this line first

3 name the acid group in front of the line.

POWERPOINT

9C 1 Preparation of an ester

Preparation

Methods of ester preparation are called esterification. In the laboratory esters are made by the reaction of alcohols with either carboxylic acids or acyl chlorides.

Preparation from carboxylic acids

The reaction of an alcohol with a carboxylic acid is slow. It can be speeded up by:

1 heat. The reaction is done under reflux (condenser is vertical, volatile substances drip back into the reaction vessel).

2 a catalyst. Concentrated sulfuric acid is added. The presence of H^+ ions speeds up the reaction. Sulfuric acid is best because it is a dehydrating agent and removes one of the products—the water—thus driving the reaction further to completion.

Separation of the ester from the reaction mixture is achieved by distillation (condenser horizontal) and collection of the fraction with the appropriate boiling point (normally the ester will come off first).

Preparation from acyl chlorides

Acyl chlorides react rapidly with alcohols to form esters, and the loss of HCl gas drives the reaction to completion. Since no heat or catalyst is required this is the preferred method of esterification in most cases.

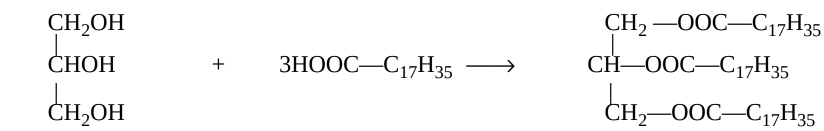
$$\underset{\text{propanoyl chloride}}{CH_3CH_2COCl} + \underset{\text{methanol}}{CH_3OH} \longrightarrow \underset{\text{methyl propanoate}}{CH_3CH_2COOCH_3} + HCl$$

Physical properties

Unlike the acids and alcohols from which they are derived, esters have no free –OH groups. They are therefore volatile compared to acids and alcohols of similar molar mass, and they are not very soluble in water. Esters are colourless, oily liquids with characteristic smells and low boiling points.

Fats and oils

Most fats and oils are derived from propan-1, 2, 3-triol (glycerol) and a variety of long-chain carboxylic acids (also called fatty acids), the carbon chain usually consisting of an even number of carbon atoms. Since they contain three ester links based on glycerol, they are often called *triglycerides*.



propan-1, 2, 3-triol   stearic acid   a fat

The three fatty acids bonded to a single glycerol molecule need not be the same. Solid fats contain a large proportion of the saturated esters, whereas the oils have much more unsaturated ester.

Some common fatty acids

Structure	Systematic name	Common name	Occurrence
$C_{17}H_{35}COOH$	octadecanoic acid	stearic acid	animal fats
$C_{11}H_{23}COOH$	dodecanoic acid	lauric acid	coconut oil
$C_{15}H_{31}COOH$	hexadecanoic acid	palmitic acid	palm-kernel oil
$C_8H_{17}CH{=}CHC_7H_{14}COOH$	octadec-9-enoic acid	oleic acid	olive oil

Chemical reactions

Hydrolysis

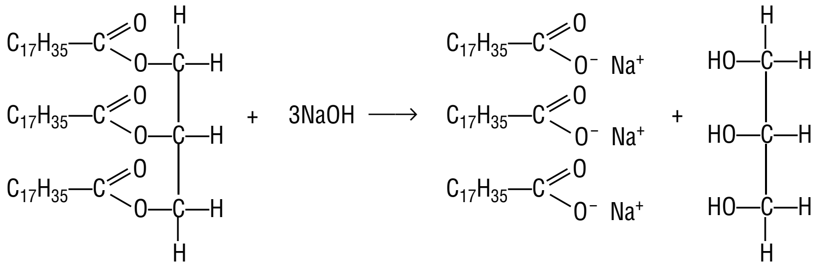
The reaction between alcohol and carboxylic acid is an equilibrium and so when esters are mixed with water the equilibrium goes the other way.

$$\text{ester} + \text{water} \rightleftharpoons \text{alcohol} + \text{carboxylic acid}$$

This hydrolysis reaction is catalysed by dilute acid or alkali; however in the presence of alkali the carboxylic acid formed will be converted to a salt—this helps shift the equilibrium to the right, increasing hydrolysis. So we can show the reaction between an ester and NaOH(aq) as

$$\underset{\text{ester}}{RCOOR'} + NaOH \longrightarrow \underset{\text{sodium salt of carboxylic acid}}{RCOONa} + \underset{\text{alcohol}}{R'OH}$$

These sodium salts are soluble and fully ionised in aqueous solution. If the ester comes from a fat, the process is called *saponification*—soap-making.



triglyceride (fat) + 3NaOH ⟶ soap (sodium stearate) + glycerol

Hydrolysis occurs whenever a water molecule splits another molecule.

POWERPOINT

9C 2 Making soap (revision)

ENCOUNTER

9C1 Michel Eugène Chevreul

9C2 Biodiesel from tallow

Reaction with ammonia

Like acyl chlorides, esters react with alcoholic ammonia to form amides:

$$\underset{\text{ester}}{RCOOR'} + NH_3(alc) \longrightarrow \underset{\text{amide}}{RCONH_2} + \underset{\text{alcohol}}{R'OH}$$

$$\underset{\text{ethyl methanoate}}{HCOOCH_2CH_3} + NH_3(alc) \longrightarrow \underset{\text{methanamide}}{HCONH_2} + \underset{\text{ethanol}}{CH_3CH_2OH}$$

The reaction is slow, so the preferred method of forming amides is with the acyl chloride.

REVISION

9C 2a Completing organic reactions 8

9C 2b Choosing the product (2)

9C 2c Choosing the product (3)

9C 2d Choosing the reagent

Quizzes 9C 1, 9C 2a, 9C 2b

Test yourself 9C Esters

1 Name these.

a $HCOOCH_2CH_2CH_3$ ____________________

b $CH_3CH_2COOCH_3$ ____________________

c $CH_3CH_2CH_2COOCH_2CH_3$ ____________________

2 Write condensed structural formulae for these.

a methyl ethanoate ____________________ **b** butyl propanoate ____________________

3 What are the special conditions necessary to form an ester from a carboxylic acid and an alcohol?

____

____

____

4 Compare the physical properties of an alcohol with the ester it will form.

5 Write equations for the reactions between:

a ethyl propanoate and dilute hydrochloric acid

b methyl butanoate and dilute sodium hydroxide solution.

c methyl ethanoate and alcoholic ammonia.

6 Write an equation for the formation of pentyl butanoate (which smells like apricot) from an acyl chloride.

WARNING: Do not confuse amide ($RCONH_2$) with amine ($R\text{-}NH_2$).

Amides

An amide is a carboxylic acid derivative. The –OH from the acid is replaced by an NH_2 (for primary amides), NH (for secondary amides) or N (for tertiary amides).

Primary amide: $R{-}\underset{\underset{O}{\|}}{C}{-}NH_2$ Secondary amide: $R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{-}R'$

Naming

You only need to know how to name primary amides. Their names end in –anamide, eg CH_3CONH_2 = ethanamide (acetamide).

Preparation

Amides can be prepared by the reaction of acyl chlorides and alcoholic ammonia:

$$\underset{\text{acyl chloride}}{R{-}\underset{\underset{O}{\|}}{C}{-}Cl} + \underset{\text{ammonia}}{H{-}NH_2} \longrightarrow \underset{\text{amide}}{R{-}\underset{\underset{O}{\|}}{C}{-}NH_2} + HCl$$

The HCl produced in this reaction will then react with more ammonia to produce NH_4Cl.

Amides are also formed by the reaction of an ester and alcoholic ammonia:

$$\underset{\text{ester}}{R{-}\underset{\underset{O}{\|}}{C}{-}OR'} + \underset{\text{ammonia}}{H{-}NH_2} \longrightarrow \underset{\text{amide}}{R{-}\underset{\underset{O}{\|}}{C}{-}NH_2} + R'{-}OH$$

The ester reaction is slow, so the acyl chloride method is the preferred preparation technique.

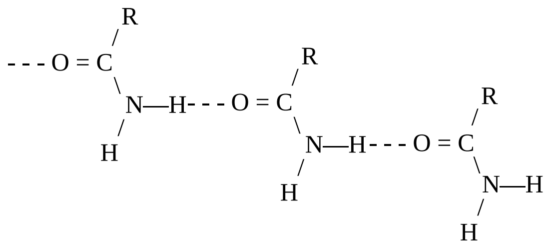
Amides can also be prepared by thermal decomposition of the ammonium salt of the carboxylic acid:

$$R\text{-}COO^-NH_4^+ \xrightarrow{\text{heat}} R\text{-}CO\text{-}NH_2 + H_2O$$

Note: The ammonium salt can be made by reacting ammonia or an ammonium compound (esp $(NH_4)_2CO_3$) with the carboxylic acid. Ammonia does **not** form an amide by reacting with the carboxylic acid directly.

Physical properties

With the exception of methanamide (MP 2 °C), amides are white crystalline solids at room temperature. The lower members are soluble in water; all amides are soluble in organic solvents. Impure ethanamide has the characteristic smell of mice, although the pure substance has no smell. The high melting points and boiling points (almost 200 °C higher than the MP) of amides are due to the formation of hydrogen bonds between the oxygen atom of one molecule and the amino-hydrogen of another.



Hydrogen bonding in amides

Chemical properties

Amides are much weaker bases than amines, even though both contain the group $–NH_2$; thus amides are neutral to litmus and do not react with hydrochloric acid to form salts.

PRACTICALS

9.2 P 184 Amide hydrolysis

Hydrolysis

Amides are hydrolysed by heating with a mineral acid (usually HCl).

eg $CH_3CONH_2 + H_3O^+(aq) \longrightarrow CH_3COOH + NH_4^+$

They are also hydrolysed by heating with alkalis (eg NaOH):

eg $CH_3CONH_2 + OH^-(aq) \longrightarrow CH_3COO^- + NH_3$

This hydrolysis reaction is similar to that of esters and acyl chlorides.

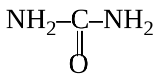
The hydrolysis reactions of amides in acid or base are popular with examiners.

Polymerisation

One of the first artificial polymers was nylon. This is a polyamide formed by the condensation reaction between a dicarboxylic acid and a diamine. We study nylon and other polymers below.

Natural amides

The most familiar amide is the diamide of methanoic acid—urea.



This is the nitrogen-containing compound present in all mammal urine as the product of protein breakdown.

Urea is an important industrial chemical. It is made in New Zealand by heating ammonia (made by the Haber process) and CO_2 (from natural gas) under pressure.

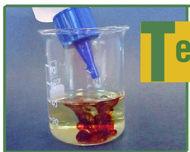
$$CO_2 + 2NH_3 \longrightarrow NH_2CONH_2 + H_2O$$

Urea is used –as a fertiliser
–to manufacture urea-formaldehyde plastics
–in the manufacture of barbiturates.

REVISION

9D 2 Completing organic reactions 9

Quizzes 9D 1, 9D 2a, 9D 2b



Test yourself 9D Amides

1 Write the structural formulae for, and name, a 3-carbon amine and a 3-carbon amide.

2 Write balanced equations for

a the preparation of ethanamide from ethanoyl chloride

b the reaction between ethyl propanoate and alcoholic ammonia

c the hydrolysis of butanamide by dilute hydrochloric acid.

d the hydrolysis of propanamide by dilute sodium hydroxide.

3 Compare the physical and chemical properties of amines and amides.

PRACTICALS

9.3 P 185 Identification of organic unknowns

REVISION

9E 1a Organic observations (1)

9E 1b Reagents in organic chemistry

9E 1c Organic observations (2)

9E 2a Using chemical reactions to identify organic compounds

9E 2b Laboratory tests of organic compounds

Quizzes 9E 2a, 9E 2b

ENCOUNTER

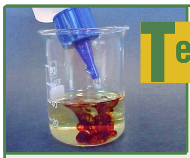
9E Sniffing out trouble

Tests for organic compounds

Once we know the physical and chemical properties of different families of organic compounds, we can used the properties to distinguish between them.

You are likely to be given a collection of 4 or 5 possible compounds and asked to sort them out. The key to such problems is to begin with the simplest tests, rather than doing every possible test on each one. For example, damp red and blue litmus papers will immediately identify an amine (turns blue), an acyl chloride (vapour turns litmus red), and a carboxylic acid (liquid turns litmus red). Acidified dichromate will turn green with 1° and 2° alcohols, and with aldehyde. Don’t just look for the colour change though — pay attention to whether the liquid is miscible in the aqueous dichromate or not. Low mass alcohols, aldehydes and ketones will be miscible, while the esters, haloalkanes and hydrocarbons will form two separate layers. More specific tests, such as with Lucas or Tollen’s reagent or bromine water should only be done on those compounds which repond appropriately to these first tests.

In an assessment you will normally be required to demonstrate your understanding of the chemistry involved with each test by writing equations for any of the reactions which occur — including the formation of H_3O^+ or OH^- to change the colour of litmus.



Test yourself 9E Tests for unknown organic compounds

1 Five unknown organic liquids are known to have the following structures:

CH_3COOCH_3 CH_3CH_2CHO $CH_3CH_2CH_2OH$ CH_3COCH_3 $CH_3COH(CH_3)_2$

- Acidified dichromate solution remained orange with compounds A, B and C, while compounds D and E turned it green. Compound C formed two layers, while the others formed a single layer.
- Lucas reagent turns cloudy with compound A and remains clear with compound B.
- Tollen's reagent does not react with compound D, but forms a silver mirror with compound E.

Name compounds A to E.

A ____________ B ____________ C ____________

D ____________ E ____________

2 Write equations to show why 2-aminopropane and propanoic acid change the colour of damp litmus paper.

____

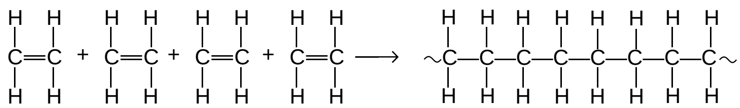
____

Polymers—natural and synthetic

Polymers are made up of many (poly) repeating units (mers). Simple polymers are made up of single **monomers** joined together in either addition or condensation polymerisation.

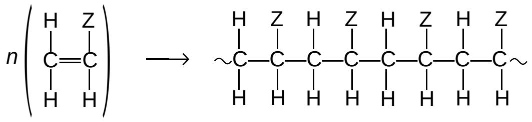
Addition polymers

In **addition polymers** the monomers contain double bonds which are broken to join the small molecules together in one long chain. Polythene is an addition polymer made from ethene:



ethene polythene

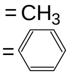
Other addition polymers include polyvinyl chloride (PVC) and polystyrene. The general equation for these polymers is:



monomer polymer

For PVC, Z = Cl

For polypropylene, Z = CH_3

For polystyrene, Z = 

PRACTICALS

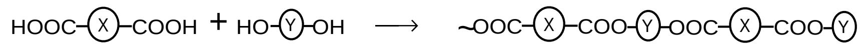
9.4 P 187 Making an addition polymer: slime

Condensation polymers

When **condensation polymers** form, a small molecule such as H_2O or HCl is lost at each join.

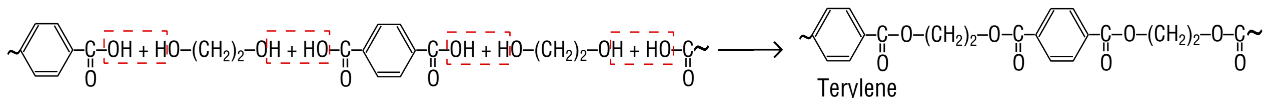
Polyesters

Esters are formed by the reaction of an alcohol and either a carboxylic acid or an acyl chloride. **Polyesters** are made by reacting "double-ended" molecules such as a diol and a dicarboxylic acid.



dicarboxylic acid diol polyester + $2H_2O$

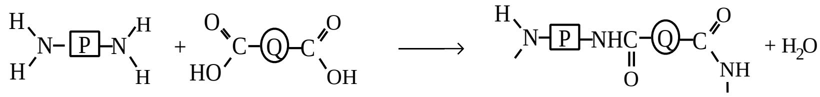
By far the most common polyester is terylene. Terylene is made from the esterification of ethane-1, 2-diol, $HOCH_2CH_2OH$, and benzene-1, 4-dicarboxylic acid, $HOOC—C_6H_6—COOH$ (terephthalic acid).



ethan-1, 2-diol terephthalic acid Terylene + $4H_2O$

Polyamides

Polyamides can be made by combining a diamine and a dicarboxylic acid or acyl chloride. Nylon, the first synthetic fibre, is a polyamide. It was developed in the United States in the 1930s and quickly became a cheap alternative to silk.



diamine dicarboxylic acid nylon

There are many types of nylons but the most important is nylon 6, 6; so called because each monomer contains six carbon atoms. Nylon 6, 6 both as a fibre and as a plastic has a rare combination of properties—high strength, elasticity, toughness and abrasion resistance. It therefore has a wide range of uses—from gear wheels to fine strands for pantyhose. Nylon 6,10 is another important nylon with very similar properties.

- Nylon 6, 6 is made from hexanedioic acid and 1, 6 diaminohexane.
- Nylon 6, 10 is made from decanedioic acid and 1, 6 diaminohexane.

POWERPOINT

9E Preparation of nylon

PRACTICALS

9.5 P 187 Making a condensation polymer: nylon 6, 6

ENCOUNTER

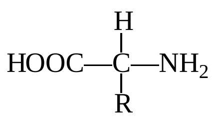
9F The story of nylon

Natural polymers

Protein

Proteins are polymers made of **amino acid** monomers.

Each amino acid contains the NH_2 group of an amine and the COOH group of an acid:



amino acid

The simplest amino acid is glycine, where R = H
The next simplest is alanine where R = CH_3

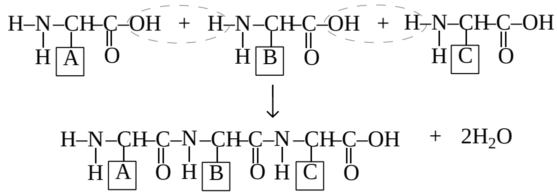
Apart from glycine, all amino acids have a *chiral* carbon (one with four different groups off it) and form optical isomers. Normally only one of the optical isomers is useful in our bodies (see page 75).

All the amino acids in proteins have the $–NH_2$ group joined to the *same carbon* as the –COOH group. There are 20 amino acids involved in proteins required by humans. Eight of these cannot be made in our bodies and must be part of our diet. Amino acids needed by the body but which cannot be made by that body are called **essential** amino acids.

You will have seen references to 'essential oils' in cosmetic advertisements. Here 'essential' simply means 'derived from the essence', ie obtained by squeezing or distillation.

In proteins, amino acids join together in condensation polymerisation:

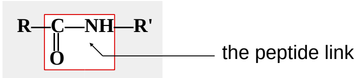
amino acid amino acid amino acid



protein

Since each amino acid contains the two active sites for the polymerisation reaction, the amino acids can be assembled in any order, providing an almost infinite number of different protein molecules. Most common proteins contain more than 100 amino acids.

Joining the amino acids together is the **peptide link**:



When protein is digested, the polymer is *hydrolysed* in exactly the same way that amides are. The acid in the stomach breaks each peptide link

$$R{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}NH{-}R' + H_2O \xrightarrow{\text{dil HCl}} R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}OH + H{-}NH{-}R'$$

Glucose and fructose are structural isomers.

Carbohydrates

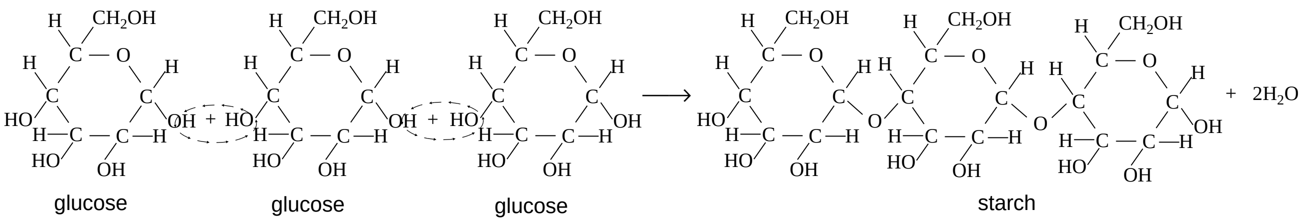
Glucose, fructose (found in honey) sucrose (table sugar), starch and cellulose are all types of **carbohydrate**.

Glucose and fructose are **monosaccharides**— single sugar units. Sucrose is a **disaccharide**, because it is composed of a glucose and a fructose molecule joined together.

$$\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O$$

The reaction is a condensation reaction because a water molecule is lost.

Starch is a condensation polymer made from glucose monomers.



When starch is hydrolysed, either by the action of enzymes or acid, water is added to reform the glucose monomers.

Soluble starch consists of long, straight chains of glucose molecules, while the insoluble forms of starch contain branches.

In **cellulose**, the glucose molecules are arranged in long, straight chains, but the arrangement is a little different from that in soluble starch, and it allows the chains to hydrogen-bond with each other. The chains combine to form long fibres which resist most solvents and chemicals. Only a few specialised bacteria have the ability to hydrolyse cellulose. Without those bacteria in their stomachs, grass-eating animals such as cows and sheep would starve.

REVISION

9F 1 Carboxylic acid derivatives and polymers key facts

9F 2 Monomers and polymers

Quizzes 9F 1, 9F 2

Test yourself 9F Polymers—natural and synthetic

1 Name two examples of:

a addition polymers ______

b synthetic condensation polymers ______

c natural condensation polymers ______

2 Explain why dilute acid makes holes in nylon pantyhose.

______

______

3 The general formula for an amino acid is HOOC—CRH—NH_2. In glycine R = H, in alanine R = CH_3. Draw the graphic formulae for two dipeptides formed by joining glycine and alanine and circle the peptide links.

Key learning outcomes for Chapter 9

By now you should be able to:

1 Name and write condensed structural formulae for given carboxylic acids.
2 Describe the physical and chemical properties of carboxylic acids including:
- hydrolysis with water and action as weak acids
- reaction with PCl_3, PCl_5 or $SOCl_2$ to give acyl chlorides
- react with alcohols to give esters.

3 Name or write the condensed structural formula for a given acyl chloride.
4 Describe the physical and chemical properties of acyl chlorides including:
- hydrolysis with water
- reaction with alcohols to form esters
- reaction with ammonia or amines to form 1° or 2° amides.

5 Write the formula of a given ester and name an ester given its formula.
6 Recall the conditions needed when esters are prepared from carboxylic acids.
7 Describe the physical and chemical properties of esters including:
- characteristic smell and solubility in water
- hydrolysis—acid or alkaline
- reaction with ammonia to form amides.

8 Describe the structure of a fat and write an equation for the saponification of a given fat.
9 Write the formula of a given amide and name an amide given its formula.
10 Describe physical and chemical properties of amides including:
- acid and alkaline hydrolysis
- action with litmus.

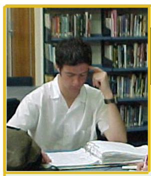
11 Use physical and chemical tests to identify supplied organic compounds.
12 Explain how addition and condensation polymers differ in the way they are formed.
13 State the reagents for the formation of the polyester *Terylene* and draw the repeating unit.
14 Describe the preparation of polyamides (nylons) and draw the repeating unit for a given nylon.
15 Give the general formula for amino acids and recognise that most amino acids have optical isomers.
16 Show how amino acids join, and identify the peptide link.
17 Show what happens in the hydrolysis of polyamides and polypeptides.

REVISION

9F 3 Organic synthesis 1
9F 4 Organic synthesis 2
Organic key facts flash cards
Chemistry 3.5 key facts crossword
Chemistry 3.5 key facts flip cards

EXAM QUESTIONS

Practice questions
Sample examination papers



Review questions for Chapter 9

1 Complete these equations and name all reagents. **A M**

a $CH_3COOCH_2CH_3 + H_2O \xrightarrow{H^+}$

b $CH_3CH_2COOCH_2CH_3 + NH_3 \longrightarrow$

c $CH_3CH_2CH_2OH + CH_3COCl \longrightarrow$

d $CH_3CONH_2 + H_2O \xrightarrow{H^+}$

2 Write balanced equations for the following reactions: **A M**

a the preparation of methanoyl chloride using PCl_5

b the reaction of butanoyl chloride with water

c the formation of propanamide from propanoyl chloride

d the reaction between ethanoyl chloride and 1-aminopropane.

3 Given the following monomers or pairs of monomers, draw the repeating unit of the polymer formed. **A M**

a $CH_2{=}CHCl$

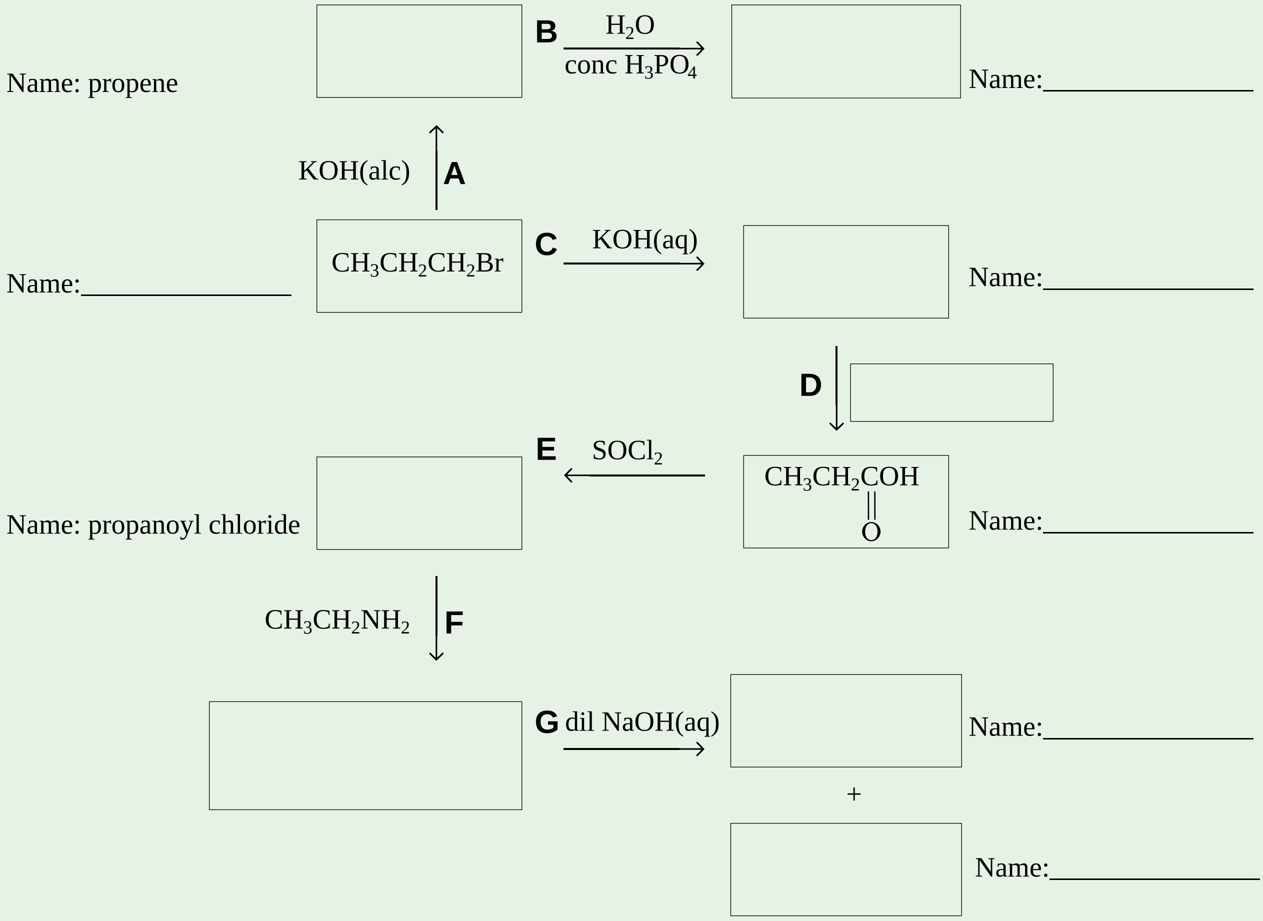
b $CH_2{=}CHCH_3$

c $HOOC–C_6H_4–COOH$ and $HOCH_2CH_2OH$

d $H_2N–(CH_2)_6–NH_2$ and $ClOC(CH_2)_4COCl$

4 Describe how you could distinguish the following compounds in the laboratory. Justify each step, writing equations for reactions where appropriate.
Compounds: aminoethane, cyclohexane, ethanoyl chloride, ethyl methanoate and propanamide. **A M E**

5 This question refers to the reaction scheme shown below.



a Complete the diagram by filling in the names or formulae of the missing compounds. A M E

b Name the reagent used in reaction E. A

c What *type* of reactions are these? A M

i Reaction A

ii Reaction C

iii Reaction D

iv Reaction G

d Name two compounds in this scheme which are *isomers*. A

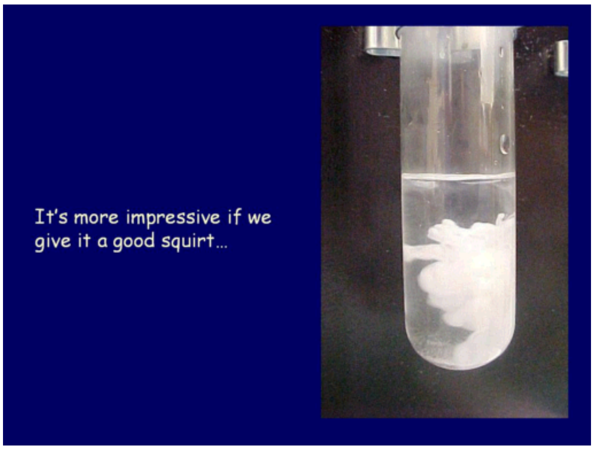
e Under what special conditions must Reaction D be done? Explain your answer. A M

Section 4

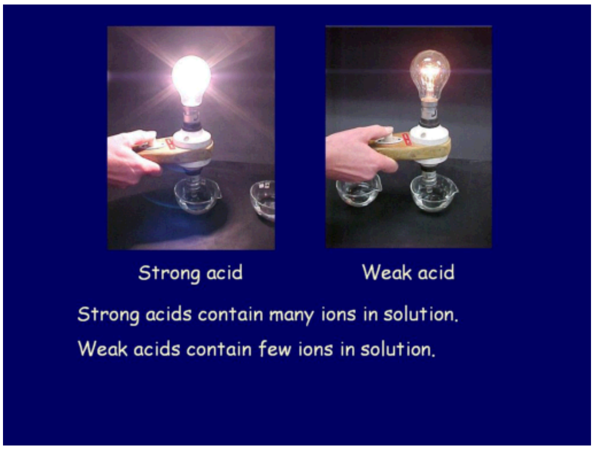
Aqueous systems

Chemistry 3.7
5 credits

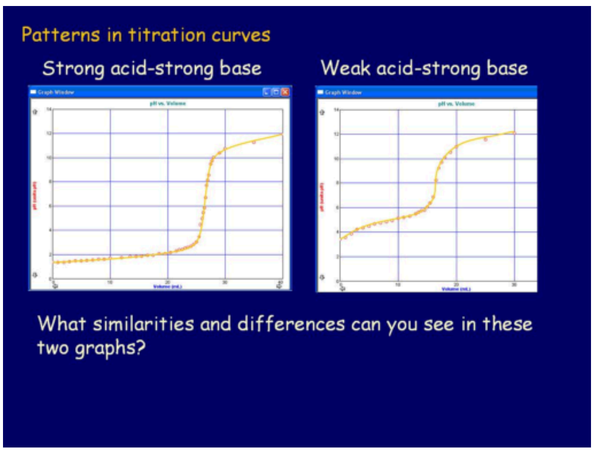
AS60700 Describe properties of aqueous systems
External



10 Solubility equilibria



11 Acids and bases



12 Buffers and titration curves

10

Solubility equilibria

Solubility, precipitation reactions and K_s

Consider solid calcium carbonate in equilibrium with a saturated solution of calcium carbonate. We could write an equation:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

and an equilibrium expression

$$K = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]}$$

But we never write solids in equilibrium constants (because the concentration of a solid is a constant), so we simply write:

$$K_s = [Ca^{2+}][CO_3^{2-}]$$

where K_s is a special equilibrium constant related to saturated solutions. We call it the *solubility constant* or **solubility product**.

This year we are concerned with the K_s of sparingly soluble or 'insoluble' compounds. (No matter how 'insoluble' a substance is, a very tiny amount will still dissolve, even if it is only one ion in 10^{20} solid ions.)

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

$$K_s = [Mg^{2+}][OH^-]^2$$

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$K_s = [Ca^{2+}]^3[PO_4^{3-}]^2$$

A large K_s indicates a high solubility.
Substances called 'insoluble' have small K_s, eg $K_s(BaSO_4) = 1.1 \times 10^{-10}$.

Example 10.1 K_s from solubility

The solubility of CaF_2 in pure water is given as 2.3×10^{-4} mol L^{-1}. Find $K_s(CaF_2)$.

First write the equilbrium equation for the system, and then the K_s:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

$$K_s = [Ca^{2+}][F^-]^2$$

Now plug in the numbers:

From the fact that the solubility is 2.3×10^{-4} mol L^{-1} we know that:

$[Ca^{2+}] = 2.3 \times 10^{-4}$ mol L^{-1} and $[F^-] = 2 \times 2.3 \times 10^{-4}$ mol L^{-1} $= 4.6 \times 10^{-4}$ mol L^{-1}

So $K_s = (2.3 \times 10^{-4}) \times (4.6 \times 10^{-4})^2 = 4.87 \times 10^{-11}$

POWERPOINT

10A 1 K_s from solubility

REVISION

10A 1 Calculator practice

10A 2a Writing expressions for K_s

Quiz 10A 2a

Example 10.2 Solubility from K_s

The solubility product of silver chromate (Ag_2CrO_4) is 9.0×10^{-12}. Calculate the solubility of silver chromate in water.

First write the equilbrium equation for the system, and then the K_s:

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

$$K_s = [Ag^+]^2[CrO_4^{-2}]$$
$$= 9.0 \times 10^{-12}$$

Finding the solubility requires us to use both chemistry and algebra:

Let the solubility of silver chromate be s.

Then $[Ag^+] = 2s$ and $[CrO_4^{-2}] = s$

$$K_s = (2s)^2(s)$$
$$= 4s^3$$
$$4s^3 = 9.0 \times 10^{-12}$$
$$s = \sqrt[3]{\frac{9.0 \times 10^{-12}}{4}}$$
$$s = 1.310 \times 10^{-4} \text{ mol L}^{-1}$$

The solubility of silver chromate is 1.310×10^{-4} mol L^{-1}.

POWERPOINT

10A 2 Solubility from K_s

PRACTICALS

10.1 P 188 Determination of the solubility of barium hydroxide

10.2 P 189 Solubility and solubility products

REVISION

10A 2b Calculating solubility product

Quiz 10A 2b

Test yourself 10A The solubility product—K_s

1 Strontium fluoride, SrF_2, has a solubility of 0.012 g per 100 g of water. $M(SrF_2) = 125.6$ g mol^{-1}.

a Write the equilibrium equation for SrF_2 dissolving in water.

____

b Calculate the solubility of SrF_2 in mol L^{-1}.

____

____

c State the concentration of each ion in the saturated solution:

$[Sr^{2+}]$ = ____________________ $[F^-]$ = ____________________

d Write the expression for $K_s(SrF_2)$ and hence calculate the value of $K_s(SrF_2)$

____

____

____

2 Silver iodide has a solubility of 2.8×10^{-6} g L^{-1}.

a What is the solubility of silver iodide in mol L^{-1}?

____

b Write the equilibrium equation for the formation of saturated silver iodide solution.

____

c Write the expression for K_s for silver iodide.

____

d Calculate the value of K_s.

3 The K_s for lead bromide is 6.3×10^{-6}.

a Write an equation for the formation of lead bromide solution.

b Write an expression for K_s.

c Calculate the solubility of lead bromide in mol L^{-1}.

4 Calculate the solubility of $Fe(OH)_2$ if $K_s(Fe(OH)_2) = 1.64 \times 10^{-14}$.

Ionic products and predicting precipitates

The ionic product is also known as the **reaction quotient**, symbolised Q, or Q_c.

K_s applies to saturated solutions in equilibrium; however the same, square-bracket expression is equal to the **ionic product** (IP) when the solution is not in equilibrium.

Saturated solution: $K_s(AgCl) = [Ag^+][Cl^-]$

Any solution: Ionic product $= [Ag^+][Cl^-]$

The solution could be a very dilute solution of silver chloride, or it could be a mixture of a silver nitrate solution and a sodium chloride solution.

In any solution if IP is greater than K_s a precipitate will form.

POWERPOINT

10B 1 Ionic product calculations

Example 10.3 Concentration to form a precipitate

If solid sodium chloride is added to a 0.01 mol L^{-1} $AgNO_3$ solution, what is the minimum concentration needed to give a precipitate of AgCl? $K_s(AgCl) = 2 \times 10^{-10}$.

First write the equilbrium equation for the system, and then the K_s:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_s = [Ag^+][Cl^-]$$

We know $[Ag^+] = 0.01$ mol L^{-1}; we want to find $[Cl^-]$.

Rearrange the K_s expression to find [Cl⁻]:

$$K_s = [Ag^+][Cl^-]$$

$$[Cl^-] > \frac{K_s}{[Ag^+]}$$

$$> \frac{2 \times 10^{-10}}{0.01}$$

$$[Cl^-] > 2 \times 10^{-8} \text{ mol L}^{-1}$$

A precipitate will form if the concentration of NaCl exceeds 2×10^{-8} mol L^{-1}.

Example 10.4 **Mixing solutions to form a precipitate**

Will a precipitate form when 75 mL of 4.0×10^{-3} mol L^{-1} NaCl solution and 25 mL of 6.0×10^{-5} mol L^{-1} $AgNO_3$ solution are mixed? $K_s(AgCl) = 1.8 \times 10^{-10}$.

Calculate the concentration of the relevant ions in the mixed solution:

Volume of mixed solutions = 75 mL + 25 mL = 100 mL

$$[Ag^+] = 6.0 \times 10^{-5} \text{ mol L}^{-1} \times \frac{25 \text{ mL}}{100 \text{ mL}}$$

$$= 1.5 \times 10^{-5} \text{ mol L}^{-1}$$

$$[Cl^-] = 4.0 \times 10^{-3} \text{ mol L}^{-1} \times \frac{75 \text{ mL}}{100 \text{ mL}}$$

$$= 3.0 \times 10^{-3} \text{ mol L}^{-1}$$

Now write the expression for the ionic product and plug in the numbers:

$$\text{ionic product} = [Ag^+][Cl^-]$$

$$= (1.5 \times 10^{-5})(3.0 \times 10^{-3})$$

$$= 4.5 \times 10^{-8}$$

Compare the ionic product with the K_s to determine whether a precipitate will form:

The ionic product (4.5×10^{-8}) is larger than the solubility product (1.8×10^{-10}) so there will be a precipitate.

The common ion effect

POWERPOINT

10B 2 The common ion effect

PRACTICALS

10.3 P 190 The common ion effect

If we take a saturated solution of sodium chloride and try to dissolve more sodium chloride, we just get solid sodium chloride at the bottom of the beaker. But we also get solid sodium chloride if a few drops of concentrated hydrochloric acid are added to saturated sodium chloride solution. Why?

In a saturated solution the ionic product equals the solubility product:

$$K_s = [Na^+][Cl^-]$$

By adding HCl the concentration of the *common ion*, Cl^-, is increased. With the ionic product now exceeding the solubility product, precipitation of sodium chloride must occur.

In soap-making, the soap (the sodium salts of fatty acids) is precipitated out of solution by adding brine—sodium chloride solution—because of this **common ion effect**.

Example 10.5 Common ion effect

What is the concentration of silver ions which will dissolve in 0.1 mol L^{-1} HCl solution? $K_s(AgCl) = 1.8 \times 10^{-10}$.

Write the expression for the K_s, substitute in $[Cl^-] = 0.1$ mol L^{-1} and solve for $[Ag^+]$:

$$K_s = [Ag^+][Cl^-]$$

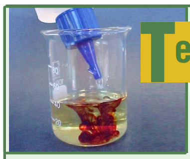
$$[Ag^+] = \frac{K_s}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.1} = 1.8 \times 10^{-9} \text{ mol L}^{-1}$$

REVISION

10B 1 Solubility key facts

10B 2 Concentrations of ions in mixed solutions

Quizzes 10B 1, 10B 2



Test yourself 10B Predicting precipitates and the common ion effect

1 10.0 mL of 0.001 mol L^{-1} $CaCl_2$ are mixed with 10.0 mL of 0.001 mol L^{-1} Na_2SO_4 solution. Will a precipitate of calcium sulfate form? $K_s(CaSO_4) = 2 \times 10^{-5}$.

2 A sample of water contains 0.025 mg L^{-1} of Pb^{2+}. In a test for Pb^{2+}, 1.0 mL of 0.100 mol L^{-1} K_2CrO_4 solution is added to 9.0 mL of the water sample. $K_s(PbCrO_4) = 3.0 \times 10^{-13}$, $M(Pb) = 207.2$ g mol^{-1}.

a $[Pb^{2+}]$ in the water sample = ______

b $[Pb^{2+}]$ in mixed solution = ______

c $[CrO_4^{2-}]$ in the mixed solution = ______

d Write the expression for the ionic product and hence determine whether a precipitate will form.

3 Calculate the solubility of $Mg(OH)_2$ at pH 13. $K_s(Mg(OH)_2) = 1 \times 10^{-11}$.

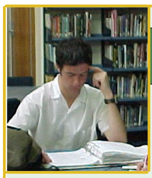
Key learning outcomes for Chapter 10

By now you should be able to:

1 Recognise a saturated solution as a system in equilibrium.
2 Define the solubility product, K_s, for a sparingly soluble ionic solid in a saturated solution.
3 Calculate solubility in mol L^{-1} and g L^{-1} using K_s.
4 Calculate K_s given solubility.
5 Define ionic product as an expression similar to K_s.
6 Use ionic product to predict precipitation.
7 Predict the effect of a common ion on solubility of a sparingly soluble ionic compound.

EXAM QUESTIONS

Practice questions



Review questions for Chapter 10

1 a Write an expression for the solubility product of zinc carbonate. A

b If the solubility of zinc carbonate is 4.86×10^{-4} g L^{-1} at 25 °C, calculate the value of K_s for zinc carbonate. A M

2 a Calculate the solubility of calcium hydroxide given $K_s(Ca(OH)_2) = 7.9 \times 10^{-6}$. A M

b 5.0 mL of 0.1 mol L^{-1} NaOH solution are added to 95.0 mL of 0.1 mol L^{-1} $CaCl_2$ solution. Will a precipitate form? **A M E**

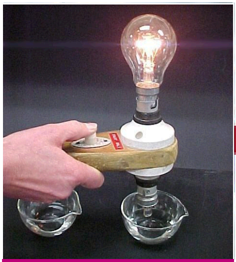
3 A 'barium meal' given to some patients to examine their stomach and intestines by X-ray (to reveal whether an ulcer has healed, for example), contains barium sulfate. $K_s(BaSO_4) = 1.5 \times 10^{-9}$.

a Write an expression for the solubility product, K_s, for barium sulfate. **A**

b Calculate the concentration of barium ions in a saturated solution of barium sulfate. **A M**

c Calculate the concentration of barium ions which will dissolve in 1.0 mol L^{-1} K_2SO_4. **A M**

d Barium ions are toxic. Explain why the 'barium meal' is a slurry of barium sulfate in potassium sulfate solution. **A M**



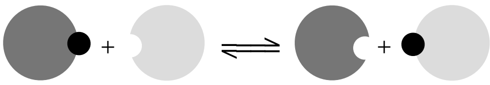
11

Acids and bases

Principles of acids and bases

Definitions

- ***An acid is a proton donor*.**
  When hydrogen chloride is dissolved in water it donates a proton to the water molecule to form ions:
  $$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
- ***A base is a proton acceptor*.**
  $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
  The ammonia molecule accepts a proton from water, leaving behind OH^-.
- ***When we remove a proton from an acid we form its* conjugate base.**
  The conjugate base of HCl is Cl^-. When we donate a proton to a base we form its **conjugate acid** (the conjugate acid of NH_3 is NH_4^+).



- **Amphiprotic *substances can either donate or accept protons.***
  Water and the bicarbonate ion are amphiprotic. In the reaction with HCl water acts as a base, because it accepts a proton. In the reaction with NH_3 it acts as an acid by donating a proton.
  $$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}$$
  $$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

You should remember all this material from your Level 2 Chemistry. If it is not familiar to you, go back and read your Level 2 notes.

Do not confuse **amphiprotic** with **amphoteric** which means 'reacts with both acids and bases'.

Strong and weak

- ***A* strong acid *is one which dissociates completely.***
  The mineral acids HCl, HBr, H_2SO_4 and HNO_3 are all strong acids. Their reactions with water all go to completion: every hydrogen chloride molecule donates its proton to a water molecule to form H_3O^+ and Cl^-.
  $$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
  Thus, in a 1 mol L^{-1} solution of HCl there will be 1 mol L^{-1} of H_3O^+ and 1 mol L^{-1} of Cl^- ions. Strong bases are also completely ionised in water. Examples are NaOH and KOH.

- **Weak acids *are only partially dissociated.***
  Acetic acid is a weak acid. In a solution of acetic acid only a tiny fraction (roughly one in a thousand) of the acetic acid molecules is broken up into ions. Weak acids release few hydrogen ions into solution.
  $$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$
  All the organic acids are weak acids, along with a few inorganic acids which you will learn. **Weak bases** too do not dissociate completely (eg NH_3).

POWERPOINT

11A1 Strong and weak acids (revision)

PRACTICAL

11.1 P 191 Species in solution

POWERPOINT

11A2 Acidic, basic and neutral salts

Quiz 11A 1

Acidic, basic and neutral salts

Sodium chloride is formed when the strong acid, HCl, reacts with the strong base, NaOH. Solutions of sodium chloride in water are neutral, which is why we say that sodium hydroxide *neutralises* hydrochloric acid.

Ammonium chloride is formed when hydrochloric acid reacts with ammonia (a weak base). Solutions of ammonium chloride are slightly acidic, because the ammonium ion hydrolyses in water:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

The salts of weak bases will be slightly acidic.

Similarly, sodium ethanoate (sodium acetate) is formed when ethanoic (acetic) acid—a weak acid—reacts with sodium hydroxide. Solutions of sodium ethanoate are slightly basic:

This reaction gives flavour to salt & vinegar potato chips.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

The salts of weak acids will be slightly basic.

Test yourself 11A Principles of acids and bases

1 Complete these equations to show that these acids are proton donors.

a $HNO_3 + H_2O \longrightarrow$ ____________________

b $CH_3COOH + H_2O \rightleftharpoons$ ____________________

2 Write the conjugate acid of these bases.

a OH^- __________ **b** HS^- __________ **c** CH_3NH_2 __________

3 Write equations to show that HSO_3^- is amphiprotic.

$HSO_3^- + H_3O^+ \rightleftharpoons$ ____________________

$HSO_3^- + OH^- \rightleftharpoons$ ____________________

4 Explain the difference between a *strong* acid and a *concentrated* acid.

____

____

5 Write an equation to show why a solution of sodium carbonate in water has a pH of about 10.

____

pH

The **pH** of a solution is a measure of the number of hydrogen ions in solution.

$$\mathbf{pH = -log_{10}[H^+]}$$

(Actually, all H^+ ions in aqueous solution are surrounded by water molecules, which is why we write H_3O^+, but it is simpler to keep on referring to, and sometimes writing, H^+ anyway.)

It follows from the definition of pH that we can calculate the hydrogen ion concentration from pH using this formula:

$$\mathbf{[H^+] = 10^{-pH}}$$

The pH of pure water is 7, which corresponds to a hydrogen ion concentration of 10^{-7} mol L^{-1}. Since the dissociation of water is:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The expression for the equilibrium constant for this reaction, K_w is:

$$K_w = [H_3O^+][OH^-]$$

K_w is often called the ionic product for water.
Since in pure water $[H_3O^+] = 10^{-7}$ mol L^{-1} and $[OH^-] = 10^{-7}$ mol L^{-1} then:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (10^{-7})^2 \\ K_w &= 10^{-14} \end{aligned}$$

Calculating pH for strong acids and bases

A strong acid or base dissociates completely:

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

If we take 1 L of water ($[H_3O^+] = 10^{-7}$ mol L^{-1}) and dissolve 3.6 g of HCl gas (0.1 mol L^{-1}), the hydrogen ion concentration is going to be 0.100 000 1 mol L^{-1}. The contribution of hydrogen ions from the water will be neglibible compared to the contribution from the acid. When looking at strong acids or bases, we *assume* that the concentration of H_3O^+ (for acids) or OH^- (for bases) is equal to the concentration of that acid or base solution.

Example 11.1 pH of a strong acid

Calculate the pH of 0.001 mol L^{-1} HCl.
Assume $[H_3O^+] = 0.001$ mol L^{-1}

$$\begin{aligned} pH &= -\log_{10}[H^+] \\ &= -\log_{10}(0.001 \text{ mol L}^{-1}) \\ pH &= 3 \end{aligned}$$

Example 11.2 pH of a strong base

Calculate the pH of 0.01 mol L^{-1} sodium hydroxide solution.
Sodium hydroxide is a strong base which dissolves in water to release hydroxide ions:

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

Assume $[OH^-] = 0.01$ mol L^{-1}.
Since $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$

$$\begin{aligned} [H_3O^+] &= \frac{1 \times 10^{-14}}{[OH^-]} \\ &= \frac{1 \times 10^{-14}}{0.01} \\ &= 1 \times 10^{-12} \text{ mol L}^{-1} \\ pH &= -\log_{10}[H_3O^+] \\ &= -\log_{10}(1 \times 10^{-12} \text{ mol L}^{-1}) \\ &= 12 \end{aligned}$$

Another way to do this problem is to calculate the pOH instead.

$$\begin{aligned} pOH &= -\log10[OH^-] \\ &= -\log10(0.01 \text{ mol L}^{-1}) \\ pOH &= 2 \\ pH &= 14 - pOH \\ &= 14 - 2 \\ pH &= 12 \end{aligned}$$

Example 11.3 $[H_3O^+]$ from pH

What is the concentration of H_3O^+ in a solution whose pH is 9.78?

$$\begin{aligned} [H_3O^+] &= 10^{-pH} \\ &= 10^{-9.78} \\ &= 1.66 \times 10^{-10} \text{ mol L}^{-1} \end{aligned}$$

Make sure you can do calculations of the kind shown above, and that you know how to use your calculator to get these answers.

POWERPOINT
11B pH of strong acids and bases

REVISION
11B 1 Strong base calculations
Quiz 11B 1

Test yourself 11B pH of strong acids and bases

1 Calculate the pH of 0.0250 mol L^{-1} HCl solution.

2 What is the concentration of a solution of HCl whose pH is 2.8?

3 Calculate the pH of a 0.004 00 mol L^{-1} KOH solution.

4 What is $[H_3O^+]$ of a solution whose pH is 4.31?

K_a and pK_a

Strong acids dissociate completely. Weak acids are in equilibrium:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

We can write the equilibrium expression:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Notice that we don't write $[H_2O]$, because in aqueous solutions the concentration of water is essentially a constant.

K_a is called the **acid dissociation constant**.

Since the stronger the acid the more it dissociates, a strong acid will have a large K_a and a weak acid will have a small K_a.

$K_a(\text{HCN}) = 4.0 \times 10^{-10}$ $\qquad$ $K_a(\text{HCl}) = 10^7$

The larger the K_a the stronger the acid.

Like all equilibrium constants, K_a is only constant for a given temperature. Most K_a values are quoted for a temperature of 25 °C —assume this temperature if none is given.

p(anything) = –log$_{10}$(anything)

Just as pH is $-\log_{10}(H^+)$, so:

$$pK_a = -\log_{10}K_a$$

$$K_a = 10^{-pK_a}$$

It is easier to write pK_a since there are no powers of 10.

pK_a(HCN) = 9.40 $\qquad$ pK_a(HCl) = –7

The larger the pK_a the weaker the acid.

You will be required to convert between K_a and pK_a.

Calculating the pH of weak acids

Finding the pH of a strong acid is simple, since we assume all the hydrogen ions come from the acid, which dissociates completely. With weak acids, there is an equilibrium between the acid molecules and the hydrogen ions. To find the $[H_3O^+]$ we must use the equilibrium constant—K_a.

Example 11.3 pH of a weak acid

Find the pH of 0.10 mol L^{-1} acetic acid solution.
$K_a(CH_3COOH) = 1.74 \times 10^{-5}$.

Write the equilibrium equation for the dissociation of the acid, and hence write the expression for the dissociation constant:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.74 \times 10^{-5}$$

Make the assumptions:

We assume two things

1 $[H_3O^+] = [CH_3COO^-]$ (ie we assume no H_3O^+ from the water.)

2 $[CH_3COOH]$ = starting concentration of 0.10 mol L^{-1}. This assumes that none of the acid has dissociated—some has (we are trying to work out how much), but it is such a small amount that we can discount it. After all, if one in a thousand has dissociated, there isn't a lot of difference between dividing by 1000 and dividing by 999.

Put the assumptions into the equation and rearrange to calculate $[H_3O^+]$:

$$\begin{aligned} 1.74 \times 10^{-5} &= \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \\ &= \frac{[H_3O^+]^2}{0.10} \\ 1.74 \times 10^{-5} \times 0.10 &= [H_3O^+]^2 \\ \sqrt{1.74 \times 10^{-5} \times 0.10} &= [H_3O^+] \\ 1.319 \times 10^{-3}\ \text{mol L}^{-1} &= [H_3O^+] \end{aligned}$$

Use $[H_3O^+]$ to calculate pH:

$$\begin{aligned} \text{pH} &= -\log_{10}[H_3O^+] \\ &= -\log_{10}(1.319 \times 10^{-3}\ \text{mol L}^{-1}) \\ \text{pH} &= 2.88 \end{aligned}$$

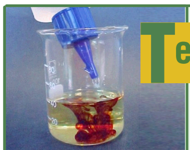
Data books often list the pK_a of weak acids, rather than their K_a. To calculate the pH of a weak acid using the pK_a, first calculate the K_a.

REVISION

11C 1 Acids and bases key facts

11C 2 Steps in weak acid calculations

Quiz 11C 1, 11C 2



Test yourself 11C K_a, pK_a and the pH of weak acids

1 HNO_2 is a weak acid.

a Write the equilibrium equation for the dissociation of HNO_2.

____

b Write the expression for K_a for HNO_2.

____

c The value of $K_a(HNO_2)$ is 4.5×10^{-4}. What is its pK_a? ______________________________

2 Write these acids from strongest to weakest: $K_a(HOCN) = 3.5 \times 10^{-4}$ $K_a(H_2SO_3) = 1.2 \times 10^{-2}$ $K_a(HCO_3^-) = 4.8 \times 10^{-11}$ $K_a(HCOOH) = 1.8 \times 10^{-4}$.

3 Find the pH of 0.0500 mol L^{-1} HF. $K_a(HF) = 7.2 \times 10^{-4}$.

4 Find the pH of 1.50 mol L^{-1} of HOBr. $pK_a = 8.62$.

Calculating the pH of weak bases

PRACTICAL

11.2 P 192 Determination of K_a and K_b

K_b and pK_b

Weak bases react with water according to the following equilibrium equation:

$$B^- + H_2O \rightleftharpoons HB + OH^-$$

eg $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The expression for the equilibrium constant, K_b is:

$$K_b = \frac{[HB][OH^-]}{[B^-]}$$

If we multiply K_a and K_b we get K_w.

Acetic acid is a weak acid. Its conjugate base, the acetate ion, is basic. The relevant equations are:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Multiplying the expressions for K_a and K_b:

$$K_a \times K_b = \frac{[CH_3\cancel{COO}^-][H_3O^+]}{[CH_3\cancel{COOH}]} \times \frac{[CH_3\cancel{COOH}][OH^-]}{[CH_3\cancel{COO}^-]}$$

$$K_w = [H_3O^+][OH^-]$$

That means K_b can be calculated from the K_a using K_w:

$$K_a \times K_b = K_w$$

$$K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{1 \times 10^{-14}}{K_a}$$

REVISION

11D 1 K_a, pK_a and K_b

pH of weak bases

In calculating the pH of weak bases we first find [OH−], then convert that to [H_3O^+] to find the pH.

Example 11.5 pH of a weak base

Calculate the pH of 2.00 mol L^{-1} NH_3 if $K_a(NH_4^+) = 5.75 \times 10^{-10}$.

Write the equilibrium equation for the dissociation of the acid, and hence write the expression for the dissociation constant:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

This equation produces OH^-, so we need to write an expression for K_b:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Write the equilibrium equation first, then decide whether the expression to write next will be a K_a or a K_b.

As a value for K_b has not been given, we need to calculate it:

$$K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{5.75 \times 10^{-10}} = 1.74 \times 10^{-5}$$

Data books often don't supply values for K_b, which is why you may be given the K_a for the conjugate acid of the base in the question.

Make the assumptions:

Assume **1** $[NH_4^+] = [OH^-]$

2 $[NH_3] = 2.00$ mol L^{-1}

Put the assumptions into the equation and rearrange to calculate [OH−]:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.74 \times 10^{-5} = \frac{[OH^-]^2}{(2.00)}$$

$$1.74 \times 10^{-5} \times 2.00 = [OH^-]^2$$

$$\sqrt{1.74 \times 10^{-5} \times 2.00} = [OH^-]$$

$$5.90 \times 10^{-3} \text{ mol L}^{-1} = [OH^-]$$

POWERPOINT

11D pH of weak acids and bases

Convert [OH−] to [H_3O^+] and hence calculate the pH:

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]} = \frac{1 \times 10^{-14}}{5.90 \times 10^{-3}} = 1.69 \times 10^{-12} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}(1.69 \times 10^{-12} \text{ mol L}^{-1}) = 11.8$$

REVISION

11D 2 Calculating the pH of a weak base

There's a good chance you won't be asked to calculate the pH of a given solution of acidic or basic salt, but it is likely that you will be asked to calculate the pH of a salt formed during a titration reaction, which is exactly the same calculation.

pH of salts of weak acids or bases

The pH of a solution of an acidic salt (such as ammonium chloride) or a basic salt (such as sodium acetate) can be calculated in exactly the same way as that of acids and bases such as acetic acid or ammonia.

The salts which hydrolyse in water are the conjugate bases (or acids) of weak acids (or bases). If you can't remember whether the salt will be acidic or basic, don't worry: just write both hydrolysis equations—one will end up with recognisable species, the other with ridiculous species:

$$CH_3COO^-(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CH_2COO^{2-}(aq) \quad ✗$$
$$CH_3COO^-(aq) + H_2O \rightleftharpoons OH^-(aq) + CH_3COOH(aq) \quad ✓$$

Example 11.6 pH of an acidic salt

Calculate the pH of a 0.20 mol L^{-1} solution of NH_4NO_3 if $K_a(NH_4^+) = 5.75 \times 10^{-10}$.

Write the hydrolysis equation, and hence write the expression for the dissociation constant:

When ionic salts dissolve in water, the ions separate:

$$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$$

The ammonium ion hydrolises in water:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Make the assumptions:

Assume 1 $[NH_3] = [H_3O^+]$

2 $[NH_4^+] = 0.20$ mol L^{-1}

Put the assumptions into the equation and rearrange to calculate $[H_3O^+]$ and hence calculate the pH:

$$\begin{aligned} 5.75 \times 10^{-10} &= \frac{[NH_3][H_3O^+]}{[NH_4^+]} \\ &= \frac{[H_3O^+]^2}{0.20} \\ \sqrt{5.75 \times 10^{-10} \times 0.20} &= [H_3O^+] \\ 1.072 \times 10^{-5}\text{ mol L}^{-1} &= [H_3O^+] \\ \text{pH} &= -\log_{10}[H_3O^+] \\ &= -\log_{10}(1.072 \times 10^{-5}\text{ mol L}^{-1}) \\ &= 4.97 \end{aligned}$$

The pH of a 0.20 mol L^{-1} solution of ammonium nitrate is 4.97.

Example 11.7 pH of a basic salt

Calculate the pH of a 0.53 mol L^{-1} solution of sodium ethanoate (sodium acetate). $K_a(CH_3COOH) = 1.74 \times 10^{-5}$.

Write the hydrolysis equation, and hence write the expression for the dissociation constant:

$$CH_3COONa(s) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

As a value for K_b has not been given, we need to calculate it:

$$K_b = \frac{1.0 \times 10^{-14}}{K_a}$$
$$= 5.75 \times 10^{-10}$$

Make the assumptions:

Assume **1** $[CH_3COOH] = [OH^-]$

2 $[CH_3COO^-] = 0.53$ mol L^{-1}

Put the assumptions into the equation and rearrange to calculate $[OH^-]$:

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$
$$5.75 \times 10^{-10} = \frac{[OH^-]^2}{0.53}$$
$$\sqrt{5.75 \times 10^{-10} \times 0.53} = [OH^-]$$
$$1.75 \times 10^{-5} \text{ mol L}^{-1} = [OH^-]$$

Convert $[OH^-]$ to $[H_3O^+]$ and hence calculate the pH:

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
$$= 5.73 \times 10^{-10} \text{ mol L}^{-1}$$
$$\text{pH} = -\log_{10}[H_3O^+]$$
$$= 9.24$$

The pH of a 0.53 mol L^{-1} solution of sodium ethanoate is 9.24.

Test yourself 11D pH of weak bases and salts

1 Calculate the pH of 0.100 mol L^{-1} NH_3 solution. $K_a(NH_4^+) = 5.75 \times 10^{-10}$.

2 5.00 g of ammonium chloride crystals are dissolved in water and made up to 30.0 mL. Calculate the concentration of the solution formed and hence its pH. $K_a(NH_4^+) = 5.75 \times 10^{-10}$.

POWERPOINT

11E Aqueous solutions

ENCOUNTER

11E Svante Arrhenius

Aqueous solutions

An aqueous solution forms when a solute dissolves in water. The species present in solution depend on the nature of the solute.

- Ionic compounds will break up into separate ions; each ion becoming surrounded by water molecules. The solutions formed conduct electricity well.
- Molecular substances will separate into separate molecules which become surrounded by water molecules. Unless these molecules react with water molecules (hydrolise), the solutions formed do not conduct electricity any better than water itself.
- Strong acids and bases react with water to completion, forming H_3O^+ or OH^- and the conjugate base or acid ions.
- Weak acids or bases (and the conjugate bases or acids of weak acids or bases) partially react with water, so that both conjugate acid/base pairs are present in the solution.
- In all aqueous solutions the main component will be $H_2O(l)$, while the product of $[H_3O^+]$ and $[OH^-]$ must always equal 10^{-14}.

The composition of aqueous solutions

0.1 mol L^{-1} $CaCl_2$ solution

Calcium chloride is ionic, and neither the calcium ion nor the chloride ion react with water, so the solution will be neutral.
$[Ca^{2+}] = 0.1$; $[Cl^-] = 0.2$; $[H_3O^+] = [OH^-] = 10^{-7}$.

0.01 mol L^{-1} NaOH solution

Sodium hydroxide is a strong base, and a 0.01 mol L^{-1} solution of NaOH has a pH of 12.
$[Na^+] = [OH^-] = 0.01$ or 10^{-2}; $[H_3O^+] = 10^{-12}$.

1.0 mol L^{-1} NH_4Cl solution

Ammonium chloride is ionic. It is the salt of a weak base, so the solution will be slightly acidic and has a pH of about 5. First the solid dissolves in water:

$$NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

Then the ammonium ion reacts with water:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

This reaction produces the same amount of NH_3 as H_3O^+, but there will be a little extra H_3O^+ from the water already present, so, in order of concentration we will have:
$[Cl^-] = 1.0$; $[NH_4^+] = 1.0 - 10^{-5}$; $[H_3O^+] = 10^{-5}$ $[NH_3] < 10^{-5}$; $[OH^-] = 10^{-9}$.

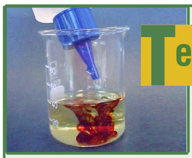
REVISION

11E 1 Species in solution (1–4)

11E 2 Order pH (1–2)

11E 3 Predicting pH

Quiz 11E 1



Test yourself 11E Species in solution

1 List the species in solution, from highest to lowest concentration, for each of the following aqueous solutions.

a HCOOH (methanoic acid)

b Na_2SO_4

c NaF (solution is alkaline)

d glucose

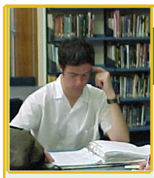
Key learning outcomes for Chapter 11

By now you should be able to:

1. Define acids, bases and conjugate acid-base pairs in terms of proton transfer.
2. Identify amphiprotic species.
3. Predict the acid-base character of the salts of weak acids or bases and write the relevant hydrolysis equations.
4. Calculate the pH of a solution of a strong acid and a strong base given their concentrations.
5. Write an equation for the dissociation of a monoprotic weak acid and write an expression for K_a from it.
6. Define and use appropriately pH, K_a, pK_a, and K_w.
7. Use K_a and pK_a to measure acid and base strengths.
8. Calculate the pH of a solution of a weak acid, weak base and a salt given their concentrations and appropriate K_a or K_b values.
9. List the species present in aqueous solutions in order of concentration.

EXAM QUESTIONS

Practice questions



Review questions for Chapter 11

1 Calculate the pHs of the following solutions:

a 0.0350 mol L^{-1} HNO_3 solution. **A**

b 1.37×10^{-3} $Ca(OH)_2$ solution. **A M**

2 Hypobromous acid, HOBr, has a pK_a of 8.62. **A**

a What is K_a(HOBr)?

b What is $K_b(OBr^-)$?

c pK_a(HOCl) (hypochlorous acid) is 7.54. Which is the stronger acid?

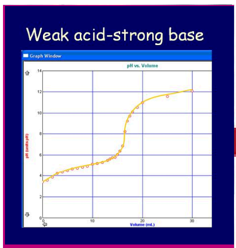
3 Calculate the pH of 0.120 mol L^{-1} HCOOH solution. $K_a(HCOOH) = 1.8 \times 10^{-4}$. **A M**

4 Calculate the pH of 0.100 mol L^{-1} CH_3NH_2 solution. $K_a(CH_3NH_3^+) = 2.0 \times 10^{-11}$. **A M E**

5 Calculate the pH of 0.250 mol L^{-1} CH_3COONa solution. $K_a(CH_3COOH) = 1.8 \times 10^{-5}$. A M E

6 List all the species present in a 0.2 mol L^{-1} aqueous solution of ammonium nitrate, in order of concentration from the highest to the lowest. Write equations to justify your answer. A M E

7 Determine the concentration of an ethanoic acid solution whose pH is 4.00. $K_a(CH_3COOH) = 1.74 \times 10^{-5}$. A M



12

Buffers and titration curves

POWERPOINT

12A 1 Buffer solutions

PRACTICALS

12.1 P 193 Buffer action

Buffers

What are buffers?

In English a *buffer* is something which ‘lessens shock or protects from damaging impact’. In chemistry

a buffer solution is one which resists changes in pH caused by addition of moderate amounts of acid or base.

If a few drops of dilute hydrochloric acid are added to a beaker of water, the pH drops sharply, and likewise when a few drops of dilute sodium hydroxide solution are added to water the pH rises sharply. With buffer solutions this doesn’t happen. Adding even a moderate amount (several mL) of acid or base to a buffer does not alter the pH, or rather, only alters it a small amount.

The key to buffer solutions are weak acids (or bases) and their conjugates.

Look what happens when we add OH^- ions to CH_3COOH. The acid is a proton donor:

$$OH^-(aq) + CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O$$

And when we add H_3O^+ to CH_3COO^- the base acts as a proton acceptor:

$$H_3O^+(aq) + CH_3COO^-(aq) \rightleftharpoons CH_3COOH(aq) + H_2O$$

So if we had a mixture of acetic acid and acetate ions it wouldn’t matter whether we added acid or base, the excess OH^- and H_3O^+ would be neutralised.

Making buffers

A buffer solution contains significant amounts of both a weak acid (or base) and its conjugate base (or acid).

Buffer solutions can be made in two ways:

1 By dissolving the calculated amount of salt into the appropriate weak acid or base.

2 By adding a calculated amount of strong base/acid to the weak acid/base (so that the required salt is formed).

For example, the acetic acid/acetate buffer could be made by dissolving sodium acetate in acetic acid solution, or by taking acetic acid and adding sodium hydroxide to form sodium acetate in solution.

Important buffers

Solutions which absorb acid and base are very important, both in biochemical systems (eg blood) and industrially. Many reactions only occur above or below a certain pH, others have undesirable side reactions at the wrong pH, and still other reactions (usually organic) will produce the best yield only at the right pH. Using the correct buffer will ensure the pH is held at the right level.

The normal pH of blood is about 7.40. If your blood pH falls outside the 7.35 to 7.45 range you will become seriously ill. Digestion produces a range of products, many of them acidic. The blood pH is maintained, in spite of this addition of H^+ ions, through HCO_3^-/H_2CO_3 buffers in the red blood cells and the blood plasma.

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq)$$
$$OH^-(aq) + H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq)$$

Phosphate buffers ($HPO_4^{2-}/H_2PO_4^-$) are also important in maintaining constant pH in cells and urine.

Buffers and K_a

Remember that for a general acid, HA, we can write the dissociation equation:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

and the expression for K_a:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The expression for K_a can be rearranged to give $[H_3O^+]$:

$$\frac{K_a[HA]}{[A^-]} = [H_3O^+]$$

From this relationship we can either calculate the pH of a given buffer mixture (ie we know K_a, [HA] and $[A^-]$) or we can calculate the amount of acid/base or salt needed to make a buffer of a given concentration.

Look what happens when the concentrations of the acid (HA) and its conjugate base (A^-) are equal:

$$\frac{K_a\cancel{[HA]}}{\cancel{[A^-]}} = [H_3O^+]$$
$$K_a = [H_3O^+]$$
$$\mathbf{p}\boldsymbol{K_a} = \mathbf{pH}$$

While it is theoretically possible to make a buffer of any pH from any acid, the buffer is most effective when $[A^-] = [HA]$, and thus we choose an acid with pK_a closest to the desired pH.

Example 12.1 Making a buffer solution

What mass of sodium methanoate must be added to one litre of 1.00 mol L^{-1} methanoic acid to make a buffer solution of pH 4.5? pK_a(HCOOH) = 3.75.

Write the hydrolysis equation (for methanoic acid), and hence write the expression for the dissociation constant:

$$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+$$
$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

Rearrange to solve for $[H_3O^+]$

$$\frac{K_a[HCOOH]}{[HCOO^-]} = [H_3O^+]$$

'p' both sides ($-\log_{10}$) to turn $[H_3O^+]$ into pH

$$pK_a = -\log_{10}\left(\frac{[HCOO^-]}{[HCOOH]}\right) + pH$$

Rearrange some more.

$$\log_{10}\left(\frac{[HCOO^-]}{[HCOOH]}\right) = pH - pK_a$$
$$= 4.5 - 3.75$$
$$= 0.75$$

Get rid of the logs by finding powers of 10:

$$\frac{[HCOO^-]}{[HCOOH]} = 10^{0.75}$$
$$= 5.62$$

Find $[HCOO^-]$ by multiplying both sides by [HCOOH]:

$$[HCOO^-] = 5.62 \times 1.00 \text{ mol L}^{-1}$$
$$[HCOO^-] = 5.62 \text{ mol L}^{-1}$$

Calculate the mass of sodium methanoate required in the one litre solution:

$$m(HCOONa) = nM$$
$$= 5.62 \text{ mol} \times 68 \text{ g mol}^{-1}$$
$$= 382 \text{ g}$$

A word about logs

Two rules about logs that you may have forgotten:

- $\log(A \times B) = \log A + \log B$
- $-\log\left(\frac{A}{B}\right) = +\log\left(\frac{B}{A}\right)$

It is always possible to avoid using logs to solve buffer problems, but if the data involves both pH and pK_a, it is often faster to use logs rather than converting to K_a and $[H_3O^+]$. The choice is yours.

Mole ratios in buffer solutions

The effectiveness of a given buffer solution to absorb H_3O^+ or OH^- depends on the relative amounts of HA and A^- present. If it contains a large amount of A^-, then it will be able to absorb lots of H_3O^+, while large amounts of HA will mop up lots of OH^-.

POWERPOINT

12A 2 Buffer calculations

REVISION

12A 1 Making up a buffer solution

Quiz 12A 1, 12A 2

Example 12.2 Mole ratios in buffer solutions

A mixture of nitrous acid, HNO_2, and potassium nitrite, KNO_2, has a pH of 3.85. Which species is present in the greater concentration — HNO_2 or NO_2^-? $K_a(HNO_2) = 7.24 \times 10^{-4}$.

Write the hydrolysis equation (for nitrous acid), and hence write the expression for the dissociation constant:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+$$

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$$

Rearrange to find the ratio of $[HNO_2]$ to $[NO_2^-]$:

$$\frac{[HNO_2]}{[NO_2^-]} = \frac{[H_3O^+]}{K_a}$$

Convert pH into $[H_3O^+]$:

$$[H_3O^+] = 10^{-pH}$$
$$= 10^{-3.85}$$
$$= 1.41 \times 10^{-4}$$

Find the value of the ratio of $[HNO_2]$ to $[NO_2^-]$:

$$\frac{[HNO_2]}{[NO_2^-]} = \frac{1.41 \times 10^{-4}}{7.24 \times 10^{-4}}$$
$$= 0.195$$

Since this ratio is less than 1:

$$[NO_2^-] > [HNO_2]$$

It is easy to tell whether [HA] or [A–] predominates by comparing the pH of the solution to the pK_a of the acid.

pH < pK_a then [HA] > [A–]
pH = pK_a then [HA] = [A–]
pH > pK_a then [HA] < [A–]

If the buffer is more acidic than its pK_a, then the acid form predominates: if it is more basic than its pK_a, then the basic form predominates.

ENCOUNTER

12A Medicinal chemistry

pH changes when solutions are diluted

pH is a measure of [H_3O^+]. You might think that working out the pH of a diluted solution was a simple matter of dividing [H_3O^+] by the dilution factor to find the new pH. *Sometimes* it is that simple. Sometimes you don't even have to do that much. And (of course—this is Year 13 Chemistry after all) sometimes it is much harder. The trick is knowing which times are which!

Strong acids and bases are fully dissociated: every possible H_3O^+ ion is already in solution. With these solutions it is easy to find the new [H_3O^+] and new pH.

Example 12.3 pH of a diluted solution of a strong acid

A solution of HCl has a pH of 2.2. What will be the pH of the solution after it has been diluted by a factor of 5?

$$\begin{aligned}
[H_3O^+]_{old} &= 10^{-pH} \\
&= 10^{-2.2} \\
&= 6.31 \times 10^{-3}\ \text{mol L}^{-1} \\
[H_3O^+]_{new} &= [H_3O^+]_{old} \div 5 \\
&= 6.31 \times 10^{-3}\ \text{mol L}^{-1} \div 5 \\
&= 1.26 \times 10^{-3}\ \text{mol L}^{-1} \\
pH_{new} &= -\log(1.26 \times 10^{-3}\ \text{mol L}^{-1}) \\
&= 2.90
\end{aligned}$$

Weak acids are only partially dissociated. As H_2O is added, the equilibrium shifts to the right, causing more H_3O^+ to be formed. Thus the [H_3O^+] in the diluted solution is greater than you might expect. To find the new pH you must work out the new concentration of the acid (or base) and calculate its pH in the normal way.

The pH of a buffer solution is calculated from the ratio of [HA] and [A–]. If we dilute the buffer solution, we dilute both concentrations equally.

$$\frac{K_a[HA] \div 5}{[A^-] \div 5} = [H_3O^+]$$

The dilution factors cancel out and we are left with the same calculation, and the same pH as before.

When buffer solutions are diluted the pH does not change.

Test yourself 12A Buffer solutions

1 What are the properties of a buffer solution? ______________________________

____

2 Give an example of the composition of a buffer solution. ______________________________

____

____

3 Use the example from **2** to show how your buffer solution responds to addition of

a H_3O^+ ions: ______

b OH^- ions: ______

4 When does the pH of a buffer equal the pK_a of the acid? ______

5 pK_a(H_2CO_3) = 6.38. Describe how you would make up 1 L of a carbonic acid/bicarbonate buffer whose pH is 6.38.

6 A buffer solution is made by dissolving 5.0×10^{-3} mol of methanoic acid (K_a=1.8×10^{-4}) and 7.0×10^{-3} mol of sodium methanoate to form 1.00 L of aqueous solution.

a Calculate the concentration of acid and base present.

b Write the expression for [H_3O^+] in terms of the concentration of acid and base present.

c Calculate the pH of the buffer solution.

d What is the effect on the pH of a 10-fold dilution of this mixture? Why?

7 HCN is a weak acid, K_a = 6.0×10^{-10}. In a mixture of NaCN and HCN with a pH of 9.0, which species is present in the greater concentration — HCN or CN^-? Justify your answer with a calculation.

pH titration curves

Four graphs to learn

You will have done acid-base titrations in your Level 2 chemistry course, using a variety of acid-base indicators (such as phenolphthalein or methyl orange) that change colour at a particular pH. You could also have done the same titration using a pH meter.

The way pH changes as we add acid or base depends upon the strengths of the acid and base involved. Four characteristic graphs can be produced for the various combinations of strong and weak acid and base (for monobasic acids and bases), as shown.

POWERPOINT

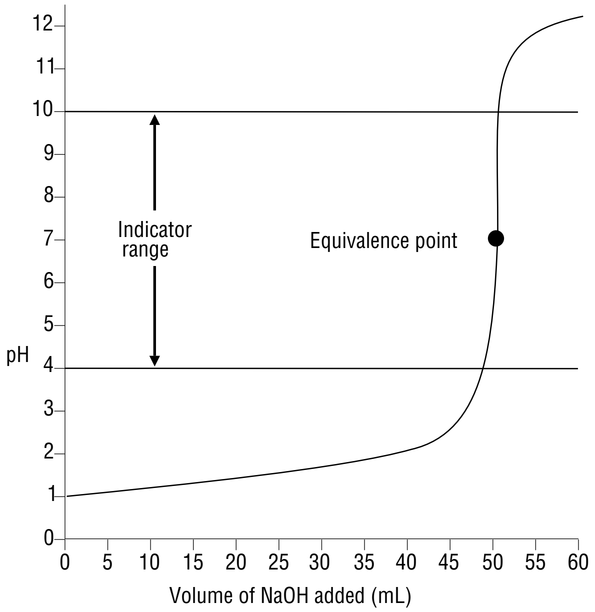
12B 1 Titration curves

PRACTICALS

12.2 P 194 Titration curves

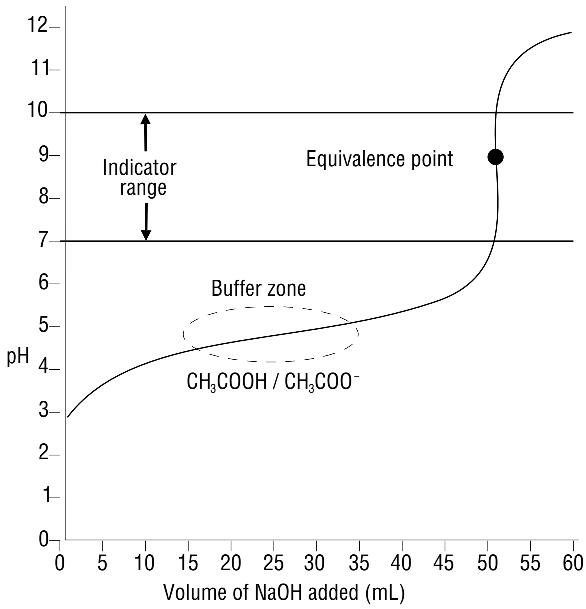
Strong base added to strong acid

0.100 mol L^{-1} NaOH added to 50.0 mL of 0.100 mol L^{-1} HCl



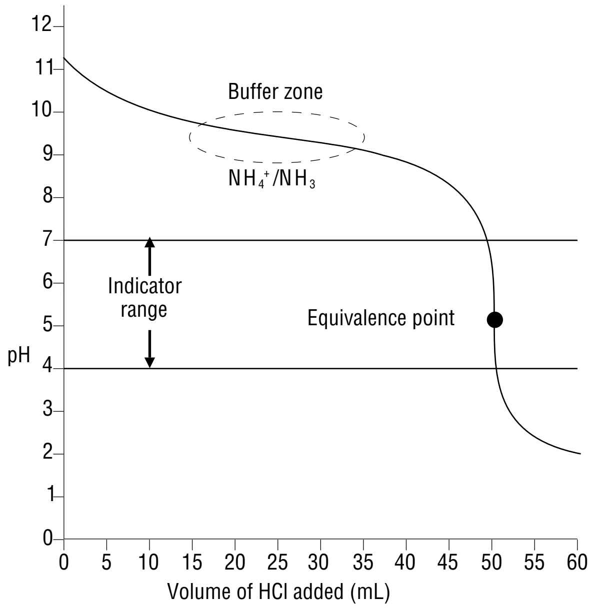
Strong base added to weak acid

0.100 mol L^{-1} NaOH added to 50.0 mL of 0.100 mol L^{-1} CH_3COOH



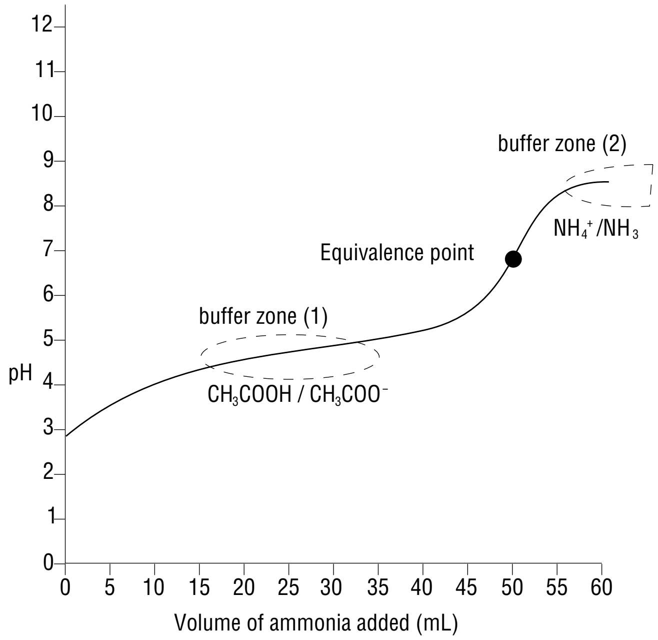
Strong acid added to weak base

0.100 mol L^{-1} HCl added to 50.0 mL of 0.100 mol L^{-1} NH_3



Weak base added to weak acid

0.100 mol L^{-1} NH_3 added to 50.0 mL of 0.100 mol L^{-1} CH_3COOH



Equivalence point

The **equivalence point** (marked on each graph) is

the point at which the amount of acid and base are present in equivalent amounts according to the balanced equation for the reaction.

Notice that close to the equivalence point a small addition from the burette will cause a large change in the pH. The equivalence point itself can be read off the graph by taking the centre of the vertical section.

For the strong acid/strong base titration the equivalence point is at a pH of 7 indicating that $[H^+] = [OH^-]$ (since the conjugates of strong acids or bases do not hydrolyse in water).

For the weak acid/strong base titration the equivalence point has a pH of about 9, indicating that $[H^+] < [OH^-]$. Excess OH^- must have been produced by hydrolysis. Hydrolysis of what? The ions present in the example shown are CH_3COO^- and Na^+. We know that Na^+ is 'well-behaved'—so CH_3COO^- must be the ion responsible.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

The reverse situation occurs in the strong acid/weak base titration. The equivalence point is acidic due to hydrolysis of (in this case) NH_4^+.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

In the case of weak acid/weak base the equivalence point is approximately 7, but it is not sharply defined. While it is possible to read off a value at the place where the slope changes the most, it would be better to change the method of analysis completely.

Buffer zone

Since buffers are formed when we mix weak acids (or bases) with their conjugate bases (or acids), whenever a weak acid (or base) is involved in an acid-base titration, we are going to form a buffer. On the pH graphs we can see the **buffer zone** is centred half-way to the equivalence point, ie that point at which the concentration of the acid (or base) and its salt are equal. At that point the pH of the solution will be equal to the pK_a of the acid.

pH = pK_a exactly half-way to the equivalence point of a titration.

Acid-base indicators

Indicators are just weak acids whose conjugate bases are different colours from their acids. The acidic form of bromothymol blue (HBrom) is yellow, while its conjugate base, $Brom^-$, is blue. At low pH, the yellow form predominates and the solution appears yellow. At high pH it is the blue form which predominates. The mixture will change colour when $[HBrom] = [Brom^-]$, and the pH of this colour change will be equal to pK_a(HBrom).

Indicators change colour when the pH of the solution is equal to the pK_a of that indicator:

methyl orange	pK_a = 4	pH range 3–5
methyl red	pK_a = 5	pH range 4–6
bromothymol blue	pK_a = 7	pH range 6–8
phenolphthalein	pK_a = 9	pH range 8–10
cresyl blue	pK_a = 11	pH range 10–12

You will be required to choose an appropriate indicator for a given titration. It must be one which changes colour on the vertical portion of the pH graph—for example phenophthalein for weak acid/strong base and methyl red for strong acid/ weak base.

REVISION

12B 1 Buffers and titration curves key facts

12B 2 Titration curves 1–4

Quiz 12B 1, 12B 2a, 12B 2b, 12B 2c, 12B 2d

Sketching titration curves

You will be expected to either sketch titration curves, especially for weak acid-strong base or weak base-strong acid titrations. Start by calculating (or estimating, if you are told to do a sketch without calculations) the key points on the curve, then join these points using your knowledge of general shape of titration curves.

POWERPOINT

12B 2 Drawing titration curves

Example 12.4 Drawing a titration curve

Draw the titration curve formed when 20.0 mL of 0.0800 mol L^{-1} ammonia solution is titrated against 0.0500 mol L^{-1} HNO_3.
$K_a(NH_4^+) = 5.75 \times 10^{-10}$.

Calculate the pH of the ammonia solution before any HNO_3 is added:

See page 123 if you've forgotten how to calculate the pH of a weak base.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + H_3O^+(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Assume 1 $[NH_4^+] = [OH^-]$
2 $[NH_3] = 0.0800$ mol L^{-1}

$$\frac{1 \times 10^{-14}}{K_a} = \frac{[OH^-]^2}{0.0800 \text{ mol L}^{-1}}$$

$$\sqrt{(1.74 \times 10^{-5} \times 0.0800)} = [OH^-]$$

$$1.18 \times 10^{-3} = [OH^-]$$

$$pOH = 2.93$$

$$pH = 11.1 \text{ (3 sig fig)}$$

Calculate the volume of HNO_3 required at the equivalence point:

$$NH_3(aq) + HNO_3(aq) \longrightarrow NH_4^+(aq) + NO_3^-(aq) + H_2O(l)$$

$$\begin{aligned} n(NH_3) &= cV \\ &= 0.0800 \text{ mol L}^{-1} \times 20.0 \times 10^{-3} \text{ L} \\ &= 1.60 \times 10^{-3} \text{ mol} \\ n(HNO_3) &= n(NH_3) \\ &= 1.60 \times 10^{-3} \text{ mol} \\ V(HNO_3) &= \frac{n}{c} \\ &= \frac{1.60 \times 10^{-3} \text{ mol}}{0.0500 \text{ mol L}^{-1}} \\ &= 0.0320 \text{ L} \quad \text{or} \quad 32.0 \text{ mL} \end{aligned}$$

Calculate the pH at the equivalence point:

At the equivalence point we have 1.60×10^{-3} mol of NH_4^+ in (32.0 + 20.0) = 52.0 mL of solution.

$$\begin{aligned} [NH_4^+] &= \frac{1.60 \times 10^{-3} \text{ mol}}{52.0 \times 10^{-3} \text{ L}} \\ &= 0.0308 \text{ mol L}^{-1} \end{aligned}$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Assume 1 $[NH_3] = [H_3O^+]$
2 $[NH_4^+] = 0.0308$ mol L^{-1}

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$5.75 \times 10^{-10} = \frac{[H_3O^+]^2}{0.0308 \text{ mol L}^{-1}}$$

$$\sqrt{5.75 \times 10^{-10} \times 0.0308} = [H_3O^+]$$
$$4.21 \times 10^{-6}\ \text{mol L}^{-1} = [H_3O^+]$$
$$\text{pH} = 5.38$$

Calculate the pH after 50.0 mL of HNO_3 have been added.

The total volume after 50.0 mL of HNO_3 have been added is 70.0 mL. Since 32.0 mL of acid is required to react with the ammonia, the excess acid is 18.0 mL.

$$c(HNO_3)_{\text{unreacted}} = \frac{18.0\ \text{mL}}{70.0\ \text{mL}} \times 0.0500\ \text{mol L}^{-1}$$
$$= 0.0129\ \text{mol L}^{-1}$$

Assume $[H_3O^+] = 0.0129$ mol L^{-1}

$$\text{pH} = -\log[H_3O^+]$$
$$= -\log(0.0129\ \text{mol L}^{-1})$$
$$= 1.89$$

Identify the buffer zone.

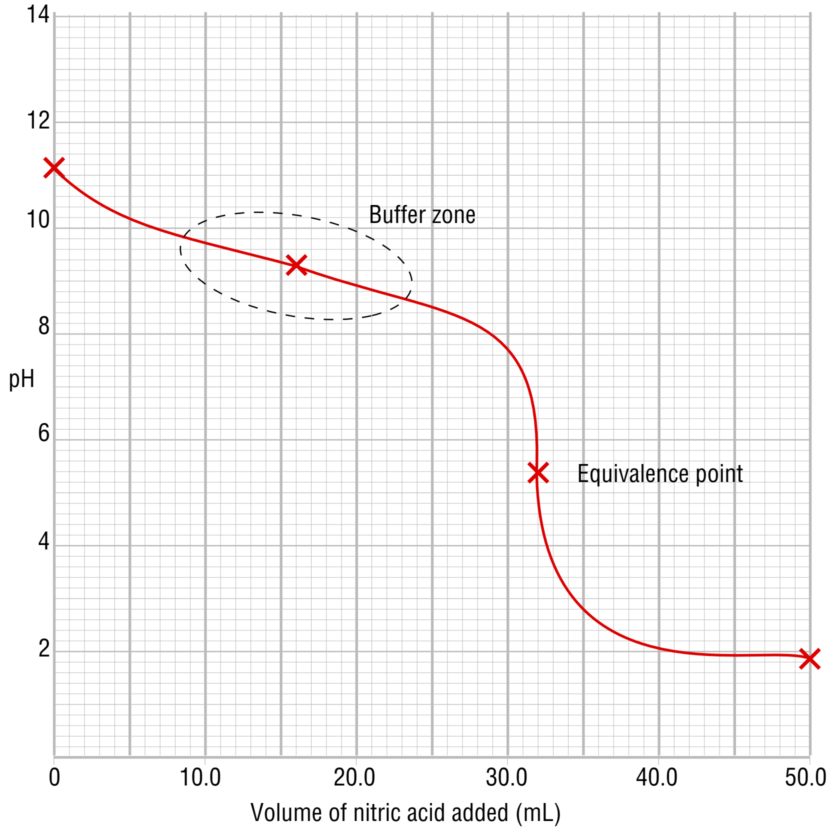
Since the equivalence point is at 32.0 mL, pH = pK_a at 16.0 mL

$$pK_a(NH_4^+) = -\log(5.75 \times 10^{-10})$$
$$= 9.24$$

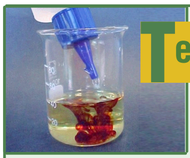
Plot the known points and sketch the graph:

On the graph, the pH will change by 1 pH unit between ¼ to the equivalence point and ¾ to the equivalence point.
At the equivalence point it will be nearly vertical for about 2 pH units above and below the equivalence point.

Titration curve for 20.0 mL of 0.0800 mol L^{-1} ammonia titrated against 0.0500 mol L^{-1} nitric acid

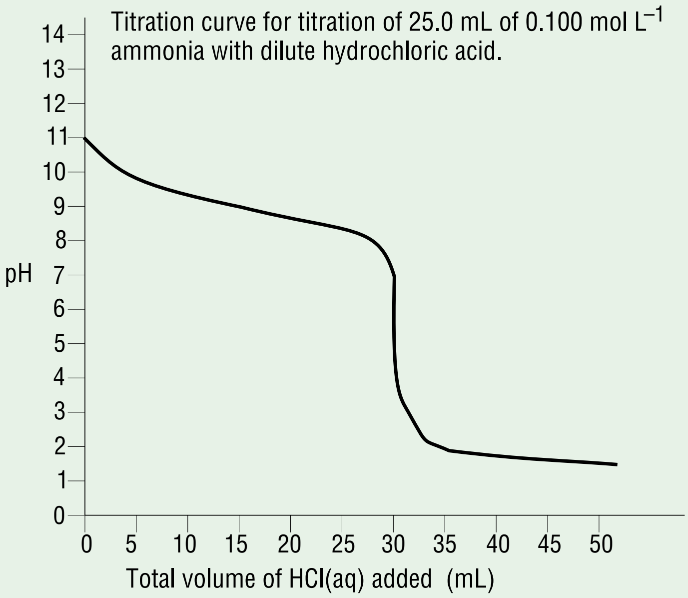


12B 3



Test yourself 12B Titration curves

1 Use this graph to answer the following questions.



a What is the pH at the beginning of the titration? ______________________

b What volume of acid has been added at the equivalence point?

____

c Label the buffer zone.

d What volume of HCl has been added when the pH of the solution equals the pK_a? ______________________

e Reading from the curve, what is the magnitude of pK_a (NH_4^+)? ______________________

f Name a suitable indicator for this titration. ______________________

g Write the equation for the reaction that occurs during this titration.

____

h Calculate the concentration of the hydrochloric acid.

____

____

____

____

____

____

i Calculate the pH of the solution at the equivalence point.

____

____

____

____

____

____

____

____

____

Key learning outcomes for Chapter 12

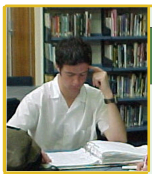
By now you should be able to:
1 Define a buffer solution.
2 Explain buffer action by writing equations for the reactions that occur when H_3O^+ or OH^- is added to to a given buffer solution.
3 Give examples of buffers.
4 Calculate the pH of a buffer solution given suitable data, or complete calculations to make up a buffer solution of given pH.
5 Given the pH of a buffer solution, determine the mole ratio of [HA] : [A^-] or [B] : [HB^+].
6 Be able to sketch the general shape of the titration curves for:
   a strong acid vs strong base
   b weak acid vs strong base
   c strong acid vs weak base.
7 Discuss the characteristics of the titration curves in 6 and perform appropriate calculations to find the pH at different points on the curve or calculate the concentration of the acid or base.
8 Explain the colour change of acid-base indicators by describing each indicator as a weak acid with a certain pK_a.
9 Choose an appropriate indicator for a titration given pH of the equivalence point and the K_a or pK_a of the indicator.

REVISION

- Chemistry 3.7 key facts crossword
- Chemistry 3.7 key facts flip cards

EXAM QUESTIONS

- Practice questions
- Sample examination papers



Review questions for Chapter 12

1 Two test tubes, one containing 10 mL of a mixture of ammonia solution and ammonium chloride, and the other 10 mL of distilled water, each have a drop of universal indicator added. Both solutions are green. What will happen when 0.5 mL of 2 mol L^{-1} hydrochloric acid solution is added to each tube? Why? **A M**

2 A 0.10 mol L^{-1} solution of the weak acid HA has a pH of 3.40.

a Write the equation for the reaction of HA with water. **A**

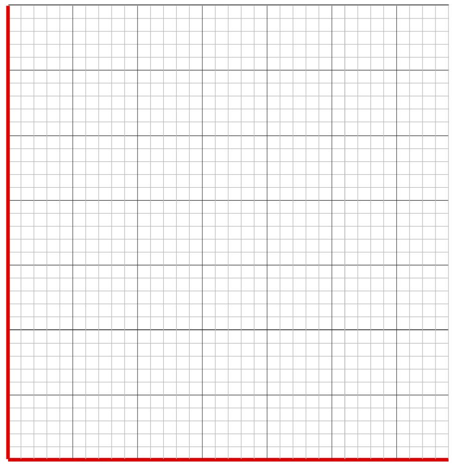
b Calculate K_a for HA and hence pK_a. **A M**

c Enough NaA is added to make [A^-] equal 0.10 mol L^{-1}. What is the pH of the resulting solution? **A**

3 On the axes opposite, sketch the titration curves you would get from the following titrations: **A M**

a 20.0 mL of 0.001 mol L^{-1} HCl against 0.001 mol L^{-1} NaOH.

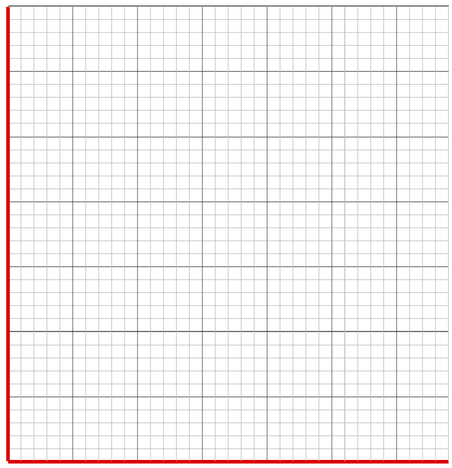
b 20.0 mL of 0.1 mol L^{-1} CH_3COOH against 0.1 mol L^{-1} NaOH.



4 A student took 25.0 mL of a commercial ammonia solution, diluted it to 250.0 mL in a volumetric flask and pipetted out 20.0 mL samples into 6 conical flasks. He titrated these solutions against 0.100 mol L^{-1} HCl solution. When he used phenolphthalein indicator he required an average of 12.5 mL HCl, and with methyl red indicator he required an average of 19.2 mL.

a Write an equation for the reaction between ammonia and hydrochloric acid. **A**

b Sketch a graph showing change in pH as the hydrochloric acid is added to the ammonia solution and use it to explain which of the two indicators is the more appropriate to use. **A M**



c Calculate the concentration of ammonia in the diluted solution and hence the percentage of ammonia in the commercial solution. **A M E**

5 Benzoic acid, C_6H_5COOH, is used as a preservative in fruit juices. What is the mole ratio of benzoic acid to the benzoate ion, $C_6H_5COO^-$, for a buffer solution whose pH is 3.5? pK_a of benzoic acid is 4.20. **A M**

6 You are to make one litre of ammonia/ammonium chloride buffer of pH = 9.75. Calculate the masses of ammonia and ammonium chloride required. $pK_b(NH_3) = 4.75$. **A M E**

Section 5

Extended practical

Chemistry 3.1
4 credits

AS60694 Internal Carry out an extended practical investigation involving quantitative analysis

13 Extended practical

13

Extended practical

POWERPOINT

13A 1 Excellent investigations

Note: changes may have been made to the criteria for this Achievement Standard since the publication of these Notes. Pay close attention to the instructions your teacher gives you, especially concerning the kinds of investigations you could do and the assessment guidelines.

The Canterbury University Outreach website contains a growing collection of analytical methods suitable for your practical investigation: www.outreach.canterbury.ac.nz/chemistry

Getting started

You are to carry out an extended investigation involving quantitative analysis. While most of your *time* will be spent in collecting, preparing and analysing your samples, the bulk of the *marks* are gained from the work you do before, and after, the 'wet' chemistry.

What's the question?

The achievement standard requires you to 'collect data in relation to a possible trend in the amount of a substance'. In other words, an experiment is valid if it would be possible for you to plot your results on a line graph. Your dependent variable (the one on the *y* axis) is almost certainly the concentration of some species, while the independent variable (*x* axis) may be time, or temperature, or distance, or the concentration of another species, or some other factor. If you're doing the unit standard (US 6341) then results that form a bar graph are also permitted.

Who cares?

It helps if you can show why your topic is important. Does it matter if there are high levels of lead in shellfish collected close to a stormwater drain? Why? How could it get there? How high is too high?

This is a chemistry project, not a social studies project, so you don't need to go into pages of detail, but a few paragraphs discussing the relevance of your results is appropriate.

Logging in

Buy an exercise book (today) and use it to record *everything*. Not only is a log book a requirement of the Standard, but it will tell your teacher that you did do steps that perhaps you forgot to mention in the formal report. Use it to record your research notes and preliminary ideas as well as your experimental data, calculations and rough notes for the report.

Don't treat your log book as a scribble pad. Date every entry, and identify every number so that you, and your teacher, know what it means later. Get into the habit of writing '$c(S_2O_3^{2-}) = 0.0934$ mol L^{-1}', and not just 'conc = 0.0934'. Identify each web address with the name or a description of the site and record the name, author(s), publisher, publication date and page number(s) of each book you use.

The practical work

Method

Your report needs to clearly describe the method you used for your experiment. The method for your *analysis* will probably be given to you — but that's not the method for your whole experiment! You'll have to decide how and where to collect your samples, how to prepare them for analysis, how many samples to collect, and so on. You may also need to modify the analytical method—changing the concentration of solutions because your material contains more, or less, of the substance than the method was designed for, or using slightly different ingredients because the exact compounds listed are not available. So under the heading **Method** you should detail all the steps involved in your experiment and the reasons for the decisions you made.

Being sure

The whole point behind doing a number of analyses is to be sure of your answer.

- You'll need to do some preliminary trials to sort out your method. Should those river water samples be taken every 20 m or every 1 km? Should you be sampling the fermenting wine every 2 hours for three days, or every week for four months?
- In most cases, you should be repeating titrations on a single solution several times to get concordant results.
- It is hard to get accurate results when your titres are very small, so dilute the reagents as necessary so that your titres fall in the range 10–40 mL.
- Collect and analyse several samples for each value of the indpendent variable and average the results. This provides a check on your results, and indicates the range of values at that point.
- Is it possible that the concentration in your samples will change between sampling and analysis? If so, is there a way to store or treat your sample to prevent this change? A useful check on your method is to make up a solution of known concentration, store it as planned, and then analyse it.
- Most analytical procedures are carried out on small amounts of the sample—2 g, 5.0 mL etc. If your sample is not homogeneous (the same throughout), that can make a big difference to your results. *Make* your material homogeneous before analysing it. Take a large sample (200 g), cut, crush or pulp it finely, mix thoroughly and then take three or four 2 g samples of the mixture for analysis and average the results. To be really sure, do it all again with another 200 g sample.
- If possible, collect more samples than you expect to need. That way if things go wrong you'll be able to redo the analysis and get back on track without stress.

Results

Data processing

You are required to show exactly how your data is calculated, and to demonstrate understanding of the chemistry involved. In other words, you need to 'show working' as you would for a calculation in an exam. However, you are not expected to repeat that page-long worked calculation for every one of perhaps 40 data points! Do one calculation out in full, and then either use a spread sheet to do the calculations, or convert the calculation into a simple formula such as:

$$\text{oxygen content (mg L}^{-1}) = \text{titre} \times 0.8$$

Pay attention to the accuracy of your equipment. If you are doing titrations and using volumetric glassware, your work is probably accurate to 3 significant figures, so it would be foolish to quote your final concentration as 10.361 mg L^{-1}. If your calculator drops a '0' that is significant though, you should record it (eg 39.3 – 28.3 = 11.0, not 11).

You cannot get Excellence unless your use of significant figures is correct.

POWERPOINT

- 13A 2 Understanding concentration
- 13A 3 Understanding back titrations
- 13A 4 Understanding colorimetric analysis

PRACTICALS

- 13.1 P 196 A back titration
- 13.2 P 197 Colorimetric analysis

Pay particular attention to small readings that may become incorporated into your final calculation. For example, if at some point you end up with a mass of 0.012 g of sample, your whole result is now only accurate to 2 sig fig.

There is also the possibility that the manufacturer's claims about the concentration of the active ingredient are wrong, but you should be very sure of your results before making your findings public.

Always quote the units with your figures—either right beside the number, or at the top of the column in a table.

Check that your results are reasonable. You wouldn't normally expect the concentration of chloride in river water to be greater than that found in sea-water. On the other hand, the vitamin C content of a fruit drink *could* be significantly greater than the 'not less than' value printed on the packet.

Tables and graphs

You should record your results in table form. Your log book needs to have a record of burette and meter readings—including the duds—plus the results of every calculation. That also includes the results of preliminary trials you needed to do to find out if your method was going to work. Your report needs to show your results in sufficient detail so that someone reading it can see that your conclusions are valid. Only include the concordant titres in your final report.

In most cases, you should present a line graph showing how the concentration of your dependent variable varies with different values of the independent variable. Plot the final average concentration — not the titres. Error 'whiskers' on each data point are appropriate, if you know how to do that.

			Conc	Average conc
Site A	Sample 1	Titre 1		
		Titre 2		
		Titre 3		
	Sample 2	Titre 1		
		Titre 2		
		Titre 3		
	Sample 3	Titre 1		
		Titre 2		
		Titre 3		
Site B	Sample 1	Titre 1		
		Titre 2		
		Titre 3		
	Sample 2	Titre 1		
		Titre 2		
		Titre 3		
	Sample 3	Titre 1		
		Titre 2		
		Titre 3		
Site C	Sample 1	Titre 1		
		Titre 2		
		Titre 3		

A table like this in your final report makes it clear how many samples were tested, shows the reproducibility of your results, and the average concentration at each site. It is not necessary to list every burette reading and every step in the calculations in your final report.

So… what?

Conclusion

Having gone through all those weeks of chemical analyses and calculations, we want to know what the final answer is and what it means. Be detailed in your conclusion: from an initial concentration of 72.4 g L^{-1} the concentration decreased an average of 3.7 g L^{-1} per day. It is recommended that the product be consumed within four days of opening, after which time the concentration was 57.6 g L^{-1}, which is still well above the manufacturer's claim of 50 g L^{-1}.

Errors

Experimental error is an important issue when discussing the reliability of your results. An *error* is not a *mistake*. If you make a mistake—such as forgetting to shake the bottle before removing a sample of a diluted solution—then you need to do it again correctly.

Causes of error are weaknesses in the equipment or method that will produce inaccuracies even when no mistake has been made.

Here are a few possibilities:

- Your result is only as accurate as the equipment you are using. The glassware is probably accurate to ±1%, the balance to ± 0.01 g or perhaps ± 0.001 g, and so on.
- There may be contaminants in your sample which will also react, making it look like you have a higher, or lower, concentration of *y* than there really is. For example, there may be other oxidising agents present that will oxidise I^- to I_2, other acids that will react with the sodium hydroxide, other halides to react with the silver nitrate, and so on.
- Some samples and reagents degrade on storage, perhaps due to the action of microbes or a reaction with something in the air. You will need to consider whether this is a concern for your particular reaction, and if so, what you are going to do to make sure that your results are trustworthy.
- If you are using the concentration of one species to indicate some other factor—such as chloride concentration to show where the sea-

water is, or oxygen concentration to indicate polluted water—then you need to consider other factors that could change that concentration. For example, a high chloride ion concentration may be due to factory discharge rather than sea-water, and low oxygen concentration could be due to a high temperature rather than a high bacteria count.

Bibliography

A bibliography is a list of the sources of information you used when preparing your report. You don't have to list all the ones you looked at that did not contain anything useful: just the ones you used. You need to provide sufficient information so that someone else could find the same information you found.

- If it is a book, list the full title, author(s), publisher and publication date, the edition, and the relevant chapter or page numbers.
- An internet address should take the person directly to the relevant page, not simply to the website.
- If you used an encyclopaedia (print or electronic), give its name, publisher, the date of publication and the title of the article(s).

Final hints

Most of the practical work you do at school has been carefully prepared for you, so that it works. Real life isn't like that! Just about everything you do will go wrong at first. The book you want won't be in the library; the chemical you need will have run out; someone else will be using the glassware you want; you'll discover the solution you spent all day yesterday making should have been stored in the fridge—or it was in the fridge and someone threw it out! Be prepared for everything to take at least twice as long as you think it is going to take so you can handle the inevitable frustrations.

Label all your solutions clearly, with your name, the solution name and concentration and the date. Labelled solutions are much less likely to be confused or thrown out.

To get Excellence you need to do a thorough investigation and produce a comprehensive report, but to get Achievement all you need to do is have a clear aim, perform a valid analysis, process the results correctly and come up with a sensible conclusion. If you're running out of time, scale back the range and the number of repeats you're doing. Modify the aim if necessary until you have one you can satisfactorily answer in the time left you. A really great investigation will earn you no credits if it never gets finished, so do what you can to get *something* finished, then write that up as well as you can.

Allow yourself at least 4 days to write up your investigation after you have completed the practical work—and don't forget to put your name on it!

On the final pages of these *Notes* are checklists and Milestone sheets to guide your work. Your teacher may ask you to detach these sheets from your book and hand them in. Once you get them back, include them in your log book.

PLAN AHEAD

Section 6

Practicals

The practical part of your chemistry course is an important as the theory. Your examiners expect you to have done a comprehensive programme of practical work and will test you on your knowledge of practical chemistry.

Although you may be working in pairs for some of these investigations, it is important that you make your own observations, record all the results and process the data yourself. Sample results and model answers to these investigations are on the CD.

Contents

Safety notes

Those substances identified as CORROSIVE will quickly make holes in your skin or clothes. If you get even a single drop on your skin, wash it off immediately (within a few seconds). Those susbtances identified as TOXIC are particularly poisonous. You should wash your hands after handling them. Most dilute solutions are safe under normal circumstances, but can still harm you if you get some in your eye or mouth.

Safety glasses should be worn for all practical work
Always fill pipettes with a pipette filler.

Inv 1.1 Redox reactions: some examples

Many redox reactions involve colour changes. The reactions below illustrate the behaviour of some common redox reagents.

Carry out each reaction using CLEAN test tubes and SMALL quantities.

Reaction one (iron powder and copper sulfate solution)

1 a To 2 mL of copper sulfate solution add half a spatula full of iron powder, mix well and allow to stand.

Observations:____

b Use a dropper to remove most of the liquid and add it to 2 mL of dilute sodium hydroxide solution.

Observation and conclusion:____

c Add two drops of concentrated nitric acid (corrosive) to the solid remaining in the test tube.

Observation and conclusion:____

____

d What species was oxidised in this reaction?___________To what?_____________

e Write the oxidation half-equation.

____

f What species was reduced in this reaction?__________To what? _____________.

g Write the reduction half-equation.

____

h Combine the two half-equations into an ionic equation.

____

Reaction two (potassium dichromate and ethanol)

2 a Place 2 mL of potassium dichromate solution in a test tube, add 2 mL of dilute sulfuric acid and warm in a water bath for two minutes. Then add 1 mL of ethanol.

Observations:____

b Chromium ions you may have met are: CrO_4^{2-} (yellow), $Cr_2O_7^{2-}$ (orange), Cr^{3+} (green), Cr^{2+} (blue). Identify the reacting and product chromium ions for the reaction in a.

Reactant species:______________ Product species: ______________

c Write the ion-electron half-equation for the chromium species and state whether chromium has been oxidised or reduced.

____

d Assume that the ethanol (CH_3CH_2OH) reacts to form ethanal (CH_3CHO). Write the ion-electron half-equation for the conversion of ethanol to ethanal and state whether this is oxidation or reduction.

____

e Combine these two half-equations to form an ionic redox equation.

____

____

Reaction three (acidified hydrogen peroxide and potassium permanganate)

3 a To 2 mL of 6% hydrogen peroxide add 2 mL of dilute sulfuric acid followed by a few drops of potassium permanganate solution.

Observations:____

b Manganese species you have met include: Mn^{2+} (colourless/very pale pink), Mn^{3+} (red), MnO_2 (brown), MnO_4^{2-} (green), MnO_4^{-} (purple). Identify the reactant and product manganese species.

Reactant species:_______________ Product species: _______________

c Write the ion-electron half-equation for the manganese species and state whether it is oxidation or reduction.

____

d Hydrogen peroxide can be oxidised to form oxygen gas or reduced to form water. Decide whether it has been oxidised or reduced and write the appropriate ion-electron half equation.

____

e Combine these two half-equations to form an ionic redox equation.

____

____

Reaction four (iron(II) sulfate and neutral potassium permanganate)

4 a To 2 mL of iron(II) sulfate solution add a few drops of potassium permanganate solution.

Observations:____

b Add a drop of potassium thiocyanate solution.

Observation and conclusion:____

c Refer to **3b** to identify the reactant and product manganese species.

Reactant species:_______________ Product species: _______________

d Write the ion-electron half-equation for the manganese species and state whether it is oxidation or reduction.

____

e Write the relevant ion-electron half equation for the Fe^{2+} reaction.

____

f Combine these two half-equations to form an ionic redox equation.

____

Reaction five (oxalic acid and potassium permanganate)

5 a To 2 mL of oxalic acid solution (toxic) add 2 mL of dilute sulfuric acid solution and warm in a water bath for 2 minutes, then add a few drops of potassium permanganate solution.

Observations:____

b Use a dropper to take a sample of gas from just above the surface of the liquid. Bubble this gas through 2 mL of limewater.

Observation and conclusion:________________________________

c Refer to **3b** to identify the reactant and product manganese species.

Reactant species:_______________ Product species: _______________

d Write the ion-electron half-equation for the manganese species and state whether it is oxidation or reduction.

____

e Oxalic acid is present as the $C_2O_4^{2-}$ ion. What does this ion form in this reaction? __________

f Write the ion-electron half-equation for the $C_2O_4^{2-}$ reaction and state whether it is oxidation or reduction.

____

g Combine these two half-equations to form an ionic redox equation.

____

Reaction six (alkaline potassium permanganate)

6 a To 2 mL of sodium hydrogen sulfite solution add 4 drops of potassium permanganate solution followed by 4 mL of dilute sodium hydroxide solution.

Observations:____

b In a separate test tube place 2 mL of dilute hydrochloric acid and 1 mL of barium chloride solution. Add a few drops of your solution from a.

Observation and conclusion:________________________________

c Write the oxidation ion-electron half equation for *alkaline conditions*.

____

d Refer to **3b** to identify the reactant and product manganese species.

Reactant species:_______________ Product species: _______________

e Write the reduction ion-electron half equation in *alkaline conditions*.

____

f Combine these two half-equations to form an ionic redox equation.

____

Inv 1.2 Redox reactions involving the halogens

Group 17 elements are important redox reagents which exhibit a range of oxidation states.

Carry out each reaction using CLEAN test tubes and SMALL quantities.
Note ALL observations. Identify new substances if you can.

Reaction one (lead(IV) oxide and concentrated hydrochloric acid)

1 a To 1 mL of concentrated hydrochloric acid (corrosive) in a test tube add a rice-grain sized sample of solid lead(IV) oxide (toxic) powder. Hold a piece of damp starch-iodide paper near the top of the test tube.

Observation and conclusion:____

____

b Use a dropper to remove a few drops of the solution from a then add to them 1 mL of dilute potassium iodide solution

Observation and conclusion:____

c Write two ion-electron half equations and hence a full ionic reaction for the reaction in **a**.

____

____

____

Reaction two (potassium iodide and hydrogen peroxide)

2 a To 2 mL of dilute potassium iodide solution add 2 mL of dilute sulfuric acid solution followed by 1 mL of 6% hydrogen peroxide.

Observations:____

b Add a few drops of starch solution.

Observation and conclusion:____

c What species was oxidised during the above redox reaction? _______________

d Write the oxidation half equation.

____

e What was the oxidising agent during the above redox reaction? _______________

f Write the reduction half equation.

____

g Combine these two half-equations to form an ionic redox equation.

____

Reaction three (sodium thiosulfate and iodine)

3 **a** To 2 mL of sodium thiosulfate add 1 mL of iodine solution.

Observations:____

b Add a few drops of silver nitrate solution.

Observation and conclusion:________________________________

c Write the reduction half-equation.

____

d $S_2O_3^{2-}$ is oxidised to the tetrathionate ion, $S_4O_6^{2-}$. What colour is this ion?____________

e Write the oxidation half equation.

____

f Combine the two half-equations into a full ionic equation.

____

Reaction four (potassium iodate and sodium sulfite)

4 **a** Acidify 2 mL of potassium iodate solution with 2 mL of dilute hydrochloric acid solution, then add 3 mL of sodium sulfite solution.

Observations:____

b Withdraw 1 mL of solution from a and add it to 1 mL of barium chloride solution.

Observation and conclusion:________________________________

c Add 1 drop of starch to the remaining solution from **a**.

Observation and conclusion:________________________________

d Write the iodate half-equation and state whether the iodate ion was oxidised or reduced.

____

e Write the sulfite half-equation and state whether the sulfite ion was oxidised or reduced.

____

f Combine the two half-equations into a full ionic equation.

____

____

Reaction five (potassium iodide and potassium iodate)

5 **a** To 4 mL of potassium iodide solution add 2 mL of dilute sulfuric acid solution followed by 2 mL of potassium iodide solution.

Observations:____

b Add a drop of starch solution.

Observation and conclusion:____________________________________

c What is formed when iodide ions are oxidised?__________________________

d What is formed when iodate ions are reduced?__________________________

e Write two ion-electron half equations and hence a full ionic reaction for the reaction in **a**.

____

____

____

____

Reaction six (potassium iodide and copper sulfate)

6 **a** To 2 mL of potassium iodide solution add 1 mL of copper sulfate solution. Filter the resulting mixture.

Observations:____

____

____

b Copper species you may have met include blue $Cu^{2+}(aq)$, black $CuO(s)$, red $Cu_2O(s)$, white $CuI(s)$ and brown/pink $Cu(s)$. Identify the reactant and product copper species in **a**.

Reactant:________________ Product:________________

c Write an ion-electron half equation for the copper reaction and state whether it is oxidation or reduction.

____

d What is the product of the iodide reaction?____________________________

e Write an ion-electron half equation for the iodide reaction.

____

Combine the two half equations into one full ionic equation.

____

____

Inv 2.1 Preparation of standard iron(II) ammonium sulfate

Iron(II) ammonium sulfate is suitable as a primary standard for quantitative analysis because it is a stable solid easily obtained in a pure form. It reacts with a number of oxidising agents. The solution prepared here can be used to standardise potassium permanganate solution (Inv 2.2).

1 Calculate the molar mass of $FeSO_4(NH_4)_2SO_4.6H_2O$. $M(FeSO_4(NH_4)_2SO_4.6H_2O)$ = __________

2 What size of volumetric flask will you use? $V(FeSO_4(NH_4)_2SO_4.6H_2O)$ = __________

3 What is the required concentration of the iron(II) ammonium sulfate solution? $c(FeSO_4(NH_4)_2SO_4.6H_2O)$ = __________

4 Write the formula relating the amount in moles, concentration and volume. ____________________

5 Calculate the amount, in moles, of iron(II) ammonium sulfate solution required. $n(FeSO_4(NH_4)_2SO_4.6H_2O)$ = __________

6 Write the formula relating the amount in moles, mass and molar mass. ____________________

7 Calculate the mass of iron(II) ammonium sulfate required. $m(FeSO_4(NH_4)_2SO_4.6H_2O)$ = __________

8 Weigh a small, clean, dry beaker. mass = __________

9 Add about (within about 0.3 g) the required mass of iron(II) ammonium sulfate required and reweigh. mass = __________

10 Calculate the mass of iron(II) ammonium sulfate used. $m(FeSO_4(NH_4)_2SO_4.6H_2O)$ = __________

11 Calculate the number of moles of iron(II) ammonium sulfate used. $n(FeSO_4(NH_4)_2SO_4.6H_2O)$ = __________

12 Dissolve the powder in about half a beaker of distilled water. Rinse the clean volumetric flask with distilled water. Use a funnel to carefully transfer the iron(II) ammonium sulfate solution to the volumetric flask and rinse in any remainder using distilled water. Make sure to wash down the sides of the funnel. Shake until dissolved and make up to the mark. Stopper and shake to mix thoroughly.

13 Calculate the exact concentration of the solution. $c(FeSO_4(NH_4)_2SO_4.6H_2O)$ = __________

Inv 2.2 Standardising potassium permanganate solution

We can use a standard solution of iron(II) ammonium sulfate to find the concentration of an unknown solution of potassium permanganate.

1 Rinse and fill a burette with the potassium permanganate solution (approximately 0.02 mol L^{-1}).

2 Using a pipette filler, pipette out 20.0 mL samples of the iron(II) ammonium sulfate solution into conical flasks and add 20 mL of dilute sulfuric acid to each flask. $V(Fe^{2+})$ = ________________

3 What is the concentration of this iron(II) ammonium sulfate solution? $c(Fe^{2+})$ = ________________

4 Calculate the amount, in moles, of iron(II) ammonium sulfate solution used in each titre. $n(Fe^{2+})$ = ________________

5 Titrate the permanganate solution into the acidified iron(II) ammonium sulfate solution until the pink colour remains. Repeat until 3 concordant results are obtained.

Burette reading	1st titration	2nd titration	3rd titration	4th titration	5th titration
Initial reading					
Final reading					
Titre					

6 Calculate the average of the concordant titres. $V(MnO_4^-)$ = ________________

The ionic equation for this redox reaction is

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

7 What is the ratio of MnO_4^- to Fe^{2+}? $n(MnO_4^-)$ = __$n(Fe^{2+})$

8 Calculate the amount, in moles, of permanganate reacting. $n(MnO_4^-)$ = ________________

9 Calculate the concentration of the permanganate solution. $c(MnO_4^-)$ = ________________

Inv 2.3 Standardising potassium permanganate solution with oxalic acid

Oxalic acid, used to reduce potassium permanganate, is poisonous. Pipette fillers must be used.

1 Weigh accurately about 1.3 g of oxalic acid (toxic) into a small,

m(oxalic) = ________________

2 Dissolve the oxalic acid in distilled water and transfer the solution to a 200.0 mL volumetric flask. Rinse the beaker into the flask several times. Mix well, make up to the mark with distilled water and mix again. Label your flask.

$V(Fe^{2+})$ = ________________

3 Calculate the exact concentration of this solution, M(oxalic acid) = 126 g mol^{-1}.

c(oxalic) = ________________

4 Rinse and fill a burette with the permanganate solution (approximately 0.02 mol L^{-1}).

5 Using a pipette filler, pipette out 20.0 mL (or 25.0 mL) samples of the oxalic acid solution into conical flasks and add 20 mL of dilute sulfuric acid to each flask. Heat each solution on a water bath or over a Bunsen flame until it is about 80 °C.

V(oxalic) = ________________

6 Calculate the amount, in moles, of oxalic acid used in each titre.

n(oxalic) = ________________

7 Titrate the permanganate solution into the acidified oxalic acid until the pink colour remains for 15 s. Repeat until 3 concordant results are obtained.

Burette reading	1st titration	2nd titration	3rd titration	4th titration	5th titration
Initial reading					
Final reading					
Titre					

8 Calculate the average of the concordant titres.

$V(MnO_4^-)$ = ________________

9 The ionic equation for this redox reaction is

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

What is the ratio of MnO_4^- to $C_2O_4^{2-}$?

$n(MnO_4^-)$ = ____ $n(C_2O_4^{2-})$

10 Calculate the amount, in moles, of permanganate reacting.

$n(MnO_4^-)$ = ________________

11 Calculate the concentration of the permanganate solution.

$c(MnO_4^-)$ = ________________

Inv 2.4 Standardising sodium thiosulfate solution

Potassium permanganate (standardised in Inv 2.2) can be used to standardise sodium thiosulfate solution by combining two redox reactions.
First, potassium permanganate oxidises iodide ions (I^-) to iodine (I_2):

$$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

then the iodine liberated is titrated against the thiosulfate solution:

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

The endpoint is found by adding a little starch solution when the iodine has faded to pale yellow. Starch is blue-black in the presence of iodine, but turns colourless when all the iodine has reacted.

1 What is the exact concentration of the potassium permanganate solution you are using? $c(MnO_4^-)$ = ________________

2 Pipette 20.0 mL samples of standard potassium permanganate solution into three conical flasks. $V(MnO_4^-)$ = ________________

3 Calculate the amount, in moles, of permanganate used. $n(MnO_4^-)$ = ________________

4 To each flask, add about 20 mL of dilute sulfuric acid solution and about 10 mL of 10% potassium iodide solution.

5 Rinse and fill a burette with the thiosulfate solution. Slowly titrate in the thiosulfate solution to each flask, adding a few drops of starch solution when the brown colour has faded to yellow. Repeat until three concordant results are obtained.

Burette reading	1st titration	2nd titration	3rd titration	4th titration	5th titration
Initial reading					
Final reading					
Titre					

6 Calculate the average of concordant titres. $V(S_2O_3^{2-})$ = ________________

7 From the two equations above, what is the relationship between $n(S_2O_3^{2-})$ and $n(MnO_4^-)$? $n(S_2O_3^{2-})$ = __$n(MnO_4^-)$

8 Calculate the amount, in moles, of thiosulfate present. $n(S_2O_3^{2-})$ = ________________

9 Calculate the concentration of the thiosulfate solution. $c(S_2O_3^{2-})$ = ________________

Inv 2.5 Standardising sodium thiosulfate using potassium iodate

Thiosulfate can be standardised by titrating against iodine solution. However, iodine is not easy to prepare as a primary standard because it sublimes as it is being weighed out.
To avoid this problem, we make the iodine during the reaction as follows:
A standard solution of iodate ions is reacted with excess iodide in acid conditions:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3H_2O + 3I_2$$

The liberated iodine is then titrated against the unknown thiosulfate solution.

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

1 Weigh out accurately about 0.71 g of dry analytical reagent grade potassium iodate, KIO_3. m(iodate) = ________________

2 Dissolve it in water in a 200 mL volumetric flask; shake well and make up to the mark. Again shake the solution thoroughly. Calculate the exact concentration of this solution. $c(IO_3^-)$ = ________________

3 Pipette 20 mL of the solution into a clean conical flask and add about 1.5 g of potassium iodide (an excess). Shake to dissolve then add 15 mL dilute H_2SO_4. $V(IO_3^-)$ = ________________

4 Calculate the amount, in moles, of iodate used. $n(IO_3^-)$ = ________________

5 Rinse and fill a burette with the thiosulfate solution. Slowly titrate the liberated iodine against the thiosulfate solution, adding a few drops of starch solution when the brown colour has faded to yellow. Repeat until three concordant results are obtained.

Burette reading	1st titration	2nd titration	3rd titration	4th titration	5th titration
Initial reading					
Final reading					
Titre					

6 Calculate the average of concordant titres. $V(S_2O_3^{2-})$ = ________________

7 From the two equations above, what is the relationship between n($S_2O_3^{2-}$) and n(IO_3^-)? $n(S_2O_3^{2-})$ = __$n(IO_3^-)$

8 Calculate the amount, in moles, of thiosulfate present. $n(S_2O_3^{2-})$ = ________________

9 Calculate the concentration of the thiosulfate solution. $c(S_2O_3^{2-})$ = ________________

Inv 2.6 Analysis of copper

The concentration of a Cu^{2+} solution can be found by reducing the Cu^{2+} to Cu^{+} with iodide, then titrating the iodine formed with thiosulfate:

$$2Cu^{2+} + 4I^{-} \longrightarrow 2CuI(s) + I_2$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^{-} + S_4O_6^{2-}$$

1 Pipette 20.0 mL samples of the Cu^{2+} solution you have been given into separate conical flasks. Use a measuring cylinder to add 10 mL of 10% potassium iodide solution to each flask.

2 Rinse and fill the burette with sodium thiosulfate solution. $c(S_2O_3^{2-})$ = ________________

3 Titrate thiosulfate into the flask until the colour changes to a pale yellow colour. (It will be cloudy due to the formation of the white CuI precipitate.) Then add starch solution and continue to add thiosulfate until the blue colour is gone. (The blue colour will return on standing.) Repeat until concordant results are obtained.

Burette reading	1st titration	2nd titration	3rd titration	4th titration	5th titration
Initial reading					
Final reading					
Titre					

4 Average the concordant titres. $V(S_2O_3^{2-})$ = ________________

5 Calculate the amount, in moles, of thiosulfate present. $n(S_2O_3^{2-})$ = ________________

6 Complete the expression:

$$\frac{n(Cu^{2+})}{n(I_2)} \times \frac{n(I_2)}{n(S_2O_3^{2-})} = \_\_\_\_\_\_ \times \_\_\_\_\_\_$$

$n(Cu^{2+})$ = ___ $\times\, n(S_2O_3^{2-})$

7 Calculate the amount, in moles, of Cu^{2+} in solution. $n(Cu^{2+})$ = ________________

8 Calculate the concentration of Cu^{2+}. $c(Cu^{2+})$ = ________________

9 Assume that this solution was prepared by dissolving brass in concentrated nitric acid and making it up to 1000.0 mL with water.
What mass of Cu was in the brass? (M(Cu) = 63.5 g mol^{-1}) $m(Cu^{2+})$ = ________________

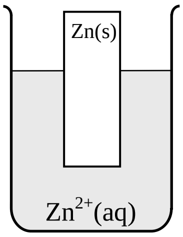
10 Calculate the percentage of copper in the brass if it had a mass of 5.70 g. %Cu = ________________

Inv 3.1 Electrochemical cells 1

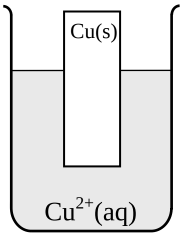
All redox reactions involve electron transfer. This can happen even when the two reactants are physically separated, say, electrons transferring from one to another through a wire. This is what happens in an electrochemical cell.

1 Clean the surface of the metal strips you use.

2 Prepare a Zn^{2+}/Zn half cell by placing a strip of zinc into a beaker of zinc sulfate solution so that the solution covers three-quarters of the zinc strip.



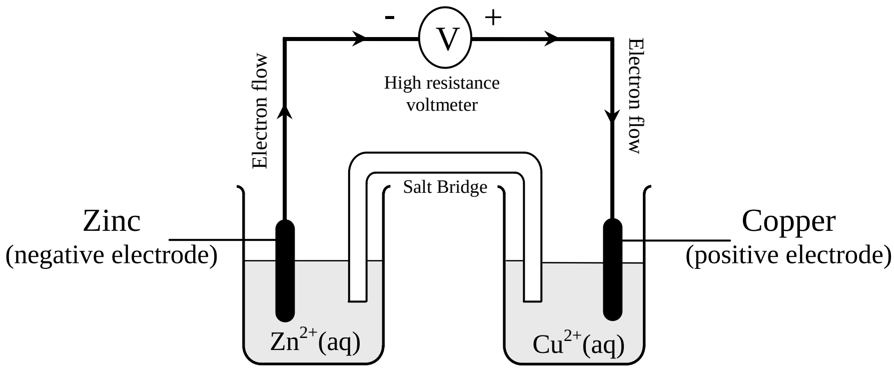
3 Prepare a Cu^{2+}/Cu half cell in a similar manner using a copper strip and copper sulfate.



4 Connect a wire from the zinc electrode (strip) to the negative terminal of a multimeter set on voltage. Record the reading on the meter.________________

5 Connect a wire from the copper electrode (strip) to the positive terminal of the meter. Record the reading on the meter.________________

6 Place the half cells next to each other and connect them via a salt bridge. Record the reading on the meter.________________



7 Which way do electrons flow in the circuit? ________________

8 What is the cathode? ________________

9 What is the anode? ________________

10 Write the half equation for the reaction occurring in the Zn^{2+}/Zn half cell.

____

11 Is this oxidation or reduction? ________________

12 Write the half equation for the reaction occurring in the Cu^{2+}/Cu half cell.

____

13 Is this oxidation or reduction? ________________

14 Combine your half equations from **11** and **13** above to give the overall cell reaction.

____

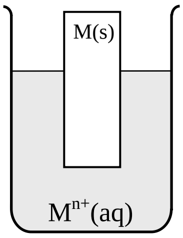
15 What is the EMF of the above cell? ________________

Inv 3.2 Electrochemical cells 2

We can use the electrode potentials of redox systems to determine the relative strengths of oxidants and reductants. Your teacher will give you a range of oxidants and reductants from which you can prepare different half-cells. Electrochemical cells are made by combining two half-cells.

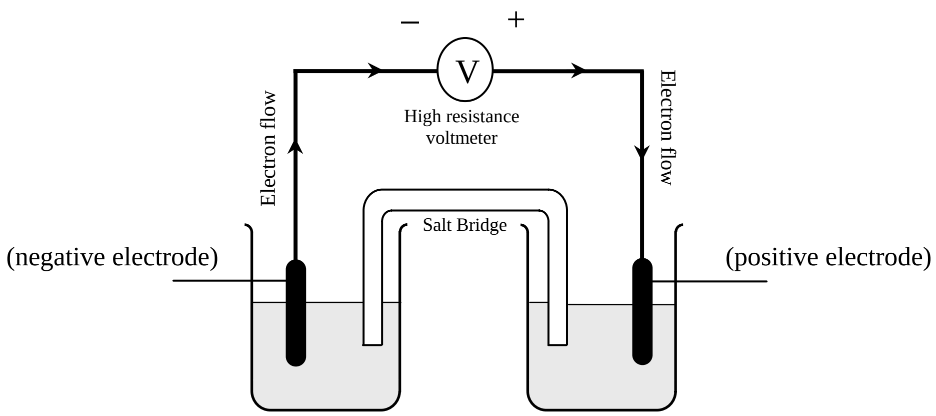
1 Clean the surface of the metal strips you use.

2 Prepare M^{n+}/M half cells by placing a strip of metal into a beaker of the metal sulfate solution so that the solution covers three-quarters of the metal strip.



3 Prepare a Fe^{3+}/Fe^{2+} half cell using a carbon electrode in equal volumes of iron(II) sulfate and iron(III) nitrate and an I_2/I^- half cell using a carbon electrode in equal volumes of iodine solution and potassium iodide solution.

4 Prepare cells by combining two half cells, connecting the two electrodes with a voltmeter and the solutions with a salt bridge.



5 For each cell measure the voltage (EMF) and record it in the table shown along with the direction of electron flow and the oxidant and reductant for each cell.

Cell	Cell voltage		Electron flow			
	measured	calculate	from	to	Oxidant	Reductant

6 Calculate the cell voltages from E° values from data tables and compare with the measured values. Suggest any reasons for differences.

7 Arrange the oxidants in order of increasing ability to be reduced.

Inv 3.3 The lead-acid cell

One of the most useful practical electrochemical cells is the lead-acid cell used in car batteries. It is so useful because its electrode reactions can be reversed by passing an electric current back through the cell.

1 Clean the surface of two lead plates and place them in a 250 mL beaker. Add about 150 mL of about 2 mol L^{-1} of sulfuric acid.

2 Connect a voltmeter between the plates and record the voltage.

Voltage reading: _______________

3 Remove the voltmeter and replace it with a DC power supply. Adjust the supply to about 3 V, switch on and wait and observe for about 10 minutes. Note any changes that take place.

Observations:____

____

4 Replace the DC supply with the voltmeter and measure the voltage. (Make sure of the polarity.)

Voltage reading: _______________

5 Replace the voltmeter with a 1.5 V bulb and observe.

Observation:____

During the charging of the cell the lead, Pb(s), of the cathode is converted to lead (IV) oxide, PbO_2(s).

6 Write equations for the reactions that take place at each electrode during discharge.

Anode: ____

Cathode: ____

Inv 4.1 Heat and phase changes

When a substance changes state from one phase to another the temperature remains the same, but heat is still absorbed or given out in the process.

1 Weigh a clean, dry 250 mL beaker. m_1 = ____________________

2 Add about 200 mL of hot water from the tap (about 55 °C) and reweigh. m_2 = ____________________

Initial temperature is: T_1 = ____________________

The mass of the water added is: $m_{Water} = m_2 - m_1$

= ____________________

3 Add about 80 g of ice, stir and note the temperature when all of the ice has melted. T_2 = ____________________

4 Reweigh the beaker and contents to find the mass of ice that was added. m_3 = ____________________

The mass of the ice added is: $m_{Ice} = m_3 - m_2$

= ____________________

The change in temperature of the water is: $\Delta T_1 = T_2 - T_1$

= ____________________

The change in temperature of the ice is: $\Delta T_2 = T_2 - 0°C$

= ____________________

Calculations: The heat lost by the water cooling from its original temperature to the final temperature is equal to the heat gained by the ice as it melts, plus that gained by the melted ice raising from 0°C to the final temperature.

$$m_{Water} \times \text{specific heat} \times \Delta T_1 = m_{Ice} \times \text{latent heat} + m_{Ice} \times \text{specific heat} \times \Delta T_2$$

Heat lost by water: ________________ × 4.2 × ________________ = __________ J (1)

Heat gained by melted ice warming: __________ × 4.2 × _________ = __________ J (2)

The difference is the energy required to melt the ice: (1) – (2) = ____________________ J

This is the heat needed to melt m_{Ice} i.e. __________ g of ice.

5 Calculate the amount of heat needed to melt 1.00 mol of ice.

6 How do your results compare with those of other groups and latent heat from data tables?

____

____

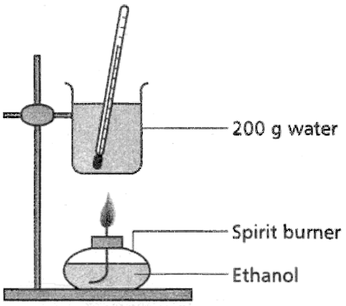
Inv 4.2 Heats of combustion

The heat of combustion of a substance is the quantity of heat liberated when one mole of that substance is burnt completely in air (oxygen). This is of value in determining such things as the relative merits of various fuels and in calculating other quantities such as heats of formation.

An experiment to compare the energy output of different alcohols can be performed by using the apparatus shown.

The alcohols to be tested are burnt in a small spirit burner.

With such simple equipment it is not possible to absorb all the heat produced, only a fraction of it. Hence, everything must be kept the same, except the fuel, to ensure this fraction is the same for each of the alcohols tested.



1 Accurately measure 200 g of tap water into the 250 mL beaker (or conical flask). Clamp in position and record the initial temperature of the water to the nearest 0.2 °C in Table 1.

2 Place approximately 10 mL of methanol in the spirit burner, replace the top, weigh the burner and contents, and record this mass in Table 1.

3 Place the burner under the centre of the flask, shield it from drafts and light the burner. Stir the water with the thermometer and when the temperature has risen 10 °C, extinguish the burner.

4 Continue stirring for 10 seconds, then record the temperature in Table 1.

5 Re-weigh the burner and record its mass in Table 1.

6 Empty the beaker (or flask) and rinse it with tap water to cool it to room temperature. Discard the remaining methanol, and sponge the methanol from the lower part of the wick with filter paper. (Do not disturb the wick protruding through the top.) Now repeat steps **1– 6** for each of the other alcohols.

Table 1

Alcohol	**Temperature of water (°C)**			**Energy absorbed (kJ)**	**Mass of burner and alcohol (g)**		
	initial	**final**	**change**		**initial**	**final**	**loss**
Methanol							
Ethanol							
Propan-1-ol							
Butan-1-ol							

7 Calculate the change in temperature of the water, and hence calculate the energy absorbed by the water in kJ, assuming that 1.0 mL of water requires 4.18 J to raise its temperature by 1 °C.

8 Calculate the mass of each alcohol burnt and record this in column 8 of Table 1, then calculate the amount, in moles, of each alcohol burnt and record this in column 4 of Table 2.

9 Use your values for column 5 of Table 1 and column 4 of Table 2 to calculate the apparent $\Delta_c H$ for each alcohol (apparent, because we know only a fraction of the energy produced has been absorbed by the water).

Table 2

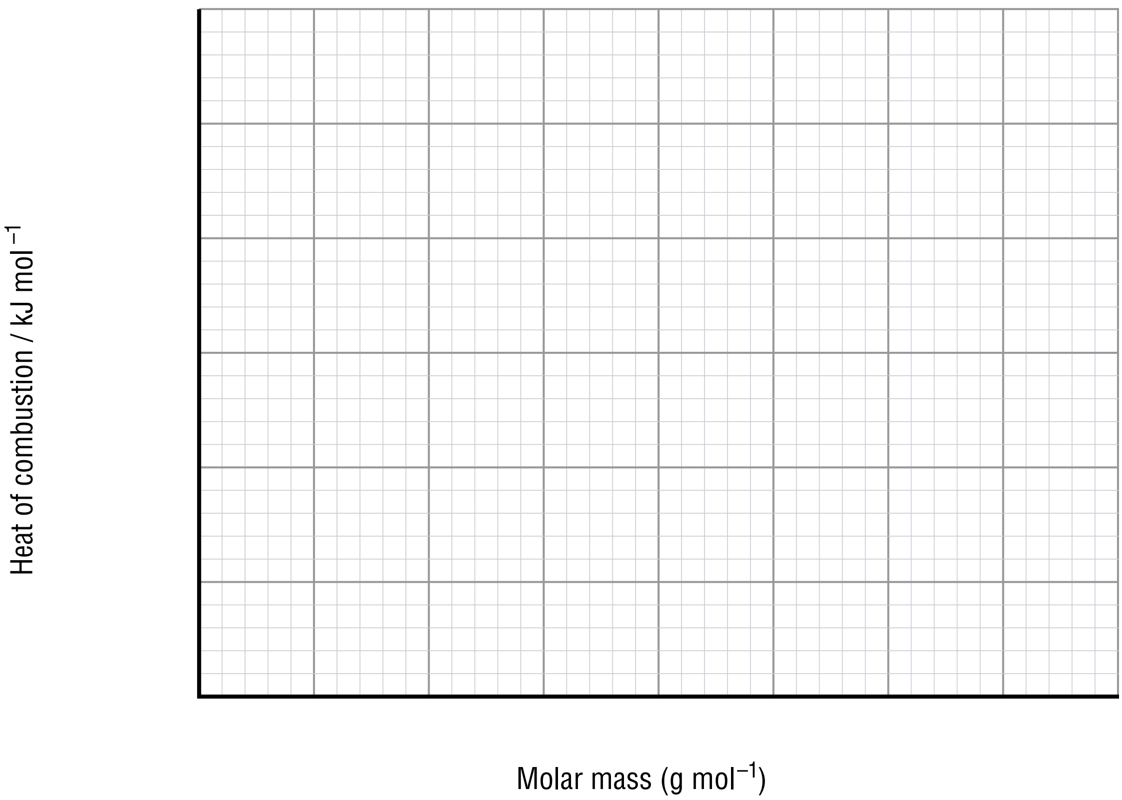
Alcohol	**Molecular formula**	**Molar mass (g mol⁻¹)**	**Amount burnt (mol)**	**Apparent Δ_cH (kJ mol⁻¹)**	**Adjusted Δ_cH (kJ mol⁻¹)**	**Book Δ_cH (kJ mol⁻¹)**
Methanol		32				715
Ethanol	C_2H_5OH	46			1372	1372
Propan-1-ol		60				2012
Butan-1-ol		74				2670

10 The book value for Δ_cH(ethanol) is 1372 kJ mol^{-1}. Use your apparent Δ_cH(ethanol) to calculate the fraction of energy produced that was absorbed by the water.

$$\text{Fraction absorbed} = \frac{\Delta_c H(\text{book})}{\Delta_c H(\text{apparent})} = \frac{\qquad}{} = $$

11 Multiply your apparent Δ_cH by the fraction calculated in **10** to find the adjusted Δ_cH for each of the other alcohols.

12 Plot a graph of molar mass versus heat of combustion for these alcohols, using your adjusted values. Draw the line of best.



13 Comment on the shape of the graph and the comparison between your values and the book values.

Inv 4.3 Finding the enthalpy change for redox reactions

The heat of reaction when one metal displaces another from a solution of its ions can be measured and compared to the $E°$ value for the same cell reaction.

Note: wash your hands after handling metal powders – they can cause eye damage.

1 Use a measuring cylinder to carefully measure out 25 mL of 0.4 mol L^{-1} copper(II) sulfate solution into a clean polystyrene cup jacketed inside another polystyrene cup.

2 Measure the starting temperature to 0.5 °C t_s =________________

3 Add 1 g (an excess) of zinc powder, and stir thoroughly with a glass rod.

4 Record the peak temperature. t_f =________________

5 Determine the rise in temperature Δt =________________

6 The equation for the reaction can be written as:

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

7 Calculate the number of moles of Cu^{2+} used in this reaction. $n(Cu)$ = ________________

8 Use the following formula to determine the amount of heat released in the reaction:

Heat = mass × specific heat × temperature change

(where specific heat capacity of water = 4.2 J g^{-1} °C^{-1} and 1 mL water = 1 g)

heat = ________________

9 Calculate the heat released, ΔH, per mole of Cu ΔH = ________________

10 Repeat the above experiment using (a) iron powder and (b) magnesium powder or turnings. (For Mg, 0.5 g should be sufficient.)

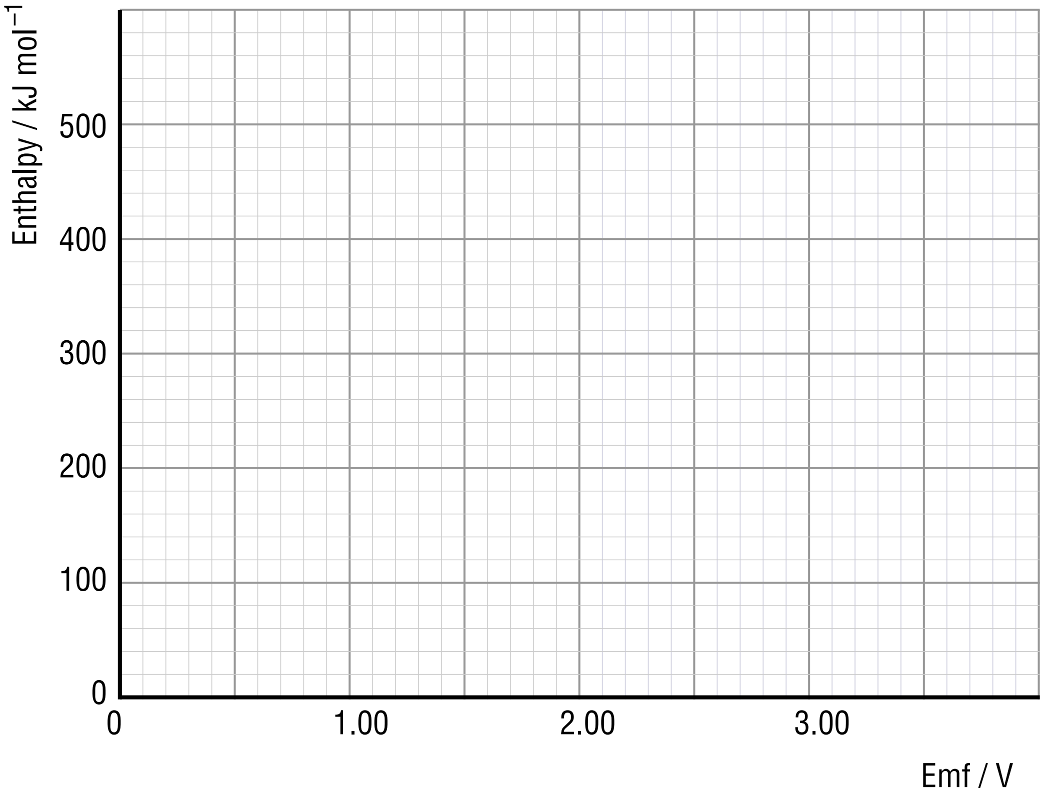
Cell reaction	***E*°(LHE)**	***E*°(RHE)**	$E°_{cell}$	ΔH
$Zn(s) / Zn^{2+}(aq) // Cu^{2+}(aq) / Cu(s)$	–0.76 V	+0.34 V		
$Fe(s) / Fe^{2+}(aq) // Cu^{2+}(aq) / Cu(s)$	–0.47 V	+0.34 V		
$Mg(s) / Mg^{2+}(aq) // Cu^{2+}(aq) / Cu(s)$	–2.36 V	+0.34 V		

11 Calculate the $E°_{cell}$ for each reaction using the formula

$$E°_{cell} = E°_{RHE} - E°_{LHE}$$

12 Plot the ΔH values against the $E°_{cell}$ for the three cell reactions. The plot should go through the origin.

Enthalpy (ΔH) *vs* Cell emf ($E°$)



13 Is there a relationship between the energy released as heat, and energy released as electricity?

____

____

14 What would happen if the metals were partly oxidised before the reactions? Explain.

____

____

____

____

Inv 4.4 Hess's law: the law of heat summation

The heat of a reaction is determined only by the difference in enthalpy between the reactants and products and is independent of the path of the reaction and the manner by which it is brought about. This is illustrated by the formation of sodium chloride by two different reaction paths.

A The two-stage path:

1. The reaction between solid sodium hydroxide and water

$$NaOH(s) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) \quad \Delta_r H_1$$

2. The reaction between sodium hydroxide solution and dilute hydrochloric acid

$$Na^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) \longrightarrow H_2O(l) + Na^+(aq) + Cl^-(aq) \quad \Delta_r H_2$$

B The single-stage path:

The reaction between solid sodium hydroxide and dilute hydrochloric acid

$$NaOH(s) + H^+(aq) + Cl^-(aq) \longrightarrow H_2O(l) + Na^+(aq) + Cl^-(aq) \quad \Delta_r H_3$$

If Hess's law is correct then, within experimental error,

$$\Delta_r H_1 + \Delta_r H_2 = \Delta_r H_3$$

$\Delta_r H_1$ heat of reaction for dissolution of sodium hydroxide

1 Place one styrofoam cup inside another one to form a calorimeter.

2 Place 100 mL of water in the styrofoam cup and note the temperature. T_1 =________________

3 Weigh out rapidly 0.05 mol (2 g) of sodium hydroxide pellets (corrosive) to the nearest 0.1 g (about 20 pellets). m =________________

4 Calculate the amount of sodium hydroxide used. n(NaOH) = ________________

5 Add the solid sodium hydroxide to the water, stir gently with a thermometer and record the highest temperature. T_2 =________________

6 Determine the rise in temperature. ΔT =________________

7 Heat energy (ΔH_1) = mass of water × temperature rise × 4.2 ΔH_1 =________________

8 Calculate the heat energy in joules for 1 mole of NaOH $\Delta_r H_1$ =________________

$\Delta_r H_2$ heat of reaction of sodium hydroxide solution with hydrochloric acid

9 Rinse the styrofoam cup and add 50 mL of 1 mol L^{-1} NaOH(aq) (0.05 mol). Measure out 50 mL of 1 mol L^{-1} HCl(aq) (0.05 mol) into a measuring cylinder and record both temperatures. The initial temperature is the mean of the two. T_1 =________________

10 Add the acid to the hydroxide solution, stir gently with a thermometer and record the highest temperature. T_2 =________________

11 Determine the rise in temperature. ΔT =________________

12 Calculate the amount of sodium hydroxide used in the reaction. n(NaOH) = ________________

13 Calculate the heat energy released in the reaction:
Heat energy (ΔH_2) = mass of solution × temperature rise × 4.2 ΔH_2 =________________

14 Calculate the heat energy in joules for 1 mole of reactants $\Delta_r H_2$ =________________

$\Delta_r H_3$ heat of reaction between solid sodium hydroxide and hydrochloric acid

11 Rinse the styrofoam cup and add 100 mL of 0.5 mol L^{-1} HCl(aq) (0.05 mol) and record initial temperature. T_1 =________________

12 Weigh out rapidly 0.05 mol (2 g) of sodium hydroxide pellets (corrosive) to the nearest 0.1 g (about 20 pellets) as in **3**. m =________________

13 Add the sodium hydroxide to the styrofoam cup and stir gently with a thermometer and record the highest temperature. T_2 =________________

14 Determine the rise in temperature. ΔT =________________

15 Calculate the amount of sodium hydroxide used in the reaction. n(NaOH) = ________________

16 Calculate the heat energy released in the reaction:
Heat energy (ΔH_3) = mass of solution × temperature rise × 4.2 ΔH_3 =________________

17 Calculate the heat energy in joules for 1 mole of reactants $\Delta_r H_3$ =________________

Comparing $\Delta_r H_1$ + $\Delta_r H_2$ to $\Delta_r H_3$

18 How does the value of $\Delta_r H_1$ + $\Delta_r H_2$ compare to the value of $\Delta_r H_3$, considering possible sources of experimental error and their magnitude? Draw a conclusion.

$\Delta_r H_1$ + $\Delta_r H_2$ =

$\Delta_r H_3$ =

____

____

____

Inv 5.1 Transition metal chemistry 1: Manganese

Transition metals can have a number of different oxidation states and their compounds and complexes are almost always coloured.

1 Manganese (II) sulfate and potassium permanganate are common laboratory reagents. What are their colours and what are the oxidation states of manganese in each compound?

____

____

2 Add a little dilute NaOH(aq) to about 2 mL of $MnSO_4$(aq) in a test tube. What do you observe?

____

Filter and allow the precipitate to stand in air. What do you observe?

____

3 Write an ionic equation for the reaction that occurs in **2**.

____

4 MnO(OH) is the product formed in 3. Write an ion-electron half-equation for its formation.

____

5 What is the oxidation state for manganese in MnO(OH)? ______________________

6 Add a few drops of $KMnO_4$(aq) to $MnSO_4$(aq) in a test tube. What do you observe?

____

7 The product formed in **6** is MnO_2. Write an ion-electron half-equation for its formation from MnO_4^-.

____

8 What is the oxidation state for manganese in MnO_2?______________________

9 Add 3 drops of $KMnO_4$(aq) to each of two test tubes containing a few mL of 30% NaOH(aq). Then add 1 drop of 1 mol L^{-1} $NaHSO_3$(aq) to one test tube and 5 drops to the other. Carefully shake the test tubes and leave to stand for a couple of minutes. What do you observe?

____

____

10 MnO_4^{3-}(aq) is blue and MnO_4^{2-}(aq) is green. Write ion-electron half-equations for their formation in **9**.

____

____

11 What are the oxidaton states for the two manganese species formed in **9**?

____

Inv 5.2 Transition metal chemistry 2: Vanadium

Transition metals can have a number of different oxidation states and their compounds and complexes are almost always coloured. Vanadium has the following: violet [V(II)], V^{2+}; green [V(III)], V^{3+}; blue [V(VI)], VO^{2+}; yellow/orange [V(V)], VO_2^{+}.

1 Put half a spatula of solid ammonium vanadate, NH_4VO_3, (TOXIC) into a conical flask, then add about 20 mL of dilute sulfuric acid (2 mol L^{-1}). Swirl the liquid to dissolve the solid.

Colour of the solution:______________ Oxidation state of vanadium:______________

2 Decant off the liquid from 1 into a clean conical flask, add 20 mL of sulfuric acid (2 mol L^{-1}) and a spatula of zinc powder. Place some cotton wool loosely in the top of the flask and swirl the flask gently. Note the colour changes that occur in the mixture.

Colour changes:____

3 Leave the flask with the cotton wool plug until the final colour is violet.

Colour: violet Oxidation state of vanadium:______________

4 Pour 10 mL of this solution into each of two 100 mL beakers. Leave one beaker exposed to the air, and the other other add about 10 mL dilute nitric acid (1–2 mol L^{-1}) and swirl the mixture. Note the colour changes in each beaker.

a In air — colour change_________________________ Oxidation state of vanadium ______

b In HNO_3 — colour change _____________________ Oxidation state of vanadium ______

5 **a** Write ion-electron half-equation for the conversion of VO_2^{+} to VO^{2+}.

____

b What would you see during this reaction?

____

6 **a** Write ion-electron half-equation for the conversion of V^{3+} to VO^{2+}.

____

b What would you see during this reaction?

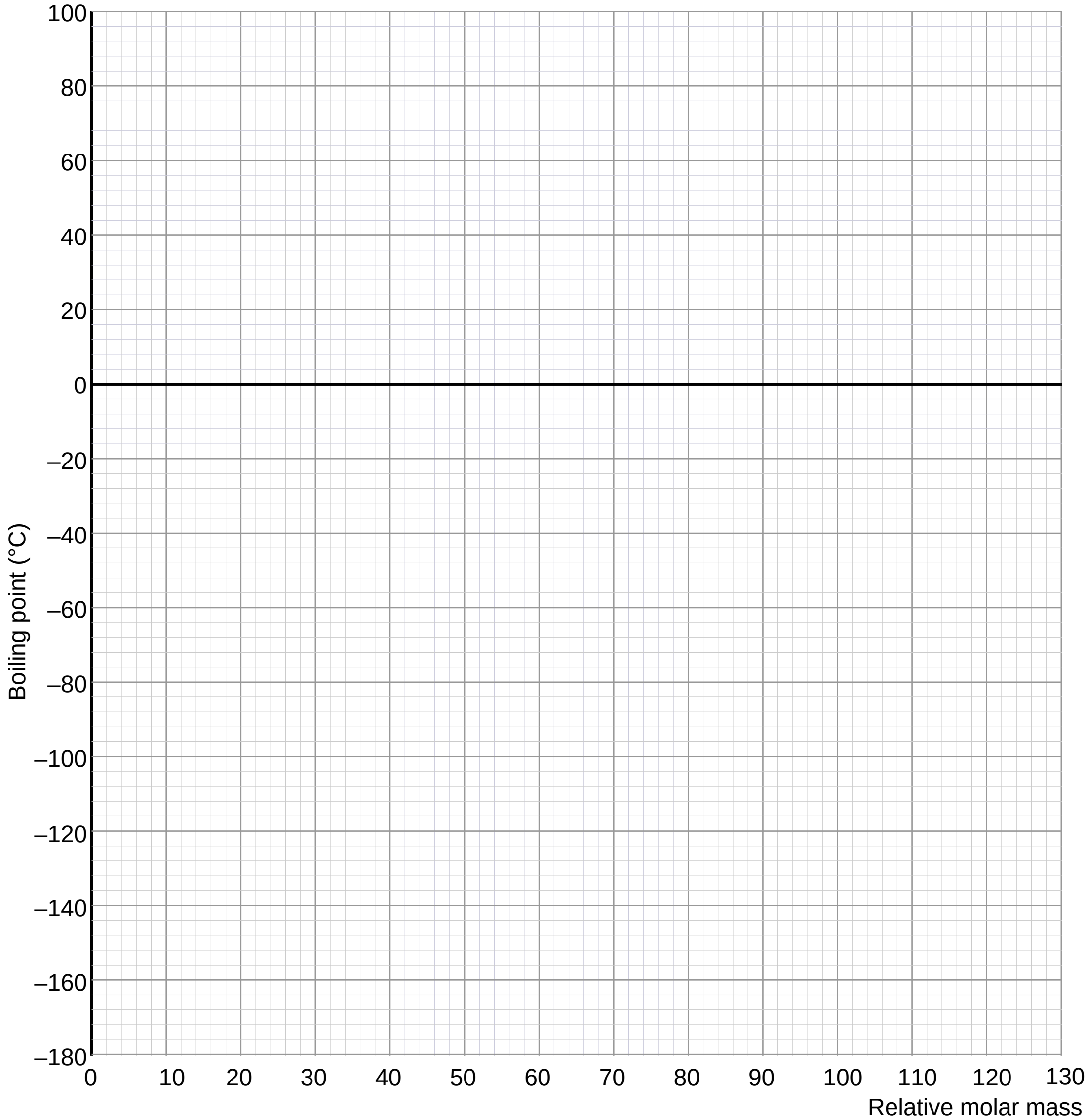
____

Inv 6.1 Hydrogen bonding

Some compounds do not follow the same trend in properties, such as boiling point, as do other members of their group. This is due to a very strong dipole-dipole force called hydrogen bonding.

Group 17	M_r	BP °C	Group 16	M_r	BP °C	Group 15	M_r	BP °C	Group 14	M_r	BP °C
HF	20		H_2O	18		NH_3	17		CH_4	16	
HCl	36.5	–85	H_2S	34	–83	PH_3	34	–88	SiH_4	32	–112
HBr	81	–67	H_2Se	81	–66	AsH_3	78	–57	GeH_4	76.6	–88
HI	128	–35	H_2Te	129.6	–49	SbH_3	125	–17	SnH_4	122.7	–52

1 On the grid following draw graphs of the boiling points of the 4 groups against their relative molar masses, using just the data above. Use a different colour for each group.



2 What trend do you observe?

3 Explain this trend.

4 Using the trends and the graphs you have drawn, what do you think the missing boiling points in the table should be? Write your estimations in the table in pencil.

5 The actual boiling points are: HF (19 °C), H_2O (100 °C), NH_3 (–33 °C), CH_4 (–162 °C). Add these points to the graphs you have drawn. What do you observe?

When hydrogen is bonded to a very electronegative element – fluorine, oxygen or nitrogen – the bond formed is highly polar; the hydrogen is almost a bare proton. Consequently, the hydrogen of one molecule exerts a strong electrostatic attraction for the very electronegative atom in a neighbouring molecule. This inter-molecular bond is called a "hydrogen bond" and the boiling point is thus higher than would be expected.

Inv 7.1 Structures of organic molecules

We use molecular models to help us understand the structures, geometries and properties of molecules. In most model sets black represents carbon, white is used for hydrogen, red for oxygen and green for chlorine.

1 Build a model of CH_2Cl_2.

a What is this compound called?______________________________

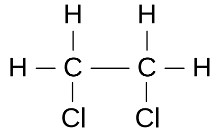
b Is this compound polar? Explain your answer.

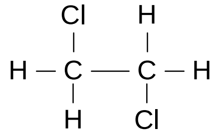
2 Rebuild your molecule putting the chlorines in different places.

Is this the same compound or different?______________________________

3 Make a model of ethane, CH_3CH_3. Firmly hold one of the carbon atoms. Now try to rotate the other CH_3 group about the C–C bond. Is rotation possible? ______________________________

4 Build each of the molecules shown on the right.





a Are they identical or are they isomers?

____

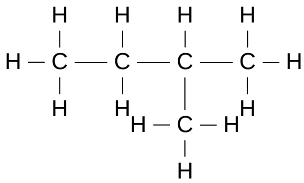
Explain why. ______________________________

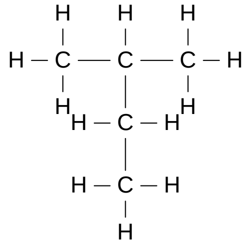
b Is the above compound polar or non-polar?________________

5 Build each of these molecules in turn:

Are the two compounds identical?

____





6 Build a model of ethene, CH_2CH_2.

a Is this a planar molecule? ________________

b Is it possible to rotate one end of the molecule as with ethane?________________

c What is the effect of double bonds on rotation?________________

7 Replace two hydrogens with chlorines.

How many *isomeric* molecules can you make of $C_2H_2Cl_2$?________________

8 Two of these isomers are cis -1,2-dichloroethene and trans-1,2-dichloroethene. Build both models.

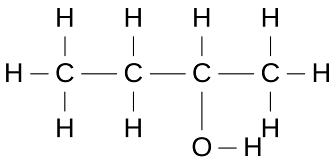
a Why are these two compounds not identical?________________

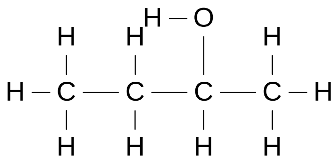
b Which isomer is polar: *cis*- or *trans*-1,2-dichloroethene?________________

9 The *cis* and *trans* forms are called geometrical isomers of each other. Build a third isomeric $C_2H_2Cl_2$ which is related to the above two by structural isomerism.

What is its name?________________

10 Build a model of butan-2-ol, $CH_3CH_2CHOHCH_3$. Compare your model with those made by other students. You should find that there are two distinct groups.





These two different molecules are OPTICAL ISOMERS. What is it about these models that shows that there are two different compounds present?

____

____

____

Inv 8.1 Oxidation of alcohols

Primary (1°), secondary (2°) and tertiary (3°) alcohols react differently with oxidising agents. These oxidation reactions can be used to distinguish between the different types of alcohols.

1 Mix 1 mL of ethanol with 5 drops of potassium dichromate solution and 10 drops of dilute sulphuric acid in a test tube. Place the test tube in a beaker of hot water to warm the mixture. What do you observe? Note the smell.

____

____

2 Repeat **1** using 1 mL of propan-2-ol instead of ethanol. What do you observe? Note the smell.

____

____

3 Repeat **1** this time using 2-methylpropan-2-ol (tertiary butyl alcohol). What do you observe?

____

4 Repeat **1** to **3** using potassium permanganate solution instead of potassium dichromate solution. What do you observe?

i ______________________________

____

ii ______________________________

____

iii ______________________________

A **primary alcohol** is oxidised to an aldehyde (alkanal) and eventually to a carboxylic acid. A **secondary alcohol** is oxidised to the corresponding ketone (alkanone). **Tertiary alcohols** do not undergo oxidation under the above conditions.

5 Write equations giving the organic reactants and products for the reactions that have taken place.

1 : ______________________________

2 : ______________________________

6 Give the name and colour of the oxidising species in each case and the name and colour of the species to which they were reduced.

____

____

____

____

Inv 8.2 Reactions of alcohols with Lucas reagent

A test that can be used to distinguish between the three types of alcohol is the Lucas test.

1 Put about 1 mL of ethanol in a dry test tube. Add 10 drops of Lucas reagent (a mixture of concentrated hydrochloric acid (corrosive) and anhydrous zinc chloride) and shake to mix well. Stand the test tube in a test tube rack. What do you observe?

2 Repeat **1** using 1 mL of propan-2-ol instead of ethanol. What do you observe?

3 Repeat **1**, this time using 2-methylpropan-2-ol (tertiary butyl alcohol). What do you observe?

Leave any unreacted test tubes in the rack until the end of the lesson.

4 List the alcohols in order of their rate of reaction with the Lucas' reagent. Put the fastest first.

5 Put the alcohols in order of increasing strength of the R- O bond.

6 Write equations for reaction of each alcohol with concentrated hydrochloric acid (the zinc chloride is a catalyst). Use structural formulae and in each case name both products and reactants.

7 Using the above information, suggest what might have caused the cloudiness in the reactions.

Inv 8.3 Preparation of 2-chloro-2-methylpropane

Haloalkanes can be prepared by nucleophilic substitution of the corresponding alcohol using a suitable halogenating agent

Note: your teacher will show you how to use the equipment safely.

1 Mix 10 mL of methylpropan-2-ol with 20 mL of concentrated hydrochloric acid (corrosive) in a separating funnel. What do you observe?

____

2 Shake for 10 minutes and allow the mixture to settle and leave overnight. What do you observe?

____

3 Run off the acid layer into a beaker and discard it. Slowly add 10 mL of sodium bicarbonate solution. What was the purpose of this? What was the gas given off?

____

____

4 Observe the mixture. What do you notice?

____

5 Shake gently and release the pressure build-up frequently. Discard the aqueous layer. Run the haloalkane into a test tube, add a spatula tip of anhydrous sodium sulfate. Stopper the tube and shake. What is the purpose of this process?

____

6 Use a data book to find the boiling point of 2-chloro-2-methylpropane. Boiling point: ______________

7 Record the mass of an empty receiving flask ready for distillation. Mass: ______________

8 Decant the sample into a clean distillation flask and distil it, collecting the fraction that distils within 2 °C of the expected boiling point. Weigh the flask and distillate. Mass: ______________

9 Complete this table with your experimental data.

	Volume	Density	Mass	Molar mass	Amount present
methylpropan-2-ol		0.78 g mL^{-1}		74.1 g mol^{-1}	
2-chloro 2-methylpropane				92.6 g mol^{-1}	

10 Write an equation for the overall reaction.

____

11 Calculate the expected yield of 2-chloro 2-methylpropane.

amount = ______________

12 Calculate the percentage yield of the experiment.

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{expected yield}} \times 100\%$$

% Yield: ______________

Inv 8.4 Hydrolysis of haloalkanes (alkyl halides)

Haloalkanes can readily be converted to alcohols by substitution and to alkenes by elimination.

1 Place 1 mL of ethanol into 3 separate test tubes and place in a beaker of water at about 60 °C.

2 Add 5 drops of 1-chlorobutane, 1-bromobutane and 1-iodobutane (or similar) into the separate test tubes followed by about 2 mL of silver nitrate solution. Shake the test tubes and leave in the 'water bath' and observe over several minutes. What do you observe?

1-chlorobutane: ______________________________

____

1-bromobutane: ______________________________

____

1-iodobutane: ______________________________

____

3 Using your observations, place the haloalkanes in order of decreasing reactivity.

____

4 Using the bond energies in the table below, suggest a possible explanation for the different rates of hydrolysis.

Bond	**Average bond energy kJ mol^{-1}**
C—Cl	339
C—Br	285
C—I	218

____

____

____

____

____

____

____

Inv 8.5 Properties of amines

Amines can be considered as derivatives of ammonia with one or more hydrogen atoms replaced by alkyl groups, and they have similar properties. Caution: Amines have strong, lingering smells. Take care not to spill the amines, especially on your school uniform.

1 Cautiously smell the amines and ammonia provided. Describe the smells and compare them.

____

____

2 Hold small pieces of damp red and blue litmus above the amines and the ammonia. Note the results.

____

____

3 Place a drop of each amine solution and ammonia on separate pieces of universal indicator paper. Estimate and record the pHs.

____

____

4 Write a general equation for the reaction of an amine with water to explain the pH values.

____

5 Prepare separate test tubes containing copper sulfate solution (about 0.5 mL). Add 3 drops of an amine solution or ammonia to each of the test tubes. Mix each solution and describe what you observe.

____

____

6 Now add an excess of each amine or ammonia to the appropriate test tube, mix the solutions vigorously, and again record your observations.

____

____

____

7 Write an equation for the reaction between ethylamine and Cu^{2+}(aq).

____

Inv 8.6 Reactions of aldehydes and ketones

Aldehydes are better reducing agents than ketones. This property can be used to distinguish between the two classes of compound.

1 **Tollens reagent:** To 1 mL of silver nitrate solution add 1 drop of sodium hydroxide solution to form a precipitate of silver oxide. Add dilute ammonium hydroxide solution, drop by drop, till the brown precipitate just disappears. Pour this solution into a clean test tube.

Add 3 drops of ethanal (acetaldehyde) and warm the test tube in a beaker of hot water. What do you observe?

______

Write the half-equation for the reduction reaction.

______

2 **Fehlings reagent:** To 1 ml of solution A (copper sulfate solution) add solution B (an alkaline solution of sodium potassium tartrate) until the blue precipitate just redissolves to give a deep blue solution. (Benedict's reagent can be used instead.)

Add 3 drops of ethanal (acetaldehyde) and boil the mixture for a few minutes. What do you observe?

______

Write two half-equations, and hence the overall ionic equation for the reaction in alkaline conditions. (The organic product will be a negative ion.)

______

______

______

3 To 5 drops of potassium dichromate solution (or potassium permanganate solution) add 10 drops of dilute sulphuric acid solution followed by 5 drops of ethanal. Warm carefully on a water bath. What do you observe?

______

Write two half-equations, and hence the overall ionic equation for the reaction.

______

______

______

4 Repeat the above reactions with using propanone (acetone) in place of ethanal. What do you observe?

______

5 What do the above tests show?

______

Inv 9.1 Reactions of acyl chlorides (teacher demo)

Acyl chlorides (acid chlorides) are derivatives of carboxylic acids (alkanoic acids). They are very reactive, undergoing exothermic reactions with water, alcohols and ammonia to give the corresponding carboxylic acids, esters and amides. (These reactions should be done in a fume cupboard or under a fume hood.) All acyl chlorides are corrosive.

1 In a dry test tube place 5 drops of ethanoyl chloride (acetyl chloride). Carefully add 5 drops of water. What do you observe? Test any gas given off with damp litmus.

____

____

2 Add a few drops of silver nitrate solution. What do you observe? What does this indicate?

____

____

3 Write an equation for the reaction between ethanoyl chloride and water

____

4 In a dry test tube place 5 drops of ethanoyl chloride. Carefully add 5 drops of ethanol. Shake carefully for about a minute and then carefully add a few drops of water. Carefully smell the product. Describe the smell.

____

5 Write an equation for the reaction between ethanoyl chloride and ethanol. Name the products.

____

____

6 (IN A FUME CUPBOARD) Put 10 mL of 0.880 ammonia in a 100 mL beaker, then carefully add a few drops of ethanoyl chloride. What do you observe?

____

7 What are the fumes that are given off? ____________________________________

8 Write a balanced equation for the reaction between ethanoyl chloride and ammonia and name the products.

____

____

Inv 9.2 Amide hydrolysis

Amides can be hydrolysed either by acid or alkali.

1 In a test tube place a few crystals of ethanamide. Add 3 to 4 mL of dilute sodium hydroxide solution. Warm gently and then carefully smell the gas produced. Observation:

____

2 Test the gas with damp red and blue litmus. Observation:

____

3 Write an equation for the reaction.

____

4 Cool and keep the mixture.

5 Now add 4 mL, a slight excess, of dilute sulfuric acid and warm the test tube and smell carefully. Observation:

____

6 What gas is formed? ______________________________

7 What effect does it have on litmus? ______________________________

8 Write an equation for the reaction.

____

9 Take a fresh sample of ethanamide. Add 2 mL of dilute sulfuric acid. Warm gently and then carefully smell the gas produced. Observation:

____

10 Test the gas with damp red and blue litmus. Observation:

____

11 Write an equation for the reaction.

____

12 Cool and keep the mixture.

13 Now add 4 mL of sodium hydroxide solution. Warm the test tube and smell carefully. Observation:

____

14 What gas is formed? ______________________________

15 What effect does it have on litmus? ______________________________

16 Write an equation for the reaction.

____

Inv 9.3 Identification of organic unknowns

Classes of organic compounds have characteristic physical and chemical properties due to the functional group(s) they contain. Unknown compounds may be identified using these characteristics.

1 Give the physical or chemical characteristics of the following classes of compounds that will allow you to distinguish between them.

Characteristics of alkanes

Characteristics of alkenes

Characteristics of alkyl halides

Characteristics of alcohols

Characteristics of aldehydes

Characteristics of ketones

Characteristics of amines

Characteristics of carboxylic acids

Characteristics of esters

Characteristics of acid chlorides

___

___

Characteristics of amides

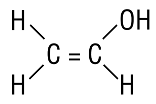
___

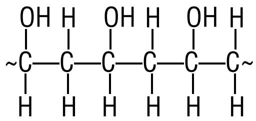
___

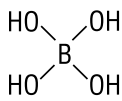
2 Use the characteristics you have listed to identify each of the 4 unknown compounds your teacher will give you, labelled W, X, Y and Z. Present your results in the form of a flow-diagram or table that includes all relevant information. Write equations for any chemical reactions that occur.

Inv 9.4 Making an addition polymer: slime

Vinyl alcohol (or 1-hydroxyethene) undergoes addition polymerisation to form the linear polymer polyvinyl alcohol. Slime is made from polyvinyl alcohol and borax, which contains the borate ion. The polar –OH group on the polymer and the –OH group on the borate ion undergo hydrogen bonding. The linear chains are thus held together in a loose network with water trapped between them. The result is a gel-like slime in which the hydrogen bonds can break and reform easily.


vinyl alcohol


polyvinyl alcohol


borax

1 Pour 50 mL of 6% polyvinyl alcohol into a 100 mL beaker and add a few drops of food colouring.

2 Add 10 mL of 4% borax solution and stir with a glass rod. (It takes a few minutes for the slime to appear.)

3 Describe the properties of the slime.

____

____

4 How can the properties of the slime be explained by its structure and bonding?

____

____

____

Inv 9.5 Making a condensation polymer: nylon 6, 6

Nylon 6, 6 is one type of copolymer formed by the condensation polymerisation of two monomers: hexanedioyl (adipyl) chloride and 1,6-diaminohexane, hydrogen chloride being eliminated.

1 Pour 10 mL of adipyl chloride (corrosive) (5% solution in hexane) into a beaker that has been coated on the inside with paraffin oil. (Dye can be added if desired.)

2 Add 5 g of hydrated sodium carbonate and stir with a glass rod.

3 What is the purpose of the sodium carbonate?

____

3 Carefully add 10 mL of the 5% solution of 1,6-diaminohexane so that the two solutions do not mix.

A small amount of solid will form at the interface of the two liquids.

4 Using a glass rod or tweezers, pull out a little of this solid and carefully wind the thread around a glass rod. (The thread will go on forming until the solutions are used up.)

5 Write an equation using structural formulae to illustrate this condensation reaction.

____

Inv 10.1 Determination of the solubility of barium hyroxide

The solubility of barium hydroxide can be determined by titration of a saturated solution with standard sulfuric acid solution.

Note: barium hydroxide is toxic, and the solid is also corrosive. Do not touch the solid, and wash your hands after the experiment.

1 Prepare a saturated solution of barium hydroxide by adding about 5 g of $Ba(OH)_2.8H_2O$ to 60 mL of water and shaking periodically for about 10 minutes. Filter the solution and pipette 10 mL aliquots of the filtrate into conical flasks.

2 Titrate with standard H_2SO_4 using methyl orange indicator.

Burette reading	1st titration	2nd titration	3rd titration	4th titration
Initial reading				
Final reading				
Titre				

3 Calculate the average of concordant titres. $V(H_2SO_4)$ = ________________

4 What was the concentration of the sulfuric acid used? $c(H_2SO_4)$ = ________________

5 Calculate the amount, in moles, of acid used. $n(H_2SO_4)$ = ________________

6 Write a balanced equation for the reaction between barium hydroxide and sulfuric acid.

____

7 Complete the expression:

$$\frac{n(Ba(OH)_2)}{n(H_2SO_4)} = \_\_\_$$

$$n(Ba(OH)_2) = \_\_\_ \times n(H_2SO_4)$$

8 Calculate the amount, in moles, of $Ba(OH)_2$ present. $n(Ba(OH)_2)$ = ________________

9 Calculate the concentration of the $Ba(OH)_2$)solution. $c(Ba(OH)_2)$ = ________________

10 If the molar mass of the barium hydroxide is 315.5 g mol^{-1} calculate the solubility in g L^{-1}.

____

____

11 How does this value compare with the data table value? Comment on any difference.

____

____

____

Inv 10.2 Solubility and solubility products

Silver halides are sparingly soluble in water and silver ions form an ammine complex with ammonia.

1 Place 2 mL of silver nitrate solution into each of 3 test tubes.

2 To the first tube add 3 or 4 drops of potassium chloride solution, to the second add the same amount of potassium bromide solution and to the third add the same amount of potassium iodide solution. What do you observe in each case? Write balanced ionic equations for any reactions.

Chloride: ______________________________

____

Bromide: ______________________________

____

Iodide: ______________________________

____

3 Divide the contents of each of the 3 test tubes from **2** into 2 equal parts.

4 To the first sample of each add dilute ammonia solution in excess and shake. What do you observe in each case? Write balanced ionic equations for any reactions.

Chloride: ______________________________

____

Bromide: ______________________________

Iodide: ______________________________

5 To the second sample of each add concentrated ammonia solution (corrosive) in excess and shake. What do you observe in each case? Write balanced ionic equations for any reactions.

Chloride: ______________________________

____

Bromide: ______________________________

____

Iodide: ______________________________

The solubility products of the silver halides are: $K_s(AgCl) = 2 \times 10^{-10}$, $K_s(AgBr) = 5 \times 10^{-13}$, $K_s(AgI) = 8 \times 10^{-17}$.

6 Use the above data to explain your observations.

____

____

____

Inv 10.3 The common ion effect

If the ionic product is greater than the solubility product then precipitation can occur. The introduction of a common ion upsets the equilibrium.

1 Pour about 5 mL of saturated salt solution into a clean test tube.
How do you know that the solution is saturated?

____

____

2 Add concentrated hydrochloric acid (corrosive) drop by drop. What do you notice?

____

3 Write the equilibrium equation for the saturated sodium chloride:

____

4 Write the expression for the equilibrium constant, K_s:

____

5 List the ions present in concentrated hydrochloric acid solution ________________

6 Name the common ion that has been added: ______________________

7 What does this do to the ionic product?

____

8 What can you say about the solubility of a compound in the presence of another compound with a common ion?

____

____

Inv 11.1 Species in solution

An acid or base can be an ion or a neutral molecule.

1 To each of the following approximately equal concentration solutions add 2 drops of universal indicator. Record your observations in the table below.

Solution	Colour in Universal Indicator	pH
Ammonium chloride NH_4Cl		
Sodium hydrogen carbonate $NaHCO_3$		
Sodium dihydrogen phosphate NaH_2PO_4		
Sodium carbonate Na_2CO_3		
Sodium sulfite Na_2SO_3		

2 Which ions behave as acids towards water? ______________________

3 Which ions behave as bases towards water? ______________________

4 Which ion is the **strongest acid**? ______________________

5 Which ion is the **strongest base**? ______________________

6 Write balanced ionic equations to represent the proton transfer reactions that occur when:

a $NaHCO_3$ dissolves in water

____

b NaH_2PO_4 dissolves in water

____

c Na_2CO_3 dissolves in water

____

d Na_2SO_3 dissolves in water

____

Inv 11.2 Determination of K_a and K_b

If the total concentration of a weak acid is known, then a determination of the $[H_3O^+]$ at equilibrium will give the concentrations of all species in the equilibrium expression. A numerical value of K_a can then be calculated. Similarly K_b can be determined for a base.

1 Standardise the pH meter (or probe) with a suitable acid buffer (potassium hydrogen tetroxalate – pH 2.16).

2 Rinse the electrode thoroughly in distilled water then measure the pH for the following in the order given. Thoroughly rinse the electrode between each measurement.

Solution	pH	$[H_3O^+]$	K_a (see **3** below)	α (see **5** below)
0.01 mol L^{-1} HCOOH				
0.1 mol L^{-1} HCOOH				
1 mol L^{-1} HCOOH				

3 From the pH values measured for each of the 3 different HCOOH solutions, calculate the equilibrium $[H_3O^+]$ and hence values for K_a (methanoic or formic acid) using the following:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

Assumption: at equilibrium $[H_3O^+] = [A^-]$

4 Compare the 3 values for K_a obtained and comment on how well they agree.

____

____

____

5 From the pH values measured for HCOOH, calculate for each of the three solutions the degree of ionisation, $\alpha = [H_3O^+]/y$ (where y = total acid concentration). Comment on the trend in values of α.

____

____

6 Standardise the pH meter with a suitable basic buffer (borax – pH 9.18).

7 Rinse the electrode thoroughly in distilled water then measure the pH of 1 mol L^{-1} NH_3 solution.

pH = ____________

8 Calculate $[OH^-]$. $[OH^-]$ = ________________

9 Use the information below to calculate a value for K_b.

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Assumption: at equilibrium $[BH^+] = [OH^-]$

K_b = ________________

Inv 12.1 Buffer action

This experiment demonstrates the buffer action (or lack of it) for selected systems when small amounts of a strong acid or strong base are added to these systems and the change in pH noted.

1 Measure the pH of aliquots (measuring cylinder) of the following solutions and note the change in pH after addition by pipette of 1 mL of strong acid and/or strong base (2 mL of NaOH for the last two) provided.

Solution	pH	pH after adding 1 mL of 0.2 mol L^{-1} HCl	pH after adding 1 mL of 0.2 mol L^{-1} NaOH
40 mL distilled water			
40 mL of 10^{-3} mol L^{-1} HCl			
100 mL of sea water $[HCO_3^-]$ = 0 004 mol L^{-1} and $[CO_3^{2-}]$ = 0.006 mol L^{-1}			
40 mL of 0.1 mol L^{-1} ethanoic acid /0.1 mol L^{-1} sodium ethanoate solution			
40 mL of 0.1 mol L^{-1} ammonium chloride / 0.1 mol L^{-1} ammonia solution			

2 How does the behaviour of buffer solutions differ from that of other solutions?

____

____

____

____

3 Write a brief explanation for their buffer action.

____

____

____

____

____

4 Milk contains, in addition to fats and proteins, a mixture of lactic acid ($CH_3CH(OH)COOH$), calcium and potassium lactates, amino acids, $H_2PO_4^-$ and HPO_4^{2-}. Will it show buffer action? Explain your answer.

____

____

____

Inv 12.2 Titration curves

During an acid-base titration the pH changes in a characteristic way. A titration curve is a graph which shows the change in pH as the titration proceeds.

1 Fill a burette with sodium hydroxide solution (0.1 mol L^{-1}).

2 Pipette 20 mL of hydrochloric acid (or ethanoic acid), 0.1 mol L^{-1}, into a 100 mL beaker. Place a magnetic stirrer in the solution and place on a hotplate/stirrer.

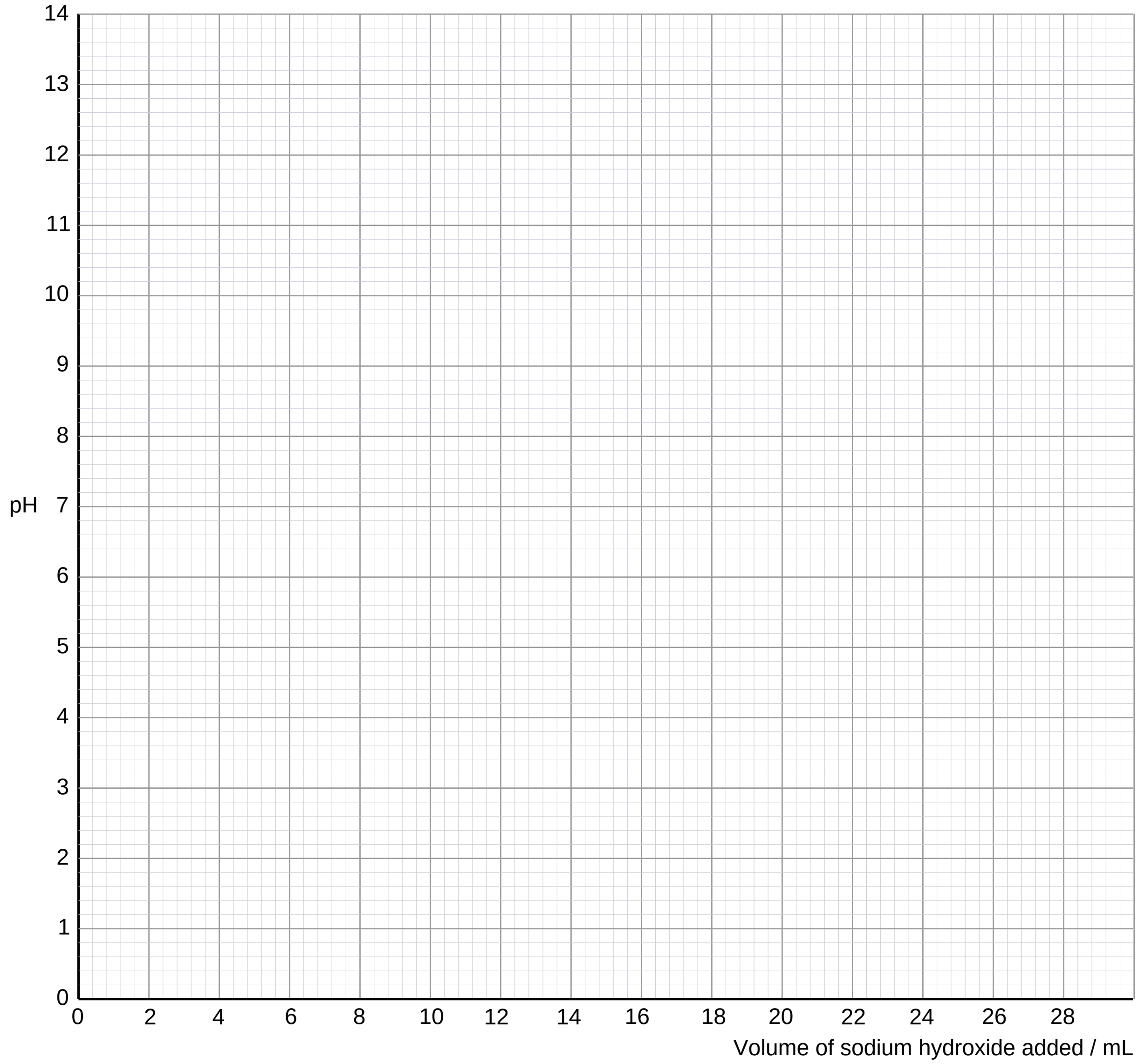
3 Use a pH meter or pH data logger probe to measure the pH at the start. pH = ______________

4 Add 2.0 mL of the sodium hydroxide solution and measure the pH. pH = ______________

5 Continue to add the sodium hydroxide solution 2. 0 mL at a time and record the pH each time.

Volume of NaOH (mL)	pH	Volume of NaOH (mL)	pH	Volume of NaOH (mL)	pH
0		10		20	
2		12		22	
4		14		24	
6		16		26	
8		18		28	

6 On the grid below plot a graph of pH (vertical axis) against volume of sodium hydroxide added. Join the points with a smooth curve of best fit.



7 What is the initial pH of the acid? pH = ____________

8 How many mL of sodium hydroxide were added at the equivalence point? V(NaOH) = ____________

9 What is the pH at the equivalence point? pH = ____________

10 Name a suitable indicator for the reaction. ____

Inv 13.1 A back titration

Many reactions are not suitable for analysis by a standard titration, perhaps because the reaction is very slow, or because other reaction products form that get in the way of an exact result. Chemists often avoid these problems by doing a *back titration.*

Calcium carbonate is a common ingredient in indigestion tablets. It reacts with acid, but the reaction with solid $CaCO_3$ takes time, and the CO_2 produced is acidic.

These factors make a direct titration difficult. Instead, we react the crushed tablets with a known volume of excess of standard HCl, heat the mixture to remove all CO_2, and then titrate in standard NaOH until the rest of the acid has reacted.

1 Crush a Quick-Eze tablet and transfer completely to a 100 mL conical flask. Repeat for two other tablets.

2 Pipette 20.0 mL (excess) of standard hydrochloric acid into each flask.

3 Boil the mixtures for 2 minutes to remove all the CO_2, and allow to cool..

4 Write an equation for the reaction between HCl and $CaCO_3$.

____

5 Write an equation for the reaction between HCl and NaOH.

____

6 Titrate the excess hydrochloric acid against standard sodium hydroxide from the burette using phenolphthalein indicator.

Burette reading	**1st tablet**	**2nd tablet**	**3rd tablet**
Initial reading			
Final reading			
Titre			

			1st tablet	2nd tablet	3rd tablet
7	Record the concentration of hydrochloric acid added.	c(HCl) =			
8	Record the volume of hydrochloric acid added.	V_{Tot}(HCl) =			
9	Calculate the amount of hydrochloric acid added.	n_{Tot}(HCl) =			
10	Record the concentration of NaOH used.	c(NaOH)			
11	Record the volume of NaOH required.	V(NaOH) =			
12	Calculate the amount of NaOH required for each tablet.	n(NaOH) =			

13	Use the titration data to calculate the amount of HCl reacting with the NaOH.	$n_{unreacted}$(HCl) =			
14	Calculate the amount of HCl reacting with the $CaCO_3$ in the tablets.	n(HCl) =			
15	Calculate the amount of $CaCO_3$ present in each tablet.	$n(CaCO_3)$ =			
16	Calculate the mass of calcium carbonate in each tablet. $M(CaCO_3)$ = 100.0 g mol^{-1}.	$m(CaCO_3)$ =			

17 Calculate the average mass of calcium carbonate in the Quick-Eze tablets.

____

Inv 13.2 Colorimetric analysis

Brass is an alloy of copper and zinc. It dissolves in nitric acid. The amount of copper in a sample can be found by colorimetry.

1. Weigh accurately about 1 g of brass. m(brass) = ______________
2. Dissolve the metal in concentrated nitric acid (corrosive) using the minimum amount of acid possible. WORK IN A FUME CUPBOARD.
3. Transfer the solution to a 100.0 mL volumetric flask and make it up to volume with dilute sulfuric acid.
4. Use a standard 0.100 mol L^{-1} copper sulfate solution to prepare standard copper ion solutions as shown below

Concentration (mol L^{-1})	0.010	0.030	0.050	0.060	0.070	0.090
Volume of 0.100 mol L^{-1}) solution required	1 mL	3 mL	5 mL	6 mL	7 mL	9 mL
Volume of dilute sulfuric acid required	9 mL	7 mL	5 mL	4 mL	3 mL	1 mL

5. Measure the absorbance of each standard solution, and the sample, using a colorimeter with a red filter. Set the colorimeter to 0 absorbance, or take the base measurement, for the dilute sulfuric acid.

Solution (mol L^{-1})	0.010	0.030	0.050	0.060	0.070	0.090	Sample
Absorbance							

6 Plot a calibration curve of your results and use it to determine the concentration of copper ions in the sample solution

$c(Cu^{2+})$ = ________________

7 Calculate the amount, in moles, of copper in the 100.0 mL flask.

____

____

____

____

8 Calculate the mass of copper in the brass sample.

____

____

____

9 Calculate the percentage of copper in the brass.

____

____

____

Answers

Test yourself 1A

1 Oxidation is a loss of electrons; reduction is a gain of electrons.

2 **a** +1 **b** +6 **c** +4 **d** +4 **e** –2

3 **a** Not redox
b Redox: Cl oxidised, N reduced
c Not redox
d Redox: C oxidised, Fe reduced
e Redox: Mn reduced, S oxidised

4 **a** Oxidising agent = CuO, reducing agent = H_2
b Oxidising agent = Ag^+, reducing agent = Fe^{2+}
c Oxidising agent = IO_3^-, reducing agent = I^-

Test yourself 1B

1 **a** Goes from orange to green/blue.
b Goes from colourless to orange/brown.
c Goes from colourless to dark brown.
d Colourless liquid gives off a colourless gas.

2 **a** The blue/black solution will go colourless.
b The pink/purple solution will go colourless; a colourless gas may be seen.
c The grey solid starts to disappear, and a colourless gas is given off.

Test yourself 1C

1 $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$
$I_2 + 2e^- \longrightarrow 2I^-$
$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

2 $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ × 5
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ × 2
$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

3 $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$
$2I^- \longrightarrow I_2 + 2e^-$ × 3
$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$

4 $TeO_3^{2-} + 3H_2O + 4e^- \longrightarrow Te + 6OH^-$
$V^{4+} \longrightarrow V^{5+} + e^-$ × 4
$TeO_3^{2-} + 4V^{4+} + 3H_2O \longrightarrow Te + 4V^{5+} + 6OH^-$

Review questions for Chapter 1

1 **a** $\overset{+6\ -2}{Cr_2O_7^{2-}} + \overset{+1}{2H^+} + \overset{+4\ -2}{3SO_2} \longrightarrow \overset{+3}{2Cr^{3+}} + \overset{+1\ -2}{H_2O} + \overset{+6\ -2}{3SO_4^{2-}}$
Oxidising agent = $Cr_2O_7^{2-}$, reducing agent = SO_2
You would see a colourless gas bubbling through an orange solution that would slowly turn blue/green.

b $\overset{0}{Cu} + \overset{+1\ +5\ -2}{4HNO_3} \longrightarrow \overset{+2\ +5\ -2}{Cu(NO_3)_2} + \overset{+4\ -2}{2NO_2} + \overset{+1\ -2}{2H_2O}$
Oxidising agent = HNO_3, reducing agent = Cu
You would see a colourless liquid react with a brown metal to produce a heavy brown gas and a blue solution.

c $\overset{+7\ -2}{2MnO_4^-} + \overset{+1\ -1}{5H_2O_2} + \overset{+1}{6H^+} \longrightarrow \overset{+2}{2Mn^{2+}} + \overset{0}{5O_2} + \overset{+1\ -2}{8H_2O}$
Oxidising agent = MnO_4^-, reducing agent = H_2O_2
You would see a colourless liquid reacting with a purple liquid to form a colourless (very pale pink) liquid and a colourless gas.

A = correct oxidation numbers and correct agents for two reactions, **M** = plus correct observations for two reactions

2 **a** brown **b** brown **c** brown
d orange **e** colourless **f** blue
g green **h** green **i** colourless
A = 7 correct

3 **a** chlorine gas **b** $Fe^{3+}(aq)$
c SO_4^{2-} **d** $I_2(aq)$ **A** = 3 correct

4 **a** $PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O$
$2Cl^- \longrightarrow Cl_2 + 2e^-$
$PbO_2 + 2Cl^- + 4H^+ \longrightarrow Pb^{2+} + Cl_2 + 2H_2O$

b $Cu^{2+} + 2e^- \longrightarrow Cu$
$Fe \longrightarrow Fe^{2+} + 2e^-$
$Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+}$

c $Cu^{2+} + e^- \longrightarrow Cu^+$ × 2
$2I^- \longrightarrow I_2 + 2e^-$
$2Cu^{2+} + 2I^- \longrightarrow 2Cu^+ + I_2$

d $Cl_2 + 2e^- \longrightarrow 2Cl^-$
$2Br^- \longrightarrow Br_2 + 2e^-$
$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$

e $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ × 2
$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$
$2MnO_4^- + 2S_2O_3^{2-} \longrightarrow 2MnO_4^{2-} + S_4O_6^{2-}$

For each equation: **A** = 1 half-equation correct, **M** = both half equations correct **E** = correct combined equn

5 **a** Aluminium acts as a reducing agent because the nitrogen is reduced from its +5 oxidation state in nitrate to the –3 state in ammonia.
A = correct answer, **M** = plus correct reason

b $NO_3^- + 6H_2O + 8e^- \longrightarrow NH_3 + 9OH^-$ × 3
$Al + 4OH^- \longrightarrow [Al(OH)_4]^- + 3e^-$ × 8
$3NO_3^- + 18H_2O + 8Al + 5OH^- \longrightarrow 3NH_3 + 8[Al(OH)_4]^-$
M = correct half equations, **E** = correct ionic equation

6 **a** You would see a colourless/pale green gas bubbling into a colourless solution. The solution would slowly turn brown.
b You would see a brown electrode left in a colourless solution. The solution would slowly turn pale blue, while white/grey crystals would form on the brown metal.
c You would see bright orange filter paper held in a colourless gas. The filter paper would turn blue/green.
A = correct observations for start and finish for one reaction, **M** = correct observations for start and finish in two or three with minor errors

Test yourself 2A

1 NaOH is not suitable as a primary standard—use Na_2CO_3 instead. Part-fill flask, then mix, then fill and remix. Rinse burette with solution. Add indicator to flask, not burette. Rinse flask in water, not solution.

2 $M(Na_2CO_3) = 106 \text{ g mol}^{-1}$

$$c(Na_2CO_3) = \frac{1.000 \text{ g}}{106 \text{ g mol}^{-1}} = 9.434 \times 10^{-3} \text{ mol L}^{-1}$$

3 $M(KIO_3) = 214 \text{ g mol}^{-1}$

$$n = \frac{m}{M} = cV$$
$$m = cVM$$
$$m(KIO_3) = 0.200 \times 250.0 \times 10^{-3} \times 214 = 10.7 \text{ g}$$

4 $M(H_2O_2) = 34 \text{ g mol}^{-1}$

$$c(H_2O_2) = 1.80 \text{ mol L}^{-1} \times 34 \text{ g mol}^{-1} = 61.2 \text{ g L}^{-1} = 6.12 \text{ g/100 mL}$$

5 **a** **i** 5.167×10^8 **ii** 1.7×10^{-4} **iii** 8.4×10^{-17}
b **i** 5.58×10^5 **ii** 2.27×10^{-11}
iii 5.73 **iv** 6.10×10^{-6}

Test yourself 2B

1 **a** Acidify with sulfuric acid and heat reaction flask.
b (22.42 + 22.28 + 22.46 + 22.44) ml/ 4 = 22.40 mL
c
$$\begin{aligned} n(C_2O_4^{2-}) &= cV \\ &= 0.172 \text{ mol L}^{-1} \times 20.0 \times 10^{-3} \\ &= 3.44 \times 10^{-3} \text{ mol} \end{aligned}$$
d
$$\begin{aligned} \frac{n(MnO_4^-)}{n(C_2O_4^{2-})} &= \frac{2}{5} \\ n(MnO_4^-) &= \frac{2}{5} \times n(C_2O_4^{2-}) \\ &= 0.4 \times 3.44 \times 10^{-3} \text{ mol} \\ &= 1.376 \times 10^{-3} \text{ mol} \end{aligned}$$
e
$$\begin{aligned} c(MnO_4^-) &= \frac{n}{V} \\ &= \frac{1.376 \times 10^{-3} \text{ mol}}{22.4 \times 10^{-3} \text{ L}} \end{aligned}$$

2 **a** Add starch solution near the endpoint and look for the blue colour to disappear.
b
$$\begin{aligned} n(S_2O_3^{2-}) &= cV \\ &= 0.0964 \text{ mol L}^{-1} \times 25.3 \times 10^{-3} \text{ L} \\ &= 2.439 \times 10^{-3} \text{ mol } (2.44 \times 10^{-3} \text{ to 3 sig fig}) \end{aligned}$$
c
$$\begin{aligned} \frac{n(OCl^-)}{n(I_2)} \times \frac{n(I_2)}{n(S_2O_3^{2-})} &= \frac{1}{1} \times \frac{1}{2} \\ n(OCl^-) &= \frac{1}{2} n(S_2O_3^{2-}) \\ &= \frac{1}{2} \times 2.439 \times 10^{-3} \text{ mol} \\ &= 1.219 \times 10^{-3} \text{ mol} \end{aligned}$$
d
$$\begin{aligned} c(OCl^-_{dil}) &= \frac{n}{V} \\ &= \frac{1.219 \times 10^{-3} \text{ mol}}{25.0 \times 10^{-3} \text{ L}} \\ &= 0.048\ 76 \text{ mol L}^{-1} \\ &\quad (0.0488 \text{ to 3 sig fig}) \\ c(OCl^-_{bleach}) &= c(OCl^-_{dil}) \times \frac{250.0}{25.0} \\ &= 0.4876 \text{ mol L}^{-1} \\ &\quad (0.488 \text{ to 3 sig fig}) \end{aligned}$$
e
$$\begin{aligned} M(NaOCl) &= 74.5 \text{ g mol}^{-1} \\ c(NaOCl) &= 0.4876 \text{ mol L}^{-1} \times 74.5 \text{ g mol}^{-1} \\ &= 36.3 \text{ g L}^{-1} \\ &= 3.63 \text{ g/100 mL} \end{aligned}$$

Review questions for Chapter 2

1
$$\begin{aligned} n = \frac{m}{M} &= cV \\ m(Na_2CO_3) &= cVM \\ &= 0.0500 \text{ mol L}^{-1} \times 250.0 \times 10^{-3} \text{ L} \times 106 \text{ g mol}^{-1} \\ &= 1.33 \text{ g (to 3 sig fig)} \end{aligned}$$

A = correct formula, but minor substitution error,
M = correct answer

2
$$\begin{aligned} n(HCl) &= cV \\ &= 0.107 \text{ mol L}^{-1} \times 41.3 \times 10^{-3} \text{ L} \\ &= 4.419 \times 10^{-3} \text{ mol} \\ \frac{n(Na_2CO_3)}{n(HCl)} &= \frac{1}{2} \\ n(Na_2CO_3) &= \frac{1}{2} n(HCl) \\ &= \frac{1}{2} \times 4.419 \times 10^{-3} \text{ mol} \\ &= 2.210 \times 10^{-3} \text{ mol} \\ m(Na_2CO_3) &= nM \\ &= 2.210 \times 10^{-3} \text{ mol} \times 106 \text{ g mol}^{-1} \\ &= 0.234 \text{ g} \\ \%\text{ purity} &= \frac{m(Na_2CO_3)}{m(\text{impure})} \times 100 \\ &= \frac{0.234 \text{ g}}{0.714 \text{ g}} \times 100 \\ &= 32.8\ \% \end{aligned}$$

A = correct moles of sodium carbonate, **M** = correct % purity of sodium carbonate, **E** = correct answer to 3 sig fig

3 **a** The endpoint is reached when the first drop of $KMnO_4$ remains coloured. **A**
b
$$\begin{aligned} &MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \\ &Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad \times 5 \\ &MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \end{aligned}$$
A = correct equation
c
$$\begin{aligned} n(MnO_4^-) &= cV \\ &= 0.0100 \text{ mol L}^{-1} \times 8.7 \times 10^{-3} \\ &= 8.7 \times 10^{-5} \text{ mol} \\ n(Fe^{2+}) &= 5 \times n(MnO_4^-) \\ &= 5 \times 8.7 \times 10^{-5} \text{ mol} \\ &= 4.35 \times 10^{-4} \text{ mol} \\ c(Fe^{2+}) &= \frac{n}{V} \\ &= \frac{4.35 \times 10^{-4} \text{ mol}}{25.0 \times 10^{-3} \text{ L}} \\ &= 0.0174 \text{ mol L}^{-1} \end{aligned}$$
A = correct moles of iron, **M** = correct concentration of iron

d
$$\begin{aligned} c(Fe^{2+}_{original}) &= c(Fe^{2+}_{dilute}) \times \frac{250.0 \text{ mL}}{25.0 \text{ mL}} \\ &= 0.0174 \text{ mol L}^{-1} \times 10 \\ &= 0.174 \text{ mol L}^{-1} \\ M(FeSO_4.7H_2O) &= 278 \text{ g mol}^{-1} \\ m(FeSO_4.7H_2O) &= cVM \\ &= 0.174 \times 250.0 \times 10^{-3} \times 278 \\ &= 12.09 \text{ g} \\ \%\text{ purity} &= \frac{m(FeSO_4.7H_2O)}{m(\text{impure})} \times 100 \\ &= \frac{12.09 \text{ g}}{14.8 \text{ g}} \times 100 \\ &= 81.7\ \% \end{aligned}$$

A = correct mass of iron in original solution, **M** = correct % purity to 3 sig fig

4 **a** $n(MnO_4^-) = cV$

$= 0.104 \text{ mol L}^{-1} \times 13.2 \times 10^{-3} \text{ L}$

$= 1.373 \times 10^{-3} \text{ mol}$ $(1.37 \times 10^{-3}$ to 3 sig fig)

b $n(H_2O_2) = 5 \times n(MnO_4^-)$

$= 3.432 \times 10^{-3} \text{ mol}$ $(3.43 \times 10^{-3}$ to 3 sig fig)

c $c(H_2O_2) = \dfrac{n}{V}$

$= \dfrac{3.432 \times 10^{-3} \text{ mol}}{20.0 \times 10^{-3} \text{ L}}$

$= 0.172 \text{ mol L}^{-1}$

$M(H_2O_2) = 34 \text{ g mol}^{-1}$

$c(H_2O_2) = 0.172 \text{ mol L}^{-1} \times 34 \text{ g mol}^{-1}$

$= 5.83 \text{ g L}^{-1}$

A = correct amount of peroxide, **M** = correct concentration of peroxide

5 $n(KIO_3) = cV$

$= 0.0153 \text{ mol L}^{-1} \times 20.0 \times 10^{-3} \text{ L}$

$= 3.06 \times 10^{-4} \text{ mol}$

$\dfrac{n(S_2O_3^{2-})}{n(I_2)} \times \dfrac{n(I_2)}{n(IO_3^-)} = \dfrac{2}{1} \times \dfrac{3}{1}$

$n(S_2O_3^{2-}) = 6 \times n(IO_3^-)$

$= 6 \times 3.06 \times 10^{-4} \text{ mol}$

$= 1.836 \times 10^{-3} \text{ mol}$

$c(S_2O_3^{2-}) = \dfrac{n}{V}$

$= \dfrac{1.836 \times 10^{-3} \text{ mol}}{17.8 \times 10^{-3} \text{ L}}$

$= 0.103 \text{ mol L}^{-1}$

A = correct amount of thiosulfate, **M** = correct concentration of thiosulfate, **E** = correct answer to 3 sig fig

6 **a** $V(\text{average}) = \dfrac{24.9 + 25.0 + 24.9}{3}$

$= 24.93 \text{ mL}$

b $n(S_2O_3^{2-}) = cV$

$= 0.115 \text{ mol L}^{-1} \times 24.93 \times 10^{-3} \text{ L}$

$= 2.867 \times 10^{-3} \text{ mol}$

$\dfrac{n(Cu^{2+})}{n(I_2)} \times \dfrac{n(I_2)}{n(S_2O_3^{2-})} = \dfrac{2}{1} \times \dfrac{1}{2}$

$n(Cu^{2+}) = n(S_2O_3^{2-})$

$= 2.867 \times 10^{-3} \text{ mol}$

$C(Cu^{2+}) = \dfrac{n}{V}$

$= \dfrac{2.867 \times 10^{-3} \text{ mol}}{25.0 \times 10^{-3} \text{ mol}}$

$= 0.1147 \text{ mol L}^{-1}$

c $m(Cu) = cVM$

$= 0.1147 \times 250.0 \times 10^{-3} \times 63.55$

$= 1.822 \text{ g}$

$\%Cu = \dfrac{m(Cu)}{m(\text{brass})} \times 100$

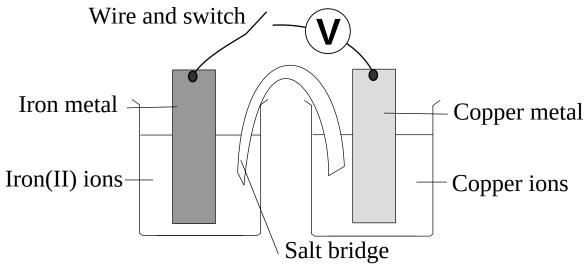
$= \dfrac{1.822 \text{ g}}{2.916 \text{ g}} \times 100$

$= 62.5\ \%$

A = correct titres used, **M** = correct method, but minor error in calculating mass of Cu, **E** = correct % to 3 sig fig

Test yourself 3A

1



2 It completes the circuit by allowing the movement of ions.

3 Temperature of 25 °C (298 K); all solutions at 1.0 mol L^{-1}; gas pressures of 1 atmosphere or 101.3 kPa.

4 $Fe(s) / Fe^{2+}(aq) // Cu^{2+}(aq) / Cu(s)$

5 $C(s) / Fe^{2+}(aq), Fe^{3}(aq) // Cu^{2+}(aq) / Cu(s)$

6 LHE $2Cl^- \longrightarrow Cl_2 + 2e^-$

RHE $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$

Test yourself 3B

1 **a** $E°_{cell} = E°_{RHE} - E°_{LHE}$

$= +0.34 \text{ V} - (-2.36 \text{ V})$

$= +2.70 \text{ V}$

b $E°_{cell} = E°_{RHE} - E°_{LHE}$

$= -1.66 \text{ V} - (+1.50 \text{ V})$

$= -3.16 \text{ V}$

c $E°_{cell} = E°_{RHE} - E°_{LHE}$

$= +1.51 \text{ V} - (+0.77 \text{ V})$

$= +0.74 \text{ V}$

2 **a** $Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$

b $Al(s) + Au^{3+}(aq) \longrightarrow Al^{3+}(aq) + Au(s)$

c $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

3 **a** When the Cl_2,Cl^- and Al^{3+} / Al half-cells are combined, will reduction occur in the Al^{3+} / Al cell and oxidation in the Cl_2 / Cl^- cell?

$E°_{cell} = E°_{Red} - E°_{Ox}$

$= -1.66 \text{ V} - (+1.40 \text{ V})$

$= -3.06 \text{ V}$

The $E°_{cell}$ is negative, so the Cl^- will not reduce Al^{3+} to Al.

b Is Cl^- oxidised and Au^{3+} reduced when the Cl_2 / Cl^- and Au^{3+} / Au half-cells are combined?

$E°_{cell} = E°_{Red} - E°_{Ox}$

$= +1.50 \text{ V} - (+1.40 \text{ V})$

$= +0.10 \text{ V}$

The $E°_{cell}$ is positive, so Cl^- will be oxidised by Au^{3+}.

c Is I^- oxidised and MnO_4^- reduced when the I_2 / I^- and MnO_4^- / Mn^{2+} half-cells are combined?

$E°_{cell} = E°_{Red} - E°_{Ox}$

$= +1.51 \text{ V} - (+0.54 \text{ V})$

$= +0.97 \text{ V}$

The $E°_{cell}$ is positive, so MnO_4^- will oxidise I^- to I_2.

4 **a** Au **d** Cl_2

b MnO_4^- **e** Fe^{2+}

c Cl^- **f** Na^+

Test yourself 3C

1 **a** Pb(s) **b** $PbO_2(s)$

2 Because water is produced in the reaction and this dilutes the acid.

3 a $Zn(s)$ b MnO_2

c It acts as the positive electrode.

4 a $Zn(s) / Zn^{2+}(aq) // Ag^{+}(aq) / Ag(s)$

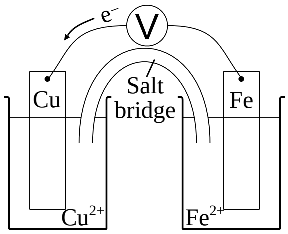
b $2Ag(s) + Zn^{2+}(aq) \longrightarrow 2Ag^{+}(aq) + Zn(s)$

Review questions for Chapter 3

1 The cells were not set up under standard conditions of temperature and concentration.

A = one point mentioned, **M** = standard conditions stated

2



c Solid copper will form in the left-hand beaker—either coating the electrode, or as a brown precipitate on the bottom of the beaker. The blue colour of the Cu^{2+} solution will fade. The liquid in the right-hand beaker will turn to a pale green colour and the iron electrode will get thinner.

A = diagram completed (allow minor error) and one point mentioned, **M** = cell correct and two observations, **E** = complete answer

3 a Yes. The MnO_4^- half-cell is more positive than the Cl^- half-cell, so it will be reduced, and Cl^- oxidised to Cl_2.

b No. The Fe^{3+}, Fe^{2+} half-cell is more positive than the S / H_2S half-cell, so Fe^{3+} would be reduced, and H_2S oxidised.

c No. The Cl_2/Cl^- half-cell is more positive, so Cl_2 will be reduced to Cl^- and Cr^{3+} oxidised to $Cr_2O_7^{2-}$.

A = two correct predictions, **M** = two correct with reasoning, **E** = complete answers to each part

4 a Ag^+ **A** b Cr^{2+} **A** c Ag **A**

d i $Cu(s) / Cu^{2+}(aq) // Sn^{4+}(aq), Sn^{2+}(aq) / Pt$

A = cell correct with minor error, **M** = all correct

ii
$$\begin{aligned} E°_{cell} &= E°_{RHE} - E°_{LHE} \\ &= +0.15\ V - (+0.34\ V) \\ &= -0.19\ V \end{aligned}$$

A = correct, but no units or incorrect sign, **M** = correct

iii The $E°_{cell}$ is negative, so oxidation occurs on the right and reduction on the left.

$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

$Cu^{2+} + 2e^- \longrightarrow Cu$

$Sn^{2+} + Cu^{2+} \longrightarrow Sn^{4+} + Cu$

A = correct with minor error, **M** = correct

5 a $Pt(s) / I^-(aq), I_2(aq) // Fe^{3+}(aq), Fe^{2+}(aq) /Pt(s)$

A = correct with minor error eg. no state symbols, **M** = correct

b The two / signs represent a change in phase with the species in direct contact; the // is a salt bridge; and the commas separate species within a half-cell which are in the same phase.

A = correct with minor error, **M** = correct

c We cannot connect wires directly to the reductant (I^-) or the oxidant (Fe^{3+}) since they are both ions in aqueous solution, so we connect wires to the platinum electrodes instead.

A = correct with minor error, **M** = correct

6 In acid conditions:

$$\begin{aligned} E°_{cell} &= E°_{Red} - E°_{Ox} \\ &= +1.23\ V - 0.54\ V \\ &= +0.69\ V \end{aligned}$$

This reaction is spontaneous.

In alkaline conditions:

$$\begin{aligned} E°_{cell} &= E°_{Red} - E°_{Ox} \\ &= +0.40\ V - 0.54\ V \\ &= -0.14\ V \end{aligned}$$

This reaction is not spontaneous.

Thus iodide is only oxidised to iodine by oxygen in acid conditions.

A = acidic conditions, **M** = correct answer with emfs calculated, **E** = plus idea of positive being spontaneous and negative not.

7 a $Zn + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+} + 2e^-$

$2NH_4^+ + 2MnO_2 + 2H_2O + 2e^- \longrightarrow 2Mn(OH)_3 + 2NH_3$

$Zn + 2NH_3 + 2NH_4^+ + 2MnO_2 + 2H_2O \longrightarrow [Zn(NH_3)_4]^{2+} + 2Mn(OH)_3$

A = correct equation

b
$$\begin{aligned} E°_{cell} &= E°_{RHE} - E°_{LHE} \\ &= +1.0\ V - (-1.03\ V) \\ &= +2.03\ V \end{aligned}$$

A = correct, but units or sign incorrect, **M** = correct

c Elements are in pure form; solutions are at 1.0 mol L^{-1}; temperature is 25 °C; pressure is 101.3 kPa.

A = all correct

Test yourself 4A

1 a If the temperature of the mixture is *higher* after the reaction, it is exothermic; if the temperature is *lower* the reaction is endothermic.

b If the reactants have *more* enthalpy than the products the reaction is exothermic; if they have *less* enthalpy than the products the reaction is endothermic.

c If the $\Delta_r H$ is positive the reaction is endothermic; if it is negative the reaction is exothermic.

2 Solids cannot be compressed whereas gases are easily compressed.

3 A crystal of $KMnO_4$ is carefully placed in a beaker of hot water, and a beaker of cold water. The spread of colour is much faster in the hot water than the cold.

4 Heat energy is needed to melt the ice cubes and this is at the expense of heating up the surrounding liquid.

5 a
$$\begin{aligned} E &= \textit{mass} \times \textit{specific heat} \times \textit{temperature change} \\ &= m \times s \times \Delta T \\ &= 1500\ g \times 4.18\ J\ g^{-1}\ °C^{-1} \times 65\ °C \\ &= 407\ 550\ J = 408\ kJ \end{aligned}$$

b
$$\begin{aligned} E &= m \times s \times \Delta T \\ &= 30.0\ g \times 4.18\ J\ g^{-1}\ °C^{-1} \times (42.0 - 20.0)\ °C \\ &= 2758.8\ J \\ \Delta T &= \frac{E}{ms} \\ &= \frac{2758.8\ J}{30.0\ g \times 2.46\ J\ g^{-1}\ °C^{-1}} \\ &= 37.4\ °C \\ T_{final} &= T_{initial} + \Delta T \\ &= 20.0\ °C + 37.4\ °C \\ &= 57.7\ °C \end{aligned}$$

6 The energy required to change 1 mole of a substance from a solid to a liquid at that substance's melting point.

7 NH_3(l at –33° C) $\rightarrow$ NH_3(g at –33° C) $\Delta_{vap}H$ = 5.65 kJ mol^{-1}

8 $\Delta_{sub}H$ is the standard heat of sublimation ie.for a substance changing from a solid to a gas. The change in energy in going from a solid to a gas can be estimated by adding the energy for a solid to liquid plus the liquid to gas.

9 N_2 CO_2 Br_2 Hg I_2 $C_6H_{12}O_6$ Na NaCl Fe MgO C

Test yourself 4B

1 The standard enthalpy of combustion is the enthalpy change when *one mole* of the substance is *completely burnt*, with all reactants and products in their standard states.

2 There is an enthalpy change when substances change states, so for example, there will be a different Δ_rH if the products are gaseous rather than liquid.

3 a $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

b $H_2(g) + ½O_2(g) \longrightarrow H_2O(l)$

4 The standard enthalpy of formation is the enthalpy change when one mole of that compound is formed from its elements, with all reactants and products in their standard states.

5 a $Na(s) + ½Cl_2(g) \longrightarrow NaCl(s)$

b $C(s) + 2H_2(g) + ½O_2(g) \longrightarrow CH_3OH(l)$

6 Δ_fH for an element will not be zero if the standard conditions are not met, such as the element is in a liquid state rather than its standard solid state, or it is at a different temperature eg. 80 °C rather than 25 °C.

Test yourself 4C

1
$$\Delta E = m(\text{water}) \times \Delta T \times s$$
$$= 100\text{ g} \times 18.0\text{ °C} \times 4.18\text{ J g}^{-1}\text{ °C}^{-1}$$
$$= 7524\text{ J or } 7.524\text{ kJ}$$
$$n(\text{Zn}) = \frac{m}{M}$$
$$= \frac{0.250\text{ g}}{65.4\text{ g mol}^{-1}}$$
$$= 3.823 \times 10^{-3}\text{ mol}$$
$$\Delta_rH = \frac{\Delta E}{n}$$
$$= \frac{7.524\text{ kJ}}{3.823 \times 10^{-3}\text{ mol}}$$
$$= 1970\text{ kJ mol}^{-1}\ (3\text{ sig fig})$$

Since reaction is exothermic, Δ_rH = –1970 kJ mol^{-1}

2 a
$$\Delta_rH^\circ = [\Delta_fH^\circ(CaO) + \Delta_fH^\circ(CO_2)] - [\Delta_fH^\circ(CaCO_3)]$$
$$= [-635.5 - 393] - [-1207]$$
$$= +178.5\text{ kJ mol}^{-1}$$

b
$$\Delta_rH^\circ = [6 \times \Delta_fH^\circ(H_2O) + 4 \times \Delta_fH^\circ(NO)] - [4 \times \Delta_fH^\circ(NH_3) + 5 \times \Delta_fH^\circ(O_2)]$$
$$= [(6 \times -241.8) + (4 \times 90.25)] - [(4 \times -46.11) + (5 \times 0)]$$
$$= -905.4\text{ kJ mol}^{-1}$$

3 a The amount of $CuSO_4$ is known because the final solution is colourless, indicating that all the Cu^{2+} has reacted. (OR because the unreacted zinc remaining shows that zinc was in excess.)

b
$$n(CuSO_4) = cV$$
$$= 0.125\text{ mol L}^{-1} \times 100.0 \times 10^{-3}\text{ L}$$
$$= 0.0125\text{ mol}$$
$$\Delta T = T_{final} - T_{initial}$$
$$= 20.5\text{ °C} - 16.0\text{ °C}$$
$$= 4.5\text{ °C}$$
$$E = m \times s \times \Delta T$$
$$= 100.0\text{ g} \times 4.18\text{ J g}^{-1}\text{ °C}^{-1}$$
$$= 1881\text{ J}$$
$$\Delta H = \frac{E}{n}$$
$$= \frac{-1881\text{ J}}{0.0125\text{ mol}}$$
$$= 150\ 488\text{ J}$$
$$= 150\text{ kJ (3 sig fig)}$$

Test yourself 4D

1
$$4HBr(g) \longrightarrow \cancel{2H_2(g)} + 2Br_2(l) \quad \Delta H = +72.8\text{ kJ mol}^{-1} \times 2$$
$$\cancel{2H_2(g)} + O_2(g) \longrightarrow 2H_2O(g) \quad \Delta H = -483.7\text{ kJ mol}^{-1}$$
$$4HBr(g) + O_2(g) \longrightarrow 2Br_2(l) + 2H_2O(g) \quad \Delta H = -338.1\text{ kJ mol}^{-1}$$

2
$$C(s) + \cancel{O_2(g)} \longrightarrow \cancel{CO_2(g)} \quad \Delta H = -394\text{ kJ mol}^{-1}$$
$$H_2O(g) \longrightarrow H_2(g) + \cancel{½O_2(g)} \quad \Delta H = +242\text{ kJ mol}^{-1}$$
$$\cancel{CO_2(g)} \longrightarrow CO(g) + \cancel{½O_2(g)} \quad \Delta H = +282\text{ kJ mol}^{-1}$$
$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) \quad \Delta H = +130\text{ kJ mol}^{-1}$$

3 $HCl(g) \longrightarrow H(g) + Cl(g)$ ΔH = + 431 kJ mol^{-1}

4 a

Bond breaking		Bond making	
C = C	+598 kJ mol^{-1}	C–C	–346 kJ mol^{-1}
Br–Br	+192 kJ mol^{-1}	2 × C–Br	2 × –276 kJ mol^{-1}
	+790 kJ mol^{-1}		–898 kJ mol^{-1}

Δ_rH = +790 – 898 = –108 kJ mol^{-1}

b

Bond breaking		Bond making	
4 × C–H	4 × + 414 kJ mol^{-1}	4 × C=O	4 × –724 kJ mol^{-1}
C=C	+598 kJ mol^{-1}	4 × H–O	4 × –464 kJ mol^{-1}
3 × O=O	3 × + 494 kJ mol^{-1}		
	+3736 kJ mol^{-1}		–4752 kJ mol^{-1}

Δ_rH = +3736 – 4752 = –1016 kJ mol^{-1}

Review questions for Chapter 4

1 a The statement means that 9.2 kJ of heat energy are required to convert 1 mole of CH_4 liquid at its boiling point to CH_4 gas at the same temperature.
A = partial answer with minor error eg. no mention of 1 mole or same temperature, **M** = complete answer

b MgO, because it has the greatest $\Delta_{fus}H$ and $\Delta_{vap}H$.
A = answer, **M** = plus reason

c $\Delta_{fus}H < \Delta_{vap}H$ because in changing from a liquid to a gas the attractive forces between the particles must be completely overcome whereas in the change from solid to liquid those forces are only partially overcome.
A = partial answer with minor error eg. no mention of number of forces overcome, **M** = complete answer

2 Δ_cH(Al) will be half of $\Delta_fH(Al_2O_3)$ since there are two moles of Al in each mole of Al_2O_3, therefore Δ_cH(Al) = –838 kJ mol^{-1}. **A**

3
$$\Delta_rH = [2 \times \Delta_fH(H_2O) + 2 \times \Delta_fH(SO_2)] - [2 \times \Delta_fH(H_2S) + 3 \times \Delta_fH(O_2)]$$
$$= [(2 \times -241.8) + (2 \times -296.8)] - [(2 \times -20.6) + (3 \times 0)]$$
$$= -1036\text{ kJ mol}^{-1}$$

A = correct method, but error such as missing sign, **M** = complete answer

4
$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393\ \text{kJ mol}^{-1}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -285\ \text{kJ mol}^{-1}$$
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -888\ \text{kJ mol}^{-1}$$

$$C(s) + \cancel{O_2}(g) \longrightarrow \cancel{CO_2}(g) \quad \Delta H = -393\ \text{kJ mol}^{-1}$$
$$2H_2(g) + \cancel{O_2}(g) \longrightarrow \cancel{2H_2O(l)} \quad \Delta H = -285\ \text{kJ mol}^{-1} \times 2$$
$$\cancel{CO_2}(g) + \cancel{2H_2O(l)} \longrightarrow CH_4(g) + \cancel{2O_2}(g) \quad \Delta H = +888\ \text{kJ mol}^{-1}$$
$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \quad \Delta_f H = -75\ \text{kJ mol}^{-1}$$

A = a correct method attempted, **M** = correct substitutions, but error in final calculation, **E** = answer correct with unit

5
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow \cancel{H_2O(l)} \quad \Delta H = -286\ \text{kJ mol}^{-1}$$
$$\cancel{H_2O(l)} + \tfrac{1}{2}O_2(g) \longrightarrow H_2O_2(l) \quad \Delta H = +52\ \text{kJ mol}^{-1}$$
$$H_2(g) + O_2(g) \longrightarrow H_2O_2(l) \quad \Delta_f H = -234\ \text{kJ mol}^{-1}$$

A = correct method, but minor error, **M** = correct answer with correct working

6

Bond breaking		Bond making	
H–H	$+436\ \text{kJ mol}^{-1}$	$2 \times$ H–I	$2 \times -299\ \text{kJ mol}^{-1}$
I–I	$+151\ \text{kJ mol}^{-1}$		
	$+587\ \text{kJ mol}^{-1}$		$-598\ \text{kJ mol}^{-1}$

$$\Delta_r H = 587 - 598 = -11\ \text{kJ mol}^{-1}$$

A = correct method, but minor error, **M** = correct answer with correct working

7 For 8 sulfur atoms forming an S_8 ring 1808 kJ mol^{-1} of energy are released rather than just 1408 kJ mol^{-1} for 4 S_2 molecules. But for oxygen it's 1168 kJ for O_8 compared to 1976 kJ for 4 O_2.
A = valid attempt shown, **M** = energy released for each species correctly calculated, **E** = links correct conclusion to working or reasoning

Test yourself 5A

1 Atomic radii decrease. For each successive element, the extra electron goes into the same shell while the extra proton in the nucleus attracts the electron shell more strongly, thus decreasing the radius.
2 Largest: Mg, S, Na, K^+, P^{3-}, N^{3-}, Ca, K^+
3 The fluoride ion is larger than the fluorine atom because an extra electron has been added to the outer shell repelling the other electrons. The effective nuclear charge is the same (no proton added), so the radius increases.
4 **a** increases across a period **b** decreases down a group
5 **a** covalent **d** polar covalent
b ionic **e** polar covalent
c polar covalent **f** ionic

Test yourself 5B

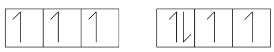
1 $Al(g) \longrightarrow Al^+(g) + e^-$ $\Delta H = 578$ kJ mol^{-1}
2 **a** The valence electrons of argon are further from the nucleus than those of neon, so it takes less energy to remove one electron from argon than from neon.
b Lithium's nuclear charge is +3, while neon's is +10, so neon's valence electrons are held more strongly than lithium's.
3 **a** ${}_{7}N^{3-}$: $1s^22s^22p^6$ **b** ${}_{33}As$: [Ar] $3d^{10}4s^24p^3$
c ${}_{28}Ni^{2+}$: [Ar] 3d **d** ${}_{24}Cr$: [Ar] $3d^54s^1$
e ${}_{35}Br^-$: [Ar] $3d^{10}4s^24p^6$ **f** ${}_{12}Mg^{2+}$: $1s^22s^22p^6$

Test yourself 5C

1 **a** +5 **b** yellow
2 **a** Almost all transition elements have the electron configuration $3d^n\,4s^2$. Loss of the $4s^2$ electrons gives a +2 oxidation state.
b Scandium has the electronic configuration [Ar] $3d^1\,4s^2$ and loss of the three outer electrons gives a +3 oxidation state.
c Copper has the electronic configuration [Ar] $3d^{10}\,4s^1$ so loss of $4s^1$ will result in an oxidation state of +1.
3 **a** Fe^{2+}, MnO_4^{2-}, V^{3+} **d** Fe^{3+}, $Cr_2O_7^{2-}$
b CrO_4^{2-}, VO_2^+ **e** MnO_4^-, V^{2+}
c Cu^{2+}, Cr^{3+}, VO^2 **f** CuO, MnO_2
4 Zinc's 3d orbital is full. Hence, there is no movement of electrons within this energy level, so no energy is absorbed in the visible region of the spectrum and therefore no colour.

Review questions for Chapter 5

1 **a** 2 There is a large jump in energy after the removal of the second electron, so this is a new shell.
A = correct number, **M** = correct reasoning
b $Q^+(g) \longrightarrow Q^{2+}(g) + e^-$ $\Delta H = 1144$ kJ mol^{-1}
A = correct equation, but error such as state signs missing, **M** = completely correct
2 **a** ${}_{31}Ga$ **c** ${}_{29}Cu$
b ${}_{16}S^{2-}$ **d** ${}_{25}Mn^{2+}$
A = 3 correct
3 **a** ${}_{14}Si$: $1s^22s^22p^63s^23p^2$ **d** ${}_{23}V$: [Ar] $3d^34s^2$
b ${}_{34}Se^{2-}$: [Ar] $3d^{10}4s^24p^6$ **e** ${}_{20}Ca^*$:[Ar]$4s^14p^1$ (example)
c ${}_{13}Al^{3+}$: $1s^22s^22p^6$ **f** ${}_{26}Fe^{2+}$: [Ar] $3d^6$
A = 4 correct
4 **a** The first IE decreases down a group in the periodic table because the outermost electron is further away from the nucleus and so easier to remove.
A = correct description, **M** = correct reasoning
b The general trend in IE moving across a period is for IE to increase because the effective nuclear charge is increasing while the electrons are going into the same shell. So, we would normally expect oxygen to have a higher IE than nitrogen. The fact that it is slightly lower means that oxygen's electron arrangement is less stable than nitrogen's:



Nitrogen Oxygen

Oxygen's least tightly held electron is paired, making it easier to remove.
A = mention of correct trend across the period and why, **M** = plus mentions fact that O has less stable electronic arrangement than N, **E** = offers explanation for lower stability of arrangement in O.
5 The orange/yellow brass dissolves in the colourless acid to form a green/blue solution and a brown gas, plus much heat. When water is added the solution turns pale blue. When colourless KI solution is added to the blue solution the colour changes to brown with a white precipitate. On titrating with colourless thiosulfate solution the brown colour fades to colourless.
A = gives 6 correct observations, M = gives 8 correct observations
6 **a** $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$
A = correct equation
b hydroxide ions
A = correct answer
7 **a** ${}_{24}Cr$: [Ar] $3d^5\,4s^1$ or $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$

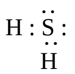
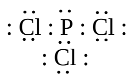
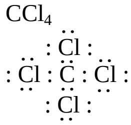
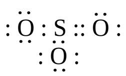
b $_{28}Ni$: $[Ar]\ 3d^8\ 4s^2$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
c $_{23}V^{3+}$: $[Ar]\ 3d^2$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$
d $_{26}Fe^{2+}$: $[Ar]\ 3d^5$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
A = 3 correct

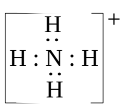
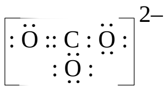
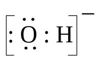
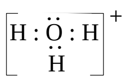
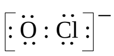
8 I: $\underline{Cu}_2O$, pink/brown or $\underline{Cu}I$, white
II: $\underline{Fe}SO_4$, pale green, or $\underline{V}^{2+}$, purple
III: $\underline{Fe}Cl_3$, orange/brown or $\underline{Cr}_2O_3$, dark green or $\underline{V}^{3+}$, green
IV: $\underline{Mn}O_2$, dark brown/black, or $\underline{V}O^{2+}$, blue
V: $\underline{V}_2O_5$, yellow
VI: $K_2\underline{Cr}_2O_7$, orange or $K_2\underline{Cr}O_4$, yellow
VII: $K\underline{Mn}O_4$, purple
A = 5 correct compounds and colours (others possible)

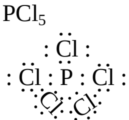
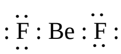
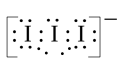
9 Sodium and magnesium compounds such as NaCl and MgO are white, whereas transition compounds are coloured ($FeCl_3$ is brown, $CuCl_2$ is green/blue). Transition elements make good catalysts—iron catalyses the Haber process and copper the oxidation of methanol—whereas sodium and magnesium are not used as catalysts. Transition metals form complexes such as $[FeSCN]^{2+}$ and $[Cu(NH_3)_4]^{2+}$, but sodium and magnesium don't form complexes. Sodium and magnesium have only one oxidation state each (Na^+ and Mg^{2+} apart from the element), but transition elements have many (Fe^{2+} and Fe^{3+}, Cu^+ and Cu^{2+}). Transition metals tend to be much harder and have higher melting points than non-transition metals. Sodium can be cut with a spatula and melts at 98 °C, whereas iron is very hard and melts at about 1500 °C.
A = mentions 2 points of diffence with examples,
M = mentions 3 points of difference with examples,
E = mentions 4 points of difference with examples

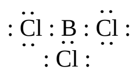
10 The Na atom is larger than the Cl atom because the extra electrons go into the same shell but the effective nuclear charge is +7 in Cl compared with +1 in Na, so they are pulled closer to the nucleus.
The Na^+ ion is smaller than the Cl^- ion because there is one shell less in Na^+ than in Cl^-.
A = correct explanation for one part, or incomplete explanations for both, **M** = correct explanations for both parts

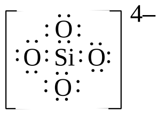
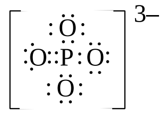
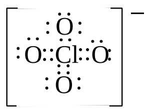
Test yourself 6A

1 **a** H_2S

b PCl_3

c CCl_4

d SO_3

e CO


2 **a** NH_4^+

b CO_3^{2-}

c OH^-

d H_3O^+

e OCl^-


3 **a** PCl_5

b BeF_2

c I_3^-

d NO

e BCl_3


4 **a** SiO_4^{4-}

b PO_4^{3-}

c ClO_4^-


Test yourself 6B

1 **a** bent **b** trigonal pyramidal **c** tetrahedral
d trigonal planar **e** linear

2 **a** Polar, because hydrogen and sulfur form polar bonds (different electronegativities) the molecule is not symetrical and the dipoles do not balance.
b Polar, because phosphorous and chlorine form polar bonds (different electronegativities) the molecule is not symmetrical and the dipoles do not balance.
c Non polar: polar bonds but symmetrical molecule so the dipoles balance.
d Non polar: polar bonds but symmetrical molecule so the dipoles balance.
e Polar, because carbon and oxygen form polar bonds and the molecule is not symmetrical and the dipoles do not balance.

3 **a** tetrahedral **b** trigonal planar **c** linear
d trigonal pyramidal **e** linear

4 **a** trigonal bipyramid **b** linear **c** linear
d linear **e** trigonal planar

5 **d** only

6 **a** 180° **b** 120° **c** 120° **d** 109°

7 Oxygen has a much greater electronegativity than hydrogen and attracts the electrons in the bond more strongly, hence the bond between O and H is polar. There are two O–H bonds, and there are also two pairs of non-bonding electrons. The four electron clouds are arranged tetrahedrally around the oxygen atom. The sum of the two dipoles is not zero, so the molecule is polar.

Test yourself 6C

1 **a** molecular **b** cov network **c** ionic
d metallic **e** molecular **f** cov network
g cov network **h** ionic **i** molecular

2 Water has a low boiling point, which is characteristic of molecular substances. In the vapour phase it exists as molecular $H_2O(g)$. If it had separated into discrete H and O atoms, then a spark would cause water vapour to explode. This does not happen. At a temperature of over 2000 °C the molecules do break up into atoms—which proves they have not broken into atoms at a lower temperature.

3 **a** covalent network **b** molecular
c molecular **d** ionic
e metallic **f** molecular

Test yourself 6D

1 **a** London (dispersion) forces **b** ionic bonds
c hydrogen bonds **d** London (dispersion) forces
e metallic bonds **f** permanent dipole forces

2 Compounds **a**, **d**, **g** and **h**

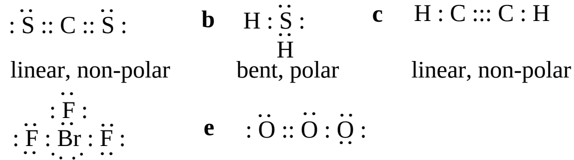
3 propane < butane < chloroethane < propanone < ethanol

4 Normal increase from HCl to HI as number of electrons per molecule increases. HF has an abnormally high melting point due to hydrogen bonding.

Review questions for Chapter 6

1 There are no angles of 180° or 90°. The angles involving the C=C carbons are 120°, as are the angles involving the C=O carbon. All other angles are 109°.
A = 1 correct angle marked, **M** = 2 correct angles marked

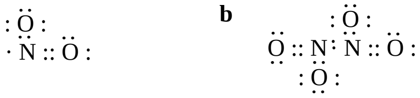
2



a linear, non-polar **b** bent, polar **c** linear, non-polar
d T-shaped, polar **e** bent, polar

A = 3 fully correct, **M** = 4 fully correct, **E** = all correct

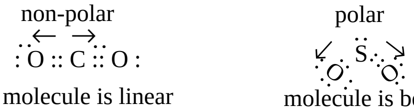
3 **a**, **b**



c At low temperatures the unpaired electrons in NO_2 can combine to form N_2O_4.
A = **a** correct, **M** = **a** and **b** correct, **E** = plus correct reason

4

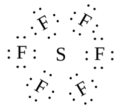
non-polar | polar



molecule is linear, dipoles are balanced | molecule is bent, dipoles unbalanced

A = correct, but some omission eg dipoles not mentioned, **M** = correct answer

5 **a** See below **b** octahedral **c** non-polar



A = correct Lewis diagram, **M** = all correct

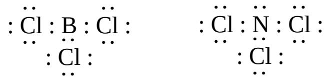
6 **a** trigonal planar **A** = correct answer
b The HCH bond will be slightly smaller than the HCO bond because the double bond C=O, which contains four electrons, has a slightly greater repulsion than the two single H–C bonds and will push those two bonds more closely together.
A = correct answer, **M** = plus correct explanation

7 We would expect H_2O to have the lowest BP and CH_3OCH_3 to have the highest based on molar mass only. However, H_2O molecules are hydrogen bonded because hydrogen is bonded to oxygen, a very electronegative atom, giving water a very high boiling point for its molecular size. CH_3OCH_3 is polar because of the electronegativity of oxygen and the bent shape of the molecule, so the molecule has a permanent dipole. The forces between these molecules are therefore stronger than those between the non-polar oxygen molecules (O_2) where only instantaneous dipole/induced dipole interactions occur.
A = correctly identifies the type of bonding and the effect on BP for each of the three substances, **M** = plus correctly accounts for the mechanism of two of the three inter-molecular forces, **E** = correctly accounts for all three mechanisms or mentions the expected trend due to molar mass only

8 Vegetable oils contain many double bonds, and it so happens that these are almost always *cis* bonds. The double bond is rigid, and the *cis* bonds put C-shaped kinks in the molecules, making the long-chain vegetable oil molecules difficult to fit closely together, which lowers the strength of the inter-molecular forces and thus their melting points.
Hydrogenating the oils breaks the double bonds, making the molecules more flexible and without those awkward kinks. The molecules are able to fit more closely together, increasing the inter-molecular forces and their melting points.
A = correctly states that breaking the double bonds results in molecules with increased forces between them and thus a higher MP, **M** = correctly explains that the cis- bonds results in molecules which are difficult to pack so have a low MP, **E** = complete explanation linking causes and effects

9 When salt melts, the ions separate as strong ionic bonds are broken. When sugar melts the molecules separate as weak van der Waals' forces are overcome. In each case, the solute-solvent attractive forces are greater than the solute-solute and solvent-solvent attractive forces.
A = correctly identifies the paticles and forces in each case, **M** = plus idea of relative strengths of various interactions

10 The Lewis diagrams for these two compounds are shown below:

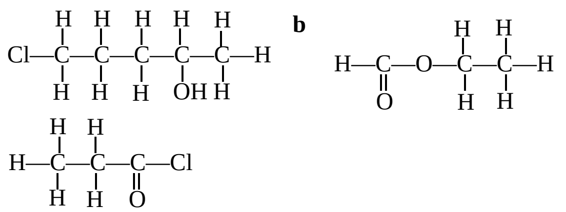


BCl_3 will be trigonal planar and non-polar, because the dipoles from the three polar B–Cl bonds are balanced. NCl_3 is trigonal pyramidal because there is a lone pair of electrons on the nitrogen atom which pushes the three polar N–Cl bonds below the plane. This gives rise to a polar molecule since the dipoles do not cancel. The inter-molecular forces between the polar NCl_3 molecule are much greater than those between non-polar BCl_3, so NCl_3 has a greater boiling point.
A = correctly states polarity of the molecules and relates this to the BP, **M** = plus correctly explains the polarity in terms of shape and dipoles, **E** = complete account linking answer to electronic structures stated or illustrated

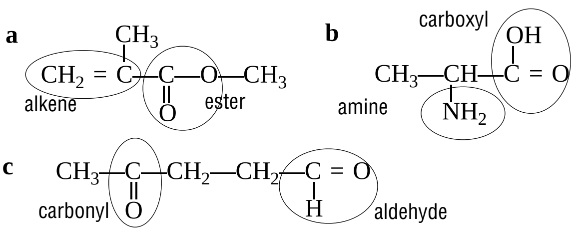
Test yourself 7A

1 **a** $NH_2(CH_2)_2COOH$ **b** $(CH_3)_2COHCH_2CH_3$
c $CH_2 = CHCH_2COCH_3$ **d** CH_3COOCH_3
e $(CH_3)_2CHNH_2$

2 **a**, **b**, **c**



3 **a**, **b**, **c**

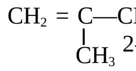


4 **a** butanone **b** propanamide
c 2-chloropropene **d** methylpropan-2-ol
e methyl ethanoate **f** ethanoyl chloride

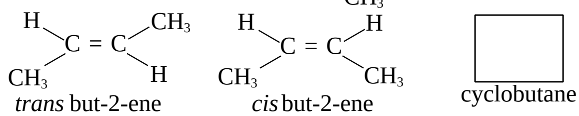
5 **a** CH_2ClCH_2COOH **b** $CH_2{=}CHCH(CH_3)_2$
c $CH_3CHBrCH_2OH$ **d** CH_3CH_2CHO
e $CH_3C(NH_2)ClCH_3$ **f** $CH_3CH_2COOCH_2CH_3$

Test yourself 7B

1 $CH_2 = CH—CH_2—CH_3$ but-1-ene



2-methylpropene

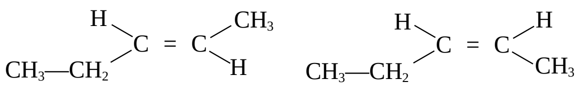


trans but-2-ene *cis* but-2-ene cyclobutane

2 a **ii** and **iv**

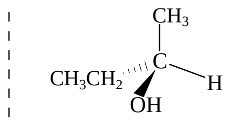
b

trans 1, 2 dichloropropene *cis* 1, 2 dichloropropene



trans pent-2-ene *cis* pent-2-ene

3



4 **a** and **d**

5 a The only physical difference is that the isomers rotate plane-polarised light in equal but opposite directions.

b In the majority of cases only one isomer is biologically active.

Test yourself 7C

1 $\longrightarrow CH_3CH_2C(CH_3)BrCH_2CH_3$ addition (2nd carbon got richer)

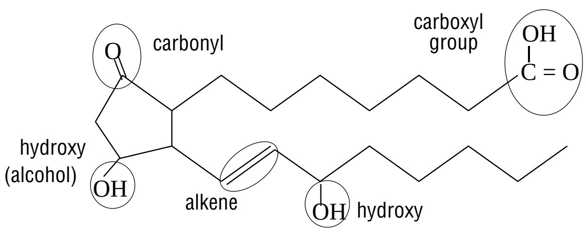
2 $\longrightarrow HCOOCH_2CH_2CH_3 + H_2O$ condensation

3 $\longrightarrow CH_3CH_2Br + HBr$ substitution

4 $\longrightarrow CH_3CH_2CH = C(CH_3)_2$ elimination (4th carbon got poorer)

Review questions for Chapter 7

1



A = 3 correct

2 a ethanal

b 3, 3-dichlorobut-1-ene

c 2-methyl, 3-aminobutane

d propanoyl chloride

e 2-methylbut-2-ene

A = 4 correct

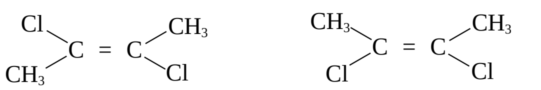
3 a CH_3CONH_2

b $CH_3(CH_2)_2COCH_3$

c HCOCl

A = 2 correct

4 a



trans 2, 3 dichlorobut-2-ene *cis* 2, 3 dichlorobut-2-ene

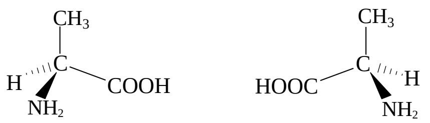
A = both correct

b *trans* **A**

c One. The chloro groups are not both on the double bond, and the double bond is on the end carbon.

A = correct answer, **M** = plus correct reasoning

5 a



A = both correct

b They will have identical chemical and physical properties except they will rotate plane-polarised light equal amounts in opposite directions. They may also behave differently in biochemical systems, reacting with bioactive chemicals differently.

A = correct affect on plane-polarised light, **M** = plus same physical and chemical properties, **E** = complete answer

6 a $CH_3CH = CHCH_3 + HCl \longrightarrow CH_3CH_2CHClCH_3$

b $CH_3CH_2OH + CH_3CH_2CH_2COOH \xrightarrow{\text{conc } H_2SO_4} CH_3CH_2CH_2COOCH_2CH_3$ $(+ H_2O)$

c $CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2CHO$

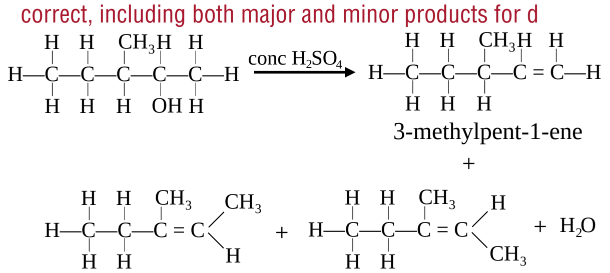
d $CH_3CH_2CH=CH_2 + H_2O \xrightarrow{\text{conc } H_3PO_4} CH_3CH_2CHOHCH_3 + CH_3CH_2CH_2CH_2OH$

major product minor product

e $CH_3(CH_2)_3CHO \longrightarrow CH_3(CH_2)_3COOH$

A = two correct, **M** = four organic products correct, **E** = all correct, including both major and minor products for d

7



3-methylpent-1-ene

\+

cis 3-methylpent-2-ene *trans* 3-methylpent-2-ene

A = one organic product with name correct, **M** = two organic products with names correct, **E** = all products and names correct

Test yourself 8A

1 CH_2OHCH_2OH ethan-1, 2-diol (ethylene glycol)

$CH_2OHCHOHCH_2OH$ propan-1, 2, 3-triol (glycerol)

2 a $CH_3(CH_2)_3CH_2OH$ pentan-1-ol

b $CH_3CH_2CH_2CHOHCH_3$ pentan-2-ol

c $CH_3CH_2C(CH_3)OHCH_3$ 2-methylbutan-2-ol

3 1° alcohols are oxidised to aldehydes, then to carboxylic acids; 2° alcohols are oxidised to ketones; 3° alcohols are not oxidised by $H^+/Cr_2O_7^{2-}$.

4 1° very slow (no apparent reaction); 2° slow (reacts in 10–20 minutes); 3° rapid.

5 a $CH_3CH(CH_3)CH_2OH \xrightarrow[\text{distillation}]{H^+/MnO_4^-} CH_3CH(CH_3)CHO$

b $CH_3OH \xrightarrow[\text{reflux}]{H^+/MnO_4^-} HCOOH$

c $CH_3CH_2CH_2CH(OH)CH_3 \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3CH_2CH_2COCH_3$

d $(CH_3)_3COH \xrightarrow{HCl/ZnCl_2} (CH_3)_3CCl$

e $CH_3(CH_2)_2CH_2OH \xrightarrow{PCl_5} CH_3(CH_2)_2CH_2Cl + POCl_3 + HCl$

f $CH_3CH_2OH \xrightarrow{SOCl_2} CH_3CH_2Cl + SO_2 + HCl$

Test yourself 8B

1 a $CH_3(CH_2)_3CH_2Cl$ 1-chloropentane

b $CH_3CH_2CH_2CHBrCH_3$ 2-bromopentane

c $CH_3CH_2C(CH_3)ClCH_3$ 2-methyl 2-chlorobutane

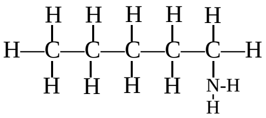
2 MP and BP are greater than the corresponding alkane, but less than the corresponding alcohols; haloalkanes are less soluble in water than the corresponding alcohol.

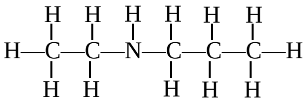
3 A nucleophile is any species which is attracted to a positive charge, eg OH^- or NH_3(alc).

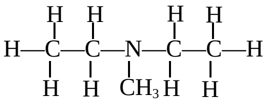
4 a $CH_3CH_2Br + KOH(aq) \longrightarrow CH_3CH_2OH + KBr(aq)$
b $CH_3CH_2CHICH_3 + NH_3(alc) \longrightarrow CH_3CH_2CH(NH_2)CH_3 + HI(alc)$

5 a $CH_3CH_2C(CH_3)_2OH + KOH(alc) \longrightarrow CH_3CH = C(CH_3)_2 + H_2O$
b elimination

Test yourself 8C

1 a


b


c


2 Test it with litmus paper—an amine will turn damp litmus paper blue. Or hold an open bottle of conc HCl beside the open bottle of suspected amine. Dense white fumes should form.

3 a $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$
methyl ammonium hydroxide
b $CH_3CH_2NH_2 + HCl \longrightarrow CH_3CH_2NH_3^+Cl^-$
ethyl ammonium chloride
c $Cu^{2+}(aq) + 4CH_3CH_2CH_2NH_2 \longrightarrow [Cu(CH_3CH_2CH_2NH_2)_4]^{2+}(aq)$

Test yourself 8D

1 Aldehydes (except methanal) are colourless liquids with pungent, unpleasant smells, more volatile and with lower melting points than the corresponding alcohols. Although both are oxidised by $H^+/Cr_2O_7^{2-}$, only aldehydes are oxidised by Tollens or Benedict reagents.

2 The diammine silver complex, $[Ag(NH_3)_2]^+$. A positive test is a silver mirror or a black precipitate and it is used to distinguish between aldehydes and ketones.

3 a The blue solution turns green to yellow to an orange precipitate.
b $Cu^{2+}(aq)$ (blue) and Cu_2O (orange)

4 They are structural isomers.

Review questions for chapter eight

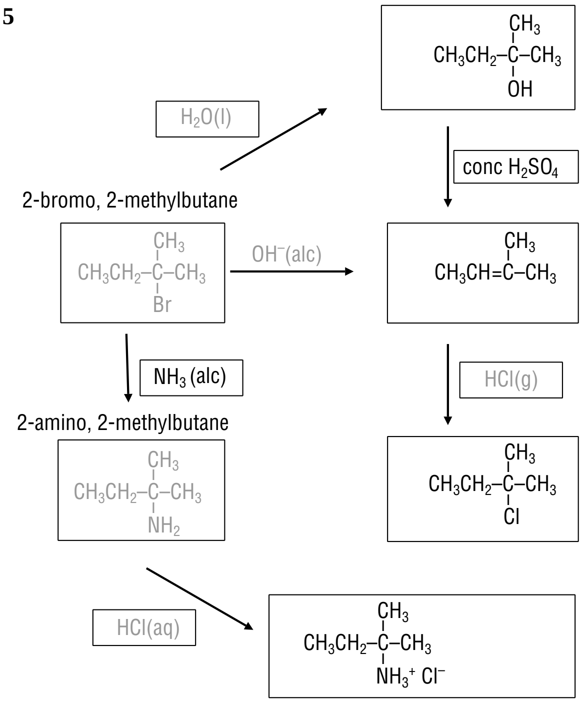
1 a They are both aldehydes. **A**
b $CH_3CH(CH_3)CHO$ methyl propanal **M** = both correct
c pent-1-ene **A**
d primary **A**
e $CH_3COOCH_2CH_2CH_2CH_3$ **A**

2 a CH_3CH_2Cl chloroethane
b $CH_3CH_2NH_3^+Cl^-$ ethyl ammonium chloride
c $CH_3CHNH_2CH_3$ 2-aminopropane
d CH_3COCH_3 propanone
e $CH_3CH = CHCH_3$ but-2-ene
A = 3 correct, **M** = all correct

3 a $CH_3CH_2C(CH_3)OHCH_2CH_3 \xrightarrow{HCl/ZnCl_2} CH_3CH_2C(CH_3)ClCH_2CH_3$
b $CH_3Cl + OH^-(aq) \longrightarrow CH_3OH + Cl^-(aq)$
c $CH_3CH_2CH_2CHO \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3CH_2CH_2COOH$
d $CH_2 = CHCH_2CH_3 \xrightarrow[\text{conc } H_3PO_4]{H_2O} CH_3CHOHCH_2CH_3$
e $CH_3CH_2CH_2CH_2CHO \xrightarrow{[Ag(NH_3)_2]^+} CH_3CH_2CH_2CH_2COOH$

A = 3 correct, **M** = 4 correct including reagents, **E** = all correct including reagents

4 a 2-aminobutane is basic to litmus paper—2-chlorobutane is not.
b Propanal will form a silver mirror with Tollens reagent; propan-1-ol will not react with Tollens reagent.
c Butan-2-ol will turn Lucas reagent cloudy in 10–20 minutes while butan-1-ol will not appear to react at all.
A = 2 correct, **M** = 3 correct

5


A = 4 names or structures correct, **M** = 6 names or structures correct, **E** = all correct including special conditions

Test yourself 9A

1 Carboxylic acids have higher MP and BP than their corresponding alcohols; the lower acids are soluble in water; lower acids have strong smells. They react with bases, metals and carbonates in the same way as inorganic acids.

2 Organic acids are weaker acids than hydrochloric acid, reacting more slowly.

3 a $2HCOOH + CaCO_3 \longrightarrow (HCOO^-)_2Ca^{2+} + CO_2 + H_2O$
calcium methanoate
b $CH_3CH_2CH_2COOH + KOH \longrightarrow CH_3CH_2CH_2COO^- K^+ + H_2O$
potassium butanoate
c $2CH_3COOH + Na \longrightarrow 2CH_3COO^- Na^+ + H_2$
sodium ethanoate
d $HCOOH + CH_3CH_2OH \xrightarrow{\text{conc } H_2SO_4} HCOOCH_2CH_3 + H_2O$
ethyl methanoate
e $CH_3CH_2COOH + SOCl_2 \longrightarrow CH_3CH_2COCl + SO_2 + HCl$
propanoyl chloride

4 The butanoic acid reacts with the baking soda to form sodium butanoate which is an ionic salt and thus has no smell.

Test yourself 9B

1 $CH_3CH_2COOH + PCl_5 \longrightarrow CH_3CH_2COCl + POCl_3 + HCl$

2 It reacts with the moisture in the air to release HCl gas.

3 a $CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$
b $CH_3CH_2CH_2COCl + CH_3OH \longrightarrow CH_3CH_2CH_2COOCH_3 + HCl$
c $HCOCl + CH_3CH_2NH_2 \longrightarrow HCONHCH_2CH_3 + HCl$
d $CH_3CH_2COCl + H_2O \longrightarrow CH_3CH_2COOH + HCl$

Test yourself 9C

1 a propyl methanoate b methyl propanoate
c ethyl butanoate

2 a CH_3COOCH_3 b $CH_3CH_2COOCH_2CH_2CH_2CH_3$

3 Heat and an acid catalyst. Using conc H_2SO_4 also drives the reaction to the right by absorbing the H_2O formed.

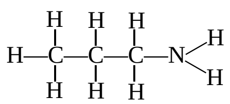
4 Low-mass alcohols are miscible in water and have higher melting points than the esters they form. Esters are immiscible in water.

5 a $CH_3CH_2COOCH_2CH_3 + H_2O \xrightarrow{\text{dil HCl}} CH_3CH_2COOH + CH_3CH_2OH$
b $CH_3CH_2CH_2COOCH_3 + NaOH(aq) \longrightarrow CH_3CH_2CH_2COO^-Na^+ + CH_3OH$
c $CH_3COOCH_3 + NH_3(alc) \longrightarrow CH_3CONH_2 + CH_3OH$

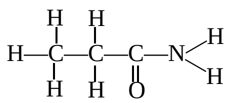
6 $CH_3(CH_2)_2COCl + CH_3(CH_2)_3CH_2OH \longrightarrow CH_3(CH_2)_2COOCH_2(CH_2)_3CH_3 + HCl$

Test yourself 9D

1



1-aminopropane



propanamide

2 a $CH_3COCl + NH_3(alc) \longrightarrow CH_3CONH_2 + HCl$
b $CH_3CH_2COOCH_2CH_3 + NH_3(alc) \longrightarrow CH_3CH_2CONH_2 + CH_3CH_2OH$
c $CH_3CH_2CH_2CONH_2 + H_3O^+Cl^- \longrightarrow CH_3CH_2CH_2COOH + NH_4^+Cl^-$
d $CH_3CH_2CONH_2 + Na^+OH^- \longrightarrow CH_3CH_2COO^-Na^+ + NH_3$

3 Except for methanamide, all amides are odourless, white, crystalline solids at room temperature, while low-mass amines are liquids with strong smells. Both amines and amides are soluble in water. Amines are strong bases, while amides are much weaker bases. Amines react with HCl to form salts, while amides are hydrolysed by HCl to form the carboxylic acid and ammonium chloride.

Test yourself 9E

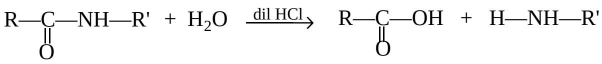
1 A = 2-methylpropan-2-ol B = propanone
C = methyl ethanoate D = propan-1-ol
E = propanal

2 $CH_3CH(NH_2)CH_3 + H_2O \longrightarrow CH_3CH(NH_3^+)CH_3 + OH^-$
$CH_3CH_2COOH + H_2O \longrightarrow CH_3CH_2COO^- + H_3O^+$

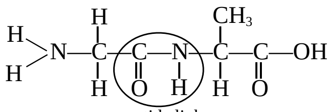
Test yourself 9F

1 a polythene, PVC b urea-formaldehyde, nylon, polyester
c starch, protein

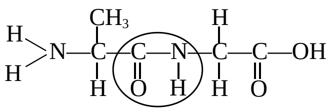
2 Nylon is a polyamide containing many peptide links. In aqueous acid, these links hydrolyse, breaking the polymer into its constituent monomers:



3



peptide link

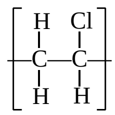


Review questions for Chapter 9

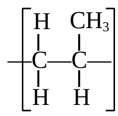
1 a $CH_3COOCH_2CH_3 + H_2O \longrightarrow CH_3COOH + CH_3CH_2OH$
ethyl ethanoate + water ethanoic acid + ethanol
b $CH_3CH_2COOC_2H_5 + NH_3 \longrightarrow CH_3CH_2CONH_2 + CH_3CH_2OH$
ethyl propanoate + ammonia propanamide + ethanol
c $CH_3CH_2CH_2OH + CH_3COCl \longrightarrow CH_3COOCH_2CH_2CH_3 + HCl$
propan-1-ol + ethanoyl chloride propyl ethanoate + hydrogen chloride
d $CH_3CONH_2 + H_2O \longrightarrow CH_3COOH + NH_3$
ethanamide + water ethanoic acid + ammonia
A = 3 correct, **M** = 4 correct

2 a $HCOOH + PCl_5 \longrightarrow HCOCl + POCl_3 + HCl$
b $CH_3CH_2CH_2COCl + H_2O \longrightarrow CH_3CH_2CH_2COOH + HCl$
c $CH_3CH_2COCl + NH_3 \longrightarrow CH_3CH_2CONH_2 + HCl$
d $CH_3COCl + CH_3CH_2CH_2NH_2 \longrightarrow CH_3CO—NH—CH_2CH_2CH_3 + HCl$
A = 3 correct, **M** = 4 correct

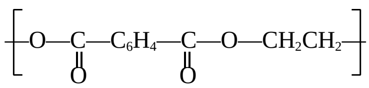
3 a



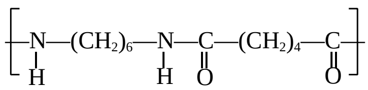
b



c



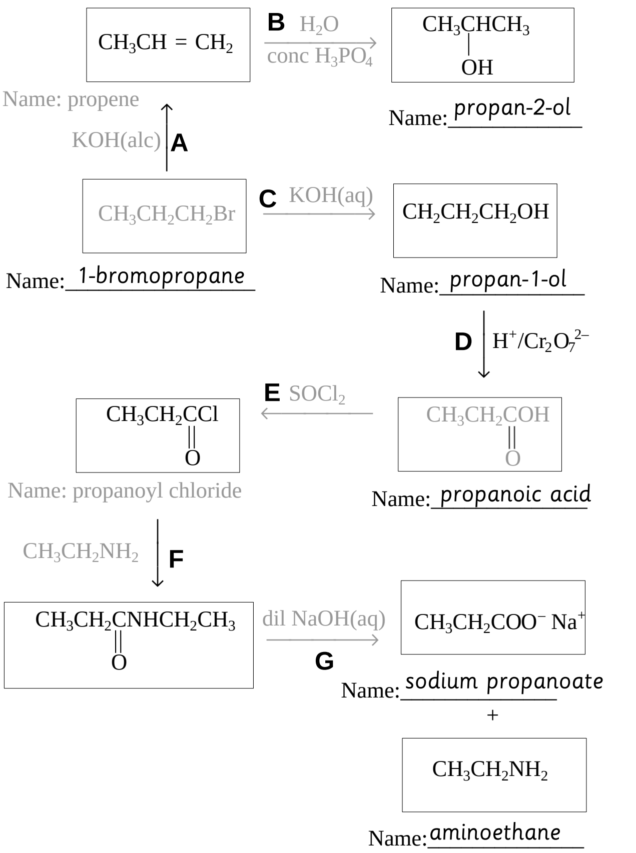
d



A = 3 correct, **M** = 4 correct

4 Propanamide will be a solid (while all the others are liquids). Amides have significantly higher melting points than other compounds of similar molar mass. They are soluble in water and form neutral solutions.
Hold damp red and blue litmus paper over the samples.
Aminoethane will turn litmus blue:
$CH_3CH_2NH_2 + H_2O \longrightarrow CH_3CH_2NH_3^+ + OH^-$
Ethanoyl chloride will turn litmus red:
$CH_3COCl + H_2O \longrightarrow CH_3COOH + H^+ + Cl^-$
Ethyl methanoate and cyclohexane do not dissolve in water: cyclohexane is non-polar, and although ethyl methanoate is polar, it does not form hydrogen bonds with water. Ethyl methanoate is volatile with a distinctly fruity smell, while cyclohexane has no smell.
A = correctly identifies 4 compounds, **M** = 4 compounds identified with justification for 2 compounds, including one correct equation, **E** = all compounds identified with 2 equations and one other compound justified

5 a See below:



A = 8 blanks correctly filled, M = 10 of the 14 blanks correctly filled, E = all reactants, reagents and names correct

b Thionyl chloride. A

c **i** elimination **iii** oxidation
ii (nucleophilic) substitution **iv** hydrolysis

A = 3 correct, M = 4 correct

d propan-1-ol and propan-2-ol A

e The reaction must be done under reflux because the alcohol is first oxidised to an aldehyde, which has a low boiling point and would boil away if not returned to the reaction vessel for further oxidation to the acid.

A = correct conditions, M = 4 correct explanation

Test yourself 10A

1 a $SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$

b s = 0.012 g per 100 g of water
$= 0.12\ g\ L^{-1}$
$= 9.6 \times 10^{-4}\ mol\ L^{-1}$

c $[Sr^{2+}] = 9.6 \times 10^{-4}\ mol\ L^{-1}$, $[F^-] = 2 \times 9.6 \times 10^{-4}\ mol\ L^{-1}$

d $K_s = [Sr^{2+}][F^-]^2$
$= [9.6 \times 10^{-4}][2 \times 9.6 \times 10^{-4}]^2$
$= 3.5 \times 10^{-9}$

2 a $M(AgI) = 234.77\ g\ mol^{-1}$

$$\text{solubility} = \frac{2.8 \times 10^{-6}\ g\ L^{-1}}{234.77\ g\ mol^{-1}} = 1.19 \times 10^{-8}\ mol\ L^{-1}$$

b $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

c $K_s = [Ag^+][I^-]$

d $[Ag^+] = [I^-] = 1.19 \times 10^{-8}$
$K_s = (1.19 \times 10^{-8})^2$
$= 1.4 \times 10^{-16}$

3 a $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$

b $K_s = [Pb^{2+}][Br^-]^2$

c Let the solubility be s.
$[Pb^{2+}] = s \quad [Br^-] = 2s$
$K_s = 4s^3$
$$\sqrt[3]{\frac{K_s}{4}} = s$$
$$\sqrt[3]{\frac{6.3 \times 10^{-6}}{4}} = s$$
$0.012\ mol\ L^{-1} = s$

4 $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$
$K_s = [Fe^{2+}][OH^-]^2$
Let the solubility be s, $[Fe^{2+}] = s \quad [OH^-] = 2s$
$K_s = s(2s)^2$
$1.64 \times 10^{-14} = 4s^3$
$$\sqrt[3]{\frac{1.64 \times 10^{-14}}{4}} = s$$
$1.6 \times 10^{-5}\ mol\ L^{-1} = s$

Test yourself 10B

1 $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

$$[Ca^{2+}] = [SO_4^{2-}] = \frac{10\ mL}{20\ mL} \times 0.001\ mol\ L^{-1} = 5 \times 10^{-4}\ mol\ L^{-1}$$

Ionic product $= [Ca^{2+}][SO_4^{2-}]$
$= (5 \times 10^{-4})^2$
$= 2.5 \times 10^{-7}$

Ionic product $< K_s$ so no precipitate will form.

2 a $[Pb^{2+}] = 0.025\ mg\ L^{-1}$
$= 2.5 \times 10^{-5}\ g\ L^{-1}$
$$= \frac{2.5 \times 10^{-5}\ g\ L^{-1}}{207.2\ g\ mol^{-1}}$$
$= 1.2 \times 10^{-7}\ mol\ L^{-1}$

b $$[Pb^{2+}] = \frac{9\ mL \times 1.2066 \times 10^{-7}\ mol\ L^{-1}}{(9\ mL + 1\ mL)}$$
$= 1.1 \times 10^{-7}\ mol\ L^{-1}$

c $$[CrO_4^{2-}] = \frac{1\ mL \times 0.100\ mol\ L^{-1}}{(9\ mL + 1\ mL)}$$
$= 0.0100\ mol\ L^{-1}$

d IP $= [Pb^{2+}][CrO_4^{2-}]$
$= (1.1 \times 10^{-7}\ mol\ L^{-1})(0.0100\ mol\ L^{-1})$
$= 1.1 \times 10^{-9}\ mol\ L^{-1}$
IP $> K_s$ so precipitation will occur

3 At pH = 13, $[OH^-] = 0.1\ mol\ L^{-1}$.
$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$
$K_s = [Mg^{2+}][OH^-]^2$
$$\frac{K_s}{[OH^-]^2} = [Mg^{2+}]$$
$$\frac{1 \times 10^{-11}}{(0.1)^2} = [Mg^{2+}]$$
$1 \times 10^{-9}\ mol\ L^{-1} = [Mg^{2+}]$

Review questions for Chapter 10

1 a $K_s = [Zn^{2+}][CO_3^{2-}]$ **A**

b $M(ZnCO_3) = 125.39 \text{ g mol}^{-1}$

$$\text{solubility} = \frac{4.86 \times 10^{-4} \text{ g L}^{-1}}{125.39 \text{ g mol}^{-1}}$$
$$= 3.88 \times 10^{-6} \text{ mol L}^{-1} = [Zn^{2+}] = [CO_3^{2-}]$$
$$K_s = [Zn^{2+}][CO_3^{2-}]$$
$$= (3.88 \times 10^{-6} \text{ mol L}^{-1})^2$$
$$= 1.50 \times 10^{-11}$$

A = correct method, but minor error, **M** = correct answer

2 a $Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$

$$K_s = [Ca^{2+}][OH^-]^2$$

Let the solubility be s

$$K_s = 4s^3$$
$$\sqrt[3]{\frac{K_s}{4}} = s$$
$$\sqrt[3]{\frac{7.9 \times 10^{-6}}{4}} = s$$
$$0.013 \text{ mol L}^{-1} = s$$

A = correct method, but minor error, **M** = correct answer

b
$$[OH^-] = \frac{5 \text{ mL}}{100 \text{ mL}} \times 0.1 \text{ mol L}^{-1}$$
$$= 5 \times 10^{-3} \text{ mol L}^{-1}$$
$$[Ca^{2+}] = \frac{95 \text{ mL}}{100 \text{ mL}} \times 0.1 \text{ mol L}^{-1}$$
$$= 0.095 \text{ mol L}^{-1}$$
$$IP = [Ca^{2+}][OH^-]^2$$
$$= (0.095)(5 \times 10^{-3})^2$$
$$= 2.4 \times 10^{-6}$$

IP < K_s so a precipitate will *not* form.

A = correct method, but total volume ignored, **M** = correct with minor error, **E** = correct working and correct reasoning

3 a $K_s = [Ba^{2+}][SO_4^{2-}]$ **A**

b Let the solubility be s, then $[Ba^{2+}] = [SO_4^{2-}] = s$

$$K_s = [Ba^{2+}]^2$$
$$\sqrt{K_s} = [Ba^{2+}]$$
$$\sqrt{1.5 \times 10^{-9}} = [Ba^{2+}]$$
$$3.9 \times 10^{-5} = [Ba^{2+}]$$

A = correct method, but minor error, **M** = correct answer

c
$$[SO_4^{2-}] = 1.0 \text{ mol L}^{-1}$$
$$K_s = [Ba^{2+}][SO_4^{2-}]$$
$$\frac{K_s}{[SO_4^{2-}]} = [Ba^{2+}]$$
$$\frac{1.5 \times 10^{-9}}{1.0} = [Ba^{2+}]$$
$$1.5 \times 10^{-9} = [Ba^{2+}]$$

A = correct method, but minor error, **M** = correct answer

d Using K_2SO_4 reduces the concentration of poisonous Ba^{2+} ions by a factor of 10 000.

A = reduces concentration, **M** = plus correct factor

Test yourself 11A

1 a $\longrightarrow NO_3^-(aq) + H_3O^+(aq)$

b $\rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

2 a H_2O **b** H_2S **c** $CH_3NH_3^+$

3 $HSO_3^-(aq) + H_3O^+(aq) \rightleftharpoons H_2SO_3(aq) + H_2O(l)$

$HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$

4 A strong acid is one that donates protons readily or dissociates completely.
A concentrated acid is one which contains a high concentration of acid, either dissociated or undissociated.

5 $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$
Hence excess hydroxide ions, so alkaline solution.

Test yourself 11B

1
$$[H^+] = 0.0250 \text{ mol L}^{-1}$$
$$pH = -\log_{10}[H^+]$$
$$= -\log_{10}(0.0250)$$
$$= 1.60$$

2
$$[H^+] = 10^{-pH}$$
$$= 10^{-2.8}$$
$$= 1.58 \times 10^{-3} \text{ mol L}^{-1}$$
$$c(HCl) = 1.58 \times 10^{-3} \text{ mol L}^{-1}$$

3
$$[OH^-] = 0.004\,00 \text{ mol L}^{-1}$$
$$[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$
$$= \frac{1 \times 10^{-14}}{0.004\,00}$$
$$= 2.5 \times 10^{-12}$$
$$pH = -\log_{10}[H^+]$$
$$= -\log_{10}(2.5 \times 10^{-12})$$
$$= 11.6$$

4
$$[H_3O^+] = 10^{-pH}$$
$$= 10^{-4.31}$$
$$= 4.90 \times 10^{-5} \text{ mol L}^{-1}$$

Test yourself 11C

1 a $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$

b $K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$

c $pK_a = -\log_{10}(K_a) = 3.3$

2 $H_2SO_3 > HOCN > HCOOH > HCO_3^-$

3 $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

Assume $[HF] = 0.0500 \text{ mol L}^{-1}$, $[H_3O^+] = [F^-]$

$$K_a = \frac{[H_3O^+]^2}{0.0500}$$
$$\sqrt{7.2 \times 10^{-4} \times 0.0500} = [H_3O^+]$$
$$6.0 \times 10^{-3} = [H_3O^+]$$
$$pH = 2.22$$

4 $HOBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OBr^-(aq)$

$$K_a = \frac{[H_3O^+][OBr^-]}{[HOBr]}$$

Assume $[HOBr] = 1.50 \text{ mol L}^{-1}$, $[H_3O^+] = [OBr^-]$

$$K_a = \frac{[H_3O^+]^2}{1.50}$$
$$\sqrt{2.40 \times 10^{-9} \times 1.50} = [H_3O^+]$$
$$6.00 \times 10^{-5} = [H_3O^+]$$
$$pH = 4.22$$

$$\boxed{\begin{aligned} K_a &= 10^{-pK_a} \\ &= 10^{-8.62} \\ &= 2.40 \times 10^{-9} \end{aligned}}$$

Test yourself 11D

1 $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Assume $[NH_3] = 0.100$ mol L^{-1}; $[NH_4^+] = [OH^-]$

$$K_b = \frac{[OH^-]^2}{0.100}$$

$$\sqrt{1.74 \times 10^{-5} \times 0.100} = [OH^-]$$

$$1.32 \times 10^{-3} = [OH^-]$$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$= 7.58 \times 10^{-12}$$

$$pH = 11.1$$

$$\boxed{K_b = \frac{1 \times 10^{-14}}{K_a} = \frac{1 \times 10^{-14}}{5.75 \times 10^{-10}} = 1.74 \times 10^{-5}}$$

2 $M(NH_4Cl) = 53.5$ g mol^{-1}

$$n = \frac{m}{M} = cV$$

$$c = \frac{m}{MV}$$

$$c(NH_4Cl) = \frac{5.00 \text{ g}}{53.5 \text{ g mol}^{-1} \times 30.0 \times 10^{-3} \text{ L}}$$

$$= 3.12 \text{ mol L}^{-1}$$

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Assume $[NH_4^+] = 3.12$ mol L^{-1}; $[NH_3] = [H_3O^+]$

$$K_a = \frac{[H_3O^+]^2}{3.12}$$

$$\sqrt{5.75 \times 10^{-10} \times 3.12} = [H_3O^+]$$

$$4.24 \times 10^{-5} = [H_3O^+]$$

$$4.37 = pH$$

Test yourself 11E

1 **a** $[H_2O(l)] > [HCOOH(aq)] > [H_3O^+(aq)] > [HCOO^-(aq)] > [OH^-(aq)]$

b $[H_2O(l)] > [Na^+(aq)] > [SO_4^{2-}(aq)] > [H_3O^+(aq)] = [OH^-(aq)]$

c $[H_2O(l)] > [Na^+(aq)] > [F^-(aq)] > [OH^-(aq)] > [HF(aq)] > [H_3O^+(aq)]$

d $[H_2O(l)] > [C_6H_{12}O_6(aq)] > [H_3O^+(aq)] = [OH^-(aq)]$

Review questions for Chapter 11

1 **a** $[H_3O^+] = 0.0350$ mol L^{-1}

$$pH = -\log_{10}[H_3O^+]$$

$$= 1.46$$

A

b $[OH^-] = 2 \times 1.37 \times 10^{-3}$ mol L^{-1}

$$= 2.74 \times 10^{-3} \text{ mol L}^{-1}$$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$= 3.65 \times 10^{-12} \text{ mol L}^{-1}$$

$$pH = 11.4$$

A = correct method, but minor error, **M** = correct pH

2 **a** $K_a = 2.40 \times 10^{-9}$

b
$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{2.40 \times 10^{-9}} = 4.17 \times 10^{-6}$$

c HOCl is the stronger acid (smaller pK_a)

A = 2 of 3 correct

3 $HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

Assume $[HCOOH] = 0.120$ mol L^{-1}; $[HCOO^-] = [H_3O^+]$

$$K_a = \frac{[H_3O^+]^2}{0.120}$$

$$\sqrt{1.8 \times 10^{-4} \times 0.120} = [H_3O^+]$$

$$4.65 \times 10^{-3} \text{ mol L}^{-1} = [H_3O^+]$$

$$2.33 = pH$$

A = correct method, but minor error, **M** = correct pH

4 $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

Assume $[CH_3NH_2] = 0.100$ mol L^{-1}; $[CH_3NH_3^+] = [OH^-]$

$$K_b = \frac{[OH^-]^2}{0.100}$$

$$\sqrt{5.0 \times 10^{-4} \times 0.100} = [OH^-]$$

$$7.07 \times 10^{-3} \text{ mol L}^{-1} = [OH^-]$$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$= 1.41 \times 10^{-12}$$

$$pH = 11.8$$

$$\boxed{K_b = \frac{1 \times 10^{-14}}{K_a} = \frac{1 \times 10^{-14}}{2.0 \times 10^{-11}} = 5.0 \times 10^{-4}}$$

A = correct method, **M** = correct working, but with minor error, **E** = correct working and correct pH

5 $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Assume $[CH_3COO^-] = 0.250$ mol L^{-1}; $[CH_3COOH] = [OH^-]$

$$K_b = \frac{[OH^-]^2}{0.250}$$

$$\sqrt{5.56 \times 10^{-10} \times 0.250} = [OH^-]$$

$$1.18 \times 10^{-5} \text{ mol L}^{-1} = [OH^-]$$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$= 8.49 \times 10^{-10}$$

$$pH = 9.07$$

$$\boxed{K_b = \frac{1 \times 10^{-14}}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}}$$

A = correct method, **M** = correct working, but with minor error, **E** = correct working and correct pH

6 $NH_4NO_3(s) + \text{water} \longrightarrow NH_4^+(aq) + NO_3^-(aq)$ complete

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ incomplete

$H_2O > NO_3^-(aq) > NH_4^+(aq) > H_3O^+(aq) > NH_3(aq) > OH^-(aq)$

A = 4 species in correct order, **M** = plus equations, **E** = 6 species in correct order and equations correct

7 $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$\text{Assume } [H_3O^+] = [CH_3COO^-]$$

$$1.74 \times 10^{-5} = \frac{(1 \times 10^{-4}\text{ mol L}^{-1})^2}{[CH_3COOH]}$$

$$[CH_3COOH] = \frac{(1 \times 10^{-4}\text{ mol L}^{-1})^2}{1.74 \times 10^{-5}}$$

$$= 5.75 \times 10^{-4}\text{ mol L}^{-1}$$

A = correct method, but minor error, **M** = correct answer

Test yourself 12A

1 The pH remains essentially constant when moderate amounts of either acid or base are added.

2 Ethanoic acid/sodium ethanoate or ammonia/ammonium chloride.

3 **a** $CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$
b $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

4 When [HA] = [A−]

5 Dissolve 84 g (1 mol) of solid $NaHCO_3$ in 1 L of 1.0 mol L^{-1} H_2CO_3 solution (or 8.4 g in 1 L of 0.1 mol L^{-1} H_2CO_3 solution).

6 **a** $[HCOOH] = 5 \times 10^{-3}\text{ mol L}^{-1}$, $[HCOO^-] = 7 \times 10^{-3}\text{ mol L}^{-1}$.

b
$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

$$\frac{K_a[HCOOH]}{[HCOO^-]} = [H_3O^+]$$

c
$$\frac{1.8 \times 10^{-4} \times 5.0 \times 10^{-3}}{7.0 \times 10^{-3}} = [H_3O^+]$$

$$1.286 \times 10^{-4} = [H_3O^+]$$

$$3.89 = \text{pH}$$

d Since both [HCOOH] and [HCOO−] are reduced by a factor of 10, the pH will remain constant.

7 $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$

$$K_a = \frac{[CN^-][H_3O^+]}{[HCN]}$$

$$\frac{[CN^-]}{[HCN]} = \frac{K_a}{[H_3O^+]}$$

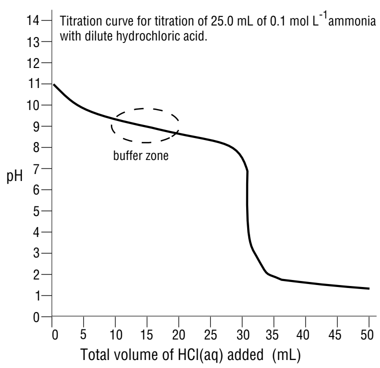
$$= \frac{6.0 \times 10^{-10}}{1 \times 10^{-9}}$$

$$= 0.6$$

Hence, [HCN] > [CN−]

Test yourself 12B

1 **a** 11 **b** 30 mL **c** See below.



d 15 mL **e** $pK_a = 9$

f methyl red

g $NH_3(aq) + HCl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$

h
$$n(NH_3) = cV$$
$$= 0.100\text{ mol L}^{-1} \times 25.0 \times 10^{-3}\text{ L}$$
$$= 2.5 \times 10^{-3}\text{ mol}$$
$$n(HCl) = n(NH_3)$$
$$= 2.5 \times 10^{-3}\text{ mol}$$
$$c(HCl) = \frac{n}{V}$$
$$= \frac{2.5 \times 10^{-3}\text{ mol}}{30.0 \times 10^{-3}\text{ L}}$$
$$= 0.083\text{ mol L}^{-1}$$

i Total volume at equivalence point = 25.0 mL + 30.0 ml
At equivalence point $n(NH_4Cl) = 2.5 \times 10^{-3}$ mol

$$c(NH_4Cl) = \frac{2.5 \times 10^{-3}\text{ mol}}{55 \times 10^{-3}\text{ L}}$$
$$= 0.045\text{ mol L}^{-1}$$

$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$
$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$
$pK_a = 9.0$, hence $K_a = 1.0 \times 10^{-9}$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$\text{Assume } [H_3O^+] = [NH_3]$$
$$[NH_4^+] = [\text{salt}]$$
$$\therefore 1.0 \times 10^{-9} = \frac{[H_3O^+]^2}{0.045\text{ mol L}^{-1}}$$
$$[H_3O^+]^2 = (1.0 \times 10^{-9})(0.045\text{ mol L}^{-1})$$
$$= 4.5 \times 10^{-11}$$
$$\therefore [H_3O^+] = \sqrt{4.5 \times 10^{-11}}$$
$$= 6.7 \times 10^{-6}$$
$$\therefore \text{pH} = 5.2$$

Review questions for Chapter 12

1 When acid is added to the water the indicator turns red due to the excess of H_3O^+ ions. When acid is added to the other solution the indicator remains green (or turns slightly yellow). The second tube contains a buffer which resists changes in pH.
A = correct observations, **M** = correct explanations

2 **a** $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$ **A**

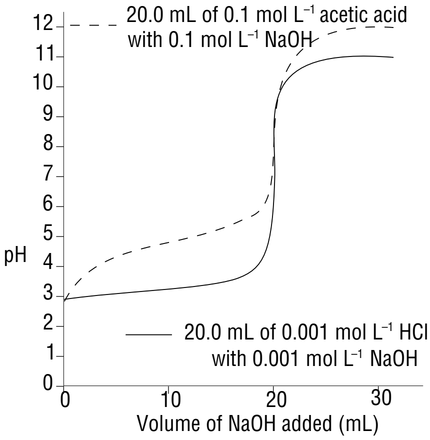
b Assume $[HA] = 0.10\text{ mol L}^{-1}$; $[H_3O^+] = [A^-]$

$$[H_3O^+] = 10^{-3.40}$$
$$= 3.98 \times 10^{-4}$$
$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$
$$= \frac{(3.98 \times 10^{-4})^2}{0.10}$$
$$= 1.58 \times 10^{-6}$$
$$pK_a = -\log_{10} K_a$$
$$= 5.8$$

A = correct method but minor error, **M** = correct pK_a

c $[HA] = [A^-]$ so $pH = pK_a = 5.8$
A = correct value

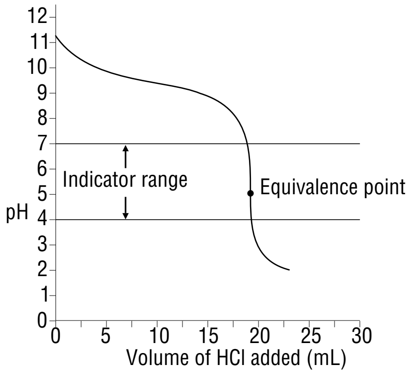
3 See below. Note especially the pH at the beginning and end of each titration.



A = rough sketches but insufficient detail, **M** = all parts correct

4 **a** $NH_3(aq) + HCl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$ **A**

b See below. Use methyl red which changes colour in the range from pH 4–6, which is in the vertical portion of the graph.



A = suitable rough sketches, **M** = correct sketch with appropriate points and indicator range shown

c

$$\begin{aligned}
n(HCl) &= cV \\
&= 0.100 \text{ mol L}^{-1} \times 19.2 \times 10^{-3} \text{ L} \\
&= 1.92 \times 10^{-3} \text{ mol} \\
n(NH_3) &= n(HCl) \\
&= 1.92 \times 10^{-3} \text{ mol} \\
c(NH_3)_{dil} &= \frac{n}{V} \\
&= \frac{1.92 \times 10^{-3} \text{ mol}}{20.0 \times 10^{-3} \text{ L}} \\
&= 0.096 \text{ mol L}^{-1} \\
c(NH_3)_{commercial} &= c(NH_3)_{dil} \times \frac{250.0 \text{ mL}}{25.0 \text{ mL}} \\
&= 0.96 \text{ mol L}^{-1} \\
c(NH_3)_{commercial} &= 0.96 \text{ mol L}^{-1} \times 17 \text{ g mol}^{-1} \\
&= 16.32 \text{ g L}^{-1} \\
&= 1.63\%
\end{aligned}$$

A = correct $n(NH_3)$, **M** = correct throughout but minor error, **E** = all correct

5 $C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$

$$\begin{aligned}
K_a &= \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]} \\
pH &= 3.5 \\
\therefore [H_3O^+] &= 3.16 \times 10^{-4} \text{ mol L}^{-1} \\
pK_a &= 4.20 \\
\therefore K_a &= 6.31 \times 10^{-5}
\end{aligned}$$

$$\text{Hence, } \frac{[C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{6.31 \times 10^{-5}}{3.16 \times 10^{-4}} = 0.1997 = 0.20$$

Hence, the ratio of benzoic acid to benzoate ion is 5:1.

A = correct method but minor error, **M** = correct ratio

6 $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$\begin{aligned}
K_b &= \frac{[NH_4^+][OH^-]}{[NH_3]} \\
\frac{K_b[NH_3]}{[NH_4^+]} &= [OH^-] \\
-\log_{10}K_b - \log_{10}\left(\frac{[NH_3]}{[NH_4^+]}\right) &= -\log_{10}[OH^-] \\
pK_b + \log_{10}\left(\frac{[NH_4^+]}{[NH_3]}\right) &= pOH \\
\log_{10}\left(\frac{[NH_4^+]}{[NH_3]}\right) &= (14 - pH) - pK_b \\
&= 14 - 9.75 - 4.75 \\
&= -0.5 \\
\frac{[NH_4^+]}{[NH_3]} &= 10^{-0.5} \\
&= 0.316
\end{aligned}$$

So make up the buffer by dissolving 1.0 mol of ammonia in one litre of water and adding 0.316 mol of ammonium chloride.

$M(NH_3) = 17 \text{ g mol}^{-1}$, so $m(NH_3) = 17$ g.

$M(NH_4^+) = 53.5 \text{ g mol}^{-1}$, $m(NH_4Cl) = 53.5 \times 0.316 = 16.9$ g.

This is an alternative method, not involving logs.

$$\begin{aligned}
K_b &= \frac{[NH_4^+][OH^-]}{[NH_3]} \\
\frac{K_b[NH_3]}{[NH_4^+]} &= [OH^-] \\
[H_3O^+] &= 10^{-pH} \\
&= 10^{-9.75} \\
&= 1.778 \times 10^{-10} \\
[OH^-] &= \frac{[1 \times 10^{-14}]}{[H_3O^+]} \\
&= \frac{1 \times 10^{-14}}{1.778 \times 10^{-10}} \\
&= 5.623 \times 10^{-5} \\
\frac{[NH_3]}{[NH_4^+]} &= \frac{[OH^-]}{K_b} \\
&= \frac{5.623 \times 10^{-5}}{1.778 \times 10^{-5}} \\
&= 3.16
\end{aligned}$$

$$\boxed{\begin{aligned} K_b &= 10^{-pK_b} \\ &= 10^{-4.75} \\ &= 1.778 \times 10^{-5} \end{aligned}}$$

Make up a solution containing 1 mol of NH_4Cl and 3.16 mol of NH_3.

$M(NH_4^+) = 53.5 \text{ g mol}^{-1}$, $m(NH_4Cl) = 53.5$ g

$M(NH_3) = 17 \text{ g mol}^{-1}$, so $m(NH_3) = 17 \times 3.16 = 53.7$ g.

Note: although these methods produce apparently completely different answers, they are both correct. There are an infinite number of ways to prepare solutions with the same ratio of $[NH_3]$ to $[NH_4^+]$; providing the ratio is correct, the buffer will have the required pH.

A = suitable method attempted but incorrect substitution(s), **M** = suitable method with correct working but minor error(s), **E** = correct masses or ratio calculated

[This page is blank]

Final checklist	Good enough for Achieve	Going for Excellence
Have I done enough practical work?		
Have all the necessary solutions been standardised?		
Is there sufficient replication for valid results?		
Is the range appropriate?		
Have I done enough to be sure my results are reliable?		
Is my log book ready?		
Are all entries dated?		
Is everything recorded in the log book? (If you have data or notes written on other scraps of paper, paste them into your log book.)		
Is everything labelled clearly so that someone else can follow it?		
Is my report complete?		
The aim		
Have you stated your aim clearly?		
Have you included background information related to your aim?		
The method		
Have you summarised your experimental procedure including a description of your analytical method?		
Have you discussed how the method works and any areas of special concern related to this method?		
Have you justified any modifications made to your method?		
Have you discussed how the relevant variables are controlled?		
The results		
Is your raw data clearly accessible in your log book?		
Does your report contain a sample calculation that someone else can follow?		
Is your use of significant figures and units in calculations correct throughout?		
Have you presented your final results with appropriate table(s) and/or graph(s)?		
The conclusion		
Have you written a conclusion, based on your results, that answers your aim?		
The evaluation		
Have you discussed the reliability of your results?		
Have you discussed the quality or accuracy of your results?		
Have you discussed how you could improve this experiment if you had more time or equipment?		
The bibliography		
Have you included a bibliography showing where your information came from?		

Equipment and chemicals required

Equipment

List the equipment you will need. Include any bottles required for storage of reagents and/or sample solutions.

Chemicals

Estimate the total number of analyses you propose to do.

Complete this table to estimate the volume of each reagent required. Also indicate whether this solution will be made up for you, or whether you need to make it up yourself.

Reagent	Concentration	Volume required per analysis	Volume required for all analyses	Is this solution supplied?

Highlight those solutions on the table above whose concentration must be accurately known. These are solutions you will need to either prepare or standardise yourself.

Summarise the method you will use to determine the concentration of each of these solutions.

Milestone 2 Will my experiment work?

Name ____________________

Does the method work on my substance?

Date due____________________

Analyse a sample of your substance, using the proposed method. It is not necessary to use standardised solutions for this trial, provided the concentrations are approximately those recommended.

Record your data here.

Do the calculations required to estimate the concentration of your test sample.

Are your titres or other measurements large enough to give accurate answers? (Normal titres should be between about 12 mL and 30 mL; with back titrations the difference between the sample and blank should be between 12 mL and 30 mL.) If not, dilute the solutions accordingly.

Is your proposed range still suitable?

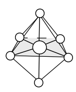
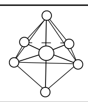
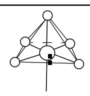
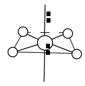
What modifications are needed to your proposed method?

Continue overleaf

[This page is blank]

Milestone 1 Is my experiment OK? Name______________________________

	Date due______________________
What is your **aim**?	
What is your **dependent variable** (what you are testing for)?	
What is your **independent variable** (the thing you change)?	
What is the **range** of your independent variable?	
State the factors that need to be **controlled** (kept constant) and how you propose to control them.	
State what you will do to make sure your results are **reliable**.	
What kind of analytical technique will you use (circle)?	Titration Colorimetry Gravimetric Other (specify)
Attach a copy of your proposed method.	
Name the **chemicals** and **special equipment** required.	

No. of electron clouds around central atom	Arrangement of electron clouds	Possible shapes of final molecule	
6			
		octahedral	square-based pyramid
	bond angle 90°		
		square planar	

Intermolecular forces

74	Van der Waals' forces between ___ molecules are also known as dispersion forces or London forces.	non-polar
75	___ bonding occurs when H is bonded to N, O or F.	hydrogen
76	Molecules with ___ surface areas have strong van der Waals' forces between them.	large
77	Straight-chain alkanes have ___ boiling points than their branched-chain isomers.	higher
78	Hydrogen bonds are about __% the strength of covalent bonds.	10
79	The many unusual properties of ___ are mainly due to hydrogen bonding.	water
80	Their more awkward ___ keeps molecules of cis isomers further apart than their trans equivalents.	shape
81	Molecular substances have relatively low melting points because __ __ __ __ are weak.	van der Waals forces

Continuing Chemistry

Key Facts
for Level 3 Chemistry

Anne Wignall and Terry Wales

Pearson Education New Zealand

Name ____________________

How to use this booklet

No matter how clever you are (or are not), some aspects of Level 3 Chemistry just have to be learnt. The better you know the statements in this booklet, the easier you will find it to understand the questions in tests and exams and the faster you will be able to answer them.

Use a small card to cover up either the clue or the answer, then slide the card down one clue at a time as you say each answer out loud, or write it. (Remember: you need to be good at writing down your answers for the exam.)

The Revision Tasks on the CD will help you to learn these facts and your teacher may test you on them using the Quizzes.

Just knowing the contents of this booklet will not be enough to get your through the exams. Your study should also include answering lots of written questions — such as those found in Continuing Chemistry, and the exam papers on the CD.

To be adequately prepared for the external examinations you need to have done about 25 hours of exam revision. Don't leave it all until November!

© Pearson Education 2007

Ions you should know

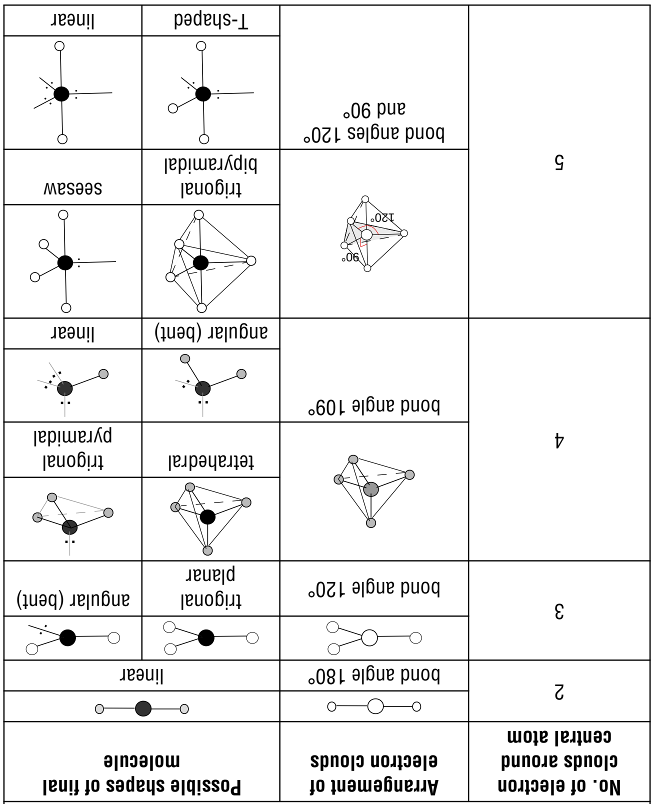
Positive ions		Negative ions	
Al^{3+}	aluminium	Br^{-}	bromide
NH_4^+	ammonium	CO_3^{2-}	carbonate
Ba^{2+}	barium	Cl^{-}	chloride
Ca^{2+}	calcium	CrO_4^{2-}	chromate
Cr^{3+}	chromium(III)	$Cr_2O_7^{2-}$	dichromate
Cu^{+}	copper(I) [cuprous]	F^{-}	fluoride
Cu^{2+}	copper(II) [cupric]	HCO_3^{-}	hydrogen carbonate [bicarbonate]
H^{+}	hydrogen	HSO_3^{-}	hydrogen sulfite [bisulfite]
Fe^{2+}	iron(II) [ferrous]	OH^{-}	hydroxide
Fe^{3+}	iron(III) [ferric]	OCl^{-}	hypochlorite
Pb^{2+}	lead	I^{-}	iodide
Li^{+}	lithium	NO_3^{-}	nitrate
Mg^{2+}	magnesium	O^{2-}	oxide
Hg^{2+}	mercury(II) [mercuric]	MnO_4^{-}	permanganate
K^{+}	potassium	PO_4^{3-}	phosphate [orthophosphate]
Ag^{+}	silver	SO_4^{2-}	sulfate
Na^{+}	sodium	S^{2-}	sulfide
Sn^{2+}	tin	SO_3^{2-}	sulfite
Zn^{2+}	zinc	SCN^{-}	thiocyanate
		$S_2O_3^{2-}$	thiosulfate

Naming organic compounds

The IUPAC system for naming carbon chains

Number of carbons	Prefix	Side chain	Number of carbons	Prefix	Side chain
1	meth-	methyl	5	pent-	pentyl
2	eth-	ethyl	6	hex-	hexyl
3	prop-	propyl	7	hept-	heptyl
4	but-	butyl	8	oct-	octyl

Homologous series	**Suffix**	
Alkenes	-ene	indicate position of C=C eg but-e-ene
Alcohols	-anol	indicate position of –OH eg propan-1-ol
Haloalkanes	-ane	indicate position of halogens eg 2, 3-dichlorobutane
Aldehydes	-anal	eg pentanal
Ketones	-anone	indicate position of C=O eg pentan-2-one
Carboxylic acids	-anoic acid	eg methanoic acid
Amines	-ane	indicate position of NH_2 eg 3-aminopentane
Esters	-anoate	eg propyl ethanoate
Acyl chlorides	-anoyl chloride	eg ethanoyl chloride
Amides	-anamide	eg propanamide



Shapes of molecules

No. of electron clouds around central atom	Arrangement of electron clouds	Possible shapes of final molecule	
2	bond angle 180°	linear	
3	bond angle 120°	trigonal planar	angular (bent)
4	bond angle 109°	tetrahedral	trigonal pyramidal
		angular (bent)	linear
5	bond angles 120° and 90°	trigonal bipyramidal	seesaw
		T-shaped	linear

Buffers and titration curves

146	A ___ solution is one that resists changes in pH caused by addition of moderate amounts of acid or base.	buffer
147	Buffer solutions contain a mixture of a weak acid (or base) and its ___ base (or acid)	conjugate
148	In a buffer solution, if [HA] = [A–], then __ = pK_a.	pH
149	When buffer solutions are ___ the pH remains constant.	diluted
150	When stoichiometric amounts of acid and base are present the titration is at its ___ point.	equivalence
151	Acid-base indicators change colour when the pH of the solution is equal to the ___ of the indicator.	pK_a
152	Choose an ___ for a pH titration that changes colour closest to the pH at the equivalence point.	indicator
153	The equivalence point is at the midpoint of the ___ part of a pH titration curve.	vertical

Oxidation and reduction

1	An oxidising agent is also called an ___.	oxidant
2	During reduction the oxidation number of a species goes ___.	down
3	A reductant is a ___.	reducing agent
4	Reducing agents are ___ during reactions.	oxidised
5	Oxidation is a ___ of electrons.	loss
6	Oxidising agents are ___ during reactions.	reduced
7	During oxidation the oxidation number of a species goes ___.	up
8	Oxidising agents ___ electrons to/from species.	remove
9	Reduction is a ___ of electrons.	donate
10	Reducing agents ___ electrons to/from species.	gain

Volumetric analysis

11	The shape makes it easy to swirl the reaction mixture for quick mixing of reagents.	conical flask
12	When writing mole ratios for titration problems, the unknown goes on the ___.	top

Transition elements

70	Almost all transition elements have several different ___ states	oxidation
71	Transition elements tend to form ___ compounds.	coloured
72	Almost all transition elements have ___ d-orbitals	incomplete
73	Many transition elements are useful ___ in industrial reactions.	catalysts

Species	ON	Colour	Species	ON	Colour
V^{2+}	+2	purple	MnO_4^{2-}	+6	green
V^{3+}	+3	green	MnO_4^-	+7	purple
VO^{2+}	+4	blue	Fe^{2+}	+2	green
VO_2^+	+5	yellow	Fe^{3+}	+3	orange
Cr^{3+}	+3	blue/green	CuI(s)	+1	white
CrO_4^{2-}	+6	yellow	Cu2O(s)	+1	brick-red
$Cr_2O_7^{2-}$	+6	orange	Cu2+	+2	blue
Mn^{2+}	+2	pale pink	CuO(s)	+2	black
MnO_2(s)	+4	brown	ZnO(s)	+2	white (yellow when hot)

Complexes

$[Cu(NH_3)_4]^{2+}$ is royal blue; $FeSCN^{2+}$ is blood-red;

$[Cu(H_2O)_6]^{2+}$ is pale blue

Group	Group name	Homologous series
C = C	double bond	alkenes
–OH	hydroxyl group	alcohols
–C(=O)—OH	carboxyl group	carboxylic acids
–O—C(=O)–	ester	esters
–Cl	chloro group	chloroalkanes
–C(=O)–	carbonyl group	ketones
–C(=O)—H	aldehyde group	aldehydes
$–NH_2$	amino group	amines
–C(=O)—Cl	acyl chloride	acyl chlorides
–C(=O)—NH_2	amide	amides

Reduced form		Oxidised form	
Formula	**Appearance**	**Formula**	**Appearance**
Cu	brown solid	Cu^{2+}	blue ion
SO_2	colourless gas	SO_4^{2-}	colourless ion
Mn^{2+}	colourless ion	H^+/MnO_4^-	purple ion
H_2O_2	colourless liquid	O_2	colourless gas
H_2O	colourless liquid	H_2O_2	colourless liquid
Cr^{3+}	blue/green ion	$Cr_2O_7^{2-}$	orange ion
Fe^{2+}	pale green ion	Fe^{3+}	orange ion
Cl^-	colourless ion	Cl_2	pale green gas
Br^-	colourless ion	Br_2	red/orange liquid
H_2	colourless gas	H^+	colourless ion
MnO_2	brown precipitate	H_2O/MnO_4^-	purple ion
MnO_4^{2-}	green ion	OH^-/MnO_4^-	purple ion
I^-	colourless ion	I_2 (in $I^- = I_3^-$)	brown solution
I_2 (in $I^- = I_3^-$)	brown solution	IO_3^-	colourless ion
H_2S	colourless gas	S	yellow/white solid
Pb^{2+}	colourless ion	PbO_2	brown solid
NO_2	brown gas	NO_3^-	colourless ion
$C_2O_4^{2-}$	colourless ion	CO_2	colourless gas
$S_2O_3^{2-}$	colourless ion	$S_4O_6^{2-}$	colourless ion
Br_2	red-orange liquid	BrO_3^-	colourless ion

132 The ___ product is the same as the expression for K_s but applies when the system is not in equilibrium. — ionic

133 If the ionic product is ___ than the solubility product, then a precipitate will form. — greater

134 The solubility of an ionic compound ___ in a solution containing a common ion. — decreases

Acids and bases

135 An acid is a proton ___. — donor

136 A base is a proton ___. — acceptor

137 When we remove a proton from an acid we form its ___ base. — conjugate

138 ___ substances can either donate or accept protons. — amphiprotic

139 Strong acids or bases ___ completely — dissociate

140 Weak acids and bases are only ___ dissociated. — partially

141 The salts of weak acids will be slightly ___. — basic

142 K_a is known as the acid ___ constant. — dissociation

143 The larger the K_a the ___ the acid. — stronger

144 The larger the pK_a the ___ the acid. — weaker

145 Salts of weak acids or bases ___ in water to form solutions which are not neutral. — hydrolise

Hydrocarbons

82 A ___ series is a family of organic compounds with different numbers of CH_2 groups. — homologous

83 The 'interesting' part of an organic molecule, responsible for its distinctive properties, is its ___ group. — functional

84 ___ isomers differ in the order in which the atoms are arranged within the molecule. — structural

85 Stereoisomers are different because of the ___ arrangement of the atoms. — spatial

86 *Cis-trans* isomers are also known as ___ isomers. — geometric

87 Geometric isomers occur because the ___ bond is rigid and does not rotate. — double

88 'The poor get poorer' applies to some ___ reactions. — elimination

89 'The rich get richer' is a summary of ___'s rule. — Markovnikov

90 Markovnikov's rule applies during ___ reactions involving unsymmetric compounds. — addition

59 The tendency of an atom to attract electrons to itself is its ___. — electronegativity

60 Non-metals have ___ electronegativities — high

61 Atomic radii decrease going ___ ___ ___ of the periodic table. — across a period

Ionisation energy

62 Ionisation energies are always measured on ___ atoms or ions. — gaseous

63 The second ionisation energy of an element is always ___ than the first. — greater

64 Ionisation energies always have ___ (positive or negative?) enthalpies. — positive

65 The energy required to remove the least tightly bound electron from each particle of one mole of gaseous atoms or ions. — ionisation energy

66 Ionisation energies relate to the formation of ___ ions only. — positive

67 First ionisation energies ___ going down a group (eg He to Kr). — decrease

68 The general trend is for first ionisation energies to ___ going across a period (from Na to Ar). — increase

69 The zig-zag shape of the graph showing first ionisation energies against atomic number reveals evidence of the electron ___ within — orbitals

13	A volumetric flask should be rinsed with ___.	water
14	In calculations, the accuracy of the final answer should be the same as the accuracy of the ___ accurate data.	least
15	The volume of liquid used in a titration is called the ___.	titre
16	A ___ standard must be available in pure form. be stable in air, react to completion and have a relatively large molar mass.	primary
17	Used to measure volumes of liquid with moderate accuracy.	measuring cylinder
18	A ___ accurately delivers a fixed volume of liquid.	pipette
19	To standardise a solution is to find its ___.	concentration
20	Pipettes and burettes should be rinsed with the solution they will ___.	contain
21	Used to make up accurate solutions of one fixed volume.	volumetric flask
22	A ___ accurately delivers a variable volume of liquid.	burette
23	Titration results that are very close together are called ___ results.	concordant
24	A solution whose concentration is accurately known is a ___ solution.	standard

Thermochemistry

47	Heats of combustion are determined on substances in their ___ states.	standard
48	Enthalpies of combustion relate to the complete combustion of ___ of the substance.	one mole
49	Enthalpies of combustion are always ___ (positive or negative?).	negative
50	Bond energies are always measured on substances in the ___ state.	gaseous
51	Bond energies relate to the breaking of a bond to form separate ___.	atoms
52	Bond breaking is an ___ process.	endothermic
53	Tables of bond energies show the ___ energy from bonds in many compounds.	average
54	Bond making is an ___ process.	exothermic

Atoms

55	Atomic radii increase going ___ __ ___ of the periodic table.	down a group
56	The ionic radius of a positive ion is ___ than the atomic radius of its parent atom.	smaller
57	Metal atoms have ___ electronegativities.	low
58	The ionic radius of a negative ion is ___ than the atomic radius of its parent atom.	larger

Optical isomerism

91	___ isomers contain a carbon atom with 4 different groups attached to it.	optical
92	Optical isomers rotate plane-polarised light in ___ directions.	opposite
93	The molecules of opposite optical isomers cannot be ___.	superimposed
94	Optical isomers have molecules which are __ __ of each other.	mirror images
95	Optical isomers have identical physical and chemical properties but behave differently in ___ organisms..	living
96	Optically active compounds ___ plane-polarised light.	rotate
97	An asymmetric carbon is also called a ___ centre.	chiral
98	In optically active compounds, the carbon atom with four different groups on it is sometimes called the ___ carbon.	asymmetric

121	A condensation polymer made from about 300 glucose monomers is ___.	starch
122	The link between each amino acid unit in a protein molecule is called a ___ link.	peptide
123	___ is a disaccharide, made by joining a glucose molecule and a fructose molecule.	sucrose
124	Nylon, polyester and protein are all ___ polymers.	condensation
125	Polythene, PVC and polypropylene are all ___ polymers.	addition
126	PCl_3, PCl_5 or $SOCl_2$ can be used to convert a carboxylic acid into an ___ ___.	acyl chloride

Solubility

127	A saturated solution is in ___ with undissolved solid.	equilibrium
128	K_s – the ___ product – is the equilibrium constant for a saturated solution.	solubility
129	Soluble substances have ___ solubility products.	high
130	When writing equilibrium equations for solubility, always put the solid on the ___.	left
131	The most common unit for solubility is ___ per ___.	moles per litre

Phase changes

37	$\Delta_{vap}H$ indicates the strength of the forces holding the particles together in the ___ state.	liquid
38	A substance's molar heat of fusion is measured at its ___ point.	melting
39	Temperature measures the ___ kinetic energy of all the particles in a sample.	average
40	$\Delta_{fus}H$ indicates the strength of the forces holding the particles together in the ___ state.	solid
41	Heat measures the ___ of the kinetic energies of all the particles in a sample.	sum
42	The greater the ___, the greater the melting point.	$\Delta_{fus}H$
43	At 0 Kelvin particles have no ___ energy.	kinetic
44	The greater the ___, the greater the boiling point.	$\Delta_{vap}H$
45	A substance's molar heat of vaporisation is measured at its ___ point.	boiling
46	When substances change phase (state) the ___ energy of the particles is changing.	potential

Alcohols, haloalkanes and amines

99	H_2O, OH^-, Cl^- and NH_3(alc) are all ___.	nucleophiles
100	___ alcohols are oxidised to ketones.	secondary
101	___ alcohols and haloalkanes are the most easily substituted.	tertiary
102	___ alcohols are oxidised to aldehydes.	primary
103	___ reagent is used to classify alcohols.	Lucas
104	Amines have a characteristic ___ smell.	fishy
105	Alcoholic ammonia reacts with haloalkanes to form an ___.	amine
106	___ KOH reacts with haloalkanes to form an alcohol.	aqueous
107	Amines react with acids to form odourless ___.	salts
108	____ solution forms a royal blue complex with amines.	copper sulfate
109	___ KOH react with haloalkanes to form an alkene.	alcoholic
110	Amines are relatively strong ___.	bases

Electrochemical cells

25	In cell diagrams, the left-hand cell is written as ___.	oxidation
26	Standard $E°$ potentials are measured at a temperature of __ °C.	25
27	A salt bridge provides a path for ___ to move from one half-cell to the other.	ions
28	Standard $E°$ potentials are measured with respect to the standard ___ half-cell.	hydrogen
29	In cell diagrams, the right-hand cell is written as ___.	reduction
30	The electrode where oxidation occurs is the ___.	anode
31	In cell diagrams, the symbol // means a ___.	salt bridge
32	The electrode where reduction occur is the ___.	cathode
33	Standard $E°$ potentials are measured at a concentration of ___ mol L^{-1}.	1.0
34	In cell diagrams, the symbol / means a change of ___.	phase
35	Standard $E°$ potentials are measured at a pressure of ___ kPa.	100
36	A series of electrochemical cells connected together forms a ___.	battery

Aldehydes and ketones

111	If you are lucky, a silver mirror will form using ___ reagent.	Tollens
112	During a positive test with Benedict solution, the mixture turns ___.	brick-red
113	Tollens, Benedict or Fehling's solutions are all ___ agents.	oxidising
114	Anhydrous sodium sulfate is used to remove ___ from an organic product.	water
115	Mixtures of organic compounds can be separated by ___ distillation.	fractional
116	When using a condenser, the ___ hose should be connected to the tap.	bottom
117	Benedict and Fehling's solutions both contain the ___ ion.	Cu^{2+}
118	Sodium carbonate solution is used to ___ excess acid during the preparation of a haloalkane.	neutralise

Carboxylic acid derivatives and polymers

119	Esters, amides and acyl chlorides all undergo ___ reactions with water.	hydrolysis
120	All reactions involving acyl chlorides produce ___ gas as one product.	HCl