NUFFIELD

ADVANCED CHEMISTRY

TEACHERS' GUIDE

FOURTH
EDITION

Longman

Nuffield Advanced Chemistry

Teachers' Guide

Fourth edition

Published for the Nuffield Foundation by Pearson Education

Acknowledgements
We are indebted to Chem 13 News for permission to reproduce the poem 'Solubility Rules' and author's agents PFD for the poem 'Carbon' by Roger McGough from DEFYING GRAVITY published by Penguin © Roger McGough.

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ISBN 0582 328365

First published 1970
Revised edition published 1984
Third edition published 1994
Fourth edition published 2000
Fourth impression 2005
Printed in China
NPCC/04

The Publisher's policy is to use paper manufactured from sustainable forests.

Note
All references to the **Book of Data** are to the Nuffield Advanced Science book published by Longman.

www.nufieldfoundation.org/curriculum

Nuffield Advanced Chemistry
4th edition

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This edition of Nuffield Advanced Chemistry is dedicated to Michael Vokins.

Contents

Appendices

Foreword

In 1961 the Nuffield Foundation's Trustees took the momentous decision to make a major investment into the reform of science education. One of their key principles was to identify talented people and to give them the freedom and resources to develop up-to-date, challenging new courses. This, the fourth edition of Nuffield Advanced Chemistry, is a testament to the rightness of that principle, and to the vision of those who first developed the course.

The major themes of Nuffield Chemistry were identified in the 1960s by Frank Halliwell, Ernest Coulson, Gordon Van Praagh, and Bryan Stokes. These themes have stood the test of time. In this edition, as in the previous revisions, it has been enthusiastic teachers from a wide range of schools and colleges who have helped to reinterpret the ideas and refresh the teaching approaches. Generations of able and creative teachers have kept the course fresh and lively so that it is as relevant today as it was when first published in 1970. The Foundation owes an enormous debt to the current team of editors many of whom were there at the start to pilot the course and teach from pre-publication versions of the material. Their energy, combined with the quality of the examiners has been vital to the continuing success of the course.

Nuffield projects have always explored new ways to reinterpret science at the frontiers so that it can be taught intelligently in schools. The Nuffield physicists, for example, showed that it was possible to introduce a statistical approach to thermodynamics in a way which would allow post-16 students to pursue the ideas in their thinking. This work has found its natural place in the Chemistry project. Nuffield projects have also featured up-to-date and authentic examples of the applications of science. In Advanced Chemistry this is most obvious in the Special Studies which are regularly updated with the help of experts in the various fields of applied chemistry.

The Nuffield Foundation seeks to maintain high standards in the quality of its publications and in this respect our partnerships with publishers are vital to our project. We are particularly grateful to Longman who have been active partners in the Chemistry project and who have brought their own flair and expertise to succeeding editions.

Similarly, the Nuffield science projects have taken it as a firm principle that it is essential to have ways of assessing the students' performance that reflect the spirit of the teaching. Nuffield Chemistry led the way in partnership with London Examinations, now part of Edexcel. The Foundation is very appreciative of the work of the staff of the Awarding Body and for their contribution to the development of a distinctive and challenging qualification.

This edition was devised and written by a team led by Michael Vokins and supported by the Nuffield Curriculum Projects Centre. The team included a core group of editors, a number of enthusiastic contributors, and a wider group of teachers who value Nuffield Chemistry and generously offered their advice and expertise so that the new course and publications could reflect the best of current practice.

Michael Vokins edited the fourth edition while undergoing treatment for cancer and completed work on the new students' book shortly before he died. He retained his mental energy, enthusiasm and creativity to the end. He was a member of the original development team in the 1960s, he was an associate editor of the second edition, and then took the lead to ensure that there would be third and now fourth editions of the project.

The Foundation, and all the many teachers and students who have valued and benefited from Nuffield Advanced Chemistry, owe Michael an enormous debt of gratitude.

Anthony Tomei
Director, Nuffield Foundation

Introduction

The Nuffield Advanced Chemistry course was first published in 1970, revised in 1984 and restructured in 1994, so this is the fourth edition of what has proved to be a most successful venture.

The core publications of the fourth edition are the *Students' Book* and the *Teachers' Guide* for the two years of the course. They are supported by a *Book of data* which students will need to consult regularly. Later in the course students study one of several Special Studies: each study has a separate booklet and they are designed to help students appreciate the links between chemistry and its applications.

The structure of the course

As in previous editions the editors have consulted widely and revised the topics in the light of detailed comments and advice from teachers. The team has also had to take into account the subject criteria from QCA when planning the number and sequence of topics and the approach to assessing practical work.

The QCA criteria specify core content for the two parts of the course, AS and A2. As a result, some chemical ideas which used to appear in the first year of the course have been moved to year 2, including the Born–Haber cycle, the chemistry of benzene and the quantitative study of rates of reaction. Some material is studied qualitatively in year 1 before being approached quantitatively in year 2, for example rates of reaction and dynamic equilibrium. The study of the alkaline earth elements, which featured in the second edition, now reappears.

The topics

The new Topic 1 at the start of the AS programme meets the needs of students who come to the course with a wide range of previous experience. Some will take the topic in their stride while others need additional support available in a photocopiable format in the *Teachers' Guide.* For all students we have aimed to provide a framework of interesting practical work at the start of their post-16 studies.

Topic 2 is broadly the same as in the third edition. The chemistry of alcohols is rewarding at this stage because of the variety of changes which can be observed. Substitution and esterification are left to later topics.

The next three topics introduce ideas about atomic structure, ionic bonding, acids and bases, the alkaline earth elements, and enthalpy changes. This completes the first unit of the specification and is the point at which some students may take their first examination.

Topic 6 introduces oxidation numbers in the context of a study of halogen chemistry. Topic 7 develops students' understanding of the covalent bond and energetics which leads to bond enthalpies and hence activation energies in a short, qualitative treatment of reaction rates and reversible reactions. In Topic 8, students' knowledge of organic compounds is extended to hydrocarbons and a mechanistic classification of reactions is introduced; this is followed by a study of intermolecular forces in Topic 9. Then Topic 10 completes the content for the second examination unit with the chemistry of halogenoalkanes.

The A2 course begins with a quantitative study of rates of reactions, similar to that of the third edition. Topics 12 and 15 continue to develop organic chemistry with an exploration of the chemistry of benzene, phenol and organic acids with their derivatives. The treatment of entropy in Topic 13 is similar to that of the third edition and is followed by a quantitative study of equilibria in Topic 14. This completes the first A2 examination unit.

The final examination unit of the course consists of topics which introduce new content in ways which help to review the concepts of the course as a whole. This means that they help to prepare for synoptic assessment. Topic 16 revisits enthalpy changes and bonding while introducing the Born–Haber cycle. It goes on to apply the concepts of structure and bonding to the chlorides and oxides of the elements in Period 3. Topic 17 picks up on the study of redox reactions with the study of electrode potentials leading to a review of the methods which chemists use to predict the direction and extent of change.

In this edition the concept of free energy changes is not included. A short study of amines precedes work on proteins and synthetic polymers in Topic 18. Topic 19 is the culmination of the inorganic chemistry with a colourful treatment of the transition elements. The course ends with a look at organic synthesis in Topic 20 which revisits all the organic reactions covered in the course. Topic 21 is for reference. Students should study the various instrumental techniques at appropriate points during the course.

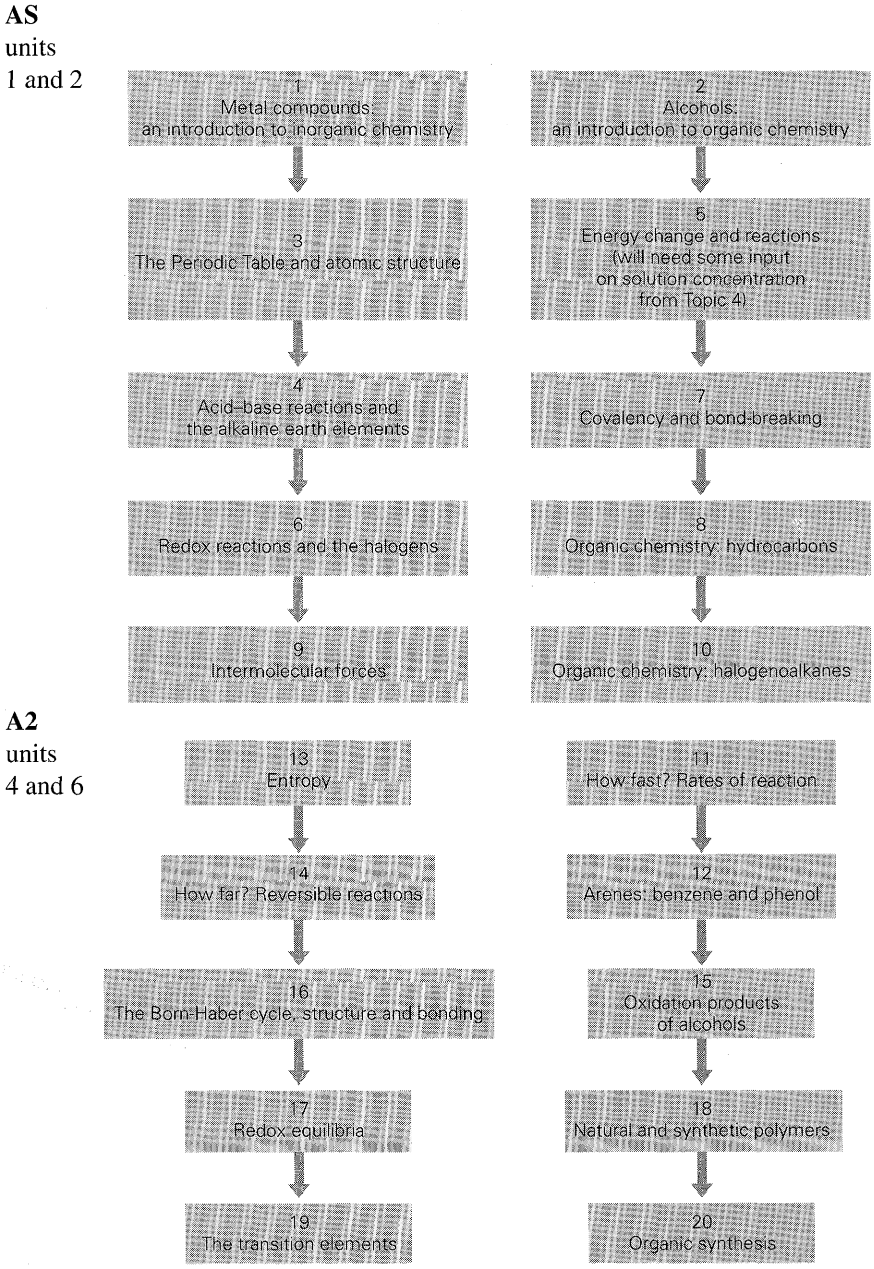
The timing of the course

We have assumed that 4.5 to 5 hours of contact time are available per week. On that basis we estimate that the whole course could be taught in 46 to 52 weeks. This includes 4 weeks for a Special Study and 1 week for a practical investigation, both in the second year. Any remaining time will be needed for tests, revision, reviewing homework and other necessary tasks. Many schools and colleges may find the time available for teaching reduced not only by pressures to cut contact time internally but also by the need to prepare students for AS examinations at the end of the first year.

Topic title		**Timing/weeks**
1	Metal compounds: an introduction to inorganic chemistry	2.5
2	Alcohols: an introduction to organic chemistry	2
3	The Periodic Table and atomic structure	2
4	Acid–base reactions and the alkaline earth elements	2
5	Energy change and reactions	1.5
6	Redox reactions and the halogens	3
7	Covalency and bond-breaking	2.5
8	Organic chemistry: hydrocarbons	2
9	Intermolecular forces	2
10	Organic chemistry: halogenoalkanes	1.5
11	How fast? Rates of reaction	3
12	Arenes: benzene and phenol	2
13	Entropy	1
14	How far? Reversible reactions	4
15	Oxidation products of alcohols	2
16	The Born–Haber cycle, structure and bonding	1
17	Redox equilibria	2
18	Natural and synthetic polymers	2
19	The transition elements	2
20	Organic synthesis	2
21	Instrumental methods	0
A Special Study		4
Practical investigation		1
Total		47

Alternative routes through the course

Some schools and colleges choose to timetable two teachers to work with a group of students. Teachers have developed a number of ways of doing this effectively. It becomes more difficult now that the examination is divided into units, especially in centres which choose to enter candidates for January as well as June examinations. The chart below shows a possible approach with one strand focusing on inorganic chemistry and related theory while the other covers the organic.



The Students' Book

Like its predecessors, the *Students' Book* contains instructions for practical work, interpretations of the experiments, background reading, and questions to help students develop their understanding of chemical ideas. All topics have several features in common that are used repeatedly during the course to help students with their learning.

There are instructions for **experiments**. In this course experiments are the core activity from which understanding is built. Ideas and experiments should go hand in hand: experiments lead to ideas and ideas to further experiments. We have organised this book on this pattern, in the hope that your students' study of chemistry will be both successful and enjoyable. Students are asked to try to interpret their experiments – to look for patterns, and to explain what they observe in terms of changes to molecules, ions and atoms. Merely describing what they see happening in an experiment will not significantly improve their understanding.

At the beginning of most experiments there is information about **health and safety**, listing the specific hazards involved in that experiment. (See the section on health and safety on page xiv of this Introduction.) There is an appendix on 'Laboratory safety' in the *Students' Book* which provides general guidelines for safe working in laboratories and notes on how to carry out risk assessments.

Prompts and questions headed **In your notes** are usually short and planned to guide students through the interpretation of their experimental results. **Questions** interspersed in the text of each topic help students to develop their understanding of the key ideas. **Study tasks** are more extensive and are designed to help students develop their understanding and their ability to extract appropriate information from their reading and to report their findings clearly in well-expressed English. The study tasks can be useful as homework.

Sometimes there is a short **comment**. These comments give extra information: sometimes curious facts and sometimes more advanced explanations which students may find helpful but are not part of the main development of the course.

Each topic includes suggestions for activities which will help students to develop their **key skills** of communication, application of number and IT.

Schools and colleges will adopt a variety of approaches to key skills, but in many centres the students will be expected to build up a portfolio of evidence from their whole study programme. The suggestions in the *Students' Book* will help them to do so.

We have not itemised the opportunities for developing the other key skills but there is no shortage of them in an advanced course based on a Nuffield approach. The *Students' Book* is designed to help students to improve their own learning and performance. Practical experiments and investigations offer many opportunities for problem solving. Laboratory work, study tasks, Special Studies and discussion activities all provide different ways of teaching students to work effectively with others.

The **topic reviews** suggest ways in which students can organise an outline of a topic so that they concentrate on learning the main ideas. Students can be encouraged to add some fun in the form of cartoons, verses, or coloured charts which can all help them learn chemistry.

Each topic ends with **review questions** and **examination questions**. Review questions are short items to help students practise the use of the ideas introduced in the topic; examination questions are taken from recent examination papers. Good answers to the examination questions will require a broad understanding of the topic and may require students to draw on ideas from earlier topics. They may be rather difficult if attempted without a period of review and revision of the set of topics in a unit of the examination specification.

Background information and **background reading** are not examinable for their content. Much of the background reading is in the AS topics and is based on passages provided as comprehension exercises in previous examinations. These passages should not only add interest to the course and show the practical relevance of the chemical ideas but also help students prepare for the comprehension/summary exercise in the unit 2 examination.

The A2 topics include the introductions to the **investigations** approved by Edexcel. Full details of the assessment are given in the coursework booklet published by Edexcel which also includes detailed general guidance for teachers and students. In an investigation students are expected to work out their own experimental procedure to answer the problem posed. The investigations are designed to develop students' understanding of practical procedures and how they can be used to collect evidence for solutions to problems. Students are likely to make several mistakes in their procedure during an investigation and have to go back and start again – but that is to be expected. We recommend that students carry out brief trial tests before attempting to plan the details of their work. The Edexcel booklet also includes one investigation for each of the Special Studies.

The naming of chemicals and the use of units in this course generally follow the recommendations of the Association for Science Education, which are published in *Chemical nomenclature, symbols, and terminology for use in school* *science*, (3rd edn, 1985). *Signs, symbols and systematics* (ASE, 2000), which replaces this publication, was published too late to be followed in this *Teachers' Guide*. In a few cases of natural products short non-systematic names have been used where knowledge of the structure is not needed. The most important aspect of this, of course, must be safety. Nothing should be done which could possibly damage the health or safety of a student or technician because of a confusion over names, and particular care should be taken to see that any such risk is avoided. For this reason the copiable section on 'Hazardous laboratory chemicals' in this *Teachers' Guide* often gives both systematic and non-systematic names.

The Teachers' Guide

This book is designed to guide you and your laboratory technician through the 21 topics in the *Students' Book*.

Each Topic starts with a summary of content, estimates of the teaching time needed, and teaching objectives based on the Edexcel specification. Most sections of topics include a **suggested treatment** which is a guide to teaching the material, and there are **answers to selected questions** and **study tasks**. At the end of each topic there are **answers to all of the review and the examination questions** in the *Students' Book*. Those provided for the examination questions should be taken as only a guide to what would be an acceptable answer in an operational AS or A-level examination. Some examination questions have been adapted to suit a particular topic, and parts have been deleted because of changes in the course.

There is also a guide to each **experiment**. As well as lists of the resources needed, there is information about the health and safety **hazards** associated with all the chemicals. The hazards are listed in a different style from that used in the *Students' Book* and are intended to help technicians, particularly when making up solutions from pure solids or liquids. A few topics (particularly Topic 1) include alternative experiments not given in the *Students' Book*. The instructions for these experiments can be photocopied for use in your laboratory.

Hazardous laboratory chemicals is a section at the end of this book which gives you further information about the nature of the health and safety hazards associated with each chemical you are likely to handle when preparing for the experiments. The safety precautions to be taken will depend on the facilities available in your own laboratories; the information is now based on the CHIP98 Approved Supply List (Chemical Hazard: Information and Packaging).

Special Studies

Towards the end of the course, provision is made for a four-week study of an applied aspect of science which is based on chemical principles. The main purpose of this section of the course is to help students to see something of the scope of a related subject, and to appreciate its dependence upon chemical ideas. In doing this, they will automatically revise some of the basic concepts of chemistry, such as structure and its relation to physical and chemical properties; equilibria; rates; and energy changes. The Special Studies are also designed to show students something of the applications of the subjects, and of their social and economic effects. They should come to regard chemistry as *useful* knowledge – useful in processing mineral resources, useful to dieticians, useful to manufacturers of metals and polymers, and useful in the production of the multitude of products that we find so valuable every day.

Like the rest of the course, the Special Studies are based on experimental work. There is one book for each study containing chapters on the necessary underlying ideas and knowledge, the details of the experimental work, and applications in industry, agriculture, and medicine. Each has its own *Teachers' Guide*. In the new specification students carry out one investigation in the context of their chosen Special Study.

Each student has to complete one Special Study. The choice of a Special Study is likely to be based on balancing the resources available against any special expertise in the department and the interests of the students. In large departments several Special Studies might be time-tabled simultaneously and students allowed to attend the study of their choice. Well-resourced departments have found that the Special Study booklets are sufficiently self-contained to be a sound basis for individualised learning, and the experimental work of several studies can be managed by one teacher in one laboratory.

Another aspect that involves careful planning is the position that the selected special study is to occupy in the teaching sequence: *Biochemistry* and *Food science* are probably best taught after Topic 18, *Materials science* after Topic 19, and *Mineral process chemistry* can be taught after Topic 17 or 19.

Teaching the course

This course is based on the belief that courses should not only be based on the principles of the subject but must also seek to develop imaginative thinking. The approach to the teaching of the subject must also encourage students to attempt interpretation and explanation of phenomena for themselves. The goal should be understanding rather than the rote recall of facts. Not that factual information is unimportant, but that observations and measurements should be given their proper place in the study of the subject. They are indispensable as the basis for speculation about possible explanations of the behaviour of matter, playing a crucial role in disciplining such speculation. Hence the importance of the *Book of data* in the Nuffield course. Theory which outruns the results of experiments can have no lasting place in science, but it is part of scientific thinking to make imaginative leaps forward, provided these are checked against known evidence, or are used to guide the search for further information, against which the new ideas can be tested.

An AS/A2 Chemistry course must fulfil the needs of three groups of students:

- those who hope to become professional chemists and will proceed to a further study of the subject in considerable depth,
- those who need chemistry as a service subject to other science disciplines and who may or may not undertake further formal study of the subject,
- those who will subsequently embark on a career in which the methods of science are not of prime importance.

In order to provide for these varying needs, a course must be flexible so that it can be used with students of a fairly wide range of abilities, while being both satisfying and complete in itself and at the same time providing a foundation for more advanced study. It should be a course that will be intellectually stimulating and, hence, exciting to follow. From the students it should demand a high degree of involvement in all that they do. They must be encouraged to approach their work critically, to cultivate the ability to reason clearly, and to appreciate that the collection of information occupies a central place in scientific investigation.

The treatment of chemistry described in this book is based on the establishment and use of three principles currently seen as being fundamental to the study of chemical systems. These are:

- the way in which energy transfers can determine the feasibility and outcome of reactions,
- the relationship between structure (both atomic and molecular) and the properties of substances,
- the use of the Periodic Table as a means of providing a unifying pattern for the diverse properties of elements and compounds.

These principles are applied to the experimental study of both organic and inorganic systems, but in a way that does not involve the neglect of preparative work. As a servant of the community, not the least important function of the chemist is to make new substances.

What has been attempted in this course is a realistic appraisal of the amount of ground that can be covered in this way and the assembling of ideas and methods from many sources, strengthened by additional experimental work and by the introduction of modern explanatory concepts, into an integrated whole.

In planning the presentation of chemistry as an integrated subject it is essential to be clear about what this entails, since there are many aspects of integration which could be involved. Four areas of integration are given prominence in the course.

1. The integration of facts and concepts. An attempt has been made to achieve this as completely as possible. The evolution of a major concept is accompanied by the collection of factual information to lead to the emergence of an underlying principle, which is then tested and often modified by appeal to further experiment. Time and laboratory resources do not always permit the necessary evidence to be obtained experimentally, but this is done where circumstances permit.
2. The integration of theory and practical work. Chemistry is predominantly an experimental subject and can only be fully understood by frequent recourse to the laboratory bench. Consequently, in this course, the theory and relevant practical experience are integrated as fully as possible. In a few areas, in particular when dealing with structure, the practical work is somewhat meagre, but these are rare. As the course proceeds, students gain experience in using theoretical principles to predict the outcome of reactions, and in testing their predictions experimentally.
3. The integration of 'pure' and 'applied' chemistry. The boundaries between these aspects of the subject are by no means clearly defined. The academic chemist and the technologist work on broadly similar lines although their aims and outlook may differ. It is important also to break down the rigid divisions which have in the past tended to separate advanced chemistry courses from related subjects such as metallurgy, biochemistry, and chemical engineering. The essential unity of these disciplines demands that this be attempted; in addition, it is important to make students aware of the nature, scope, and challenge of the technological subjects so that they may be in a position to consider a career in one of these fields.
4. The possibility of breaking down the boundaries between the traditional divisions of the subject into inorganic, organic, and physical chemistry. This has been realised to some extent in the treatment of physico-chemical principles, which are introduced at intervals throughout the course. Examples of chemical systems to show the need for or to illustrate concepts are taken from both the inorganic and organic areas of the subject.

In dealing with technological and other applications, the social and economic results of advances in chemistry are discussed, as are the moral and ethical implications. The technological importance of chemistry and its value to society feature in two main ways. Firstly, throughout the *Students' Book* a number of descriptions of chemistry in a variety of contexts are provided as reading material. In some cases these are quite short accounts, but in other cases an extended treatment is given in the form of background reading. Secondly, towards the end of the course each student undertakes one Special Study, during which the basic principles explored earlier can be applied in new contexts of a technological nature.

Teaching method

Each teacher will interpret the course in his or her own way and apply the teaching techniques that seem most appropriate to each learning situation. There are, however, some approaches to the Nuffield course that many teachers have found valuable, so we mention them here.

The course relies heavily on class discussion. Such discussion may be relatively lengthy, involving the whole class, or occupy a few minutes only and a small number of students. Ideally these discussions should be held at the time when they are relevant.

Questions and study tasks which promote discussion are included at frequent intervals in both the *Students' Book* and the *Teachers' Guide*. Discussion of these questions in the laboratory as they arise from practical work is especially valuable.

This edition of the *Students' Book* is more consistent than earlier editions in providing guidance about what students should record in their notes while in the laboratory and after completing experiments.

The questions at the ends of the topics in the *Students' Book* provide useful tests of understanding and application. In addition, students should tackle lengthier pieces of written work which require them to select facts, marshal evidence, and present ideas in a lucid and not too wordy form. Not only does this help them to learn chemistry but it also provides opportunities to develop key skills. Examples are provided in some of the study tasks and the passages of background reading. We hope that students' interest will take their research beyond the *Students' Book* to other books and to relevant websites. The Nuffield Curriculum Projects Centre website is being developed to encourage this kind of exploratory activity.

An integrated course of this type demands careful planning for each lesson, especially in the first few years of its use. Without this preliminary work much valuable time can be lost. The contents of this *Teachers' Guide* are intended to give as much help as possible in this process. An Advanced Chemistry course features many abstract ideas. Models, overhead projector transparencies, videos and computer software can all help students to visualise theoretical models, understand their significance and learn to apply them.

Health and safety

Health and safety in school and college science affects all concerned: teachers and technicians, their employers, students, their parents or guardians, as well as authors and publishers.

As part of the reviewing process, these publications have been checked for health and safety. In particular, we have attempted to ensure that:

- all recognised hazards have been identified,
- suitable precautions are suggested,
- where possible, the procedures are in accordance with commonly adopted model (general) risk assessments,
- if a special risk assessment is likely to be necessary this has been pointed out,
- where model (general) risk assessments are not available, we have done our best to judge the procedures to be satisfactory and of an equivalent standard.

It is assumed that:

- practical work is conducted in a properly equipped and maintained laboratory,
- rules for student behaviour are strictly enforced,
- mains-operated equipment is regularly inspected, properly maintained and appropriate records are kept,
- care is taken with normal laboratory operations such as heating substances and handling heavy objects,
- good laboratory practice is observed when chemicals are handled,
- eye protection is worn whenever the risk assessment requires it,
- any fume cupboard required operates at least to the standard of Building Bulletin 88,
- students are taught safe techniques for such activities as heating chemicals, smelling them, or pouring from bottles,
- hand-washing facilities are readily available in the laboratory.

Under the COSSH and Management of Health and Safety at Work regulations, employers are responsible for carrying out risk assessments before hazardous procedures are undertaken or hazardous chemicals used or made. Teachers are required to co-operate with their employers by complying with such risk assessments.

However, teachers should be aware that mistakes can be made and, in any case, different employers adopt different standards. Therefore, before carrying out any practical activity, teachers should always check that what they are proposing is compatible with their employer's risk assessments and does not need modification for their particular circumstances. Any local rules issued by the employer must always be followed, whatever is recommended here.

Model (general) risk assessments have been taken from, or are compatible with:
Topics in safety, Association for Science Education, 2nd edn, 1988
Hazcards, CLEAPSS, 1995 (or 1998 update)
Safeguards in the school laboratory, Association for Science Education, 10th edn, 1996
Hazardous chemicals: a manual for science education, SSERC, 1998.

Clearly, you must follow whatever procedures for risk assessment your employers have laid down. As far as we know, all the practical work and demonstrations in this course are covered by the model (general) risk assessments detailed in the above publications, and so, in most schools and colleges, you will not need to take further action.

If you or your students decide to try some procedure with hazardous substances beyond what is in this course, and you cannot find it in these or other model (general) assessments, then your employer will have to make a special risk assessment. If your employer is a member, then CLEAPSS will act for them. Otherwise the ASE may be able to help.

Only you can know when your school or college needs a special risk assessment. But thereafter, the responsibility for taking all the steps demanded by the regulations lies with your employer.

Investigations will involve independent action by the student. Our notes on investigations warn students to carry out a risk assessment; students should be responsible for safety in the first instance and credited in any assessment for making safe plans. Nevertheless, proposals must be seen by you the teacher, and you must ensure that you make an appropriate check, particularly with respect to safety, on what will go on. You will need to take particular care if students consult library books published before modern safety standards came into force or get ideas from the internet.

Technical note

The authors of the topics drew up the lists of apparatus and chemicals for the experiments. The lists were then checked by teachers and technicians. The editors then found considerable variation in the expectations of staff. Some people take it for granted, for example, that a burette will be supplied with a stand, burette funnel and white tile or that burners and spatulas will be readily available. Also in some laboratories the reagent bottles for solutions all come with built-in droppers while in others the practice is to supply dropping pipettes. These sorts of variations are reflected to some extent in the lists in this book. What this means is that when starting to use this file, staff in each school or college will have to annotate the lists to correspond to local practice.

Appendix 2 on pages 306–324 gives extensive information about the hazards associated with most of the chemicals used in the course. When annotating the chemicals in the equipment lists in this file with their hazard categories the authors have borne in mind the circumstance of the member of staff doing the preparatory work, so the hazard alongside a dilute solution may be that which refers to the pure solid. In the *Students' Book*, however, the hazards refer to the chemicals in the form in which they are supplied.

The authors and editors have aimed to use solutions which are as dilute as practicable in order to reduce the hazard category.

Publications

The complete list of publications in print in 2000 is as follows.

For the student
Students' Book. Topics 1 to 21 of the basic course in one volume, with an appendix 'Laboratory safety'.
The Special Studies: *Biochemistry*, *Food science*, *Metals as materials*, and *Mineral process chemistry.*
Book of data.

For the teacher
Teachers' Guide. A guide for teachers and technicians to Topics 1 to 21 of the basic course. There are appendices on Hazardous laboratory chemicals, Microscale chemistry, and Help with mathematics.
Teachers' Guides to the Special Studies: individual Teachers' Guides are published for each of the Special Studies.

Examinations

Edexcel is the Awarding Body for Nuffield Advanced Chemistry at AS and A-level. Edexcel issues the 'Specification', 'Internal assessment of practical coursework for AS and Advanced GCE chemistry (Nuffield)' including the criteria for the assessment of investigations and, each year, a 'Mark scheme with examiners' report'. The specification contains full details of the type and pattern of the papers, and of the proportion of marks allocated to the various skills which the examination seeks to assess.

Contributors

This edition was devised and written by a team led by Michael Vokins. This included a core group of editors, a number of enthusiastic contributors, and a wider group of teachers who value Nuffield Chemistry and generously offered their advice and expertise so that the new course and publications could reflect the best of current practice.

Michael Vokins and the three editors have helped to shape Nuffield Chemistry throughout the life of the project as teachers, writers and examiners. The editors have contributed an enormous amount to this edition. Alan Furse edited the inorganic topics, Glyn James the organic and Robin Hillman the physical chemistry. Their experience was enriched by new contributions from John Apsey, Pamela Butler, David Craggs, Elwyn Davies, and Douglas Snowden all of whom helped to produce a new version of the course to meet the needs of students today based on their experience of teaching the course in schools and colleges and on their awareness of what students find hard in examinations.

We appreciate the support and advice of Colin Osborne of The Royal Society of Chemistry. Likewise we hugely value the advice from Peter Borrows of the Association for Science Education, who has checked all the publications from the point of view of health and safety.

We are fortunate to have the advice and support of Longman and especially the input from James Newall, who listened hard to the advice from teachers and has been the project champion throughout the publication phase. We are also grateful to Rebecca Harman and the team at Pearson Education.

The new course was developed in close collaboration with Edexcel who led the team of examiners writing the new specification. We are very grateful to Samina Khan, Sharon Nixon and Ray Vincent for all their work. The chair of the Edexcel Nuffield examiners is always very important and we are pleased that Mary Ratcliffe is continuing this work. There is no doubt that the quality of the examining team and the support of the Awarding Body have been crucial to the success of Nuffield Advanced Chemistry.

Finally, all those involved would acknowledge that the publications would never have appeared but for the determination, tact and sheer persistence of Sarah Codrington of the Nuffield Curriculum Projects Centre. First as a support to Michael Vokins and latterly as the sole project manager she held the scattered team together and harnessed their energies to great effect.

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TOPIC 1

Metal compounds: an introduction to inorganic chemistry

Introduction

Students come to this course from a wide variety of backgrounds and experiences of chemistry. The intention of this first topic is to ensure that by the time they have finished it they can:

- recognise a variety of types of inorganic chemical reactions
- write equations for inorganic reactions, both in a full form and reduced to their simplest ionic terms where appropriate
- work practically with inorganic substances
- do calculations involving quantities measured out by mass in the case of solids or by volume if gaseous.

Some teachers may feel that their students can already do these things with confidence. For such classes Topic 1 can be disposed of quite quickly; the practical work might be done selectively and the exercises and questions used merely as a confidence-builders.

Other teachers may feel that the questions in this topic are well beyond the scope and experience of their students. The 'Alternative approach' on pages 15–25 of this *Teachers' Guide* is intended for them; the explanations are fuller, the pace steadier. Pages can be photocopied for student use.

It is expected that most students will have enough experience to tackle the topic as it is set out and suggested timings are based on this assumption.

Students should be encouraged to keep careful records of the work they do and the opportunity has been taken to suggest ways in which note-taking can be done. In this topic, as in later ones, the Topic review at the end should act as a checking mechanism.

A few assumptions have been made about previous experience. Acids, alkalis and the use of indicators are expected to be familiar ground, and so is a basic familiarity with the Periodic Table and the use of chemical symbols. Some appreciation of structure and bonding is also expected, although the 'Alternative approach' assumes only a little of this.

There is always a danger with introductory topics that those who can already do the things being taught are merely reinforced in their confidence and those who began in a confused state will finish even more confused. It is hoped that by providing a variety of possible approaches every student will learn something new and no student will be put off. The 'learning curve' may be quite exhilarating for some!

Timing		Students' Book
1.1	8 hours	Pages 2–12
1.2	2 hours	Pages 12–14
1.3	$\frac{1}{2}$ hour	Pages 15–16
1.4	1 hour	Pages 16–19
Total about $2\frac{1}{2}$ weeks		

Content

1.1 Types of inorganic reaction – thermal decomposition, precipitation, redox reactions. Solubility rules, reactivity series, exothermic and endothermic reactions, some oxidising and reducing agents, applications of the mole concept in practical situations.

1.2 Making salts – more applications of the mole concept; practical preparation of a single salt and a double salt.

1.3 The chemists' toolkit: writing formulae and balancing equations – a revision aid for those who already have experience.

1.4 The chemists' toolkit: the mole, molar mass and molar volume – relative atomic mass; relative formula mass; moles; the Avogadro constant; using moles; moles of gases.

1.5 Background reading: A golden opportunity.

Objectives

1. To reinforce students' experience of inorganic reaction types.
2. To provide opportunities to use the mole concept in practical situations.
3. To revise and amplify basic chemical ideas and procedures such as solubility, exothermic and endothermic reactions, hydrated salts, reactivity series, redox, equation writing.
4. To provide some experience in preparative inorganic chemistry.

1.1 Types of inorganic reaction

Timing About 8 hours will be needed

Suggested treatment

The time taken in introducing this topic will depend on the students' previous experience and on how confident the teacher feels about this experience. There should be a reminder of hazard symbols and basic safety procedure. Students then carry out a variety of reactions with compounds of some metals. After each experiment, students are asked to think about what they have done and seen, prompted by questions. The results of experiments and any associated theory should be recorded in a notebook and the answers to the questions should be written out in such a way as to make it clear what each question was asking. The answers should be discussed before going on to the next experiment.

Students should study sections 1.3 and 1.4 (the Chemists' toolkit sections) in parallel with sections 1.1 and 1.2. These may be used, either in the version given in the *Students' Book* or in the 'Alternative approach' photocopied from the *Teachers' Guide*.

Thermal decomposition reactions

There is a short introduction in the *Students' Book* which explains what to look out for when heating inorganic solids. The importance of safe working should be stressed in a positive way: knowing the hazards, safe methods can be planned. Students can be introduced to (or reminded of) *Hazcards* or other sources of information, such as the Hazardous laboratory chemicals appendix in this *Teachers' Guide*.

EXPERIMENT 1.1a Thermal decomposition reactions

Each group of students will need:
Eye protection
Bunsen burner and mat
Test tube and rack
5 dry hard-glass test tubes
Test tube holder
Delivery tube with bung to fit test tubes
Full-range indicator paper or blue litmus paper
Wooden splint
Spatula

HAZARD

Ammonium dichromate(VI) is a very hazardous material. If confined it can explode. It is a very powerful oxidant and forms explosive mixtures with reducing agents, e.g. foreign matter such as dust. Toxic if swallowed, irritating to skin, category 2 carcinogen. Dust or very fine crystals are particularly hazardous.

Access to:
Fume cupboard
Limewater
Solid samples (about 2 g each) of
  Hydrated cobalt(II) chloride HARMFUL
  Hydrated copper(II) nitrate HARMFUL AND OXIDISING
  Hydrated iron(II) sulphate HARMFUL
  Zinc carbonate
  Sodium nitrate OXIDISING

For the demonstration:
Ammonium dichromate(VI) POWERFUL OXIDANT, VERY TOXIC BY INHALATION, CATEGORY 2 CARCINOGEN.

For the alternative approach on the copiable sheets:
Hydrated cobalt(II) sulphate
Hydrated copper(II) nitrate HARMFUL, OXIDISING
Zinc carbonate

Procedure

Full details of the procedure are given in the *Students' Book.*

Demonstrate the decomposition of ammonium dichromate(VI) in a fume cupboard or in a vessel with a mineral wool plug to prevent escape of particles.

If a fume cupboard is used, wear gloves when placing a heap of solid of no more than 50 mm diameter on a heat-resistant mat. Heat the edge of the pile with a Bunsen flame directed downwards until the reaction starts. The residue may contain unreacted dichromate dust; wear gloves and sweep it into a plastic bag containing sand.

Alternatively, heat no more than 1g of ammonium dichromate(VI) in a borosilicate boiling tube with a mineral wool plug inserted at the mouth.

To avoid cracking test tubes, tell students that if a liquid appears they should continue heating until there are no further changes.

If students are working in pairs it is generally advisable for one partner to concentrate on heating the solid while the other watches carefully and notes down all observations.

Key points for students to include in their notes (page 3):

1. All the compounds changed permanently. This was apparent either because gases etc. were produced or because the solid changed in appearance.
2. The compounds decomposed on heating.
3. Zinc oxide is yellow when hot, white when cold.
4. The zinc carbonate decomposed (chemical change) and the resulting zinc oxide undergoes a reversible colour change (physical change).
5. The cobalt(II) chloride and the copper(II) nitrate gave off so much water that they dissolved in it. In the process they seemed to melt with the application of very little heat. The formulae are $CoCl_2.6H_2O$ and $Cu(NO_3)_2.6H_2O$ respectively, so the crystals do contain a high proportion of water.
6. Carbon dioxide is often produced when carbonates are heated, nitrates often give off nitrogen oxides and oxygen, and sulphates give off oxides of sulphur. The behaviour of sodium nitrate is, perhaps, unexpected because it gives off oxygen but no nitrogen oxides.
7. The residue from the heating of cobalt chloride can be used to test a liquid to see if it contains water. It turns from blue to red if water is added to it.

As practice in equation-writing, the equations for some of these reactions should be discussed. The zinc carbonate equation is reasonably straightforward, although zinc carbonate is a basic carbonate and produces water on heating as well as carbon dioxide. The hydrated iron(II) sulphate produces sulphur dioxide and sulphur trioxide, leaving iron(III) oxide. Copper(II) nitrate produces oxygen, nitrogen dioxide and water, leaving copper(II) oxide. Sodium nitrate produces oxygen and leaves sodium nitrite, $NaNO_2$.

Key points for students to include in their notes after the demonstration (page 4):

1. The decomposition is, unusually, exothermic. A glow can be seen while the reaction is happening and it is not necessary to heat continuously.
2. The pieces of solid are thrown up into the air by the gases being evolved.
3. The solid left behind seems much less dense than the original ammonium dichromate. (This is an illusion; the product is more finely divided than the ammonium dichromate and the pieces of product have a good deal of space between them.)

The balancing of the equation for this reaction is discussed in Topic 6 as an example of the use of oxidation numbers.

Precipitation reactions

EXPERIMENT 1.1b

Solubility and precipitation reactions

There is a microscale alternative to this experiment. See Microscale appendix, M2.

Each group of students will need:
Eye protection
Full rack of test tubes
Spatula

Access to:
Solid samples of
  Hydrated copper(II) chloride TOXIC
  Hydrated iron(III) nitrate IRRITANT
  Hydrated iron(II) sulphate HARMFUL
  Potassium carbonate
  Magnesium carbonate
  Iron(III) oxide

For the alternative approach on the copiable sheets:
Hydrated copper(II) chloride TOXIC
Hydrated iron(III) chloride IRRITANT
Hydrated iron(II) sulphate HARMFUL, IRRITANT
Hydrated cobalt(II) sulphate HARMFUL

For both approaches:
0.4 M sodium hydroxide solution (about 10 cm^3) IRRITANT
Approximately 0.1 M solutions of the following (about 20 cm^3 of each)
  Sodium chloride
  Sodium sulphate
  Sodium hydroxide IRRITANT
  Copper(II) sulphate
  Lead nitrate TOXIC
  Sodium carbonate

Key points for students to include in their notes (page 5):

1. The copper and iron compounds were coloured. Copper and iron are both transition elements.
2. The formulae for copper(II) chloride, iron(II) sulphate and iron(III) nitrate all contain water; they are 'hydrated' solids. These solids might reasonably be expected to be soluble in water.
3. The solubility rules were obeyed by all the compounds.

After the first part of the experiment, the results should be discussed with the class and the interpretation given in the *Students' Book* should be read and understood.

The 'Further precipitation reactions' can then be attempted. If mixing 15 pairs of solutions seems excessive, consider cutting the number of mixtures or sharing them amongst the class. The microscale version is quicker.

Redox reactions (1)

EXPERIMENT 1.1c

Demonstration of the Thermit reaction

The concept of 'redox' as loss or gain of oxygen is discussed. Before the experiment starts, the reacting masses needed are worked out from the equation to give practice in the use of mole calculations.

Procedure

HAZARDS

The mixture is relatively stable and a more vigorous starter is often suggested than magnesium ribbon alone. A 1:3 ratio of aluminium to metal oxide can be used and Cr_2O_3 or Mn_3O_4 used instead of Fe_2O_3.
On no account use CuO, Cu_2O, MnO_2, CrO_3, or lead oxides with aluminium as the reaction can be violent.

This reaction should be demonstrated (after a description of the technique) from behind a safety screen.

Each student will need:
Eye protection

The teacher will need:
Eye protection
Safety screen
Filter paper (and paper clip)
Tray full of **dry** sand
Iron(III) oxide, **dry**, three portions of 8.0 g (0.05 mol) stored in a desiccator
Aluminium powder, fine, 2.7 g (0.1 mol) FLAMMABLE
Copper powder, 9.5 g (0.15 mol)
Magnesium ribbon
Magnesium powder, a small amount FLAMMABLE
Zinc powder, 9.8 g (0.15 mol) FLAMMABLE
Balance, to weigh to ±0.1 g
Weighing bottle

For more information on the Thermit reaction consult CLEAPSS *Laboratory Handbook*, 1992 update.

Procedure

This teacher demonstration is described in the *Students' Book*. 8.0 g of iron(III) oxide is mixed with 2.7 g of aluminium (or 9.8 g zinc or 9.5 g copper). A fireclay pot could be used but it will probably be destroyed during the demonstration. A cheaper alternative is to use a filter paper folded in the normal way and then embedded in the sand. To light the fuse of magnesium ribbon a piezoelectric lighter with butane fuel (Aldrich) is convenient. Alternatively a strong Bunsen flame from a hand-held burner can be used, but the flame must be directed upwards away from the Thermit mixture. If the Thermit mixture does not ignite, approach with great caution as delayed ignition can occur.

This is a spectacular demonstration of a 'competition' reaction, the importance of which is explained in the *Students' Book*. The mixture of copper and iron(III) oxide has been included to highlight the nature of the 'competition' reactions and relate them to the reactivity series and exothermic and endothermic reactions.

Key points for students to include in their notes (page 8):

1. The mixtures of aluminium powder with iron oxide and zinc powder with iron oxide react.
2. A great deal of heat is given out by the first of these reactions, considerably less by the second of them.
3. You could test to see that iron is produced by applying a magnet – iron would be attracted to it.

Redox reactions (2)

The redox concept is extended in this section to cover gain and loss of electrons. There is no intention at this stage to develop the subject beyond showing that redox reactions involving iron ions can be brought about by substances called reducing agents and oxidising agents. The students should become familiar with the names of the agents used but time should not be taken up in writing full equations. This section provides a useful curtain-raiser to the development in Topic 6.

EXPERIMENT 1.1d

Redox reactions

Each group of students will need:
Eye protection
Full rack of test tubes
0.4 M sodium hydroxide solution, about 20 cm^3 IRRITANT
0.1 M ammonium iron(II) sulphate to which a little 1 M sulphuric acid has been added, labelled 'acidified iron(II) sulphate solution', about 15 cm^3 IRRITANT
0.1 M ammonium iron(III) sulphate to which a little dilute sulphuric acid has been added, labelled 'acidified iron(III) sulphate solution', about 10 cm^3 IRRITANT
20 volume hydrogen peroxide solution, about 10 cm^3 IRRITANT
0.04 M potassium manganate(VII) solution acidified with an equal volume of 1 M sulphuric acid labelled 'acidified potassium manganate(VII) solution', about 10 cm^3 IRRITANT
Concentrated nitric acid (a few drops) CORROSIVE, OXIDISING
Zinc, foil or granulated, about 0.5 g
0.01 M sodium disulphate(IV) (metabisulphite) solution or 0.1 M sodium sulphite solution, about 10 cm^3 HARMFUL

Procedure

Details of the procedure are given in the *Students' Book.*

Students should use very small quantities of the iron compounds; too much may lead to incomplete conversion. The mixture involving concentrated nitric acid may require very cautious warming. When the mixture involving zinc is tested with sodium hydroxide there may be signs of a white precipitate of zinc hydroxide as well as the expected green of iron(II) hydroxide. Sodium disulphate(IV) ($Na_2S_2O_5$) solution gives a more convincing green precipitate than other sulphur oxoanions after the initial red coloration fades on warming.

There is no intention to write complete equations. The processes can be recorded by reaction schemes such as:

$$Fe^{2+}(aq) \xrightarrow[H_2O_2(aq)]{} Fe^{3+}(aq)$$

Redox reactions (3) The reaction of iron with copper(II) sulphate

The students carry out an investigation to find out which of two possible equations for this reaction is the correct one.

EXPERIMENT 1.1e

Deciding which equation is correct

Each group of students will need:
Eye protection
Bunsen burner, tripod, gauze and heatproof mat
Beaker, 100 cm^3
Filter funnel and paper
Conical flask, 150cm^3
Stirring rod
50 cm^3 Measuring cylinder
1 M copper(II) sulphate, 15 cm^3 HARMFUL
Iron powder, fine, 1 g
Propanone, 20 cm^3 HIGHLY FLAMMABLE
Balance, to weigh to ±0.01 g
Weighing bottle or dish
Oven at 100 °C
Spatula

Procedure

Weigh a dry piece of filter paper, fold it, place it inside the filter funnel, and stand this inside a conical flask ready for a filtration which will be necessary near the end of this experiment.

Weigh exactly 0.56 g iron powder into a 100 cm^3 beaker and add to it at least 15 cm^3 of 1 M copper(II) sulphate solution. Heat the mixture to boiling, stirring well all the time, and allow it to boil for 1 minute. Now allow the contents of the beaker to cool and the precipitate of copper to settle. Pour off as much of the liquid as you can, being careful not to lose any copper.

Add pure water until the beaker is about one-third full, and stir the mixture. Allow the copper to settle and pour off as much liquid as possible. Repeat this process with more pure water, and after two or three 'washings' carefully pour off as much water as you can, without losing any of the copper down the sink. Now add about 20 cm^3 of propanone and stir the mixture.

Filter the mixture through the apparatus you set up at the start of the experiment, and leave the residue of copper in the filter paper to dry naturally as the propanone evaporates. Next, drive off the remainder of the propanone by removing the funnel and heating it in an oven at 100 °C for about 5 minutes.Allow the funnel to cool, remove the filter paper carefully and weigh it, together with the residue of copper which it contains.

Key points for students to include in their notes (page 12):

3 Students should find that the first of the suggested equations is the correct one.

4 The purpose of the propanone is to help to dry the copper. Propanone mixes with water and then evaporates easily itself, leaving the copper reasonably water free.

1.2 Making salts

Timing About 2 hours will be needed

Suggested treatment

In this section more practice is provided at calculating quantities using the mole concept. While the two preparations are being carried out, it is important for the teacher to check that the students know what they are doing and why and that they

EXPERIMENT 1.2a

The preparation of nickel sulphate, $NiSO_4.7H_2O$

HAZARD

Nickel salts and their solutions are harmful, and may cause sensitisation by skin contact.
Do not use black nickel oxide, NiO, rather than nickel carbonate, although it overcomes the calculation problem. It is toxic, and may cause cancer by inhalation of dust: it is a category 1 carcinogen.

Each group of students will need:
Eye protection
100 cm^3 beaker
Weighing dish
Measuring cylinder, 50 cm^3
Spatula
Bunsen burner, tripod, gauze and heatproof mat
Filter funnel and paper
Evaporating basin
Petri dish or other flat dish for crystallising
Nickel carbonate (basic), about 4 g HARMFUL
1 M sulphuric acid, about 25 cm^3 IRRITANT
Balance, to weigh to ±0.1 g

Procedure

Full instructions are given in the *Students' Book.*

The procedure has been described using nickel carbonate as a starting material. The calculation is thus invalidated because nickel carbonate is a basic carbonate and actually contains rather more nickel hydroxide than nickel carbonate. It is still worth getting the students to do the calculation and the results of it are not too much in error.

Key points for students to include in their notes (page 13)

7.0 g of hydrated nickel sulphate could theoretically have been prepared, but some remained in solution and was poured away.

EXPERIMENT 1.2b

The preparation of ammonium iron(II) sulphate (Mohr's salt), $(NH_4)_2SO_4.FeSO_4.6H_2O$

This is a rather more elaborate preparation resulting in the formation of a double salt, an explanation of which is given at the beginning of the sub-section in the *Students' Book.* This experiment also contains the only reference in this topic to acids, alkalis and neutralisation, ideas which could be drawn out at an appropriate point in the practical work.

Each group of students will need:
Eye protection
Bunsen burner, tripod, gauze and heatproof mat
Measuring cylinder, 50 cm^3
Measuring cylinder, 10 cm^3
Conical flask, wide neck, 250 cm^3
2 beakers, 250 cm^3
Dropping pipette
Filter funnel and paper
Cotton wool
Red litmus paper
Crystallising dish and cover
Weighing bottle

Access to:
2 M sulphuric acid, 60 cm^3 CORROSIVE
2 M ammonia solution, 60 cm^3 IRRITANT
Iron filings
Balance, to weigh to ±0.1 g

Procedure

The procedure is detailed in the *Students' Book*. Students calculate the amount of iron (2.8 g) and volume of ammonia solution (50 cm^3) required to react with $\frac{1}{20}$ mole of sulphuric acid to make the single salts ammonium sulphate and iron(II) sulphate. They then make ammonium iron(II) sulphate by making equimolar solutions of the single salts and then crystallising them together as the double salt. 2 M sulphuric acid is used in this experiment rather than 1 M to avoid having to evaporate solutions with unduly large volumes.

The iron(II) sulphate is filtered into dilute sulphuric acid to prevent hydrolysis. Light green monoclinic crystals of ammonium iron(II) sulphate are formed. These are more stable in air than crystals of iron(II) sulphate. The latter slowly effloresce in air and turn yellow by partial oxidation to basic iron(III) sulphate. Students should realise that the double salt behaves merely as a mixture of its component sulphates. Ammonium iron(II) sulphate provides an example of a group of double salts of formula $(M^+)_2SO_4.M^{2+}SO_4.6H_2O$ where the iron(II) may be replaced by V, Cr, Mn, Co, Ni, Cu or Zn in the +2 oxidation state without change in crystal form.

Key points for students to include in their notes (page 14)

1 The crystals are light green.
2 The crystals do not change over a long period of time.
3 Fe^{2+}, NH_4^+ and SO_4^{2-}
4 About 20 g of product could be made.
5 Iron and sulphuric acid; redox ammonia and sulphuric acid; neutralisation.

1.3 The chemists' toolkit: writing formulae and balancing equations

Timing About half an hour will be needed

Suggested treatment

This section should be worked over during the carrying out of the experiments in section 1.1. After discussion between teacher and class this section might be set for homework, the essential tasks being to learn the formulae for the ions referred to and to be able to combine them into formulae for compounds. The relevant Review Questions from the end of the topic should then be done.

Some classes of students, depending on their previous experience, may lack the confidence to carry out Experiments 1.1a and 1.1b as they are set out in the *Students' Book.* An alternative version of this toolkit, incorporating these experiments is provided in this *Teachers' Guide* on pages 15–25. These pages may be photocopied and issued to students to use. Some of the examples used in the experiments are different from those used in the *Students' Book.*

1.4 The chemists' toolkit: the mole, molar mass and molar volume

Timing About 1 hour will be needed, but timing will vary depending on past experience.

Suggested treatment

In this topic the mole is placed in the practical context of its value for calculating reacting masses of substances. In section 1.4 of the *Students' Book* a very pragmatic approach has been adopted, avoiding some of the technicalities of precise definition and focusing on what will be most useful for the student.

Students should, however, be aware of precise definitions and class discussion may bring these out. The main points to be covered can be summarised as follows:

1 For chemists, equal amounts of various substances are those amounts which each contain the same number of entities such as molecules, atoms, ions and formula units.

2 To compare equal amounts of different substances it is necessary to weigh out, not equal masses, but masses of substances in the ratio of the masses of the entities present in those substances.

3 Historically, one gram of hydrogen was chosen as a basis for comparison.

4 The number of hydrogen atoms, H, in 1 g of hydrogen, or the number of hydrogen molecules, H_2, in 2 g of hydrogen, was called first the Avogadro number. Later the Avogadro constant was introduced.

5 In 1961 the ^{12}C scale of relative atomic masses was internationally agreed and the following definition was adopted.

> The *relative atomic mass* of an element is the mass of one atom of the element on a scale chosen so that the mass of one atom of the ^{12}C isotope of carbon is 12 'units' exactly.

6 The *mole* is the SI unit of amount of substance and is also defined in terms of the ^{12}C isotope:

> One *mole* of any substance is the amount of substance which contains as many elementary entities as there are carbon atoms in 12 g (exactly) of pure carbon-12.

The elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

The word entities (that which makes a thing what it is) has been used rather than 'units' because the former conveys more accurately the idea of atoms, groups of atoms etc. The word 'unit' has a specific scientific meaning and it is preferable not to use the term in more than one context.

7 In using moles, it is necessary to specify precisely what entities are referred to. For example, the phrase 'one mole of chlorine' is ambiguous; it could mean one mole of chlorine atoms, Cl, that is 35.5 g, or one mole of chlorine molecules, Cl_2, that is 71.0 g. For this reason, the formula of the substance being considered must always be stated and the correct phrases should be 'one mole of chlorine atoms, Cl' and 'one mole of chlorine molecules, Cl_2'.

In substances consisting of giant lattices, whether they are covalent such as silicon dioxide, SiO_2, or ionic such as sodium chloride, Na^+Cl^-, the formula specifies the entities to which the mole refers. Students should notice for example, that one mole of sodium chloride contains one mole of sodium ions and one mole of chloride ions, whereas one mole of calcium chloride, $CaCl_2$, consists of one mole of calcium ions, Ca^{2+}, and two moles of chloride ions, Cl^-. Difficulties which might arise are dealt with by stating the formula being considered in each case, knowing the charges on the individual ions.

8 The Avogadro number has been superseded by the Avogadro constant defined as follows.

> The *Avogadro constant* is the constant of proportionality between the amount of substance and the number of specified entities of that substance. It is represented by the symbol *L*, and has units mol^{-1}.

The mole, which is the unit of amount of substance is defined in terms of a number of entities, and so we have the relation:

$$\begin{array}{c}\text{amount of substance}\\ \text{in mol}\end{array} \times \begin{array}{c}\text{Avogadro constant}\\ L\ (\text{mol}^{-1})\end{array} = \text{number of specified entities}$$

The unit of *amount of substance* is the *mole*, symbol mol. The *Avogadro constant* has units mol^{-1}, as it is the number of entities per mole.

9 The *molar mass* of a substance is defined as the mass of one mole of the substance; the entities must be specified. The symbol for molar mass is M and the unit is g mol^{-1}.

If we want to calculate the amount of substance in moles, knowing its mass in grams, we simply divide this mass by the molar mass of the substance concerned. The relation is

$$\text{amount in moles} = \frac{\text{mass in grams}}{\text{molar mass in grams per mole}}$$

It is suggested that students be asked to include the units in this type of calculation. To take a simple example, the amount in moles, of magnesium atoms in 48 g of magnesium (molar mass 24 g mol^{-1}) is:

$$\frac{48\ \text{g}}{24\ \text{g mol}^{-1}} = 2\ \text{mol}$$

1.5 Background reading: a golden opportunity

ANSWERS TO QUESTIONS

Questions, page 19

1 **Particles** of gold are **trapped** in a **mineral lattice structure**.

2 The mineral mixture acts as an impervious physical **barrier shielding** most of the gold particles from attack by cyanide ions.

3 Sulphur in refractory minerals is converted to sulphur dioxide, and arsenic to arsenic(III) oxide, which have environmental and economic implications.

4 Fresh water contains dissolved **oxygen** needed to oxidise sulphur minerals.

5 High recovery of base metals OR any two named metals.

6 Summary exercise, see below.

Advice on summary exercises

The summary exercises given for most background reading passages are based on examination requirements. Point out to students that they must read the task carefully because they are often *not* asked to summarise the *whole* of the passage.

They should get in the habit of stating the number of words at the end of their summaries. In the examinations, numbers count as words, as do standard abbreviations and hyphenated words, but the words in any title are not counted.

Summaries should be grammatical and written in complete sentences. At first many students find it hard to understand what it means to digest a passage and then to express it concisely in their own words. They must avoid the temptation to copy long sections from the original text.

It may be worthwhile discussing with students situations where scientists have to apply these summarising skills in their work. Examples include abstracts for scientific papers, book reviews as well as press releases. See also the copiable advice to students, page 26.

Key points to include in the summary

A title, for example, 'The Bactech process of extracting gold from its ore', is not essential and does not count towards word total, but helps to focus the student's thoughts on the task.

- Gold ore is **crushed** and **ground**.
- **Refractory minerals** are **separated** from the **oxide ore** and other **non-metallic minerals** by **froth flotation** to produce a **sulphide concentrate**.
- The concentrate is treated with the thermophilic bacterium ***Sulpholobus acidocalderius***.
- This **catalyses** atmospheric **oxidation** of **sulphide** minerals.
- This helps the **products** to **dissolve** OR **products** are **water soluble**.
- The **bacteria**, **concentrate** and **fresh water** are mixed together in **stirred** tanks.
- The **pH** is **adjusted** or **altered** by **adding lime**, then **sodium cyanide solution** is **added**.
- This is reacted with **zinc shavings** to produce gold.

Answers to Topic 1 questions

Review questions

1.1

a	Sulphuric acid	(1)	**i**	Calcium hydroxide	(1)
b	Nitric acid	(1)	**j**	Hydrogen peroxide	(1)
c	Ammonia	(1)	**k**	Ammonium sulphate	(1)
d	Sodium carbonate	(1)	**l**	Manganese(II) carbonate	(1)
e	Potassium sulphate	(1)	**m**	Cobalt(II) bromide	(1)
f	Potassium hydrogencarbonate	(1)	**n**	Chromium(III) oxide	(1)
g	Ammonium chloride	(1)	**o**	Calcium fluoride	(1)
h	Silver nitrate	(1)			

Total 15 marks

1.2

a	$H_2(g)$	(1)	**e**	$Cl_2(g)$	(1)	**i**	$Hg(l)$	(1)
b	$He(g)$	(1)	**f**	$K(s)$	(1)	**j**	$S(s)$	(1)
c	$N_2(g)$	(1)	**g**	$Br_2(l)$	(1)			
d	$O_2(g)$	(1)	**h**	$I_2(s)$	(1)			

Total 10 marks

1.3

a	$CuSO_4$	(1)	**e**	K_2CO_3	(1)	**i**	$Fe_2(SO_4)_3$	(1)
b	KNO_3	(1)	**f**	NH_4NO_3	(1)	**j**	$Mg(OH)_2$	(1)
c	$CaCl_2$	(1)	**g**	FeI_2	(1)			
d	ZnO	(1)	**h**	$Al(NO_3)_3$	(1)			

Total 10 marks

1.4

a $2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$ (2)
b $2Zn(NO_3)_2(s) \longrightarrow 2ZnO(s) + 4NO_2(g) + O_2(g)$(2)
c $Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$ (2)
d $2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$ (2)
e $2Al(OH)_3(s) \longrightarrow Al_2O_3(s) + 3H_2O(l)$ (2)

Total 10 marks

1.5

a i $Na^+, CO_3^{2-}, Ca^{2+}, Cl^-$ (1)
ii $CaCO_3$, calcium carbonate (1)
iii $Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$ (2)
b i $Mg^{2+}, SO_4^{2-}, K^+, OH^-$ (1)
ii $Mg(OH)_2$, magnesium hydroxide (1)
iii $Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$ (2)
c i $Zn^{2+}, NO_3^-, Na^+, OH^-$ (1)
ii $Zn(OH)_2$, zinc hydroxide (1)
iii $Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$ (2)
d i $Al^{3+}, SO_4^{2-}, K^+, OH^-$ (1)
ii $Al(OH)_3$, aluminium hydroxide (1)
iii $Al^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s)$ (2)
e i $Pb^{2+}, NO_3^-, K^+, CrO_4^{2-}$ (1)
ii Lead chromate, $PbCrO_4$ (1)
iii $Pb^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$ (2)

Total 20 marks

1.6

a Thermal decomposition (1); the $CaCO_3$ is broken down by heating. (1)
b Precipitation (1); solid zinc hydroxide is produced when two solutions are mixed together. (1)
c Redox (1); Fe_2O_3 loses oxygen *or* Fe^{3+} gains electrons (1)
or reduction (1); reason as above (1)
or oxidation (1); CO gains oxygen (1)
d Precipitation (1); ions in solution produce a solid. (1)
e Redox (1); Fe^{2+} loses electrons forming Fe^{3+} (1)
or charge on Fe^{2+} ion increases (1)
or Cl_2 gains electrons (1)

Total 10 marks

1.7

a $3Mg(s) + Fe_2O_3(s) \longrightarrow 3MgO(s) + 2Fe(s)$ (2)
b $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$ (2)
c $Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$ (2)
d $2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$ (2)
e $NH_3(g) + HNO_3(aq) \longrightarrow NH_4NO_3(aq)$ (2)

Total 10 marks

1.8

a 63 (1) **c** 270.5 (1) **e** 964 (1)
b 162.5 (1) **d** 286 (1)

Total 5 marks

1.9

a 6.5 g (1) **c** 100 g (2) **e** 5.1 g (3)
b 4.8 g (1) **d** 33 g (3)

Total 10 marks

1.10

a 0.50 (2) **c** 0.050 (2) **e** 50 (2)
b 0.13 (2) **d** 0.050 (2)

Total 10 marks

1.11

a Moles of $Fe_2O_3 = \frac{8}{160}$ (1); moles of Mg $= 3 \times \frac{8}{160}$ (1)
Mass of Mg $= 24 \times 3 \times \frac{8}{160} = 3.6$ g (1)

b Moles of HgO $= \frac{4.32}{216}$ (1) $= 0.02$ (1)
Mass of Hg $= 0.02 \times 200 = 4.0$ g (1)
Volume of $O_2 = 0.02 \times \frac{24}{2}$ (1) $= 0.24$ dm^3 or 240 cm^3 (1)

c Moles of Zn $= \frac{15}{65.4}$ (1)
Volume of $H_2 = \frac{15}{65.4} \times 24$ (1) $= 5.50$ dm^3 or 5500 cm^3 (2SF) (1)

d 4.8 $dm^3 = \frac{4.8}{24} = 0.2$ mol (1)
moles of Al $= \frac{2}{3} \times 0.2$ (1)
mass of Al $= \frac{2}{3} \times 0.2 \times 27 = 3.6$ g (1)

e Moles of ammonia $= \frac{0.6}{24} = 0.025$ (1)
Moles of $NH_4NO_3 = 0.025$ (1)
Mass of $NH_4NO_3 = 0.025 \times 80 = 2.0$ g (1)

Total 17 marks

1.12

a $MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$ (2)
b 0.05 moles of MgO required (1); $0.05 \times 40 = 2.0$ g (1)
c 0.05 mole of crystals. Molar mass of $MgCl_2.6H_2O = 203$ (1)
mass of crystals $= 0.05 \times 203 = 10.15$ g (1)
d Crystals remain in solution (1); $MgCl_2$ lost during transfer operations. (1)

Total 8 marks

Examination questions

1.13

a $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$ (2)
b Evaporate *some* water (1); set aside/cool (1);
filter and dry crystals on paper (1)
c 65.4 g Zn gives 287.4 g of hydrated salt (1)
2.0 g Zn gives $287.4 \times \frac{2}{65.4}$ g (1)
$= 8.8$ or 8.79 g (2 or 3 SF) (1)

Total 8 marks

1.14

a V^{3+} (1)

b Molar mass of $V_2(SO_4)_3.3H_2O$ = 444 (g mol^{-1})
Molar mass of K_2SO_4 = 174 g mol^{-1} (1)
$\frac{1}{100}$ mol required (1)
$\therefore$ 1.74 g required (1)

c V_2O_3 (1)
Least oxygen per V atom (1)
Smallest ionic charge, V^{3+} (1)

Total 7 marks

1.15

a i (Dilute) sulphuric acid (1)
ii Bubbles/effervescence (1); metal dissolves. (1)

b i 0.1 (1)
ii $\frac{6}{55}$ = 0.109 or 0.11 (1)
iii Excess Mn used to ensure complete reaction of acid (1)
iv To remove unreacted Mn (1)
v The salt would be decomposed/dehydrated (1)
vi Molar mass = 223 (1); 0.1 mole = 22.3 g (1)
vii Some $MnSO_4$ remains in solution (1); (or other sensible, practical reason)

c i Hardness/toughness/strength/malleability (1)
ii Reduction (1)
iii Ratio Mn: Fe is $\frac{80}{55}:\frac{20}{56}$ which is almost 4:1 (1)

Total 14 marks

NUFFIELD ADVANCED CHEMISTRY TOPIC 1

AN ALTERNATIVE APPROACH

1.1 The chemists' toolkit: writing formulae and balancing equations

In this toolkit we are going to start with the construction of chemical formulae.

A formula conveys two pieces of information; it gives the identity of the elements present, and it also tells us the ratio in which the atoms or ions are combined together. For example, the formula for sucrose, $C_{12}H_{22}O_{11}$, tells chemists that there are three elements present in the compound: carbon, hydrogen and oxygen, and that in one molecule there are 12 carbon atoms, 22 hydrogen atoms and 11 oxygen atoms all linked together.

COMMENT

Compounds can be classified as ionic or covalent on the basis of the type of bonding present.

Ionic compounds

Atoms of metals lose electrons in order to achieve **stable** electronic structures, and you should be able to recall that this often results in the formation of a noble gas structure.

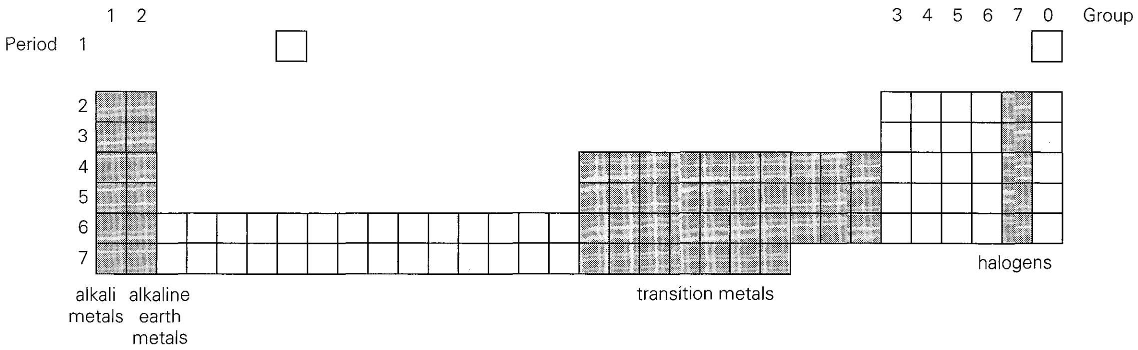


Figure 1.1 Periodic Table of the elements (in outline)

From the position of many metals in the Periodic Table it is possible to deduce how many outermost electrons are lost when they form positive ions. Thus the formulae of some simple metal ions are:

Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}

Look at the detailed Periodic Table in the Students' Book to see how this pattern is related to the columns (groups) in the Table.

The transition metals also form positive ions, but the rules which govern just how many electrons are lost from their atoms are complicated. Transition metals can form a variety of different positive ions, for example:

Fe^+, Fe^{2+}, Cu^+, Cu^{2+}, Mn^{2+}

Balancing the loss of electrons by metals, the **non-metals** on the **right-hand side** of the table **gain electrons** to achieve noble gas structures. From their position in the Periodic Table it is again possible to deduce how many electrons are gained when they form negative ions, for example:

F^-, Cl^-, Br^-, O^{2-}, S^{2-}, N^{3-}

STUDY TASK

Obtain a copy of the Periodic Table, and use a coloured pen to mark the formulae of the ions listed above in the appropriate places in the table alongside the symbols for the elements. Use table 5.3 in the *Book of data* to find the formulae of the common ions formed by other elements in Groups 1, 2, 3, 5, 6 and 7 and also enter these onto your table.

1 What patterns can you see?

2 Where are the positive ions found? Where are the negative ions found?

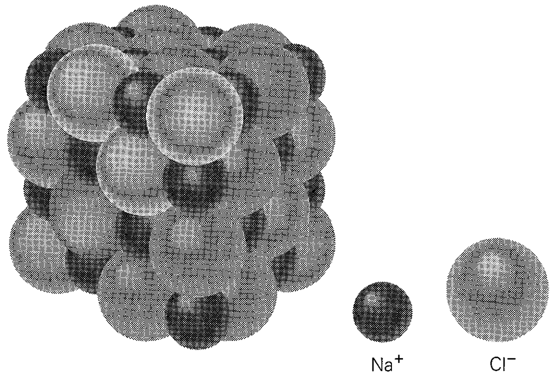


Figure 1.2 Space-filling model of sodium chloride

For the electric charges to be balanced in an ionic compound, positive and negative ions are present in compounds in a ratio which gives the compound overall neutrality, and this ratio gives the formula.

For example, with lithium oxide, containing Li^+ ions and O^{2-} ions, there must be twice as many Li^+ ions as there are O^{2-} so the formula can be written $Li^+{}_2O^{2-}$ or, more simply as Li_2O, with the charges omitted. Notice that the $_2$ referring to the Li^+ ions, follows the symbol, and does not precede it.

With aluminium oxide, containing Al^{3+} ions and O^{2-} ions, the ions will combine in a 2 to 3 ratio, so the formula can be written $(Al^{3+})_2(O^{2-})_3$, or, more simply as Al_2O_3 (with the charges omitted). Notice once again that the $_2$ and the $_3$ follow the symbols of the elements to which these numbers refer.

When an element can form more than one type of ion, Roman numerals in brackets after the name of the element give us the number of charges on the ion, for example:

the compound containing Fe^{2+} ions and Cl^- ions is called iron(II) chloride, and the formula is $FeCl_2$.

the compound containing Fe^{3+} ions and Cl^- ions is called iron(III) chloride, and the formula is $FeCl_3$.

These compounds, although they both contain the same elements, are *different* compounds, and therefore must be given their full names; the name *iron chloride* is ambiguous and should not be used.

COMMENT

The Roman numerals in each name indicate the degree of oxidation of a metal. In iron(II) chloride there are two chlorine atoms to every atom of iron; in iron(III) chloride there are three chlorine atoms to every atom of iron. The uncombined element is described as iron(0) because the iron atoms are not oxidised at all.

When Roman numerals are used in chemical formulae they are known as 'oxidation numbers'. You will be studying oxidation numbers in Topic 6. Here are some more examples of numerals:

Roman	Arabic
I	1
IV	4
V	5
VI	6
VII	7

STUDY TASK

Use your Periodic Table to construct the formulae for the following ionic compounds:

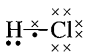
magnesium bromide
aluminium fluoride
copper(I) oxide
chromium(III) chloride
aluminium oxide
potassium sulphide
iron(II) oxide
copper(II) oxide
barium bromide.

Covalent compounds

Atoms of non-metals are characterised by having outermost electron shells which are almost complete. This is why when non-metals combine with each other they do so by sharing electrons in order to achieve noble gas structures with full outermost electronic shells. From their position in the Periodic Table it is possible to deduce how many electrons need to be involved in sharing so that this noble gas structure can be achieved.

Let us take an example: hydrogen combining with chlorine. A hydrogen atom needs to gain one electron to achieve a noble gas structure, so its only electron must be shared with an electron from another atom.

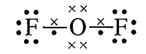
Chlorine atoms also need to gain one electron to achieve the same goal. One of the chlorine atom's outermost electrons must be shared with an electron from another atom. Thus one hydrogen atom will share its electron with an electron from the chlorine atom and a single covalent bond is formed between them.



$\mathrm{H}\overset{\times}{\cdot}\overset{\times\times}{\underset{\times\times}{\mathrm{Cl}}}\overset{\times}{\underset{\times}{}}$ or just H—Cl

The formula of a hydrogen chloride molecule is therefore HCl.

Another example is oxygen combining with fluorine. Oxygen atoms need to gain two electrons to achieve a noble gas structure, so two of its outermost electrons must be shared with another atom. Fluorine atoms need to gain only one electron to achieve a noble gas structure, so only one of these outermost electrons must be involved in sharing. Thus to satisfy the requirements of both types of atom, two electrons from one oxygen atom will share with one electron from each of two fluorine atoms and two single covalent bonds are formed between them.



$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\overset{\times}{\cdot}\overset{\times\times}{\underset{\times\times}{\mathrm{O}}}\overset{\times}{\cdot}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:$ or just F—O—F

The formula of an oxygen difluoride molecule is therefore OF_2.

You will see that the number of covalent bonds which the common non-metals form with each other follows a pattern:

H 1				
	C 4	N 3	O 2	F 1
	Si 4	P 3	S 2	Cl 1
				Br 1

You should realise that this method of finding the formulae of covalent compounds only works for simple compounds. You will come across other covalent compounds like hydrogen peroxide (H_2O_2) and carbon monoxide (CO), where the electron sharing is more complicated.

STUDY TASK

Use the table above to predict the formulae of the following simple covalent compounds:

sulphur bromide
silicon fluoride
phosphorus chloride
ammonia
hydrogen sulphide
carbon disulphide.

Compounds with both ionic and covalent bonding

Many inorganic compounds contain three or more elements, in which the ions are assemblies of atoms held together by covalent bonds. At this stage, you do not need to be concerned about their structure, but you do need to know their formulae, because a large number of inorganic compounds are composed of these ions.
The commonest are listed below:

Positive ions (cations)	Negative ions (anions)	
ammonium ion NH_4^+	hydroxide ion	OH^-
	carbonate ion	CO_3^{2-}
	hydrogencarbonate ion	HCO_3^-
	nitrate ion	NO_3^-
	sulphate ion	SO_4^{2-}
	phosphate ion	PO_4^{3-}

You will see that most ions of this type are negatively charged.

We can use the same rules to construct formulae as we used for simple ionic compounds. For example, sodium carbonate contains sodium ions, Na^+ and carbonate ions, CO_3^{2-}, and so the formula must be $(Na^+)_2CO_3^{2-}$, but this is normally written without the charges as Na_2CO_3.

In the case of a compound such as calcium hydroxide, containing Ca^{2+} ions and OH^- ions, we must write the formula as $Ca(OH)_2$, and *not* $CaOH_2$ (no brackets). Without the brackets the formula would imply that there were two hydrogen atoms but only one oxygen atom, whereas there are actually *two hydroxide* ions present.

STUDY TASK

Use the list of ions you have entered on your copy of the Periodic Table and the list of ions given above to work out the formulae of the following compounds:

potassium nitrate
sodium phosphate
magnesium sulphate
ammonium bromide
sodium hydrogencarbonate

calcium carbonate
aluminium hydroxide
copper(II) nitrate
chromium(III) sulphate
barium hydroxide.

Balancing equations

Now that you have practised constructing formulae you need to be able to construct balanced chemical equations. Equations in chemistry are very important:

- They convey information about the nature of the reactants and the products of the reaction.
- They give us the ratio in which the reactants combine and the products are formed. This is important information, because it enables us to mix the reactants in the correct mass ratio and to predict what mass of products we should expect to obtain.
- Finally in more advanced cases, an equation can sometimes predict the feasibility of a reaction. However, even a correctly balanced equation does not necessarily indicate that a reaction will take place.

To construct equations, there are four stages.

1. You need to be able to write down the **word equation** and to be certain that you know the names for all the reactants and products.
2. You must convert the names of all the substances into **correct formulae**. This is what we have been practising above.
3. Since atoms can neither be created nor destroyed, the **equation needs to be balanced** so that there are the same numbers of atoms of each element on both sides of the equation. You can only do this by altering the proportions of the substances reacting together, and also those of the substances created.

4 Next add abbreviations to show whether the substances are solids, liquids or gases or dissolved in water. These are known as **state symbols**. The four commonest state symbols, which are always enclosed in brackets, are listed in the margin.

COMMENT

The state symbols are solid (s), gas (g), liquid (l), and solution in water (aq). (aq) is from the Latin for water, *aqua*.

COMMENT

Many non-metal elements have two atoms in their molecules:
H_2 N_2 O_2 Cl_2 Br_2 I_2

To see these stages in operation let us consider the combustion of methane, CH_4, with oxygen:

1 From your work in an earlier course you should know that carbon dioxide and water are formed:

$$\text{methane} + \text{oxygen} \longrightarrow \text{carbon dioxide} + \text{water}$$

2 The formulae for each reactant and product must now be constructed, and we can write:

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O$$

3 The equation above, however, shows us the destination of the single carbon atom within the methane molecule. It forms part of the carbon dioxide molecule.

However, out of the four hydrogen atoms in the methane molecule, only two can be accounted for in the water molecule. So two water molecules must be formed, and we write this as $2H_2O$.

Now two water molecules must contain two oxygen atoms, and, together with the two oxygen atoms within the carbon dioxide molecule, this makes a total of four oxygen atoms appearing in the products. Yet there are only two oxygen atoms within the oxygen molecule. So there must be two oxygen molecules to start with, and we write this as $2O_2$. So we can write:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

And as the fourth stage we add the state symbols:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

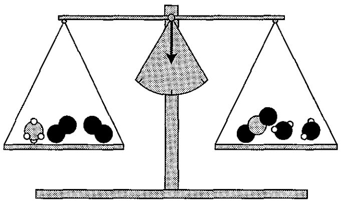


Figure 1.3 The reactants and products of a reaction always have exactly the same mass

Study this equation carefully and compare it with the models shown on the scales in figure 1.3. There are four hydrogen atoms, four oxygen atoms and one carbon atom on each side, and the equation is balanced.

When you write balanced equations, **you must never change the formula to suit the balancing process**. You can only change the *proportions* of the substances reacting and those of the substances formed, by putting numbers in front of the formulae, until all the atoms are accounted for.

The construction of balanced equations in chemistry is a very important skill to acquire. We have mentioned already that equations can help you to work out the reacting masses involved in a reaction. You will see patterns of reactions far more clearly than you would from any word equation.

Understanding inorganic reactions

EXPERIMENT 1.1a Thermal decomposition

Procedure

Only do this experiment in a fume cupboard because toxic fumes are produced.

a In separate experiments heat small samples of cobalt(II) sulphate, copper(II) nitrate (TAKE CARE), and zinc carbonate.

In your notes:
Design a table in which you can record the names, appearance and formulae of the compounds you heated. Describe the changes you see when the substances are heated and their final colour.

Try to identify any gases evolved.

b The action of heat on ammonium dichromate(VI) will be demonstrated to you.

In your notes:
To your table add a description of the effect of heat on ammonium dichromate(VI). From the formula try to deduce the gases likely to have been evolved.

SAFETY

Hydrochloric, nitric and sulphuric acids and sodium hydroxide are corrosive even when dilute, but be especially careful when using concentrated solutions; nitrogen oxides and sulphur dioxide are toxic materials and should be treated with care.

BACKGROUND

Simple tests for gases likely to be produced in experiments:

- **Water vapour** – when cooled down, water vapour condenses into droplets of liquid. This liquid turns cobalt chloride paper from blue to pink.
- **Carbon dioxide** – has no smell. When bubbled through lime water (calcium hydroxide solution), the solution turns cloudy.
- **Oxygen** – has no smell. Use a glowing splint to test: this will burst into flames.
- **Oxides of sulphur** – have a choking smell. Colourless, sometimes produce misty fumes when moist and are strongly acidic, so test with moist Full-range Indicator paper.
- **Nitrogen dioxide** – a brown acidic gas, so observe the colour and use moist Full-range Indicator paper.

SAFETY

Cobalt(II) sulphate is harmful.
Copper(II) nitrate is harmful and oxidising.
Unfamiliar solids must be heated in a fume cupboard.
Ammonium(VI) dichromate is explosive and toxic by inhalation. It is a category 2 carcinogen. It must be heated only in an efficient fume cupboard, or in a vessel with a mineral wool plug to prevent particles escaping.

Interpretation of the experiment

Cobalt(II) sulphate

You used hydrated cobalt(II) sulphate crystals for your first experiment. These pink crystals have the formula $CoSO_4.7H_2O$. The $7H_2O$, known as water of crystallisation, tells us that seven water molecules are present in the solid, for each cobalt ion and for every sulphate ion.

The pure crystals are not damp, because the water is chemically combined inside the solid. However, when gently heated, the crystals release this water as vapour, which you would have seen condensing inside the upper, colder part of the test tube. The amount of water produced is sometimes surprisingly large. When this dehydration is complete, the solid, which was once hydrated, is now said to be anhydrous. You should also have seen that a colour change occurred, from pink to mauve.

Copper(II) nitrate

Copper(II) nitrate crystals have the formula $Cu(NO_3)_2.6H_2O$. When you gently heated these crystals, the water would have been evolved, leaving anhydrous copper(II) nitrate. Then when you heated this anhydrous powder, a black powder of copper(II) oxide formed and nitrogen dioxide, NO_2, and oxygen, O_2, were released.

Zinc carbonate

Zinc carbonate decomposes fairly readily, giving off a colourless odourless gas that you should have identified as carbon dioxide. The zinc oxide residue has the unusual property of appearing yellow when hot but regaining its normal white colour when cooled. This colour change is reversible and is a physical process, since no new substance is formed.

QUESTIONS

Construct balanced equations, including state symbols, for:

1 the dehydration of hydrated cobalt(II) sulphate
2 the decomposition of zinc carbonate
3 the decomposition of hydrated copper(II) nitrate.

Ammonium dichromate(VI)

Ammonium dichromate(VI) is an orange solid with the formula $(NH_4)_2Cr_2O_7$.

On heating it leaves a dark green residue of chromium(III) oxide, and water vapour is evolved, along with another well known gas that will not have reacted to any of your gas tests.

Most decompositions are endothermic, but this particular reaction is strongly exothermic. Once started, it continues of its own accord, accompanied by a spectacular and extensive display of sparks, reminiscent of Roman Candle fireworks. The hot gases produced propel the tiny solid particles of chromium(III) oxide upwards in an effect similar to that of an erupting volcano. As well as its ability to decompose in this spectacular fashion, ammonium dichromate(VI) is also an oxidising agent, so it is a useful laboratory chemical.

COMMENT

When chemicals react and give off energy to their surroundings we say an **exothermic reaction** has taken place. Some reactions 'pull in' energy from their surroundings and in these cases we say an **endothermic reaction** has taken place.

QUESTION

Use the formula for ammonium dichromate(VI) and the other information given above to construct a balanced equation for the decomposition of this solid.

Precipitation reactions

You are going to mix solutions of a few representative metal compounds, all of which are encountered frequently in the laboratory, with aqueous sodium hydroxide.

EXPERIMENT 1.1b Precipitation reactions

SAFETY

Cobalt(II) chloride is toxic.
Iron(II) sulphate is harmful.
Iron(III) chloride is irritant.
Cobalt(II) sulphate is harmful.
0.4 M sodium hydroxide is an irritant.

Procedure

Design a table in your notes. You could use one like that shown below.

Name	Formula	Colour before mixing	Colour after mixing
copper(II) chloride			
iron(II) sulphate			
iron(III) chloride			
cobalt(II) sulphate			

As you carry out the experiment enter your observations in the table as you go along, otherwise you will forget important details which need to be recorded.

Mix small volumes of fresh solutions of each of the four salts in separate test tubes with dilute sodium hydroxide solution.

Enter your results in the table, noting in the final column the production of any cloudiness, which indicates the formation of an insoluble solid, known as a precipitate. Record the colour of any precipitate. When a precipitate is formed, use the solubility information in the background box to decide what it is, and write an equation for the reaction.

BACKGROUND: SOLUBILITY

1 Sodium, potassium and ammonium compounds are always soluble in water.

2 All nitrates are soluble in water.

3 Most chlorides are soluble in water; lead chloride and silver chloride are common exceptions to this rule.

4 Most sulphates are soluble in water; lead sulphate and barium sulphate are common exceptions to this rule.

5 Most oxides, hydroxides and carbonates are insoluble in water; calcium hydroxide is slightly soluble in water. All sodium, potassium and ammonium compounds are soluble.

Interpretation of the experiment

It is important that you understand what is going on when a precipitate is formed. In all the experiments which you have just carried out, the chemicals were ionic and in solution, so, before mixing, the ions were independent of each other.

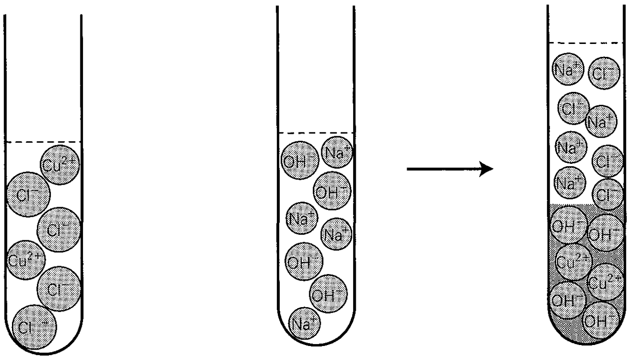
Consider the first experiment between aqueous copper(II) chloride and aqueous sodium hydroxide:

- the solution of copper(II) chloride contains $Cu^{2+}(aq)$ and $Cl^{-}(aq)$ ions
- the solution of sodium hydroxide contains $Na^{+}(aq)$ and $OH^{-}(aq)$ ions.

You will have noticed that a blue precipitate was formed in this reaction, so presumably two of the ions must have been attracted to each other. For the four ions above, the interaction must have been between oppositely charged ions, so the precipitate must have been formed either between the Na^{+} and Cl^{-} ions or between the Cu^{2+} and OH^{-} ions. This reaction cannot have been between the Na^{+} and Cl^{-} ions, because sodium chloride is a soluble substance (see the solubility information).

However, copper(II) hydroxide is insoluble, as are most hydroxides, so it must be the blue precipitate. Its formula is $Cu(OH)_2$ and it was created when the copper(II) ions in the copper(II) chloride solution combined with the hydroxide ions in the sodium hydroxide solution in a 1:2 ratio.

$$Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$$



Before mixing

the Cu^{2+} and Cl^- ions move about randomly in solution

the Na^+ and OH^- ions move about randomly in solution

After mixing

the Cu^{2+} and OH^- ions come together to form a precipitate of solid copper(II) hydroxide;

the Na^+ and Cl^- ions have not taken part in the reaction: these are the 'spectator ions'

Figure 1.4 Forming a precipitate

Notice that the sodium ions, $Na^+(aq)$ and the chloride ions $Cl^-(aq)$ do not feature in the reaction at all. They are present in the mixture, of course, at the end of the reaction. For this reason they are often known as **spectator ions**. If you had filtered the mixture, they would have passed through the filter paper and formed the filtrate as a solution of sodium chloride, whereas the solid blue copper(II) hydroxide would have been the residue on the filter paper.

The type of equation above is known as an **ionic equation**, because it involves the interaction of ions. Spectator ions are often omitted in ionic equations, because the intention is to illustrate precisely what is happening in the solution, without mentioning any ions which are not involved in the process.

The full equation for the reaction is:

$$CuCl_2(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + 2NaCl(aq)$$

STUDY TASK

Write the ionic equation between copper(II) and hydroxide ions, and then construct balanced equations for the other precipitation reactions which occurred.

You should have noticed and recorded in your table that coloured precipitates were formed with Cu^{2+}, Fe^{2+}, Fe^{3+} and Co^{2+} ions:

- $Cu^{2+}(aq)$ ions form a blue precipitate with aqueous sodium hydroxide
- $Fe^{2+}(aq)$ ions form a dirty green precipitate with aqueous sodium hydroxide
- $Fe^{3+}(aq)$ ions form a rusty brown precipitate with aqueous sodium hydroxide
- $Co^{2+}(aq)$ ions form a precipitate with aqueous sodium hydroxide.

COMMENT

The different colours of precipitates formed by $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ ions when added to aqueous sodium hydroxide are very useful means of distinguishing between them.

STUDY TASK

Use the ideas you have met to construct balanced equations for the following reactions. In some cases the products are given, and in others you must work them out for yourself. Include state symbols in your equations.

1 sodium(s) + oxygen(g)

2 iron(s) + copper(II) sulphate(aq)

3 aluminium + chlorine gas

4 carbon dioxide(g) + calcium hydroxide (lime water)(aq)
⟶ calcium carbonate(s) + water(l)

5 calcium carbonate(s) + hydrochloric acid(aq)
⟶ calcium chloride(aq) + carbon dioxide(g) + water(l)

6 barium chloride(aq) + potassium sulphate(aq)

7 ammonia(g) + oxygen(g) ⟶ nitrogen(II) oxide, NO(g) + water(l)

COMMENT

When you balance equations, you **must never change the formula to suit the balancing process**. You can only change the **proportions** of the substances reacting and those of the substances formed, by putting numbers in front of the formulae, until all the atoms are accounted for.

Answers to Topic 1: An alternative approach

STUDY TASK

'Obtain a copy of the Periodic Table ...'

1 All the ions with one positive charge are in Group 1 (the first vertical column of elements); those with two and three positive charges are in Groups 2 and 3 respectively.

Those ions with one negative charge are in Group 7 (think of this as being one place to the left of the noble gases); those with two and three negative charges are in Groups 6 and 5 respectively.

2 Metals form positive ions (left and middle of the Periodic Table); non-metals form negative ions (right of the Periodic Table).

STUDY TASK

'Use your Periodic Table ...'

The formulae are:

$MgBr_2$
AlF_3
Cu_2O
$CrCl_3$
Al_2O_3
K_2S
FeO
CuO
$BaBr_2$

STUDY TASK

'Use the table above to predict the formulae ...'

The predicted formulae are:

SBr_2
SiF_4
PCl_3
NH_3
H_2S
CS_2

STUDY TASK

'Use the list of ions you have entered ...'

The formulae are:

KNO_3
Na_3PO_4
$MgSO_4$
NH_4Br
$NaHCO_3$
$CaCO_3$
$Al(OH)_3$
$Cu(NO_3)_2$
$Cr_2(SO_4)_3$
$Ba(OH)_2$

QUESTIONS

'Construct balanced equations, including …'

1 $CoSO_4.7H_2O(s) \longrightarrow CoSO_4(s) + 7H_2O(g)$

2 $ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$

3 $2Cu(NO_3)_2.6H_2O(s) \longrightarrow 2CuO(s) + 4NO_2(g) + O_2(g) + 12H_2O(g)$

QUESTIONS

'Use the formula for ammonium dichromate …'

$(NH_4)_2Cr_2O_7(s) \longrightarrow Cr_2O_3(s) + 4H_2O(g) + N_2(g)$

STUDY TASK

'Write the ionic equation between copper(II) …'

$Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$
$Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$
$Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$
$Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$

STUDY TASK

'Use the ideas you have met to construct …'

1 $4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$

2 $Fe(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Fe^{2+}(aq)$

3 $2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$

4 $CO_2(g) + Ca(OH)_2(aq) \longrightarrow CaCO_3(s) + H_2O(l)$

5 $CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

6 $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

7 $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$

Answering summary comprehension questions

The usual advice for answering examination questions also applies to summary comprehension questions.

RTQ^2 is a useful mnemonic. It stands for **read the question twice**.

The difference when answering summary comprehension questions is that you are given a passage on which the questions are based. As with a question, you should read the passage at least twice.

The passage should be read first at normal reading speed, the sort of speed you would use to read a novel or a magazine. The second time you read the passage you should read it as you were first taught to read, either placing your finger under every word, or running a pencil along under each word. **Make sure that you read every word.** If you use a pencil, or a highlighter you may wish to underline key words or phrases.

The comprehension questions should then be read in the same way, once at normal reading speed and then carefully reading every word. Again, it may be helpful to underline or highlight keywords or phrases.

There are usually two types of comprehension question. The first type of question is designed to find out how well you understand the passage. The answer to this type of question would usually be found in the passage itself. It is important to be as full and precise as possible in your answer. Unlike in an English comprehension, you are not expected to find new phrases to answer the questions, but you are expected to find the relevant parts of the passage and express them as succinctly and accurately as possible.

The second type of comprehension question is designed to see if you can relate your knowledge of chemistry to the ideas, concepts or principles expressed in the passage. This type of question will sometimes involve applying some of the chemistry learned in the module to the situation described in the passage or it may involve applying more general chemical ideas learned in the rest of the course. The best way of *preparing* for this type of question is to have thoroughly learned the material covered in each module. The way to *identify* this type of question is to look out for questions which ask for specific chemical knowledge like 'Give the formula of ... ' or 'What reagents and conditions would you use for ... ?'. The other clue is that the answer will not be found in the passage!

THE SUMMARY

The summary question will usually be in the form of an instruction like 'Write a summary in continuous prose, in no more than 100 words, describing ... '. Read the instructions carefully. The instruction will usually help you to write a title for your summary, and this is the next step. It is very helpful to write a title for your summary, because it will help you to *focus* your ideas on the appropriate key points. You can usually work out how many key points are expected. The number of key points is equal to the number of marks for the question. Although this will not always be exactly true, it is a very useful guide and will help you not to write too much or too little.

Once you have focused your ideas by writing a title, and you know how many key points you are trying to find, you are ready to go back to the passage and search for them. Many students find it helpful to underline or highlight the key points in the passage. Once you have done this, you are ready to start writing down the key points. The best thing to do is to write on alternate lines of the paper. This will make it much easier to edit your passage and make it flow without having to rewrite it. As with the comprehension questions, do not be frightened of copying phrases or sentences from the passage. You do not need to change the wording. If you do change the wording, you need to be very careful not to lose the precise chemical meaning of the point.

When you have finished writing down the key points you are ready to edit your passage. Make sure that your key points are in a logical sequence. This will usually be the sequence in which they appear in the passage. Your passage should consist of a number of sentences. Remember that each sentence must have a verb – a 'doing word'. Make sure that your key points are *not* in note form, but that they are written in good, flowing English using appropriate articles ('a' and 'the' are articles). You should avoid using any abbreviations. It is probably best to use chemical names rather than chemical formulae, unless a formula is essential to convey a key point.

It is useful to add an **introductory sentence** and a **closing sentence** to your passage. Sometimes you will find that you can join points together if they are connected in some way. Use conjunctions like 'and' and 'but'. Some of the marks for your summary will be for quality of language.

Your writing must be legible. The examiners must be able to read your writing at normal reading pace.

Finally, **count your words**. There is a penalty for exceeding the stated number of words. The easiest way to count your words is to count 20 at a time and make a pencil line every 20 words on your script. Then you will not have to start counting from the beginning if you lose count. If you do go over the target number of words, you need to be brutal to cut them. Remember your title does not count towards the number of words in your summary and a number with a unit counts as two words.

Solubility rules, OK?

Potassium, sodium and ammonium salts,
Whatever they may be
Can always be depended on
For solubility.

When asked about the nitrates,
The answer's always clear,
They each and all are soluble,
Is all we want to hear.

'Most every chloride's soluble,
At least we've always read,
Save silver, mercurous mercury,
And (slightly) chloride of lead.

Every single sulphate,
Is soluble, 'tis said,
'Cept barium and calcium
And strontium and lead.

Hydroxides of metals won't dissolve,
That is all but three,
Potassium, sodium and ammonium
Dissolve quite readily.

And then you must remember
That you must not forget
Calcium and barium
Dissolve a little bit.

Metallic sulphides will not mix
With water it is true
But if you read the two above
You'll find out which ones do.

The carbonates, insoluble,
It's lucky that it's so,
Or else our marble buildings
Would melt away like snow.

(Repeat with feeling)
Potassium, sodium and ammonium salts,
Whatever they may be,
Can always be depended on
For solubility.

Anon.

We are grateful to Chem 13 News for permission to reproduce the above poem.

TOPIC 2

Alcohols: an introduction to organic chemistry

Introduction

Students may already have some knowledge of alkanes and perhaps alcohols from their pre-A-level courses. This introduction to the chemistry of carbon compounds allows students an insight into the chemistry and formulae of simple alcohols and carbonyl compounds, and the chemistry of alcohols.

Organic chemistry is introduced at this point to give students an early experience of practical procedures and laboratory preparations and to allow a more equitable distribution of carbon chemistry throughout the course.

The students' appreciation of oxidation–reduction reactions is extended to include some simple examples from organic chemistry. The use of molar masses and the calculation of the correct molar proportions to use in reactions involving organic compounds serves to reinforce the material in Topic 1. The functional group chosen for study, alcohol —OH, allows a range of reaction types to be discussed. Students are encouraged to consider simple interpretations of the organic reactions they have studied and classify them as oxidation, reduction or dehydration (elimination) reactions.

Organic mechanisms are not introduced at this stage; this is reserved for Topic 8. The importance of alcohol in fermentation is discussed.

Content

Timing		Students' Book
2.1	2 hours	pages 27–31
2.2	2 hours	pages 31–36
2.3	2 hours	pages 37–39
2.4	Homework	pages 40–41
Total about 2 weeks		

2.1 The chemists' toolkit: naming carbon compounds – bonding in alkanes; molecular, structural and displayed formulae, structural isomers; names for compounds containing carbon atom chains; naming primary alcohols; naming more complicated alcohols; secondary and tertiary alcohols diols and triols.

2.2 Reactions of alcohols – experiments with alcohols; solubility, reaction with sodium, oxidation, dehydration; preparation of propene, propanal and propanoic acid from propan-1-ol; interpretation of reactions of alcohols.

2.3 How much? – molar masses of organic compounds; stages in a laboratory preparation; laboratory preparation of cyclohexene from cyclohexanol.

2.4 Background reading: the history of alcohol

Objectives

1 To introduce the nomenclature of alkanes and primary alcohols and the concept of functional groups.

2 To develop an understanding of molecular, structural, and displayed formulae and structural isomers.

3 To introduce the concept of homologous series.

4 To introduce a range of organic reactions: oxidation, reduction and dehydration (elimination).

5 To develop a knowledge of some of the reactions of alcohols, aldehydes and ketones, especially oxidation reactions.

6 To develop an understanding of the stages in the laboratory preparation of an organic compound.

7 To appreciate the historical and social significance of alcohol.

2.1 The chemists' toolkit: naming carbon compounds

Timing About 2 hours

Suggested treatment

This section is designed to provide the necessary introduction for naming straight-chain alkanes and alcohols before progressing to the experimental work on alcohols. Molecular, structural and displayed formulae are explained as well as isomers. The nomenclature of straight-chain alkane molecules is given. It is *not* intended at this stage that the nomenclature of organic compounds with branched chains be attempted.

It is suggested that, wherever possible, models are used to reinforce a knowledge of structure. By constructing models, students are more readily able to appreciate the spatial relationships between the atoms in molecules. Open rather than space-filling models are preferable at this stage because they relate most closely to the displayed formulae.

A Review task allows students to revise covalent bonding, which should have been covered in pre-A-level courses. Some students may need more help with this section. Teachers may wish to go over the main ideas of covalent bond formation in terms of sharing electron pairs before students embark on this task.

ANSWERS

Study task, page 29

3 $CH_3(CH_2)_3CH_3$; $(CH_3)_2CHCH_2CH_3$; $C(CH_3)_4$.

4 Hexane and cyclohexane do not have the same molecular formula.

Naming more complicated alcohols

Each group of students will need:

Molecular model kits to make models of propan-1-ol, propanal and propanoic acid. In this section primary, secondary and tertiary alcohols, diols and triols are distinguished but a full discussion of nomenclature is left until Topic 8.

2.2 Reactions of alcohols

Timing 2 hours will be needed

Suggested treatment

This section begins by introducing the term *functional group* and then proceeds with a study of some reactions of alcohols: reaction with sodium, oxidation, dehydration. Substitution is considered in Topics 8 and 10 and esterification is studied in Topic 15 when carboxylic acids are considered. Since the emphasis is intended to be on the reactions of alcohols and on basic practical procedures, there is no attempt to purify the products. Students should be encouraged to write an account of each section of the experiment and answer the questions on it before proceeding to the next section.

EXPERIMENT 2.2a Experiments with alcohols

HAZARDS

Teachers should provide freshly cut pieces of sodium. When preparing these, wear eye protection and ensure all equipment is dry. Place a piece of sodium on a white tile and cut with a knife. After use, place all equipment in a bowl of water to destroy any remaining sodium. Any residual sodium should be disposed of by reaction with propan-1-ol.

Hydrogen gas, which is extremely flammable, is produced by the reaction of sodium with the alcohols, although the quantities produced will be small if small pieces of sodium are used. The sodium alkoxides produced during this reaction are corrosive and highly flammable.

The ethanal produced during the oxidation of ethanol is harmful with a possible risk of irreversible effects.

Each group of students will need:
Eye protection
Bunsen burner and heatproof mat
Full rack of test tubes and boiling tubes
Test tube holder
Small evaporating basin
Dropping pipette

Access to:
Butan-1-ol FLAMMABLE, HARMFUL
Ethanol HIGHLY FLAMMABLE
Methanol HIGHLY FLAMMABLE, TOXIC
Pentan-1-ol FLAMMABLE, HARMFUL
Propan-1-ol HIGHLY FLAMMABLE
Sodium, 2 mm cubes FLAMMABLE, CORROSIVE
0.1 M sodium dichromate(VI) TOXIC SOLUTION, SKIN SENSITISER
1.0 M sulphuric acid IRRITANT
Full-range Indicator paper

Procedure

Full instructions are given in the *Students' Book.* The following points should be discussed with the students.

1 Solubility in water

The longer the carbon chains, the less soluble the alcohol. After pentan-1-ol, the solubility of the alcohols is less than 1g in 100 g of water. Solutions of alcohols in water should be neutral. The trend in solubility of the alcohols can be explained in terms of the greater proportion of 'insoluble hydrocarbon chain' as the molar mass increases. Students should realise at this stage that the —OH group makes the alcohols more soluble than the corresponding hydrocarbon but an explanation in terms of hydrogen bonding is left until Topic 9.

2 Reaction with sodium

Students will see little or no reaction unless the sodium is freshly cut. Details of the reaction are given in the *Students' Book.* The trend in the rate of reaction with different alcohols reflects the proportion of hydrocarbon chain in the alcohol molecules.

3 Oxidation

Students should be able to discern a pungent smell of ethanal. The green colour of the Cr^{3+} ion should be obvious, indicating reduction of dichromate(VI). The reaction of the alcohols becomes progressively slower with increasing length of carbon chain but the reaction with methanol is also quite slow.

EXPERIMENT 2.2b Preparations using propan-1-ol

There is a microscale alternative to parts of this experiment (see M3 pages 294 and 300).

Each group of students will need:
Eye protection and protective gloves
Test tubes and rack
Bunsen burner, tripod, gauze and heatproof mat
Apparatus for gas collection (see figure 2.1)
Ceramic fibre
3 test tubes with corks

Apparatus for refluxing and distillation with pear-shaped flask, 50 cm^3 (see figure 2.2 and 2.3)
Anti-bumping granules
Boiling tube
Dropping pipettes, 3
Measuring cylinders, 10 cm^3
Weighing boat
Aluminium oxide, 4–8 mesh granules, 5 g
Propan-1-ol, 6 cm^3 HIGHLY FLAMMABLE
Sodium dichromate(VI), 6 g and 3 g VERY TOXIC, SKIN SENSITISER
Concentrated sulphuric acid, 2 cm^3 CORROSIVE
1 M sulphuric acid, 15 cm^3 IRRITANT

Access to:
Benedict's solution HARMFUL PRODUCT
0.1 M sodium hydroxide IRRITANT
0.05 M bromine water HARMFUL, IRRITANT
0.01 M potassium manganate(VII)
0.1 M sodium carbonate
Balance, to weigh to ±0.1 g

HAZARD

Sodium dichromate(VI) may cause sensitisation by skin contact so gloves should always be worn when using the solid and preferably when using the solution.
The products are hazardous: propene gas is highly flammable; propanoic acid is corrosive; propanal is highly flammable and irritant.

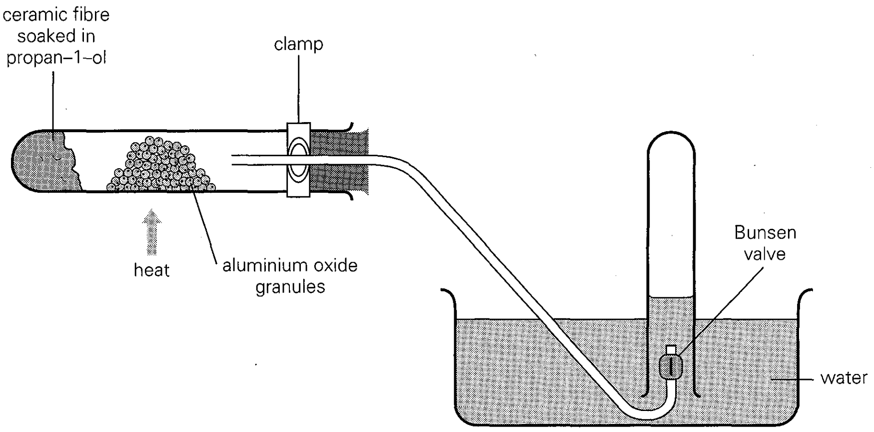


Figure 2.1 Apparatus for gas collection

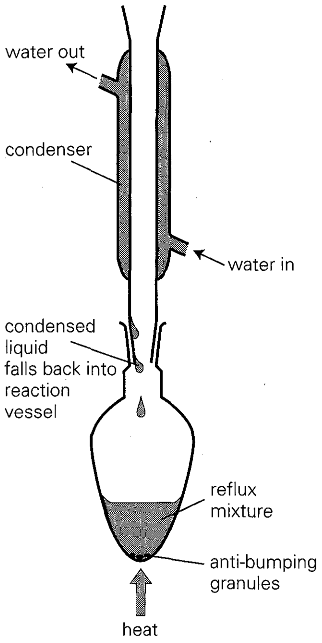


Figure 2.2 Apparatus for refluxing

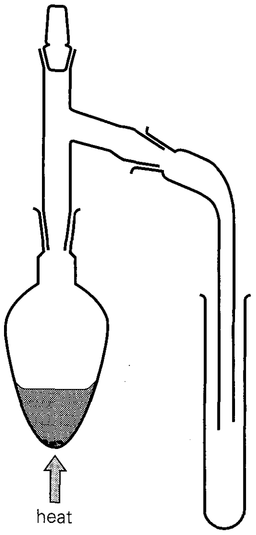


Figure 2.3 Apparatus for distillation

Procedure

Full instructions are given in the *Students' Book*. Benedict's solution is used to test for the aldehyde produced in reaction 3 rather than Fehling's solution because the former is less hazardous and gives more consistent results. It works better if a little sodium hydroxide solution is added before warming.

1 The dehydration of propan-1-ol

Bromine water and acidified potassium manganate(VII) are decolorised. The product is therefore unsaturated. This is an elimination reaction producing a good yield of propene. To prepare approximately 0.05 M bromine water, crush a small (1 cm^3) ampoule of bromine under 200 cm^3 of water. Decant the liquid into a bottle and make up to 500 cm^3. Alternatively, add 1 cm^3 of liquid bromine to 500 cm^3 water. WEAR RUBBER GLOVES and work in fume cupboard.

2 The oxidation of propan-1-ol

Teachers should advise pupils of the necessary care to be taken when refluxing, for example, tightly fitting joints, use of anti-bumping granules etc. The sodium dichromate(VI) is added as a solution down the condenser in the reflux position; this allows more control over the reaction.

A simplified equation for this reaction is given in the *Students' Book*. At this early stage, it is not advisable to give students the full equation. The product will have an acrid smell and neutralises a relatively large volume of sodium carbonate solution. It should not give an orange precipitate with Benedict's solution.

3 The partial oxidation of propan-1-ol

The propanal produced in this reaction should only neutralise one or two drops of sodium carbonate but will give a brick red precipitate on heating with Benedict's solution confirming that a different product has been obtained. Students should see the colour of the solution change gradually from blue through green to yellow and finally to red as the aldehyde reduces the copper(II) ions. This series of colour changes is seen most clearly if the reaction is carried out in a boiling water bath.

Benedict's solution

Benedict's solution can be purchased or prepared. To make about 100 cm^3 of the solution dissolve 17.3 g of sodium citrate and 27 g of sodium carbonate-10-water (IRRITANT) in 70 cm^3 of pure water. Then dissolve 1.73 g of copper sulphate-5-water (HARMFUL) in 15 cm^3 of water and add this to the citrate-carbonate solution with constant stirring.

Interpretation of the reactions of alcohols

Each group of students will need:
Molecular model kits.

This section summarises the reactions of primary alcohols which the students have just carried out. The simplified equations are all that is necessary at this stage. The oxidation of secondary alcohols is also discussed, and this use of models can help show why tertiary alcohols cannot be oxidised in this way.

Teachers might find it useful to introduce the naming of simple aldehydes and carboxylic acids in order to answer question 3. The students are asked to make molecular models of some of the compounds they have encountered.

ANSWERS

Study task, page 36

2 a $2C_4H_9OH + 2Na \longrightarrow 2C_4H_9O^-Na^+ + H_2$ **b** sodium butoxide

3 **a** ethene **b** butene or but-1-ene **c** ethanoic acid

2.3 How much?

Timing About 2 hours will be needed

Suggested treatment

The chemists' toolkit: molar masses of organic compounds

This introductory section gives students further practice at working out molar masses.

ANSWERS

Questions, page 37

1 The molar mass of linalool is 126 g mol^{-1}.

2 Volumes occupied by one mole are: water, 18.0 cm^3; ethanol, 58.4 cm^3; cyclohexanol, 104.2 cm^3.

Stages in a laboratory preparation

This section and the experiment which follows reinforces the students' knowledge of dehydration reactions and mole calculations by considering the laboratory preparation of cyclohexene from cyclohexanol. The stages in a laboratory preparation are listed in the *Students' Book*, and teachers should spend some time discussing these before students start the experiment. A discussion of how to calculate the percentage yield should also be included here.

EXPERIMENT 2.3 How much cyclohexene can you get from cyclohexanol?

There is a microscale alternative to this experiment (see pages 294 and 301) (M4).

Each group of students will need:
Eye protection and protective gloves
Test tubes and rack
Bunsen burner, tripod, gauze and heatproof mat
Distillation apparatus with 50 cm^3 flasks (see figure 2.4)
Beaker, 100 cm^3
Conical flask, 50 cm^3, with stopper for drying
2 measuring cylinders, 10 cm^3
2 dropping pipettes, 10 cm^3
Thermometer, 0–110 °C
Separating funnel, 50 cm^3
Sample tube or weighing bottle

Access to:
Cyclohexanol, 15 cm^3 HARMFUL
Concentrated phosphoric(V) acid (85% syrupy, boil before use), 4 cm^3 CORROSIVE
Calcium chloride, anhydrous granular IRRITANT
0.05 M bromine water HARMFUL AND IRRITANT
0.01 M potassium manganate(VII)
Sodium chloride, saturated solution, 20 cm^3
1 M sulphuric acid IRRITANT
Balance, to weigh to ±0.1 g

HAZARDS

The fumes are unpleasant; do the experiment in a fume cupboard if possible. The product, cyclohexene, is highly flammable and harmful with a flash point of −6 °C. The receiver adaptor has a vent to which a length of tubing can be connected to lead the flammable vapours below bench level down the sink. If receiver adaptors with vents are not available or if insufficient flasks are available, side arm test tubes could be used in their place.

The product should not be stored since it may form unstable by-products.

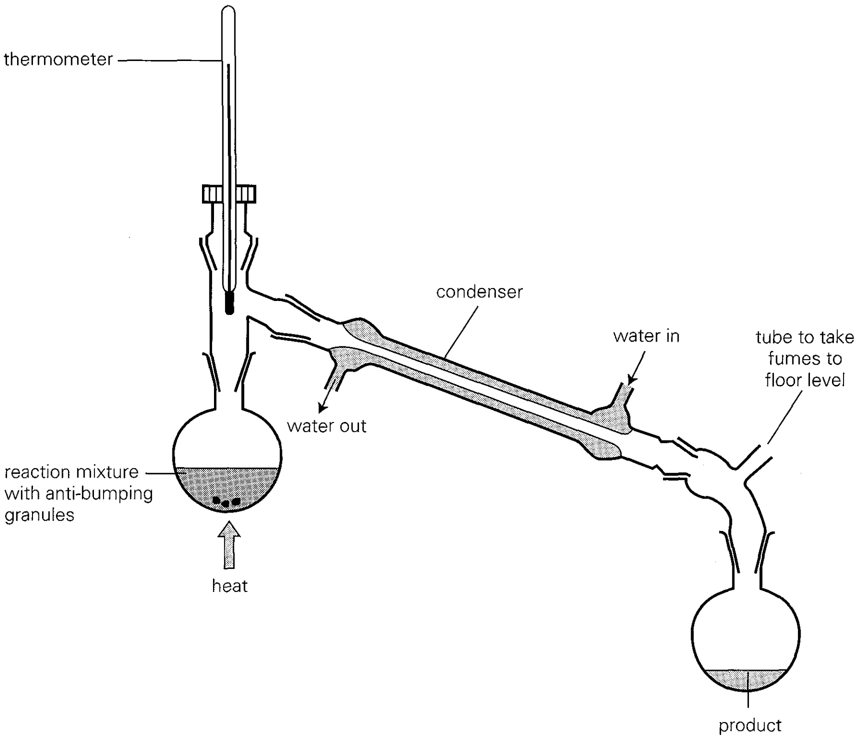


Figure 2.4 Apparatus for distillation with vent

Procedure

Full instructions for the experiment are given in the *Students' Book*. The introductory questions focus on the nature of the reactant and product and should be answered by the student before starting the experiment. A discussion of the difference in solubility between cyclohexanol and cyclohexene is a prerequisite for answering some of the questions following the preparation.

The volume of cyclohexanol required is 10.4 cm^3.

The dehydration of alcohols to alkenes is carried out by heating with phosphoric(v) acid. This method gives high yields with little decomposition, whereas the alternative method of dehydration using concentrated sulphuric acid produces extensive charring. However, should the yields be small, it may be better to collect together all the students' samples for a single distillation. The receiver adaptor has a vent to lead off flammable vapours to below bench level down the sink by means of rubber tubing. Although the boiling point of cyclohexene is approximately 84 °C, it fractionates with water at about 70–72 °C and so the distillate is collected over a relatively wide temperature range. This is probably the first time that students have used a separating funnel and teachers should take a few minutes explaining its use.

The notes the students are expected to write following the experiment should focus on the important points of the procedure. Students should appreciate that distillation is used to separate the product from the rest of the reaction mixture. The purification stages involve:

1. separation of cyclohexene from water-soluble contaminants using a separating funnel
2. removing water from the organic layer using anhydrous calcium chloride
3. redistillation to separate the more volatile cyclohexene from less volatile impurities.

A yield of up to 80% can be obtained. Teachers should discuss reasons why the yield is less than 100%, not only in terms of the incomplete conversion of reactant to product, but also in relation to losses of product during purification.

2.4 Background reading: the history of alcohol

This may be set for homework.

ANSWERS TO QUESTIONS

1 Sugar content; stored in a limited supply of air.

2 The conversion of glucose into ethanol and carbon dioxide is an exothermic reaction. The energy released enables the cells to stay alive and to replicate.

3 The ethanol in alcoholic drinks is absorbed and distributed throughout the drinker's body without any chemical change.
Chemical reactions that remove ethanol from our systems depend on a catalyst that is only present in small amounts. It takes a long time to metabolise even a small quantity of alcohol like the amount contained in two pints of beer.

4 Summary exercise, see below.

Key points to include in the summary

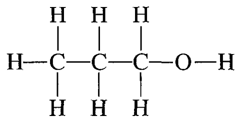
- **Grapes** are crushed to separate the juice as soon as possible after picking.
- **Sulphur dioxide** is used to kill wild yeasts.
- **Sugar** and **tartaric acid** are added to get the best balance.
- **Fermentation** is started by the addition of a **yeast** selected for its properties or, if suitable, using the natural yeasts in the grape skins.
- **Oxygen** is needed for the multiplication of yeast cells.
- The **temperature** needs to be kept at about 20 °C.
- Wine is stored for one year in the presence of a limited amount of air.
- The wine is **filtered**.

Answers to Topic 2 questions

Review questions

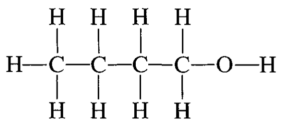
2.1

a



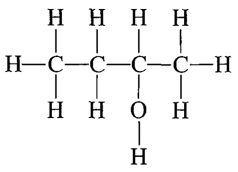
(1)

b



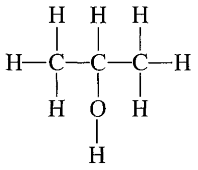
(1)

c



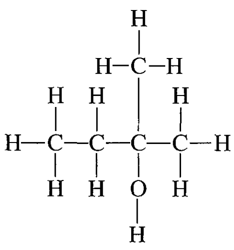
(1)

d



(1)

e

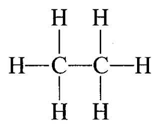


(1)

Total 5 marks

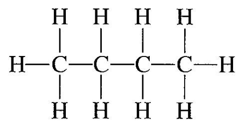
2.2

a



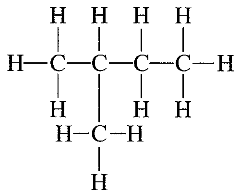
(1)

b



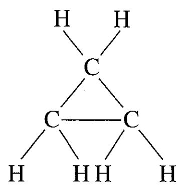
(1)

c



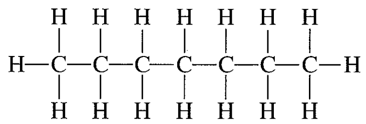
(1)

d



(1)

e



(1)

Total 5 marks

2.3

a	Methanol	(1)	**d**	Ethane-1,2-diol	(1)
b	3-methylpropan-1-ol	(1)	**e**	Sodium ethoxide	(1)
c	2-methylpropan-2-ol	(1)			

Total 5 marks

2.4

a	Propane	(1)	**d**	Cyclobutane	(1)
b	Pentane	(1)	**e**	Propene	(1)
c	2-methylpentane	(1)			

Total 5 marks

2.5

a $2CH_3OH(l) + 2Na(s) \longrightarrow 2CH_3O^-Na^+(s) + H_2(g)$ (2)

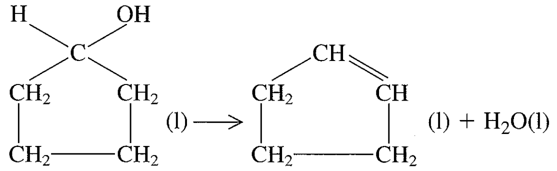
b $2C_2H_5OH(l) + 2Na(s) \longrightarrow 2C_2H_5O^-Na^+(s) + H_2(g)$ (2)

c $2C_3H_7OH(l) + 2Na(s) \longrightarrow 2C_3H_7O^-Na^+(s) + H_2(g)$ (2)

d $CH_3CH_2OH(l) \longrightarrow CH_2{=}CH_2(g) + H_2O(l)$ (2)

e $CH_3CH_2CH_2OH(l) \longrightarrow CH_3CH{=}CH_2(g) + H_2O(l)$ (2)

f

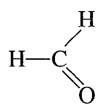


(2)

Total 12 marks

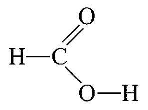
2.6

a



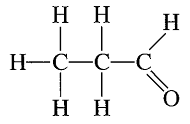
(1) methanal (1)

b



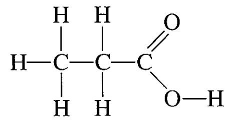
(1) methanoic acid (1)

c

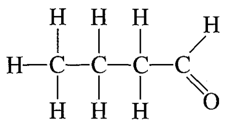


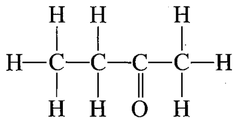
(1) propanal (1)

d



(1) propanoic acid (1)

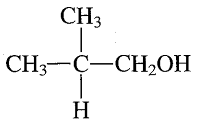
e  (1) butanal (1)

f  (1) butanone (1)

Total 12 marks

2.7 Isomers have same molecular formula but different structural formulae. (1)
Both have same molecular formula, C_3H_8O. (1)
They have different structural formulae, $CH_3CH_2CH_2OH$ and $CH_3CHOHCH_3$. (1)

Total 3 marks

2.8 

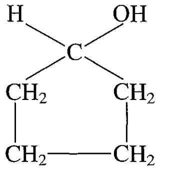
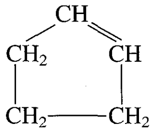
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH_2OH$$

(1); primary (1)

Total 2 marks

2.9
a 74 (1) **c** 102 (1) **e** 70 (1)
b 74 (1) **d** 88 (1)

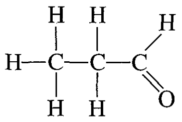
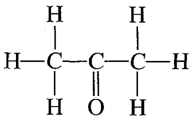
Total 5 marks

2.10
a HCHO (1); 30 (1)
b $CH_3O^-Na^+$ (1); 54 (1)
c  (1); 86 (1)
d  (1); 68 (1)
e CH_3COCH_3 (1); 58 (1)

Total 10 marks

2.11
a But-1-ene (1)
$CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH{=}CH_2 + H_2O$ (1)
b Molar masses of butan-1-ol and but-1-ene are 74 and 56. (1)
So 3.7g = 0.05 mole. (1)
Theoretical yield = 0.05 × 56 = 2.8 g (1)
c $\%\ \text{yield} = \frac{1.8}{2.8} \times 100 = 64\%$ (2)
d Unwanted (side) reactions. (1)
Loss of product during purification. (1)
e Dehydrating agent. (1)

Total 10 marks

2.12
a Blue (1)
b Cu^{2+} (1)
c Warm/heat (1)
d  (1); propanal (1)
e  (1); propanone (1)
f Copper(I) oxide, red (2)
g Precipitate (1)

Total 10 marks

2.13 **a** D (1) **c** B (1) **e** 88 (1)

b B, C, D (2) **d** A (1)

Total 6 marks

Examination questions

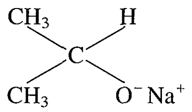
2.14 **a** **i** Dehydration (1)

ii Phosphoric acid, H_3PO_4 or aluminium oxide, Al_2O_3 (1)

iii Alkene/unsaturated (1)

b **i** $CH_3CH_2CH_2O^-Na^+$ (2, 1 if charges not clearly shown)

or

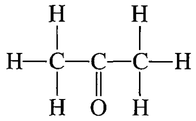
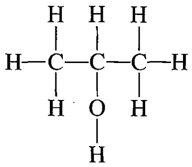


ii Hydrogen (1)

c **i** Oxidation (1)

ii Sodium/potassium dichromate (1); sulphuric acid (1)

d

Y =  (2) alcohol =  (2)

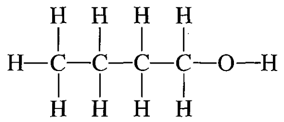
$$Y = \begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & \| & & | & & \\ & & H & & O & & H & & \end{array} \quad (2) \qquad \text{alcohol} = \begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & O & & H & & \\ & & & & | & & & & \\ & & & & H & & & & \end{array} \quad (2)$$

e Propan-1-ol, $CH_3CH_2CH_2OH$ (1)

Contains same number of carbon atoms (1)

Total 15 marks

2.15 **a**



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & & & \\ & & | & & | & & | & & | & & & & \\ H & - & C & - & C & - & C & - & C & - & O & - & H \\ & & | & & | & & | & & | & & & & \\ & & H & & H & & H & & H & & & & \end{array}$$

(1)

b Sodium (1)

c **i** Oxidation/redox (1)

ii Sodium/potassium dichromate or $Na_2/K_2Cr_2O_7$ (1)

Sulphuric acid/H_2SO_4 (1)

iii Distillation (1)

iv Reflux/excess oxidising agent (1)

d Substance B: Benedict's solution + heat (1)

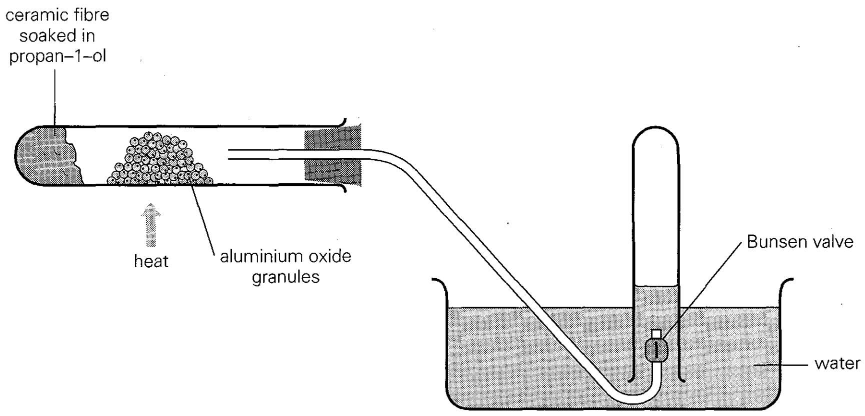
From blue solution to orange/red precipitate (1)

Substance C: any practical test for an acid (1)

Result (1)

e Reaction 1 (1)

f **i**



Should show collection of gas over water (1);

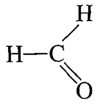
butane-1-ol + mineral wool at bottom of test tube (1);

Al_2O_3 higher up (1); heat (1) (−1 for any fault, e.g. not sealed)

ii Purple colour (1); becomes colourless (1)
iii $C_4H_8(g) + 6O_2(g) \longrightarrow 4CO_2(g) + 4H_2O(l)$
Four correct formulae (1); correct balancing (1)

Total 20 marks

2.16 **a** (1)



b **i** Oxygen (1)
ii Exothermic reaction (1)
c **i** Sodium/potassium dichromate (1)
Sulphuric acid (1)
ii Distil off product (1)
Use half the amount/calculated amount of oxidising agent (1)
d Blue (1) to orange/red (1)

Total 9 marks

2.1

Carbon

I am an atom of carbon
And carbon is the key
I am the element of life
And you owe yours to me

I am the glue of the Universe
The fixative
used by the Great Model-maker
I play a waiting game
Lie low that's my secret
Take a breath every millennium

But though set in my ways
Don't be misled. I'm not inert
I will go down in cosmic history
as an adventurer
For when I do make a move
Things happen and fast

I am an atom of carbon
And carbon is the key
I am the element of life
And you owe yours to me

When the tune is called
I carry the message
to the piper
Take the lead
in the decorous dance
of life and death

Patient, single minded and stable
I keep my talents hidden
Bide my time
Until by time am bidden.

Roger McGough

We are grateful to PFD for permission to reproduce the above poem from DEFYING GRAVITY published by Penguin.

TOPIC 3

The Periodic Table and atomic structure

Introduction

The main theme running through this topic is the relationship of the properties of atoms and ions to the arrangement of the electrons in their outer shells. It is assumed that students have already gained some knowledge of atomic structure and electron arrangement from their previous courses.

The topic starts by looking, briefly, at the Periodic Table and its essential characteristics. It continues by considering how the evidence from emission spectra and ionisation energy values have been used to determine electron arrangements. The success of the Periodic Table in rationalising chemical knowledge is then shown to arise from its basis in the electron structures of the elements. Consideration is given to the electron configuration of ions before concluding with a very short description of the bonding in metals.

Teachers should be aware that there is a sharp gear change in this topic from relatively undemanding introductory work to a model of the atom which can be quite demanding for students relatively fresh from GCSE. The time taken to teach this topic will vary considerably depending upon students' previous experience. It should not be rushed as many very significant ideas are being established. Inevitably, there is little opportunity for practical work but teachers should seek to enthuse students with a sense of the excitement that attended the gradual development of the atomic model which is used in this course. Of course, it is only a model and, therefore, suffers from many of the faults of models. Moreover, it is without the finer points of the more sophisticated models that students may well encounter in their further studies in higher education. The strength of a particular model lies in what it can do and the model established is more than satisfactory for the needs of the rest of the A-level course.

Content

3.1 The Periodic Table – Mendeleev's table; the modern Periodic Table; periodicity of physical properties.

3.2 The story of the atom – evidence for the atom; development of the model of the atom.

3.3 Flame colours and emission spectra – flame colours of elements of Groups 1 and 2; interpretation of line emission spectra, evidence for the existence of electron energy levels; ionisation energies.

3.4 The arrangement of electrons in atoms – patterns of ionisation energies; the arrangement of electrons in quantum shells and subshells.

3.5 Evidence for the ionic model – properties of ionic compounds; the shape of ions; electron arrangements in ions.

3.6 Metallic bonds – a simple picture of metallic bonding allows a simple explanation of characteristic metallic properties.

Timing		**Students' Book**
3.1	$1\frac{1}{2}$ hours	pages 48–52
3.2	$\frac{1}{2}$ hour	pages 52–54
3.3	2 hours	pages 54–57
3.4	3 hours	pages 57–62
3.5	$2\frac{1}{2}$ hours	pages 63–69
3.6	$\frac{1}{2}$ hour	pages 69–71
Total about 2 weeks		

Objectives

1 To revise simple ideas of atomic structure and isotopes.

2 To appreciate the basis of the modern Periodic Table and the idea of periodicity of physical properties.

3 To look at some of the evidence for the pattern of electron distribution in atoms.

4 To study trends in atomic and ionic radii, and ionisation energy, linking these to atomic structure.

5 To review the evidence for the existence of ions, their formation in terms of electron transfer, and the characteristic properties of ionic compounds.

6 To introduce a simple picture of metallic bonding.

3.1 The Periodic Table

Timing About 1.5 hours will be required

Suggested treatment

The topic begins straight away with Mendeleev's Periodic Table. Teachers may wish to refer to earlier attempts to classify the elements including those of Lavoisier, Döbereiner and Newlands. Mendeleev's table stands out for two main reasons: he left spaces for elements which he believed still had to be discovered, and he was able to predict their properties with remarkable accuracy. The features of a modern Periodic Table, based on the number and arrangement of electrons in the atoms of the elements, are then considered.

Teachers must ensure that one use of the mass spectrometer included in Topic 21 is studied at this point as it is required in AS. This is the use of the mass spectrometer for determining the molar mass of an element. Students should be required to read section 21.1 as far as the beginning of the study task and then to answer the question in the *Students' Book* on the molar mass of naturally occurring silicon. They should be reminded to give answers to 3 significant figures, as in the data supplied. See Appendix 4, section 3, 'Significant figures'.

Teachers could refer students to one of the many computer databases on the Periodic Table (see the Nuffield Advanced Chemistry website).

ANSWERS

Questions, page 51

1 $^{28}_{14}Si$, $^{29}_{14}Si$, $^{30}_{14}Si$

2 14, 15 and 16 neutrons

3 The mean relative atomic mass = $(0.922 \times 28.0) + (0.047 \times 29.0) + (0.031 \times 30.0) = 28.1$

The study task in section 21.1 could be set for homework. See Topic 21 for answers.

Periodicity of physical properties

Following these discussions the word *periodicity* can be introduced. It will be necessary to clarify the meaning of this term. In this context it is used to imply that when elements are arranged in order of atomic number, those having similar chemical and physical properties recur periodically, that is, at regular intervals. For an example of periodicity, students can be shown models of atomic volumes of a number of elements and can then carry out the first part of the study task in which they calculate the atomic volumes for the first 18 elements and draw up a bar chart using the results.

ANSWER

Study task, page 51

1 The atomic volumes of the first 18 elements (to 2 significant figures) are (in $cm^3\ mol^{-1}$)

H	14	0	14	Al	10
He	27	N	17	Si	12
Li	13	F	13	P	17
Be	4.9	Ne	17	S	16
B	4.6	Na	24	Cl	23
C	5.3	Mg	14	Ar	29

The unit used for atomic volume is cubic centimetre per mole; students should be encouraged to include units at each stage of the calculations that they are asked to do, thus:

$$\text{atomic volume } (\text{cm}^3\ \text{mol}^{-1}) = \frac{\text{mass of 1 mole of atoms } (\text{g mol}^{-1})}{\text{density } (\text{g cm}^{-3})}$$

Students should note that in the calculations of atomic volume, the density used for elements which are liquids or gases at room temperature is the density of the liquid element at its boiling point. A computer spreadsheet should be used, if available, to show the variation of atomic volume with atomic number and to plot patterns of atomic volume within particular groups of elements.

The graph of atomic volume plotted against atomic number is important in a historical context, for it was Lothar Meyer who first drew attention to periodic maxima and minima and noted that similar elements occupied similar positions on the graph. In doing this, he also drew attention to the idea of arranging the elements in order of increasing relative atomic mass. The elements at the peaks of the chart are the alkali metals (although helium has an atomic volume greater than that of lithium, and the data on francium is not sufficiently accurately known). The elements at the troughs belong to Group 3, if the transition metals are ignored.

It should be pointed out to the students that the periodicity shown by atomic volumes is also exhibited by other properties such as the enthalpy changes of fusion and vaporisation, and the melting and boiling points. The relevant information for all the elements is given in the *Book of data.* The study task then asks students to plot the melting and boiling points of elements 1–18 in the Periodic Table and to look for patterns in the data. Copies of these graphs are shown in figure 3.2.

Students' attention should be drawn to the sharp change in the values of all the physical data between carbon and nitrogen and between silicon and phosphorus, reflecting the change in structure from giant lattices to molecules.

Finally, students may be interested to look at the abundances of the elements given in the *Book of data.* There is no evidence of any periodicity to be found amongst those figures.

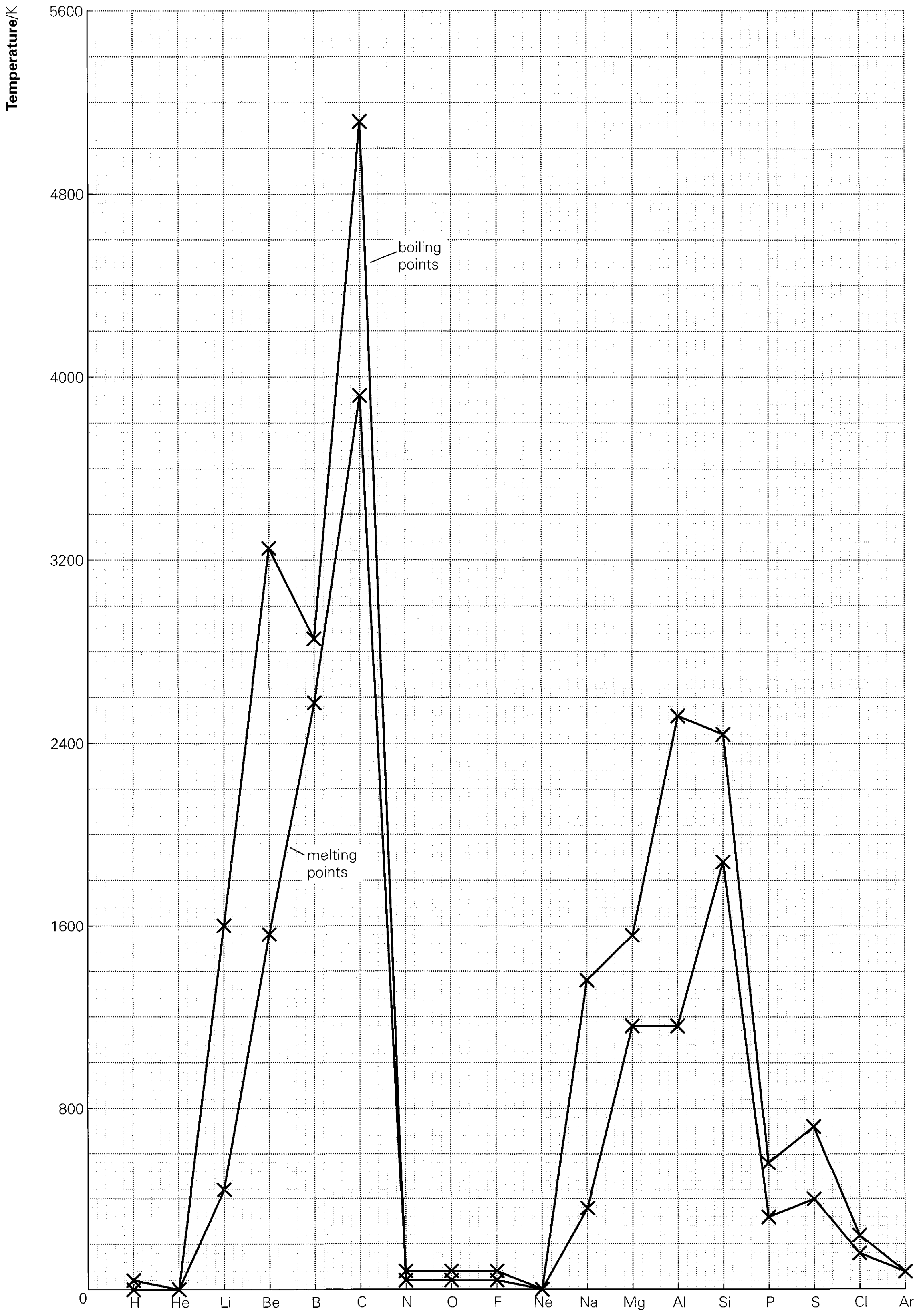


Figure 3.2 Melting and boiling points of the first 18 elements

3.2 The story of the atom

Timing About $\frac{1}{2}$ hour will be required excluding the study task

Suggested treatment

Students will have a basic knowledge of atomic structure from their GCSE work. The study task, which is suitable for group work or for homework, asks students to gather information from various sources about the evidence for the nature of the atom. This section is intended for background knowledge only; students do not need to remember detailed information. A scanning tunnelling microscope can be found by visiting a website (see the Nuffield Advanced Chemistry site for links).

A short chronology of important stages in the development of our understanding of the atom is given at the end of this topic (copiable). Teachers may set students a further task to investigate the work of some of the other key names included in this chronology.

3.3 Flame colours and emission spectra

Timing About 2 hours will be required

Suggested treatment

Students examine the colours which metal compounds impart to a flame and observe the emission spectra which arise. The relationship between the emission spectra and ionisation energies is then developed.

EXPERIMENT 3.3 The flame colours of the elements of Groups 1 and 2

Each group of students will need:
Eye protection
Diffraction grating or direct vision spectroscope
Cobalt blue glass (if available)
Each station will need:
Bunsen burner and heatproof mat
Nichrome wire in insulating handle
Spatula
Dropping pipette
Concentrated hydrochloric acid in a small beaker CORROSIVE
Sample of a salt on a watch glass, one for each station, chosen from the chlorides of Li to Cs and Mg to Ba (calcium chloride is IRRITANT; barium chloride is TOXIC).
Darkened room

HAZARD

Risk assessments will be necessary for the salts chosen. If chlorides are not available, carbonates may be substituted; nitrates are less suitable because they are oxidising and some will produce toxic nitrogen dioxide on heating.

Procedure

Full details are given in the *Students' Book.* It is convenient to set up a series of 'stations', one for each element, around which the students circulate in order to observe the various flame colours. This arrangement avoids the need for cleaning the nichrome wires between each test.

It is difficult to see the lines in the spectrum using either a diffraction grating or a direct vision spectroscope unless the flame is viewed in a darkened corner of the laboratory. Ideally, the experiment should be done in a dark room or a blacked-out laboratory, if the lines are to be seen clearly.

The lilac colour of the potassium flame may be masked by the intense yellow colour of the sodium compounds present as impurities. Potassium chloride of analytical reagent quality should therefore be used or the potassium flame should be viewed through cobalt blue glass which cuts out the colour of the sodium flame. Owing to the high cost of caesium and rubidium compounds, teachers may prefer to demonstrate the flame colours of these elements. The emission spectrum of magnesium cannot be observed in the visible region but it is worth while letting the students discover this for themselves.

The spectra are better observed using gas discharge tubes; an optional experiment is given below together with details of what the students should observe from both experiments.

EXPERIMENT 3.3a (optional) A study of the atomic spectra of some elements

Each group of students will need:
Diffraction grating or direct vision spectroscope

Access to:
The following gas discharge tubes together with appropriate power supplies: sodium, mercury, hydrogen, helium, neon, oxygen and others as available.

Procedure

The usual care should be taken when dealing with the power supplies. This experiment could be done in addition to the 'flame colour' experiment. It gives more reproducible results and has the advantage that the spectral lines can be observed at leisure. If sufficient gas discharge tubes, spectroscopes and power supplies are available, the students could observe each tube in a circus arrangement.

Students are asked to note the main features of the spectral lines. The spectrum of atomic hydrogen is of fundamental importance, but it is difficult to see when using ordinary hydrogen tubes. Colour photographs of the spectra of various elements are therefore provided in the *Book of data*. Students should note the increase in complexity of the spectra with increase in atomic number (and hence number of electrons) and also the fact that each element is characterised by its own particular set of lines.

Interpretation of the emission spectra of elements

The relationship between atomic spectra and ionisation energies is now developed. The atomic emission spectrum of hydrogen may be examined more closely by reference to figure 3.11 in the *Students' Book*. From this the convergence of the lines should be noted. This seems to indicate that the lines do not occur at random but are governed by some law. The distribution of the lines should then be interpreted by means of an energy level diagram such as that shown in figure 3.12 in the *Students' Book*. The students should understand that an electron in an atom can only exist in certain well-defined energy levels (as required by the quantum theory). The interpretation of the spectral lines coming closer together (converging) is that the energy levels are also converging.

Energy is required to promote an electron from a lower energy level to a higher one (excitation) and energy is released, as a quantum of radiation, when the electron falls from a higher to a lower energy level. The difference in energy levels determines the energy change and hence the frequency of the emitted radiation, since $\Delta E = h\nu$. A change in level from $n = 3$ to $n = 2$ results in a line in the red region of the spectrum, while one from $n = 4$ to $n = 2$, representing a larger energy change, produces a line in the higher energy region of the spectrum, namely green.

It is sufficient for students to understand that the different lines represent transitions from different energy levels and that the higher the frequency of the lines, the greater the difference between the energy levels.

At the convergence limit, the electron possesses sufficient energy to escape from the atom and ionisation results. By finding the convergence limit for the series of lines in the ultraviolet part of the spectrum known as the Lyman series which involve transitions back to the $n = 1$ level, it is possible to obtain a value for the ionisation energy. Figure 3.12 in the *Students' Book* indicates the existence of several series of lines other than those observed in the visible region. As the ultraviolet series represents transitions back to the $n = 1$ or ground state, the convergence limit for this series of lines gives a measure of the ionisation energy for a ground state atom of hydrogen.

The ultraviolet convergence limits for the alkali metals and the corresponding ionisation energies obtained from these are shown in the table below.

Element	**Series limit/10^{15} Hz**	**Ionisation energy/kJ mol^{-1}**
Li	1.30	519
Na	1.24	495
K	1.05	419
Rb	1.01	403
Cs	0.94	375

The section is completed by a formal definition of ionisation energy.

3.4 The arrangement of electrons in atoms

Timing About 3 hours – the study task could be set as a homework

Suggested treatment

The introductory work is presented as a study task.

ANSWERS

Study task, page 58

1 Students use the values of the ionisation energies given in the *Book of data* or a suitable spreadsheet program to draw a graph of successive ionisation energies of sodium plotted against the number of electrons removed. The graph emphasises that large energy jumps are involved at certain points.

2 The logarithm (to the base 10) of the ionisation energy is then plotted and the pattern noted; one electron in the $n = 3$ level is relatively easy to remove, eight electrons in the $n = 2$ level are removed with difficulty and two electrons in the $n = 1$ level are extremely difficult to remove.

Students might also plot the values of successive ionisation energies for a number of other elements to show that there is a consistent pattern of arrangement of the inner shell electrons, for example, potassium is 2,8,8,1, sulphur is 2,8,6 and so on. In this way, students should see that the number of outer shell electrons is the same as the group number.

Interpretation of the patterns in the ionisation energies

This section serves to explain the patterns which the students found in the previous section through graph plotting exercises. A display board can be useful aid for this section.

For sodium, successive ionisation energies show that two electrons in the $n = 1$ level are closer to the nucleus than the other electrons and are said to be in the first quantum shell. The eight electrons in the $n = 2$ level are further from the nucleus and are said to be in the second quantum shell. The single electron in the $n = 3$ level is said to be in the third quantum shell and is even further from the nucleus. Strictly speaking we should say that the two electrons in the $n = 1$ level spend most of their time closer to the nucleus than the other electrons rather than saying that they are closer to the nucleus.

This approach has been taken in order for pupils to appreciate general principles rather than to worry over much about detail. However, teachers may wish to move to a more sophisticated model. Thus there are two ways of looking at electrons in atoms: from the point of view of their energy level, $n = 1, 2, 3$ etc. and from the point of view of how far from the nucleus they are on average.

The pattern of successive ionisation energies for potassium is also discussed as is the pattern for the first six ionisation energies of another element; this leads to the conclusion that it must be in Group 4 (it is, in fact, silicon).

A graph of the first ionisation energies of the elements plotted against atomic number is then examined. A study task asks students to observe the pattern of first ionisation energies down a group.

ANSWERS

Study task, page 60

Down a group, the first ionisation energy decreases because the attraction between the nucleus and the outer electrons decreases markedly with distance and there is an increased shielding of the outer electrons from the nuclear charge. Although the positive charge on the nucleus gets larger as the group is descended, this is balanced by a corresponding increase in the number of shielding electrons.

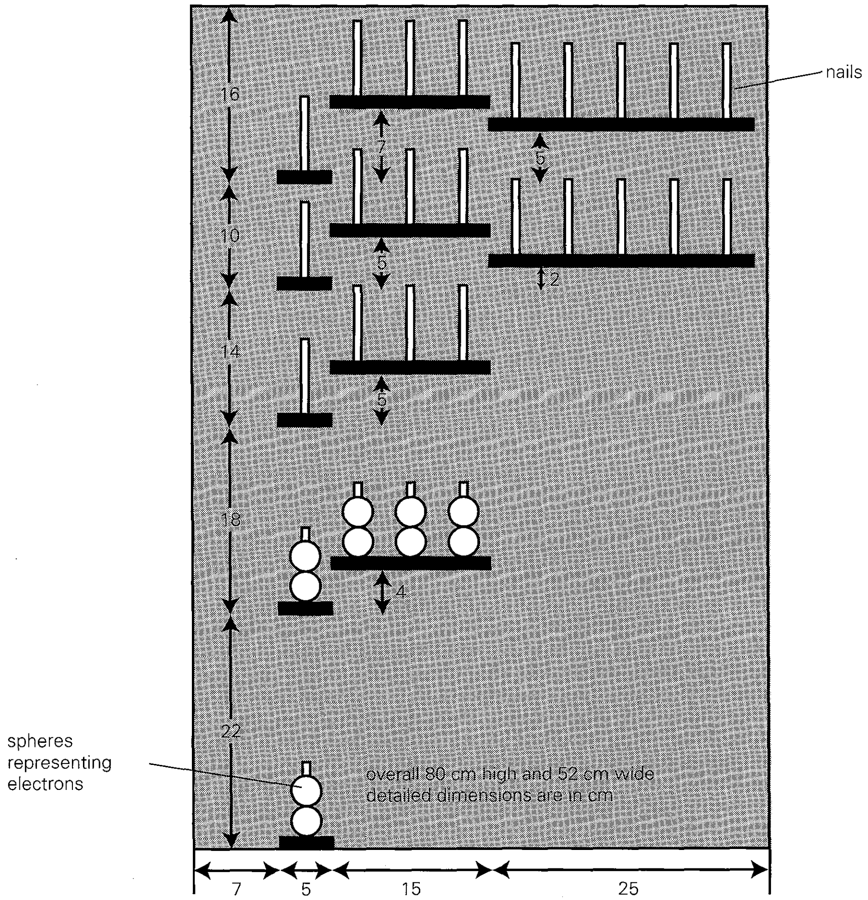


Figure 3.4 Dimensions for a display board.

In the plot of the first ionisation energies for the first 20 elements, groups of 2,8,8 electrons are apparent. The groups have sharp breaks between them which indicates the filling of different quantum shells. The groups of eight electrons are subdivided into sub-groups of 2,3,3 and this is evidence that not all the electrons in a given quantum shell possess the same energy.

This may be followed by a study of the graph showing the first ionisation energy for each of the elements in the Periodic Table (figure 3.16 in the *Students' Book*). From this, the break in the 2,8,8 pattern caused by the transition elements is apparent and the existence of d-electrons may be introduced in the energy level diagram. Because of the symbols which are used for the electrons in energy levels, and because of the 3,3 grouping of the p electrons, the *Students' Book* mentions electron spin. It is not intended that any evidence for this in terms of spectral line splitting etc. should be discussed. An energy level diagram showing s and p-levels should now be used (see figure 3.18 in the *Students' Book*).

The s, p, d notation for electronic structure, for example, $1s^22s^22p^6$ for neon, is then introduced and the order of filling the levels from the lowest energy levels is discussed. Energy level diagrams can now be drawn for several elements to consolidate the ideas connecting the atomic number with the number of electrons and the allocation of the correct number of electrons to each level. It is important to note that the energy levels do not correspond exactly to the positions at which electrons spend most of their time. The concept of electrons being distributed as diffuse clouds of negative charge and the shapes of the s, p and d charge clouds are only revealed by wave mechanics and it is not possible at this level to provide evidence for such shapes.

When writing electron configurations either to show main shells or sub-shells, it is always the arrangement of electrons in the ground state (that is in the lowest possible energy state) which is represented and not the arrangement in an excited state of the type referred to in section 3.3.

ANSWERS

Questions, page 61

1 The pattern is broken by ten electrons after calcium.

2 The pattern changes because the number of sub-shells increases as the number of the main shell increases.

3 The elements responsible for the break are the transition metals.

The electron configurations of the elements are then related to the position of an element in the Periodic Table. Students should realise that the chemical similarities existing among members of a group of elements arise because of the similar configurations of the outer electron shells of their atoms.

The section ends with a brief consideration of electron affinity.

3.5 Evidence for the ionic model

Timing About $2\frac{1}{2}$ hours will be required

Suggested treatment

In their previous courses, students may have seen demonstrations of the electrical conductivity of melts of substances such as lead bromide and discussed the conductivity of molten salts in general. Some students may also have seen experiments on the separation of coloured ions when an ionic compound in solution is subjected to an electric field. As an introduction to this section, students undertake a study task to recall the properties of ionic compounds. They then carry out experiments on the conductance and migration of ions in an electric field and consider the shape and pattern of cleavage of sodium chloride crystals or calcite (calcium carbonate) crystals in relation to the regular packing of the ions.

Less time may be spent on this section with students who are already conversant with some of the material.

The next experiment can be organised as a circus and the requirements are listed in that form.

EXPERIMENT 3.5 Properties of ionic compounds

1 The electrical conductivity of solutions

Each station will need:
Low-voltage power pack
Torch bulb
Carbon rods to dip into the test solutions
5 clean beakers, 100 cm^3
0.1 M solutions of the following
  Hydrochloric acid
  Sodium hydroxide IRRITANT
  Sodium chloride
  Magnesium sulphate
  Aluminium nitrate

The conductivity of these solutions is investigated in conditions which do not allow electrolysis to occur.

2 Migration of ions

a Using copper(II) sulphate

Eye protection
Bunsen burner, tripod, gauze and heatproof mat
U-tube and measuring cylinder of similar capacity
2 carbon electrodes in bungs with nicked edges, to fit the U-tube
2 100 cm^3 beakers
0.2 M copper(II) sulphate HARMFUL SOLID
Gelatin
Saturated potassium nitrate OXIDISING
Ice bath
Balance, to weigh to 1 g
20 V dc power supply with crocodile clip leads

b Using potassium manganate(VII)

Chromatography paper, 1 cm reel
2 microscope slides
Tweezers
Potassium manganate(VII), few large crystals HARMFUL, OXIDISING
20 V dc power supply with crocodile clip leads

Procedure

It is suggested that half the class set up Experiment 2a while the other half set up Experiment 2b, and then observe each others' results. The experiments show the migration of cations and anions in an electric field. In Experiment 2a the colour associated with the Cu^{2+} ion moves to the cathode while in Experiment 2b, the coloured MnO_4^- ion moves towards the anode.

To save time, the solution of agar for Experiment 2a could be prepared beforehand and kept liquid in a hot water-bath until required.

3 Examination of ionic crystals

Eye protection
Microscope and/or hand lens
Microscope slide, preferably cavity type
Robust knife

Light hammer
Crystals of sodium chloride and calcite
Large demonstration crystal of sodium chloride
Model showing the structure of sodium chloride

Procedure

Students should wear eye protection in case fragments of crystals fly up when they are struck with the hammer or cleaved with a knife.

This section introduces the idea that the regular shape of crystals reflects regular packing of the ions. The shape and pattern of cleavage of sodium chloride crystals is briefly explored by reference to a model of the structure. Alternate sodium and chloride ions, arranged in three planes mutually at right angles to each other result in cubic crystals and cleavage takes place parallel to these planes. Examination of the model also shows that there are planes made up entirely of sodium ions or chloride ions and these planes 'cut off' the corners of the cube. Cleavage along these planes may produce an octahedral crystal. Students are not expected to know the different types of arrangement of ions in such crystal structures.

If there is time, students could grow their own crystals and note that although different crystals of a particular compound may be of different sizes and lengths of side, they all have the same angles at the corners.

The *Book of data* lists crystal systems in table 4.8, and also includes coloured photographs of models of zinc blende, marcasite, calcite, mica and beryl. A collection of good mineral specimens would be an attractive addition to this experiment.

Interpretation of the experiments

The properties of ionic compounds in relation to solubility in water and in hydrocarbons, and to their melting and boiling points is then briefly considered. The difference in the size of atoms and of the cations and anions which they form is also examined, aided by a diagram.

The shape of ions

Electron density maps obtained from X-ray diffraction data are used as evidence for the spherical shapes of some simple ions. The electron density maps in figure 3.24 in the *Students' Book* are contour maps in which the individual lines are drawn through positions of equal electron density. The electron densities decrease towards the outside of the ions but the actual values are not important in the present context. The distribution of electrons in both the sodium and chloride ions is seen to be spherical out to a region of very low electron density; after this there is a slight distortion of the electron cloud. A similar situation exists with calcium fluoride. Not too much should be read into these diagrams; it is sufficient to point out that they are consistent with the idea that these ions have a spherical shape.

The problem of where to draw the boundary of the ion in an electron density map is then raised. The students are asked how they might attempt to locate the boundary between the outer contours in figure 3.24. Dividing the gap in the same proportion as the radii associated with the equivalent electron densities might be suggested. Such a procedure assumes that the electron density falls off in a linear manner whereas in reality it does not. X-ray diffraction allows us to determine the internuclear distances accurately but not the actual ionic radii. In order to compile a table of ionic radii, one ionic radius must be arbitrarily fixed; the others can then be based on internuclear distance determinations. Several different methods have been used for assigning an ionic radius used as a basis for a scale, and consequently the tables of ionic radii compiled by different workers are not consistent with each other. Furthermore, ions are 'soft' not 'hard', more like rubber balls than cricket balls. Evidence for this comes from the compressibility of crystals such as sodium chloride. Also the precise size of the ion depends on its environment; for instance, the size of a sodium ion varies very slightly depending on the anion it is associated with. Each of these features is what we would expect to be the behaviour of a diffuse charge cloud of electrons.

Electron arrangements in ions

The section is concluded with a brief discussion of electron arrangements in ions using dot and cross diagrams to show electron transfer. Most students should be familiar with such diagrams from their pre-A-level courses and the time spent on this section will therefore depend on their previous experience. Students should be able to write electronic configurations for ions with the noble gas structure, but should also realise that not all ions have such a structure.

The section ends with reference to ions derived from more than one element such as ammonium ions and hydroxide ions. It is suggested that teachers should confine their attention only to the ammonium and hydroxide ions, as a full study of the covalent bonding in ions such as carbonate, nitrate or sulphate requires some understanding of delocalisation.

3.6 Metallic bonds

Timing about $\frac{1}{2}$ hour

Suggested treatment

It is necessary to account for the relatively high melting points of most metals, and for their good electrical and thermal conductivities. The simplest picture, that of a lattice of positive metal ions in a 'sea' of mobile electrons, will be adequate for this course. The shared electron 'sea' bonds the metal ions tightly into the lattice and confers a relatively high melting point, while the mobile electrons provide a means of conducting an electric current and thermal energy. The mobile electrons are another example of delocalisation.

Any discussion of energy bands is not required in this chemistry course. When an element is in the solid state the energy levels of each atom do not remain undisturbed; each atom is affected by adjacent ones and the individual energy levels become fused into a series of levels very close to each other, known as energy level bands. The arrangement of these bands, and the extent to which they are occupied by electrons, determine whether the element will be a conductor, an insulator, or a semiconductor.

Answers to Topic 3 questions

Review questions

3.1

Protons	Neutrons	Electrons
53	74	53
53	74	54
21	24	21
21	24	18
1	1	2

(1 mark for each correct answer)

Total 15 marks

3.2 **a** Only one type of F atom ($^{19}_{9}$F) (1)
but two isotopes of bromine ($^{79}_{35}$Br and $^{81}_{35}$Br) (1)

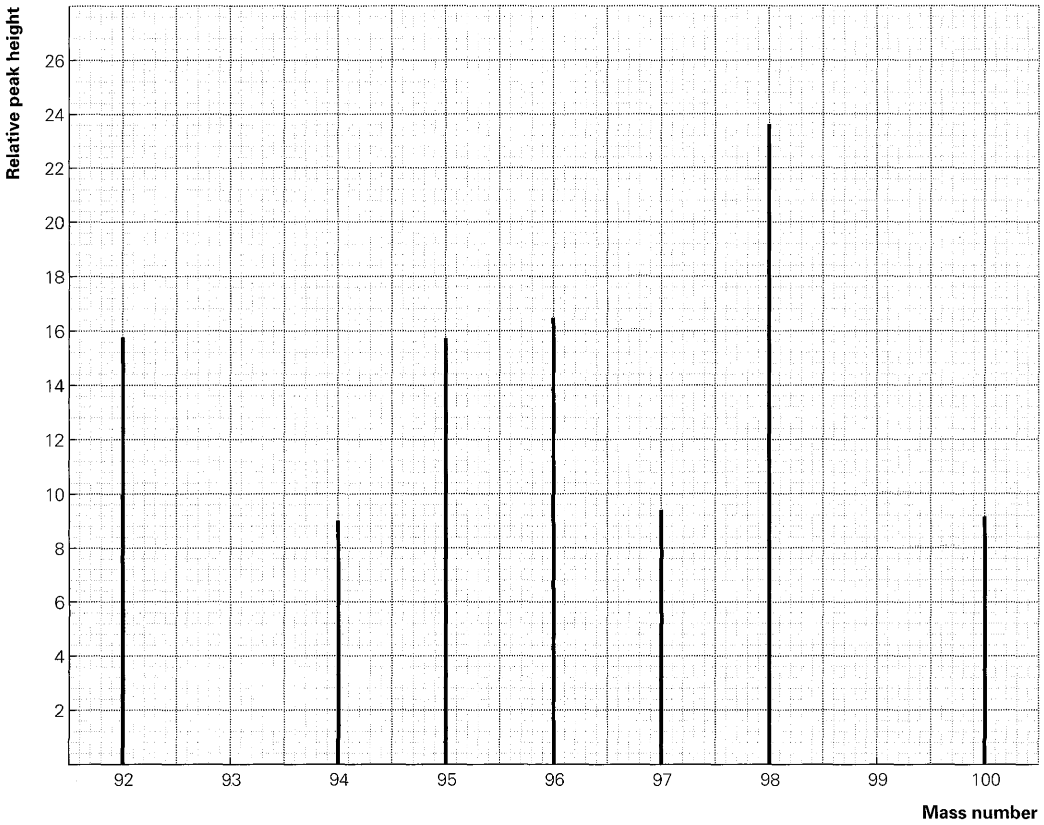
b Relative atomic mass of Ti

$$= \frac{(46 \times 0.8) + (47 \times 0.73) + (48 \times 7.4) + (49 \times 0.55) + (50 \times 0.52)}{0.8 + 0.73 + 7.4 + 0.55 + 0.52} \quad (1)$$

$$= \frac{479.26}{10.00} \quad (1)$$

$$= 48 \text{ (2SF)} \quad (1)$$

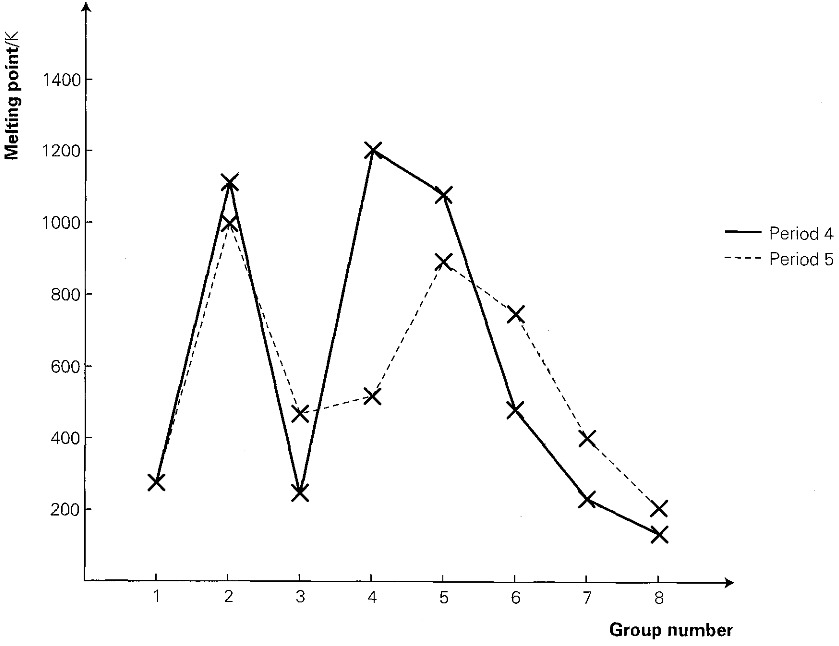
c



(5)

Total 10 marks

3.3 **a**



(4)

b Similarities: Group 1 low, Group 2 high, Groups 7 and 8 low. (1)
Differences: In Periods 2 and 3, Group 4 element has much the highest melting point. (1)

Groups 5 and 6 elements have much higher melting point in Periods 3, 4 and 5 than in Period 2. (1)
Group 3 elements have high melting point in Periods 2 and 3, low in Periods 4 and 5. (1)

Total 8 marks

3.4
a NaF; MgF_2; AlF_3; SiF_4; PF_5; SF_6 (2)
b The number of moles of F atoms per mole of atoms of the other element increases by one from group to group (or similar, clear statement). (2)
c Similar pattern for oxides but increase by $\frac{1}{2}$ mole of oxygen atoms. (1)
d F atoms have seven outer electrons but O atoms have six, so twice as many electrons must be provided to fill the outer shell of an O atom. (2)

Total 7 marks

3.5
a Not true. Whilst all transition elements are metals, there are many metals which are not transition elements (e.g. elements in Groups 1 and 2; tin, lead etc.). (2)
b Groups 1 and 2 consist entirely of metals and Groups 7 and 8 are non-metals. But Group 4 contains the non-metals C and Si as well as the metals Sn and Pb. (2)
Other examples may be given and 'in-between' elements such as Ge may be discussed.

Total 4 marks

3.6
a Sodium (1) **b** Potassium (1) **c** Calcium (1)
d Barium (1) **e** Magnesium or beryllium (1)

Total 5 marks

3.7
a Heating promotes electrons to higher energy levels. (1)
When electrons 'fall' to lower levels, energy is given out. (1)
Frequency/wavelength of this energy corresponds to light of the colours seen. (1)
b Sr atoms contain more electrons than Na atoms. (1)
c Energy emitted of wavelengths/frequencies not in the visible region of the spectrum. (2)

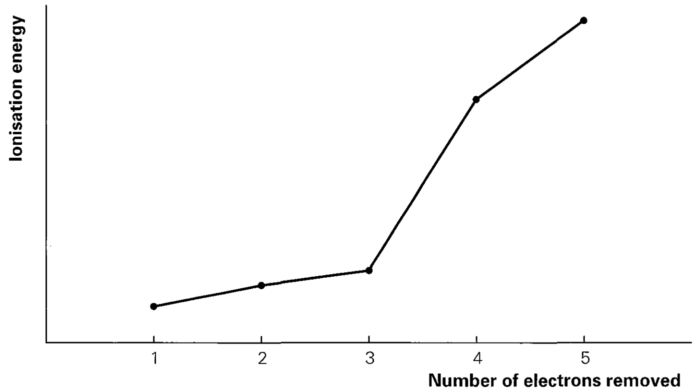
Total 6 marks

3.8
a **i** 496 (1); **ii** 2189 (1); **iii** 5140 (1); **iv** 9954 (1)
(all in kJ mol^{-1})
b Energy needed to form $Na^+(g)$ from Na(g) very much less than that needed to form $Si^{4+}(g)$ from Si(g). (1)
c Magnesium probably ionic: low energy needed to form Mg^{2+}. (1)
Aluminium could be either: energy needed to form Al^{3+} considerably more than for Mg^{2+} but much less than for Si^{4+}. (1)

Total 7 marks

3.9
Mark by impression

The graph should be similar in form to the figure below. It should show a sudden rise from the third to the fourth ionisation energy, and fairly regular, but smaller, rises between the first and second, and the second and third.



Total 5 marks

3.10

a	Group 0 (or 8)	(1)	**d**	Group 2	(1)
b	Group 5	(1)	**e**	Group 7	(1)
c	Group 3	(1)			

Total 5 marks

3.11

Sodium bromide, NaBr	(1)	Sodium oxide, Na_2O	(1)
Sodium nitride, Na_3N	(1)	Magnesium bromide, $MgBr_2$	(1)
Magnesium oxide, MgO	(1)	Magnesium nitride, Mg_3N_2	(1)
Aluminium bromide, $AlBr_3$	(1)	Aluminium oxide, Al_2O_3	(1)
Aluminium nitride, AlN	(1)		

Total 9 marks

3.12

a **i** Cu^{2+} **ii** CrO_4^{2-} (2)

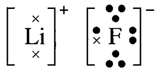
b Green (1)

Because it contains a mixture of the blue and yellow ions. (1)

Total 4 marks

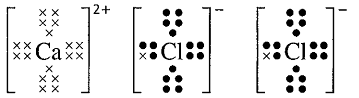
3.13

a



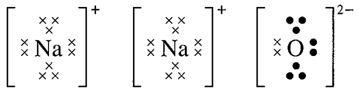
(2) for each correct compound. Dots and crosses need not be shown differently.

b



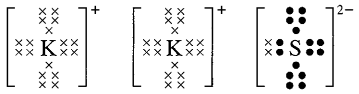
(2)

c



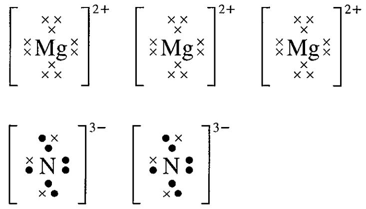
(2)

d



(2)

e



(2)

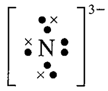
Total 10 marks

Examination questions

3.14

a $1s^22s^22p^6$ (2) −1 per error (2)

b (1)



c Li_3N (1)

d **i** Net attraction of nucleus lower in negative ions or increased repulsion between electrons (1)

ii Nuclear charge greater or more protons in oxygen (1)

e **i** Red or crimson (1)

ii Electrons promoted to higher (excited) energy levels (1)

fall back emitting light (1)

iii Radiation emitted is outside visible region (1)

Total 10 marks

3.15

a $2Al(OH)_3(s) \longrightarrow Al_2O_3(s) + 3H_2O(l)$ (2)
−1 for missing state symbols.

b **i** Molar mass of $Al_2O_3 = 102$
so 5.1/102 (or 0.05) mole (1)
so mass of NaOH $= 0.05 \times 2 \times 40 = 4.0$ g (1)

ii To ensure complete reaction of Al_2O_3 (1)

c **i** 13 (1)

ii $x = 2 \quad y = 1$ (2)

d **i** Clean nichrome wire by dipping in concentrated hydrochloric acid and holding in flame until no colour visible. (2)
Dip wire in acid again, then in sample and hold in flame. (1)

ii Yellow (1)

iii Intensity of yellow colour could be compared with known amounts/standards. (2)

Total 14 marks

3.16

a **K** 1600 ±100 kJ mol^{-1} (less than **C**) (1)
L 400 ± 50 kJ mol^{-1} (less than **D**) (1)

b **i** **C** and **K** (1)

ii **D** and **L** (1)

iii **A** and **B** (1)

iv **F** (1)

v **EI**, $\mathbf{E_3H_2}$, **EA**, $\mathbf{EB_2}$ (any 2, 1 each) (2)

c Increasing nuclear charge as a quantum shell is filling. (2)

Total 10 marks

3.17

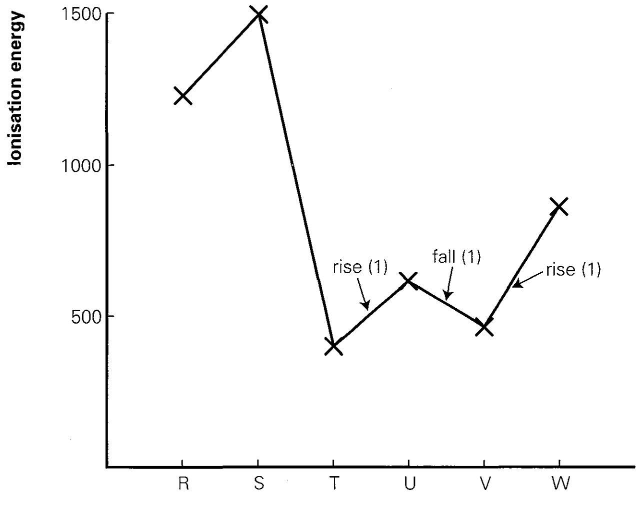
a Group 1 big increase from 1st to 2nd ionisation energy. (2)

b 14 000 − 15 000 13 000 or 16 000 (2)

c p-electron (1)

d $\mathbf{T}^+(g) \longrightarrow \mathbf{T}^{2+}(g) + e^-$ (2)

e



(3)

f **M** is in Group 2 (1)
Cannot be Be (Be only has 4 electrons) (1)
∴ must be Mg or higher. (1)
OR
2 s-electrons outermost (1)
4 electrons which must be part of 8 (1)
must be 2 more electrons inside these (1)

Total 13 marks

NUFFIELD ADVANCED CHEMISTRY TOPIC 3

3.1

The development of thought about atoms

• 430–280 BC	Greek thinkers especially Leucippus, Democritus and Epicurus develop basic ideas of an atomic theory for matter.
• 4th century BC	Aristotle opposes an atomic theory.
• 1st century BC	Lucretius in a poem 'De Rerum Naturae' collects together and expands on the ideas of the earlier 'atomists'.
• 2nd century AD	Galen, a leading physician, supports Aristotle's views leading to the almost total eclipse of the atomic theory for nearly 1400 years.
• 3rd–16th century AD	There was only occasional and sporadic interest in an atomic theory by Moslem scientists and medieval Christian scholars.
• 17th century	Gassendi, a strong supporter of an atomic theory, brings it back into prominence through his arguments with Descartes.
• 1661	Robert Boyle accepts an atomic theory of matter.
• 1687	Sir Isaac Newton applies the atomic theory to speculate about the nature of gases – the first time the theory is applied in a scientific manner.
• 1789	Higgins publishes an atomic theory but it is generally ignored.
• 1803–8	Dalton establishes the modern atomic theory in a form that could be experimentally verified.
• 1811	Avogadro distinguishes between atoms and molecules.
• 1834–55	Faraday's experiments on electricity: he establishes the laws of electrolysis and the importance of the fundamental unit of electric charge.
• 1895	Becquerel discovers radioactivity.
• 1897	Sir J. J. Thomson's recognition of the electron as a constituent of atoms. He proposes a 'plum pudding' model of an atom in which electrons are distributed through a 'dough' of positive charge.
• 1909	Geiger and Marsden publish the results of a series of experiments carried out under Rutherford at Manchester University which establish the existence of a very small nucleus in an atom.
• 1911	Rutherford proposes a planetary model of the atom in which electrons revolve round a positively charged nucleus rather like the planets revolve round the Sun.
• 1912	Bohr establishes a shell arrangement for the electrons of an atom using Planck's Quantum Theory.
• 1913	Soddy coins the word 'isotope' for atoms of the same element with different relative atomic mass.
• 1913–14	Moseley, working at Manchester University and, subsequently at Oxford University, establishes the fundamental importance of the number of positive charges in the nucleus as the atomic number of the element.
• 1914	Rutherford uses the term 'proton' for the particle of positive charge in an atom.
• 1925	Prince Louis-Victor de Broglie suggests that electrons have a wave nature.

1926	Heisenberg states his Uncertainty Principle pointing out that it is not possible to measure both the position and energy of any particle simultaneously.
1926	Schrödinger determines the probability of finding electrons at defined positions within a hydrogen atom using his wave equation: he indicates this probability in the form of electron clouds (atomic orbitals) which are mathematically-defined regions of space in which there was a high probability of finding an electron.
1932	Chadwick confirms the existence of the neutron in the nucleus of an atom.
1935	Yukawa proposes that a third particle binds the protons and neutrons together in the nucleus of an atom. This is named a meson.
1938	The first meson is discovered by C. D. Anderson while carrying out experiments on a mountain in Colorado, USA.
1938	Lisa Meitner and her nephew, Otto Frisch, realise the possibility of nuclear fission.
1945	First atomic weapon explodes in New Mexico, followed by the use of atomic bombs on Hiroshima and Nagasaki.
1952	First hydrogen bomb explodes.
1966	Nucleus pictured as having a shell structure in which protons and neutrons are kept from exploding apart by mesons shared between them.
1970s	Over 200 sub-atomic particles are known. The picture of the nucleus of the atom becomes increasingly complex.

TOPIC 4

Acid–base reactions and the alkaline earth elements

Introduction

The main theme running through this topic is the nature of acids and bases. Many of the compounds of the alkaline earth metals are basic and are familiar compounds to students. All elementary science courses introduce the ideas of acids, alkalis and indicators so these, too, are familiar concepts. The topic develops both sets of ideas and links them together.

After an introduction in which the importance of many of the compounds of the elements of Group 2 is referred to, the topic starts with a set of experiments on acids and bases. This leads to the development of the Brønsted–Lowry theory of acidity and the concept of weak and strong acids and bases in terms of extent of ionisation. The Brønsted–Lowry theory is not required for AS but introducing it here lays the foundations for the A2 work in Topic 14. Solution concentration is then introduced in the context of acid–base reactions to enable students to tackle problems involving molarities.

The topic continues with experiments and data-gathering exercises on the properties of the alkaline earth elements and their compounds.

Content

Timing		Students' Book
4.1	3 hours	pages 78–81
4.2	3 hours	pages 81–86
4.3	2 hours	pages 87–89
4.4	2 hours	pages 89–92
Total about 2 weeks		

4.1 Acids and bases – characteristics of acids; Brønsted–Lowry theory of acid–base behaviour; strong and weak acids and bases.

4.2 The chemists' toolkit: solution concentration – preparing solutions of known concentration, calculations using molarities; finding the solubility of calcium hydroxide in water by titration.

4.3 The properties of the alkaline earth elements – physical appearance and physical properties; reactions with oxygen and water.

4.4 Some compounds of the elements of Group 2 – basic nature of oxides; formulae and solubility of some salts; effect of heat on carbonates and nitrates.

4.5 Background reading: the role of calcium in agriculture.

Objectives

1. To extend the concept of acids and bases by considering the Brønsted–Lowry theory of acid–base behaviour.
2. To consider the strengths of different acids and bases and the effect of strength on the pH of the solution.
3. To provide an opportunity to perform simple calculations using molar masses and concentrations in mol dm^{-3}.
4. To observe and record patterns in physical properties and behaviour in the elements of Group 2.
5. To observe and record patterns in the physical and chemical behaviour of the oxides, hydroxides, carbonates and nitrates of the alkaline earth elements.

4.1 Acids and bases

Timing About 3 hours will be required

Suggested treatment

The section is introduced by means of a study task. Students are asked to work in groups to pool their knowledge of properties which typify acids and bases. After a brief revision of neutralisation and the use of indicators, students are then asked to write ionic equations for the reactions they have studied. Students are then introduced to acid–base reactions, first in terms of the Arrhenius theory and then in terms of proton transfer. This leads to a consideration of the words strong and weak as applied to acids and bases.

EXPERIMENT 4.1

What is an acid?

Each group of students will need:
Eye protection
Full rack of test tubes
Dropping pipettes
Drinking straws
2 small basins
2 beakers, 100 cm^3

Access to:
A selection of 0.01 M solutions of acids and alkalis, including phosphoric(V) acid, urea and saturated calcium hydroxide (0.01 M NaOH is IRRITANT)
A selection of indicators
8 M ammonia CORROSIVE
Hydrogen chloride in hydrocarbon solvent (prepared in advance, see page 62) HIGHLY FLAMMABLE, TOXIC, CORROSIVE
Magnesium ribbon
Sodium carbonate, anhydrous (kept in a desiccator) IRRITANT
Conductivity meter
'Stick' pH meter
Full-range Indicator paper (kept in a desiccator)

Optional (see notes):
Ethanoic acid, dry CORROSIVE, FLAMMABLE
Box with circular hole in the side

The teacher or technician will need:
Eye protection and protective gloves
Apparatus for generating hydrogen chloride (CORROSIVE AND TOXIC gas; uses concentrated sulphuric acid, CORROSIVE)
Flask with stopper
Anhydrous calcium chloride IRRITANT
Methylbenzene (toluene) or petroleum spirit, boiling range 120–160 °C HIGHLY FLAMMABLE, HARMFUL
Rock salt or sodium chloride
Concentrated sulphuric acid CORROSIVE

HAZARD

Stock bottles of ammonia build up pressure in warm weather and should be opened with great caution. 8 M ammonia is prepared by mixing 450 cm^3 ammonia, density 0.880 g cm^{-3}, with 550 cm^3 of pure water.

Procedure

Full details are given in the *Students' Book*.
For experiments 2 and 3 a solution of hydrogen chloride in hydrocarbon solvent needs to be prepared in advance and details are given below.
The following notes on the experiments may be helpful.

1 This experiment serves as a brief revision of neutralisation and leads to a consideration of ionic equations. Students should not spend too long on this section and only a selection of acids, alkalis and indicators should be used. The reactions should be carried out in test tubes. It is not the intention at this stage to perform a full-scale titration; this will be left until Experiment 4.2.

Students should be reminded to shake the tubes after each addition of alkali to the acid.

2 Preparation of hydrogen chloride in hydrocarbon solvent methylbenzene is harmful, so petroleum spirit, boiling range 120–160 °C, could be used as an alternative solvent; the solvent should be dried over anhydrous calcium chloride before use. Rock salt is used in preference to pure sodium chloride because the latter can produce a large amount of froth during the reaction. The preparation should be done in a fume cupboard.

Drip concentrated sulphuric acid onto crushed rock salt, heating the mixture of salt and acid gently to obtain the gas. When the gas is prepared in this way there is no need to dry it. The rim of the funnel should be positioned so that it just touches the surface of the hydrocarbon solvent. When sufficient hydrogen chloride gas has been dissolved in the hydrocarbon solvent, the solution should be transferred to a stoppered flask and a few granules of anhydrous calcium chloride added to ensure that the solution remains absolutely dry.

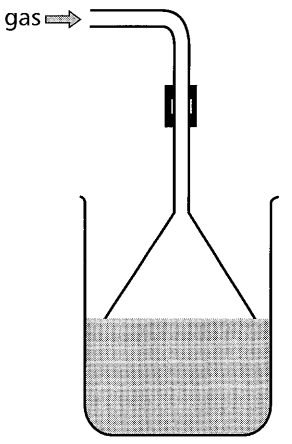


Figure 4.1 Apparatus for dissolving hydrogen chloride gas in hydrocarbon solvent.

This part of the experiment draws attention to the role of water in causing hydrogen chloride to behave as an acid. Students investigate the properties of a dry solution of hydrogen chloride in hydrocarbon solvent, and find that the expected acid reactions only occur on the addition of water.

Dry ethanoic acid could also be provided for students to test. This can be made by adding 2 or 3 cm^3 of ethanoic anhydride to 100 cm^3 of ‘glacial’ ethanoic acid, and allowing to stand overnight.

Students carry out the following tests on the solution of hydrogen chloride in hydrocarbon solvent, using clean, dry test tubes.

- **i** To about 2 cm^3 of the solution add a piece of dry, blue litmus paper. Tweezers can be used to prevent contamination by moisture; alternatively a drop of the solution can be transferred to the paper using a glass rod. Little change will be seen but on the addition of a drop or two of water the indicator will turn red.
- **ii** To about 2 cm^3 of the solution add a clean, dry piece of magnesium ribbon. No effervescence will occur, but it will be seen on adding a few drops of water.
- **iii** To about 2 cm^3 of the solution add about 1 g of anhydrous sodium carbonate. Again, no effervescence will occur, until a few drops of water are added.
- **iv** Finally, the electrical conductivity of the solution is tested. It will be found to be very low, but on addition of a few drops of water, it increases markedly.

3 On placing the two dishes close to each other and creating a gentle air current, a white ‘smoke’ of ammonium chloride should be seen. The effect is more dramatic when the dishes are placed in a box with a circular hole at one end of about 5 cm diameter: on tapping the lid attractive smoke rings can be produced.

4 This may be the first time that students have used a pH meter, so some explanation of the apparatus may be necessary. ‘Stick’ type meters are ideal for this experiment; they have the advantage that they are easy to use, give a simple digital readout and require little maintenance.

Make sure that the students wash the pH electrodes between readings. As a result of this experiment, students should realise that equimolar solutions of acids (or bases) do not necessarily have the same pH and that this is related to the concentration of hydrogen ions present. This is considered further in the next section and in Topic 14.

The drinking straws should be disposed of as soon as they have been used to make ‘carbonic acid’ solution; they should not be used by more than one person.

Interpretation of acid–base reactions

The Brønsted–Lowry theory of acid–base reactions is introduced and the importance of the solvent is made clear. In interpreting acid–base reactions, it may be mentioned that hydrogen chloride does not just separate into ions when it dissolves in water. The dissolving of hydrogen chloride in water is an exothermic process, so bond-forming processes must be involved as well as bond breaking. The H^+ ion is an isolated proton with very high charge density and hence it is readily attracted to water molecules to form the hydroxonium ion. There is no consensus of opinion on naming the H_3O^+ ion. In this course, the term oxonium ion has been used throughout because this name can be identified clearly with the formula for this species. The terms hydroxonium and hydronium ions are also acceptable.

Strong and weak acids and bases

This last part of this section distinguishes strong and weak acids and bases in terms of the extent to which they donate or accept protons.

4.2 The chemists' toolkit: solution concentration

Timing About 3 hours will be needed

Suggested treatment

This section gives students the opportunity to use moles and molarities in the context of neutralisation reactions. Concentrations of solutions are often conveniently expressed in units of moles of specified entities (ions, molecules etc.) per cubic decimetre of solution. Dissolving a mole of substance in sufficient water to make 1 cubic decimetre of solution gives a solution concentration of 1 mole per cubic decimetre, sometimes known as a molar solution. The abbreviation 'M' is sometimes used to indicate this concentration.

Teachers should note that for calculations the concentration of a solution is expressed more helpfully as moles per cubic decimetre (abbreviated mol dm^{-3}). In laboratories the convenient system of labelling solutions as 'M', '2 M' is usual; students should be familiar with both practices.

As a preliminary to the practical work in Experiment 4.2, students are introduced to calculations involving concentrations of solutions. A number of examples involving the calculation of concentration in mol dm^{-3} (from a knowledge of the mass of dissolved substance in a given volume) and the calculation of volume of solution required to neutralise a solution of known concentration should be given.

Students should be able to use the relationship:

$$\text{concentration (in mol dm}^{-3}) = \frac{\text{amount of substance (in mol)}}{\text{volume (in dm}^3)}$$

or

$$\text{concentration (in mol dm}^{-3}) = \frac{\text{amount of substance (in mol)}}{\text{volume (in cm}^3)/1000}$$

ANSWERS TO THE BACKGROUND QUESTIONS

Questions, page 82

1	**a** 0.038	**b** 0.03
2	**a** 36.5 g	**b** 2.72 g
3	**a** 0.125	**b** 0.1

EXPERIMENT 4.2

To find the solubility of calcium hydroxide in water by titration

Each group of students will need 24 hours in advance:
Eye protection
Conical flask, 250 cm^3, with stopper
Calcium hydroxide IRRITANT

For the titration:
Conical flask
Filter funnel and filter paper
0–110 °C thermometer
Titration apparatus with 10 cm^3 pipette and filler
0.050 M hydrochloric acid
Indicator, methyl orange or bromophenol blue FLAMMABLE

Procedure

The solubility of calcium hydroxide in water can be found by titrating a saturated solution with a standard acid. Details are given in the *Students' Book*. Depending on the experience of the students, it may be necessary to demonstrate the correct use of titration technique. As an alternative to a pipette and pipette filler, a second burette may be used.

Students should obtain values for the solubility of calcium hydroxide of about 1.65 g dm^{-3} at 20 °C.

4.3 The properties of the alkaline earth elements

Timing About 2 hours will be required plus homework time

Suggested treatment

The students are asked to draw up a number of tables in their notebooks, and then to look up or observe the required information and record it in the tables. Much of the information can be observed using a Periodic Table database on CD-ROM or the Web. The tables are:

- the physical appearance of the elements,
- the radii of the atoms and ions of the elements,
- the reactions of the metals with oxygen and water.

Class time can be spent helping students to begin to collect the numerical data and in demonstrating the reactions of some of the elements with oxygen and water.

TEACHER DEMONSTRATION 4.3

Reactions of alkaline earth elements with oxygen and with water

For the reactions with oxygen the teacher will need:
1 strip of cleaned magnesium ribbon, 10 cm long
A few calcium granules, fresh and shiny
2 gas-jars of oxygen
1 pair of tongs
1 combustion spoon
Eye protection and safety screen

Procedure

Hold the piece of magnesium by one end in a pair of tongs. Ignite the other end in a Bunsen burner flame. Immediately transfer the burning magnesium into a gas-jar of oxygen. The flame is very bright indeed and students and teacher should not look directly at the flame but concentrate on a point about a metre to one side.

Burning calcium in oxygen is very capricious and carries a high failure rate. The calcium should be fresh and have a shiny appearance but, even so, when hot it tends to acquire a coating of calcium oxide which prevents attack by further oxygen. Sputtering of hot particles can occur – use a safety screen.

Put the calcium granules in a combustion spoon and get them as hot as possible as quickly as possible. Watch for signs of a glow or spark. Transfer into the oxygen. When it does burn there is a very quick reaction with a red tinge to a very bright flame.

It is not recommended that strontium or barium be burned in oxygen.

HAZARD

Magnesium and calcium are highly flammable. Barium and petroleum ether are flammable. Barium is harmful

For the reactions with water the teacher will need:

1 piece of cleaned magnesium ribbon, 4–5 cm long
A few calcium granules
2–3 small (3 mm) pieces of barium (if available) stored under oil
1 small beaker (5 cm^3) containing petroleum ether (80–100 or 100–120)
1 spatula
3 glass Petri dishes
1 piece of filter paper
Overhead projector
Universal indicator solution
Eye protection

Procedure

Put water in the first Petri dish and put it on the overhead projector. Put the magnesium in the water and focus the projector on the magnesium. No reaction is visible initially but a few bubbles of gas may appear around the magnesium after a time.

Put a second Petri dish of water on the overhead projector and add the calcium granules. Bubbles of gas are immediately seen and a white precipitate of calcium hydroxide appears. This obscures the light from the projector so that the image on the screen appears black.

Using the spatula, remove the barium pieces from their protective oil and transfer them into the small beaker of petroleum ether. This washes off the oil. Remove the pieces from the petroleum ether and blot them dry using filter paper. Put a third Petri dish of water on the overhead projector and add the barium pieces. The reaction is comparable in vigour to the reactions involving alkali metals.

Add a few drops of universal indicator to each Petri dish. There will be no alkaline indications in the case of the magnesium – there is very little reaction and in any case magnesium hydroxide is virtually insoluble – but the calcium and barium hydroxides will show a blue colour.

Interpretation

Each table is followed by a question or questions about the data. The intention is that students should write the answers in the form of sentences which stand on their own. For example, the answer to the question: 'What generalisation can be made about the sizes of the ions of these metals, relative to the sizes of their atoms?' might be: 'The table shows that the ions of these elements are much smaller than the corresponding atoms.'

Throughout this and later topics, students should be encouraged to make sure that their notebooks are used to collect information logically and to record the outcome of discussions. At this stage it is not intended to do more than draw attention to the similarities and trends in the properties. Several of the points raised are taken up in later topics, or may be discussed in the light of later concepts. At this stage, it would clearly not be a good idea to try, for example, to teach possible reasons for differences between atomic and ionic radii. The fact that ionic radii do show a trend is used in Experiments 4.4c and 4.4d, which is why attention is drawn to the trend now.

For the teacher's convenience, the numerical data required in the various tables are collected below.

The physical appearance of the elements

Element	T_m/°C	T_b/°C	Density/g cm^{-3}
beryllium	1278	2970	1.85
magnesium	649	1107	1.74
calcium	839	1484	1.55
strontium	769	1384	2.54
barium	725	1640	3.51

Suggested comments

There is a general tendency for the melting points to decrease down the Group but there seems to be little pattern in the boiling points.

The radii of the atoms and ions of the elements

Element	r_m/nm	Cation formed	r_i/nm	Electronic structure
beryllium	0.112	Be^{2+}	0.027	[He]$2s^2$
magnesium	0.160	Mg^{2+}	0.072	[Ne]$3s^2$
calcium	0.197	Ca^{2+}	0.100	[Ar]$4s^2$
strontium	0.215	Sr^{2+}	0.113	[Kr]$5s^2$
barium	0.224	Ba^{2+}	0.136	[Xe]$6s^2$

Suggested comments

Both the atomic and ionic radii increase with atomic number. The ion of each of the elements is smaller than the corresponding atom. All the ions have the same charge. The outer electronic configuration of each atom is similar.

The reactions of the metals with oxygen and water

Suggested comments

The reaction with water gets more vigorous with increasing atomic number. The reaction with oxygen shows little variation in vigour.

4.4 Some compounds of the elements of Group 2

Timing About 2 hours will be required plus homework time

Suggested treatment

The students continue their acquisition of information about Group 2 by completing further tables. Much of this information is obtained as a result of the associated practical work, but again some may be found on a CD-ROM database. The tables are:

- the action of water on some Group 2 oxides,
- the formulae of some salts and their flame colours,
- the decomposition of carbonates,
- the decomposition of nitrates.

EXPERIMENT 4.4a The action of water on some Group 2 oxides

HAZARD

It is important to emphasise the danger associated with strong alkalis. There is a safety warning at the beginning of Experiment 4.4a in the *Students' Book*.

Each student or pair of students will need:
Eye protection
Rack of test tubes
Tiny samples of magnesium oxide, and calcium oxide CORROSIVE
Distilled water
1 M hydrochloric acid, about 20 cm^3 IRRITANT
Full-range Indicator paper

For safety's sake it is important that the students should not use more than 0.1 g of each oxide in each test.

One way of arranging this is to have 0.1 g samples on display so that students can take an amount similar to the displayed amount.

Specifically, the danger is that strong alkalis will hydrolyse delicate protein such as the cornea of the eye and once this has happened the tissue does not grow again; furthermore the hydrolysis occurs very rapidly. In these respects solutions of alkalis are often much more hazardous than solutions of acids of comparable strength, though to the lay mind, the latter are much more feared.

Samples of calcium and magnesium oxides often contain the respective carbonates so that effervescence may be seen on adding acid. Teachers could use the explanation of this observation to reinforce the idea of the basic nature of these oxides.

In the discussion following Experiment 4.4a, the teacher should see that the students have correctly interpreted the results. The questions that follow the experiment in the *Students' Book* are designed to help. Answers to these questions should be along the following lines.

Key points for students to include in their notes (page 90)

1 One of the signs that a reaction occurred when water was added to the oxides was the evolution of heat.

2 The evidence that the oxides were basic was the fact that the pH of their mixtures with water was, in each case, above 7, indicating alkaline solutions.

3 Equations for the reactions of the oxides with water are:

$$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(aq)$$
$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

4 Equations for the reactions of the hydroxides with hydrochloric acid are:

$$Mg(OH)_2(aq) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$$
$$Ca(OH)_2(aq) + 2HCl(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$$

5 The chlorides are all soluble in water.

6 Of the sulphates only calcium sulphate is sparingly soluble, and so that reaction may be affected.

EXPERIMENT 4.4b Formulae and flame colours of some salts

Each group of students will require:
Access to samples of as many of the following as possible (preferably in colourless, stoppered containers):
Hydrated magnesium chloride
Calcium chloride (hydrated or anhydrous) IRRITANT
Hydrated strontium chloride
Hydrated barium chloride TOXIC
Calcium sulphate (hydrated or anhydrous)
Hydrated magnesium sulphate
Strontium sulphate
Barium sulphate

Students should examine samples of the salts without handling them. The information needed to complete the table can be obtained from the *Book of data*. Beryllium compounds are not recommended for use in schools, but appear in the *Book of data*.

The formulae of some salts

Element	Chloride	Sulphate	Flame colour
beryllium	$BeCl_2.4H_2O$	$BeSO_4.4H_2O$	–
magnesium	$MgCl_2.6H_2O$	$MgSO_4.7H_2O$	–
calcium	$CaCl_2.6H_2O$	$CaSO_4.2H_2O$	brick red
strontium	$SrCl_2.6H_2O$	$SrSO_4$	bright red
barium	$BaCl_2.2H_2O$	$BaSO_4$	apple green

Key points for students to include in their notes (page 90):

As a general rule, the compounds of Group 2 elements are more heavily hydrated at the top of the group than at the bottom. (The teacher might like to discuss with the class the possible reason for this – the smaller cations are more intensely charged and attract water molecules more strongly.) Three of the elements show distinctive flame colours.

EXPERIMENT 4.4c Heating the carbonates

Each group of students will need:
Rack of hard-glass test tubes, 100 × 16 mm or crucibles (see notes below)
Delivery tubes
Lime water
Bunsen burner and mat

Access to samples of:
Anhydrous magnesium carbonate
Anhydrous calcium carbonate
Anhydrous strontium carbonate
Anhydrous barium carbonate HARMFUL

It may be preferable for students to view these experiments on CD-ROM. There is a practical problem here. The obvious method, heating the carbonate samples and testing for the evolution of carbon dioxide, really only works in the case of magnesium carbonate. Borosilicate glass melts at about 820 °C. The teacher may adopt one of the following alternative strategies:

- encourage the class to weigh samples of the carbonates and heat them strongly in crucibles, allowing them to cool, followed by reweighing.
- tell them the temperatures at which the carbonates decompose freely and invite them to show by experiment that the ease of decomposition is consistent with this temperature information.

The relevant temperatures are:

Carbonate	Temperature/°C	Ionic radius of cation/nm
$MgCO_3$	540	0.072
$CaCO_3$	900	0.100
$SrCO_3$	1290	0.113
$BaCO_3$	1300	0.136

Key points for students to include in their notes (page 91):

The discussion should lead to the idea that if a carbonate decomposes into an oxide, the carbonate ion CO_3^{2-} has to be decomposed into an oxide ion O^{2-} and carbon dioxide, CO_2. This is more likely to happen if the positive ion is small and/or highly charged, because a small, intensively positive ion can pull electrons towards itself and thus towards one of the oxygen atoms better than a larger, less positive ion. A detailed appreciation of the structure of the carbonate ion involves a knowledge of delocalisation of electrons and is not expected at this stage.

EXPERIMENT 4.4d Heating the nitrates

HAZARD

Barium nitrate is toxic. Oxides of nitrogen are very toxic and corrosive; this experiment should be performed on a very small scale in a well-ventilated laboratory, or preferably in a fume cupboard.

Each group of students will need:

Small samples (not more than 0.5 g) of:
  Magnesium nitrate
  Calcium nitrate
  Strontium nitrate OXIDISING
  Barium nitrate TOXIC
Hard glass test tubes, 100 × 16 mm
Bunsen burner and mat

Again, viewing on CD-ROM may be preferred to laboratory work.

Key points for students to include in their notes (page 91):

The trend in the decomposition of the nitrates is similar to that for the carbonates but the nitrates decompose much more readily after the water of crystallisation has been lost.

4.5 Background reading: the role of calcium in agriculture

Timing This task may be set for homework

This section gives students an insight into how plant growth is affected by soil pH, and the importance of cation exchange in the soil.

ANSWERS TO THE BACKGROUND READING QUESTIONS

Questions, page 92

1 Calcium compounds are added as lime or calcium carbonate. Liming not only neutralises excess acidity in the soil but is also necessary for good crop growth. For the benefit of teachers, calcium is necessary for cell wall formation in plants and an acute shortage (which rarely occurs) causes death. High concentrations of calcium tend to precipitate many substances and may be useful in preventing the toxic effects of some dissolved cations.

2 Particular plants grow best within narrow pH ranges. Outside these ranges, the plants have stunted growth or die.

3 Particular (named) plants grow best at a particular pH (ranges given). Very few plants are able to tolerate soils with pH values greater than 8.

4 Factors include removal of calcium by plants, removal by reaction with acids in the soil including the effect of acid precipitation on dissolving carbonate rocks and the cation exchange capacity of the soil (which is affected by the acidity).

Answers to Topic 4 questions

Review questions

4.1

a	The hydrogen atom consists of one proton and one electron.	(1)
	H^+ represents what is left when the electron is removed.	(1)
b	Protons are very small so charge density would be very high.	(1)
	They will combine with water molecules, forming H_3O^+.	(1)
		Total 4 marks

4.2

a	$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$	(1)
b	$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$	(1)
c	$HSO_4^- + H_2O \longrightarrow H_3O^+ + SO_4^{2-}$	(1)
d	$H_3PO_4 + H_2O \longrightarrow H_3O^+ + H_2PO_4^-$	(1)
e	$HCO_2H + H_2O \longrightarrow H_3O^+ + HCO_2^-$	(1)
f	$H_2CO_3 + H_2O \longrightarrow H_3O^+ + HCO_3^-$	(1)
		Total 6 marks

4.3

a	Acid HCN	(1);	base H_2O	(1)
b	Acid NH_4^+	(1);	base H_2O	(1)
c	Acid H_3O^+	(1);	base HCO_3^-	(1)
d	Acid HCO_3^-	(1);	base H_2O	(1)
e	Acid $H_2PO_4^-$	(1);	base H_2O	(1)
f	Acid NH_4^+	(1);	base NH_2^-	(1)

Total 12 marks

4.4

a	$2Ba(s) + O_2(g) \longrightarrow 2BaO(s)$	(2)
b	$Sr(s) + Cl_2(g) \longrightarrow SrCl_2(s)$	(2)
c	$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$	(2)
d	$Ba(OH)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2H_2O(l)$	(2)
e	$Sr(OH)_2(s) + 2HNO_3(aq) \longrightarrow Sr(NO_3)_2(aq) + 2H_2O(l)$	(2)
		Total 10 marks

4.5

a	The compound is broken down into two or more products when heated.	(1)
b	**i** $SrCO_3(s) \longrightarrow SrO(s) + CO_2(g)$	(2)
	ii $2Mg(NO_3)_2(s) \longrightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$	(2)
	iii $2Mg(NO_3)_2.6H_2O(s) \longrightarrow 2MgO(s) + 4NO_2(g) + O_2(g) + 6H_2O(l)$	(1)
		Total 6 marks

4.6

a	$36.5 \times 0.025 = 0.913$ g	(2)
b	$98 \times 0.025 = 2.45$ g	(2)
c	$40 \times 0.025 = 1.00$ g	(2)
d	$158 \times 0.025 = 3.95$ g	(2)
e	$248 \times 0.025 = 6.20$ g	(2)

Total 10 marks

4.7

a	$\frac{25}{1000} \times 0.100 = 2.5 \times 10^{-3}$	(2)
b	$\frac{10}{1000} \times 2.00 = 0.02$	(2)
c	$\frac{20}{1000} \times 0.05 = 1 \times 10^{-3}$	(2)
d	$\frac{17.5}{1000} \times 0.200 = 3.5 \times 10^{-3}$	(2)
e	$\frac{30}{1000} \times 0.04 = 1.2 \times 10^{-3}$	(2)

Total 10 marks

4.8

a	$\frac{5.85}{58.5} \times \frac{1000}{100} = 1.00\ (\text{mol dm}^{-3})$	(2)
b	$\frac{1.70}{170} \times \frac{1000}{250} = 0.04$	(2)
c	$\frac{3.16}{158} \times \frac{1000}{2000} = 0.01$	(2)
d	$\frac{5.04}{126} \times \frac{1000}{500} = 0.08$	(2)
e	$\frac{7.15}{286} \times \frac{1000}{250} = 0.1$	(2)

Total 10 marks

4.9

a $1.50\ \text{g cm}^{-3}$ (1)

b $\frac{63}{1.5} = 42\ \text{cm}^3$ (2)

c $\frac{42}{4} = 10.5\ \text{cm}^3$ (1)

d **i** Graduated pipette or burette (1)
ii Volumetric flask (1)

Total 6 marks

4.10

Density of $H_2SO_4 = 1.84\ \text{g cm}^{-3}$ (1)

Volume of 1 mole $= \frac{98}{1.84}$ ($= 53.3\ \text{cm}^3$) (1)

Volume required $= \frac{98}{1.84} \times 5$ (1)

$= 266\ \text{cm}^3$ (3SF) (1)

Total 4 marks

4.11

a $[\text{HCl}] = \frac{3.65}{36.5} = 0.1\ \text{mol dm}^{-3}$
$[\text{H}^+] = 0.1\ \text{mol dm}^{-3}$ (2)

b $[\text{Ba(OH)}_2] = \frac{17.1}{171} = 0.1\ \text{mol dm}^{-3}$
$[\text{Ba}^{2+}] = 0.1\ \text{mol dm}^{-3}$ (2)

c $[\text{OH}^-] = 2 \times [\text{Ba}^{2+}] = 0.2\ \text{mol dm}^{-3}$ (2)

d $[\text{SO}_4^{2-}] = 0.1 \times 3 = 0.3\ \text{mol dm}^{-3}$ (2)

e $[\text{Al}^{3+}] = 0.1 \times 2 = 0.2\ \text{mol dm}^{-3}$ (2)

Total 10 marks

4.12

a Any named single acid/alkali indicator (1)
Correct colour change (1)

b $\text{Sr(OH)}_2\text{(aq)} + 2\text{HCl(aq)} \longrightarrow \text{SrCl}_2\text{(aq)} + 2\text{H}_2\text{O(l)}$ (2)

c $\frac{13}{1000} \times 0.1 = 1.3 \times 10^{-3}$ (1)

d $\frac{1.3 \times 10^{-3}}{2} = 6.5 \times 10^{-4}$ (2)

e $6.5 \times 10^{-4} \times \frac{1000}{10}$
$= 6.5 \times 10^{-2}$ (1)

f Molar mass of $\text{Sr(OH)}_2 = 122$ (or 121.6) (1)
Solubility $= 6.5 \times 10^{-2} \times 122 = 7.93\ \text{g dm}^{-3}$ (1)
or
$6.5 \times 10^{-2} \times 121.6 = 7.97\ \text{g dm}^{-3}$ (1)

Total 10 marks

4.13

$\text{Sr(OH)}_2\text{(aq)} + \text{H}_2\text{SO}_4\text{(aq)} \longrightarrow \text{SrSO}_4\text{(aq)} + 2\text{H}_2\text{O(l)}$ (2)

Moles of $H_2SO_4 = \frac{16.3}{1000} \times 0.100 = 1.63 \times 10^{-3}$ (2)

Moles of Sr(OH)_2 in $25\ \text{cm}^3 = 1.63 \times 10^{-3}$ (1)

Moles of Sr(OH)_2 in $1000\ \text{cm}^3 = 1.63 \times 10^{-3} \times \frac{1000}{25} = 0.0652$ (1)

Mass of Sr(OH)_2 in $1000\ \text{cm}^3 = 0.0652 \times 122 = 7.95\ \text{g}$ (2)
Solubility $= 7.95\ \text{g dm}^{-3}$

Total 8 marks

4.14

a $HCl + NaOH \longrightarrow NaCl + H_2O$ (1)

moles of NaOH $= \frac{20}{1000} \times 0.05 = 1 \times 10^{-3}$ (1)

volume of HCl $= \frac{1 \times 10^{-3} \times 1000}{0.1} = 10\ cm^3$ (1)

b $HNO_3 + KOH \longrightarrow KNO_3 + H_2O$ (1)

moles of KOH $= \frac{25}{1000} \times 0.08 = 2 \times 10^{-3}$ (1)

volume of $HNO_3 = \frac{2 \times 10^{-3} \times 1000}{0.05} = 40\ cm^3$ (1)

c $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$ (1)

moles of NaOH $= \frac{50}{1000} \times 0.01 = 5 \times 10^{-4}$ (1)

volume of $H_2SO_4 = \frac{5 \times 10^{-4} \times 1000}{2 \times 0.02} = 12.5\ cm^3$ (1)

d $HCl + NaOH \longrightarrow NaCl + H_2O$ (1)

moles of HCl $= \frac{12.5}{1000} \times 0.01 = 1.25 \times 10^{-3}$ (1)

Concentration of NaOH $= 1.25 \times 10^{-3} \times \frac{1000}{10} = 0.125\ mol\ dm^{-3}$ (1)

e $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$ (1)

Moles of NaOH $= \frac{25}{1000} \times 0.05 = 1.25 \times 10^{-3}$ (1)

Concentration of $H_2SO_4 = \frac{1.25 \times 10^{-3} \times 1000}{2 \times 20} = 0.0313\ mol\ dm^{-3}$ (3SF) (1)

Total 15 marks

Examination questions

4.15

a **i** $1s^2 2s^2$ (1)

ii $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ (1)

b **i** Ba^{2+} (1)

ii The first two ionisation energies are relatively low; the third is much higher as the third electron is removed from a new main quantum shell. (1)

c **i** Be, because the electron is removed from a shell close to the nucleus. (2)

ii Smaller, electrons are pulled closer by net positive charge. (2)

Total 8 marks

4.16

a Fume cupboard; CO is poisonous. (2)

b Filter off precipitated $Sr(OH)_2$; wash + dry; heat strongly to decompose to SrO. (3)

c **i** $Sr(OH)_2(s) \longrightarrow SrO(s) + H_2O(l)$ (2)

ii 184 g $SrSO_4 \longrightarrow$ 104 g SrO (1)

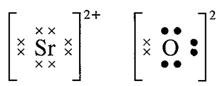
so 4.6 g $\longrightarrow \frac{104 \times 4.6\ g}{184} = 2.6\ g$ (1)

% yield $= \frac{1.3}{2.6} \times 100 = 50\%$ (1)

d **i** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ (1)

ii Sr^{2+} has no 5s electrons. (1)

iii (1)



e **i** Dip in HCl, then in sample, then in flame. (2)
ii Red (1)
iii Electrons promoted to higher energy levels by absorption of energy; fall back to lower levels, emitting energy having frequency of red light. (2)
f H_3O^+ from water; H_2O from OH^-. (2)

Total 20 marks

4.17

a Molar mass of $HCO_2H = 46$ (1)
Mass required = 4.6 g (1)
b $HCO_2H(l) + H_2O(l) \longrightarrow H_3O^+(aq) + HCO_2^-(aq)$ (2)
c Weak acid (1)

Total 5 marks

4.18

a Volumetric flask (1)
b **i** $H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$ (1)
ii $\frac{18.5}{1000} \times 0.2 = 3.7 \times 10^{-3}$ (1)
iii 1.85×10^{-3} (1)
iv 18.5 (1)
c **i** Does not give sharp colour change at end point. (1)
ii Any named single acid/alkali indicator. (1)
d **i** $\frac{1.84 \times 1000}{98} = 18.8$ (3SF) (1)
ii Titrated sample less concentrated: may have picked up water. (1)
e Conducts electricity (1)
f **i** Ca^{2+}; PO_4^{3-} (2)
ii $Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$ (1)
iii Sell $CaSO_4$ (1)

Total 14 marks

4.19

a Named single indicator correct colours. (3)
b **i** 17.7 cm^3 (1)
ii 1.77×10^{-3} (1)
iii 8.85×10^{-4} (1)
iv Molar mass $MgCO_3 = 84$ ($g\ mol^{-1}$)
Mass $MgCO_3 = 0.0743$ g (3SF) (1)
v 59.9% (3SF) (accept 60.0%) (1)
c **i** Accepts protons (2)
ii $HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$ (2)
d CO_3^{2-}; H_2CO_3 (2)

Total 14 marks

4.20

a Molar mass = 236 (1)
Mass required $= \frac{236 \times 0.2 \times 10}{1000} = 4.72$ g (1)
b Calcium carbonate calcium ethanedioate (2)
c $Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$ (1)
$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow CaC_2O_4(s)$ (1)
d 20 cm^3 (2)

Total 8 marks

TOPIC 5

Energy change and reactions

Introduction

'What makes a reaction take place?' is the most interesting and most demanding question that chemists can ask. A rigorous answer is not possible at this level but an insight into the answer is possible. This topic starts the search for an answer by establishing the way in which energy transfers are described by chemists. The search continues in Topic 13 when the need to consider the system as well as the surroundings is introduced. In Topic 14 our ideas about entropy are applied to equilibrium reactions. The development of these ideas is mainly qualitative and the only calculations are straightforward.

When the story is told well students will gain an insight into chemistry that should last long after the detail of individual reactions has been forgotten.

In this topic enthalpy changes are introduced, defined, measured and used to solve specific problems. Careful attention should be given throughout to a precise understanding of the terms used.

Content

5.1 Energy from chemical reactions – measuring energy changes of some reactions in solution; enthalpy changes, the meaning of standard enthalpy change for a reaction, standard enthalpy change of formation.

5.2 Hess's Law – determining standard enthalpy changes of reaction; measuring the enthalpy change of acid–base reactions.

5.3 Uses of standard enthalpy changes of formation – range of values of standard enthalpy changes; the importance and uses of Hess's Law.

Timing		**Students' Book**
5.1	$2\frac{1}{2}$ hours	pages 100–3
5.2	$2\frac{1}{2}$ hours	pages 103–5
5.3	$2\frac{1}{2}$ hours	pages 105–7

Total about $1\frac{1}{2}$ weeks

Objectives

1 To study the enthalpy changes that take place during chemical reactions and to measure some of these by experiment.

2 To gain an understanding of a range of enthalpy changes including the enthalpy changes of formation and reaction.

3 To examine the evidence for Hess's Law and to use this law to evaluate enthalpy changes that cannot be measured directly.

5.1 Energy from chemical reactions

Timing About $2\frac{1}{2}$ hours will be needed

Suggested treatment

It is suggested that students are introduced to energy changes through experiments involving exothermic and endothermic reactions.

EXPERIMENT 5.1 Measuring some energy changes

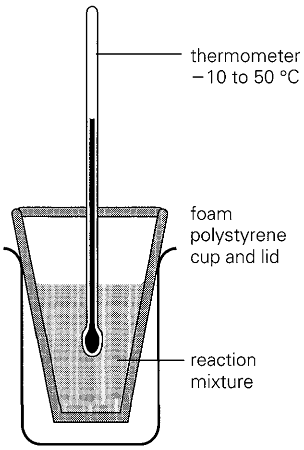


Figure 5.1 Apparatus for measuring energy changes

Each group of students will need:
Apparatus as in figure 5.1
Thermometer, −10 to 50 °C in 0.1 °C intervals
2 measuring cylinders, 25 cm^3
Weighing bottle for zinc powder, large watch glass (or other vessel for weighing sodium hydrogencarbonate), spatula
1.0 M citric acid, 25 cm^3
0.2 M copper(II) sulphate, 25 cm^3 HARMFUL SOLID
Sodium hydrogencarbonate, 10 g
Zinc powder, 1 g HIGHLY FLAMMABLE
Access to:
Balance, to weigh to ±0.01 g

Procedure

Before proceeding with the experiment, students are asked to calculate the mass of solid reagents to use. The required quantities are 0.65 g of zinc and 8.4 g of sodium hydrogencarbonate. Zinc powder should be used and it should not be oxidised on the surface; zinc dust is unsatisfactory.

The change in temperature of the solution is recorded in each case and the energy change in joules is calculated.

How to do the calculation

The energy change in joules is calculated from the relation:

energy exchanged between reactants and surroundings =
specific heat capacity × mass of the solution × temperature change

The mass of solution is taken as the mass of the same volume of water and the specific heat capacity is taken as 4.18 $J\ g^{-1}\ K^{-1}$, the value for water in the *Book of data*. The reactions are detailed below, the value for the first of these being based on figures in the *Book of data* and the second on a class experiment.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq) \qquad \Delta H^{\ominus} = -219\ kJ\ mol^{-1}$$

$$C_6H_8O_7(aq) + 3NaHCO_3(s) \longrightarrow C_6H_5O_7^{3-}(aq) + 3Na^+(aq) + 3CO_2(g) + 3H_2O(l) \qquad \Delta H^{\ominus} = +70\ kJ\ mol^{-1}$$

Recording energy changes

Following the experiments, a more detailed study of energy changes and the language of thermochemistry is undertaken. Some further notes are given below.

- In this course, chemical reactions are studied in open systems at constant pressure and it is enthalpy changes which are considered rather than internal energy changes ΔU, which pertain to closed systems at constant volume. When a reaction occurs at constant pressure, if the volume increases then the system must do work against the atmosphere; if the volume decreases then work will be done by the atmosphere on the system. This means that the enthalpy change, ΔH, will be different from the internal energy change ΔU.

- Enthalpy, H, and heat content are synonymous terms, as are enthalpy change, ΔH, and heat. It is correct to refer to the enthalpy change of formation or the heat of formation, but not to the enthalpy of formation.
- $\Delta H^{\ominus}$ is usually spoken of as 'delta H standard'. The standard sign is not always used in the same way in different books. The meaning of standard as used in this course is clearly set out in the *Students' Book* and on page 5 of the *Book of data*. The meaning of standard enthalpy change of formation is explained in the *Students' Book*.
- Exothermic and endothermic reactions can be shown as in figure 5.2.

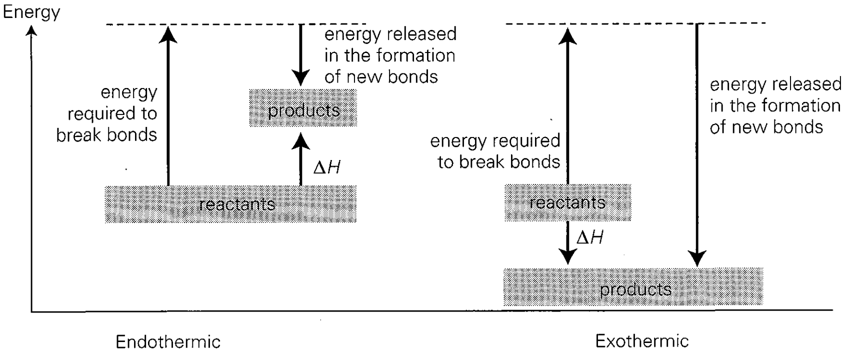


Figure 5.2 Energy level diagram for exothermic and endothermic changes

- For the benefit of teachers, the values of $\Delta H^{\ominus}$ (298) can be changed to values at other temperatures quite easily since:

$$\frac{d(\Delta H)}{dT} = \Delta C_p$$

where ΔC_p is the difference between the sum of the specific heat capacities of the reactants and products at constant pressure.

5.2 Hess's Law

Timing About $2\frac{1}{2}$ hours will be needed

Suggested treatment

A formal definition of Hess's Law is given in the *Students' Book*. It is a particular form of the law of conservation of energy and its validity can be demonstrated by experiment. The *Students' Book* contains some experimental results in support of the law, involving some metal displacement reactions.

Determining standard enthalpy changes of reaction

Once attention has been drawn to the law, it can be used to construct energy cycles to calculate standard enthalpy changes of formation of compounds that cannot be determined directly. The method for doing this is shown for a postulated reaction which was discussed in Topic 1:

$$Fe_2O_3(s) + 3Cu(s) \longrightarrow 2Fe(s) + 3CuO(s)$$

Further examples should be given by reference to the questions at the end of the topic or other examples using enthalpy changes of formation and reaction (see also section 5.3). This gives students the necessary practice required before they attempt Experiment 5.2.

EXPERIMENT 5.2 Measuring the enthalpy change of acid–base reactions

HAZARD

Solid sodium hydroxide and solid potassium hydroxide are corrosive and cause severe burns.
Solutions of sodium hydroxide (0.5 M) and potassium hydroxide 0.4 M or more are corrosive.
Solutions of sodium hydroxide (0.05 M to 0.49 M) and potassium hydroxide 0.1 M to 0.39 M are irritant.
Solutions of hydrochloric acid 6.5 M or more are corrosive.
Solutions of hydrochloric acid 2.0 M to 6.4 M are irritant.

Students are asked to design experiments to determine the enthalpy changes for the neutralisation of hydrochloric acid by sodium hydroxide and by potassium hydroxide. Time will be required for library research and trial experiments, and it is essential that students submit a risk assessment.

When students have completed their plans, these should be shown to the teacher for checking before they carry out their experiments.

Students should obtain similar values for the two experiments and it will be profitable to discuss the reason for this. Further values can be found in table 5.7 in the *Book of data*.

5.3 Uses of standard enthalpy changes of formation

Timing About $2\frac{1}{2}$ hours will be needed

Suggested treatment

The introduction to this section provides students with an opportunity to extract values for standard enthalpy changes of formation from the *Book of data*. The values are shown in table 5.1.
Students may notice some trends in these data. The value of $\Delta H_f^{\ominus}$:

- becomes more negative down the Group 1 chlorides (as the size of the cation increases)
- for metallic oxides becomes more negative from Groups 1 to 3 (as the size of the cation decreases and its charge increases)
- becomes less negative (more positive) down the series of hydrogen halides (as the size of the halogen atom increases)
- is much more negative for silicon dioxide (giant structure) than it is for carbon dioxide and nitrogen dioxide (molecular structures)
- the values for liquid water and water vapour are both negative, but the value for liquid water is more so.

	$\Delta H_f^{\ominus}$/kJ mol^{-1}
LiCl	−408.6
NaCl	−411.2
KCl	−436.7
Na_2O	−414.2
MgO	−601.7
Al_2O_3	−1675.7
HCl	−92.3
HBr	−36.4
HI	+26.5
CO_2	−393.5
SiO_2 (quartz)	−910.9
NO_2	+33.2
$H_2O(l)$	−285.8
$H_2O(g)$	−241.8

Table 5.1

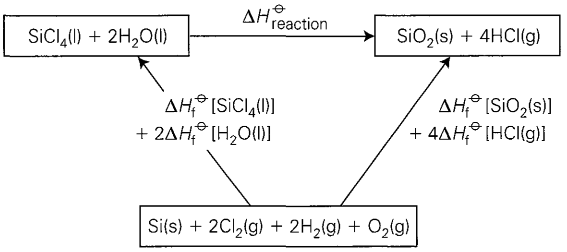
An explanation of these patterns should not be attempted at present although it might form extension work. The $\Delta H_f^{\ominus}$ values for the decomposition of hydrogen halides is relevant to the experiment on these gases in Topic 6.

The section is completed by giving a further example of the use of a Hess cycle. The example of this type of calculation given in the *Students' Book* is the reaction between ammonia gas and hydrogen chloride gas to form solid ammonium chloride. An additional example which might be used is the hydrolysis of silicon tetrachloride:

$$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(g)$$

If only enough water to react with the silicon tetrachloride is added, all of the hydrogen chloride formed can be considered to be evolved as gas, i.e. there is no surplus water to dissolve the gas.

First write down the equation of the reaction in which you are interested, then add the formation equations, from the same elements to both sides of the equation.



The value of $\Delta H_f^\ominus$ (298) used for silicon dioxide is that for quartz, marginally the most energetically stable form of $SiO_2(s)$.

Figure 5.1 Energy cycle for the reaction of silicon tetrachloride with water

The total enthalpy change must be the same by whatever route the $SiO_2 + 4HCl$ is formed (whether they are formed directly from their elements or through the intermediate of $SiCl_4 + H_2O$).
Therefore:

$$\Delta H_f^\ominus[SiO_2(s)] + 4\Delta H_f^\ominus[HCl(g)] = \Delta H_f^\ominus[SiCl_4(l)] + 2\,\Delta H_f^\ominus[H_2O(l)] + \Delta H^\ominus_{reaction}$$

That is

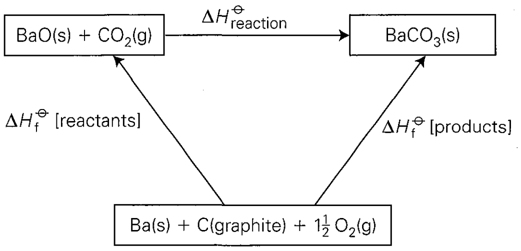
$$-910.9\text{ kJ mol}^{-1} + 4(-92.3)\text{ kJ mol}^{-1} = -687.0\text{ kJ mol}^{-1} + 2(-285.8)\text{ kJ mol}^{-1} + \Delta H^\ominus_{reaction}$$

So, $\Delta H^\ominus_{reaction} = -21.5\text{ kJ mol}^{-1}$

ANSWERS

Study task, page 107

1 **a** The required Hess cycle is



b The required enthalpy changes are

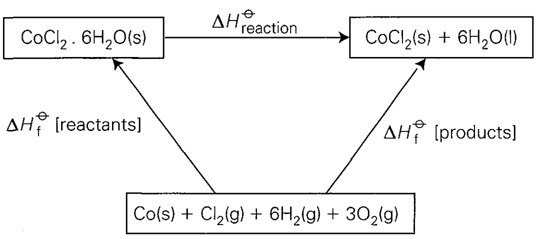
$\Delta H_f^\ominus[BaO(s)] = -553.5\text{ kJ mol}^{-1}$
$\Delta H_f^\ominus[CO_2(g)] = -393.5\text{ kJ mol}^{-1}$
$\Delta H_f^\ominus[BaCO_3(s)] = -1216.5\text{ kJ mol}^{-1}$

c and d From the relationship

$$\begin{aligned}\Delta H^\ominus_{reaction} &= \Delta H_f^\ominus[\text{products}] - \Delta H_f^\ominus[\text{reactants}]\\ \Delta H^\ominus_{reaction} &= -1216.3\text{ kJ mol}^{-1} - [-553.3 - 393.5]\text{ kJ mol}^{-1}\\ &= -1216.3\text{ kJ mol}^{-1} + 946.8\text{ kJ mol}^{-1}\\ &= -269.5\text{ kJ mol}^{-1}\end{aligned}$$

2 **a** $CoCl_2.6H_2O(s) \longrightarrow CoCl_2(s) + 6H_2O(l)$

The required Hess cycle will therefore be:



The required enthalpy changes are:

$\Delta H^{\ominus}_f [CoCl_2.6H_2O(s)] = -2115.4\ kJ\ mol^{-1}$
$\Delta H^{\ominus}_f [CoCl_2(s)] = -312.5\ kJ\ mol^{-1}$
$\Delta H^{\ominus}_f [H_2O(l)] = -285.8\ kJ\ mol^{-1}$

Using the relationship:

$\Delta H^{\ominus}_{reaction} = \Delta H^{\ominus}_f\ [products] - \Delta H^{\ominus}_f\ [reactants]$

it follows that:

$$\begin{aligned}\Delta H^{\ominus}_{reaction} &= -312.5\ kJ\ mol^{-1} + 6(-285.8)\ kJ\ mol^{-1} - [-2115.4]\ kJ\ mol^{-1}\\ &= -312.5\ kJ\ mol^{-1} - 1714.8\ kJ\ mol^{-1} + 2115.4\ kJ\ mol^{-1}\\ &= -2027.3\ kJ\ mol^{-1} + 2115.4\ kJ\ mol^{-1}\\ &= +88.1\ kJ\ mol^{-1}\end{aligned}$$

b To keep the reaction going it had to be heated continuously, suggesting that the reaction is endothermic; this conclusion is in line with the result of the calculation.

Answers to Topic 5 questions

Review questions

5.1

a Heat evolved $= 100 \times 4.2 \times 6.9$ (1)
$= 2898\ J$ (1)

b $\Delta H = -\dfrac{2898 \times 1000}{50 \times 1000} = -58.0\ kJ\ mol^{-1}$ (3SF) (1)

c Experiment 2: Heat produced $= 40 \times 4.2 \times 13.8 = 2318.4\ J$ (1)
$\Delta H = -\dfrac{2318.4 \times 1000}{2 \times 20 \times 1000} = -58.0\ kJ\ mol^{-1}$ (3SF) (1)
Experiment 3: Heat produced $= 40 \times 4.2 \times 13.8 = 2318.4\ J$ (1)
$\Delta H = -\dfrac{2318.4 \times 1000}{20 \times 1000} = -116\ kJ\ mol^{-1}$ (3SF) (1)

d ΔH is the same for reactions 1 and 2 because both HCl and HNO_3 are strong acids, and NaOH and KOH are both strong alkalis (or fully ionised). (1)
So essentially the same reaction occurs in both cases:
$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ (1)
ΔH for reaction 3 is twice that for reactions 1 and 2 because H_2SO_4 produces twice as many H^+ per mole. (1)

Total 10 marks

5.2

a $CuSO_4(aq) + Mg(s) \longrightarrow MgSO_4(aq) + Cu(s)$ (1)

b 2×10^{-3} (1)

c Heat produced $= 100 \times 4.2 \times 2.5 = 1050\ J$ (1)
Heat produced per mole of $Cu^{2+} = \dfrac{1050}{2 \times 10^{-3}} = 525\ 000\ J$
(or 525 kJ) (1)

d $Cu^{2+}(aq) + Mg(s) \longrightarrow Mg^{2+}(aq) + Cu(s) \quad \Delta H = -525\ kJ\ mol^{-1}$ (2)

Total 6 marks

5.3

a $Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$ (1)

b $\frac{0.05 \times 50}{1000} = 2.5 \times 10^{-3}$ (1)

c 1.25×10^{-3} (1)

d $\Delta H = -\frac{184}{1.25 \times 10^{-3} \times 1000} = -147\ \text{kJ mol}^{-1}$ (3SF) (2)

e $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$; $\Delta H = -147\ \text{kJ mol}^{-1}$ (1)

Total 6 marks

5.4

a $Ca(s) + \frac{1}{2}O_2(g) \longrightarrow CaO(s)\ \Delta H^\ominus = -635.1\ \text{kJ mol}^{-1}$ (2)

b $K(s) + \frac{1}{2}Br_2(l) \longrightarrow KBr(s)\ \Delta H^\ominus = -393.8\ \text{kJ mol}^{-1}$ (2)

c $Na(s) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) \longrightarrow NaOH(s)\ \Delta H^\ominus = -425.6\ \text{kJ mol}^{-1}$ (2)

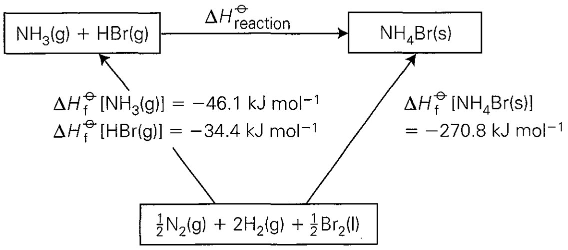
d $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)\ \Delta H^\ominus = -277.1\ \text{kJ mol}^{-1}$ (2)

e $Mg(s) + C(s) + 1\frac{1}{2}O_2(g) \longrightarrow MgCO_3(s)\ \Delta H^\ominus = -1095.8\ \text{kJ mol}^{-1}$ (2)

Total 10 marks

5.5

a and b



(3) for correct boxes and arrows

(3) for correct values of $\Delta H_f^\ominus$

c $\Delta H^\ominus_{\text{reaction}} = -270.8 - (-36.4 - 46.1)$ (1)

$= -188.3\ \text{kJ mol}^{-1}$ (1)

Total 8 marks

5.6

a $\Delta H^\ominus = -157.3 - (+82.0)$ (1)

$= -239.3\ \text{kJ mol}^{-1}$ (1)

b $\Delta H^\ominus = -46.1 - 92.3 - (-314.4)$ (1)

$= +176\ \text{kJ mol}^{-1}$ (1)

c $\Delta H^\ominus = -601.7 - 393.5 - (-1095.8)$ (1)

$= +100.6\ \text{kJ mol}^{-1}$ (1)

d $\Delta H^\ominus = (2 \times -601.7) - (-393.5)$ (1)

$= -809.9\ \text{kJ mol}^{-1}$ (1)

e $\Delta H^\ominus = -1675.7 - (-824.2)$ (1)

$= -851.5\ \text{kJ mol}^{-1}$ (1)

f $\Delta H^\ominus = (2 \times -358.7) - (2 \times -467.9)$ (1)

$= +218.4\ \text{kJ mol}^{-1}$ (1)

g $\Delta H^\ominus = (2 \times -157.3) + (4 \times 33.2) + (6 \times -285.8) - (2 \times -1217.1)$ (1)

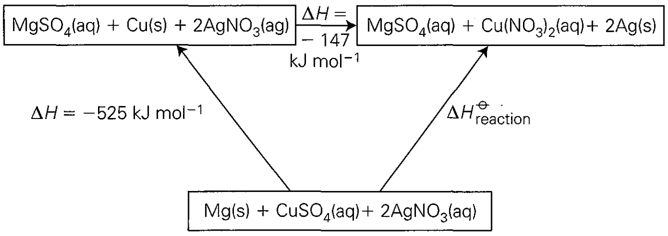
$= +537.6\ \text{kJ mol}^{-1}$ (1)

Total 14 marks

5.7

a $Mg(s) + 2AgNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + 2Ag(s)$ (1)
(could be written ionically)

b (3)



c $\Delta H^\ominus_{\text{reaction}} = -525 - 147 = -672\ \text{kJ mol}^{-1}$ (2)

d $Mg(s) + 2Ag^+(aq) \longrightarrow Mg^{2+}(aq) + 2Ag(s)\ \ \Delta H^\ominus = -672\ \text{kJ mol}^{-1}$ (2)

Total 8 marks

5.8

a None (1)
b $\Delta H_f^\ominus[CuO(s)]$ (1)
c $\Delta H_f^\ominus[CuO(s)]$ (1)

Total 3 marks

Examination questions

5.9

a Range 0° to 100 °C or 0° to 50 °C etc. (1)
Sensitivity 0.10 °C (1)
b **i** 2.1 °C (1)
ii 0.4 °C (1)
c Second experiment larger volumes minimise errors (2)
d Third experiment small temperature rise maximises errors (2)
e $Mg^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MgCO_3(s)$ (2)
f Heat produced $= 20 \times 4.18 \times 2.1 = 175.56$ J (1)
$\Delta H^\ominus = -175.56 \times 100\ \text{J mol}^{-1} = -17.6\ \text{kJ mol}^{-1}$ (3SF) (1)

Total 12 marks

5.10

a **i** **A** $4.18 \times 20 \times 2 = 167.2$ J (1)
B $4.18 \times 20 \times 12 = 1003.2$ J (1)
ii Mass of solution is mass of whole system (1)
Specific heat capacity, 4.18, is the same as that of water (1)
iii 1.25×10^{-2} (1)
iv $\Delta H_A^\ominus = -13\ \text{kJ mol}^{-1}$ (2)
$\Delta H_B^\ominus = -80\ \text{kJ mol}^{-1}$ (2)
b $\Delta H^\ominus_{\text{reaction}} = -13 - (-80)$ (1)
$= +67\ \text{kJ mol}^{-1}$ (1)
c Chalk may <u>not</u> have been pure $CaCO_3$ (1); incomplete decomposition of heated chalk (1); heat losses to surroundings (1); small temperature change (2 °C) may have been inaccurately measured. (1) any 3 to count (3)

Total 14 marks

5.11

a **i** 9.79 kJ (1)
ii $\dfrac{9790}{250 \times 4.18} = 9(.37)$ °C (2)
b **i** No; reaction so slow heat would easily dissipate
OR small temperature rise would not affect enzyme yeast. (2)
ii Yes; in such a large volume of liquid heat could not escape/might denature the enzyme
OR No; temperature rise exactly the same as in laboratory and can be controlled with suitable equipment. (2)

Total 7 marks

5.12

a Box should contain
$2Na(s) + H_2(g) + 2C(s) + 3O_2(g)$ (2)
b $\Delta H_2^\ominus = -1131 - 394 - 286 - (2 \times -951)$ (1)
$= +91$ kJ (1)

Total 4 marks

TOPIC 6

Redox reactions and the halogens

Introduction

In Topic 1, oxidation and reduction were related to changes in oxygen content and to electron transfer. This is expanded in the present topic where the concept of oxidation number is introduced and used. Oxidation numbers are also seen as an aid to balancing equations as well as being central to the Stock system for naming inorganic substances.

Students are likely to be aware from previous experience that there are trends in the physical and chemical properties of Group 7 elements and their compounds. This topic extends students' knowledge of these materials by introducing a range of halogen compounds and considering their sources and uses.

Content

6.1 Sources of the halogens – methods of extraction of halogens from their sources; the extraction of iodine from seaweed.

6.2 Redox reactions and oxidation numbers – reactions between halogens and halide ions; oxidation and reduction by electron transfer. The chemists' toolkit: oxidation numbers; rules for assigning oxidation numbers; redox and oxidation number change; Stock notation. The chemists' toolkit: balancing redox equations.

6.3 The properties of the halogens – trends in the physical and chemical properties of the halogens; electronic structures of the halide ions; variable oxidation numbers; sources and uses of the halogens.

6.4 Oxidation number −1: the halides – reactions of the halides with silver nitrate solution; action of sulphuric and phosphoric acids on solid halides; properties of the hydrogen halides.

6.5 Oxidation number 0: the halogens – reactions of various elements with chlorine; reactions of the halogens with sodium hydroxide.

6.6 Oxidation number +1: sodium chlorate(I) – oxidation of iron(III) ions and iodide ions using sodium chlorate(I).

6.7 Oxidation number +5: the potassium halates(V) – oxidations using acidified potassium halates(V).

6.8 The preparation and analysis of potassium iodate(V) – the preparation of potassium iodate(V); the reaction between iodine and sodium thiosulphate; determination of the purity of samples of potassium iodate(V).

6.9 Background reading: the halogens in human metabolism

Timing		Students' Book
6.1	2 hours	pages 115–17
6.2	3 hours	pages 117–21
6.3	2 hours	pages 121–2
6.4	3 hours	pages 123–4
6.5	1 hours	pages 124–5
6.6	$\frac{1}{2}$ hour	pages 125–6
6.7	$\frac{1}{2}$ hour	pages 126–7
6.8	3 hours	pages 127–30
6.9	Homework	pages 131–3
Total about 3 weeks		

Objectives

1 To introduce the concept of redox reactions in terms of electron transfer.

2 To introduce the idea of oxidation number and to show its meaning and use in balancing equations and in naming inorganic compounds.

3 To study by experiment, the properties of the elements in Group 7 of the Periodic Table and their compounds, noting trends in their properties wherever possible.

4 To extend students' experience of practical procedures involved in the separation of compounds.

5 To extend students' experience of titrations with specific reference to the estimation of iodine using sodium thiosulphate.

6 To evaluate information concerning the sources of the halogens and their uses.

6.1 Sources of the halogens

Timing About 2 hours

Suggested treatment

This introductory section summarises the variety of sources from which halogens may be extracted. This is a suitable exercise for homework and also provides students with experience of information retrieval using reference books, CD-ROM or other sources. The study task serves as a focus for these exercises.

ANSWER

Study task, page 116

1 1.83×10^{-1} tonnes of caliche are required to extract 1 mol of I_2 molecules. This assumes that there is no loss of iodine during the extraction procedure. In reality, only about one-tenth of the liquor obtained after nitrate crystallisation from caliche is treated for the recovery of iodine.

The extraction of iodine from seaweed serves to introduce students to the use of a hydrocarbon solvent to purify and concentrate a molecular substance.

EXPERIMENT 6.1

The extraction of iodine from seaweed

HAZARDS

If 100 volume hydrogen peroxide is purchased it must be handled with great care. 100 volume hydrogen peroxide is corrosive. Gloves should be worn when diluting the solution to 20 volume for laboratory use.

Each group of students will need:

Eye protection
Bunsen burner, tripod, gauze and heatproof mat
Tin lid, preferably new one
Beaker, 100 cm^3
Boiling tube and rack
Filter funnel and filter paper
Separating funnel, 100 cm^3
Conical flask, 50 cm^3, with stopper
Spatula
Measuring cylinder, 25 cm^3

Access to:

Dried seaweed, preferably from a *Laminaria* seaweed (see under procedure), 2 g
1 M sulphuric acid, 5 cm^3 IRRITANT
20 volume hydrogen peroxide, 10 cm^3 IRRITANT
Petroleum spirit, boiling range 120–160 °C, 10 cm^3 labelled 'Hydrocarbon solvent' HIGHLY FLAMMABLE
Balance to weigh to ±0.1 g

Procedure

Full experimental details are found in the *Students' Book.*

Laminaria may be obtained from biological supply agencies or collected as a result of liaison with biology or geography departments before they go on field trips. Seawater contains approximately 0.05 parts per million of iodine but some seaweeds of the Laminaria group have the power to absorb and concentrate iodine so that it is present at 800 parts per million. Extraction of iodine from seaweed ash was once of major importance but is now of minor significance.

The importance of solvent extraction could be discussed along the following lines: if a compound is soluble in an organic solvent which is immiscible with water, extraction of the aqueous solution with the solvent will eventually transfer the compound (in this case iodine) almost entirely into the organic solvent. Repeated extraction will result in more and more solute being transferred. The extraction solvent should not react with the solute and be readily removed by distillation or evaporation without volatilising the solute.

Students should observe the purple coloration of the iodine in the hydrocarbon solvent and although the students are not asked to evaporate the hydrocarbon solvent, the teacher may demonstrate this in a fume cupboard. The result, however, is unlikely to be convincing even when the hydrocarbon solvent is allowed to evaporate with the minimum of heating.

6.2 Redox reactions and oxidation numbers

Timing About 3 hours

Suggested treatment

This section is developed in the following ways:

1. Through practical work, students discover the pattern of the oxidation of halide ions by halogens.
2. The concept of oxidation and reduction by electron transfer is developed.
3. Oxidation numbers are introduced.
4. The rules for assigning oxidation numbers are discussed.
5. The rules for naming inorganic compounds using oxidation numbers (Stock notation) is developed.

EXPERIMENT 6.2 The reactions between halogens and halide ions

HAZARDS

The halogens are all hazardous substances that need to be used with great care. Chlorine can cause severe damage to the lungs and eyes. Bromine causes severe burns and is very toxic if inhaled. Iodine solid burns the skin and the vapour irritates the eyes and respiratory system.
To prepare the solutions* it is advisable to wear protective gloves:

- **Dilute a saturated aqueous solution of bromine (VERY TOXIC AND**

Each group of students will need:
Eye protection
12 test tubes and rack
Bungs to fit test tubes
Access to:
The following reagents, each with a dropping pipette for dispensing:
  Aqueous chlorine, saturated solution, 5 cm^3 TOXIC
  0.05 M aqueous bromine*, 5 cm^3 HARMFUL AND IRRITANT
  0.05 M aqueous iodine*, 5 cm^3
  0.1 M potassium bromide, 5 cm^3
  0.1 M potassium chloride, 5 cm^3
  0.1 M potassium iodide, 5 cm^3
Petroleum spirit, boiling range 120–160 °C, 10 cm^3, labelled 'Hydrocarbon solvent' (see 6.1)
  HIGHLY FLAMMABLE
Fume cupboard (for the aqueous chlorine and bromine)

Procedure

Full details are given in the *Students' Book*. Students should be advised to use only 1 cm^3 portions of the halide solutions, so that only small amounts of halogen need be used. The nature of the halogen product resulting from the reaction (where this

CORROSIVE) with three times its own volume of pure water.
- **Dissolve 12 g of iodine (HARMFUL) and 10 g of potassium iodide in 1 dm^3 of water.**

Store the aqueous chlorine and bromine solutions in a fume cupboard.

occurs) is found with the aid of hydrocarbon solvent when the coloured halogen migrates to the organic layer. Students should interpret this in terms of the hydrocarbon solvent being better than water for dissolving molecular substances.

Oxidation and reduction by electron transfer

A brief discussion should lead to the establishment of the following points.

- The reactions can be split up into two half reactions which are related by electron transfer.
- Oxidation–reduction reactions involve transfer of electrons. Loss of electrons is oxidation and gain of electrons is reduction.
- Oxidants (oxidising agents) are substances which gain electrons during a reaction. Reductants (reducing agents) are substances which lose electrons during a reaction.

The chemists' toolkit: oxidation numbers

Oxidation number means a number found by the application of certain rules. It is of value in describing oxidation and reduction reactions and combining powers of atoms. It does not offer physical insight, but is a type of 'book-keeping'. It is calculated directly from experimental findings, that is, the determination of empirical formulae. By reference to the empirical formulae of chlorides, hydrides and oxides of the elements of the first, second and third periods of the Periodic Table (elements from hydrogen to argon), charts can be drawn up showing the number of charges on the ions of those elements that form ions. As an optional homework, students could construct a chart similar to the one below. This could be developed as follows:

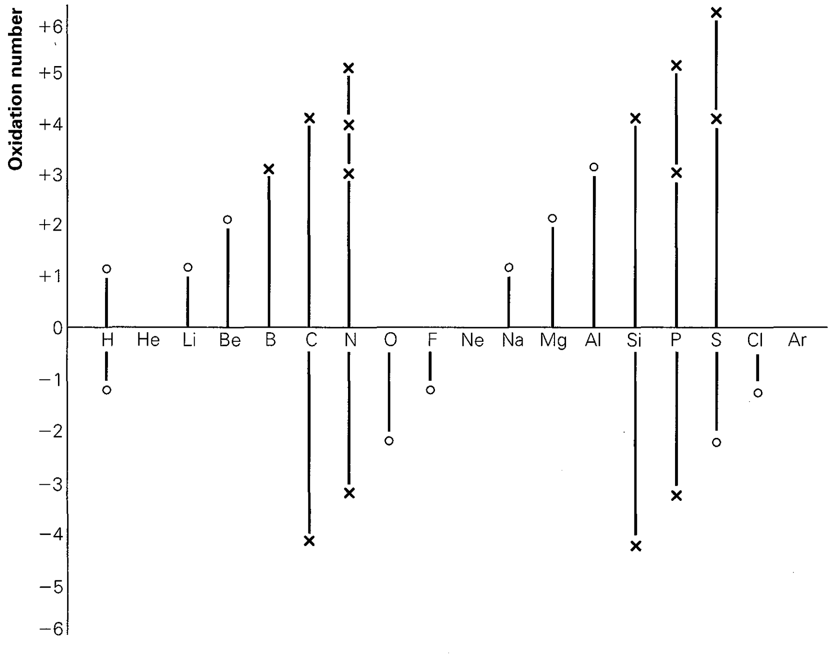


Figure 6.1 Oxidation number chart

The points indicated by a 'o' are those for simple ions. Oxidation numbers are then assigned to those elements which do not form ions by inspecting the empirical formulae of a number of covalent compounds; these are indicated by an 'x' on the chart. A name is needed for the number represented on the vertical axis of the chart and in this operational way, the term oxidation number can be introduced. Students should realise that elements have an oxidation number of zero and the total oxidation number of a compound is also zero.

Students may ask whether to put the 'x' above or below the line. An answer may be sought by inspecting compounds of the element with hydrogen on the one hand and oxygen on the other. Thus nitrogen in ammonia has an oxidation number of −3, whereas in nitrogen dioxide, it is +4 and in dinitrogen pentoxide it is +5.

Students should be encouraged to look up the formulae of the hydrides, chlorides and oxides of the elements in table 5.3 in the *Book of data*.

When the chart has been completed, the following points should be made.

- The maximum positive oxidation number shown by an element is frequently the same as the number of the group containing the element.
- The patterns in the two periods are essentially similar, except in Group 6, where sulphur forms compounds with a greater range of positive oxidation numbers than oxygen.
- Metals have oxidation numbers which are always positive.

Once the idea of oxidation number has been introduced, it will be necessary to formulate some rules so that it can be applied to a greater range of compounds.

Rules for assigning oxidation numbers

The *Students' Book* gives five rules for assigning oxidation numbers. More extensive notes are given below.

a The sign given to the oxidation number of an element in a binary compound is decided by giving one element a positive and the other a negative oxidation number. In most cases of compounds of metals with non-metals, there is no difficult in deciding which sign should be given to which element: the metal is given a positive sign and the non-metal a negative one. For many other compounds, the sign can be decided by using the invariable oxidation numbers. The signs are always relative to other elements. For example, the oxidation number of sulphur in sodium sulphide is -2 but in sulphur dioxide it is $+4$.

b The numerical value of the oxidation number of an element in a compound is found by using the empirical formula of that compound. The oxidation number of each of the atoms in the formula counts separately, and their algebraic sum is zero. In PCl_3, if the oxidation number of chlorine is taken as -1, the total chlorine contribution is -3 and so the oxidation number of phosphorus is $+3$. It follows that the oxidation number of any uncombined element is zero.

c The oxidation number of an element existing as a monatomic ion is the charge on that ion. In a polyatomic ion, the algebraic sum of the oxidation numbers of the atoms is equal to the charge on the ion. For example, in the sulphate ion, SO_4^{2-}, if the oxidation number of oxygen is taken as -2, the total oxidation number for oxygen is -8 and the oxidation number of sulphur is therefore $+6$.

d Some elements have invariable oxidation numbers in their compounds, or oxidation numbers that are invariable under certain conditions. A list is given in the *Students' Book*.

Oxidation and reduction

Oxidation and reduction are now defined in terms of increase and decrease in oxidation number, respectively.

Oxidation numbers and the Stock notation

The *Students' Book* notes that the Roman numerals which appear in the Stock system of nomenclature used for metal compounds are in fact the oxidation numbers of the metals, but that this nomenclature for distinguishing between compounds of non-metals such as nitrogen(IV) oxide and nitrogen(II) oxide is much less widely used. The point is made, however, that the salts of common mineral acids are often named without including the oxidation number, for example, nitrate rather than nitrate(V) and sulphite rather than sulphate(IV).

6.3 The properties of the halogens

Timing About 2 hours

Suggested treatment

This section gives students a further opportunity to use reference books, a computer spreadsheet or CD-ROM facilities, to collect information and to search for patterns in the physical and chemical properties of the halogens and halide ions.

1 Trends in physical properties

The following might be considered.

- The melting and boiling points of the halogens increase with increasing atomic number. These trends are also reflected in the physical states shown by the halogens at room temperature.
- The appearance of the halogens when pure and when dissolved in a hydrocarbon solvent could be revised.
- A discussion of the solubility of halogens in water, indicating the need to dissolve iodine in potassium iodide if aqueous iodine solution is required.

2 Electronic structure of the halide ions

The radii of the halide ions are greater than the radii of the corresponding halogen atoms. This situation is the reverse of that found for the elements of Groups 1 and 2. Trends in atomic and ionic radii of the halogens and halide ions should be discussed.

To form a cation requires an input of energy but the enthalpy change for the formation of gaseous halide anions from gaseous halogen atoms is negative and the latter is therefore more favourable.

3 Variable oxidation numbers

The oxidation number of a variety of types of halogen compounds should be put on an oxidation number chart. Table 5.3 in the *Book of data* gives a suitable range of compounds.

4 Sources and uses

This may be omitted if students have already covered the material in section 6.1.

6.4 Oxidation number −1: the halides

Timing About 3 hours

Suggested treatment

In this section, students compare experimentally some properties of the Group 1 chlorides, bromides and iodides. They also prepare hydrogen halides and study some of their properties.

EXPERIMENT 6.4 Some reactions of the halides

The details of these experiments are given separately here for convenience and because of safety considerations. The students investigate halides both in solid form and in solution. The solutions of the halides are tested with silver nitrate solution and the resulting precipitates with ammonia solution. The experiments with solid halides include the action of sulphuric acid and phosphoric acid. The resulting hydrogen halides are examined.

Experiment 1

HAZARDS

Stock bottles of ammonia build up a pressure in warm weather and should be opened with great caution. 8 M ammonia is prepared by mixing 450 cm^3 ammonia, density 0.880 g cm^3, with 550 cm^3 of pure water. Solid silver nitrate is corrosive.

Each group of students will need:
Eye protection
6 test tubes and rack

Access to:
The following solutions each with a dropping pipette:
8 M ammonia solution, 6 cm^3 CORROSIVE
0.1 M potassium bromide, 3 cm^3
0.1 M potassium chloride, 3 cm^3
0.1 M potassium iodide, 3 cm^3
0.1 M silver nitrate, 6 cm^3 (solid is CORROSIVE)
Lamp or brightly lit windowsill

Procedure for experiment 1

Details are given in the *Students' Book*. Students should be advised to use only small quantities of silver nitrate solution. The ammonia dissolves the silver chloride precipitate because a complex ion $Ag(NH_3)_2^+$ is formed. Silver bromide is sparingly soluble to give a similar complex ion but silver iodide is insoluble in ammonia.

Experiments 2a and 2b

HAZARDS

Add phosphorus pentoxide to about double its volume of 85% phosphoric acid. Wear gloves and a face shield for this procedure. Lead ethanoate is a toxic substance with a possible risk of irreversible effects, so students should be provided with prepared test papers rather than having access to a solution.
There are a number of harmful substances produced during the reaction of concentrated sulphuric acid with the solid halides. Bromine is very toxic and corrosive and iodine is harmful. Hydrogen halides are evolved with all the halides. These are corrosive, or irritant at lower concentrations. A small amount of hydrogen sulphide, which is toxic, is formed in the reaction between sulphuric acid and solid iodide.

Each group of students will need:
Eye protection and protective gloves
Bunsen burner and heatproof mat
6 test tubes and rack
Test tube holder

Access to:
Potassium bromide
Potassium chloride
Potassium iodide
100% phosphoric(V) acid with pipette CORROSIVE
Sodium dichromate(VI) paper VERY TOXIC if ⩾0.2 M TOXIC if ⩾0.003 M Avoid handling the papers with bare hands
Concentrated sulphuric acid with pipette CORROSIVE
Full-range Indicator paper
Fume cupboard
Lead ethanoate paper TOXIC if ⩾0.01 M
Ammonia paper CORROSIVE

Procedure for experiment 2

Because of the hazards involved in these reactions, students must be warned to use only very small quantities of the halides and fume cupboards should be used where possible. If students heat the reaction mixtures, they must be advised to do so very gently. The students test the gases evolved on heating halides using lead ethanoate paper, dichromate(VI) paper and ammonia paper. Students should hold the test papers using tweezers or gloves.

Sulphur dioxide (toxic and corrosive) can be detected when sulphuric acid reacts with bromide using the dichromate(VI) paper. Hydrogen sulphide can be detected when the iodide reacts with sulphuric acid. The results may be obscured by vaporisation of bromine or iodine if the mixture is heated too strongly. Sulphur may also be detected.

After students have had the opportunity to make their own suggestions, the reactions should be discussed with particular reference to the oxidations and reductions that are taking place. For example, students may suggest that sulphuric acid liberates hydrogen bromide and hydrogen iodide from bromides and iodides respectively and then oxidises these hydrides to free halogens while the acid itself is reduced. The likely reduction products can be discussed and sulphur dioxide, sulphur and hydrogen sulphide mentioned as possibilities. It should not be a surprise to find that the reaction which involves the halogen that is oxidised the most readily is the one in which the sulphur in the sulphuric acid is reduced the furthest. The sequence of reactions is complex and students are not expected to know the equations for the reactions.

Students should note that the reactions with phosphoric(v) acid do not appear to involve oxidation of the halides (although a slight brown colour may be noted on reaction with the potassium iodide). This is in direct contrast to the reaction with sulphuric acid which is a good oxidant.

Experiment 3

HAZARDS

See the notes for Experiment 2.

Each group of students will need:
Eye protection and protective gloves
Bunsen burner and heatproof mat
9 dry test tubes and rack
Clamp stand and clamp
9 dry corks to fit test tubes
Side-arm test tube fitted with right-angle bend delivery tube (see figure 6.2)
Beaker, 250 cm^3 or plastic tub (for the gas solubility experiment)
Length of nichrome wire in holder
Glass rod (for test with ammonia)

Access to:
Potassium chloride
Potassium bromide
Potassium iodide
100% phosphoric(v) acid with dropping pipette, 5 cm^3 CORROSIVE
8 M ammonia solution CORROSIVE
Balance to weigh ±0.1 g

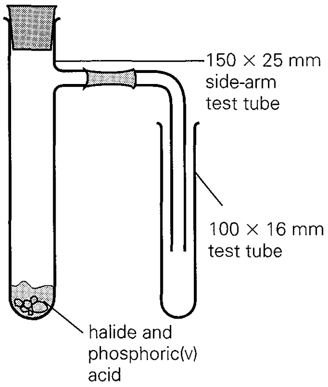


Figure 6.2 Apparatus for making hydrogen halides

Procedure for experiment 3

A wide ice-cream tub, plastic food box or washing up bowl is a suitable container for testing the solubility of the hydrogen halide gases in water. The acidic character of the hydrogen halides may also be tested using moist full-range indicator paper if wished. Students should write equations for the reactions they have observed. The decomposition of hydrogen iodide may be discussed briefly by referring to the trend of enthalpy changes of formation of the hydrogen halides, see *Book of data* table 5.3. The values of the bond energies of the hydrogen halides are discussed further in Topic 7.

A possible way of organising the carrying out of the preparation and properties of the hydrogen halides is to have three 'teams' of students preparing one of the hydrogen halides each and demonstrating, in turn, the reactions to each other. This gives the teacher the opportunity to reinforce the details of the reactions and cuts down on atmospheric pollution!

6.5 Oxidation number 0: the halogens

Timing About 1 hour will be needed

Suggested treatment

This section is intended to cover the reactions of the elements of the third period with chlorine and the reactions of the halogens with alkalis. Instructions are given for a complete range of demonstrations but a few may be selected if preferred.

Optional teacher demonstration 6.5

The action of chlorine on the elements of the third period of the Periodic Table

SAFETY

On no account must white phosphorus be used.

Sulphur should be kept away from aluminium powder. The products of some of the reactions are corrosive and should be treated with care.

The teacher will need:
Eye protection
Bunsen burner and heatproof mat
6 combustion spoons, one of which should be new
Tweezers and knife (for sodium)
Filter paper
Sandpaper (for cleaning magnesium ribbon)

Access to:
Small samples of the following:
Sodium CORROSIVE, HIGHLY FLAMMABLE
Magnesium ribbon
Aluminium powder HIGHLY FLAMMABLE
Silicon powder
RED phosphorus HIGHLY FLAMMABLE, TOXIC
Sulphur FLAMMABLE (forms TOXIC and CORROSIVE gas)
Chlorine, 6 gas jars TOXIC
Fume cupboard

Each student will need:
Eye protection

Procedure

All the experiments should be done in a fume cupboard. To demonstrate the reactions of the elements with chlorine, begin by showing the reaction of sodium with chlorine. Carefully cut away the surface coating of some sodium to obtain a cube of side 2–3 mm. Put this in a *new* combustion spoon. Heat the spoon with a Bunsen burner until the sodium is molten and the spoon is really hot but do not wait until the sodium catches fire. Lower the sodium into a gas jar of chlorine and note the vigorous reaction. Any yellow colour in the product will be due to the reaction of the chlorine with the metal of the spoon.

Repeat the reaction using about 5 cm of freshly-cleaned magnesium ribbon. Wind the ribbon round the combustion spoon, ignite it and lower it into the second gas jar of chlorine.

The demonstrations can be continued with aluminium powder, powdered silicon, red phosphorus and sulphur. Because of the nature of the reactants and the corrosive nature of the silicon, phosphorus and sulphur chlorides, these experiments should be performed in a fume cupboard. If phosphorus is used, it requires only a very slightly raised temperature to start the reaction with chlorine. The reaction with silicon may not be very convincing and teachers may wish to omit this.

Here is an alternative way of demonstrating the reaction of sodium with chlorine.

> Take a heat-resistant mat. Put a pile of dry sand on it, less than the diameter of a gas jar. Place a crucible lid on the sand and put a piece of cleaned up sodium on the lid. Ignite the sodium with a Bunsen and when it is burning, quickly invert a gas jar of chlorine over the burning sodium, removing the lid at the last minute and stand the gas jar over the sand on the mat. White NaCl fumes are easily visible.

In the interests of economy of time, teachers may prefer to get students to view these reactions using a Periodic Table database on CD-ROM.

EXPERIMENT 6.5 The reactions of halogens with alkalis

HAZARDS

It is advisable to store the aqueous chlorine and bromine in a fume cupboard and wear protective gloves when pouring the solutions as well as for dealing with spillages. For details on preparing the solutions see Experiment 6.2.

Each group of students will need:
Eye protection and protective gloves
3 test tubes and rack

Access to:
The following solutions, each with a dropping pipette:
- 0.4 M sodium hydroxide, 1 cm^3 HARMFUL AND IRRITANT
- Aqueous chlorine, saturated solution, 2 cm^3 TOXIC
- 0.05 M aqueous bromine, 2 cm^3 IRRITANT AND HARMFUL
- 0.05 M aqueous iodine, 2 cm^3

Fume cupboard (for the aqueous chlorine and bromine)

Procedure

Full details of the procedure are given in the *Students' Book.* The students should observe the colour of the halogen disappear on addition of sodium hydroxide. The aqueous chlorine should be fresh in order to observe any change.

An interpretation of the reactions of the halogens with alkalis

Equations are given for the reaction of chlorine with sodium hydroxide using cold dilute alkali and hot concentrated alkali. The students are introduced to disproportionation by answering the question 'What changes of oxidation number does the chlorine undergo?' for the reaction

$$Cl_2(aq) + 2OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

The chlorine undergoes two changes; part of it changes from 0 to −1 and part from 0 to +1.

ANSWERS

Questions, page 125

3 Chlorine changes in oxidation number from 0 to +5 and from 0 to −1.

4 $3I_2(aq) + 6KOH(aq) \longrightarrow 5KI(aq) + KIO_3(aq) + 3H_2O(l)$

6.6 Oxidation number +1: sodium chlorate(I)

Timing About $\frac{1}{2}$ hour

The content of this section is not examinable as part of AS unit 2 in the Edexcel specification.

Suggested treatment

This section provides students with the opportunity to carry out some reactions using sodium chlorate(I) solution and then to write balanced equations. They may well need to refer to the chemists' toolkit on balancing redox equations.

EXPERIMENT 6.6 Some reactions of sodium chlorate(I)

HAZARDS

Sodium chlorate(I) solutions are corrosive and dangerous to skin and eyes even in dilute solution.
The iodine released in the reaction of sodium chlorate(I) with potassium iodide is harmful but the amounts are very small so do not pose a problem.

Each group of students will need:
Eye protection
4 test tubes and rack
0.1 M iron(II) sulphate, 3 cm^3 HARMFUL SOLID
0.1 M potassium iodide, 3 cm^3
Sodium chlorate(I) solution, with dropping pipette, 4 cm^3 CORROSIVE
0.5 M sodium hydroxide solution

Procedure

Full details are given in the *Students' Book*. (Protective gloves should be worn when dispensing the sodium chlorate(I).) The reactions of sodium chlorate(I) (sodium hypochlorite) are those of an oxidising agent. Students are asked to write equations for the reactions; they may try these now or after the discussion of balancing equations using the oxidation number method in the next section.

1 Reaction with iron(II) ions

The relevant equation is:

$$2Fe^{2+}(aq) + ClO^-(aq) + H_2O(l) \longrightarrow 2Fe^{3+}(aq) + Cl^-(aq) + 2OH^-(aq)$$

Students can use a solution of sodium hydroxide to test for the presence of Fe^{3+} ions.

Students may need to be reminded of the test to distinguish aqueous iron(II) ions from iron(III) ions which was introduced in Experiment 1.1d.

2 Reaction with iodide ions

The iodine that is formed colours the solution distinctly but the colour diminishes after a short time. This is because the iodine first formed reacts with the hydroxide ions. The equation for the reaction is:

$$2I^-(aq) + ClO^-(aq) + H_2O(l) \longrightarrow I_2(aq) + Cl^-(aq) + 2OH^-(aq)$$

6.7 Oxidation number +5: the potassium halates(V)

The content of this section is not examinable as part of AS unit 2 of the Edexcel specification.

Timing About $\frac{1}{2}$ hour will be needed

The action of potassium halates as oxidising agents is discussed by reference to experiments involving their reaction with Fe^{2+} and I^- ions.

EXPERIMENT 6.7 Some reactions of the potassium halates(V)

Each group of students will need:
Eye protection and protective gloves
Test tubes and rack
Bunsen burner and heatproof mat
Test tube holder

Access to:
Potassium chlorate(V) OXIDISING, HARMFUL
Potassium bromate(V) OXIDISING, TOXIC, CATEGORY 2 CARCINOGEN
Potassium iodate(V) OXIDISING
1 M sulphuric acid, 5 cm^3 IRRITANT
0.1 M iron(II) sulphate, 5 cm^3 HARMFUL SOLID
0.1 M potassium iodide, 5 cm^3

HAZARDS

Potassium bromate(v) is a category 2 carcinogen and should therefore be used with close supervision. Concentrated sulphuric acid (used in Experiment 6.4) must not be present in the laboratory when halates(v) are in use; accidents have been caused by the inadvertent use of this in place of the dilute acid.

Procedure

Instructions for the experiment are given in the *Students' Book*. Students should identify the species which have been oxidised and reduced in the reactions but are not asked to write equations for the reactions. After discussion of the reactions teachers might ask students to use the oxidation number method to balance the equations.

1 Reaction with iron(II) ions

All the halates(V) are good oxidants. They all oxidise Fe^{2+} to Fe^{3+} in a similar manner, for example,

$$6Fe^{2+}(aq) + ClO_3^-(aq) + 6H^+(aq) \longrightarrow 6Fe^{3+}(aq) + Cl^-(aq) + 3H_2O(l)$$

2 Reaction with iodide ions

Chlorates and bromates oxidise iodide to iodine, the halates(V) being reduced to halide. The reaction of iodide with iodate produces iodine and water.

$$6I^-(aq) + ClO_3^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + Cl^-(aq) + 3H_2O(l)$$
$$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$$

6.8 The preparation and analysis of potassium iodate(v)

Timing About 3 hours will be needed

Suggested treatment

The preparation and analysis are presented as effectively one continuous exercise comprising:

- preparing samples of potassium iodate(V) and of potassium iodide
- learning the technique of titration using sodium thiosulphate solution
- using this technique to estimate the purity of either or both of the halogen compounds.

EXPERIMENT 6.8a The preparation and analysis of potassium iodate(v)

HAZARDS

Students should wear gloves when dealing with solid iodine. The concentrated solution of potassium hydroxide used in this experiment should be handled with care. It is necessary to wear face masks or goggles.
The potassium iodate(v) formed in this reaction is oxidising and harmful by ingestion.
Care should be taken with the evaporation; the impure potassium iodide has a tendency to 'spit' towards the end of the evaporation.

Each group of students will need:
Eye protection, or face masks, and protective gloves
Bunsen burner, tripod, gauze and heatproof mat
Boiling tube and rack
Beaker, 400 cm^3
Dropping pipette
Apparatus for suction filtration, small size
Evaporating basin
Measuring cylinder, 10 cm^3
Spatula
Specimen tubes, stoppered, 2
Access to:
4 M potassium hydroxide, 10 cm^3 VERY CORROSIVE (goggles must be worn, not safety spectacles)
Iodine, solid HARMFUL

Procedure

Full details are given in the *Students' Book*. The greatest possible care should be taken when using hot concentrated potassium hydroxide solution, which attacks flesh rapidly and is particularly dangerous to the eyes. On no account must the boiling tube and contents be heated directly with a Bunsen burner; the use of a water bath prevents violent expulsion of the alkali.

Since this is probably the first time that students have used the technique of suction filtration, some explanation of the procedure should be given as well as a brief discussion of how losses of potassium iodate might occur during this process.

After the experiment, the students should keep their samples of potassium iodate(v) and potassium iodide which will be required for Experiment 6.8c.

EXPERIMENT 6.8b

The reaction between iodine and sodium thiosulphate

Each group of students will need:
Eye protection
Apparatus for titration with 50 cm^3 burette and 10 cm^3 pipette

Access to:
0.01 M iodine in potassium iodide solution, 30 cm^3
0.01 M sodium thiosulphate, 50 cm^3
1% starch solution with dropping pipette

Procedure

Full details are given in the *Students' Book.* The students are asked to satisfy themselves that their results are consistent with the equation:

$$2Na_2S_2O_3(aq) + I_2(aq) \longrightarrow 2NaI(aq) + Na_2S_4O_6(aq)$$

If the students are to have confidence in the quantitative aspects of the subject, it is important that they should be able to obtain good results. This experiment is capable of giving an excellent result provided that care is taken to supply well-mixed, accurately made solutions prepared from good quality reagents.

The oxidation number of sulphur in sodium thiosulphate is +2 and in sodium tetrathionate is $+2\frac{1}{2}$. The students are asked to work these numbers out; in this way they are made aware of the possibility of fractional oxidation numbers.

EXPERIMENT 6.8c

To determine the purity of samples of potassium iodate(v)

Each group of students will need:
Eye protection
2 weighing bottles
2 volumetric flasks, 100 cm^3
2 beakers, 100 cm^3
2 filter funnels
Wash bottle with pure water
Apparatus for titration with 50 cm^3 burette and 10 cm^3 pipette
Conical flask, 100 cm^3
Measuring cylinder, 10 cm^3
Samples of potassium iodate and potassium iodide made in Experiment 6.3b

Access to:
0.1 M potassium iodide, 60 cm^3
1 M sulphuric acid, 60 cm^3 IRRITANT
0.01 M sodium thiosulphate, 100 cm^3
1% starch solution, with dropping pipette
Balance, to weigh to 0.01 g

Procedure

Full details of the procedure and method of calculation are given in the *Students' Book.*

In part 1 of this experiment, the students determine the percentage purity of the potassium iodate(V) that they made in Experiment 6.8a. Results are likely to be variable but percentages in the high nineties are to be expected.

Part 2 utilises the same method but this time, the percentage of potassium iodate(V) remaining in the potassium iodide is found. Figures of around 10% of potassium iodate should be obtained.

Depending on the students' previous experience, it may be necessary to explain the correct way to use a volumetric flask to make a solution of known concentration.

6.9 Background reading: the halogens in human metabolism

Timing This exercise may be set for homework

Suggested treatment

Part of this task requires students to summarise the important parts of a passage. This may be the first time that the students have been asked to do such a summary and some suggestions on how to go about the task might be given beforehand (see Topic 1, Sheet 1.1 on page 26 of this *Teachers' Guide*).

ANSWERS TO THE BACKGROUND READING QUESTIONS

Questions, page 131

1 The answer should relate to the oxidising action of halogens on the tissues.

2 Bones, and especially in the enamel of teeth.

3 Fluoride ions cause teeth to become mottled and at high concentrations are toxic.

4 A solution which kills bacteria.

5 1.03×10^{-1} mol dm^{-3}.

6 Iodide. Iodine can be metabolised in the body. The other halide ions are required for specific functions but there are no natural mechanisms to oxidise them. If natural mechanisms did exist, the halogens produced would be too powerful oxidants for the body to deal with.

7 Students might suggest the following order of importance $Cl > I > F > Br$. The chloride ions are present in the blood and cells and are involved in maintaining the ionic concentrations within the tissues. Larger amounts of chlorides are required by the body than other halides. Iodine is essential in animals in order to control the rate of metabolism via the hormone thyroxine but the effects of lack of iodine in the diet take some time to manifest themselves. Fluoride ions are required in minute quantities for healthy teeth but too high a concentration of fluoride can have harmful effects, as it inhibits the action of some enzymes.

8 A good summary should include most of the following points.

- The halogens are only involved as ions except for iodine.
- Fluoride ions have no known role.
- Chloride ions maintain the balance between the fluid inside and outside cells.
- Bromide ions affect the working of the brain, causing drowsiness.
- Iodide ions are oxidised to iodine in the thyroid and are then involved in the synthesis of thyroxine.

Answers to Topic 6 questions

Review questions

6.1

a	+1, 0	(1)	reduced	(1)	**f**	+2, +3	(1)	oxidised	(1)
b	0, +2	(1)	oxidised	(1)	**g**	0, +1	(1)	oxidised	(1)
c	0, +2	(1)	oxidised	(1)	**h**	−1, 0	(1)	oxidised	(1)
d	0, +1	(1)	oxidised	(1)	**i**	0, −2	(1)	reduced	(1)
e	0, −1	(1)	reduced	(1)	**j**	+2, +1	(1)	reduced	(1)

Total 20 marks

6.2

a	Copper(II) oxide	(1)	**k**	Manganese(VII) oxide	(1)
b	Copper(I) oxide	(1)	**l**	Uranium(VI) fluoride	(1)
c	Iron(III) hydroxide	(1)	**m**	Copper(II) sulphate-5-water	(1)
d	Iron(II) sulphide	(1)	**n**	Titanium(IV) iodide	(1)
e	Lead(II) carbonate	(1)	**o**	Nickel(II) oxide	(1)
f	Lead(IV) chloride	(1)	**p**	Silver(I) oxide	(1)
g	Chromium(II) bromide	(1)	**q**	Vanadium(V) oxide	(1)
h	Manganese(III) oxide	(1)	**r**	Strontium(II) nitrate	(1)
i	Manganese(IV) oxide	(1)	**s**	Osmium(VIII) oxide	(1)
j	Manganese(VI) oxide	(1)	**t**	Bismuth(III) chloride	(1)

Total 20 marks

6.3

a	Iron	(1)	Chlorine	(1)
b	Bromine or bromide ions	(1)	Chlorine	(1)
c	Iodine or iodide ions	(1)	H_2O_2 or hydrogen peroxide	(1)
d	Sulphur	(1)	Iodine	(1)
e	Copper	(1)	HNO_3 or nitric acid	(1)

Total 10 marks

6.4

a	Copper	(1)	Hydrogen	(1)
b	Bromine	(1)	I^-/iodide ions	(1)
c	Silver	(1)	Magnesium	(1)
d	Chlorine	(1)	Iron/Fe^{2+}	(1)
e	Bromine	(1)	Hydrogen sulphide/H_2S	(1)

Total 10 marks

6.5

a $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$ (1)

b $2Al(s) + 3I_2(s) \longrightarrow 2AlI_3(s)$ (1)

c $Mg(s) + Br_2(l) \longrightarrow MgBr_2(s)$ (1)

d $2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(l)$ (1)

e $H_2(g) + F_2(g) \longrightarrow 2HF(g)$ (1)

Total 5 marks

6.6

a $Zn(s) + 2Fe^{3+}(aq) \longrightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$ (2)

b $2Al(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2(g)$ (2)

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

d $3CuO(s) + 2NH_3(g) \longrightarrow 3Cu(s) + 3H_2O(l) + N_2(g)$ (2)

e $Sn(s) + 4HNO_3(l) \longrightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$ (2)

f $SO_2(g) + Br_2(aq) + 2H_2O(l) \longrightarrow 4H^+(aq) + SO_4^{2-}(aq) + 2Br^-(aq)$ (2)

g $As_2O_3(s) + 2I_2(aq) + 2H_2O(l) \longrightarrow As_2O_5(aq) + 4H^+(aq) + 4I^-(aq)$ (2)

h $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq)$
$\longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$ (2)

i $Cr_2O_7^{2-}(aq) + 6I^-(aq) + 14H^+(aq)$
$\longrightarrow 2Cr^{3+}(aq) + 3I_2(aq) + 7H_2O(l)$ (2)

j $2BrO_3^-(aq) + 3N_2H_4(aq) \longrightarrow 2Br^-(aq) + 3N_2(g) + 6H_2O(l)$ (2)

Total 20 marks

6.7	**a**	**i** Volumetric flask	(1)
		ii Pipette	(1)
		iii Burette	(1)
	b	248 (g mol^{-1})	(1)
	c	0.1	(1)
	d	2.36×10^{-3}	(1)
	e	$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$	(1)
	f	1.18×10^{-3}	(1)
	g	0.0472	(1)
	h	12.0 (g dm^{-3}) (3SF)	(1)
			Total 10 marks

6.8	Equations for reactions:	
	$Cl_2(g) + 2KI(aq) \longrightarrow I_2(aq) + 2KCl(aq)$ (or ionic equation)	(1)
	$2Na_2S_2O_3(aq) + I_2(aq) \longrightarrow Na_2S_4O_6^{2-}(aq) + 2NaI(aq)$ (or ionic equation)	(1)
	moles of $Na_2S_2O_3$ (or $S_2O_3^{2-}$) $= 4.5 \times 10^{-3}$	(1)
	moles of I_2 = moles of $Cl_2 = 2.25 \times 10^{-3}$	(1)
	mass of $Cl_2 = 2.25 \times 10^{-3} \times 71$	(1)
	= 0.160 g (3SF)	(1)
		Total 6 marks

6.9	**a**	Brings about reduction of another substance OR Decreases the oxidation number of another element OR Releases electrons in a reaction.	(2)
	b	Tin(II) ions	(1)
	c	**i** 6	(1)
		ii 2	(1)
		iii 3	(1)
		iv 6	(1)
		v $3Sn^{2+}(aq) + ClO_3^-(aq) + 6H^+(aq) \longrightarrow 3Sn^{4+}(aq) + Cl^-(aq) + 3H_2O(l)$	(3)
			Total 10 marks

Examination questions

6.10	**a**	**i** Yellow precipitate	(2)
		ii $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$ formulae state symbols	(2)
	b	**i** Precipitate darkens/turns grey/purple	(1)
		ii Photography	(1)
		iii Precipitate dissolves	(1)
		Soluble/complex compound formed	(1)
	c	**i** Hydrogen bromide	(1)
		ii $HBr(g) + NH_3(g) \longrightarrow NH_4Br(s)$	(1)
		iii Bromine	(1)
		iv Sulphur dioxide	(1)
		v Acid in **c i** oxidising agent in **c iii**	(2)
			Total 14 marks

6.11	**a**	0 in I_2; -1 in I^-	(2)
	b	-2 in SO_4^{2-} (1); -1.75 in $S_2O_8^{2-}$	(2)
	c	Persulphate ions	(1)
	d	$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$	(1)
			Total 6 marks

6.12

a **i** 0 in I_2 −1 in NaI +5 in $NaIO_3$ (3)

ii Disproportionation (1)

b **i** Pipette (1)

ii Starch (1)

blue/black to colourless (2)

iii 1.67×10^{-4} (1)

iv 8.35×10^{-5} (1)

v 2.78×10^{-4} (1)

vi $2.78 \times 10^{-4} \times 198 = 0.055\,(0)$ g (1)

$$\% \text{ purity} = \frac{0.0550 \times 100}{0.060} = 92\%$$ (1)

c $NaIO_3$ may contain water of crystallisation/less stable than KIO_3/$NaIO_3$ may be more soluble/other reasonable suggestions (1)

Total 14 marks

6.13

a 2×10^{-3} (1)

b $2S_2O_3^{2-}(aq) + 2I^-(aq) \longrightarrow I_2(aq) + S_4O_6^{2-}$ (1)

c 1×10^{-3} (1)

d 2×10^{-3} (1)

e $2Cu^{2+}(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2Cu^+(aq)$ (1)

(students will not know that CuI is precipitated)

Ratio Cu^{2+}:I_2 is 2:1

and therefore Cu^{2+}:I^- is 1:1

so oxidation number of Cu goes down to +1 (1)

(argument along these lines)

Total 6 marks

6.14

a **i** Tube which contained KBr: orange (1)

Tube which contained KI: purple/pink (1)

ii $Cl_2(aq) + 2KBr(aq) \longrightarrow Br_2(aq) + 2KCl(aq)$ (2)

(or ionic equation)

b $$\text{Moles of } I_2 = \frac{10 \times 0.0100}{1000} = 1 \times 10^{-4}$$

$$\text{moles of } Na_2S_2O_3 = \frac{20 \times 0.0100}{1000} = 2 \times 10^{-4}$$ (1)

∴ 1 mol I_2 reacts with 2 mol $Na_2S_2O_3$ (1)

$I_2(aq) + 2Na_2S_2O_3(aq) \longrightarrow Na_2S_4O_6(aq) + 2NaI(aq)$ (1)

(which is consistent with calculation)

c **i** All destroy bacteria (1)

ii Cl_2 in swimming pools or drinking water

or I_2 for cuts/wounds

or Cl_2 solution for sterilising babies' bottles. (1)

Total 9 marks

TOPIC 7

Covalency and bond-breaking

Introduction

In this topic, we consider the nature of the bonds which exist in a representative range of materials. It is emphasised that questions concerning geometry may be answered experimentally, but questions concerning bonding can only be discussed in terms of simplified models.

In this course, ideas of bonding are not based on atomic orbitals nor on molecular orbitals. These ideas are mathematical concepts, and to be significant they need to be considered in conjunction with a course in theoretical physics. These seem to be unnecessary concepts at this level.

Students have studied the electronic structure of atoms in Topic 3 and some may have had previous experience of drawing 'dot and cross' diagrams for simple covalent compounds in their pre-A-Level courses. The introduction to this topic considers the evidence for the nature of covalent bonding. Counting electrons and relating the totals to noble gas structures is used to provide an introduction to bonding and stoichiometry. The distribution of bonds in space is then considered.

The concept of electronegativity as the power of an atom in a molecule to attract electrons to itself is then used as an aid to understanding bond polarity.

The use of standard enthalpy changes of combustion to determine the enthalpy changes of formation of combustible compounds is discussed and bond energies are introduced through a study of the enthalpy changes of combustion of a homologous series of alcohols. This leads to a discussion of the factors which affect rates of reaction interpreted in terms of activation energies and a qualitative treatment of collision theory.

The topic ends with an introduction to reversible reactions and the idea of dynamic equilibrium.

Content

7.1 Electron density maps – an electron density map for a molecular substance is contrasted with that for an ionic substance.

7.2 Electron sharing in covalent molecules – electron arrangements in molecules; electron sharing to form noble gas structures; 'dot and cross' diagrams; shapes of molecules as determined by lone pairs and bonding pairs of electrons; bond angles; sigma bonds and pi bonds. Dative covalency; the oxonium ion, the ammonium ion, carbon monoxide and nitric acid.

7.3 Background reading – growing diamonds.

7.4 The chemists' toolkit: electronegativity – definition of electronegativity, bond polarisation, intermediate types of bonding; electronegativity and polar molecules.

Timing		**Students' Book**
7.1	$\frac{1}{2}$ hour	pages 139–40
7.2	4 hours	pages 141–7
7.3	homework	pages 148–9
7.4	1 hour	pages 149–50
7.5	homework	pages 150–2
7.6	4 hours	pages 152–61
7.7	3 hours	pages 161–9
Total about $2\frac{1}{2}$ weeks		

7.5 Background reading – electron spectroscopy for chemical analysis.

7.6 Bond energies – standard enthalpy change of combustion and its use in calculating enthalpy change of formation; determination of enthalpy changes of combustion of alcohols; bond lengths and bond energies, bond energies and rates of reaction.

7.7 Reversible reactions – reversible changes at a molecular level; dynamic equilibrium; the effects of concentration, temperature and pressure changes on equilibrium states; the effect of catalysts; Le Chatelier's Principle.

Objectives

1 To introduce a model of covalent bonding in terms of electron arrangements, with a view to accounting for the formulae and structures of compounds, and for the forces which hold the particles together.

2 To interpret the cohesive force in a covalent bond as being due to a sharing of an electron charge cloud between two positively charged nuclei.

3 To discuss the shapes of molecules in terms of mutual repulsion between the electron clouds in bonds and lone pairs.

4 To introduce the idea of electronegativity.

5 To interpret some properties of polar molecules in terms of electron distribution.

6 To use Hess cycles and enthalpy changes of combustion to calculate the enthalpy changes of formation of compounds.

7 To introduce bond energies.

8 To introduce a simple treatment of the collision theory of reaction rates, including the idea of activation energy.

9 To introduce the concept of dynamic equilibrium in reversible reactions and to predict qualitatively the effects of changing conditions on equilibrium.

7.1 Electron density maps

Timing About $\frac{1}{2}$ hour will be needed

Suggested treatment

The content of this section is not examinable as part of A5 unit 2 in the Edexcel specification.

This section uses electron density maps to introduce covalent bonding and distinguishes this type of bonding from ionic bonding. The sharing of an electron charge cloud leads to a lower potential energy than if the cloud were not shared, and a lower potential energy results in greater stability.

ANSWERS

Questions, page 140

Students should compare the electron density maps for sodium chloride and 4-methoxybenzoic acid. They should recognise that the electron distribution for the two is significantly different. In figure 7.2 there is a substantial electron density at all points between the two bonded nuclei. The electrons are being shared by those nuclei whereas this is not so in figure 7.1 for the ionic substances. In molecules, the force holding bonded atoms together is considered to result from a sharing of the electron charge cloud between the two positive nuclei.

7.2 Electron sharing in covalent molecules

Timing About 4 hours will be required

Suggested treatment

The teacher will need:
Molecular model kit, with orbitals, to make models of the molecules of CH_4, NH_3, H_2O, H_2, Cl_2, HCl; CH_3Cl, CH_3OH, C_2H_6, C_2H_5OH; $CH_2{=}CH_2$, O_2, CO_2 and 4-methoxybenzoic acid.

The distribution of bonds in space is considered through the approach involving the mutual repulsion of bonds and lone pairs of electrons. The rules are simple, and they work with surprisingly few exceptions.

In relation to stoichiometry, the Lewis–Langmuir approach involving the counting of electrons and relating these to a noble gas structure is used. The noble gas approach suffers from the shortcoming that it is frequently not obeyed by elements outside the second short period of the Periodic Table. PCl_5, SF_6 and SF_4 are examples of exceptions to the rule.

It is not considered appropriate to introduce the concept of the expanded octet in an introductory topic on covalent bonding. The noble gas method provides a useful guide, being particularly applicable to the elements of the first short period. It thus constitutes a suitable means for introducing bonding and stoichiometry.

Since 'dot and cross' diagrams will feature prominently in a discussion of this type of bonding it is suggested that the teacher should begin by showing the class ball-and-spoke models or space-filling models, or both, of a range of simple molecules with the intention of emphasising that they are three-dimensional structures. Suitable molecules to demonstrate would be CH_4, C_2H_6, CH_3OH, C_2H_5OH, NH_3, H_2O and HCl. They should be shown at first without any representation of lone pairs of electrons.

Discussion should bring out the noble gas structure, and the possibility of achieving this by electron sharing. Once again it should be stressed that 'dot and cross' diagrams are simply a convenient method for counting electrons; they do not represent the positions of the electrons. Nor do the diagrams give a proper indication of the shapes of the molecules, for they are two-dimensional representations of three-dimensional structures.

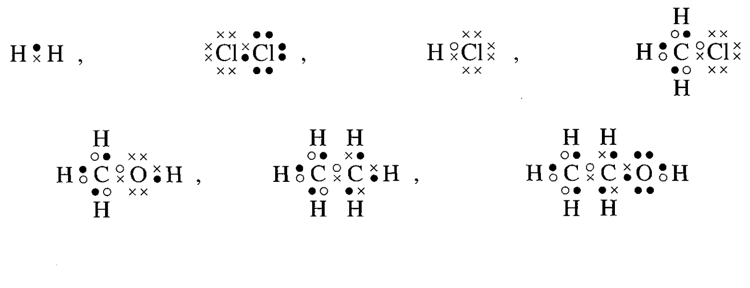
The class should make 'dot and cross' diagrams for the electronic structures of several simple molecules. The *Students' Book* gives ethane and ethene as examples in figure 7.6. It then asks that students draw 'dot and cross' diagrams for H_2, Cl_2, HCl, CH_3Cl, CH_3OH, C_2H_6, C_2H_5OH, C_2H_4, O_2, N_2 and CO_2. A number of other examples could also be given. Students then consider the shapes of molecules in terms of bonding pairs and lone pairs of electrons. This may be developed as follows.

ANSWERS

Questions, page 142

When writing 'dot and cross' diagrams at this stage, students should be reminded that each electron is actually distributed as a diffuse negative charge-cloud; it is not precisely located in space. The dots and the crosses provide a very convenient way of counting electrons, and of showing the number in any given quantum shell. They do not show the spatial distribution of the electrons.

1



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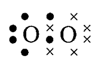
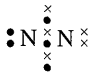
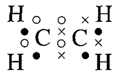
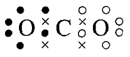








Single bonds

The teacher will need:
Models of CH_4, NH_3, H_2O and HCl, together with pear-shaped lobes representing lone pairs of electrons.

The relationship between molecular shape and electron distribution should now be considered. Models without lone pairs attached could be arranged in Periodic Table order on the demonstration bench. Students could be asked to refer to their 'dot and cross' diagrams for these electronic structures, or the 'dot and cross' diagrams might be put on the board.

The class might then be asked leading questions along the following lines.

1 What do you notice about the spatial arrangement of the bonds in the molecule CH_4?

This should elicit the fact that the bonds are as far removed from each other as is possible; no other geometric arrangement would produce a greater separation.

2 If, as seems to be the case with CH_4, the bonds attempt to arrange themselves as far apart from each other as possible, why are the molecules of ammonia and water not planar and linear respectively?

3 Considering ammonia, what is the distribution of hydrogen atoms in comparison with methane? What does this indicate?

The arrangement of the three hydrogen atoms in approximately tetrahedral positions seems to indicate that the molecule is behaving as though there were still a bond in the fourth tetrahedral position.

4 What could be occupying the space in the fourth tetrahedral position?

By looking at their diagrams, students might suggest that the non-bonded pair of electrons, the lone pair, might be occupying this space. A model of an ammonia molecule with a pear-shaped representation of a lone pair might then be discussed.

Stress that it is only the electron pairs on the central atom which determine the shape of a molecule. It is a common misconception that electron pairs on other atoms have to be considered as well.

5 Can the shape of the water molecule be interpreted by a similar argument?

This question may be pursued in a similar manner, and then discussed with a model showing two lone pair lobes.

6 Why do bonds and lone pairs repel each other?

They are negative charge clouds in close proximity.

7 What is the likely electron distribution in the hydrogen chloride molecule?

This situation may be illustrated by a model with three lone pair lobes.

8 Is there any evidence indicating whether a bond or a lone pair exerts a greater repelling force?

ANSWERS

Questions, page 142

The CH_4 molecule, being symmetrical, adopts the bond angle of a regular tetrahedron, 109.5°. In ammonia the bond angle is decreased by 2.5°. In water the bond angle is decreased by 5.0° from the tetrahedral value.

	Bond angle	**Change in bond angle from methane**
CH_4	109.5°	–
NH_3	107.0°	2.5°
H_2O	104.5°	5°

Therefore a lone pair/bond pair repulsion is greater than a bond pair/bond pair repulsion; and a lone pair/lone pair repulsion is greater than either of these. This gives the order of effectiveness in repulsion as:

lone pair/lone pair > lone pair/bond pair > bond pair/bond pair

The reason for this situation is that the region of space occupied by a lone pair is closer to the nucleus of the parent atom and is fatter than the region of space occupied by a bond pair; the latter is drawn out to form a longer, thinner distribution as it is attracted by the positive nuclei of the atoms at each end of it. The lone pair is attracted from only one direction.

Multiple bonds

The teacher will need:
Molecular models of the molecules of C_2H_6 and C_2H_4.

The stereochemistry of some molecules containing multiple bonds should now be considered on an electron charge-cloud basis.

The *Students' Book* introduces the terms 'pi bond' at this point and compares it with a sigma bond. Their description is, however, limited to a statement that double bonds consist of one bond that is symmetrical about the axis joining the atomic nuclei involved in the bond (the *sigma* bond) and one bond (the *pi* bond) that consists of two electron clouds, which are not symmetrical about this axis. This statement is intended as a foundation for further development in Topic 8, where alkenes are considered.

ANSWER

Question, page 143

Ethene, C_2H_4, is an example of a compound with a molecule containing a double bond. The molecule is planar, and the electron density is consistent with the assumption that one pair of electrons forms a σ bond, and the second pair a π bond. Carbon dioxide and oxygen also have double bonds.

As an additional activity, students could be asked to use this approach to suggest a shape for the molecule of ethyne, C_2H_2. This compound has a linear molecule, and the triple bond consists of one σ bond and two π bonds.

Covalent giant structures

A common misconception is that covalent bonds are weak bonds. Students confuse the properties associated with intermolecular forces with the properties associated with covalent bonding.

A consideration of the properties of diamond helps to emphasise that covalent bonds are both strong and highly directional so that diamond, with its continuous network of covalent bonding, has a very high melting point and is one of the hardest materials known.

A comparison of the electrical conductivities of diamond and graphite can introduce the distinction between localised electrons (as in most covalent bonds) and delocalised electrons (as in graphite).

Dative covalency

The two electrons, which form a covalent bond, do not necessarily have to come one from each atom; both may originate from one of the atoms. In earlier discussions, students may have noticed that ammonia has a lone pair of electrons and that the hydrogen ion is deficient in electrons. Students have also considered the formation of an oxonium ion from water and a proton. Dative covalency is introduced by reference to the formation of these two ions, and the electron arrangements for carbon monoxide and nitric acid molecules are also shown.

Emphasise that, once formed, a dative covalent bond is no different from any other covalent bond. So in an ammonium ion all four bonds are identical.

ANSWERS

Study task, page 147

2 In an H_3O^+ ion there is only one lone pair of electrons, whereas in an H_2O molecule there are two. The repulsion between lone pairs and bonding pairs is greater than the repulsion between bonding pairs.

7.3 Background reading: growing diamonds

ANSWERS TO BACKGROUND READING QUESTIONS

1 Allotropy: alchemists did not know that diamond and graphite are different forms of the same element, or that diamond and graphite are both made of carbon.
Appearance: gold resembles copper, diamonds do not look like graphite.
Hardness: diamond is hard, graphite is soft.

2 a Density.
b High pressure is required to force/squeeze atoms/carbons into closer/tighter packing arrangement/closer together.
c High temperatures are needed because of the energy required to break the bonds or to melt the graphite.
d Deep below the Earth's crust.

3 The time for diamonds to grow makes the process too costly or they are the wrong colour for jewellery and not of gem quality.

4 Key points to include in the summary:
To make diamonds from graphite, high pressure, 1.0×10^5 atm is needed.
High temperature, up to 2500 °C, is also needed.
Graphite is mixed with a metal which melts below 2500 °C.
The mixture is heated until the molten metal dissolves the graphite under pressure supplied by pistons.
A belt of concentric metal rings is needed to contain the mixture.

7.4 The chemists' toolkit: electronegativity

Timing About 1 hour

Suggested treatment

This section is developed in two parts.

1 The concept of electronegativity is introduced.

2 Polarity in molecules is explained in terms of differences in electronegativity between the component atoms.

In this present section students focus their attention on bond polarisation. The intention is to reinforce the idea that truly ionic and truly covalent bonds are extreme types, and that there is a complete range of intermediate situations.

When an atom of one element is bonded covalently to an atom of another element, the attractions of the nuclei for the bonding electrons will be different, and the bonding electrons will not be equally shared. This bond polarisation is clearly related to the electronegativities of the elements concerned.

Pauling defined the property known as *the electronegativity of an atom* as 'the power of an atom in a molecule to attract electrons to itself'. The concept is concerned with atoms in molecules, and is therefore a very different one from the concept of electron affinity, which is concerned with isolated atoms. An atom of a given element in different compounds will be in different environments, and its power to attract electrons is unlikely to remain constant. In addition, there is no uniquely defined electronegativity scale. For these reasons, electronegativity scales which allot numerical values to elements should only be used in the knowledge of how the values were obtained, and hence in the knowledge of the use which may justifiably be made of the values; even then they should be used with caution.

Pauling derives his values of electronegativity from values of bond energies. It will be seen in the study of bond energies later in the topic that these are average values since they are susceptible to changes in environment; also many of them are only approximate since the necessary thermochemical data are not available.

Mulliken derives his set of values from ionisation energies and electron affinities. The latter are difficult to measure with accuracy, and in some instances values had to be assumed. Allred and Rochow proposed that the electrostatic force acting on an electron at the periphery of an atom is a measure of the atom's electronegativity, see figure 7.1. Their values show the same trends as Pauling's values. Whatever the situation may be concerning individual values, the trends are clear. The safe approach is to use only an *order* of relative electronegativity.

What uses may be made of the concept of electronegativity? It may be said that bonds between elements of widely differing electronegativity will be highly polar, that is, predominantly ionic. Bonds between elements of similar electronegativity will have only slightly polar character and thus be predominantly covalent if the elements are non-metals, and metallic if the elements are metals. Thus bonds between potassium and chlorine, and between sodium and fluorine, will be predominantly ionic; and bonds between carbon, hydrogen, nitrogen, oxygen, and chlorine will be predominantly covalent, whereas bonds between sodium, calcium, copper, etc. are metallic.

The concept of electronegativity will be of use in the organic topics, in considerations of homolytic and heterolytic bond-breaking in reactions. It will be seen that the discussion on polar molecules and electronegativity produces the same pattern as did the discussion on the polarisation of ions.

Fajans' rules, as discussed in Topic 16, indicate that the beryllium–fluorine bond, for example, will be more polarised (that is more covalent) than will the rubidium–fluorine bond. The trend in electronegativities of the metals of Groups 1 and 2 indicates the same. Fajans' rules indicate that the beryllium–iodine bond will be more polarised (that is more covalent) than the beryllium–chlorine bond, and the trend in electronegativities of the halogens indicates the same.

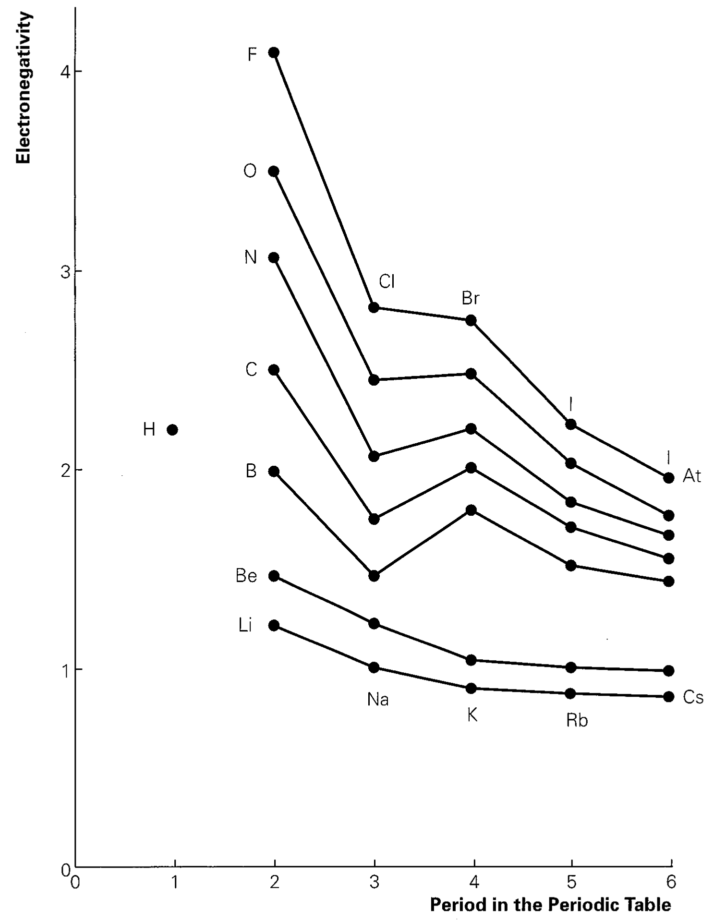


Figure 7.1 Allred–Rochow electronegativities

The two discussions were conducted from opposite extremes towards an intermediate position, from ions towards polarisation and partial covalency on the one hand, and from molecules towards increasing polarity and partial ionic character on the other hand. The important lesson is that true ionic and true covalent bonds are extreme types and that examples occur over the whole range of intermediate situations.

Although electronegativity is a useful concept, teachers should be aware that students often use electronegativity as an explanation for situations where this is not justified. Electronegativity is a rationalisation of many factors which can help to interpret various phenomena, rather than a fundamental explanation of many properties.

Electronegativity and polar molecules

Students are asked to draw 'dot and cross' diagrams for the HCl molecule and CH_3CH_2Cl molecule and then consider whether the centre of gravity of the positive charge and the centre of gravity of the negative charge coincide. The HCl molecule is a suitable one for initial discussion. The sequence of ideas should develop from electronegative elements, to lone pairs of electrons, to an imbalance in charge distribution. The latter may then be demonstrated by attaching lone pair representations to the HCl model.

The existence of polar molecules and the origins of the polarity should be made clear, but it is not necessary to define dipole moment or discuss methods of measuring dipole moments.

The section is completed by a consideration of polarity of molecules in figure 7.4 in the *Students' Book*. Students should appreciate the 3-dimensional structure of these molecules.

ANSWER

Question, page 150

The centre of positive charge and the centre of negative charge (analogous with centre of gravity) do not coincide, and a permanent dipole results. Further imbalance of charges results from bond polarisation and the final dipole includes both of these factors.

The figure shows the centres of positive and negative charge, and illustrates the establishment of a permanent dipole. Such molecules are said to be polar.

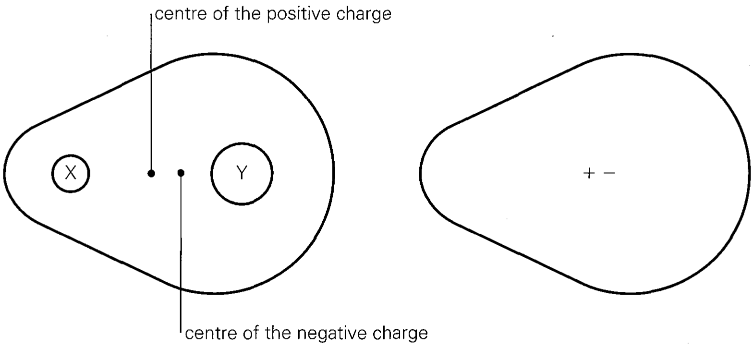


Figure 7.2 The origin of a dipole in a molecule

ANSWER

Question, pages 150

Methane molecules are not polar. All the other molecules are polar.

7.5 Background reading: electron spectroscopy for chemical analysis

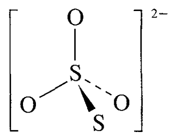
ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 150–1

1 a Charge on each H atom is +0.18; therefore charge on each N atom is −0.54.
  b Positive ions are strongly attracted to negative N atoms in ammonia (or vice-versa).

2 The charge on the sulphate ion $= 4 \times (-0.78) + (+1.12)$
$= -2(.00)$

3 c Tetrahedral or



4 a +2
  b Oxidation number represents the charge an atom would carry if all the binding electrons were attributed to the most electronegative element/does not take into account intermediate bond types (or bond polarisation)/not a good guide to charge when atoms form bonds to other atoms of the same element.

5 Key points to include in summary:

- When an atom absorbs x-radiation/x-rays an electron is expelled.
- The kinetic energy of electrons can be measured using an electron spectrometer.
- The kinetic energy of the (expelled) electrons depends on their binding energy *or* electron binding energy can be calculated from their kinetic energies.
- (Kinetic energy) depends on the effective nuclear charge.
- This in turn depends on the (partial) charge on the atom *or* partial charges can be calculated from binding/kinetic energies of electrons.

7.6 Bond energies

Timing About 4 hours will be needed

Suggested treatment

In this section, a discussion of bond energies arises from a consideration of the results of an experiment to find out whether the —CH_2— group makes a specific contribution to the enthalpy change of combustion of alcohols. It is developed along the following lines:

1. A definition of standard enthalpy change of combustion is given and its use in calculating standard enthalpy changes of formation using Hess's Law is discussed.
2. The values for the enthalpy change of combustion of a series of alcohols are determined experimentally and the specific energy contribution of each —CH_2— group noted.
3. Bond energies are introduced and the range of values of bond energies discussed.
4. The relationship between bond energy and bond length is introduced.

It is important to emphasise that bond-breaking is endothermic, and that the overall energy change on combustion is only exothermic because the energy released as new bonds form in the products is greater than the energy needed to break the bonds in the reactant molecules. It is a common misconception that bond-breaking gives out energy.

Standard enthalpy change of combustion

In Topic 5, students were introduced to a number of specific enthalpy changes and to calculations using Hess's Law. The first part of section 7.6 extends students' knowledge of enthalpy changes by defining the standard enthalpy change of combustion. The section continues by showing how values for standard enthalpy changes of combustion can be used to calculate the standard enthalpy change of formation of a compound which cannot be prepared directly from its elements. Students are asked to calculate the standard enthalpy change of formation of methanol after an example of the procedure has been given.

ANSWER

Study task, page 154
Using the figures given in the *Students' Book* an answer of -239.1 kJ mol^{-1} for the standard enthalpy change of formation of methanol should be obtained.

The question is then asked 'How can enthalpy changes of combustion give information about the energy required to break individual bonds?' This is addressed by Experiment 7.6.

EXPERIMENT 7.6

To find the enthalpy changes of combustion of some alcohols

Each group of students will need:
Eye protection
Metal calorimeter and spirit lamp
Thermometer, 10–50 °C in 0.1 °C intervals
Graph paper
Measuring cylinder 500 cm^3, or 1000 cm^3

HAZARDS

All the alcohols used, propan-1-ol to octan-1-ol, are highly flammable and most are harmful.

Access to:
Balance, to weigh to ±0.01 g
Bunsen burner, heatproof mat and splint (for lighting spirit burner)
Series of primary alcohols from propan-1-ol to octan-1-ol in separate spirit burners. (Do not allow students to pour alcohols into the burners; the technician should fill the burners and label them, so stock bottles are *not* needed in the lab.)
Molecular models of each of the alcohols should be available for inspection

Procedure

This experiment is designed to answer the question 'Does the —CH$_2$— group in a series of alcohols make any consistent contribution to the enthalpy change of combustion of the compounds?'. If it can be shown that this is the case, then this is evidence that specific bonds are making specific contributions.

The spirit lamp may cause some inaccuracy if the wick is allowed to burn. This is overcome by removing the fabric wick and replacing it with glass woven wick sold for petrol lighters. As far as possible, a narrow flame should be used. If the flame is broader than about 3 mm at the base, much of the alcohol is not completely burned and a deposit of carbon may be seen on the glass walls. This also prevents efficient energy transfer.

Full details of the procedure are given in the *Students' Book* together with a diagram of the apparatus. The method used is that first described in the article by Reed and Tordoff, 'A simplified apparatus for the determination of the enthalpy of combustion of alcohols'. *School Science Review*, **70**, 250, page 77, 1988.

When the hot burner is extinguished, considerable evaporation takes place with the lower alcohols. A glass or metal cap should be placed over the wick, and the burner should be weighed immediately after the flame is extinguished.

It should be pointed out to the students that the heat losses in a piece of apparatus such as the combustion calorimeter are considerable, but calibrating the apparatus before use reduces their effect.

Different pairs of students should do one experiment with propan-1-ol to calibrate the apparatus and one experiment with another alcohol, in such a way that the class covers the series of alcohols, from butan-1-ol to octan-1-ol.

The experiment does require quite skilful manipulation and some results may be very poor. Students should be referred to the data in table 5.5 in the *Book of data* and which for convenience are collected here.

Alcohol	$\Delta H_c^{\ominus}$/kJ mol^{-1}	Difference/kJ
propan-1-ol	−2021	
		655
butan-1-ol	−2676	
		653
pentan-1-ol	−3329	
		655
hexan-1-ol	−3984	
		654
heptan-1-ol	−4638	
		656
octan-1-ol	−5294	

A number of questions draw the students' attention to the possible sources of error. Errors result from heat losses (as discussed above) and from incomplete combustion. The methods by which experimental errors might be reduced should also be discussed.

From the results quoted above it can be seen that the difference between the enthalpy change of combustion of one alcohol and the next is nearly the same, suggesting that the —CH$_2$— group contributes a specific amount to the total. This suggests that definite contributions to the overall energy situation may be made by specific bonds.

Bond energies in other compounds

Bond energies are introduced in the following way: if there is a definite contribution to the overall energy by specific bonds then a particular quantity of energy may be associated with a C—H bond, another with a C—C bond, and so on.

The *Students' Book* then considers in detail the examples of methane and ethane in order to obtain values for *E*(C—H) and *E*(C—C). Bond energies should not be confused with bond dissociation energies or bond strengths. In the case of diatomic molecules such as oxygen or chlorine they are the same, but for methane there are four different bond dissociation energies:

	Approximate values /kJ mol^{-1}
$CH_4(g) \longrightarrow CH_3(g) + H(g)$	$\Delta H^{\ominus} = 439$
$CH_3(g) \longrightarrow CH_2(g) + H(g)$	$\Delta H^{\ominus} = 464$
$CH_2(g) \longrightarrow CH(g) + H(g)$	$\Delta H^{\ominus} = 422$
$CH(g) \longrightarrow C(g) + H(g)$	$\Delta H^{\ominus} = 338$

To avoid confusion it is better not to discuss bond dissociation energies with students at this stage.

The *Students' Book* includes values for the C—Cl bond, determined from different compounds. These show a range of values; the point should be made to the class that the value for an X—Y bond depends upon the environment of the bond, and alters as the groups attached to X and Y are altered. But average values can be very useful and are in table 4.6 in the *Book of data*.

ANSWERS

Questions, page 159

1 To work out the approximate value for the energy needed to atomise one mole of propan-1-ol, the values of the average bond energies for all the bonds are added up. Using the figures given in the *Book of data*, the answer is:

$$\begin{aligned} & 7E(\text{C—H}) + 2E(\text{C—C}) + E(\text{C—O}) + E(\text{O—H}) \\ &= 7 \times 413 + 2 \times 347 + 358 + 464 \\ &= 4407 \text{ kJ mol}^{-1} \end{aligned}$$

2 The bond energies of the hydrides required are:

C—H	N—H	O—H	F—H
413	391	464	568
F—H	Cl—H	Br—H	I—H
568	432	366	298

The trends in the ease of breaking the bonds are these: it gets more difficult to break the X—H bond with increasing atomic number across a period of the Periodic Table, but it gets easier to break the X—H bond with increasing atomic number within a group of the Periodic Table. Students could be reminded of the results they obtained when investigating the thermal stability of the hydrogen halides in Experiment 6.4.

Bond lengths and bond energies

Bond lengths and bond energies can be considered on an electron cloud charge basis. The bonding of the carbon nuclei is greater in ethene than in ethane, and the internuclear distance is smaller, as can be seen from the table.

Bond	**Bond length** /nm	**Bond energy** /kJ mol^{-1}
C—C	0.154	347
C=C	0.134	612
C≡C	0.121	838

Values for these and for some other bonds are given in the *Students' Book*. Students should notice that the bond energies of multiple bonds are not simple multiples of the bond energies of single bonds. For carbon–carbon bonds the 'second' or 'third' bonds of the double or triple bond only contribute 265 kJ mol^{-1} and 226 kJ mol^{-1} respectively to the total bond energy, reflecting the fact that they are π bonds not σ bonds. This should be referred to again in Topic 8 in which the reactivity of alkenes and alkanes is compared.

Bond energies and rates of reaction

Most students will have studied the factors affecting reaction rates as part of the National Curriculum, and they may well have carried out a GCSE investigation of one or more of these factors. It may be helpful to ask students to review and summarise their knowledge of this topic before introducing the collision theory and the concept of activation energy.

When substances react, the first stage has to involve the breaking of bonds in the reactants. Collision theory is introduced in the *Students' Book*, together with the concepts of activation energy and a transition state for a reaction. Although the bond energies of the bonds that have to be broken are important in determining the value of the activation energy for a reaction, care is taken to indicate that they are not numerically equal.

The reaction referred to involves the reaction between bromoethane and aqueous hydroxide ions. Although this type of reaction is seen and studied in more detail in Topic 10, it may be helpful to get students to carry it out on a test-tube scale at this point or, failing this, to demonstrate the reaction.

EXPERIMENT 7.6

(optional) The reaction of bromoethane with hydroxide ions

Each group of students (or the teacher) will need:
Eye protection
Test tube and rack
Dropping pipettes

Access to:
Bromoethane, 1 cm^3 HIGHLY FLAMMABLE, TOXIC VAPOUR
20% potassium hydroxide in ethanol, 2 cm^3 CORROSIVE, HIGHLY FLAMMABLE
2 M nitric acid, 2 cm^3 CORROSIVE
Universal indicator paper
0.02 M silver nitrate CORROSIVE

To 2 cm^3 of 20% potassium hydroxide in ethanol (TAKE CARE) add an equal volume of water followed by 1 cm^3 of bromoethane. Shake the tube from side to side for about 2 minutes. To test for bromide ions, add sufficient 2 M nitric acid to neutralise the potassium hydroxide (test with indicator paper to ensure that the solution is acidic). Then add a few drops of 0.02 M silver nitrate. A cream precipitate of silver bromide will confirm that bromide ions are present.

7.7 Reversible reactions

Timing About 3 hours will be needed

Suggested treatment

This topic ends with a qualitative introduction to reversible reactions, dynamic equilibrium and the factors which affect the position of equilibrium. These ideas will be explored quantitatively in Topic 14 where the equilibrium law is introduced. In this topic the key ideas are that:

- some reactions are reversible
- reversible reactions reach a state of dynamic equilibrium
- changes in concentration, pressure and temperature affect the position of equilibrium in a chemical reaction as predicted by Le Chatelier's principle
- catalysts do not change the position of equilibrium but cut down the time taken to reach an equilibrium state.

EXPERIMENT 7.7a

Reversible reactions

HAZARDS

Ammonium chloride is irritating to the eyes; it releases toxic ammonia gas on heating.
Concentrated hydrochloric acid may cause burns. Its vapour is very irritating to the respiratory system.

Each group of students will need:
Eye protection
Boiling tube
2 test tubes
Test tube rack
Bunsen burner and heatproof mat
Spatula
Test tube holder
3 Petri dishes
Dropping pipettes (unless supplied with the reagent bottles)
Solid ammonium chloride HARMFUL, IRRITANT
0.01 M aqueous iodine HARMFUL
0.1 M aqueous sodium hydroxide IRRITANT
0.1 M sulphuric acid IRRITANT
An indicator (bromocresol green, bromocresol purple, bromothymol blue and methyl red all work well, litmus is less satisfactory) FLAMMABLE
0.1 M cobalt(II) sulphate solution HARMFUL
Concentrated hydrochloric acid CORROSIVE

Full details of the experiments are given in the *Students' Book.* The experiments are followed by a section on their interpretation during which the terms reversible reaction, forward reaction, reverse reaction and a state of equilibrium are introduced and explained.

EXPERIMENT 7.7b

Dynamic equilibrium

HAZARDS

Iodine burns the skin and students should be warned not to touch its crystals.

Each group of students will need:
Eye protection
2 test tubes and rack
2 dropping pipettes
Measuring cylinder, 10 cm^3
Spatula or tweezers (for iodine)
Hydrocarbon solvent (petroleum spirit, 120–160 °C) FLAMMABLE
Iodine HARMFUL
0.1 M iodine in potassium iodide solution

Procedure

Full instructions are given in the *Students' Book.*

Students are led to the idea that equilibrium systems appear to respond to a change in conditions by counteracting the change being made. The effect of temperature and pressure on an equilibrium mixture are then studied with reference to the N_2O_4/NO_2 equilibrium.

EXPERIMENT 7.7c

The $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium

HAZARDS

The dinitrogen tetraoxide produced is toxic, with a danger of delayed effects; the demonstration should be conducted in a fume cupboard.
There is a danger of cumulative effects with lead nitrate.

The teacher will need:
Eye protection
Lead nitrate, dried and powdered, 20 g HARMFUL
Sand, fine dried, 10 g
Bunsen burner and heatproof mat
Apparatus for preparation and collection of dinitrogen tetraoxide (see figure 7.3)
Glass syringe, 100 cm^3 (the plunger must be lubricated with a thin film of a light lubricating oil)
Spatula

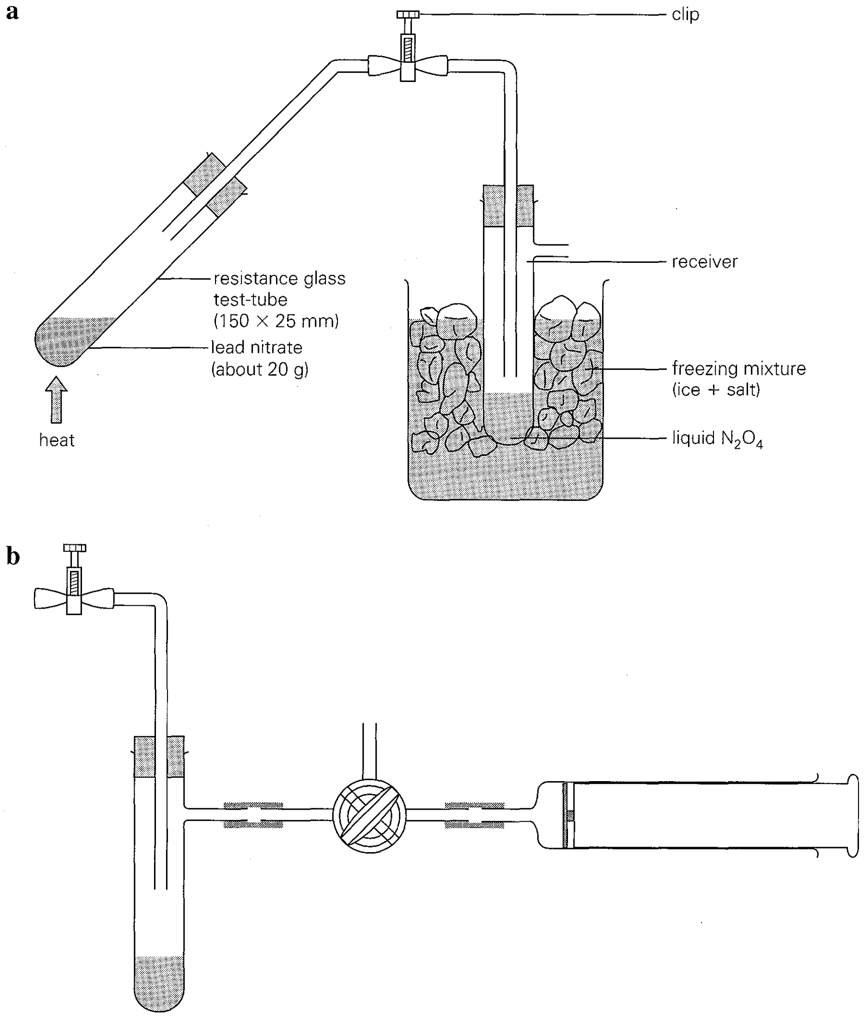


Figure 7.3 Gas preparation and method of filling the syringe

Procedure

Set up the apparatus shown in figure 7.3a in a fume cupboard to collect a few cm^3 of liquid dinitrogen tetraoxide. Use about 20 g of powdered lead nitrate which has been dried by heating in a steam oven. If the lead nitrate is mixed with dry sand the gases are given off more smoothly. Heat as gently as possible with the clip open to avoid decomposition of the product into nitrogen monoxide and oxygen. The students should note the difference in colour between the gaseous products in the hot and cold regions of the apparatus.

When sufficient liquid has been collected, stop the heating and close the clip. Remove the heated tube and its contents.

Next, remove the receiver from the freezing mixture. Dry the outside and connect it to the stopcock and syringe as shown in figure 7.3b.

As small an area of rubber as possible should be left exposed to the gas, hence glass to glass connections are important. Adjust the stopcock so that the receiver is connected to the atmosphere. Warm the receiver gently (in the hand or a beaker of warm water) so that the liquid N_2O_4 boils and the gas expels air from the apparatus. By suitable manipulation of the stopcock, rinse the syringe twice with successive quantities of about 20 cm^3 of gas, then allow it to fill to about the 40 cm^3 mark and adjust the stopcock so that the syringe is sealed. Disconnect the syringe and stopcock from the receiver. Alternatively, the stopcock can be replaced by a short length of rubber tubing with a piece of solid glass rod in one end. If a syringe is not available, any sealed item of glassware will do, although it might not be possible to show the effect of pressure change.

To demonstrate the effect of temperature, large beakers of water will need to be prepared in advance, one chilled with ice to about 10 °C, and the other warmed to about 50 °C.

An alternative way of doing this experiment is to collect three test tubes of the gaseous mixture. Each tube should be carefully stoppered and then made safe with plastic sealing tape. The three tubes can then be placed side by side in beakers of water chilled with ice, water at room temperature and water heated to about 50 °C.

To demonstrate the effect of pressure, apply pressure to the gas by pushing the plunger a short distance into the syringe and note the colour changes. First a darkening in colour occurs as the NO_2 concentration increases. This is followed by a decrease in the intensity of the colour as the equilibrium adjusts itself to the new condition (the delay is due to the rate of the reaction). Reduce the pressure on the gas and again note the colour changes.

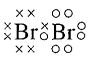
Le Chatelier's Principle

After discussion as to how equilibrium systems respond to changes in temperature and pressure and the use of a catalyst, Le Chatelier's Principle is established as a summary of the general guidelines governing the behaviour of equilibrium systems.

Answers to Topic 7 questions

Review questions

7.1

a

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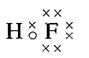
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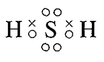
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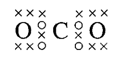
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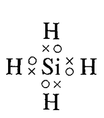
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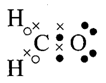
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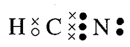
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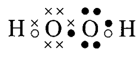
h

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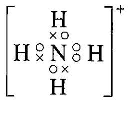
i

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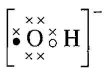
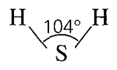
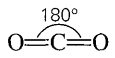
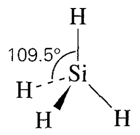

(1)

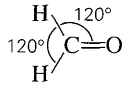
Total 10 marks

7.2

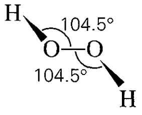
c  (2)

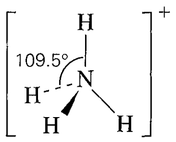
d  (2)

e  (2)

f  (2)

g  (2)

h  (2)

i  (2)

Total 14 marks

7.3

a $C_5H_{12}(l) + 8O_2(g) \longrightarrow 5CO_2(g) + 6H_2O(l)$ (2)

b $C_8H_{18}(l) + 12\frac{1}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$ (2)

c $C_5H_{10}(l) + 7\frac{1}{2}O_2(g) \longrightarrow 5CO_2(g) + 5H_2O(l)$ (2)

d $CH_3OH(l) + 1\frac{1}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ (2)

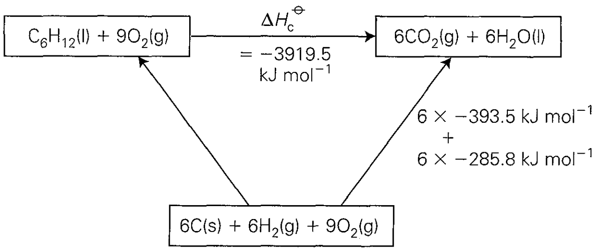
e $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ (2)

Total 10 marks

7.4

a $C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$ (2)

b



Correct cycle, including arrows (4)

c Data inserted correctly (3)

d $\Delta H_f^\ominus[C_6H_{12}(l)] = (6 \times -393.5) + (6 \times -285.8) - (-3919.5)$

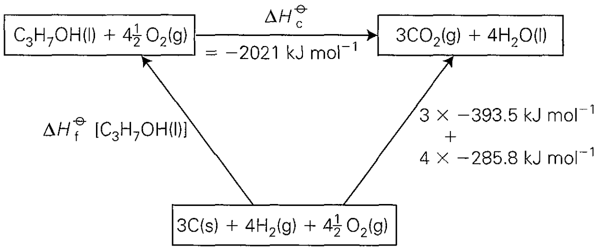
$= -156.3\ \text{kJ mol}^{-1}$ (2)

e Answer should correspond to *Book of data* value. (1)

Total 12 marks

7.5 Equation $C_3H_7OH(l) + 4\frac{1}{2}O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$ (2)

Hess cycle:



(6)

$\Delta H_f^\ominus[C_3H_7OH(l)] = (3 \times -393.5) + (4 \times -285.8) - (-2021) = -302.7\ \text{kJ mol}^{-1}$ (2)

Total 10 marks

7.6

a

Methanol	−715 kJ mol^{-1}	(1)
Ethanol	−1371 kJ mol^{-1}	(1)
Propan-1-ol	−2010 kJ mol^{-1}	(1)
Butan-1-ol	−2673 kJ mol^{-1}	(1)

b Similar increase in successive values (1)

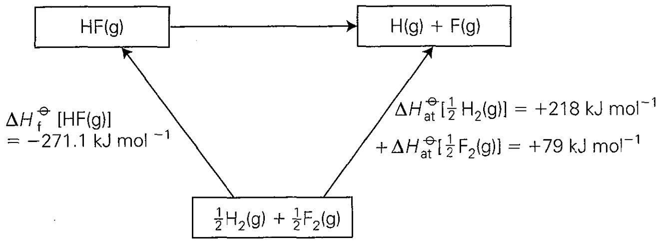
c Suitable scales for graph, up to five C atoms (1)
Axes labelled (1)
Points plotted accurately (1)
d Value read from graph (3300 – 3350 kJ mol^{-1}) (1)
cf *Book of data* value –3329 kJ mol^{-1} (1)

Total 10 marks

7.7
a $\Delta H^{\ominus}_{\mathrm{at}}$[C, graphite(s)] = +716.7 kJ mol^{-1} (1)
b $2 \times \Delta H^{\ominus}_{\mathrm{at}}[\frac{1}{2}H_2(g)]$ = +436.0 kJ mol^{-1} (1)
c $\Delta H^{\ominus}_{\mathrm{at}}[\frac{1}{2}O_2(g)]$ = +249.2 kJ mol^{-1} (1)
d $\Delta H^{\ominus}_{\mathrm{c}}[CH_4(g)]$ = –890.3 kJ mol^{-1} (1)
e 4 × E(C—H) in CH_4 = +1740 kJ mol^{-1} (1)

Total 5 marks

7.8
a (3)



b $\Delta H^{\ominus}_{\mathrm{reaction}}$ = +218 + 79 – (–271.1) = +568.1 kJ mol^{-1} (2)
c Bond energy E(H—F) = 568 kJ mol^{-1} (1)
d Bond energies E(H—Cl) = 432.0, E(H—Br) = 366.3,
E(H—I) = 298.3 kJ mol^{-1} (3)
Bonds weaker as size of halogen atom increases/longer bonds (1)

Total 10 marks

7.9
a E(P—Cl) = 983/3 = +328 kJ mol^{-1} (3SF) (2)
b E(Cl—Cl) = (–305 + 983 – 314) × $\frac{2}{3}$ = +243 kJ mol^{-1} (3SF) (2)

Total 4 marks

7.10
a Hydrogen is much more electronegative than sodium, so ions are formed. (2)
b Electronegativity of C very similar to that of H, so bonds are virtually non-polar. (2)
c Cl significantly more electronegative than H, so shared electrons strongly attracted towards Cl. (Lone pairs on Cl also contribute significantly to dipole.) (3)
d F very much more electronegative than Na, so ions are formed; F not much more electronegative than O, so covalent bonds in OF_2; OF_2 is molecular as a consequence whilst LiF has giant ionic lattice. (3)

Total 10 marks

7.11

Reaction	Temperature increase	Pressure increase	Increased surface area	Increased concentration
1	faster (1)	no effect (1)	faster (1)	faster (1)
2	faster (1)	faster (1)	faster (surface area of catalyst) (1)	not applicable (1)
3	faster (1)	no effect (1)	faster (surface area of catalyst) (1)	faster (1)

Total 12 marks

7.12

Reaction	Increased temperature	Increased pressure
1	shift to left (1)	shift to right (1)
2	shift to left (1)	no effect (1)
3	shift to right (1)	shift to right (1)

Total 6 marks

7.13

a Uncatalysed 78.7 kJ mol^{-1}; Pt catalysed 49.0 kJ mol^{-1}; enzyme-catalysed 36.4 kJ mol^{-1}. (1)

b Catalysts provide an alternative pathway having lower activation energy; enzyme catalysis is more efficient than purely chemical inorganic catalysis as shown by lowest E_A (3)

c Moles of $H_2O_2 = \frac{50}{1000} \times 2.0 = 0.1$ (1)

Moles of $O_2 = 0.05$ (1)

Volume of $O_2 = 0.05 \times 24 = 1.2\,dm^3$ or $1200\,cm^3$ (1)

d Same volume of O_2 would be produced (1)

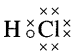
because same amount of H_2O_2 decomposed

(catalyst only affects rate of production of O_2, not the extent of the reaction) (1)

Total 9 marks

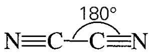
Examination questions

7.14

a **i**  (1)

 (1)

 (1)

ii  (2)

b $\Delta H_f^{\ominus}[(CN)_2(g)] = +259\,kJ\,mol^{-1}$ (3)

c HCN (CN)$_2$ SO_2, H_2S or CO_2 (3)

d **i** 0 (in Cl_2); −1 (in NaCl); +1 (in NaClO) 2 marks for all 3, 1 for 2 (2)

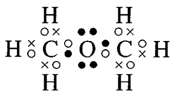
ii Element/chlorine simultaneously oxidised and reduced (1)

iii $(CN)_2 + 2NaOH \longrightarrow NaCN + NaCNO + H_2O$ (1)

e $(CN)_2$ (or HCN which may be formed) is poisonous/toxic. (1)

Total 16 marks

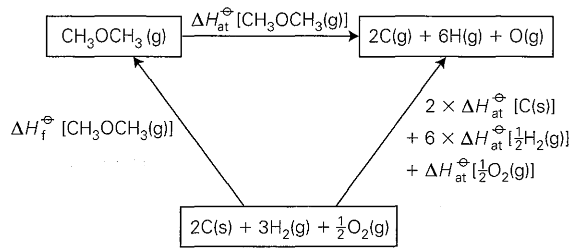
7.15

a  (1)

b $CH_3OCH_3(g) \longrightarrow 2C(g) + 6H(g) + O(g)$ (2)

c $E(C{-}O) = \frac{3194 - (6 \times 413)}{2}$

$= 358\,kJ\,mol^{-1}$ (2)

d  (4)

e $\Delta H_{at}^{\ominus}$ refers to a compound in the gaseous state which may not be its standard state. (1)

Total 10 marks

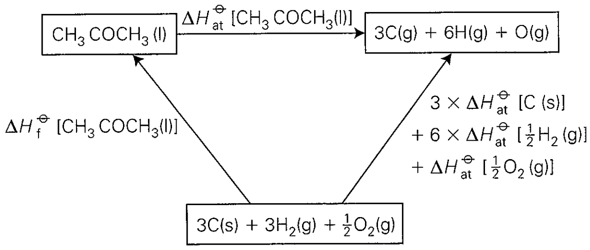
7.16 **a** **i** $3.34 \times 25.3 = 84.5$ kJ (3SF) (2)

ii $\frac{2.90}{58} = 0.05$ mol propanone used.

$\Delta H_c = \frac{84.5}{0.05} = -1690 \text{ kJ mol}^{-1}$ (2)

(sign essential in final answer)

b



(2)

$\Delta H^\ominus_{at}[CH_3COCH_3(l)] = (3 \times 715) + (6 \times 218) + 249 - (-248)$

$= +3950 \text{ kJ mol}^{-1}$ (4 SF) (2)

c $\Delta H^\ominus_{at} = (2 \times 346) + (6 \times 413) + 749$

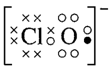
$= +3919 \text{ kJ mol}^{-1}$ (3)

d $\Delta H^\ominus_{at} = +3950 \text{ kJ mol}^{-1}$

Difference may be due to use of average bond energies, incomplete combustion in experiment, or other experimental inaccuracies. (1)

Total 12 marks

7.17 **a**



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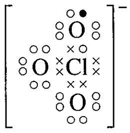

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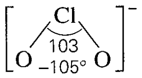
b



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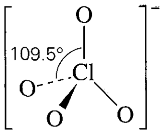
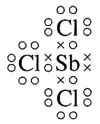


(2)

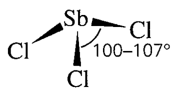
Total 8 marks

7.18 **a** **i**



(2)

ii



(2)

b **i** Yield would be reduced (1)

If temperature increased, equilibrium shifts in endothermic direction. (1)

ii Increase pressure (or amount) of oxygen (1)

Equilibrium moves so as to reduce pressure i.e. towards the products (1)

iii Sb_2O_3 (1)

iv $2SbCl_3(s) + 3H_2O(l) \longrightarrow Sb_2O_3(s) + 6HCl(aq)$ (1)

Total 10 marks

TOPIC 8

Organic chemistry: hydrocarbons

Introduction

This second topic of organic chemistry builds on the knowledge students have gained in Topic 2 about alcohols. The reasons for the diversity of carbon compounds is considered and the naming of organic compounds is extended to include those with branched chains. A wider variety of functional groups is introduced. The chemistry of the alkanes and alkenes is discussed in an experimental context. The scope of organic reactions is widened to include addition, substitution and polymerisation reactions. Organic reactions are considered in terms of bond-making and bond-breaking processes, and students are introduced to the free radical mechanism for photochemical halogenation of alkanes and electrophilic addition to alkenes.

Content

Timing		**Students' Book**
8.1	2 hours	pages 176–80
8.2	3 hours	pages 181–9
8.3	Homework	pages 190–2
8.4	5 hours	pages 192–201
8.5	Homework	pages 201–2
Total about 2 weeks		

8.1 The variety of molecular structure in organic compounds – properties of C—C bonds: rules for naming organic compounds; names and structures of functional groups.

8.2 The alkanes – the importance of alkanes in the petroleum industry: the chemical and physical properties of the alkanes; photochemical reaction of alkanes; free radical substitution: homolytic and heterolytic fission: chain reactions.

8.3 Background reading: octane number of petrol hydrocarbons.

8.4 The alkenes – the uses of alkenes: nomenclature of alkenes: the chemical and physical properties of alkenes, geometric isomerism; the extraction of limonene by steam distillation, addition reactions of alkenes: electrophiles.

8.5 Background reading: polymerisation.

Objectives

1 To extend students' knowledge of naming organic compounds and introduce geometric isomerism.

2 To introduce the fundamental types of bond-breaking in organic chemistry, homolytic and heterolytic, and the fundamental types of attacking groups, free radical, electrophilic and nucleophilic.

3 To develop understanding of the classification of organic reactions with specific reference to substitution, addition, polymerisation and free radical reactions.

4 To develop knowledge of the reactions of alkanes and alkenes.

5 To show how bond energies can be used in a discussion of reaction mechanisms in organic chemistry.

6 To appreciate how extraction procedures are used to obtain purified preparations of natural products.
7 To provide information about the economic and social importance of alkanes and alkenes.

8.1 The variety of molecular structure in organic compounds

Timing About 2 hours will be needed

Suggested treatment

Each group of students will need:
Molecular model kit

This section is introduced by asking students to revise the names and molecular, structural and displayed formulae for some simple alkanes. It is then developed in the following manner.

1 Some properties of the carbon atom which give rise to the very wide range of organic compounds are considered.
2 The IUPAC rules for naming organic compounds containing carbon and hydrogen only are introduced.
3 The names and structures of a range of functional groups are given.

It is suggested that wherever possible students should make models of the carbon compounds under consideration. This not only helps to visualise the three-dimensional structure but allows ideas such as free rotation about a C—C single bond and *cis-trans* isomerism (see section 8.4) to be explained more readily.

ANSWERS

Study task, page 178

Students are asked to make models and write down the different structural formulae of alkane molecules having the formula C_6H_{14}. The five isomers are:

$CH_3CH_2CH_2CH_2CH_2CH_3$
$CH_3CH_2CH_2CH(CH_3)CH_3$
$CH_3CH_2CH(CH_3)CH_2CH_3$
$CH_3CH(CH_3)CH(CH_3)CH_3$
$CH_3CH_2C(CH_3)_2CH_3$

8.2 The alkanes

Timing About 3 hours will be needed

Suggested treatment

This section is developed in the following way.

1 A brief introduction to the petroleum industry.
2 Students are introduced to the properties of the alkanes by a series of experiments.
3 Homolytic and heterolytic fission are introduced during a discussion of the experiments including the photochemical halogenation of alkanes.
4 The reactions of the alkanes are discussed in more detail.

A discussion of the change in T_b with increase in number of carbon atoms for the straight-chain alkanes is deferred until Topic 9.

EXPERIMENT 8.2

The properties of some alkanes

Each group of students will need:
Eye protection
Test tubes and rack
2 stoppers for test tubes
Combustion spoon or equivalent
Small trough (ice cream tubs are suitable)
Delivery tube for gas collection (see figure 8.1)
Bunsen valve
Measuring cylinder, 10 cm^3
Dropping pipettes
Metal spatula

Access to:
Aluminium oxide, 4–8 mesh granules, 5 g
2 M ammonia, 2 cm^3
0.05 M bromine water, 2 cm^3 HARMFUL AND IRRITANT
2% bromine (TOXIC AND CORROSIVE) in inert solvent, 2 cm^3
Hexane, free from aromatics, 12 cm^3 HIGHLY FLAMMABLE, HARMFUL
Paraffin, light, laboratory grade, 5 cm^3 FLAMMABLE, IRRITANT
Poly(ethene), a few granules
20% potassium hydroxide in ethanol, 2 cm^3 CORROSIVE
0.01 M potassium manganate(VII), a few drops
1 M sulphuric acid, a few drops IRRITANT
Concentrated sulphuric acid, 2 cm^3 CORROSIVE
Ceramic fibre, a small tuft

Access to:
Fume cupboard
Photoflood light or sunlight

HAZARDS

This is the students' first extended experience with organic compounds and several of the hazardous substances will be used again in this topic. It is therefore a good opportunity to check that students understand the safety symbols and are aware of safe laboratory procedures. See the 'Laboratory health and safety' and 'Hazardous laboratory chemicals' appendices.

The following additional notes may be helpful.

When preparing solutions technicians should note that:

- **Bromine can cause burns, and is very toxic by inhalation. It is difficult to pour bromine without some liquid dribbling down the outside of the bottle so it should always be dispensed in a fume cupboard.**
- **Hexane vapour is harmful and highly flammable.**
- **Potassium hydroxide can cause severe burns.**
- **Potassium manganate(VII) is HARMFUL and OXIDISING.**

The photoflood light should be in an electrically safe holder, and arranged so that it cannot shine directly into the students' eyes.

Procedure

Full instructions are given in the *Students' Book*. The following notes may be helpful.

1 Combustion

The flames should be yellow (luminous) and not too sooty. Students should notice that poly(ethene) softens and slowly becomes a liquid on gentle heating. The melting of poly(ethene) could also be carried out by touching the polymer with a hot nail.

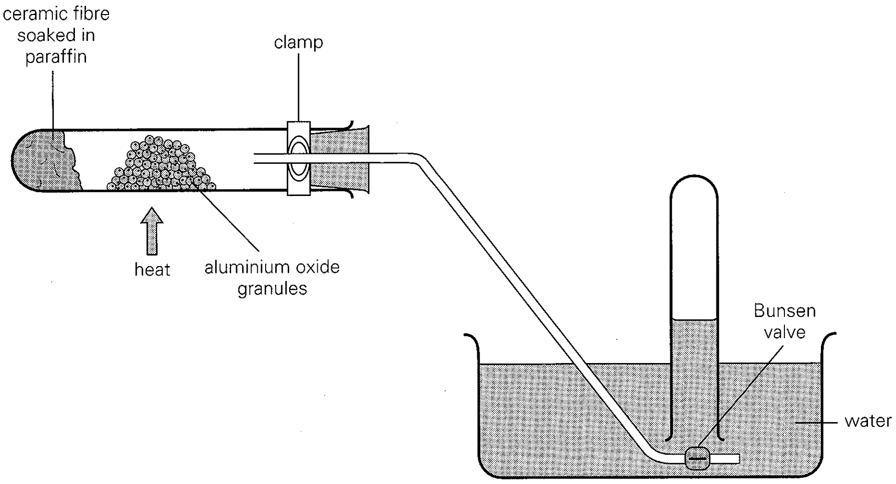


Figure 8.1 Apparatus for the catalytic cracking of an alkane

2 Oxidation

There should be no reaction, although poly(ethene) may go brown at the edges.

3 Action of bromine

No reaction, but poly(ethene) may absorb some bromine.

4 Action of bromine in sunlight

When a reaction takes place, the bromine colour fades and hydrogen bromide fumes are evolved. These can be tested with ammonia (dense white fumes). The colour of bromine fades faster when irradiated with a photoflood light or light from an overhead projector. The teacher may wish to do this part of the experiment as a demonstration, adding a drop of pure bromine to hexane, as the most suitable 'inert' solvent is hexane anyhow.

5 Action of sulphuric acid

No reaction.

6 Action of alkali

No reaction.

7 Catalytic cracking

This may be familiar to some students from their pre-A-level work: aluminium oxide is used to mimic the industrial process. Plenty of gas can be collected but it may not be particularly unsaturated (see figure 8.1).

An interpretation of the photochemical experiment with alkanes

The discussion of the photochemical reaction of alkanes with chlorine or bromine is lengthy and teachers are unlikely to undertake it in full with all groups of students. Students will not be expected to memorise the discussion, but there is an advantage in letting them see something of the way chemists organise their evidence for a hypothesis. In discussing chain reactions, a common error is to postulate a hydrogen radical instead of a methyl radical as part of the chain propagation step.

Reactions of the alkanes

At the end of this section in the *Students' Book* there is an account of the principal alkane reactions. Students are expected to learn these reactions; opportunities should be taken from time to time to test their knowledge.

Summary

Students should draw up a flow chart to summarise the reactions they have studied.

8.3 Background reading: octane number of petrol hydrocarbons

Timing This may be set for homework

Students are asked to read a passage which introduces the processes of catalytic cracking, catalytic reforming, alkylation and isomerisation of hydrocarbons and to answer questions based on the passage.

ANSWERS TO THE BACKGROUND READING QUESTIONS

Questions, page 190

1 Pre-ignition is the explosion of the fuel–air mixture by compression, before the intended ignition from a spark.

2 High octane number fuels have less tendency to pre-ignite.

3 Catalytic cracking uses zeolites, while catalytic reforming uses platinum and produces a higher proportion of arenes.

4 The equation of *unbranched hydrocarbon* ⟶ *branched hydrocarbon* should have correct structural formulae and should balance.

5 The simplest equation is:

$$CH_3(CH_2)_{18}CH_3 \longrightarrow CH_2{=}CH_2 + CH_3(CH_2)_{16}CH_3$$

6 A simple example is:

$$CH_2{=}CH_2 + H^+ \longrightarrow {}^+CH_2{-}CH_3$$

$$(CH_3)_3CH + {}^+CH_2{-}CH_3 \longrightarrow (CH_3)_3C{-}CH_2{-}CH_3 + H^+$$

7 Highly branched iso-octane has an octane number of 100; isomers with fewer side chains will have an octane number less than 100.

8 Free radicals have an odd number of electrons and are produced by the homolytic fission of a covalent bond.

9 Chain branching results in fewer reactive free radicals.

10 Key points for inclusion in a summary:

- There are four important processes for producing petrol-grade hydrocarbons.
- In catalytic cracking, large molecules are broken down into smaller molecules using crystalline aluminosilicates as the catalysts.
- In catalytic reforming, platinum is added to the cracking catalyst and highly purified alumina is used for the catalyst.
- Reforming produces arenes, branched chain alkanes, and hydrocarbons of lower molar mass.
- Alkylation is the joining of small molecules in the right way.
- Alkylation involves the reaction of a branched chain alkane with an alkene in the presence of acid catalyst.
- Isomerisation is when straight chain alkanes are converted to branched chain alkanes using a specially prepared platinum material.

8.4 The alkenes

Timing About 5 hours will be needed

Suggested treatment

This section is developed in the following way:

1. The structure and bonding in alkenes are discussed and how they are named.
2. Limonene is extracted from orange peel.
3. The reactions of alkenes are studied experimentally.
4. The reaction between an alkene and bromine is considered in mechanistic terms.
5. The reactions of the alkenes are summarised.

Wherever possible students should use molecular models as an aid to understanding the structure of alkenes, and to illustrate the bond-breaking and bond-making processes taking place during the reactions.

The *Students' Book* first discusses the production and use of alkenes in the petroleum industry. It should be possible for the teacher to supplement this with booklets and posters obtainable from the educational services of the various petroleum companies.

Geometrical isomerism is then introduced. Molecular models will be helpful here. Rules for naming alkenes are briefly reviewed; students should be given some practice in putting them into effect.

EXPERIMENT 8.4a Extracting limonene from oranges by steam distillation

Each group of students will need:
Eye protection
Bunsen burner, tripod, gauze and heatproof mat
Distillation apparatus with flask, 250 cm^3 (see figure 8.2)
Thermometer, 0–250 °C
Measuring cylinder, 50 cm^3
Dropping pipette
Test tube with stopper or specimen bottle
Kitchen grater (or sharp knife)
2 oranges, or their zest

It is likely that this is the first time that students have performed a distillation themselves. A little time should be spent on advising them of the general safety procedures, for example: never boiling to dryness, ensuring that the joints are tightly fitting, using anti-bumping granules when necessary. Remind students that cold water should enter at the lower connection of the condenser.

Procedure

The quantity of limonene obtained from the zest of two oranges is about 2 cm^3 and depends on the freshness of the oranges used. Oranges which are heavily waxed are likely to give a poor yield of product. It is important to grate the oranges thinly, removing the thin outer coating, the zest, and not the complete peel. Cut up the zest otherwise it may be difficult to empty the distillation flask at the end of the experiment. The experiment may be scaled up easily.

If students have sufficient product, they may test it with bromine water and acidified potassium manganate(VII) as part of Experiment 8.4b. If there is not sufficient time to do this straight away, the product should be stored in a closed container to prevent evaporation.

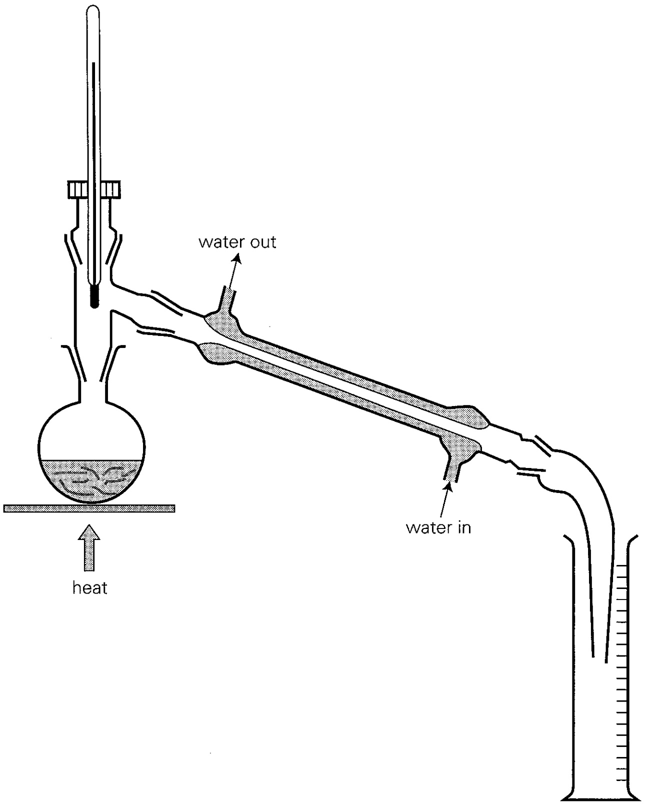


Figure 8.2 Steam distillation apparatus

Teachers may be interested to know that limonene is optically active; the (+) form being present in citrus oils whilst the (−) form is found in pine needle oil. The racemic mixture, called dipentene, is a constituent of turpentine. Chirality is introduced in Topic 18.

EXPERIMENT 8.4b The reactions of the alkenes

HAZARDS

Di(dodecanoyl) peroxide (lauroyl peroxide) is oxidising as well as being irritant. Methyl 2-methylpropenoate (methyl methacrylate) is highly flammable and irritant. It should be restricted to use in a fume cupboard under strict supervision.

Each group of students will need:
Eye protection
4 test tubes and rack
Combustion spoon, or equivalent
Beaker, 250 cm^3 (as a waterbath)
3 dropping pipettes

Access to:
0.05 M bromine water, 1 cm^3 HARMFUL AND IRRITANT
Cyclohexene, 2 cm^3 HIGHLY FLAMMABLE, IRRITANT
Di(dodecanoyl) peroxide (lauroyl peroxide), 0.1 g OXIDANT
Limonene, 1 cm^3
Methyl 2-methylpropenoate, 5 cm^3 HIGHLY FLAMMABLE, IRRITANT
0.01 M potassium manganate(VII), 1 cm^3
Concentrated sulphuric acid, 2 cm^3 CORROSIVE
1 M sulphuric acid, 1 cm^3 IRRITANT

Procedure

Full instructions are given in the *Student's Book.*

Students repeat Experiment 8.2 this time using alkenes instead of alkanes, and are thus able to compare the properties of these two classes of hydrocarbons. The tests 1, 2 and 3 should also be performed on the sample of limonene extracted from orange peel.

The following notes may be helpful.

1 Combustion

The flame should be yellow (luminous) and slightly sooty.

2 Oxidation

The alkenes should readily decolorise the 0.01 M potassium manganate(VII) solution.

3 Action of bromine

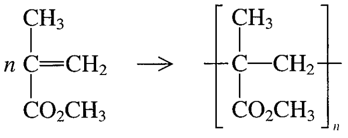
The bromine solution should be decolorised instantly. Reactions 2 and 3 should be introduced to students as indications of unsaturation.

4 Action of sulphuric acid

Some charring occurs and the reaction mixture becomes hot. If water is added (carefully!), a cloudy solution is obtained, with most of the material water-soluble.

5 Polymerisation

The use of methyl 2-methylpropenoate must be carefully controlled as the vapour is irritating and highly flammable. The reaction should be carried out only in a fume cupboard. The equation for the reaction is:



$$n\,\underset{CO_2CH_3}{\overset{CH_3}{C}}{=}CH_2 \rightarrow \left[\underset{CO_2CH_3}{\overset{CH_3}{C}}{-}CH_2\right]_n$$

An interpretation of the experiments with alkenes

The idea of electrophilic attacking groups is introduced in this section. In the reactions with electrophiles, the double bond is acting as a nucleophile. It may be helpful to students to point out that types of reagent tend to occur in pairs: acid and base, oxidising and reducing, and now electrophile and nucleophile.

ANSWERS

Questions, page 199

1 Electron rich; nucleophile.

2 Carbocation.

3 Br—Br bond can break homolytically giving free radicals, or heterolytically giving ions.

4 Electron-deficient species, e.g. Br^+.

5 Yes.

The experiments of Francis can be summarised as:

$$CH_2{=}CH_2 \xrightarrow{\overset{\delta+\quad\delta-}{Br{-}Br}} CH_2Br{-}{}^+CH_2 \xrightarrow{:NO_3^-} CH_2Br{-}CH_2{-}NO_3$$

Polarisation of the bromine molecule is a necessary part of the process of reaction: this is shown by the failure of dry ethene and bromine gases to react when mixed in a container with waxed walls, so that the bromine cannot be polarised.

Reactions of alkenes

Students should be expected to learn these reactions, and a suitable opportunity should be taken to test their knowledge.

Teachers may like to go into a little more detail with some students as optional extension work. The addition of hydrogen halides to alkenes, listed under 2 in the *Students' Book*, is a suitable example for further discussion. This reaction was described by the Russian chemist Markovnikov in 1869. The Markovnikov addition is an electrophilic one that follows a pattern of forming a carbonium ion as the intermediate in the reaction:

$$CH_3\text{—}CH{=}CH_2 + H^+ \longrightarrow CH_3\text{—}{}^+CH\text{—}CH_3$$

The positive charge appears on the carbon atom with fewest hydrogen atoms, rather than having $CH_3\text{—}CHBr\text{—}CH_2^+$ as the intermediate.

If the reaction mixture is illuminated, a different product is obtained

$$CH_3\text{—}CH{=}CH_2 + HBr \xrightarrow{hv} \underset{\text{1-bromopropane}}{CH_3\text{—}CH_2\text{—}CH_2Br}$$

This reaction is known as an anti-Markovnikov addition, and was investigated in 1933 by two American chemists, Kharasch and Mayo. They proposed that the addition proceeded by a free radical process. When illuminated, hydrogen bromide will form free radicals, H· and Br·, and the Br· radical will attack the propene, forming a carbon radical

$$CH_3\text{—}\dot{C}H\text{—}CH_2Br$$

as the intermediate in the reaction.

The odd electron appears on the carbon atom with the fewest hydrogen atoms, rather than having $CH_3\text{—}CHBr\text{—}CH_2\cdot$ as the intermediate. Further reaction with HBr gives the product and another Br· to continue the chain reaction. The free radical reaction can be initiated by peroxides as well as ultraviolet light.

To summarise:

$$CH_3\text{-}CH{=}CH_2 \xrightarrow{H^+} CH_3\text{—}\overset{+}{C}H\text{—}CH_3 \xrightarrow{Br^-} \underset{\text{Markovnikov addition}}{CH_3\text{—}CHBr\text{—}CH_3}$$

$$CH_3\text{-}CH{=}CH_2 \xrightarrow{Br\cdot} CH_3\text{—}\dot{C}H\text{—}CH_2Br$$

$$\xrightarrow{HBr} \underset{\text{anti-Markovnikov addition}}{CH_3\text{—}CH_2\text{—}CH_2Br + Br\cdot}$$

At the end of this section students should draw up a chart to record the reactions they have studied. A detailed study of polymerisation can be left until Topic 18.

8.5 Background reading: polymerisation

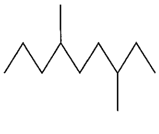
Timing This may be set for homework.

Students are asked to read a passage which introduces addition and condensation polymerisation in the context of the work of Carothers, Ziegler and others in order to demonstrate how chemists try to control reaction conditions in order to produce specific polymers.

ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 201

1 107 ethene molecules

2  and 

3 The free radical at the end of a growing chain can react with the chain in a process known as 'back-biting'; a catalyst is likely to be specific to monomer molecules.

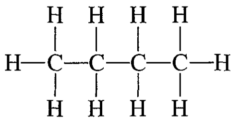
4 Key points to include in summary.

- Equal quantities of water and chloroethene, and a small quantity of the surface active agent … are stirred together in an autoclave.
- This produces a suspension of chloroethene in water.
- Potassium peroxodisulphate(VI) is added.
- This acts as an initiator which increases the rate of the reaction by producing free radicals.
- The temperature of the mixture is raised to about 60 °C.
- The droplets polymerise to form solid particles of poly(chloroethene).
- This can be recovered by filtration.
- Water dilutes the reaction mixture and helps to keep it cool.

Answers to Topic 8 questions

Review questions

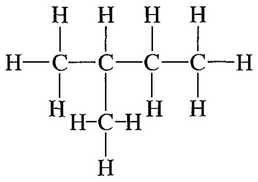
8.1 Empirical formula shows atomic proportions of each element, C_2H_5. (1)
Molecular formula shows number of atoms of each element in one molecule, C_4H_{10}. (1)
Structural formula shows how atoms are grouped in each molecule, $CH_3CH_2CH_2CH_3$. (1)
Displayed formula shows every atom and every bond.



(1)

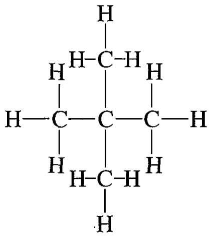
Total 4 marks

8.2 **a**



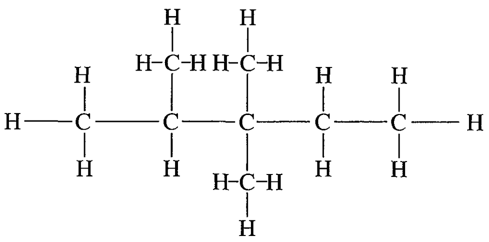
(1)

b



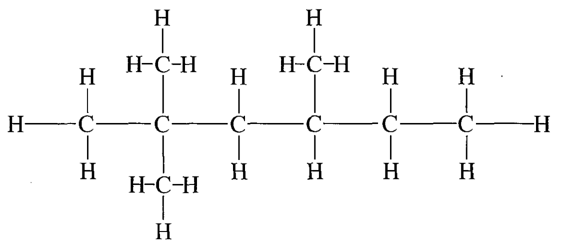
(1)

c

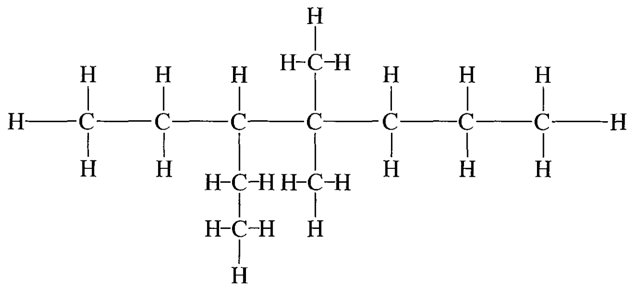


(1)

d (1)



e (1)



Total 5 marks

8.3

a C_5H_{12} (1)
b C_5H_{12} (1)
c C_8H_{18} (1)
d C_9H_{20} (1)
e $C_{11}H_{24}$ (1)

Total 5 marks

8.4

a Pentane (1)
b 2-methylbutane (or methylbutane) (1)
c 3-methylpentane (1)
d 1,2-dimethylcyclohexane (1)
e 2,3-dimethylhexane (1)

Total 5 marks

8.5

a $C_{10}H_{22} \longrightarrow C_8H_{18} + C_2H_4$ (2)
b $C_{10}H_{22} \longrightarrow C_6H_{14} + 2C_2H_4$ (2)

Total 4 marks

8.6

a $Br_2 \longrightarrow 2\,Br\bullet$ initiation (1)
$C_6H_{14} + Br\bullet \longrightarrow HBr + C_6H_{13}\bullet$ } propagation (2)
$C_6H_{13}\bullet + Br_2 \longrightarrow C_6H_{13}Br + Br\bullet$
$Br\bullet + Br\bullet \longrightarrow Br_2$
$C_6H_{13}\bullet + C_6H_{13}\bullet \longrightarrow C_{12}H_{26}$ } termination (3)
$Br\bullet + C_6H_{13}\bullet \longrightarrow C_6H_{13}Br$
b $C_6H_{14} + Br_2 \longrightarrow C_6H_{13}Br + HBr$ (2)
c Substitution (1)
d More H atoms in $C_6H_{13}Br$ could be replaced by Br atoms. (1)

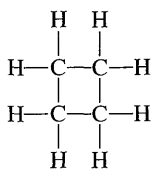
Total 10 marks

8.7

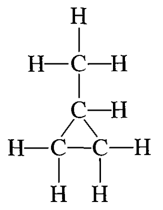
a $C_8H_{18}(l) + 12\frac{1}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$ (2)
(or doubled throughout)
b Density of octane = 0.703 g cm^{-3} (2)
Mass of 1 litre = 703 g
c Molar mass of octane = 114 g mol^{-1} (2)
703 g = 703/114 = 6.16 mol (3 SF)
d Volume of oxygen = 6.16 × 12.5 × 24 dm^3 (2)
Volume of air = 6.6 × 12.5 × 24 × 5 = 9234 dm^3
e Incomplete combustion produces carbon, carbon monoxide, unburned octane. (1)
Less energy is produced. (1)

Total 10 marks

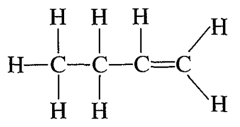
8.8



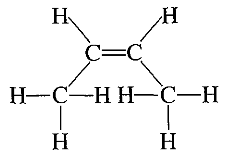
(1) cyclobutane (1)



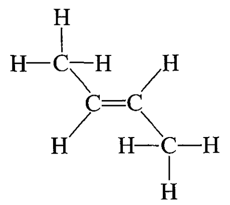
(1) methylcyclopropane (1)



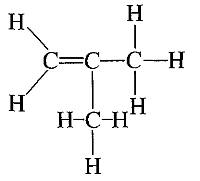
(1) but-1-ene (1)



(1) *cis*-but-2-ene (1)



(1) *trans*-but-2-ene (1)

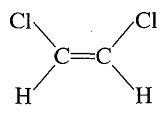


(1) methylpropene (1)

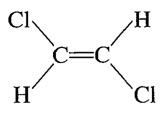
Total 12 marks

8.9 **a** $ClCH{=}CHCl$ and $CH_3CH_2CH{=}CHCH_3$ can exist as geometric isomers. (2)

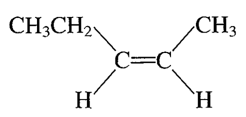
b



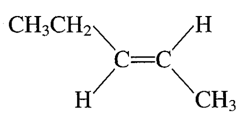
(cis)



(trans) (2)



(cis)



(trans) (2)

Total 6 marks

8.10 $Br_2(l)$; $H_2(g)$; $H_2SO_4(l)$; $HBr(g)$; $H_2O(l)$ (1 each)

Total 5 marks

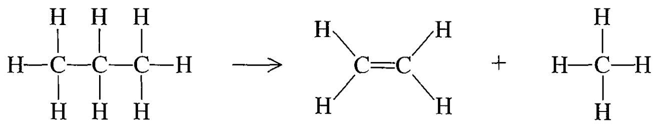
8.11 **a** Free radicals: $CH_3\bullet$, 7 outer electrons
$Cl\bullet$, 7 outer electrons (1)
Electrophiles: Br^+, 6 outer electrons
H^+, no electrons (1)
Neither free radicals nor electrophiles:
OH^-, H_2O, I^-, NH_3 (all 8 outer electrons) (1)

b Metal atoms do not usually bond covalently to carbon. (1)

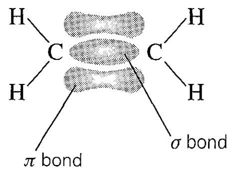
Total 4 marks

Examination questions

8.12 **a** **i** (2)

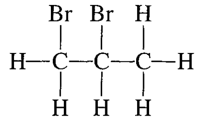


ii (2)



b $\Delta H^{\ominus} = +20.2 - (-104.5) = +124.7\,\text{kJ mol}^{-1}$ (2)

c **i** 1,2-dibromopropane (2)

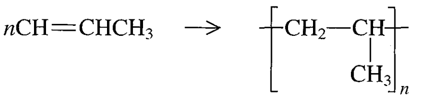


$\mathrm{H{-}\overset{Br}{\underset{H}{C}}{-}\overset{Br}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$

ii Type = addition reagent = electrophile (2)

iii B = H_3PO_4/H_2SO_4 C = H_2O (or reversed) (2)

iv (2)



$n\mathrm{CH{=}CHCH_3} \longrightarrow \left[\mathrm{-CH_2-\underset{CH_3}{CH}-}\right]_n$

v Chlorine uv or sunlight (2)

vi Free radical (1)

vii 1-chloroprop-2-ene (1)

Total 18 marks

8.13 **a** Ultraviolet or sunlight (1)

b Homolytic (fission) (1)

c Chain propagation (1)

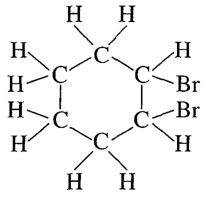
d $Cl\bullet + Cl\bullet \longrightarrow Cl_2$
or $CH_3CH_2CH_2CH_2\bullet + CH_3CH_2CH_2CH_2\bullet \longrightarrow CH_3(CH_2)_6CH_3$ (1)

e Formation of polymers/combustion of hydrocarbons/reactions in the ozone layer/hydrogen with chlorine (any one). (1)

Total 5 marks

8.14 **a** From orange to colourless (1)

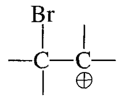
b 1,2-dibromocyclohexane (2)



c **i** Orange colour would remain (1)

ii Remove excess bromine by shaking with aqueous alkali (1)
Separate organic layer and dry with anhydrous sodium sulphate (1)
Remove hydrocarbon solvent by distillation (1)
Dry with anhydrous sodium sulphate (1)

d **i** and Br^- (2)



$-\overset{Br}{\underset{|}{C}}-\overset{|}{\underset{\oplus}{C}}-$

ii Carbocations (1)

iii Electrophile (1)

Total 12 marks

8.15

a Diagram along the lines of *Students' Book* figure 8.11.
It should show flask containing lavender blooms + water (1)
Liebig condenser with inner tube and outer jacket clearly separate (1)
Heat source (1)
Apparatus which will work (no gaps, not sealed) (1)

b **i** To dissolve the organic product/oil (1)
ii Dry/remove water (1)

c **i** —OH converted to $—O^-Na^+$ (1)
ii Addition of Br_2 to <u>both</u> double bonds (2)
iii Double bond introduced (any of 3 possible positions) (2)

d Any three from: non-toxic, economical to produce, readily available starting materials, high yield at each stage, similar physical properties e.g. volatility, stable. (3)

Total 14 marks

8.16

a **i** Type = substitution   mechanism = free radical (2)
ii To produce Cl• free radicals/break Cl—Cl bonds (1)
iii $CH_2Cl\,CHCl\,CH_3$ 1,2-dichloropropane (2)

b Double bond provides a pair of electrons (2)

c Elimination involves removal of atoms from a molecule; here these atoms make HCl. (1)

Total 8 marks

TOPIC 9

Intermolecular forces

Introduction

Intermolecular forces are most obviously relevant to an understanding of the melting and boiling points of covalent compounds.

In this topic, van der Waals forces, dipole–dipole interactions, and hydrogen bonding are discussed in a practical context. These forces are shown to be involved in a wide range of important phenomena, being particularly significant in biochemical structures and changes.

Content

Introduction – evidence for intermolecular forces.

9.1 Van der Waals forces – increase in boiling point with increasing number of electrons and increasing surface contact; van der Waals radii.

9.2 Molecules with permanent dipoles – the effect of an electrostatic field on a jet of liquid; polarisation in molecules; dipole moments; dipole–dipole interactions.

9.3 Hydrogen bonding – the type and arrangement of atoms in hydrogen bonding; relative strengths of different intermolecular forces; evidence for hydrogen bonds; measuring enthalpy changes of vaporisation; the importance of hydrogen bonding.

Timing		Students' Book
Introduction		
	1 hour	page 209
9.1	3 hours	pages 209–12
9.2	2 hours	pages 213–4
9.3	3 hours	pages 215–19
Total about 2 weeks		

Objectives

1 To consider the evidence for intermolecular forces.

2 To consider qualitatively dipole–dipole attraction, van der Waals forces and hydrogen bonding, and to appreciate the magnitude of the forces involved.

3 To demonstrate an understanding of the types of atoms involved in dipole–dipole interactions and hydrogen bonding.

4 To interpret the physical properties of substances in terms of the different types of intermolecular forces.

5 To appreciate the importance of hydrogen bonding in determining the structures of some materials including some important biological compounds such as carbohydrates and proteins.

Introduction

Timing About 1 hour

Suggested treatment

The introductory section asks students to review the magnitude of the forces involved in ionic and covalent bonding. Patterns of ionisation energy have been discussed in Topic 3 and covalent bond energies in Topic 7.

EXPERIMENT 9.0 Evidence for intermolecular forces

Each group of students will need:
7 wine bottle corks (preferably new and parallel sided)
Steel sewing needle (clean and blunt)
Aluminium foil (e.g. cut from a takeaway container)
A few small pieces of paper

Access to:
Large shallow container

Procedure

Students are introduced to some evidence for intermolecular forces by simple experiments involving floating corks and needles. A raft of seven or eight corks, wetted so that there is a layer of water around each cork, should be kept together by the weak forces. Unfortunately, used corks from wine bottles will not work as well as new unused corks.

An explanation of these experiments should be left until hydrogen bonding has been discussed in section 9.3. All that is required at this stage is to show that there are significant intermolecular forces in water and that the total force increases when the contact area increases.

INSTRUCTIONS TO STUDENTS

1 Floating corks

Put seven new wine-bottle corks in a large beaker of water. They float, of course, but can you make them float standing on their ends in the water? Try floating several of the wet corks as a group. You should be able to manage it with all seven!

INSTRUCTIONS TO STUDENTS

2 Floating needles

Steel and aluminium are obviously more dense than water yet you can float a steel sewing needle or piece of aluminium foil on the surface of water if you are very careful. Try putting the needle on a small piece of paper on the water's surface and then carefully pushing the paper away from under it.

9.1 Van der Waals forces

Timing About 3 hours

The students will need:
Molecular model kit to build space-filling models of pentane and 2,2-dimethylpropane

Suggested treatment

The origin of van der Waals forces is described in terms of the flickering dipole model. Teachers should remind students of the meaning of dipole before explaining this. The increase in the boiling point of straight-chain alkanes with increasing number of carbon atoms, and the increase in the boiling point of halogens down Group 7, can be explained in terms of the increase in van der Waals attractions.

ANSWERS

Study task, page 210

The question on the isomers of C_5H_{12} can be answered in terms of molecular shape. Pentane has a long linear molecule and there is an extensive surface area for contact with other molecules; 2,2-dimethylpropane is approximately spherical in shape and there is a much smaller surface area available for contact with other molecules. There is thus more van der Waals attraction between pentane molecules than there is between 2,2-dimethylpropane molecules, and therefore the boiling point of pentane is higher than that of 2,2-dimethylpropane.

The situation is most clearly demonstrated by means of space-filling models of the molecules, and students should make their own. It is even simpler for them to consider the relative areas of contact when a set of models is close-packed.

Van der Waals radii

The van der Waals radius of an atom is explained in the *Students' Book*, where it is contrasted with the covalent radius. Some data are given in the *Students' Book* and the attention of students should also be drawn to table 4.4 of atomic and ionic radii given in the *Book of data*.

Van der Waals forces can also make an important contribution to the structure of proteins. This point could be left until Topic 18.

ANSWERS

Study task, page 212

The section finishes with a study task which asks the students to use tables 7.7 and 7.2 in the *Book of data* to compare the tensile strength of poly(ethene) with the tensile strength of a range of metals. Poly(ethene) fibres can be produced that are a suitable material for bullet-proof vests!

9.2 Molecules with permanent dipoles

Timing About 2 hours

The students will need:
Molecular model kit to build a space-filling model of propanone

Suggested treatment

Dipoles are introduced with reference to propanone where the difference in electronegativity of the atoms causes polarity in the molecule. An experiment on the effect of an electrostatic field on a jet of liquid then leads to a discussion of how polarity in molecules can affect boiling point.

EXPERIMENT 9.2

What is the effect of an electrostatic field on a jet of liquid?

Each group of students will need:
Burette with filling funnel
Glass rod and dry piece of cloth (see figure 9.1)
Beaker, 600 cm^3, or large diameter container

HAZARDS

A risk assessment will be necessary so that appropriate precautions are taken for the liquids selected for testing.

Access to:

A range of organic hydrocarbons, alcohols and ketones for which hazard information is available, 50 cm^3 each

Suitable examples include:

Hexane	HARMFUL, HIGHLY FLAMMABLE
Cyclohexane	HARMFUL, HIGHLY FLAMMABLE
Ethanol	TOXIC, HIGHLY FLAMMABLE
Propan-1-ol	HIGHLY FLAMMABLE
Propanone	HIGHLY FLAMMABLE
Butanone	IRRITANT, HIGHLY FLAMMABLE

Water

Procedure

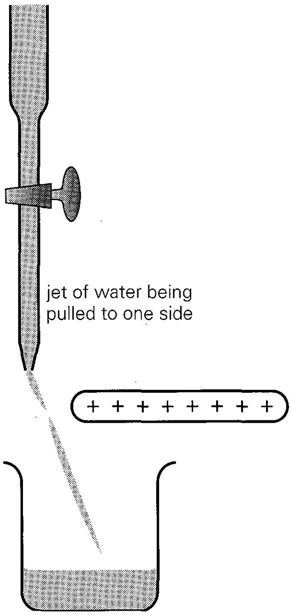


Figure 9.1 Apparatus for experiment 9.2

This experiment is intended to be operated as a circus. The students circulate repeating the experiment with a different liquid at each station.

The liquids can be returned to the stock bottle after use if placed in clean, dry burettes, and collected in clean beakers. Instead of a glass rod, students can use a ball-point pen casing.

The deflection of water suggests that water molecules are polar in character. Alkanes such as hexane show no, or almost no, deflection while alcohols such as propan-1-ol and ketones show marked deflections. The degree of polarisation of the molecules does not match the extent of deflection in a simple manner.

These results are used in the *Students' Book* to revise the idea of polar molecules (first introduced in Topic 7). The dipole moments for some molecules are then considered. This is another quantity which can be used in the determination of the structure of substances.

For the further information of teachers, dipole moments, μ, are the product of the magnitude of the electric charge in the dipole and the distance between the two charges. The unit of dipole moment is the debye, D, which is 3.3×10^{-30} coulomb metre. In the case where the charge is the charge on the electron (1.6×10^{-19} C) and the separation is about a bond length (1×10^{-10} m):

$$\mu = qd = (1.6 \times 10^{-19}) \times (1 \times 10^{-10})\ \mathrm{C\,m} \approx 5\ \mathrm{D}$$

Molecules which do not possess a permanent dipole moment are nevertheless polarised to some extent when placed in an electrical field. This effect arises because the electrical field causes a displacement of electrons relative to atomic nuclei, and a displacement of atoms relative to each other, the latter resulting in changes in bond angles and bond lengths. The total polarisation may therefore be made up of three parts: the orientation polarisation, P_O, due to a permanent dipole; the electron polarisation, P_E; and the atom polarisation, P_A.

$$P_T = P_O + P_E + P_A$$

Thus in Experiment 9.2, molecules which do not possess a permanent dipole may be observed to be very slightly deflected, as a result of the induced dipole. In the samples listed, however, the permanent dipole effect overwhelmingly predominates.

Although induced polarisation is mentioned in the *Students' Book*, polarisability and induced dipoles need not be discussed with the students in any depth.

ANSWERS

Study task, page 214

This section is completed by a comparison of the boiling points of pairs of substances with similar numbers of electrons but different polarities. The example in the *Students' Book* is:

propanone	32 electrons	boiling point 56 °C
2-methylpropane	34 electrons	boiling point −12 °C

Students are asked to find other examples, but they need to select substances with sufficiently similar shapes and molar masses for the comparison to be valid. Some possibilities are butane and propan-1-ol; cycloheptane and cyclohexanol; ethane and hydrogen chloride.

9.3 Hydrogen bonding

Timing About 3 hours

Suggested treatment

The study of hydrogen bonding is developed in the following way:

1. The specific requirements for hydrogen bonding are discussed.
2. Some experimental evidence for hydrogen bonding is introduced.
3. An experiment to measure the enthalpy change of vaporisation of water introduces a study task to estimate the hydrogen bonding contribution to the total intermolecular forces between water molecules.
4. The importance of hydrogen bonding in water and in living organisms is considered.

The teacher will need:
Models of each of the molecules ammonia, water, and hydrogen fluoride, showing the lone pairs of electrons.

The *Students' Book* contains a discussion of the specific requirements for hydrogen bonding. It gives the bond energy of typical hydrogen bonds as around 30 kJ mol^{-1}.

More details are as follows. The strongest hydrogen bonds are formed when the hydrogen atoms concerned are interposed between elements of the highest electronegativity, so the strongest hydrogen bonding may be expected in association with fluorine. It should be emphasised to students that very few elements can take part in hydrogen bonding. Such bonds can form in the following situations:

N—H···O
N—H···N
O—H···O
F—H···F but *not* C—H···C

The energy needed to rupture an H···F bond is approximately 125 kJ mol^{-1}. More usually the energy of hydrogen bonds lies between 10 and 30 kJ mol^{-1}. This is only about ten times the average thermal energy of molecules at 25 °C (2.5 kJ mol^{-1}) and therefore many molecules are able to break hydrogen bonds at room (and body) temperature. The hydrogen bond is thus strong enough to influence physical properties, but so weak that it does not change chemical reactions.

Teachers should be aware that geometric considerations apply to hydrogen bonding just as they do to covalent bonding. In the cases illustrated, such as N—H···O, significant bonding will occur when the bond angle is near to 180°. The bond angle is rarely less than 165° for significant hydrogen bonding and further deviation leads to even weaker hydrogen bonds being formed.

ANSWERS

Study task, page 216

1 Students are asked to predict from a graph the boiling point of water without its hydrogen bonding. A reasonable estimate is 200 K.

2 and 3 For a hydrogen bond to form, a hydrogen atom and a non-bonded pair of electrons are required. In the hydrogen fluoride molecule there is *one* hydrogen atom and *three* non-bonded pairs, so, in principle, four hydrogen bonds might form. However, in 100 hydrogen fluoride molecules, although there are 300 non-bonded electron pairs, there are only 100 hydrogen atoms. Therefore, only 100 hydrogen bonds can be formed – an average of one bond per molecule.

Water molecules, however, have *two* hydrogen atoms and *two* non-bonded electron pairs each and so can form an average of *two* hydrogen bonds each.

Ammonia has *three* hydrogen atoms and *one* non-bonded electron pair, and by a similar argument will only form on average *one* hydrogen bond per molecule.

As extension work students could also be asked to deduce the effect of hydrogen bonding on the enthalpy change of fusion, enthalpy change of vaporisation, and melting point, using values of these constants from the *Book of data.*

EXPERIMENT 9.3 Measuring the enthalpy change of vaporisation of water

HAZARDS

Steam is more dangerous than boiling water.

This experiment can be done in a variety of ways depending on the apparatus available. It could be done as a teacher demonstration.

Procedure 1

Each group of students (or the teacher) will need:
Electric kettle (free of scale)
Balance weighing to 2 kg
Stop clock

Procedure

Full details are given in the *Students' Book.* A value of 36 kJ mol^{-1} can be obtained. It is important to replace the lid as soon as the kettle is switched off otherwise a lot of vapour is lost. The power rating of the kettle is found by simply inspecting the plate at the base of the kettle.

This is a good experiment for students to think about an appropriate number of significant figures for their result.

Kettles can be descaled if necessary using a dilute solution of sulphamic acid (IRRITANT).

The experiment can be done with smaller groups using an alternative method, *procedure 2*, detailed below.

Procedure 2

In this method a steady Bunsen flame is used to heat a known mass of water to boiling and the time taken to do this is measured. The same Bunsen flame is then used to keep the water boiling for 10 minutes and the mass of water boiled off is found by subtraction.

The procedure is described on Sheet 9.1 (page 144) and may be photocopied if teachers wish to use this method.

Each group of students will need:
Apparatus as shown on Sheet 9.1
Measuring cylinder, 250 cm^3
Dropping pipette
Stop clock
Stirrer
Split cork
Thermometer, −10–110 °C

Teachers will realise that the calculation is straightforward using mass × specific heat capacity × temperature change, assuming that 1 kJ is needed to raise the temperature of the water by 1 °C (since 240 g of water is used).

In steps **1** and **2** the calculations assume that the energy is supplied at a constant rate. It is therefore important to keep the size of the Bunsen burner flame constant and to protect it from draughts.

Teachers should draw students' attention to the relatively high value of ΔH_{vap} for water and explain this in terms of hydrogen bonding.

ANSWERS

Study task, page 217

1 Students are asked to estimate the hydrogen bonding contribution to the enthalpy change of vaporisation of water. Depending on their method of extrapolating from limited data students will arrive at a value in the range 18.0–18.5 kJ mol^{-1} for the estimate if there were no hydrogen bonding, leading to about 11 kJ mol^{-1} for the strength of 1 mole of hydrogen bonds in water.

2 Values in the range 9–12 kJ mol^{-1} can be justified.
These values are of the correct order of magnitude, although many sources quote values of 25 kJ mol^{-1} in both cases.

Hydrogen bonding in ice

ANSWERS

Study task, page 219

Hydrogen bonds give water a skin effect (figure 9.3) and this contributes to the high surface tension. Students might be encouraged to speculate about the surface tension of other liquids; some data are given below.

Liquid	Surface tension at 20 °C /N m^{-1}
water	0.073
propane-1,2,3-triol	0.063
methanoic acid	0.037
benzene	0.029
ethanoic acid	0.028
methanol	0.023

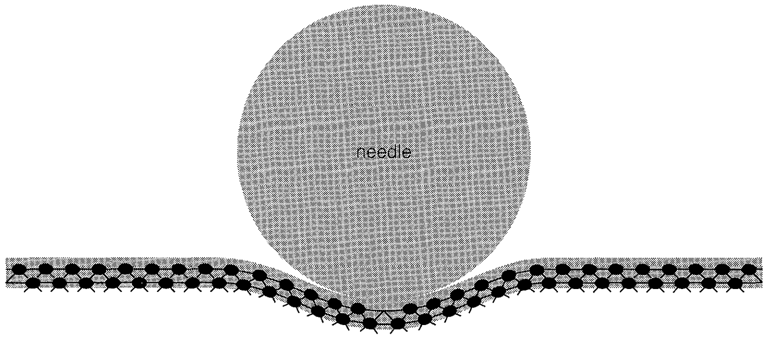


Figure 9.3 A water surface, showing how the surface tension is increased by intermolecular hydrogen bonding (not to scale).

As optional extension work for this section teachers might like to demonstrate an experiment on liquid flow in alcohols and ask the students to examine the cleavage of crystals of gypsum and anhydrite.

EXPERIMENT 9.3

(optional) To examine the rate of bubble movement in some alcohols

The teacher will need:

4 lengths of glass tubing, about 70 cm by 8 mm outside diameter

Propan-1-ol HIGHLY FLAMMABLE

Propane-1,2-diol

Propane-1,2,3-triol (glycerol)

Propane-1,2,3-triyl triethanoate (glyceryl triacetate)

Procedure

Each tube should be sealed at one end, filled with one of the liquids except for an air bubble of length about 3 cm, and then firmly sealed at the other end with a well softened cork (or a teat turned inside out over the tube end). On inversion the rate of movement of the air bubbles will be seen to be related to the viscosity of the liquids.

Liquid	**Viscosity at 20 °C** /N s m^{-2}	**Surface tension at 20 °C** /N m^{-1}
propan-1-ol	0.0023	0.023
propane-1,2-diol	0.064	0.038
propane-1,2,3-triol	0.94	0.063
propane-1,2,3-triyl triethanoate	0.023	0.036

The interpretation is in terms of hydrogen bonding. With only one hydroxyl group dimers are expected; with two groups chains of molecules are possible; and with three groups cross links may be formed, giving a three-dimensional network. Each of these phenomena impedes the movement of the molecules and therefore decreases the rate of liquid flow.

If this argument is true, then a replacement of the hydroxyl groups by some other group should markedly increase the rate of flow. A further experiment with propane-1,2,3-triyl triethanoate can be carried out and the results compared with those for propane-1,2,3-triol, confirming the argument. It is also strikingly simple to shake bottles of the two liquids and compare their mobility.

It has been shown that provided the length of the air bubble is at least twice its diameter, the rate of movement is independent of the bubble size. However, the real situation is very complex and is suitable for study as a project; for example, in narrow tubes surface tension effects become more important than viscosity.

EXPERIMENT 9.3 (optional) The cleavage of some crystals

Each group of students will need:
Eye protection
Specimens of gypsum and anhydrite to test for hardness and cleavage
Penknives for cleaving gypsum

Procedure

The students should examine the specimens for hardness, by scratching with a fingernail and tapping with a metal object, and for cleavage, using a penknife.

The gypsum is found to be very soft and readily cleavable into flat plates, while the anhydrite is very hard and does not cleave.

These differences occur because of structural differences. In gypsum the Ca^{2+} and SO_4^{2-} ions are arranged in layers with water molecules on the surfaces of the layers, and the layers are held together by means of hydrogen bonds. Since the hydrogen bonds are weak the layers are easily separated. In anhydrite the attractions are directly between Ca^{2+} ions and SO_4^{2-} ions, forming a strong lattice; and there are no well-defined planes along which cleavage might occur.

Hydrogen bonding in living organisms

This material is presented so that students will appreciate that the hydrogen bond is not an academic curiosity. It has been necessary to understand its properties in order to interpret much chemical behaviour that is of biological importance.
In DNA, the hydrogen bonds link the nitrogenous bases at right angles to the axis of the helix.

Although hydrogen bonding helps stabilise the three-dimensional structure of proteins, van der Waals forces are also of great importance in maintaining the tertiary structure of proteins.

These examples are studied in more detail in the *Biochemistry* Special Study.

When all the material in this section has been discussed with students it is desirable to summarise the basic information about the hydrogen bond, concerning participating groups, bond length, and bond angle.

Answers to Topic 9 questions

Review questions

9.1

a Van der Waals forces only (1)
b Van der Waals only (1)
c Van der Waals and dipole–dipole attractions (1)
d Van der Waals, dipole–dipole and hydrogen bonds (1)
e Van der Waals and dipole–dipole (1)
f Van der Waals, dipole–dipole and hydrogen bonds (1)
g Van der Walls and dipole–dipole attractions (1)

Total 7 marks

9.2

a Butan-1-ol and 1-chloropropane (2)
b In butan-1-ol, van der Waals, dipole–dipole and hydrogen bonds (1)
In 1-chloropropane, van der Waals and dipole–dipole attractions (1)
In pentane, van der Waals forces only (1)

c

Compound	**Molar mass** /g mol^{-1}	**Number of electrons**	**Boiling point/°C**
butan-1-ol	74	42	117
1-chloropropane	78.5	42	46
pentane	72	42	36

(3)

d Hydrogen bonds strongest of three, van der Waals forces weakest. (2)

Total 10 marks

9.3

C > **D** > **A** > **B** (2)
C and **D** are polar; van der Waals forces greater in **C** because of its shape. (3)
A and **B** are non-polar; **A** will have higher boiling-point again because of shape influencing van der Waals forces. (3)

Total 8 marks

9.4

Heptane; greater van der Waals forces because of linear shape. (3)

Total 3 marks

9.5

a iii (2)
b i (2)
c i (2)
d iii (2)
e i (2)
f ii (2)

Total 12 marks

9.6

a Ar, Ne, He; decreasing number of electrons in atoms (2)
b Pentane, butane, propane; decreasing number of electrons (2)
c HF, HI, HCl. HF is hydrogen-bonded; HI has stronger van der Waals forces (more electrons) than HCl. (2)
d Hydrazine, ammonia, disilane; hydrazine can form twice as many H-bonds per molecule as ammonia; disilane is not H-bonded. (2)

Total 8 marks

9.7 **a** **i** Displayed formulae showing H-bond between H atom of one urea molecule and either O or N of another. (2)

ii Displayed formulae showing H-bond between H atom of urea and O atom of water. (2)

iii Displayed formulae showing H-bond between H atom of water and O or N atom of urea. (2)

(**ii** and **iii** can be either way round)

b **i** Urea 32; propan-1-ol 34 (2)

ii Urea 4.56 D; propan-1-ol 1.66 D (1)

iii More in urea because it has four H atoms available to form H-bonds and two atoms (N and O) which can ‘accept’ H-bonds; propan-1-ol only has one H atom available and one ‘acceptor’ O atom. (3)

iv Urea can form more H-bonds per molecule than propan-1-ol; it has a much higher dipole moment so has stronger dipole–dipole attractions; van der Waals forces will be similar (not much difference in number of electrons). (3)

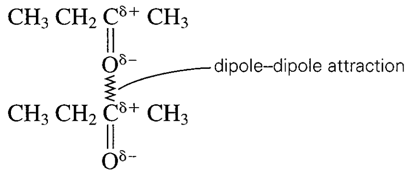
Total 15 marks

Examination questions

9.8 **a** **i** Dipole–dipole attractions (1)

ii Van der Waals forces (1)

b (2)



c Less area of contact between 2-methylbutane molecules because of shape, hence weaker intermolecular forces (may be shown in a diagram). (2)

Total 6 marks

9.9 **a** **i** Van der Waals forces (1)

ii Less area of contact between molecules of 2,2,4-trimethylpentane because of shape, hence weaker van der Waals forces (may be shown in a diagram). (2)

b **i** Stronger dipole–dipole attractions in octanoic acid because two electronegative oxygen atoms present

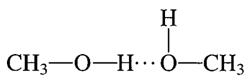
OR stronger van der Waals forces in octanoic acid because more electrons present (1)

ii Within the range 150–185 °C (1)

Octanal has van der Waals and dipole–dipole attractions; octane has only van der Waals OR octanoic acid has H-bonds as well. (1)

Total 6 marks

9.10 **a**



$$CH_3{-}O{-}H\cdots\overset{\overset{\displaystyle H}{|}}{O}{-}CH_3$$

(The O – H ··· O bond angle must be 180°) (1)

b **i** Water can form an average of two H-bonds per molecule but ethanol only one. (2)

ii Weaker van der Waals forces in methanol because it has fewer electrons. (2)

c H atoms not directly bonded to oxygen atoms (1)

Total 6 marks

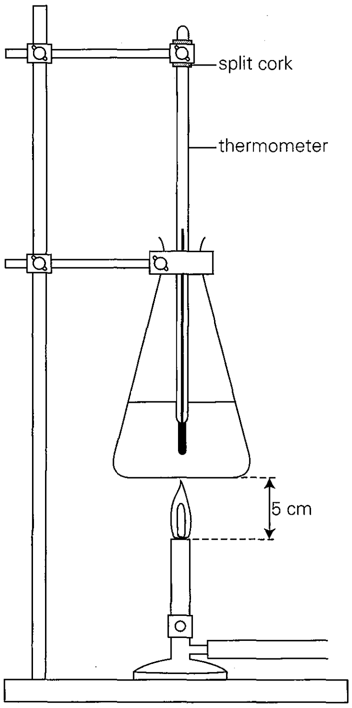
9.11	**a**	In a liquid there are intermolecular forces and energy is needed to break these bonds.	(2)
	b	Energy supplied = $1.5 \times 2 \times 60$ (kJ)	(1)
		(=180 kJ)	
		$\Delta H_{\text{vap}} = 180 \times \frac{18}{80} = 40.5$ or 41 kJ mol^{-1}	(2)
	c	**i** Axes correctly labelled, including units	(1)
		three points correctly plotted and joined (curve OR straight lines)	(1)
		ii Within range 18–18.6 kJ mol^{-1}	(1)
		iii Hydrogen bonds in water not taken into account when making prediction.	(1)
			Total 9 marks
9.12	**a**	Large number of electrons in poly(ethene) molecules	(1)
	b	Strength or high melting point	(1)
	c	Hydrogen bonds	(1)
	d	O—H bond polarised $O^{\delta-}$—$H^{\delta+}$	(1)
		so H atoms attracted to O in other molecules (or diagram)	(1)
			Total 5 marks

NUFFIELD ADVANCED CHEMISTRY TOPIC 9

9.1

ALTERNATIVE EXPERIMENT 9.3

Measuring the enthalpy change of vaporisation of water



Apparatus for Experiment 9.3

Assemble the apparatus shown in the diagram, with the conical flask empty. Remove the thermometer.

Move the Bunsen burner to one side, light it, adjust the air-hole to give a non-luminous flame, and adjust the gas supply until the flame is about 5 cm high. Replace the burner under the flask and make a final adjustment so that the tip of the flame just touches the bottom of the flask.

Remove the burner again and *do not alter the flame for the rest of the experiment.*

As accurately as you can, measure 240 cm^3 (240 g) water into the conical flask, using a measuring cylinder.

Replace the flask in the lower clamp of the apparatus and fix the thermometer in the upper clamp (CARE) so that the bulb is about 2 cm clear of the bottom of the flask.

Put the Bunsen burner under the flask so that the tip of the flame is under the centre of the flask. Read the temperature on the thermometer and at the same moment start timing.

Record temperatures (after stirring the contents of the flask) every half minute until the water is boiling steadily, and every two minutes afterwards.

Allow the water to boil for exactly 10 minutes.

Remove the Bunsen burner and allow the water to cool. Measure the volume of the remaining water as accurately as you can.

Calculation

1 Plot a graph of temperature (vertical axis) against time (horizontal axis). From the graph calculate the rate of temperature rise (in degrees per minute) from the start of the experiment until the water is boiling.

How many kilojoules of energy did the flame supply per minute?

2 How much energy was supplied by the flame during the time your water was boiling?

3 Work out the mass of water boiled away. How many moles of water were changed to steam?

4 How much energy was used to change one mole of water at the boiling point to steam?

TOPIC 10

Organic chemistry: halogenoalkanes

Introduction

This third topic of organic chemistry is a natural extension of the ideas developed in Topic 8. It is separated from it in order that the concept of bond polarisation could be developed in Topic 9.

Halogenoalkanes are first prepared by substitution reactions with alcohols. An understanding of nucleophilic substitution and elimination reactions result from an experimental investigation of halogenoalkanes.

Contents

Timing		Students' Book
10.1	1 hour	pages 226–7
10.2	5 hours	pages 228–33
10.3	Homework	pages 234–5
Total about $1\frac{1}{2}$ weeks		

10.1 Physical properties of halogenoalkanes – occurrence and uses; the naming of halogenalkanes, mass spectra, the importance of bond strength and bond polarity.

10.2 Reactions of halogenoalkanes – preparation from primary and tertiary alcohols; substitution and elimination reactions; nucleophiles, attacking and leaving groups; factors influencing the reactivity of halogenoalkanes.

10.3 Background reading: anaesthetics.

Objectives

1 To develop an understanding of organic reactions with specific reference to substitution and elimination.

2 To develop an appreciation of the practical procedures used in the preparation of halogenoalkanes from alcohols.

3 To develop a knowledge of the reactions of halogenoalkanes.

4 To show how bond energies and bond polarisation can be used in discussing reaction mechanisms in organic chemistry.

10.1 Physical properties of halogenoalkanes

Timing About 1 hour will be needed

Suggested treatment

This section develops the structure and nomenclature of the halogenoalkanes and considers the factors responsible for their reactivity.

As an introduction to the halogenoalkanes, the *Students' Book* begins this section by discussing their nomenclature, occurrence, and uses, and some physical properties including bond energies, dipole moments, and mass spectra.

ANSWER

Question, page 227

Nucleophiles are likely to attack $C^{\delta+}$ in halogenoalkanes.

The mass spectrum of 1-chlorobutane is given in the *Students' Book* in figure 10.2 and below.

In the mass spectrum the following peaks can be identified:

$C_4H_9{}^{37}Cl^+$	94.0
$C_4H_9{}^{35}Cl^+$	92.0
$C_4H_9{}^+$	57.1
$C_4H_8{}^+$	56.1
$C_3H_7{}^+$	43.1
$C_3H_5{}^+$	40.9
$C_2H_5{}^+$	29.0

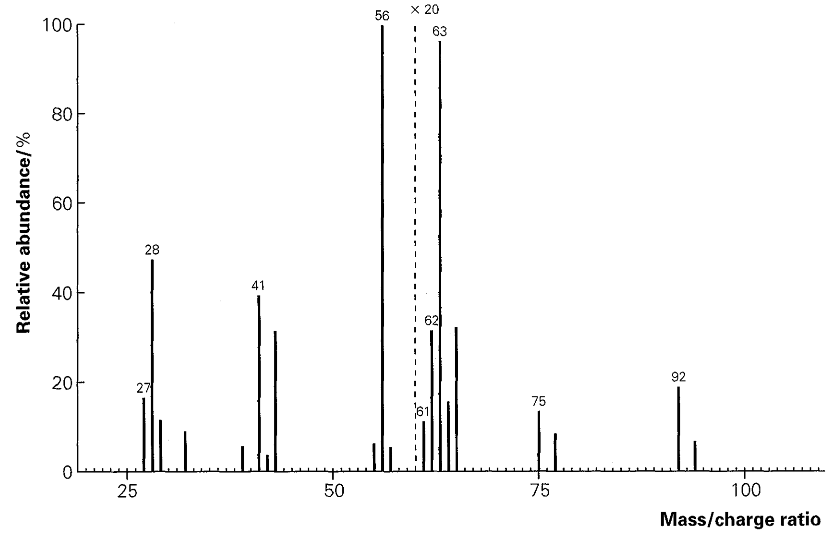


Figure 10.1 The mass spectrum of 1-chlorobutane

ANSWERS

Questions, page 227

1 There are two isotopes of chlorine: chlorine-35 and chlorine-37, so there are two peaks for any species containing chlorine atoms.

2 The chlorine-35 isotope is three times as abundant as the chlorine-37 isotope.

10.2 Reactions of halogenoalkanes

Timing About 5 hours

Suggested treatment

This section is developed in the following way:

1 Halogenoalkanes are prepared from a primary or a tertiary alcohol.

2 The reactions of the halogenoalkanes are studied experimentally.

3 The reactions of the halogenoalkanes are summarised.

EXPERIMENT 10.2a Preparation of halogenoalkanes from alcohols

Students should carry out one of the two experiments.

1 A halogenoalkane from a primary alcohol

HAZARDS

Several of the products have associated hazards: Bromoethane is harmful; bromine (by-product) is very toxic and corrosive; ethoxyethane and ethene (by-products) are both extremely flammable.

Each group of students will need:
Eye protection
Apparatus for distillation with a pear shaped flask, 50 cm^3 (see figure 10.2)
Dropping pipette
Measuring cylinder, 5 cm^3
Weighing boat
Balance, to weigh to ±0.1 g

Access to:
Ice
Ethanol, 5 cm^3 HIGHLY FLAMMABLE
Potassium bromide, 6 g
Concentrated sulphuric acid, 5 cm^3 CORROSIVE

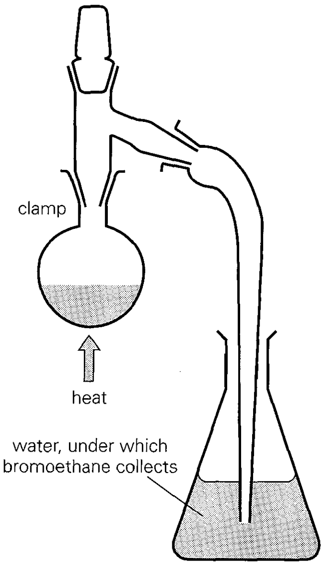


Figure 10.2 Apparatus for the preparation of a halogenoalkane

Procedure

Full details of the experiment are given in the *Students' Book*. Students should be aware of the hazards involved in the experiment and should ensure that the glass joints are tight before heating commences. The bromoethane will be seen as clear or milky globules at the bottom of the conical flask, evidence that a new compound has been formed.

In their notes, students should be able to write the equation:

$$C_2H_5OH + HBr \longrightarrow C_2H_5Br + H_2O$$

and indicate that this C—O bond is broken in ethanol.

2 A halogenoalkane from a tertiary alcohol

HAZARDS

2-chloro-2-methylpropane (product) is highly flammable and all halogenoalkanes should be treated as harmful.

Each group of students will need:
Conical flask, 250 cm^3 or larger, with stopper
Separating funnel, 100 cm^3 or larger, with stopper
Beaker, 250 cm^3 for discarded layers
Conical flask, 50 cm^3, with stopper
Filter funnel, small
Apparatus for distillation with 50 cm^3 pear-shaped flask and 0–100 °C Thermometer (see figure 10.3)
Measuring cylinder, 25 cm^3
Measuring cylinder, 100 cm^3

Access to:
Calcium chloride, powdered anhydrous, 6 g IRRITANT
Concentrated hydrochloric acid, 70 cm^3 CORROSIVE
2-methylpropan-2-ol, 20 cm^3 HIGHLY FLAMMABLE AND HARMFUL
0.1 M sodium hydrogencarbonate, 40 cm^3
Sodium sulphate, anhydrous 1 g
Cotton wool
Anti-bumping granules
Balance, to weigh to ±0.1 g

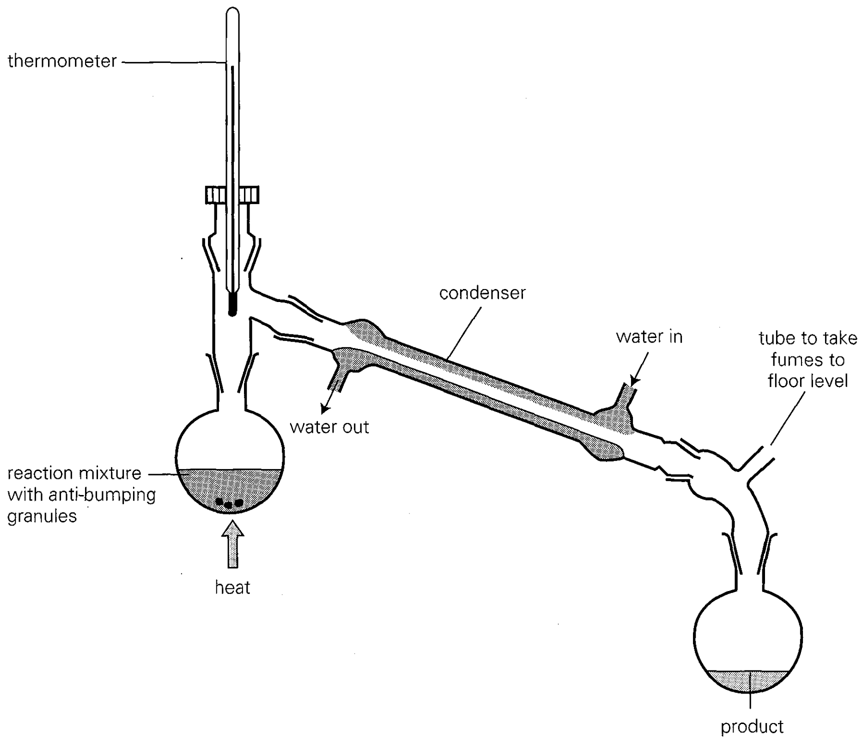


Figure 10.3 Apparatus for distillation

Procedure

Full instructions for the small-scale laboratory preparation of 2-methyl-2-chloropropane are given in the *Students' Book.* If they wish, students could weigh the tertiary halogenoalkane into the flask for greater accuracy, rather than use a measuring cylinder. The purification procedure should be discussed with the students, as well as the reasons for the yield being less than theoretical. With care a yield of 85% is possible.

Students could save their product for use in Experiment 10.2b, parts 2 and 4.

EXPERIMENT 10.2b The reactions of the halogenoalkanes

HAZARDS

All the halogenoalkanes should be treated as flammable, with harmful vapours. The products are flammable, and should be disposed of in a solvents container for chlorinated organic waste.

Each group of students will need:
Eye protection
Test tubes and rack
Combustion spoon, or equivalent
Corks for test tubes, 3
Delivery tube for gas collection and Bunsen valve
Small trough (ice cream tubs are suitable)
Dropping pipette
250 cm^3 beaker to act as hot water bath
Access to:
1-bromobutane, a few drops (see HAZARDS)
1-chlorobutane, a few drops
2-chlorobutane, a few drops
2-chloro-2-methylpropane, 1 cm^3
1-iodobutane, a few drops
Bromine water
20% potassium hydroxide in ethanol, 3 cm^3 CORROSIVE, HIGHLY FLAMMABLE
0.02 M silver nitrate
2 M nitric acid, 2 cm^3 CORROSIVE
Full-range Indicator paper
Ceramic fibre, a small tuft
Ethanol, 12 cm^3 HIGHLY FLAMMABLE

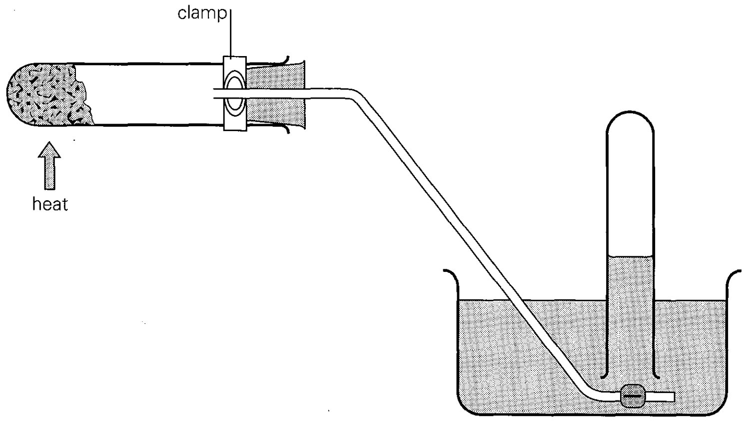


Figure 10.4 Apparatus for part 4

Procedure

Full instructions are given in the *Students' Book*. The following notes may be helpful.

1 Combustion

The flames should be yellow (luminous) and not too sooty.

2 Reaction with aqueous alkali

The chloro compound does not react as readily as the bromo or iodo compounds (but it is much cheaper).

3 A comparison of halogenoalkanes

The order of precipitation is

a *first*, iodo; *second*, bromo; *third*, chloro

b *first*, tertiary; *second*, secondary; and *third*, primary. The chloro compounds do not give heavy precipitates.

4 Reaction with alcoholic alkali

A reasonable yield of alkene should be achieved. Students should be advised to heat gently, otherwise an oily film of unchanged 2-chloro-2-methylpropane may appear in the trough.

An interpretation of the halogenoalkane experiments

A full interpretation of the reactions of halogenoalkanes requires the consideration of kinetic and stereochemical evidence; this is not considered appropriate at this stage of the course. Further consideration is given to these reactions in Topic 11 on kinetics. For now, the emphasis is intended to be on the idea of a nucleophilic attacking group, and the nature of substitution and elimination reactions. The substitution and elimination reactions are in competition with each other:

$$(CH_3)_3CCl \xrightarrow[20\%\ H_2O]{KOH\ in\ 80\%\ CH_3CH_2OH} \underset{80\%}{(CH_3)_3COH} + \underset{20\%}{(CH_3)_2C{=}CH_2}$$

and the relative amounts of products are affected by a change in temperature as well as a change in solvent.

The substitution reaction in experiment 3 is catalysed by Ag^+ ions and possible attacking groups are NO_3^- ions, OH^- ions, or H_2O molecules. For this particular reaction the bond strengths appear to be a better guide than the polarity of the bonds. This should serve to warn students that the interpretation of organic reactions is complex and should be based on the study of a large number of reactions in different conditions. The few cases that students study can only show them possibilities.

Reactions of the halogenoalkanes

An account of the reactions of halogenoalkanes together with a short description of the reaction of alcohols with hydrogen bromide is given in the *Students' Book.* At the end of this section students should draw up a chart to record the chemical properties of the halogenoalkanes together with appropriate reaction conditions. An opportunity should be taken to test the students' knowledge of these reactions at a suitable point.

10.3 Background reading: anaesthetics

Timing This may be set for homework

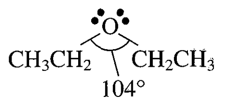
Students are asked to read an account of the properties required in molecules to produce anaesthesia and of the development of modern anaesthetics. They are asked to answer questions based upon the passage and to summarise the key ideas. Traditional names are used for the compounds concerned since these will be familiar in the medical context.

ANSWERS TO THE BACKGROUND READING QUESTIONS

1 Fluorine atoms have more electrons than hydrogen atoms, so you would expect stronger van der Waals forces between molecules containing fluorine atoms than those containing hydrogen atoms. Hence you would expect those containing fluorine atoms to have a higher boiling point.

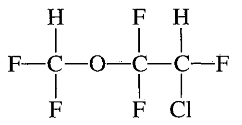
2 Hydrogen atoms in alkanes are converted into water when they burn, but halogens do not combine with oxygen when alkanes containing halogen atoms burn.

3



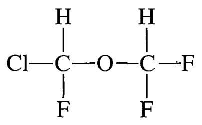
$CH_3CH_2OCH_2CH_3$

4



$F{-}CHF{-}O{-}CF_2{-}CHCl{-}F$

enflurane



$Cl{-}CHF{-}O{-}CHF{-}F$

isoflurane

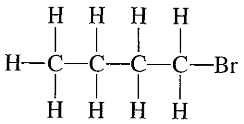
5 Key points to include in the summary
An anaesthetic should:

- produce loss of consciousness
- be potent – produce loss of consciousness at a low level of concentration
- be of low boiling point because this increases potency
- be unreactive – not converted to other compounds metabolised in the liver to toxic products
- have low flammability (to reduce risk of explosion)
- not cause hepatitis.

Answers to Topic 10 questions

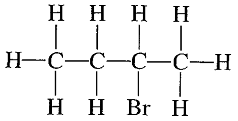
Review questions

10.1



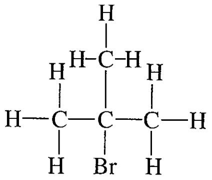
$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{Br} \\ & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

(1); 1-bromobutane (1)

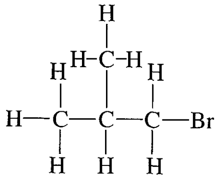


$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{Br} & & \mathrm{H} & & \end{array}$$

(1); 2-bromobutane (1)



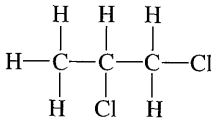
(1); 2-bromo-2-methylpropane (1)



(1); 1-bromo-2-methylpropane (1)

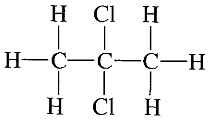
Total 8 marks

10.2



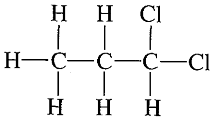
$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{Cl} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{Cl} & & \mathrm{H} & & \end{array}$$

(1); 1,2-dichloropropane (1)



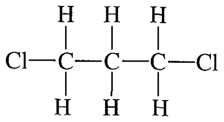
$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{Cl} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{Cl} & & \mathrm{H} & & \end{array}$$

(1); 2,2-dichloropropane (1)



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{Cl} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{Cl} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

(1); 1,1-dichloropropane (1)



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{Cl} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{Cl} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

(1); 1,3-dichloropropane (1)

Total 8 marks

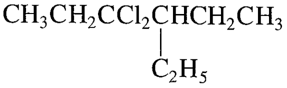
10.3

a $CH_3C(CH_3)BrCH_3$ (1)

b $CH_2ClCH_2CHClCH_3$ (1)

c $CH_3CHBrCHICH_2CH_3$ (1)

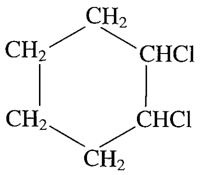
d



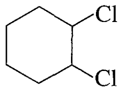
$$\underset{\displaystyle C_2H_5}{CH_3CH_2CCl_2\underset{|}{C}HCH_2CH_3}$$

(1)

e



or



(1)

Total 5 marks

10.4

a	1,2-dichloroethane	(1)
b	1-bromo-2-chloroethane	(1)
c	2-iodobutane	(1)
d	1-bromo-2-methylbutane	(1)
e	Chlorocyclopentane	(1)

Total 5 marks

10.5

a	Parent-ion is the ion produced from the complete molecule ($C_2H_6O^+$ here); molar mass	(2)
b	$C_2H_5O^+$	(1)
	$C_2H_5^+$	(1)

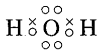
Total 4 marks

10.6

a	Bromine consists of two isotopes, mass numbers 79 and 81, so $C_2H_5Br^+$ will produce separate peaks for each isotope.	(2)
b	Equal heights means same number of ions for both mass/charge ratios. Average M/e = 109 (which is molar mass)	(2)
c	*Book of data* confirms molar mass is 109.	(1)

Total 5 marks

10.7

a		(2)
b		(2)
c		(2)
d	It has unshared electron pairs which can form bonds by attacking a positive centre.	(2)
e	Electrophile	(1)

Total 9 marks

10.8 CN^-; OH^-; H_2O; NH_3; Br^- (1 mark each)

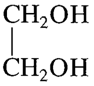
Total 5 marks

10.9

a	CH_3CH_2OH	(1)
b	OH^-	(1)
c	Br^-	(1)
d	Substitution	(1)
e	Nucleophile	(1)

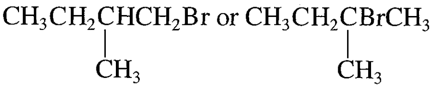
Total 5 marks

10.10

a	$CH_3CH_2CH_2NH_2$		1-aminopropane	(2)
b	$CH_3CHOHCH_3$		propan-2-ol	(2)
c	$CH_3CH{=}CHCH_3$	or	$CH_3CH_2CH{=}CH_2$	(1)
	but-2-ene	or	but-1-ene	(1)
	(Name consistent with formula)			
d	CH_3CH_2OH		ethanol	(2)
e	 $\begin{array}{l}CH_2OH\\ \mid\\ CH_2OH\end{array}$		ethanediol	(2)

Total 10 marks

10.11

a	$CH_3CH_2CH_2CH_2Br$	aqueous KOH	reflux	(3)
b	$CH_3CHBrCH_3$	aqueous KOH	reflux	(3)
c	$CH_3CH_2CH_2Br$ or $CH_3CHBrCH_3$	KOH in ethanol	heat	(3)
d	$CH_3CH_2CHBrCH_3$	KOH in ethanol	heat	(3)
e	 $CH_3CH_2\underset{\displaystyle CH_3}{\underset{\mid}{C}}HCH_2Br$ or $CH_3CH_2\underset{\displaystyle CH_3}{\underset{\mid}{C}}BrCH_3$	KOH in ethanol	heat	(3)

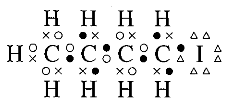
Total 15 marks

Examination questions

10.12

a $C_4H_9I(g) \longrightarrow 4C(g) + 9H(g) + I(g)$
$4C(s) + 4\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s)$ (2)
$\Delta H_{at} = (4 \times 716.7) + (9 \times 218) + 106.8 - (-52)$ (1)
$(= +4987.6\ \text{kJ mol}^{-1})$

b **i** (2)

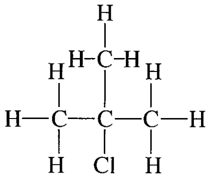


ii $E(C—I) = \Delta H^{\ominus}_{at} - 9E(C—C) - 3E(C—H)$ (2)
$= 4987.6 - (9 \times 413) - (3 \times 347)$
$= 229.6$ or $+230\ \text{kJ mol}^{-1}$ (1)

c **i** Yellow precipitate (1)
ii $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$ (2)
iii Butan-1-ol (1)

d C—Cl bond much stronger than C—I bond (2)

e **i** (1)



ii White precipitate (1)
iii Two sensible points, e.g. C—Cl bond weaker in branched compounds, tertiary carbonium ion more stable than primary. (2)

Total 18 marks

10.13

a **i** Butan-1-ol (1)
ii $C_4H_9Br + H_2O \longrightarrow C_4H_9OH + HBr$ (2)
iii (Pale) yellow (1)
iv Silver chloride (1)
$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ (2)
v Precipitate dissolves (1)
More soluble/complex compound formed (1)
vi C—I bonds weaker than C—Cl so more easily broken (2)

b **i** Test tube containing reagents and ceramic fibre, heat specified (1)
fitted with suitable delivery tube (1)
to collect gas over water (1)
ii Bromine (water/solution) OR acidified $KMnO_4$ (1)
Orange to colourless OR pink/purple to colourless (1)

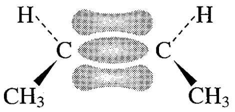
Total 16 marks

10.14

a 2-methylbutan-1-ol or 3-methylbutan-1-ol or 2,2-dimethylpropanol (1)
Correct structural formula (1)

b **i** Apparatus for reflux with addition, well drawn and fully labelled (2)
ii Bromine (1)
Oxidation of HBr/Br$^-$ by sulphuric acid (1)
iii Molar masses 88 g ($C_5H_{11}OH$) and 151 g ($C_5H_{11}Br$)
1 mole $C_5H_{11}OH$ gives 1 mole $C_5H_{11}Br$
so mass required $= \frac{88}{151} \times \frac{100}{60} \times 15 = 15$ g (2SF) (2)

c (2)



Total 10 marks

TOPIC 11

How fast? Rates of reaction

Introduction

Students will have had some previous qualitative experience of the dependence of rates of reaction on the concentration of reagents, temperature, state of subdivision of the particles and the presence or absence of catalyst. Some may also have had practical experience of following the course of a reaction quantitatively by measuring a decrease of mass of a reactant or an increase in volume of a gaseous product.

This topic extends students' knowledge of chemical kinetics by considering measurements and describes rates of reaction in a more mathematical context. It also introduces students to the use of reaction kinetics for interpreting mechanisms in terms of rate-determining steps.

A study of catalysis is also undertaken.

Content

Timing		Students' Book
11.1	1 hour	pages 242–4
11.2	5 hours	pages 244–50
11.3	2 hours	pages 251–6
11.4	3 hours	pages 256–9
11.5	4 hours	pages 259–61
11.6	Homework	pages 262–4
Total about 3 weeks		

11.1 Rates of reactions: why study them? – factors which may influence rates of reaction; measurement of rate by rate of change of concentration; rate equations; order of reaction; the rate constant.

11.2 Measuring rates of reaction – problems involved in measuring rates; effect of concentration on rate of reaction by experiment; deduction of order of reaction; half-life; methods of following a reaction; kinetics of the reaction between iodine and propanone in acid solution.

11.3 Kinetics and reaction mechanism – rate determining steps; hydrolysis of primary and tertiary halogenoalkanes; S_N1 and S_N2 mechanisms.

11.4 The effect of temperature on the rate of reaction – measurement of activation energy by experiment; collision theory of reaction kinetics; the Arrhenius equation.

11.5 Catalysis – effect of catalysts on activation energy, homogeneous catalysis; experimental study of some catalysts; study task on heterogeneous catalysis; *investigation of the rate of reaction of magnesium with acid.*

11.6 Background reading: light and chemical change.

Objectives

1 To study the factors which influence rates of reaction.

2 To study the range of practical procedures which can be used to provide information for calculating rates of reaction.

3 To show how kinetic studies provide evidence in support of reaction mechanisms.

4 To introduce a method of measuring the activation energy of a reaction and to link this quantity to a simple treatment of the collision theory of reaction kinetics.

5 To gather information on catalysts and to introduce a theoretical understanding of catalysis.

11.1 Rates of reactions: why study them?

Timing About 1 hour

Suggested treatment

With the aid of some directed questioning from the teacher, the students should be able to recall, or suggest, factors which are likely to influence the rates of reactions. A list of such factors is given in the *Students' Book.*

The students are about to embark on a study of a fairly detailed subject which will probably appear to many to be more physical and mathematical than chemical. It is important at the outset to explain why they will be going to the trouble of *measuring* reaction rates rather than being content with a qualitative knowledge. There is no need to labour the point – what is given in the *Students' Book* should be enough to establish a strategy for the topic.

The general idea of a rate equation is first introduced, and each term in it is discussed. The rate equation is an equation showing how the rate of change of concentration of a substance A, symbol r_A, depends upon the concentration of the various substances involved in the reaction.

When discussing this equation, it is particularly important to see that the students gain a clear understanding of the definitions of the various terms. Although the term *rate of reaction* is perfectly acceptable in a general sense, and when referring to purely qualitative observations, teachers should note that it should generally be avoided for quantitative observations, at least at this level, so that any possible ambiguity is avoided. The rate equation does not describe the 'rate of the reaction' but the rate of change of concentration of one named substance taking part in the reaction. It is clearly important to state to which substance the equation refers.

The *Students' Book* gives a typical rate equation:

$$r_A = k[A]^a[B]^b[C]^c$$

Each term in this rate equation is then defined. When discussing the definitions, bear in mind that students do not always realise unaided that one of the implications of a rate equation of the form

$$r_A = k[A][B]$$

is that increasing the concentrations of both A and B by a factor of two increases r_A by a factor of four.

The idea that the rate constant k is a measure of the rate of change of concentration of substance A, r_A, at unit concentration of each of the substances appearing in the rate equation needs a little stress at this point, because it is implied in the discussion of the results of Experiment 11.4.

Students should be given practice in working out for themselves the units of rate constants for particular reactions as they progress through the topic.

11.2 Measuring rates of reaction

Timing About 5 hours will be needed

Suggested treatment

In this section, students carry out two experiments in which they measure rates of reaction. The first reaction to be studied is that between hydrochloric acid and calcium carbonate. A discussion of the various experimental methods available for measuring rates then follows. The second experiment is then undertaken, measuring the rate of the reaction between iodine and propanone in acid solution.

Two methods are given for each experiment.

EXPERIMENT 11.2a

The kinetics of the reaction between calcium carbonate and hydrochloric acid

Each group of students will need:

Method 1

Measuring cylinder, 20 cm^3
Cotton wool
Conical flask, 100 cm^3
Marble, acid washed chips 1–1.5 g each, 10 g
1 M hydrochloric acid, 20 cm^3 IRRITANT
Stop clock
Balance, to weigh to ±0.01 g

Method 2

Measuring cylinder, 10 cm^3
Test tube with side-arm, 150 × 25 mm, or equivalent
Glass gas syringe, 100 cm^3
Rubber stopper to fit test tube
Rubber connecting tubing
Marble, as in Method 1
1 M hydrochloric acid, 10 cm^3 IRRITANT
Stop clock

Procedure

The marble chips need to be washed briefly in dilute hydrochloric acid to remove any surface powder. They should then be rinsed in pure water and allowed to dry at room temperature.

This is a simple experiment which gives rapid results. Two versions are offered. Method 1, using a direct-reading balance, could be done as a teacher demonstration with students assisting, if there are not sufficient balances available. Method 2 is suitable for students themselves.

Full details are given in the *Students' Book*. It is important that the acid should be saturated with carbon dioxide before readings are begun. In Method 2, the maximum volume of carbon dioxide obtainable from 10 cm^3 of 1 M hydrochloric acid is about 120 cm^3, so the timing must not be started too early or the syringe will be overfilled. Students may need advice on the choice of sensible scales and need reminding to label axes and give units in a conventional way. Sample results are shown in the graphs in figure 11.1.

Students are asked to plot the results on similar axes, and compare their results with types of graphs that would be expected from zero, first, and second order reactions (see figure 11.4 in the *Students' Book*). They should find that the rate of change of concentration of hydrochloric acid is first order with respect to hydrochloric acid.

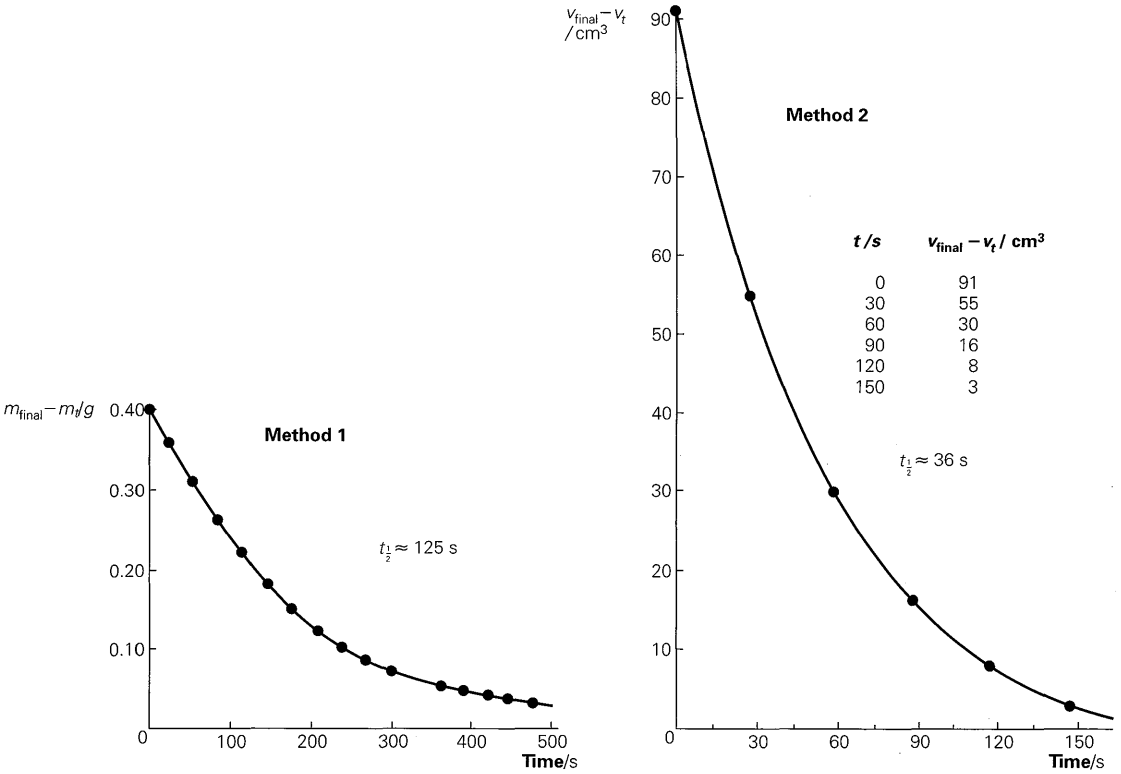


Figure 11.1 Sample results for Experiment 11.2a

After the instructions and discussion of this experiment, the *Students' Book* contains a survey of methods of following reactions. This section could be set for homework.

EXPERIMENT 11.2b

The kinetics of the reaction between iodine and propanone in acid solution

Each group of students will need:

Method 1

Eye protection
7 conical flasks
Burette, 50 cm³, and burette stand
White tile
Funnel, small
Pipette, 10 cm³, and safety filler
4 measuring cylinders, 50 cm³, 2 × 25 cm³, 10 cm³
0.02 M iodine in potassium iodide solution, labelled A, 50 cm³ IODINE SOLID IS HARMFUL
1 M propanone solution (in water), labelled B, 25 cm³ PROPANONE IS HIGHLY FLAMMABLE
1 M sulphuric acid, labelled C, 25 cm³ IRRITANT
0.5 M sodium hydrogencarbonate, labelled D, 150 cm³
0.010 M sodium thiosulphate, labelled E, 200 cm³
1% starch solution, 10 cm³
Stop clock

Method 2

Conical flask, 100 cm³
4 test tubes
Stop clock

Access to communal burettes with 'drip trays' containing:
2 M hydrochloric acid, 100 cm³ per group of students IRRITANT
2 M propanone, 40 cm³ per group of students HIGHLY FLAMMABLE
0.01 M iodine in potassium iodide solution, 20 cm³ per group of students IODINE SOLID IS HARMFUL

Procedure

For a second experiment on rates of reaction, the iodination of propanone is suggested. Again, two methods are offered. Method 1 illustrates a different method of following a reaction from that used in Experiment 11.2a, and it is used at this point because the order of the reaction with respect to iodine turns out to be zero. This point is followed up in the subsequent discussion. Method 2 illustrates an 'initial rate' method of arriving at orders of reaction. Although less sophisticated in technique, Method 2 has the advantage of finding orders with respect to all three reactants, and is quicker than Method 1.

Students should use both methods. If time is short, half the class could use one method and half the other method, the results shared and discussed by the whole class.

Full details for both methods are given in the *Students' Book.* It will probably be helpful to give the students some explanation before they begin. In particular, the sampling technique used in Method 1 needs to be emphasised, and the need for 'quenching' the reaction before titration, in this case by neutralising the acid catalyst, should be discussed.

In Method 2 it is important that the volumes are measured as accurately as possible, because of the small quantities that are used. This method is particularly impressive if all four runs are done simultaneously, which is quite possible if students work in groups.

Sample results (Method 2)

	Run A	**Run B**	**Run C**	**Run D**
Time for colour to disappear/s	115	264	243	58
Rate	4/115 =0.035	4/264 =0.015	4/243 =0.016	2/58 =0.034

ANSWERS

Questions, page 250

1 Water is added to some of the mixtures to ensure that the total volume of all four mixtures are the same. In this way the concentration of each reactant is proportional to the volume of solution that is used.

2 If the concentration of acid is halved, the rate of change of concentration of iodine is also halved.

3 The reaction is first order with respect to hydrogen ions.

4 The reaction is first order with respect to propanone, but zero order with respect to iodine.

11.3 Kinetics and reaction mechanism

Timing About 2 hours will be needed

Suggested treatment

The mechanistic implications of Experiment 11.2b are next discussed. A full account is given in the *Students' Book.* The discussion should not be rushed as this subject is often one which students find difficult.

The section ends with a discussion of the S_N1 and S_N2 mechanisms for the hydrolysis of halogenoalkanes, described in the *Students' Book* as CASE A, CASE B, and CASE C.

ANSWERS

CASE A, page 253

1 These results might have been obtained by removing portions of the reaction mixture at measured time intervals, quenching them by rapid cooling in ice, and quickly titrating them with acid of known concentration.

2 It is a second order reaction, as the half-life increases with time.

3 As measured in this experiment, this is an *overall* order, since neither of the two reactants is in large excess.

4 The S_N2 mechanism is in operation in this case. The evidence shows that the reaction is second order; the S_N1 mechanism demands first order kinetics overall.

CASE B, page 254

1 a If the concentration of 1-bromobutane is doubled, the rate of change of concentration of 1-bromobutane also doubles.

b The reaction is first order with respect to 1-bromobutane.

2 a If the concentration of hydroxide ion is increased five times, the rate of change of concentration of 1-bromobutane also increases five times.

b The reaction is first order with respect to hydroxide ions.

3 Since the rate of change of concentration of 1-bromobutane depends on the concentration of hydroxide ions, the S_N2 mechanism operates in this case.

CASE C, page 254

In Case C, students first interpret some conductivity data obtained from a study of the hydrolysis of 2-chloro-2-methylpropane and find that there are not sufficient data to determine the overall order of reaction. They then analyse some results of the hydrolysis of 2-bromo-2-methylpropane obtained by varying the concentration of hydroxide ions as well as the halogenoalkane. The graphs are based on the experimental work of Dr Rob Dickinson, using 'Datadisk'.

Hydrolysis of 2-chloro-2-methylpropane using water

1 With 0.5 cm^3 2-chloro-2-methylpropane in 15 cm^3 of solvent the rate of reaction is proportional to 35 microsiemens min^{-1}.

With 0.1 cm^3 2-chloro-2-methylpropane in 15 cm^3 of solvent the rate is proportional to 21 microsiemens min^{-1}. Students may find it difficult to estimate the initial rate as the graphs have slight curvature. The figures quoted here are based on the gradients as measured over the first 5 minutes of reaction.

2 Doubling the concentration of 2-chloro-2-methylpropane approximately doubles the rate of reaction.

3 The reaction is first order with respect to 2-chloro-2-methylpropane.

4 This is only the order with respect to 2-chloro-2-methylpropane.

5 There is insufficient information to distinguish which mechanism is occurring as the volume of water (7.5 cm^3) in the mixture is an excess. So we do not know the effect of changing the concentration of the nucleophile.

Hydrolysis of 2-bromo-2-methylpropane using sodium hydroxide solution

1 Doubling the concentration of hydroxide ions doubles the time for the indicator to change colour. This means that in the same time, the same amount is produced.

2 Increase of hydroxide ion concentration has no effect on the rate of change of concentration of 2-bromo-2-methylpropane.

3 The order of the reaction with respect to hydroxide ions is zero.

4 The S_N1 mechanism operates in this case, since the reaction is first order overall.

11.4 The effect of temperature on the rate of reaction

Timing About 3 hours will be needed

Suggested treatment

The section is developed in the following way:

1. Students carry out an experiment to collect data which provides information for rate determinations at different temperatures.
2. The collision theory of reaction kinetics is introduced and used to provide a theoretical approach to activation energy.
3. The Arrhenius equation is introduced.

EXPERIMENT 11.4 The effect of temperature on the rate of a reaction

Each group of students will need:
Eye protection
Beaker, 400 cm^3
2 boiling tubes, 150 × 25 mm
Labels
2 thermometers, 0–110 °C (one for each tube)
2 measuring cylinders, 10 cm^3
Stop clock
Small piece of plain white paper
Sticky tape
Scissors
0.10 M sodium thiosulphate, 100 cm^3
0.5 M hydrochloric acid, 100 cm^3

Procedure

Full details are given in the *Students' Book*. The following points should be emphasised when introducing this experiment.

1. Two measuring cylinders should be used. They should be labelled, one for each solution, and the two should not be confused. If they are, sulphur precipitates will start to form in them, making the experimental results invalid.
2. Similarly, the test tubes should be labelled, **A** and **B**, so that the same one can be kept for the same solution in each run of the experiment.
3. Test tube **A** should be rinsed thoroughly with water between runs. If this is not done, the acid left over from the previous run will react with the new portion of sodium thiosulphate solution whilst it is being brought up to the required temperature.
4. Careful temperature control is necessary.

Some students may have performed an experiment similar to this in their pre-A-level science course. This experiment however is a rather more sophisticated version of the practical technique that they may have used earlier.

This may be the first time that students have encountered natural logarithms. The mathematics appendix should be useful here.

Teachers should note that when completing the table, students enter the time, t, in seconds, and then work out the rate ($= 1/t$) in s^{-1}. Finally they enter the logarithm of the rate, ln(rate). Strictly speaking one can only take logarithms of dimensionless quantities; one cannot take logarithms of quantities with units. To get around this difficulty, the trick is to divide each rate by 1 second^{-1}, thus preserving the numerical value but removing the units. The *Students' Book* does not mention this complication.

Sample results are shown on the graph, figure 11.2.

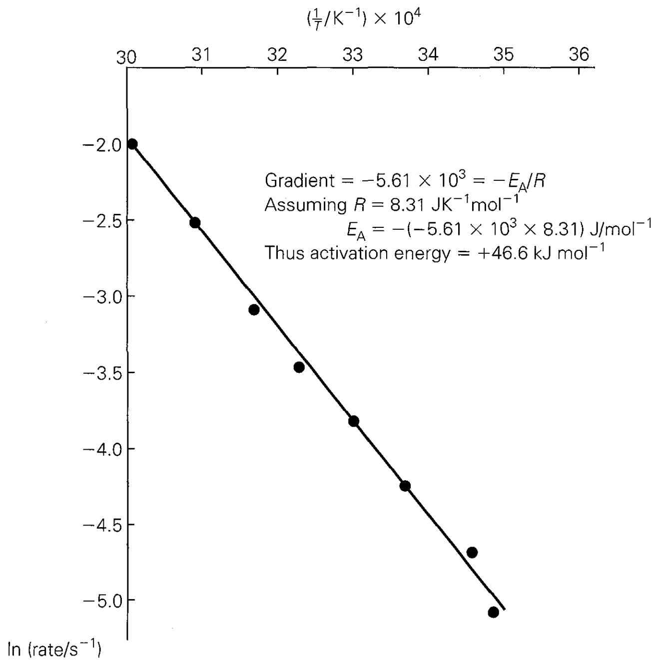


Figure 11.2 Activation energy of the thiosulphate–acid reaction: sample results

The collision theory of reaction kinetics

It is not intended that students should take the study of the collision theory of reaction kinetics any further than the treatment that is given in the *Students' Book*; it is enough for them to understand broadly what is meant by activation energy.

At the end of this section students are asked to calculate the activation energy of the reaction they studied in Experiment 11.4 by measuring the gradient of the graph. They will need to understand that the graph has a negative gradient, but since gradient = E_A/R, E_A will have a positive value. The gas constant, R, will be unfamiliar to most students, but they can simply be directed to find its value in table 1.6 in the *Book of data*. The final value of E_A should be given to a sensible number of SF: two, or at most three. Further examples of such calculations should be given in order to reinforce the idea involved.

For a fuller treatment of collision theory teachers should consult a textbook on physical chemistry.

The Arrhenius equation

Students should know the meaning of the symbols, but do not have to use the equation in its exponential form.

The large increase in the number of collisions with the minimum energy for reaction as the temperature rises is explained by reference to a graph showing the distribution of energy amongst molecules at different temperatures (figure 11.10 in the *Students' Book*).

11.5 Catalysis

Timing About 4 hours will be needed

Suggested treatment

The teaching of catalysis is difficult to place in any chemistry course because if all the ideas are to be dealt with at one time, it must be left as late as possible. If the suggested order of topics has been followed, students will not so far have studied electrode potentials or the transition elements. It is not therefore possible for them to complete their study of catalysis at this point, nor should they be left with the impression that this is the only place on the course where the subject is discussed.

The principle advance that is made at this stage is the introduction of the idea that catalysts provide reaction pathways of lower activation energy than that of the uncatalysed reaction. An example of this is given in detail in the *Students' Book.*

The section is developed in the following way:

1 A consideration in general terms of how catalysts are able to increase the rate of reaction.

2 An experimental study of a variety of catalysed reactions, including an enzyme catalysed reaction.

3 A study task which introduces students to the processes of adsorption and desorption in heterogeneous catalysis.

Introduction to catalysis

The function of a catalyst in providing a route of lower activation energy from reactants to products should be discussed, as well as the meaning of homogeneous and heterogeneous catalysis. Figure 11.13 in the *Students' Book* illustrates the relationship between reactants, products, and activated complexes. It should be noted that in a reaction profile there may be several activated states for both the catalysed and uncatalysed reactions. An activated complex is usually a theoretical situation in which some bonds are half broken and others are half formed. An activated complex is not a true intermediate. A true intermediate is relatively more stable than the activated complexes and its presence can often be deduced from spectroscopic, cryoscopic and kinetic evidence.

Students' attention should be drawn to table 6.2 in the *Book of data* which provides examples of activation energies for a number of catalysed and uncatalysed reactions.

EXPERIMENT 11.5 A study of some catalysts

HAZARDS

Biological materials should be treated as irritant and disposed of in an approved manner.

Each group of students will need:
Eye protection
Test tubes and rack
Dropping pipettes
Beaker, 250 cm^3 as a water bath
Tweezers
Spatula
Measuring cylinder, 10 cm^3
Paper tissue

Access to:
0.1 M cobalt chloride (or similar salt), 1 cm^3
2 M hydrogen peroxide, 30 cm^3 IRRITANT
0.5 M potassium sodium tartrate
2 M sodium hydroxide CORROSIVE
2 M urea, 3 cm^3
Liver, small piece of calf or pig
1% urease-active meal (a fresh sample will give more convincing results)
Selection of metal oxides (Cu_2O, MnO_2, ZnO, MgO; optional: SnO_2, TiO_2) SEVERAL ARE HARMFUL
Red litmus paper

Procedure

Before starting this section teachers should ask students for some examples of experiments involving catalysis which they have encountered in their pre-A-level courses.

For the benefit of the teacher some further notes are given here. Some or all of these could be used as extension work. The word catalysis used alone suggests an acceleration of the chemical process (Greek *catalysis* is to loosen). If a reaction is apparently slowed down by the added substance, that substance is said to be an inhibitor. Inhibitors are sometimes called 'negative' catalysts, for example, when sodium sulphate(IV) (sulphite) solution is oxidised by oxygen gas, the reaction is inhibited by a variety of alcohols.

The following notes about each experiment may be useful.

1 Students should be advised to use only 2 or 3 cm^3 of 2 M hydrogen peroxide and, as near as possible, the same tiny amount of catalyst in each tube. The range of oxides tested may be increased to include CuO, SnO_2 and TiO_2 if teachers wish. The results of adding the metal oxides to hydrogen peroxide are – MnO_2: vigorous effervescence; Cu_2O: effervescence; ZnO, MgO, SnO_2, TiO_2: no effervescence. The oxides which exhibit catalysis in these experiments are those of transition metals which have incomplete d sub-shells in their ions.

Liver contains the enzyme catalase which catalyses the breakdown of hydrogen peroxide.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Similar enzymes are found in a wide variety of plant and animal species.

The exact role of catalase in cells is uncertain but it does prevent the accumulation of hydrogen peroxide, which some enzyme systems in the body produce, for example, during the deamination of amino acids by L-amino acid oxidase. If hydrogen peroxide is allowed to build up to high concentrations it would oxidise many of the metabolites. In some organisms catalases and other similar enzymes (peroxidases) may catalyse important oxidation reactions.

2 Rochelle salt and hydrogen peroxide only effervesce slightly when brought to the boil. On adding Co^{2+} ions there is an immediate effervescence and the solution turns green. As the effervescence subsides the colour returns to a pink colour. There is no colour change when $Co^{2+}(aq)$ is added to hot hydrogen peroxide or hot Rochelle salt solutions on their own.

This experiment is used to demonstrate that the catalyst is involved in the reaction but not changed at the end of the reaction. It involves oxidation of the Co^{2+} ion and subsequent reduction of the oxidised form.

3 The enzyme urease in the jack bean meal catalyses the hydrolysis of urea:

$$CO(NH_2)_2 + H_2O \longrightarrow 2NH_3 + CO_2$$

Sodium hydroxide only reacts very slowly with urea at room temperature, but does so quite quickly on heating.

An alternative procedure for the experiment is to add a solution of the urease-active meal in water or phosphate buffer solution at pH7 to the urea solution.

Students who do biology may be surprised that the enzyme works under alkaline conditions. Unlike most enzymes, urease is fairly insensitive to alkaline pH. This is an obvious biological advantage since it has to withstand the localised alkaline conditions when ammonia is produced.

INVESTIGATION 11.5 The rate of reaction of metals with acid

Many students may well be familiar with a version of this investigation from GCSE courses and it must be made clear to them, and indeed to all students, that however similar this exercise might appear, the level of work involved is much higher. It is important that the investigation is based around detailed and sound laboratory work and that at least two areas are covered.

The students need to be fully aware of the different methods available for assessing rates of reaction, in particular the difference between an 'initial' rate method and a method which follows a reaction over a period of time when a concentration will change.

Students should be able to process results in a competent quantitative manner and be able to deal similarly with errors.

Risk assessments must be accurately and thoroughly prepared and be rather more than a direct transfer from 'Hazards'.

11.6 Background reading: light and chemical change

ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 262

1 CO_2, H^+, e^-, Mg

2 Marine plants released oxygen to the atmosphere. Molecular oxygen was converted into ozone by short wavelength ultraviolet light.

3 Chlorine radicals reduce the ozone concentration by a chain reaction. Each step in the reaction produces a new highly reactive free radical.

$Cl\bullet + O_3 = ClO\bullet + O_2$

$ClO\bullet + O\bullet = Cl\bullet + O_2$

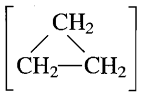
4 Key points to include in summary:

- The ozone layer absorbs ultraviolet light wavelengths below 300 nm.
- Ultraviolet light, especially with a wavelength in the range 250 nm–265 nm, kills cells.
- Pyrimidine and purine groups in DNA and RNA absorb ultraviolet at 260 nm.
- When activated they undergo chemical reactions with nearby groups, water or oxygen.
- If this type of cellular damage is heavy, the body's repair mechanisms may be swamped and allow mutant cells to survive.
- Replication of such cells leads to cancer.
- The ozone layer is depleted by reaction with nitrogen monoxide, and hydroxyl radical and chlorine free radicals.
- Nitrogen monoxide and hydroxyl radicals occur naturally.
- The main cause of the rise in chlorine free radicals is the use of chlorofluorocarbons (CFCs) as solvents, refrigerator coolants, and in aerosol cans.
- The chlorine free radicals have a dramatic effect on ozone, one molecule can break down thousands of ozone molecules through a sequence of chain reactions.

Answers to Topic 11 questions

Review questions

11.1 **a** Rate = k



(1)

b Rate = $k[N_2O]$ (1)

c Rate = $k[H_2][I_2]$ (1)

d Rate = $k[HI]^2$ (1)

e Rate = $k[C_{12}H_{22}O_{11}][H^+]$ (1)

Total 5 marks

11.2 No (1)

In **11.1b**, rate is not proportional to $[N_2O]^2$ and in **11.1e**, H^+ appears in the rate equation but not in the chemical equation. (2)

Total 3 marks

11.3

a 1 (1)
b 1 (1)
c 2 (1)
d 2 (1)
e 2 (1)

Total 5 marks

11.4

a s^{-1} (1)
b s^{-1} (1)
c $dm^3\,mol^{-1}\,s^{-1}$ (1)
d $dm^3\,mol^{-1}\,s^{-1}$ (1)
e $dm^3\,mol^{-1}\,s^{-1}$ (1)

Total 5 marks

11.5

a Measure volume of gas produced at convenient time intervals, e.g. with gas syringe. (2)
b Take out samples at convenient time intervals, quench (e.g. using ice) and titrate HBr with standard alkali. (2)
c Take out samples as in **b**, quench and titrate iodine with standard sodium thiosulphate solution OR colorimetric method. (2)
d Dilatometry: there will be a change in volume as the polymer is formed. (2)

Total 8 marks

11.6

a
i 1st order w.r.t. H_2O_2; rate is doubled if $[H_2O_2]$ doubled, rate trebled if $[H_2O_2]$ trebled (2)
ii 1st order w.r.t. I^-; rate is doubled if $[I^-]$ doubled (2)
iii Zero order w.r.t. H^+; rate unchanged if $[H^+]$ doubled (2)
iv Rate $= k[H_2O_2][I^-]$ (1)
v $k = \dfrac{\text{Rate}}{[H_2O_2][I^-]}$ (2)
Substituting values for any two runs gives $k = 0.0175$
vi $dm^3\,mol^{-1}\,s^{-1}$ (1)

b Yes: mechanism is consistent with rate equation; (1)
Slow step is the rate-determining step; (1)
H_2O_2 appears in rate-determining step; (1)
I^- appears in rate equation and rate-determining step; (1)
H^+ does not appear in rate equation or in rate-determining step. (1)

Total 15 marks

11.7

a
i Rate $= k[BrO_3^-][Br^-][H^+]^2$; (1)
Rate is doubled if $[BrO_3^-]$ doubled (runs 2 and 3); (1)
Rate is doubled if $[Br^-]$ doubled (runs 3 and 4); (1)
Rate is quadrupled if $[H^+]$ doubled (runs 1 and 2). (1)
ii $dm^9\,mol^{-3}\,s^{-1}$ (1)

b Yes. Rate-determining step contains HBr and $HBrO_3$; (1)
[HBr] depends on $[H^+]$ and $[Br^-]$; (1)
$[HBrO_3]$ depends on $[H^+]$ and $[BrO_3^-]$; (1)
so rate will depend on $[Br^-]$, $[BrO_3^-]$ and $[H^+]^2$; (1)
which is consistent with the rate equation; (1)
(Part **b** can also be marked by impression out of 5).

Total 10 marks

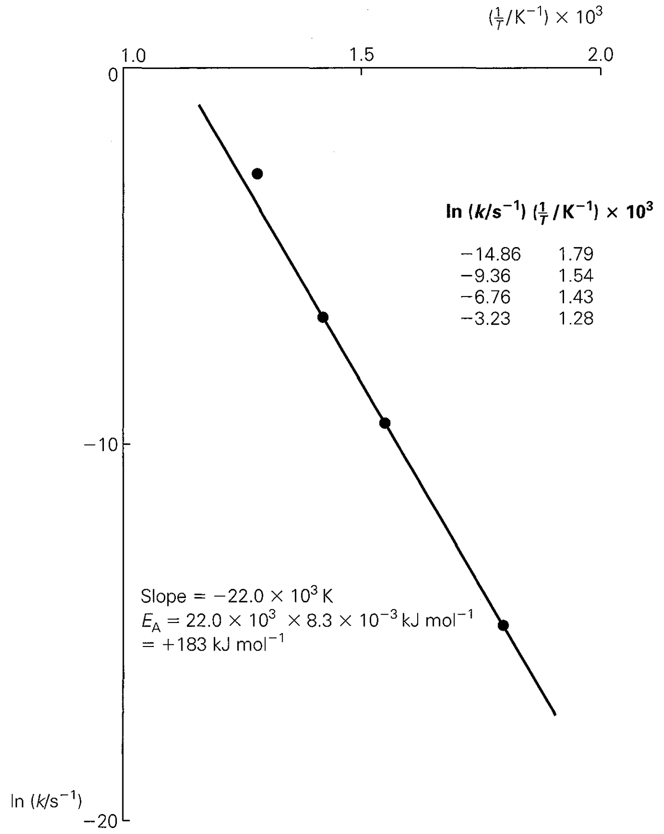
11.8

a Increased temperature means increased kinetic energy of molecules, so collisions will be more frequent; (1)
and a greater proportion of molecules will have the necessary activation energy. (1)

b For reaction to occur, collisions must be between molecules having the necessary activation energy; (1)
and molecules must be correctly aligned on impact. (1)

Total 4 marks

11.9



$\ln (k/\text{s}^{-1})$	$(\frac{1}{T}/\text{K}^{-1}) \times 10^3$
−14.86	1.79
−9.36	1.54
−6.76	1.43
−3.23	1.28

Slope = -22.0×10^3 K

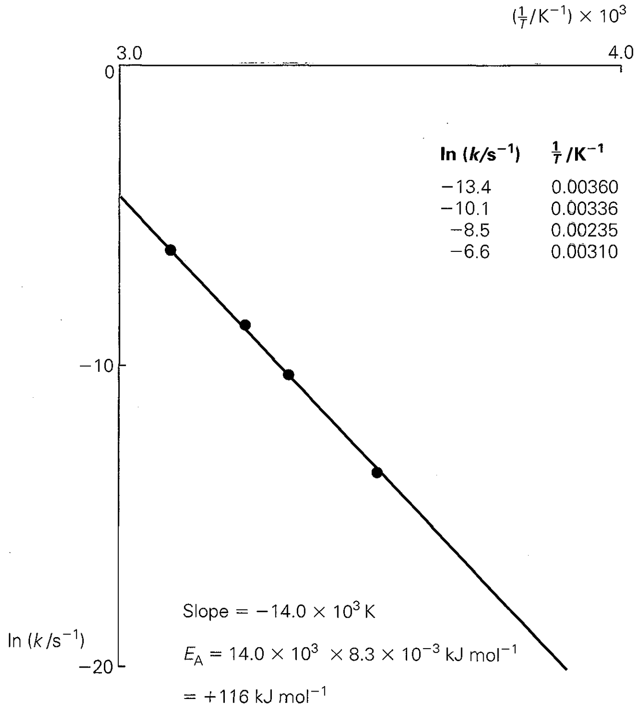
$E_A = 22.0 \times 10^3 \times 8.3 \times 10^{-3}$ kJ mol^{-1}

= +183 kJ mol^{-1}

a	Correct values of ln k;	(1)
	Correct values of $1/T$;	(1)
	Sensible scales and axes labelled;	(1)
	Points plotted correctly;	
	'Best-fit' straight line.	(1)
b	Correct gradient;	(1)
	Calculation E_A;	(1)
	Sign and units.	(1)

Total 7 marks

11.10



$\ln (k/\text{s}^{-1})$	$\frac{1}{T}/\text{K}^{-1}$
−13.4	0.00360
−10.1	0.00336
−8.5	0.00235
−6.6	0.00310

Slope = -14.0×10^3 K

$E_A = 14.0 \times 10^3 \times 8.3 \times 10^{-3}$ kJ mol^{-1}

= +116 kJ mol^{-1}

a 4 marks as in 11.9 **b** 3 marks as in 11.9

Total 7 marks

Examination questions

11.11

a Labelled axes with units; (1)
Points correctly plotted; (1)
Smooth curve. (1)
b Each correct half-life scores 1 mark
e.g. if taken at 0.25 to 0.125 and 0.125 to 0.063
275 ± 20 m 565 ± 40 m (2)
Must be successive half-lives.
c Second order; (1)
Half-life increases with time. (1)
d Equimolar solutions (neither reactant in large excess) (1)
e $C_4H_9Cl + OH^- \longrightarrow C_4H_9OH + Cl^-$ (1)

Total 9 marks

11.12

a **i** Blue/black (1)
ii As I^- reacts to form I_2, it is reduced back to I^- by $S_2O_3^{2-}$. (1)
b **i** Correctly labelled axes; (1)
Axes becoming more positive left to right and bottom to top; (1)
Points correctly plotted and joined with a single straight line. (1)
ii 1st order; (1)
because rate $\propto [S_2O_8^{2-}(aq)]$. (1)
c **i** Rate $= k[S_2O_8^{2-}][I^-]$ (1)
ii $dm^3\ mol^{-1}\ s^{-1}$ (1)

Total 9 marks

11.13

a **i** Rate $= k[HI]^2$ (1)
ii $dm^3\ mol^{-1}\ s^{-1}$ (1)
b **i** Correctly labelled axes; (1)
Points correctly plotted and best-fit straight line drawn; (1)
Axes correct way round and sensible scale. (1)
ii Gradient within range −22 500 K to −23 500 K (2)
(1 mark for value, 1 for sign)
iii E_A within range 187 to 195 kJ mol^{-1} (2)
(2, 3 or 4 SF acceptable)
iv HI absorbed on metal surface;
Weakens H—I bond;
Lowers activation energy (2)
(Any two points).

Total 11 marks

11.14

a **i** Heat in separate tubes in the same water bath. (1)
ii Attach paper marked with dark ink spot to outside of beaker; (1)
Measure time taken for spot to disappear (1)
(Other methods are possible and can be credited.)
iii Rate $= \dfrac{1}{\text{time}}$ (1)
b **i** 1/temperature $= 3.10 \times 10^{-3}\ K^{-1}$ (1)
ln rate/s^{-1}) $= -3.40$ (1)
ii Axes correctly labelled; (1)
Axes correct way round with sensible scales; (1)
Points correctly plotted, single straight line. (1)
iii Gradient in range−4200 K to −5400 K (1)
(Correct value is close to −5000)
$E_A = -8.31\ J\ K^{-1}\ mol^{-1} \times -5000\ K = +41.6\ kJ\ mol^{-1}$ (2)

Total 12 marks

TOPIC 12

Arenes: benzene and phenol

Introduction

The first organic topic of the second year of the course provides an opportunity to review many of the reactions of the first year in the light of the mechanistic principles that have been progressively developed.

The unique properties of benzene enable the concept of delocalisation to be introduced for the first time. The reactions of arenes are contrasted with those of alkane and alkene hydrocarbons, and infrared spectra are presented as an additional tool for identifying carbon compounds.

Alcohols were studied in the second topic of the course. Students may review the reactions of alcohols in the light of the ideas of bond polarity, bond strength and the processes of bond-breaking and bond-making developed in Topics 8 and 10.

The behaviour of the hydroxyl group in phenols, where the group is attached to an arene ring, is studied and contrasted with alcohols.

Aspirin and oil of wintergreen (found in 'deep heat') are prepared from 2-hydroxybenzoic acid to provide an opportunity for large scale (or microscale) preparations and the further use of infrared spectra. These preparations require a limited introduction to esters, which are considered more fully in Topic 15, but are also used to develop principles of equilibria in Topic 14. The history of aspirin shows the development of a modern drug from a herbal remedy.

Content

Timing		Students' Book
12.1	2 hours	pages 273–6
12.2	3 hours	pages 277–82
12.3	Homework	pages 283–4
12.4	3 hours	pages 284–9
12.5	2 hours	pages 289–92
12.6	Homework	pages 293–4
Total about 2 weeks		

12.1 Benzene and some substituted benzene compounds – the structure of benzene, thermochemical and X-ray diffraction evidence, delocalisation, infrared spectrum of benzene, the naming of arenes.

12.2 Reactions of arenes – experiments with arenes; electrophilic substitution reactions; reactions of the benzene ring.

12.3 Background reading: benzene

12.4 Phenols – solubility in water, acidic properties, ester formation and reactions of the benzene ring, comparison of phenol with ethanol.

12.5 Aspirin – preparation of aspirin and oil of wintergreen from 2-hydroxybenzoic acid; determination of melting points.

12.6 Background reading – aspirin: from herbal remedy to modern drug.

Objectives

1 To develop an understanding of delocalisation.

2 To develop a knowledge of how infrared spectra and simple correlation tables can be used to deduce the functional group present in an organic compound.

3 To develop a knowledge of the reactions of arenes including the mechanism of electrophilic substitution.

4 To develop a knowledge of the reactions of phenols and to compare them with alcohols.

5 To develop an appreciation of the procedures used in the preparation and purification of derivatives of 2-hydroxybenzoic acid.

6 To provide background information about the historical and social importance of a pharmaceutical product.

12.1 Benzene and some substituted benzene compounds

Timing About 2 hours will be needed

Suggested treatment

In this section the structure of benzene is considered using electron density, infrared, and thermochemical evidence. The teacher will find it helpful to have a model of the benzene molecule available throughout this section. The PEEL model is particularly useful.

The *Students' Book* describes how Kekulé came to propose the cyclic structure of benzene, and gives some modern evidence in support of delocalised bonding. Three pieces of evidence are described and should be discussed with the class. They are:

1 The length of the C—C bond in benzene, as revealed by X-ray diffraction. The electron density diagram of benzene is given in the *Students' Book* as figure 12.2.

2 The infrared absorption spectrum of benzene, which contains absorption peaks not shown in the corresponding spectra of alkanes or alkenes:

3 Thermochemical data: these call for a comparison of the enthalpy changes of hydrogenation of benzene and cyclohexene.

Students often find it difficult to appreciate that the thermochemical data indicates that benzene is more stable than expected on account of delocalisation. An energy level diagram may be helpful here.

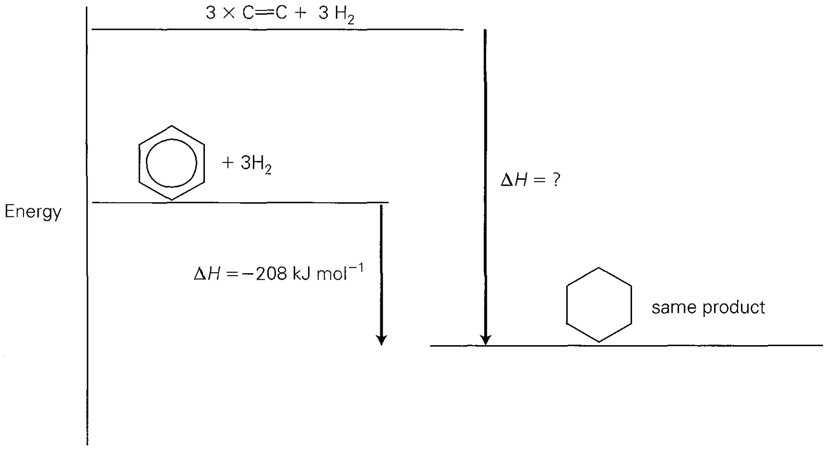


Figure 12.1 An energy level diagram

The infrared absorption spectrum of benzene is shown in figure 12.3c in the *Students' Book* and students are asked to identify the origin of the main absorption bands by reference to the *Book of data* and compare them with those of decane and oct-1-ene. Before doing this they should familiarise themselves with the method of infrared absorption spectroscopy which is described in Topic 21 of the *Students' Book*. Students are not required to memorise details of the procedure, but should be able to interpret infrared spectra with the aid of simple correlation tables. Table 3.3 from the *Book of data* gives information about stretching and bending vibrations for a variety of bonds. Students should be able to read off absorption wavenumbers from spectra, and be familiar with the non-linear scale that is used. Students could be asked to make a ball-and-spring model of the molecule of methane and ethane, and then use them to identify both stretching and bending modes of vibration.

Students should notice from figures 12.3a that the typical alkane C—H stretching absorption is just below 3000 cm^{-1}. Figure 12.3b shows that a typical alkene has the same absorption (due to the same bonds) but has in addition a C—H absorption just above 3000 cm^{-1}. These absorptions do not appear in the benzene spectrum (figure 12.3c); the typical arene C—H absorption is a doublet (two absorptions) just above 3000 cm^{-1}.

Finally in this section there is a brief review of the naming of arenes. Students may wonder why the structure of naphthalene (another example of delocalisation) is shown with double bonds whereas that of benzene has a circle inside a hexagon. This is because the circle has come to indicate *six* electrons delocalised about the hexagonal structure; in naphthalene there are *ten* electrons delocalised about *two* hexagons with one side in common, a different situation.

12.2 Reactions of arenes

Timing About 3 hours

Suggested treatment

This section is developed in the following way:

1 Students study the reactions of the arenes using methylbenzene and methoxybenzene.
2 An interpretation of the substitution reactions of the benzene rings is discussed.
3 The reactions of the benzene ring are summarised.

Experiments with arenes

Benzene is carcinogenic, and experiments with it are illegal in the UK. In Experiment 12.2 two derivatives of benzene are used to illustrate the type of chemical reactions in which arenes take part.

Methylbenzene (toluene) is used in the first part of the experiment, in which the arenes are compared with the alkanes and the alkenes. Though less harmful than benzene, methylbenzene should be used with care. Methoxybenzene (methyl phenyl ether) is then used to provide evidence for consideration when discussing the nature of the reactions of the benzene ring – that is, as a basis for developing ideas of electrophilic substitution reactions. The methoxy group activates the benzene ring, and thus makes the results of the reactions observable in a reasonable length of time.

EXPERIMENT 12.2 Experiments with arenes

Each group of students will need:
Eye protection
Gloves
Test tubes and rack
Combustion spoon or equivalent
Spatula
Glass rod (to test HCl evolved)
Beaker to act as a water-bath, 250 cm^3

HAZARDS

Methylbenzene (toluene) is harmful by inhalation.
2% bromine in hydrocarbon solvent should be prepared in a fume cupboard; a suitable solvent is hexane (free from aromatics) (highly flammable and harmful) but the solution has to be freshly prepared as the colour fades within an hour in bright daylight.

Access to:
2 M ammonia (to test HCl evolved)
Anhydrous aluminium chloride, 1 g CORROSIVE
Concentrated nitric acid, 1 cm^3 CORROSIVE
Concentrated sulphuric acid, 3 cm^3 CORROSIVE
Methoxybenzene (methyl phenyl ether, anisole), 3 cm^3 FLAMMABLE
Methylbenzene (toluene), 2 cm^3 HIGHLY FLAMMABLE
0.01 M potassium manganate(VII), 1 cm^3
2% bromine in hydrocarbon solvent, 4 cm^3 CORROSIVE, HIGHLY FLAMMABLE, TOXIC, HARMFUL
(*prepared just before use*)
Hexane HIGHLY FLAMMABLE AND HARMFUL
2-chloro-2-methylpropane, 1 cm^3 HIGHLY FLAMMABLE
0.4 M sulphuric acid, 1 cm^3
Dropping pipettes, 4
Full-range Indicator paper

Procedure

Full instructions are given in the *Students' Book*. A model of methoxybenzene would be useful. The following notes may be helpful.

1 Combustion

Arenes burn with a luminous and very sooty flame.

2 Oxidation

Slow oxidation may be observed with methylbenzene. This does not occur with benzene.

3 and 1 Bromination

No reaction with methylbenzene but copious fumes of hydrogen bromide (white smoke with ammonia) should be observed with methoxybenzene. Because of the difficulty of obtaining a suitable solvent the teacher may prefer to demonstrate these reactions, in a fume cupboard, by adding a drop of pure bromine.

HAZARD

Pure bromine is very toxic and corrosive.

4 and 2 Action of sulphuric acid

No reaction with methylbenzene but methoxybenzene dissolves with a slight yellowing and the product is soluble in water.

3 Friedel–Crafts reaction

Copious fumes of hydrogen chloride are evolved when the mixture is warmed in a water bath.

4 Nitration

Deep red and other colours are seen very clearly if the reaction mixture is poured into a white sink.

ANSWERS

Questions, page 279–80

1 On the basis of the relative electronegativities of iodine and chlorine, the expected polarisation is

$$\overset{\delta+}{\mathrm{I}}-\overset{\delta-}{\mathrm{Cl}}$$

which means that the attacking group is positively charged.

2 The leaving group is a hydrogen atom, as H^+. This is consistent with the ease of attack on methoxybenzene because the benzene ring is negatively polarised.

Students should be able to appreciate that the reactions of the benzene ring are electrophilic substitution reactions.

Reactions of the benzene ring

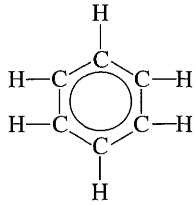
The principal reactions of the benzene ring are summarised in the *Students' Book*. Students are asked to draw up a chart summarising these in the topic review.

12.3 Background reading: benzene

ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 283

1 a



b $C_6H_{12} \longrightarrow C_6H_6 + 3H_2$

c Cheaper **or** lower pressure used

2 a Addition

b Substitution

3 Fuming sulphuric acid/sulphur trioxide

4 Key points to include in summary:

- Petroleum is fractionally distilled to produce naphtha.
- Sulphur (impurities) is removed.
- Naphtha is heated to 770 K and passed over **either** an aluminium oxide catalyst at 40 atm **or** platinum catalyst at 15 atm/platformed.
- Hexane is dehydrogenated to cyclohexane.
- Cyclohexane dehydrogenated to form benzene.
- Other products are dissolved in a solvent and distilled/fractionated.
- Residual impurities are removed and further fractionation separates benzene from other products.

12.4 Phenols

Timing 3 hours

Suggested treatment

One aim of this section is to show how the properties of the O—H group are modified in different molecular environments. The students should be asked to remind themselves of the behaviour of alcohols before considering the changes which take place when the hydroxyl group is bonded to the arene ring in phenols. They should be encouraged to review the reactions of alcohols encountered in Topics 2 and 10, in the light of bond energies and dipole moments and to classify them according to the following types of reaction:

1 reactions in which the O—H bond breaks
2 reactions in which the C—O bond breaks
3 oxidations.

There is, of course, a fourth category of reactions in which alcohols themselves behave as nucleophiles on account of the lone pair of electrons on the oxygen atom. Students have not yet encountered any reactions of this type, but the equilibrium aspects of the esterification reaction are studied in Topic 14, and the preparations from 2-hydroxybenzoic acid, in this topic, involve the formation of esters. For these reasons esters are introduced here although a full consideration of their reactions is left until acid derivatives are discussed in Topic 15. The need for acid conditions for the nucleophilic substitution of alcohols could be used to introduce the base behaviour of the lone pair of electrons. Since a base is also a nucleophile, the nucleophilic potential of alcohols becomes clear.

In the study task, which introduces the work on phenols, students are asked to predict how they think the behaviour of the O—H group may be modified on account of the delocalisation of the lone pair of electrons with the arene ring. The influence of the O—H group on the reactions of the ring itself is also considered.

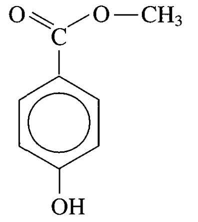
ANSWERS

Study task, page 284

1 a Displacement of the lone pair will assist ionisation of the O—H bond, so phenol is more likely than ethanol to react with sodium hydroxide.
  b Phenol might react with sodium carbonate: it will depend on whether it is a strong enough acid.
  c $C_6H_5OH + NaOH \longrightarrow C_6H_5O^-Na^+ + H_2O$

2 a Delocalisation will hinder the breaking of the C—O bond.
  b Electrophiles are used to attack arene rings.
  c Nucleophiles are used to bring about substitution reactions in alcohols.
  d Phenol is unlikely to undergo nucleophilic substitution or elimination reactions.

3 a Electrophilic substitution.
  b The delocalisation of the lone pair should make it easier for phenol to take part in reactions of this type.



Methyl 4-hydroxybenzoate

If teachers wish to take the structural comparison of phenol and ethanol further they can point out the bond shortening in phenol (C—O is 0.136 nm) compared with ethanol (C—O is 0.143 nm). Students could also be asked to calculate the delocalisation energy of phenol (180 kJ mol^{-1}) and to compare the result with the value for benzene (159 kJ mol^{-1}). This implies an additional delocalisation in phenol, accounting for 21 kJ mol^{-1}.

Because of the corrosive nature of many phenols it is suggested that methyl 4-hydroxybenzoate is used instead, using procedures based on the CLEAPSS Guide L195. Phenol itself is corrosive and causes painful blisters and it is also toxic by skin absorption. This does not preclude a demonstration by the teacher of the reactions of phenol. See also the microscale alternative.

In the *Students' Book* methyl 4-hydroxybenzoate is referred to as a 'phenolic compound' in order to draw attention to the class of compound being used, rather than the specific compound itself.

EXPERIMENT 12.4

The reactions of the phenolic functional group

There is a microscale alternative to this experiment (see pages 295 and 302 (M5))

HAZARDS

Bromine water should be prepared with great care as bromine is very toxic by inhalation. Sodium residues should be disposed in propan-1-ol, because sodium reacts dangerously with water.

Each group of students will need:

Eye protection
Test tubes and rack
Combustion spoon, or equivalent
Dropping pipettes

Access to:

0.05 M bromine water, 5 cm^3 HARMFUL, IRRITANT (bromine water is VERY TOXIC AND CORROSIVE)
2 M ethanoic acid, 2 cm^3 IRRITANT
Ethanoic anhydride, 1 cm^3 CORROSIVE, FLAMMABLE
Ethanol, 2 cm^3 HIGHLY FLAMMABLE
Full-range Indicator
Methyl 4-hydroxybenzoate
2 M nitric acid, 5 cm^3 CORROSIVE
2 M hydrochloric acid IRRITANT
Sodium, a small cube (2–3 mm side) CORROSIVE, FLAMMABLE
1 M sodium carbonate, 5 cm^3
2 M sodium hydroxide, 10 cm^3 CORROSIVE

Procedure

Full instructions are given in the *Students' Book*. The following notes may be helpful.

1 Solubility in water

The phenolic compound in water should have a pH of about 6. It is useful to compare pH of the phenol solution with that of the water used.

2 Phenolic compounds as acids

a *Action of sodium.* Clean pieces of sodium should be used to avoid unwanted effects. (Product is very corrosive.)

b *Action of sodium hydroxide.* The phenolic compound will dissolve readily in sodium hydroxide solution and will reappear as an emulsion when concentrated hydrochloric acid is added. If too much acid is added, the phenol will remain dissolved due to the combined effects of heat and extra water.

c *Action of sodium carbonate.* There is no effervescence of carbon dioxide; phenol can be distinguished from carboxylic acids by this test.

3 Reaction with an organic acid (esterification)

This experiment is less impressive but more pleasant to carry out than the alternative benzoylation using benzoyl chloride.

4 Properties of the benzene ring

a *Combustion.* The phenolic compound should burn with a typical arene smoky flame.

b *Bromine and* **c** *Nitric acid.* Typical electrophilic substitution reactions occur, similar to those observed with methoxybenzene.

Interpretation of the experiments

This section concludes with a comparison of the reactions of phenol with those of ethanol. It is suggested that the differences arise because one of the lone pairs of electrons in the oxygen atom can joint the delocalized electrons of the benzene ring, a situation not possible in the case of ethanol.

The nucleophilic nature of ethanol is also mentioned, to account for the formation of esters, thus introducing a class of compounds to be studied in Topic 15.

12.5 Aspirin

There is a microscale alternative to the preparation of aspirin experiment (see Appendix 1, Sheet M6). Pages 296 and 303 (M6).

Timing About 2 hours will be needed (more if the two experiments are done consecutively)

Suggested treatment

The preparations of aspirin and oil of wintergreen illustrate the esterification of the —OH and —CO_2H groups of 2-hydroxybenzoic acid. They give useful experience in techniques of purification needed for a solid and a liquid.

Organisation will depend on time and resources available, but all students should tackle both experiments if possible. The oil of wintergreen preparation involves a lengthy reflux period: it may be convenient for this to be happening whilst students are recrystallising aspirin or determining its melting point.

EXPERIMENT 12.5

Preparations using 2-hydroxybenzoic acid

Each group of students will need:

1 Preparation of aspirin

Eye protection
Reflux apparatus (Liebig condenser and 50 cm^3 pear-shaped flask)
Apparatus for suction filtration
250 cm^3 beaker to act as a water bath
Beaker, 100 cm^3
Dropping pipette
Ice bath
Measuring cylinder, 5 cm^3
Stirring rod
Melting-point apparatus
Thermometer, 0–250 °C

Access to:

Ethanoic anhydride, 4 cm^3 CORROSIVE, HIGHLY FLAMMABLE
2-hydroxybenzoic acid (salicylic acid), 2 g HARMFUL
Phosphoric(V) acid, 85% a few drops CORROSIVE

2 Preparation of oil of wintergreen

Eye protection
Distillation apparatus (50 cm^3 pear-shaped flask, still head, and Liebig condenser)
Reflux apparatus consisting of Liebig condenser and 50 cm^3 pear-shaped flask
Thermometer, 0–250 °C
Beaker, 100 cm^3
2 conical flasks, 100 cm^3
Dropping pipette
Measuring cylinders, 25 cm^3 and 50 cm^3
Separating funnel

Access to:

Ethyl ethanoate, 15 cm^3 HIGHLY FLAMMABLE
2-hydroxybenzoic acid (salicylic acid), 9 g HARMFUL
Methanol, 15 cm^3 TOXIC, HIGHLY FLAMMABLE
0.5 M sodium carbonate, 30 cm^3
Sodium sulphate, anhydrous
Sulphuric acid, concentrated, 2 cm^3 CORROSIVE

HAZARDS

Although ethyl ethanoate is classified as highly flammable, it has an auto-ignition temperature of 426 °C, so it is safer to use than many other solvents, some of which form emulsions with the reaction mixture.

Procedure

Full instructions are given in the *Students' Book*.

Students will need to be reminded of the techniques of recrystallisation, previously met in Experiment 6.8a. The key to success is to dissolve the impure aspirin in the *minimum* quantity of boiling water. Insoluble impurities can be removed by hot filtration (although this may result in loss of product as the solution cools in the funnel); soluble impurities remain in solution after cooling. Students need to understand that the product has to be much more soluble in the hot than in the cold solvent.

Students should be shown how to make a melting point tube by sealing one end of a capillary tube and how to use the melting point apparatus available. The 'literature' melting point of aspirin is 135 °C. Students may also need to be shown how to 'flute' filter paper, although filtration through a cotton wool plug is a suitable alternative.

Students are expected to answer a number of questions about each preparation.

- They may suggest that ethanoyl chloride could be used instead of ethanoic anhydride, but it is more expensive without improving the yield.
- The choice of phosphoric acid as catalyst for the manufacture of aspirin is based on the relatively harmless nature of phosphoric acid and its low cost. It also produces fewer side products.

- To prepare soluble aspirin you need to make an ionic salt by neutralisation. Reference to section 12.3 will remind students that esterification involves nucleophilic attack by the alcohol with loss of —OH from the acid. The reaction of methanol with the carboxylic group is much more favourable than with the phenolic group.
- Solvent extraction is used to remove the dissolved oil of wintergreen from the water and the unwanted water-soluble substances.
- Washing with sodium carbonate solution removes acid residues which might otherwise char the product during distillation.

Students are not expected to learn the details of the chemistry of aspirin, so the emphasis should be on the ethanoylation reaction.

12.6 Background reading: aspirin, from herbal remedy to modern drug

The passage on aspirin could be set as homework and used as the basis for a discussion on the use and abuse of drugs in society today. (See also background reading on drugs in Topic 20.) It is instructive to compare the cost of different brands of aspirin tablets based on their aspirin content.

ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 293

1 The use of medicines was confused by the inclusion of elements of magic and religion, together with theories that we now know were unsound.

2 Salicin.

3 The principle that many remedies lie not far off from their causes.

4 Esterification.

5 Key points to include in the summary.

- The first step of the process involves an acid–base reaction of phenol with sodium hydroxide to form sodium phenoxide.
- The second step of the reaction is an unusual electrophilic aromatic substitution. Here a carboxylate group is substituted into the benzene ring.
- This is done by adding sodium phenoxide to (solid) carbon dioxide.
- The final step of the reaction is an acid–base reaction.
- This involves adding acid to the disodium 2-hydroxybenzoate formed in the second step.
- This produces 2-hydroxybenzoic acid.

Answers to Topic 12 questions

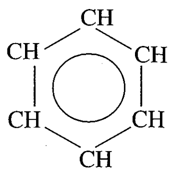
Review questions

12.1

a CH (1)

b C_6H_6 (1)

c



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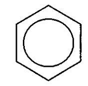
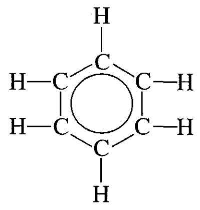


(1)

d



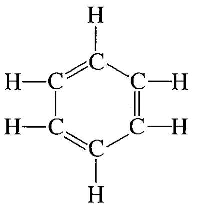
(1)

Total 4 marks

12.2 ∠C—C—C = 120° (1)
∠H—C—C = 120° (1)

Total 2 marks

12.3 **a** (1)



b C—C bond lengths 0.154 nm (1)
C=C 0.134 nm (1)

c Experimental value 0.140 nm (1)

Total 4 marks

12.4 **a**

	Cyclohexane	**Cyclohexene**	**Benzene**
C—H stretching /cm^{-1}	2962–2853 (1)	2962–2853 and 3095–3010 (1)	3030 (1)
C—H bending /cm^{-1}	1485–1365 (1)	1485–1365 (1)	750 (1)
C=C stretching /cm^{-1}	–	1669–1645 (1)	1600, 1580, 1500, 1450 (1)

b The C—H bending and C=C stretching vibrations are at different wavenumbers from those in alkenes. (2)

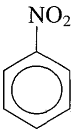
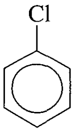
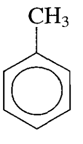
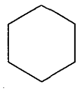
Total 10 marks

12.5 **a** $CH_2{=}CH_2(g) + H_2(g) \longrightarrow C_2H_6(g)$ (1)
$C_6H_6(l) + 3H_2(g) \longrightarrow C_6H_{12}(l)$ (1)

b Benzene has six delocalised electrons, not three C=C double bonds. (1)
This enhances stability/benzene is at a lower energy than if double bonds were present. (1)

Total 4 marks

12.6

Product	**Formula of product**	**Reagent**	**Conditions**	**Type of reaction**
nitrobenzene	 (1)	nitric acid HNO$_3$	conc HNO$_3$ + conc H$_2$SO$_4$	electrophilic substitution
chlorobenzene	 (1)	**chlorine** (1)	**iron(III) chloride catalyst** (1)	**electrophilic substitution** (1)
methylbenzene (1)		**chloromethane** (1)	**aluminium chloride catalyst** (1)	**electrophilic substitution** (1)
cyclohexane (1)	 (1)	Hydrogen, H$_2$	**Ni catalyst at 200 °C** (1)	**addition** (1)

Total 13 marks

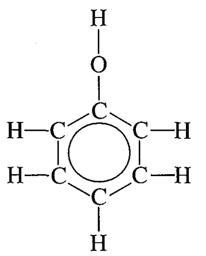
12.7 **a** Introduction of an alkyl group (e.g. CH$_3$—) (1)
in place of a hydrogen atom (1)

b Substitution (1)

c **i** $CH_3CHClCH_3$ **ii** $CH_3CH_2CH_2Cl$ (2)
Both need $AlCl_3$ to be present (1)
d Both are C_9H_{12} (2)

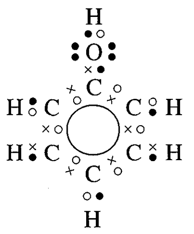
Total 8 marks

12.8 **a**



(1)

b



(2)

c ∠C—O—H = 104–105° (1)
∠C—C—O = 120°

Total 4 marks

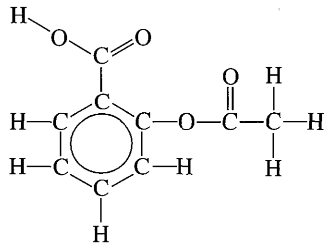
12.9 Compound **a** is a phenol (1)
because its —OH group is directly attached to a C atom in a benzene ring (1)
b and **c** are not phenols because their —OH groups are not so attached. (2)

Total 4 marks

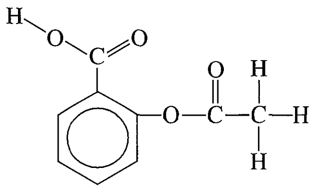
12.10 **Reaction 1:** sodium hydroxide (1)
in aqueous solution (1)
Reaction 2: nitric acid (1)
dilute (1)
Reaction 3: hydrogen (1)
Ni catalyst and heat (1)
Reaction 4: ethanoyl chloride or ethanoic anhydride (1)
phenol dissolved in NaOH (aq) (1)
Reaction 5: bromine (1)
aqueous solution/water (1)

Total 10 marks

12.11 **a**



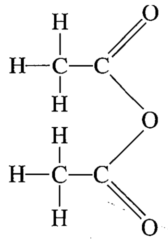
or



(2)

b $C_9H_8O_4$ (1)

c



(2)
ethanoic anhydride (1)
d Esterification (1)
the —OH group in phenol reacts with an acid derivative (1)
OR substitution (1)
the oxygen atom of the phenolic —OH acts as a nucleophile (1)

Total 8 marks

Examination questions

12.12

a **A** = cyclohexane (1)

B = hydrogen (1)

C = bromine (1)

D = iron(III) bromide (C/D can be either way round) (1)

E = bromobenzene (1)

F = conc. sulphuric acid (1)

b **i** $Br^+/Br^{\delta+}$ (1)

NO_2^+ (1)

ii Prevents further substitution (1)

iii Dyes/explosives (1)

c **i** Temperature around 200 °C (1)

Pressure around 30 atm (1)

ii $C_6H_6 + 3Cl_2 \longrightarrow C_6H_6Cl_6$ (1)

Total 13 marks

12.13

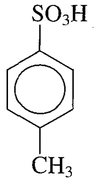
a **A** = 4-nitromethylbenzene (1)

B = conc. sulphuric acid (1)

C = conc. nitric acid (1)

(or vice-versa)

b **i** (1)



ii SO_3 (1)

iii Detergents (1)

c **i** $FeBr_3 + Br_2 \longrightarrow Br^{\delta+}—Br^{\delta-}FeBr_3$ or $Br^+ + FeBr_4^-$ (1)

ii Electrophilic substitution (2)

d **i** Step 1: hydrogen — Step 2: KOH (2)

Ni at 200 °C — in aqueous ethanol + heat (2)

ii Add bromine (water)

orange/brown to colourless

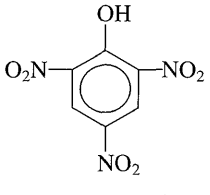
or acidified $KMnO_4$

pink/purple to colourless (2)

Total 15 marks

12.14

a (1)



b Wear gloves (picric acid yellows skin) (1)

use fume cupboard (toxic oxides of nitrogen evolved) (1)

c Diagram should show flask fitted with reflux condenser (1)

heated in water/steam bath (1)

d Buchner flask (1)

Buchner funnel (1)

e To purify product (1)

dissolve product in minimum volume (of hot water) (1)

cool using ice (1)

filter off crystals (1)

f Theoretical yield from 10 g of phenol $= \frac{10 \times 229}{94}$ g (1)

% yield $= \frac{15 \times 94 \times 100}{10 \times 229} = 61.6$ or 62% (1)

Total 13 marks

TOPIC 13

Entropy

Introduction

The concept of entropy is an important part of the Nuffield A-level Chemistry course. Entropy helps us to understand why chemical reactions occur. It knits together several topics such as equilibria and electrochemical cells so a discussion of entropy at this stage prepares the ground for further development in Topics 14 and 17. A non-mathematical approach has, on the whole, been used. Entropy can be understood on more than one level and an appreciation of the basic concepts can be achieved at this stage by using simple models and equations coupled with experimental work.

The study of entropy starts by considering chance and disorder and is then developed by looking at some endothermic reactions. Entropy changes in the system and the surroundings are then introduced and the topic ends with the recognition that the feasibility of a reaction depends on the values of ΔS_{system} and $\Delta S_{\text{surroundings}}$.

Content

Timing		Students' Book
13.1	$2\frac{1}{2}$ hours	pages 302–8
13.2	$2\frac{1}{2}$ hours	pages 308–13
Total about 1 week		

13.1 How does chance operate in chemistry? – spontaneous changes, rearranging quanta of energy; chance in chemical reactions considered in terms of order/disorder; counting numbers of ways; changes in the system and in the surroundings, total entropy change.

13.2 Measuring entropy – calculating the entropy change in the surroundings; standard entropy of substances, calculating the entropy change in the system; total entropy change; feasibility of reactions in terms of the balance between the entropy change in the system and in the surroundings.

Objectives

1. To introduce the idea of entropy change as a change in the number of ways of arranging the atoms and energy in a substance.
2. To introduce the relationship between the enthalpy change of a reaction and the entropy change in the surroundings.
3. To introduce the idea of standard entropy of substances and to show how the entropy change in a system is calculated.
4. To introduce the idea that the feasibility of a reaction depends on the balance between ΔS_{system} and $\Delta S_{\text{surroundings}}$.

13.1 How does chance operate in chemistry?

Timing About $2\frac{1}{2}$ hours

Suggested treatment

The section is developed in the following way:

1 The number of ways of sharing energy in atoms and molecules is discussed and the direction of change shown to be from order to disorder.

2 Students carry out some experiments illustrating a variety of changes. These focus their attention on the order and disorder in both the surroundings and the system.

3 The term entropy is introduced and related to the number of possible arrangements of energy quanta.

4 The direction of spontaneous change is considered in relation to entropy change in the surroundings and the system.

Students should first be reminded of the work they did in Topic 3 where the quantisation of energy was briefly discussed. They then consider assemblies of 2 and then 3 vibrating atoms having one quantum of energy each and work out the different numbers of ways of arranging the quanta. The ideas to be gained from this section are:

- The number of ways of arranging the energy will be far greater if there are more energy levels available for distributing the energy in each atom.
- What happens to an individual atom in any given situation depends on chance alone.
- Chance determines the direction of change from order to disorder.

The Background information for mathematicians is intended only for those students who are interested in this approach; it is not essential for the development of an understanding of the importance of entropy.

The *Students' Book* suggests that there are differences in the number of ways of arranging quanta of energy in solids, liquids and gases. If teachers wish, they could extend the discussion by considering the different ways energy is stored in atoms and molecules. The relative entropy values of translational, rotational and vibrational entropies for dinitrogen monoxide, which reflect these changes, could be given to students as extension work. The largest entropy component is associated with the movement of molecules from place to place (translation).

Translation entropy	$156\ \text{J mol}^{-1}\ \text{K}^{-1}$
Rotational entropy	$54\ \text{J mol}^{-1}\ \text{K}^{-1}$
Vibrational entropy	$10\ \text{J mol}^{-1}\ \text{K}^{-1}$
Total entropy	$220\ \text{J mol}^{-1}\ \text{K}^{-1}$

When we compare the possibilities for translation, rotation and vibration in gases, liquids and solids it can be seen that there are many more energy levels available for a gas than for a liquid and relatively few for a solid. Therefore the number of ways of arranging the energy decreases in the order gas > liquid > solid.

At this stage teachers could introduce an optional experiment to demonstrate the quantisation of vibrational energy in iodine molecules.

HAZARDS

Contact between iodine vapour and the eyes is particularly hazardous. When students are observing the effect they should wear eye protection.
(A fume cupboard is not necessary if the plug is efficient.)

Optional teacher demonstration

The teacher will need:

Eye protection
Low-voltage electric lamp with line filament
Fine diffraction grating (about 300 lines per millimetre)
Bunsen burner, retort stand, clamp and heatproof mat
Test tube, 150 × 25 mm, containing 2 small iodine crystals HARMFUL
Ceramic fibre

Access to:

Fume cupboard

Procedure

The test tube containing the iodine should be clean and loosely plugged with ceramic fibre to minimise the escape of iodine vapour.

The test tube is held in a clamp in front of the lamp and warmed over most of its length with a small Bunsen flame; the sides of the test tube must be warmed first to prevent the iodine vapour from condensing on them. Warming of the lower end of the test tube is continued until the iodine vaporises.

If the vapour is too dense, not enough light comes through for much to be seen. If the vapour is not dense enough, the contrast between the absorption bands and the continuous background is poor. The best method is to warm the tube until a strongly coloured vapour fills it and to observe the spectrum of the emergent light as the test tube cools. Hold the diffraction grating close to the eye with the lines of the diffraction grating parallel to the line filament of the lamp. Alternatively, a direct vision spectroscope could be used.

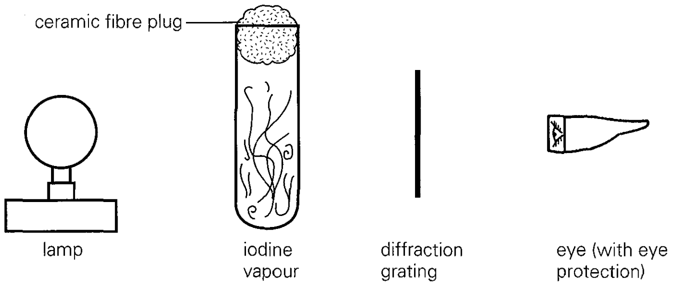


Figure 13.1 Arrangement of the apparatus for the optional experiment

The condensed iodine must be removed from the sides, by warming, before repeating an observation. Four students can share one set of apparatus if the tube is re-warmed as necessary.

The diatomic molecule of iodine, I_2, can vibrate and, by absorbing light energy, it can increase its energy of vibration. Looking at the spectrum of white light through iodine vapour reveals approximately equally spaced dark bands in the red, yellow, and part of the green regions, resulting from the absorption of light energy by the iodine molecules. The dark bands are spaced approximately evenly like the rungs of a ladder. They correspond to the energy steps in the quantised vibrations of iodine molecules. Students sometimes find these bands quite difficult to see. They should not be allowed to get the impression that the absorption is responsible for the colour of the iodine.

EXPERIMENT 13.1

Chance in chemical reactions

HAZARDS

Ammonium carbonate gives off ammonia and carbon dioxide spontaneously. Ammonium nitrate should not be heated or ground up since it may explode. The ammonium chloride–sodium nitrite mixture must not be stored premixed, and enough water should be added to produce a solution that is less than 1 M (see ASE *Topics in safety*, 1988).

Each group of students will need:
Eye protection
Test tubes and rack
Test tube holder
Crucible
Tongs
Bunsen burner, tripod, gauze, and heatproof mat
Measuring cylinder, 10 cm^3
Thermometer, −10 to 110 °C
2 beakers, 100 cm^3

Access to:
Ammonium carbonate, 3 g HARMFUL
Ammonium chloride, 3 g plus 1 g HARMFUL, IRRITANT
Ammonium nitrate, 5 g OXIDISING
Barium hydroxide, $Ba(OH)_2.8H_2O$, 3 g HARMFUL
Ethanoic acid, pure (glacial acetic acid), 5 cm^3 CORROSIVE, FLAMMABLE
Lime water
Magnesium ribbon, 5 cm length HIGHLY FLAMMABLE

Sodium nitrite, 3 g OXIDISING, TOXIC
Zinc carbonate, 2 g
Weighing boats
Balance, to weigh to ±0.1 g

Procedure

This series of experiments is designed to focus the students' attention on the extent of order or disorder in the system (the reactants and products) and the surroundings. After performing the experiments, students are asked, in a study task, which of the reactions are spontaneous. They then try to find a pattern relating spontaneity to the degree of order or disorder in the reactants and products. The meaning of spontaneous is given in the introduction to this topic in the *Students' Book*. Further notes are given below.

1 $$\underset{\text{ordered}}{NH_4^+NO_3^-(s)} + \underset{\text{disordered}}{aq} \longrightarrow \underset{\text{disordered}}{NH_4^+(aq)} + \underset{\text{disordered}}{NO_3^-(aq)}$$

The reaction is endothermic and spontaneous.

2 $$\underset{\text{disordered}}{2CH_3CO_2H(l)} + \underset{\text{ordered}}{(NH_4^+)_2CO_3^{2-}(s)} \longrightarrow \underset{\text{disordered}}{2CH_3CO_2^-NH_4^+(aq)} + \underset{\text{very disordered}}{CO_2(g)} + \underset{\text{disordered}}{H_2O(l)}$$

The reaction is endothermic and spontaneous.

3 $$\underset{\text{ordered}}{2Mg(s)} + \underset{\text{very disordered}}{O_2(g)} \longrightarrow \underset{\text{ordered}}{2MgO(s)}$$

The reaction is exothermic and spontaneous. This reaction may be regarded as spontaneous in the sense stated in the study task since, once started, it will go to completion. The entropy change of this reaction is calculated in section 13.2.

4 $$\underset{\text{ordered}}{NH_4Cl(s)} + \underset{\text{ordered}}{NaNO_2(s)} \xrightarrow{\text{aq}} \underset{\text{disordered}}{NaCl(aq)} + \underset{\text{disordered}}{2H_2O(l)} + \underset{\text{very disordered}}{N_2(g)}$$

Decomposition of ammonium nitrite takes place slowly at room temperature and hence the reaction between ammonium chloride and sodium nitrite occurs spontaneously after adding a little water. The reaction is exothermic.

5 $$\underset{\text{ordered}}{Ba(OH)_2(s)} + \underset{\text{ordered}}{2NH_4Cl(s)} \longrightarrow \underset{\text{ordered}}{BaCl_2{\cdot}2H_2O(s)} + \underset{\text{very disordered}}{2NH_3(g)}$$

This is an endothermic reaction which occurs spontaneously. The entropy change of this reaction is calculated in section 13.2 and the equation has been written to match the available data.

6 $$\underset{\text{ordered}}{ZnCO_3(s)} \longrightarrow \underset{\text{ordered}}{ZnO(s)} + \underset{\text{very disordered}}{CO_2(g)}$$

This reaction is endothermic and not spontaneous. The entropy change of this reaction is calculated in sections 13.2 and 14.4.

Questions, page 305

Students are asked to classify the above reactions as spontaneous or non-spontaneous and compare the order/disorder of the reactants and products.

Students will know that many familiar reactions occur spontaneously with a release of energy, for example the burning of fuels, acid–base reactions, the reaction of sodium with water, and many other obvious examples.

Before studying the experiments in detail, most students will think that exothermic change plays a part in determining the direction of chemical change. This is seen in reaction **3**, where the energy released when magnesium burns is sufficient to 'keep the reaction going'. Conversely, reaction **6**, which is endothermic, is not spontaneous.

Students should notice that reactions **1**, **2** and **5** are also spontaneous, despite being endothermic. The idea that only exothermic reactions are spontaneous therefore needs modification. In each of the endothermic reactions, students should be able to identify a common pattern: a greater disorder in the products compared with the reactants. For example, in reactions **2** and **5**, gas is released and in reaction **1** a solution is formed. However, a similar change also occurs in reaction **4** which is exothermic.

But such a change from order in reactants to disorder in products does not always occur if the reaction is exothermic. So increase in disorder does not appear to be as important here, as for example in the combustion of magnesium.

At the end of this section, the students should see that two factors may play a role in determining whether a reaction is spontaneous:

- the enthalpy change
- the degree of disorder in the products compared with the reactants.

Counting numbers of ways

In this section the word entropy is introduced and described as a term by which energy distribution is measured. It is then related to the 'number of ways' by the equation

$$S = k \ln W$$

Boltzmann's equation cannot be justified at this level and it is only introduced to show that the units of entropy are J mol^{-1} K^{-1}. More useful to the students is the Second Law of Thermodynamics stated in the form:

Spontaneous reactions go in the direction of increasing entropy.

Entropy and our experiments

Experiment 13.1 can now be discussed in terms of entropy changes. Students should be able to recognise that there are a number of spontaneous changes where ΔS_{system} is negative, for example the burning of magnesium.

All such changes prove to be exothermic, resulting in an increase of entropy of the surroundings by increasing the number of ways of arranging the energy. Provided that the increase in entropy of the surroundings is greater than the decrease in entropy of the system, that is

$$\Delta S_{\text{surroundings}} + \Delta S_{\text{system}} > 0$$

then the total entropy change is positive. It is thus seen to be important to be able to calculate the entropy change in the surroundings.

When a reaction is endothermic, the number of ways of arranging the energy in the surroundings decreases and the entropy of the surroundings decreases. The reaction may still be spontaneous, however, if the increase in the entropy of the system is large enough to compensate for the decrease in entropy of the surroundings.

These arguments lead to the conclusion that the criterion for spontaneous change is that ΔS_{total} is positive.

13.2 Measuring entropy

Timing About $2\frac{1}{2}$ hours

Suggested treatment

This section concentrates on the measurement of entropy and introduces some calculations. It is developed as follows:

1. Students are shown how to calculate the entropy change in the surroundings.
2. Standard entropy values for different substances are compared.
3. Students are shown how to calculate ΔS_{system} for a reaction using the *Book of data*.
4. The two calculations are combined to find values for ΔS_{total}.

Calculating the entropy change in the surroundings

The *Students' Book* states the relationship which enables the entropy change in the surroundings to be calculated:

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{reaction}}}{T}$$

Students should be able to use this relationship but it is not necessary to be able to derive it. An empirical approach has been adopted in considering how temperature affects the entropy change of the surroundings and this is described in the *Students' Book*. It is not intended that students consider this in any further depth.

Standard entropy of substances

The standard entropy values for a variety of substances are given in the *Students' Book*. From these values, students should be able to extract the patterns that gases have a much larger entropy content than solids, and that relatively soft solids have a larger entropy content than harder ones. The sharp entropy changes associated with a solid melting or a liquid vaporising can be seen in the *Students' Book* figure 13.9.

The subsection is concluded by a brief indication of how entropy content is calculated using a thermodynamic approach; it is not necessary for students to remember this information. The following notes are for the benefit of teachers only. The relationship between entropy change and thermal energy absorbed is

$$\mathrm{d}S = \frac{\mathrm{d}q_{\text{reversible}}}{T}$$

where q is the energy transferred reversibly from the surroundings. This method of expressing entropy changes is not dependent on working out the number of ways of arranging the energy. This was, in fact, the way in which entropy was originally introduced in the 19th century. The equation may be applied to finite reversible changes, a reversible change being one in which energy is transferred into the system sufficiently slowly that the system never departs significantly from equilibrium.

Entropies at temperatures other than at absolute zero can be obtained experimentally by measuring the molar heat capacity of a substance at constant pressure, C_p.

To determine the entropy change when the temperature of one mole of a substance is heated at constant pressure from 0 K to a temperature, T, the equation is

$$S_T^{\ominus} = \int_0^T \frac{C_p}{T}\,\mathrm{d}T$$

The method involves the accurate evaluation of C_p over a wide temperature range. Heat capacities cannot, however, be measured at very low temperatures, and this portion of the graph is found by extrapolation based on the Debye theory of solids.

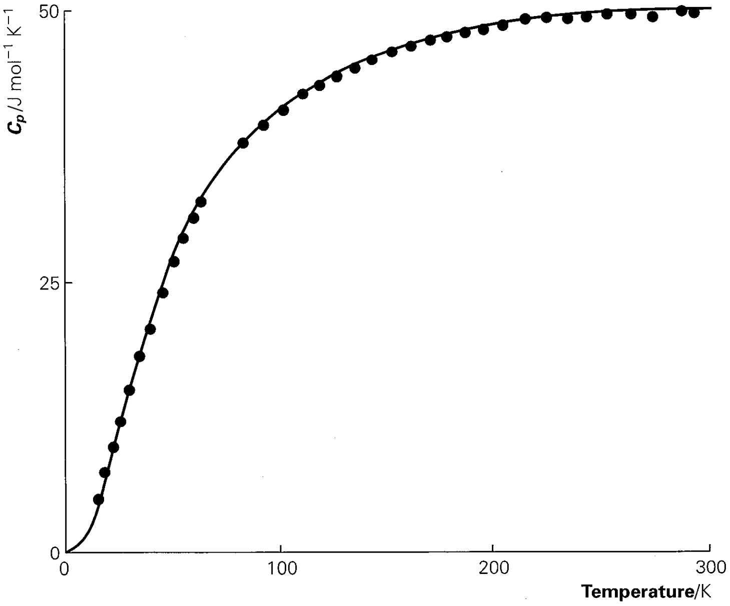


Figure 13.2 Graph of C_p against T for silver chloride

The graph of $\frac{C_p}{T}$ against T shows how entropy values are determined. The area enclosed by the curve gives the entropy of the substance at the particular temperature under consideration.

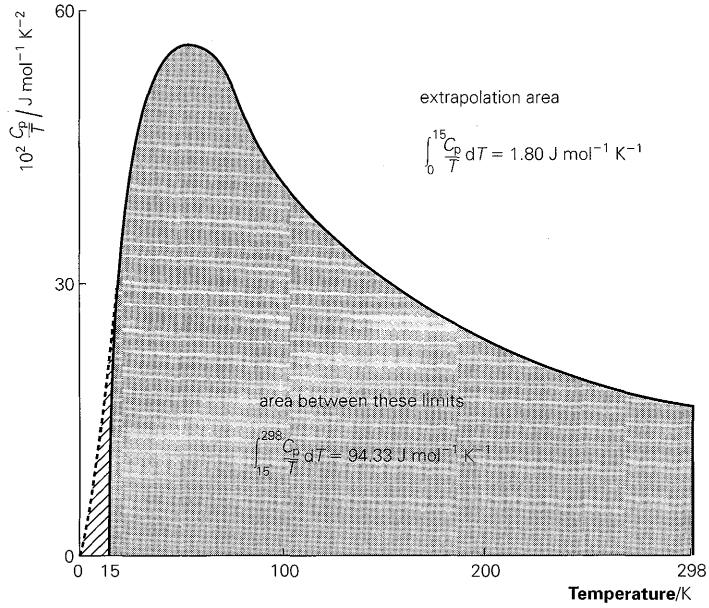


Figure 13.3 Graph of $\frac{C_p}{T}$ against T for silver chloride

Calculating the entropy change in the system

For this section, the treatment should follow the sequence given in the *Students' Book* where the method of finding the entropy change of a system as $\Delta S_{\text{products}} - \Delta S_{\text{reactants}}$ is given. Students should be given practice in extracting entropy values from tables 5.2 and 5.3 in the *Book of data* and their attention should be drawn particularly to the fact that the entropy values for the elements quoted are per mole of atoms, for example per O and not O_2.

The total entropy change

The total entropy change for the burning of magnesium in air is calculated, and the reaction is shown to be spontaneous due to the large positive enthalpy change of formation of magnesium oxide.

ANSWERS

Answers to questions on page 313 of the *Students' book* are given on copiable sheets (pages 190–91).

Answers to Topic 13 questions

Review questions

13.1 A sensible predicted order would be Fe(s), Au(s), NaCl(s), $Ca(OH)_2$(s), C_6H_6(l), C_6H_{14}(l), C_8H_{18}(l), Ne(g), CH_4(g), CO_2(g).
Actual values (J mol^{-1} K^{-1}) are: Fe(s) 27.3; Au(s) 47.4; NaCl(s) 72.1; $Ca(OH)_2$(s) 83.4; C_6H_6(l) 172.8; C_6H_{14}(l) 295.9; C_8H_{18}(l) 361.1; Ne(g) 146.2; CH_4(g) 186.2; CO_2(g) 213.6.

(Mark by impression out of 6)

Comment will depend on predicted order but would be expected to point out that **in general** solids have lower entropies than liquids or gases, but complexity of the substances may have a significant influence: here, the three gases have markedly smaller molecules than the liquids and all have lower entropies than two of the liquids.

(Mark by impression out of 3)

Total 9 marks

13.2

a	$\Delta S^{\ominus}_{\mathrm{system}} = 213.6 - (5.7 + 2 \times 102.5)$	(1)
	$+2.9\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
b	$\Delta H^{\ominus}_{\mathrm{f}}[\mathrm{CO_2(g)}] = -393.5\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -(-393500/298)$	(2)
	$= 1320\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
c	$\Delta S^{\ominus}_{\mathrm{total}} = +2.9 + 1320 = +1323\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
d	Reaction expected to be spontaneous	(1)
	because $\Delta S^{\ominus}_{\mathrm{total}}$ positive	(1)

Total 8 marks

13.3

a	$\Delta H^{\ominus} = -239.3\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -(-239\,300/298) = +803\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(3)
b	$\Delta H^{\ominus} = +176\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -176\,000/298 = -591\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(3)
c	$\Delta H^{\ominus} = -601.7\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -(-601\,700/298) = +2019\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(3)
d	$\Delta H^{\ominus} = -809.9\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -(-809\,900/298) = +2718\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(3)
e	$\Delta H^{\ominus} = -851.5\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -(-851\,500/298) = +2857\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(3)
f	$\Delta H^{\ominus} = -20.6\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -(-20\,600/298) = +69\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(3)
g	$\Delta H^{\ominus} = -411.2\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -(-411\,200/298) = +1380\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(3)

Total 21 marks

13.4

a	Little changed; solid + gas changing to solid + gas, same number of particles	(2)
b	Positive; 1 mole of solid changing to 2 moles of gas	(2)
c	Negative; solid + gas changing to solid only	(2)
d	Negative; both products are solids but one reactant is a gas	(2)
e	Little changed; similar states, similar number of particles	(2)
f	Little changed; although fewer particles, solid removed and more complex gas formed	(2)
g	Negative; solid + gas producing solid only	(2)

Total 14 marks

13.5

a	$-18.7\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
b	$+284.5\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
c	$-108.3\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
d	$-219.5\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
e	$-38.5\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
f	$+43.3\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
g	$-61.6\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(2)

Total 14 marks

13.6

a	$+784\ \mathrm{J\,mol^{-1}\,K^{-1}}$; spontaneous	(2)
b	$-306.5\ \mathrm{J\,mol^{-1}\,K^{-1}}$; not spontaneous	(2)
c	$+1911\ \mathrm{J\,mol^{-1}\,K^{-1}}$; spontaneous	(2)
d	$+2499\ \mathrm{J\,mol^{-1}\,K^{-1}}$; spontaneous	(2)
e	$+2819\ \mathrm{J\,mol^{-1}\,K^{-1}}$; spontaneous	(2)
f	$+112.3\ \mathrm{J\,mol^{-1}\,K^{-1}}$; spontaneous	(2)
g	$+1318\ \mathrm{J\,mol^{-1}\,K^{-1}}$; spontaneous	(2)

Total 14 marks

13.7

a	$\Delta H^{\ominus} = +157.3\ \mathrm{kJ\,mol^{-1}}$	
	$\Delta S^{\ominus}_{\mathrm{surroundings}} = -527.8\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
	$\Delta S^{\ominus}_{\mathrm{system}} = +93.1\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
	$\Delta S^{\ominus}_{\mathrm{total}} = -434.7\ \mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
	Not spontaneous	(1)

	b	$\Delta H^\ominus = -43.5\,\mathrm{kJ\,mol^{-1}}$	
		$\Delta S^\ominus_{\mathrm{surroundings}} = +146\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^\ominus_{\mathrm{system}} = -128.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^\ominus_{\mathrm{total}} = +17.3\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		Spontaneous	(1)
	c	$\Delta H^\ominus = -99.5\,\mathrm{kJ\,mol^{-1}}$	
		$\Delta S^\ominus_{\mathrm{surroundings}} = +333.9\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^\ominus_{\mathrm{system}} = +70.1\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^\ominus_{\mathrm{total}} = +404\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		Spontaneous	(1)
	d	$\Delta H^\ominus = +178.3\,\mathrm{kJ\,mol^{-1}}$	
		$\Delta S^\ominus_{\mathrm{surroundings}} = -598\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^\ominus_{\mathrm{system}} = +160.4\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^\ominus_{\mathrm{total}} = -437.6\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		Not spontaneous	(1)
	e	$\Delta H^\ominus = +274.7\,\mathrm{kJ\,mol^{-1}}$	
		$\Delta S^\ominus_{\mathrm{surroundings}} = -921.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^\ominus_{\mathrm{system}} = +321.4\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^\ominus_{\mathrm{total}} = -600.4\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		Not spontaneous	(1)

Total 20 marks

13.8	**a**	$+335.6\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
	b	$+5.1\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
	c	Similar type and number of reactant and product particles	(1)
	d	$\Delta S^\ominus_{\mathrm{total}} = +340.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		reaction spontaneous and expected to go to completion	(1)

Total 6 marks

13.9	**a**	$-63.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
	b	$121.5 + 56.5 - 95.9 = +82.1\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
	c	$\Delta S^\ominus_{\mathrm{total}}$ is positive	(1)
		so spontaneous process	(1)

Total 5 marks

Examination questions

13.10	**a**	$\Delta H^\ominus_{\mathrm{reaction}} = -123.8$ or $-124\,\mathrm{kJ\,mol^{-1}}$	(2)
	b	$\Delta S^\ominus_{\mathrm{surroundings}} = -(123\,800/298)$	(1)
		$+415$ (or $+415.4$) $\mathrm{J\,mol^{-1}\,K^{-1}}$	(2)
	c	**i** Number of particles decreases	(1)
		gas and liquid change to solid	(1)
		ii $\Delta S^\ominus_{\mathrm{total}} = +199.8$ (or $+199$) $\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		iii Total entropy change positive so reaction spontaneous	(1)
	d	Yield of PCl_5 decreases	(1)
		because $\Delta S^\ominus_{\mathrm{surroundings}}$ decreases so $\Delta S^\ominus_{\mathrm{total}}$ decreases	(1)

Total 11 marks

13.11	**a**	Sulphur,	(1)
		because it is a solid but the other substances are gases.	(1)
	b	**i** Negative	(1)
		because gases turn into liquid and solid	(1)
		ii $\Delta S^\ominus_{\mathrm{surroundings}}$ positive for $\Delta S^\ominus_{\mathrm{total}}$ to be positive	(1)
		$\Delta S^\ominus_{\mathrm{surroundings}}$ must be more positive than $\Delta S^\ominus_{\mathrm{system}}$ is negative	(1)
		iii $\Delta H^\ominus$ must be negative	(1)

Total 7 marks

13.12

a **i** $\Delta S^{\ominus}_{\text{surroundings}} = +128\,600/298$ (1)
$= +432\ \text{J mol}^{-1}\ \text{K}^{-1}$ (2)
ii $\Delta S^{\ominus}_{\text{system}} = -219(.1)\ \text{J mol}^{-1}\ \text{K}^{-1}$ (2)
iii Negative sign expected because number of particles decreases (1)
and gases change to liquid (1)

b **i** At equilibrium $\Delta S^{\ominus}_{\text{total}} = 0$ (1)
ii Advantage: greater yield of methanol/faster reaction/methanol easy to liquefy (1)
Disadvantage: higher capital/running costs/energy required to maintain high pressure (1)

Total 10 marks

13.13

a Solid reactants give a gaseous product (1)

b At 1250 K, $\Delta S^{\ominus}_{\text{surroundings}} = -\dfrac{237\,500}{298} = -190\ \text{J mol}^{-1}\ \text{K}^{-1}$ (2)
so for $\Delta S^{\ominus}_{\text{total}}$ to be positive, $\Delta S^{\ominus}_{\text{surroundings}}$ must be less negative than $-190\ \text{J mol}^{-1}\ \text{K}^{-1}$ so temperature must be >1250 K (1)

c $\Delta S^{\ominus}_{\text{system}}$ will be more positive because Zn will be gaseous (1)

d Temperature required will be lower because as $\Delta S^{\ominus}_{\text{system}}$ is more positive, $\Delta S^{\ominus}_{\text{surroundings}}$ can have a more negative value for $\Delta S^{\ominus}_{\text{total}}$ to remain positive. (1)

Total 6 marks

ANSWERS TO QUESTIONS ON PAGE 313

1 To calculate the entropy change for the reaction:

$Ba(OH)_2(s) + 2NH_4Cl(s) \longrightarrow BaCl_2{\cdot}2H_2O(s) + 2NH_3(g)$

you should follow the steps set out below.

You will have to start by looking up the $S^\ominus$ and $\Delta H_f^\ominus$ values at 298 K for all the reactants and products. You will find the values in the *Book of Data*.

$S^\ominus[NH_4Cl(s)] = +94.6\ J\ mol^{-1}\ K^{-1}$ $\Delta H_f^\ominus[NH_4Cl(s)] = -314.4\ kJ\ mol^{-1}$

$S^\ominus[Ba(OH)_2(s)] = +99.7\ J\ mol^{-1}\ K^{-1}$ $\Delta H_f^\ominus[Ba(OH)_2(s)] = -944.7\ kJ\ mol^{-1}$

$S^\ominus[BaCl_2{\cdot}2H_2O(s)] = +202.9\ J\ mol^{-1}\ K^{-1}$ $\Delta H_f^\ominus[BaCl_2{\cdot}2H_2O(s)] = -1460.1\ kJ\ mol^{-1}$

$S^\ominus[NH_3(g)] = +192.3\ J\ mol^{-1}\ K^{-1}$ $\Delta H_f^\ominus[NH_3(g)] = -46.1\ kJ\ mol^{-1}$

You then have to work out $\Delta S^\ominus_{system}$ for the reaction:

$\Delta S^\ominus_{system} = \Delta S^\ominus_{products} - \Delta S^\ominus_{reactants}$

$= +587.5\ J\ mol^{-1}\ K^{-1} - (+288.9\ J\ mol^{-1}\ K^{-1})$

therefore $\Delta S^\ominus_{system} = +298.6\ J\ mol^{-1}\ K^{-1} = +299\ J\ mol^{-1}\ K^{-1}$ (3SF)

$\Delta H^\ominus_{reaction}$ is calculated similarly

$\Delta H^\ominus_{reaction} = \Delta H^\ominus_{products} - \Delta H^\ominus_{reactants}$

$= -1552.3\ J\ mol^{-1}\ K^{-1} - (-1573.5\ J\ mol^{-1}\ K^{-1})$

therefore $\Delta H^\ominus_{reaction} = +21.2\ kJ\ mol^{-1}$

and from $\Delta H^\ominus_{reaction}$ you can calculate

$$\Delta S^\ominus_{surroundings} = \frac{-\Delta H^\ominus_{reaction}}{T} = -(+21.2 \times 1000 \div 298)\ J\ mol^{-1}\ K^{-1}$$

$$= -71.1\ J\ mol^{-1}\ K^{-1}$$

Finally you obtain a value for $\Delta S^\ominus_{total}$ by using the relationship

$\Delta S^\ominus_{total} = \Delta S^\ominus_{system} + \Delta S^\ominus_{surroundings}$

with the values you have already calculated

$\Delta S^\ominus_{system} = +298.6\ J\ mol^{-1}\ K^{-1}$

$\Delta S^\ominus_{surroundings} = -71.1\ J\ mol^{-1}\ K^{-1}$

therefore $\Delta S^\ominus_{total} = +298.6\ J\ mol^{-1}\ K^{-1} - 71.1\ J\ mol^{-1}\ K^{-1}$

$= +227.5\ J\ mol^{-1}\ K^{-1} = +228\ J\ mol^{-1}\ K^{-1}$ (3SF)

and the reaction will go spontaneously at 298 K.

The experiment you did matches this theoretical prediction. We have, therefore, demonstrated that entropy calculations match our practical experience, which is a test all scientific theories must pass.

Notice that the production of ammonia gas with its large entropy plays a major role in making this reaction go spontaneously.

2 We will also consider the decomposition of zinc carbonate, which you looked at in Experiment 13.1:

$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$

The standard entropy values at 298 K are

$S^\ominus[ZnCO_3(s)] = +82.4\ J\ mol^{-1}\ K^{-1}$

$S^\ominus[ZnO(s)] = +43.6\ J\ mol^{-1}\ K^{-1}$

$S^{\ominus}[CO_2(g)] = +213.6\ J\ mol^{-1}\ K^{-1}$

so $ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$

$+82.4 \quad +43.6 \quad +213.6$ in $J\ mol^{-1}\ K^{-1}$

and $\Delta S^{\ominus}_{system} = \Delta S^{\ominus}_{products} - \Delta S^{\ominus}_{reactants}$

therefore $\Delta S^{\ominus}_{system} = +257.2\ J\ mol^{-1}\ K^{-1} - 82.4\ J\ mol^{-1}\ K^{-1}$

$= +174.8\ J\ mol^{-1}\ K^{-1} = +175\ J\ mol^{-1}\ K^{-1}$ (3SF)

A positive entropy change means that this reaction might go spontaneously. But there is also the entropy change in the surroundings to be determined.

The standard enthalpies of formation at 298 K are

$\Delta H^{\ominus}_f[ZnO] = -348.3\ kJ\ mol^{-1} \qquad \Delta H^{\ominus}_f[ZnCO_3] = -812.8\ kJ\ mol^{-1}$

$\Delta H^{\ominus}_f[CO_2] = -393.5\ kJ\ mol^{-1}$

so $ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$

$-812.8 \quad -348.3 \quad -393.5$ in $kJ\ mol^{-1}$

and $\Delta H^{\ominus}_{reaction} = \Delta H^{\ominus}_{products} - \Delta H^{\ominus}_{reactants}$

therefore $\Delta H^{\ominus}_{reaction} = -348.3\ kJ\ mol^{-1} - 393.5\ kJ\ mol^{-1} - (-812.8\ kJ\ mol^{-1})$

$= +71.0\ kJ\ mol^{-1}$

and $\Delta S^{\ominus}_{surroundings} = \dfrac{-\Delta H^{\ominus}_{reaction}}{T} = -(+71.0 \times 1000 \div 298)\ J\ mol^{-1}\ K^{-1}$

$= -238\ J\ mol^{-1}\ K^{-1}$

This large negative value makes it most unlikely that the reaction will be spontaneous at 298 K. We can check this speculation by using the relationship

$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surroundings}$

with the values we have already calculated

$\Delta S^{\ominus}_{total} = +174.8 - 238$

$= -63.2\ J\ mol^{-1}\ K^{-1}$

So this reaction will not go spontaneously at 298 K. But you may remember that most carbonates decompose when heated. How does this happen when we have confirmed that the entropy change is negative? We will leave this question until later.

3 In Topic 1 you studied the thermal decomposition of hydrated cobalt(II) chloride and in Topic 5 you calculated the standard enthalpy of reaction at 298 K for:

$CoCl_2{\cdot}6H_2O(s) \longrightarrow CoCl_2(s) + 6H_2O(l)$

$\Delta H^{\ominus}_{reaction} = +88.1\ kJ\ mol^{-1}$

Here you are asked which entropy values are mainly responsible for this reaction being spontaneous when heated and what are the differences between the substances that might account for this entropy effect.

The *standard* entropy values from the *Book of data* are:

$S^{\ominus}[CoCl_2(s)] = +109.2\ J\ mol^{-1}\ K^{-1} \qquad S^{\ominus}[CoCl_2{\cdot}6H_2O(s)] = +343.0\ J\ mol^{-1}\ K^{-1}$

$S^{\ominus}[H_2O(l)] = +69.9\ J\ mol^{-1}\ K^{-1}$

Using the relationship

$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surroundings}$

You will find

$\Delta S^{\ominus}_{total} = +185.6\ J\ mol^{-1}\ K^{-1} - 295.6\ J\ mol^{-1}\ K^{-1}$

$= -110.0\ J\ mol^{-1}\ K^{-1}$

If you use the entropy value

$S^{\ominus}[H_2O(g)] = +188.7\ J\ mol^{-1}\ K^{-1}$

and calculate $\Delta S^{\ominus}_{total}$ the answer becomes $+1033\ J\ mol^{-1}\ K^{-1}$. This suggests that the formation of gases instead of liquids on heating is likely to be responsible for the reaction becoming spontaneous at a temperature somewhat above 298 K.

TOPIC 14

How far? Reversible reactions

Introduction

This topic will deal with the principles governing equilibrium reactions building on the material that was introduced in Topic 7, when the nature of reversible reactions and of the equilibrium state were established, and the effects of concentration, pressure and temperature on equilibria were considered qualitatively. In this topic the Equilibrium Law is introduced as a conclusion from many experiments, and its implications are considered for a number of equilibria, including acid–base reactions. The position of equilibrium is also related to the total entropy change of a reaction and a rationale is established for the effects of changes on equilibria summed up in Le Chatelier's Principle.

Redox equilibria are not considered until Topic 17 but basic ideas could be introduced in this topic if that approach is preferred.

The pH meter and its use are described in Topic 21.

Contents

14.1 Reversible reactions

14.2 The Equilibrium Law – equilibrium constant, K_c, units of K_c; relative concentrations at equilibrium; measurement of an equilibrium constant by experiment.

14.3 The equilibrium constant for reactions involving gases, K_p – partial pressures and mole fractions; K_p, units of K_p, calculations based on K_p.

14.4 Entropy and equilibrium reactions – the effect of product concentration on entropy change, a study of the nitrogen dioxide–dinitrogen tetraoxide equilibrium; relationship between entropy change and K_c; at equilibrium $\Delta S_{\text{total}} = 0$; effect of pressure and temperature on entropy change; how to make reactions go the way you want; Le Chatelier's principle.

14.5 Acid–base equilibria – pH values of dilute solutions of acids and salts; interpretation of acid–base reactions; competition for protons, pH and the equilibrium constant for the ionisation of water; calculations of pH from hydrogen ion concentration and vice versa.

14.6 The strengths of acids and bases – strong and weak acids; dissociation constants for acids, K_a; calculation of pH from K_a values; experimental determination of K_a for a weak acid.

14.7 Acid–base titrations – change of pH during acid–base titration; theory of indicators; *An analysis of vinegars*.

14.8 Buffer solutions – composition of buffer solutions; interpretation of buffer behaviour.

Timing		Students' Book
14.1	$\frac{1}{2}$ hour	pages 318–9
14.2	4 hours	pages 320–7
14.3	$1\frac{1}{2}$ hours	pages 327–8
14.4	2 hours	pages 329–33
14.5	3 hours	pages 333–7
14.6	3 hours	pages 337–41
14.7	3 hours	pages 341–3
14.8	3 hours	pages 344–7
Total about 4 weeks		

Objectives

1 To consider the properties which characterise the equilibrium state.
2 To consider entropy changes in an equilibrium reaction.
3 To consider the applications of Brønsted–Lowry theory to acid–base equilibria.
4 To develop a quantitative understanding of pH.

14.1 Reversible reactions

Timing About $\frac{1}{2}$ hour

Suggested treatment

This section reviews the qualitative ideas about reversible reactions which were introduced in Topic 7. Discussion can now be concentrated on the following points:

- A stable state of equilibrium can be set up only in a *closed* system – one which contains a constant amount of matter but can exchange energy with its surroundings (the contents of a stoppered vessel) or in an *isolated* system – one which contains a constant amount of both matter and energy (for example the contents of a sealed and insulated vessel). Strictly speaking stable equilibrium cannot be attained in an open system, that is, one that can exchange both matter and energy with its surroundings. In practice, however, there are systems of this kind which can be studied in open conditions because no gases are involved.
- If allowed to stand long enough, reversible reactions will reach a position of equilibrium whether the starting materials are the substances on the left of the $\rightleftharpoons$ or those on its right. The symbol $\rightleftharpoons$ indicates that equilibrium can be approached from either direction.
- The approach to equilibrium from either direction suggests that the equilibrium state is dynamic rather than static. Evidence for this is normally obtainable only by use of radioisotopes as tracer elements.
- The equilibrium state though stable under fixed conditions is sensitive to alteration in those conditions.
- The term 'position of equilibrium' is useful in such discussions.

The *Students' Book* does not introduce the terms extensive and intensive properties but some students may find the idea helpful. Intensive properties are those which are independent of the total amount of matter in the system, such as depth of colour per unit thickness of layer, density, pressure, and concentration. Properties such as mass, volume and internal energy, which vary with the total amount of matter, are called extensive properties. The equilibrium state is characterised by constancy of intensive properties in a closed or isolated system.

14.2 The Equilibrium Law

Timing About 4 hours

Suggested treatment

The section is developed in the following way:

1 The Equilibrium Law is introduced as a summary of quantitative investigations of equilibrium reactions.
2 The meaning and units of K_c are described.
3 Students are provided with data on two equilibria and asked to calculate the values of K_c.
4 The section concludes with the determination of a K_c value by experiment.

Students seem to have most difficulty in understanding that K_c has a constant value in stated conditions, but when they grasp this central idea their interpretation of equilibrium situations is usually sound; the confusion may arise because of chemists' interest in manipulating the conditions in order to improve the yield from equilibrium reactions.

The Equilibrium Law is an empirical law – it has its basis in the results of many practical experiments rather than in a rigid proof. Familiarity with the form of equilibrium expressions is gained by writing the expressions for a number of reactions.

ANSWERS

Questions, page 321

1 $$K_c = \frac{[Ce^{3+}(aq)]_{eqm}[Fe^{3+}(aq)]_{eqm}}{[Ce^{4+}(aq)]_{eqm}[Fe^{2+}(aq)]_{eqm}}$$

2 $$K_c = \frac{[CH_3OH(g)]_{eqm}}{[CO(g)]_{eqm}[H_2(g)]^2{}_{eqm}}$$

3 $$K_c = \frac{[NH_3](g)^2{}_{eqm}}{[N_2(g)]_{eqm}[H_2(g)]^3{}_{eqm}}$$

Some important conclusions from the Equilibrium Law are considered concerning the position of equilibria in relation to K_c values. Stress must also be given to the fact that K_c remains constant at a constant temperature and reactions when subjected to a change at constant temperature readjust to a new position of equilibrium accordingly.

The importance of relating the K_c expression to a specific stoichiometric equation is underlined and attention is paid to the units for K_c which vary from example to example depending upon the form of the stoichiometric equation and hence the equilibrium expression. K_c has no units only when the number of concentration terms is the same on the numerator and denominator. The units of K_c have therefore to be examined on each and every occasion.

ANSWERS

Questions, page 322

1 K_c has units of $dm^3\ mol^{-1}$ for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

2 K_c has units of $dm^{12}\ mol^{-4}$ for $Co^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq)$

Chemists and chemical engineers use the idea that if K_c is known, then the relative proportions of reactants and products can be calculated for any initially known mixture of reactants.

Relative concentrations at equilibrium

The description in the *Students' Book* of the method of determining the equilibrium constant for the ester equilibrium merely refers to it as 'a simple titration technique'. Students are probably not yet sufficiently well-informed about acid–base systems to make their own more detailed proposals for a method, but the question could be raised later in the topic or when the chemistry of esters is discussed in Topic 15.

For the benefit of teachers, more details on the method referred to are given here.

The equilibrium constant can be determined by allowing flasks containing different mixtures of ethyl ethanoate, water, and catalyst (hydrochloric acid) to stand at room temperature, and then analysing the mixtures by titrating the contents of each flask with alkali when equilibrium has been reached.

The quantity of concentrated hydrochloric acid used is titrated separately. The volume of alkali needed is subtracted from all the other results to allow for acid added as catalyst.

The amount of ethanoic acid (d mol) in the equilibrium mixture is calculated. As the original mixture contained b mol ethyl ethanoate and c mol water, there must be d mol ethanoic acid, d mol ethanol, $(b - d)$ mol ethyl ethanoate, and $(c - d)$ mol water at equilibrium.

The results were adapted from the work of sixth-form students. The experiment was carried out at about 20 °C and the results were obtained by allowing mixtures of ethyl ethanoate and water, of differing proportions (between 20 cm^3 ester + 1 cm^3 water and 15 cm^3 ester + 15 cm^3 water) plus a fixed volume (2 cm^3) of concentrated hydrochloric acid, to stand for one week. The containers were in well-sealed (ground-glass joint) apparatus. Hydrogen ions from the hydrochloric acid act catalytically in enabling equilibrium to be attained in a week.

ANSWERS

Questions, page 323

Mixture	K_c
1	0.231
2	0.280
3	0.282
4	0.272
mean	0.266 (to 3SF)

Some emphasis is then given to the point that concentrations should always be used in units of mol dm^{-3} in the equilibrium expression and therefore it is a wise policy to ensure that this is always done rather than to attempt short cuts in particular examples.

ANSWERS

Questions, page 324

This question concerns the equilibrium $2NO_2$ (solvent) $\rightleftharpoons$ N_2O_4 (solvent)

Mixture	$K_c/10^4$ mol^{-1} dm^3 at 10 °C
1	9.0
2	11.0
3	8.9
4	9.5
5	9.9
mean	9.9 (to 2SF)

The values of K_c are all of the same order of magnitude and are constant within the limits of experimental error.

ANSWERS

Study task, page 324–5

1	$\frac{[HI(g)]}{[H_2(g)][I_2(g)]}$		$\frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$
a	4.01×10^3 dm^3 mol^{-1}	a	54.3
	3.50×10^3 dm^3 mol^{-1}		54.6
	3.20×10^3 dm^3 mol^{-1}		53.9
b	15.3×10^3 dm^3 mol^{-1}	b	54.1
	14.6×10^3 dm^3 mol^{-1}		53.6
	6.47×10^3 dm^3 mol^{-1}		54.4

2 The second expression clearly gives the better constant.

3 This expression is in accordance with the Equilibrium Law.

4 $K_c = \frac{[HI(g)]}{[H_2(g)]^{1/2}[I_2(g)]^{1/2}}$

5 and 6 The values will be the square roots of those given above for $K_c = \frac{[HI(g)]^2}{[HI(g)][I_2(g)]}$ that is, about 7.4.

Students should be given plenty of practice in questions involving K_c values. A selection of suitable questions is included at the end of the topic.

EXPERIMENT 14.2 Measurement of an equilibrium constant, K_c

There is a microscale alternative to this experiment (see pages 296 and 304 (M7)).

Each group of students will need:

Eye protection
Burette
Small funnel
Pipette filler
Two 25.0 cm^3 pipettes
10.0 cm^3 pipette
Conical flask, 100 cm^3, stoppered and dry
Conical flasks for titrations
White tile

Access to:

0.10 M iron(II) sulphate (freshly made from Analar grade), 25 cm^3 (solid is HARMFUL)
0.10 M silver nitrate, 25 cm^3 (solid is CORROSIVE)
0.020 M potassium thiocyanate, 50 cm^3

Procedure

Full instructions are given in the *Students' Book*. To reduce the cost of this experiment students could share one mixture that has been allowed to reach equilibrium. The results are rather variable, because hydrolysis and oxidation make it impossible to maintain a pure solution of iron(II) sulphate. Judging the 'endpoint' is also difficult.

It may help students if the teacher discusses what might be meant by the concentration of a solid, and why it is a constant (at a given temperature) which does not appear in the expression for K_c. It may be sufficient to point out that the density is a measure of the concentration of a solid and that it does not vary with the amount of solid present.

14.3 The equilibrium constant for reactions involving gases, K_p

Timing About $1\frac{1}{2}$ hours

Suggested treatment

When dealing with reactions involving gases, it is often found to be more convenient to use an equilibrium constant expressed in terms of partial pressures (K_p) rather than in terms of concentrations (K_c).

The possibility of using partial pressures instead of concentrations for gas reactions is discussed in the *Students' Book*. Dalton's Law of partial pressures is introduced and it is pointed out that the partial pressure of a gas is proportional to its concentration. In a mixture the partial pressure of each gas can be calculated by multiplying its mole fraction by the total pressure exerted by the gas mixture.

Some students find it helpful to think of the partial pressures as the contribution each gas makes to the total pressure of the mixture. Teachers will have to ensure that students fully understand the concept of mole fraction and can calculate it. Two fully worked examples are shown for the calculation of K_p.

Teachers should stress that square brackets are not used in equilibrium expressions for K_p since the use of square brackets is specifically for concentrations given in units of mol dm^{-3}. Teachers should also stress again the need for correct units. It is most likely that students will find partial pressures quoted in kilopascals (kPa) but atmospheres (atm) or newtons per square metre (N m^{-2}) may also be encountered in questions. As with K_c values, the units in which the equilibrium constant is quoted depend on the particular form of the equilibrium expression and how many terms there are in numerator and denominator.

The relationship between K_p and K_c is shown in a comment box in the *Students' Book* but for the information of the teacher, its derivation is shown below.

For the equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K_c = \frac{[NO_2(g)]^2_{eqm}}{[N_2O_4(g)]_{eqm}}$$

and $$K_p = \frac{p^2_{NO_{2eqm}}}{p_{N_2O_{4eqm}}}$$

but $$[NO_2(g)]_{eqm} = \frac{p_{NO_{2eqm}}}{RT}$$

and $$[N_2O_4(g)]_{eqm} = \frac{p_{N_2O_{4eqm}}}{RT}$$

$$K_c = \frac{\left(\frac{p_{NO_{2eqm}}}{RT}\right)^2}{\left(\frac{p_{N_2O_{4eqm}}}{RT}\right)} = \frac{p^2_{NO_{2eqm}}}{p_{N_2O_{4eqm}}} \times \frac{1}{RT}$$

$$= \frac{K_p}{RT}$$

$$K_cRT = K_p$$

The general expression is

$$K_p = K_c(RT)^n$$

where n = the number of gas molecules on the right-hand side of the equation minus the number of gas molecules on the left-hand side of the equation.

Teachers might like to ask the students how the values of K_p and K_c would compare for reactions such as:

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

and

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

14.4 Entropy and equilibrium reactions

Timing About 2 hours

Suggested treatment

The aim of this section is to provide a molecular basis for Le Chatelier's Principle in terms of entropy changes. Students should be aware from their work in Topic 13 that for a spontaneous change ΔS_{total} is positive. The question 'How can the total entropy change for a reversible reaction be positive in both directions?' is then asked. The remainder of this section seeks to explain this apparent paradox. It is developed in the following sequence:

1. The effect of changing the temperature and pressure on the position of the nitrogen dioxide–dinitrogen tetraoxide equilibrium is studied experimentally.
2. The law of diminishing returns can be applied to the entropy change of a reversible reaction.
3. At equilibrium ΔS_{total} is zero.
4. All reactions are reversible to some extent.
5. The effect of temperature on the decomposition of zinc carbonate (from Topic 13) can now be calculated.
6. Le Chatelier's Principle is introduced as a generalisation about the direction of change in a system at equilibrium.

EXPERIMENT 14.4 The $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium

The practical details for this demonstration are included in Experiment 7.7c.

The effect of product concentration on entropy change

This section is introduced by considering the course of the decomposition of pure N_2O_4. As N_2O_4 decomposes into NO_2, more disorder is introduced into the system but as more and more NO_2 molecules are formed the extent of disorder is relatively less. Similar arguments apply to the reverse reaction. At some stage the entropy change for the system is therefore 0. This is extended intuitively to include the entropy change of the surroundings.

The equation $S^{\ominus}_{total} \propto \ln K_c$ is then given. It should be noted that this relates to the combined effect of the system and the surroundings.

Some nominal values are given for total entropy changes for the equilibrium situation and for reactions which do not go or go to completion. These values are of course not hard and fast, but serve to give an indication of the relationship of entropy to chemical equilibrium.

The relationship between ΔS_{total} and the equilibrium constant is not intended to be used by students for calculations.

The effect of pressure on entropy change

The idea is introduced that when the pressure on a gas is reduced the volume increases and the number of ways of arranging the gas particles increases. Hence the entropy of the gas increases.

The decomposition of zinc carbonate and the formation of ammonia are used as examples.

Further examples should be given to consolidate these ideas.

The effect of temperature on entropy change

This section follows on from the discussion in Topic 13 where the equation $\Delta S_{\text{surroundings}} = -\Delta H/T$ was introduced.

The effect of temperature change on the value of $\Delta S_{\text{surroundings}}$ leads to a brief discussion of how the temperature influences the feasibility of a reaction. For an endothermic reaction raising the temperature gradually decreases the extent of the unfavourable entropy change in the surroundings and therefore increases the feasibility of a reaction.

How to make reactions go the way you want

The *Students' Book* revisits Le Chatelier's Principle as a summary of the effects discussed.

14.5 Acid–base equilibria

Timing About 3 hours

Suggested treatment

After a short introduction, this part of the topic is developed along fairly orthodox lines and is dealt with in some detail in the *Students' Book.*

The Brønsted–Lowry theory of acids and bases was introduced in Topic 4. The distinction between strong and weak acids and bases was also introduced.

The content is developed in the following way:

1. Students collect data on the pH of solutions for use in the development of the section.
2. Acid–base reactions are interpreted as a competition for protons, acids being proton donors and bases proton acceptors.
3. The ionisation constant for water is introduced and the quantitative definition of pH explained.
4. pH values are calculated from $[H^+]$ values and vice versa.

As a preparation for the introductory experiments students are asked to review their previous knowledge of acids and bases. This is a useful opportunity to clear up any misconceptions.

In the *Students' Book*, pH is defined by $\text{pH} = -\lg[H^+(aq)]$ but, strictly speaking it should be written in the form

$$\text{pH} = -\lg\left(\frac{[H^+(aq)]}{\text{mol dm}^{-3}}\right)$$

so that the units on the right-hand side cancel out. The reason for this is that the log of a number can only be written for a number without units and so they are cancelled out before taking the log. It can also be stated in the form

$$\text{pH} = -\lg[H_3O^+(aq)]$$

EXPERIMENT 14.5 What is an acid?

HAZARDS

Indicator solutions are flammable when prepared in ethanolic solution.

Each group of students will need:
Test tubes and rack
Full-range Indicator
Stirring rod

Access to the following 0.1 M solutions:
Ammonium chloride (solid is HARMFUL)
Ethanoic acid (pure acid is FLAMMABLE AND CORROSIVE)
Phosphoric(V) acid (pure acid is CORROSIVE)
Sodium carbonate (solid is IRRITANT)
Sodium ethanoate
Disodium hydrogenphosphate(V)
Sodium dihydrogenphosphate(V)
Trisodium phosphate(V) (solid is IRRITANT)
Sodium hydrogen sulphate
Sodium sulphate
Sulphuric acid (concentrated acid is CORROSIVE)

and in addition:
Small pieces of clean magnesium ribbon
Indicator solutions such as:
- Bromophenol blue
- Bromothymol blue
- Methyl orange
- Phenolphthalein FLAMMABLE

Procedure

Full instructions are given in the *Students' Book*. It is useful to test the pH of 'pure' water: demineralised (deionised) water is recommended. Good results could be shared as the results are used in the subsequent development of the topic. The following notes may be helpful.

The following measurements were made with a 'stick' pH meter, as described in Topic 21. The 0.1 M solutions had pH values of about:

1

H_2SO_4	1.6	H_3PO_4	1.9
$NaHSO_4$	1.9	NaH_2PO_4	4
Na_2SO_4	7	Na_2HPO_4	9
		Na_3PO_4	10

2

CH_3CO_2H	2.9	NH_4Cl	5
Na_2CO_3	10	CH_3CO_2Na	8

3

Indicator	Colour in acidic solution	Colour in alkaline solution
bromophenol blue	yellow	blue
bromothymol blue	yellow	blue
methyl orange	red	yellow
phenolphthalein	colourless	red

14.6 The strengths of acids and bases

Timing About 3 hours

Suggested treatment

This section is developed in the following way:

1 The use of pH to distinguish between strong and weak acids is demonstrated; such a demonstration affords a good opportunity to describe how to use a pH meter for accurate measurements.

2 K_a is introduced as a special case of K_c.

3 A simplified method of converting K_a values to pH values is explained.

Converting K_a values to pH values

The reverse calculation, of converting K_a values to pH values, can conveniently be introduced at this stage. The *Students' Book* contains an example. This problem can be worked out in a similar way to the calculation of the value of K_a for a weak acid from the pH of a solution of the acid, but it involves a quadratic equation. Students are not expected to solve the quadratic equation but to make the approximation that $[H^+(aq)]_{eqm} << [HCO_2H(aq)]_{eqm}$ and that $[H^+(aq)]_{eqm} = [HCO_2^-(aq)]_{eqm}$.

For the information of the teacher the full calculation of the pH of a 0.01 M solution of methanoic acid ($K_a = 1.6 \times 10^{-4}$ mol dm^{-3}) is given here.

$$HCO_2H(aq) \rightleftharpoons HCO_2^-(aq) + H^+(aq)$$

$$K_a = \frac{[HCO_2^-(aq)]_{eqm}[H^+(aq)]_{eqm}}{[HCO_2H(aq)]_{eqm}}$$

Neglecting the hydrogen ions which arise from ionisation of the water, since the concentration of these will be very small compared with the concentration of those from the acid, we can say that

$$[H^+(aq)]_{eqm} = [HCO_2^-(aq)]_{eqm}$$

and $[HCO_2H(aq)]_{eqm} = 0.01 - [H^+(aq)]_{eqm}$

$$\therefore \quad 1.6 \times 10^{-4} = \frac{[H^+(aq)]^2_{eqm}}{10^{-2} - [H^+(aq)]_{eqm}}$$

At this point, a quadratic has to be worked out:

$$[H^+(aq)]^2_{eqm} + (1.6 \times 10^{-4}[H^+(aq)_{eqm}) - (1.6 \times 10^{-4} \times 10^{-2}) = 0$$

giving a value for $[H^+(aq)]_{eqm} = 1.35 \times 10^{-3}$ mol dm^{-3} and pH = 2.87.

Alternatively as in the *Students' Book*, making the approximation that $[H^+(aq)]_{eqm}$ will be very small for weak acids, we can omit the $1.6 \times 10^{-4}[H^+(aq)]_{eqm}$ term and simplify the calculation to

$$[H^+(aq)]^2_{eqm} - 1.6 \times 10^{-4} \times 10^{-2} = 0$$

so that $[H^+(aq)]^2_{eqm} = 1.6 \times 10^{-6}$ mol^2 dm^{-6}

and $[H^+(aq)]_{eqm} = 1.26 \times 10^{-3}$ mol dm^{-3}

from which pH = 2.9

COMMENT

The general solution to a quadratic equation of the form $ax^2 + bx + c = 0$ is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

No treatment of strength of bases is recommended. Every weak base has a conjugate acid, and K_a values can cover all possibilities in this area.

ANSWER

Question, page 339

The solution is as follows:

For 0.001 M HClO with $K_a = 3.7 \times 10^{-8}$ mol dm^{-3}

$$K_a = \frac{[H^+(aq)]^2}{0.001} = 3.7 \times 10^{-8} \text{ mol dm}^{-3}$$

$[H^+(aq)]^2 = 3.7 \times 10^{-11}$ mol^2 dm^{-6}

$[H^+(aq)] = 6.08 \times 10^{-6}$ mol dm^{-3}

and pH = 5.22

EXPERIMENT 14.6a Determination of K_a for a weak acid

HAZARDS

Ethanoic acid is corrosive and flammable; propanoic acid is corrosive.

Each group of students will require:
Eye protection
Volumetric flask, 100 cm^3
Dropping pipette
Beakers, 100 cm^3

Access to:
A weak acid (ethanoic or propanoic, for example) CORROSIVE
Balance, to weigh to ±0.01 g
pH meter, calibrated to ±0.1
or
Full-range Indicator
Narrow-range Indicator papers

Procedure

Full details are given in the *Students' Book*. Students are asked which of their measurements is likely to have been the least accurate. The pH value will have been determined to no better than 2SF and their K_a should also have no more than 2SF.

EXPERIMENT 14.6b Comparing some weak acids

HAZARDS

Ethanoic acid is corrosive and flammable; the chloroethanoic acids are toxic and corrosive.

Each group of students will require:
Eye protection
Test tubes and rack
pH meter, calibrated to ±0.1
or
Glass rod
Narrow-range Indicator papers

Access to the following 0.1 M solutions in labelled beakers:
Ethanoic acid (pure acid is FLAMMABLE and CORROSIVE)
Chloroethanoic acid (pure acid is TOXIC and CORROSIVE)
Dichloroethanoic acid (pure acid is CORROSIVE)
Trichloroethanoic acid (pure acid is CORROSIVE)

and in addition
0.5 M ethanoic acid
Methyl 4-hydroxybenzoate
Benzoic acid
0.5 M sodium carbonate

Procedure

Outline instructions are given in the *Students' Book*. Warn students that they may have to look very closely to see signs of reaction between acids and sodium carbonate solution. They have to be careful to distinguish the evolution of a gas from any bubbles of air caught up in the solutions during mixing. It is not easy to show that benzoic acid reacts with sodium carbonate solution.

ANSWERS

In your notes, page 341

1

Name of acid	Equation with conjugate base	K_a/mol dm^{-3}	pK_a
ethanoic	$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$	1.7×10^{-5}	4.8
chloroethanoic	$CH_2ClCO_2H \rightleftharpoons H^+ + CH_2ClCO_2^-$	1.3×10^{-3}	2.9
dichloroethanoic	$CHCl_2CO_2H \rightleftharpoons H^+ + CHCl_2CO_2^-$	5.0×10^{-2}	1.3
trichloroethanoic	$CCl_3CO_2H \rightleftharpoons H^+ + CCl_3CO_2$	2.3×10^{-1}	0.6
benzoic	$C_6H_5CO_2H \rightleftharpoons H^+ + C_6H_5CO_2^-$	6.3×10^{-5}	4.2
carbonic	$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$	4.5×10^{-7}	6.3
phenol	$C_6H_5OH \rightleftharpoons H^+ + C_6H_5O^-$	1.28×10^{-10}	9.9

2 In order of acid strength: benzoic > ethanoic > carbonic > phenol. You would expect the first two to displace carbonic acid from a carbonate.

3 Structural formula for the first four acids are:
$CH_3—CO_2H$
$CH_2Cl—CO_2H$
$CHCl_2—CO_2H$
$CCl_3—CO_2H$

4 The reason for the increase in acid strength ethanoic < trichloroethanoic is the electron-withdrawing effect of the chlorine atoms. It is sufficient for students to suggest that the C—Cl dipole may help to stabilise the anion.

14.7 Acid–base titrations

Timing About 3 hours

Suggested treatment

Students could begin this section by following the course of the pH change during an acid–base titration, as described in the following experiment.

EXPERIMENT 14.7 The change of pH during an acid–base titration

Each group of students will need:
Eye protection
Burette, 50 cm^3
Small funnel
Pipette, 25 cm^3, and pipette filler or second burette and second small funnel
Beaker, 100 cm^3
Magnetic stirrer, if possible

Access to:
pH meter
Computer
1.0 M ammonia, 40 cm^3 concentrated solution is CORROSIVE
1.0 M ethanoic acid, 25 cm^3 concentrated solution is CORROSIVE
1.0 M hydrochloric acid, 25 cm^3
1.0 M sodium hydroxide, 40 cm^3 CORROSIVE

Procedure

Full details of the experimental procedure are given in the *Students' Book*. Details of data capture using a computer are not provided here as it is assumed that teachers will use the instructions provided with their particular apparatus.

There are four possible combinations of acid and base:

- strong acid and strong base
- strong acid and weak base
- weak acid and strong base
- weak acid and weak base.

Time can be saved by allocating the various titrations to different students, so that each group does one titration. The results can be collected together and discussed at the end of the experiment. (See figure 14.1.)

In the graphs of volume of alkali added against pH, it is the regions of rapid pH change that are of interest to us. It will be seen that in the strong acid/strong base titration there is a rapid change of pH from about 4 to about 10 due to a very small addition of base solution around the 'end-point'. This range is smaller in the strong acid/weak base titration and covers approximately pH 4–7. This is also the case in the weak acid/strong base titration, but here the pH range of rapid change is approximately 7–10. For the weak acid/weak base system there is no marked horizontal portion in the curve and hence, no major region of rapid pH change.

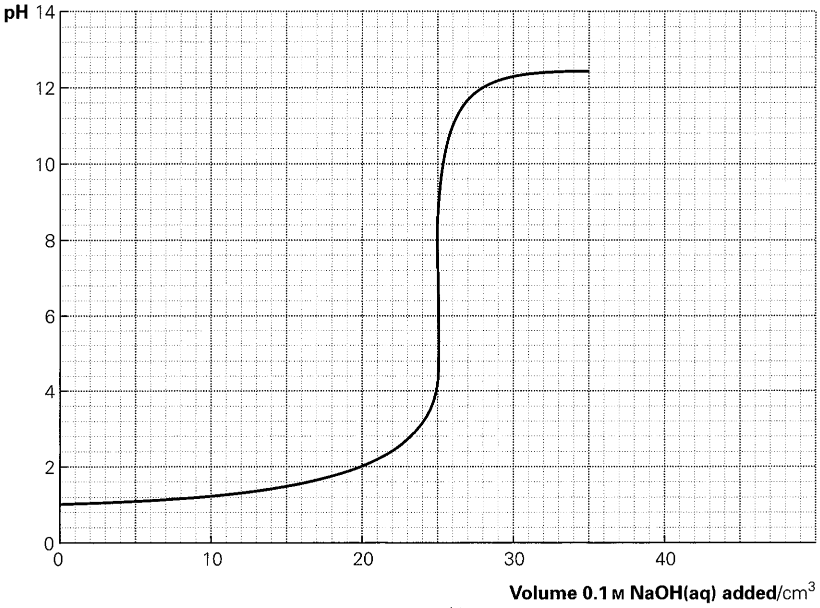


Figure 14.1a pH changes during titration of 25 cm^3 0.1 M HCl with 0.1 M NaOH(aq)

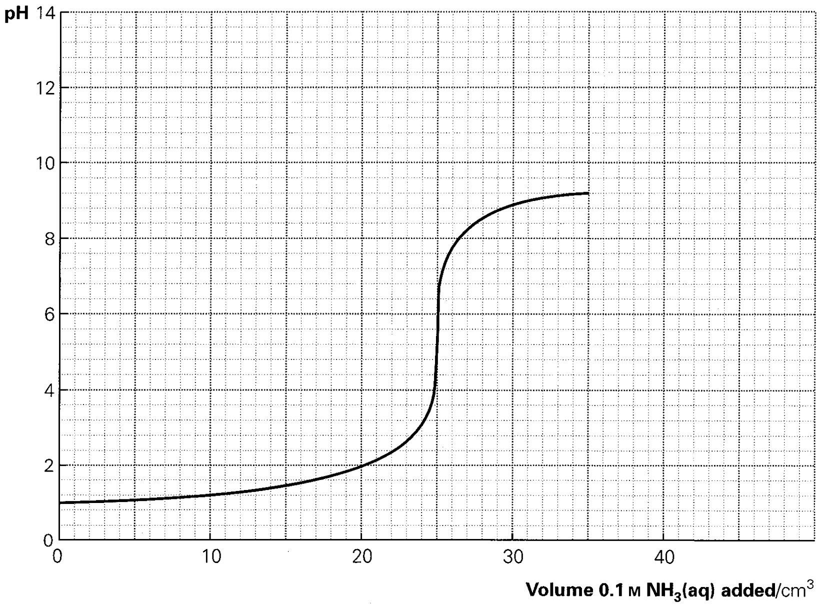


Figure 14.1b pH changes during titration of 25 cm^3 0.1 M HCl(aq) with 0.1 M NH$_3$(aq)

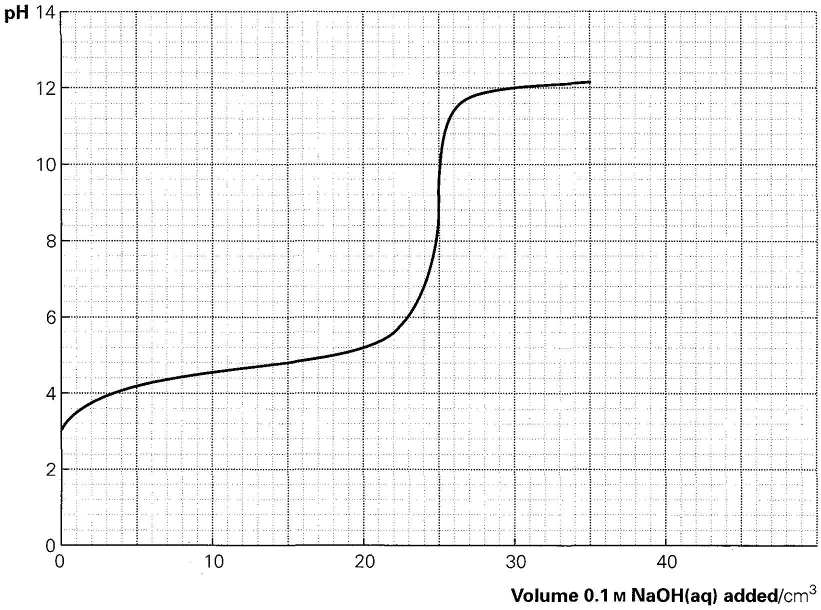


Figure 14.1c pH changes during titration of 25 cm³ 0.1 M $CH_3CO_2H(aq)$ with 0.1 M NaOH(aq)

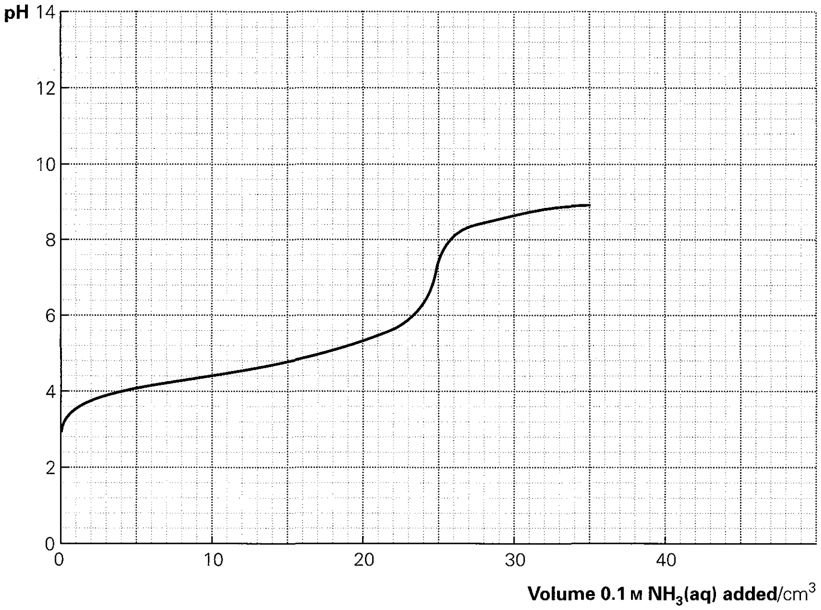


Figure 14.1d pH changes during titration of 25 cm³ 0.1 M CH_3CO_2H with 0.1 M $NH_3(aq)$

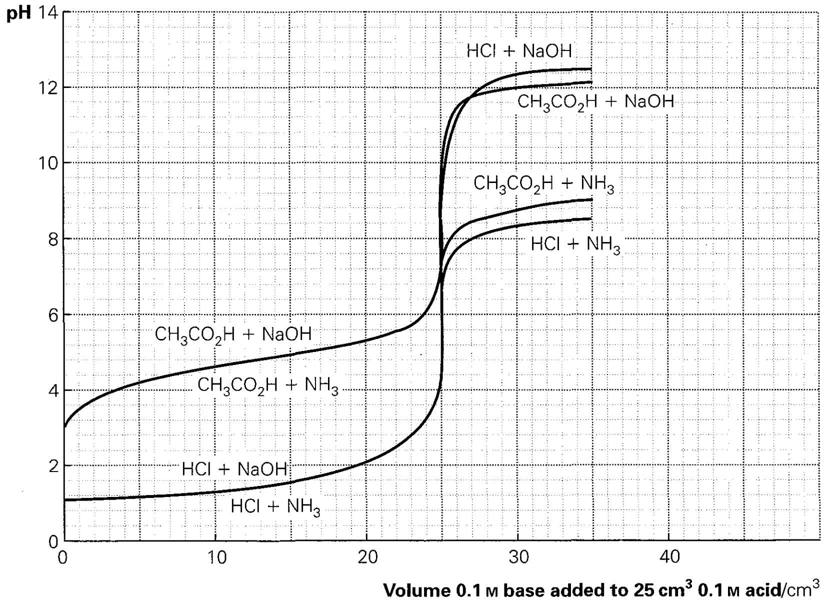


Figure 14.1e Titration curves for strong and weak acids and bases

The theory of indicators

This difference in the pH range at which equal volumes of solution react completely (25 cm^3 of each in this case) focuses attention on what exactly we mean by the end-point of a titration. In the examples under discussion, the solutions are all of the same molarity, and equal volumes should react together. The *equivalence point* occurs when the quantities of substance specified in the equation have reacted together. If this point can be made to correspond with a colour change in a suitable indicator (the end-point) we have a means of detecting the equivalence point easily and simply. Experience shows that choice of the correct indicator for use in acid–base titrations depends on the type of system used.

- For strong acids with strong bases almost any indicator can be used.
- For strong acids with weak bases the choice is restricted; methyl orange is commonly used.
- For weak acids with strong bases the choice is again restricted but indicators different from methyl orange must be used; phenolphthalein is a common choice.
- For weak acids with weak bases it is very difficult to find a suitable indicator.

The suitability of indicators for different purposes was established by trial and error long before the idea of pH was introduced. From such information we might confidently guess that the colour change with methyl orange occurs somewhere in the pH range 4–7, and for phenolphthalein somewhere in the pH range 7–10.

In cases where the use of indicators is unsuitable or impossible, a pH meter provides a simple method of following an acid–base titration.

From the titration curves it is obvious that the equivalence point in a titration does not invariably correspond with the production of a neutral solution, which would be defined as one with pH 7. In the strong acid/strong base system a solution very near to this pH value is obtained. With a strong acid and a weak base the mixture is acid (low pH), and with a weak acid and a strong base it is alkaline (high pH).

As an extension teachers might like to ask their students to calculate the origin of the rapid changes in pH at the end-point of the strong acid/strong base titration. This can be seen from a calculation of the pH value one drop (about 0.05 cm^3) before the equivalence point, and one drop after the equivalence point.

For one drop before the equivalence point there will be 25.00 cm^3 1.0 M HCl(aq) present and 24.95 cm^3 1.0 M NaOH(aq), i.e. an excess of 0.05 cm^3 1.0 M HCl(aq) in 49.95 cm^3 (near enough to 50 cm^3) total solution

$$\begin{aligned}
H^+(aq) \text{ ions per } 50\,cm^3 &= \frac{0.05 \times 1.0}{1000}\,mol \\
\therefore [H^+(aq)] &= \frac{0.05 \times 1.0 \times 1000}{1000 \times 50}\,mol\,dm^{-3} \\
&= 10^{-3}\,mol\,dm^{-3} \\
\therefore \text{pH value} &= 3
\end{aligned}$$

One drop after equivalence point we have 0.05 cm^3 1.0 M NaOH(aq) in excess

$$\begin{aligned}
OH^-(aq) \text{ ions per } 50\,cm^3 &= \frac{0.05 \times 1.0}{1000}\,mol \\
\therefore [OH^-(aq)] &= \frac{0.05 \times 1.0 \times 1000}{1000} \times 50 = 10^{-3}\,mol\,dm^{-3} \\
\text{but } [H^+(aq)][OH^-(aq)] &= K_w = 10^{-14}\,mol^2\,dm^{-6} \\
\therefore [H^+(aq)] &= \frac{10^{-14}}{10^{-3}} = 10^{-11}\,mol\,dm^{-3} \\
\therefore \text{pH value} &= 11
\end{aligned}$$

Thus there is a change in pH value of eight units during the addition of two drops of 1.0 M NaOH(aq) at the end-point of this titration.

ANSWERS

Questions, page 343

The colour of HIn for methyl orange is red.
The colour of In^- for phenolphthalein is red.

INVESTIGATION 14.7b An analysis of vinegars

It is important that students see this exercise as something rather more than a simple titration. If they seek to identify other more complex acids which may be present they may need some guidance as to the tests available. An alternative approach could be adopted via the 'construction' in the laboratory of a suitable mixture of known constitution. Students should be able to process results in a competent quantitative manner and be able to deal similarly with errors. Risk assessments must be accurately and thoroughly prepared and be rather more than a direct transfer from Hazcards.

14.8 Buffer solutions

Timing About 3 hours

Suggested treatment

The subject of buffer solutions is dealt with in some detail in the *Students' Book* and this might be read by students beforehand. Little more needs to be added here.

EXPERIMENT 14.8 Buffer solutions

Each group of students will need:
Eye protection
2 beakers, 100 cm^3
Spatula
Dropping pipette
Labels
Full-range Indicator, and colour chart
0.1 M ethanoic acid, 50 cm^3, pure ethanoic acid is CORROSIVE
0.1 M hydrochloric acid, 5 cm^3, the concentrated acid is CORROSIVE
1 M hydrochloric acid, 1 drop
Sodium ethanoate, 2 g
0.1 M sodium hydroxide, 5 cm^3 IRRITANT
Access to:
pH meter (optional)

Procedure

Full instructions are given in the *Students' Book.* After doing the experiments students should re-read the passage on the interpretation of buffer behaviour in order to interpret their results. They are likely to need help with this task.

Answers to Topic 14 questions

Review questions

14.1

i **a** $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ (1)

b $K_c = \frac{[HCl(g)]^2}{[H_2(g)][Cl_2(g)]}$ (1)

c No units (1)

ii **a** $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ (1)

b $K_c = \frac{[H_2(g)][I_2(g)]}{[HI(g)]^2}$ (1)

c No units (1)

iii **a** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3$ (1)

b $K_c = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$ (1)

c $mol^{-1}\,dm^3$ (1)

iv **a** $2O_3(g) \rightleftharpoons 3O_2(g)$ (1)

b $K_c = \frac{[O_2(g)]^3}{[O_3(g)]^2}$ (1)

c $mol\,dm^{-3}$ (1)

v **a** $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ (1)

b $K_c = \frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]}$ (1)

c No units (1)

vi **i** $CH_3OH(l) + CH_3CO_2H(l) \rightleftharpoons CH_3CO_2CH_3(l) + H_2O(l)$ (1)

b $K_c = \frac{[CH_3CO_2CH_3(l)][H_2O(l)]}{[CH_3OH(l)][CH_3CO_2H(l)]}$ (1)

c No units (1)

vii **a** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (1)

b $K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$ (1)

c $mol^{-2}\,dm^6$ (1)

viii **a** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ (1)

b $K_c = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$ (1)

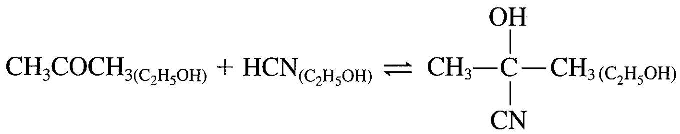
c No units (1)

ix **a** $2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$ (1)

b $K_c = \frac{[Fe^{2+}(aq)]^2[Sn^{4+}(aq)]}{[Fe^{3+}(aq)]^2[Sn^{2+}(aq)]}$ (1)

c No units (1)

x **a** (1)



$$CH_3COCH_{3(C_2H_5OH)} + HCN_{(C_2H_5OH)} \rightleftharpoons CH_3-\underset{\displaystyle CN}{\overset{\displaystyle OH}{C}}-CH_{3(C_2H_5OH)}$$

b $K_c = \frac{[CH_3C(OH)(CN)CH_{3(C_2H_5OH)}]}{[CH_3COCH_{3(C_2H_5OH)}][HCN_{(C_2H_5OH)}]}$ (1)

c $mol^{-1}\,dm^3$ (1)

Total 30 marks

14.2

$K_c = \frac{[NO_2]^2}{[N_2O_4]}$ (1)

$= \frac{(0.0014\,mol\,dm^{-3})^2}{0.19\,mol\,dm^{-3}}$ (1)

$= 1.03 \times 10^{-5}\,mol\,dm^{-3}$ (2)

Total 4 marks

14.3

a 0.02 mol − 0.009 mol = 0.011 mol (1)

b 0.01 mol − 0.009 mol = 0.001 mol (1)

c $K_c = \frac{[CH_3CO_2C_5H_{11}]}{[C_5H_{10}][CH_3CO_2H]}$ (1)

d $[C_5H_{10}]_{\text{eqm}} = \frac{0.011 \times 1000}{600}\ \text{mol dm}^{-3}$ (1)

$[CH_3CO_2H]_{\text{eqm}} = \frac{0.001 \times 1000}{600}\ \text{mol dm}^{-3}$ (1)

$[CH_3CO_2C_5H_{11}]_{\text{eqm}} = \frac{0.009 \times 1000}{600}\ \text{mol dm}^{-3}$ (1)

e $K_c = 491\ \text{mol}^{-1}\ \text{dm}^3$ (2)

Total 8 marks

14.4

a **i** To ‘freeze’ the equilibrium (1)

ii Purple iodine vapour would change to grey/black solid (1)

iii Titrate with standard (1)
sodium thiosulphate solution (1)
using starch indicator (1)

b **i** $K_c = \frac{[H_2(g)][I_2(g)]}{[HI(g)]^2}$ (1)

ii $4.8 \times 10^{-4}\ \text{mol dm}^{-3}$ (1)

iii $\frac{(4.8 \times 10^{-4}\ \text{mol dm}^{-3})^2}{[HI(g)]^2} = 0.019$ (1)

$[HI(g)] = \sqrt{\frac{(4.8 \times 10^{-4}\ \text{mol dm}^{-3})^2}{0.019}} = 3.48 \times 10^{-3}\ \text{mol dm}^{-3}$ (1)

Total 9 marks

14.5

i $K_p = \frac{p^2_{HCl}}{p_{H_2}p_{Cl_2}}$ no units (2)

ii $K_p = \frac{p_{H_2}p_{I_2}}{p^2_{HI}}$ no units (2)

iii $K_p = \frac{p^2_{SO_3}}{p^2_{SO_2}p_{O_2}}$ atm^{-1} (2)

iv $K_p = \frac{p^3_{O_2}}{p^2_{O_3}}$ atm (2)

v $K_p = \frac{p_{CO_2}p_{H_2}}{p_{CO}p_{H_2O}}$ no units (2)

vi $K_p = \frac{p^2_{NH_3}}{p_{N_2}p^3_{H_2}}$ atm^{-2} (2)

vii $K_p = \frac{p^2_{NO}}{p_{N_2}p_{O_2}}$ no units (2)

Total 14 marks

14.6

Mole fraction of $N_2 = \frac{4}{5}$ (1)

Partial pressure $= \frac{4}{5} \times 1 = 0.8$ atm (1)

Mole fraction of $O_2 = \frac{1}{5}$ (1)

Partial pressure $= \frac{1}{5} \times 1 = 0.2$ atm (1)

Total 4 marks

14.7

a $p_{NO_2} = \frac{0.96}{1.02} \times 0.2 = 0.188$ atm (2)

$p_{NO} = \frac{0.04}{1.02} \times 0.2 = 7.84 \times 10^{-3}$ atm (2)

$p_{O_2} = \frac{0.02}{1.02} \times 0.2 = 3.92 \times 10^{-3}$ atm (2)

b $K_p = \frac{p^2_{NO}p_{O_2}}{p^2_{NO_2}}$ (1)

c $K_p = 6.82 \times 10^{-6}$ atm (2)

Total 9 marks

14.8

a The value of K_p decreases with increase of temperature, so proportion of ammonia at equilibrium decreases. (2)

b Forward reaction is exothermic (K_p lower at higher temperatures) (2)

c **i** Less ammonia at equilibrium (lower yield) (1)

Faster reaction (1)

ii More ammonia at equilibrium (1)

Slower reaction (1)

Total 8 marks

14.9

a $\Delta S^{\ominus}_{\text{system}} = 512.2 - 205 - 496.2 = -189\ \text{J mol}^{-1}\ \text{K}^{-1}$ (2)

b $\Delta S^{\ominus}_{\text{surroundings}} = +661\ \text{J mol}^{-1}\ \text{K}^{-1}$ (1)

c $\Delta S^{\ominus}_{\text{total}} = +472\ \text{J mol}^{-1}\ \text{K}^{-1}$ (1)

Equilibrium lies well to right-hand side (1)

d At 700 K, $\Delta S_{\text{surroundings}} = +281\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta S_{\text{total}} = +92\ \text{J mol}^{-1}\ \text{K}^{-1}$ (1)

At 1100 K, $\Delta S_{\text{surroundings}} = +179\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta S_{\text{total}} = -10\ \text{J mol}^{-1}\ \text{K}^{-1}$ (1)

e ΔS_{total} decreases as temperature increases so equilibrium shifting towards left-hand side. (1)

f $K_p = 4.0 \times 10^{-24}\ \text{atm}^{-1}$(298 K); $3.0 \times 10^{-4}\ \text{atm}^{-1}$(700 K); $1.3 \times 10^{-1}\ \text{atm}^{-1}$(1100 K) (2)

Consistent with answers to **e**

g For $\Delta S_{\text{total}} = 0$, $\Delta S_{\text{surroundings}} = +189\ \text{J mol}^{-1}\ \text{K}^{-1}$

$T = -\frac{(-197\,000\ \text{J mol}^{-1})}{189\ \text{J mol}^{-1}\ \text{K}^{-1}} = 1042\ \text{K}$ (1)

Eqm. position is 'central' (1)

Total 12 marks

14.10

a 1.7 (1)

b 1.3 (1)

c 3.0 (1)

d 13.9 (1)

e 12.6 (1)

f 14.6 (1)

Total 6 marks

14.11

a $K_a = \frac{[H^+][C_6H_5CO_2^-]}{[C_6H_5CO_2H]}$ (1)

b $K_a = \frac{[H^+][C_6H_5O^-]}{[C_6H_5OH]}$ (1)

c $K_a = \frac{[H^+][CH_3(CH_2)_2CO_2^-]}{[CH_3(CH_2)_2CO_2H]}$ (1)

d $K_a = \frac{[H^+][CN^-]}{[HCN]}$ (1)

Total 4 marks

14.12

a $K_a = 6.3 \times 10^{-5}\ \text{mol dm}^{-3} = \frac{[H^+]^2}{0.001}\ \text{mol dm}^{-3}$ (1)

$[H^+]^2 = 6.3 \times 10^{-8}$

$[H^+] = 2.5 \times 10^{-4}$ (1)

pH = 3.6 (1)

b 6.6 (method as for **a**) (3)

c 3.7 (method as for **a**) (3)

d 5.1 (method as for **a**) (3)

Total 12 marks

14.13

a $[H^+] = 7.94 \times 10^{-6}\ \text{mol dm}^{-3}$ (1)

$K_a = (7.94 \times 10^{-6})^2/0.1$ (1)

$= 6.3 \times 10^{-10}\ \text{mol dm}^{-3}$ (1)

b $[H^+] = 1.26 \times 10^{-5}\ \text{mol dm}^{-3}$ (1)

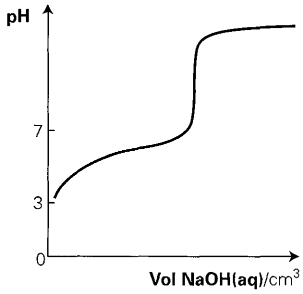
$K_a = (1.26 \times 10^{-5})^2/0.025$ (1)

$= 6.3 \times 10^{-9}\ \text{mol dm}^{-3}$ (1)

Total 6 marks

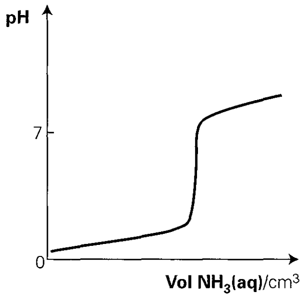
14.14

a



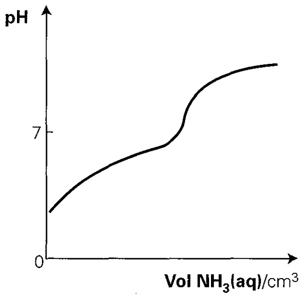
for original pH (1)
for form of graph (1)
for final pH (1)

b



marks as in **a** (3)

c



marks as in **a** (3)

d There is no sharp change in pH around the end-point (1)

Total 10 marks

14.15

a $\text{pH} = -\lg K_a - \lg\,[\text{acid}]/[\text{base}]$ (1)

$= 4.9 - \lg\,(0.05)/(0.075)$ (2)

$= 5.1$ (1)

b 9.5 (method as in **a**) (4)

c 9.5 (method as in **a**) (2)

d Same pH because ratio [acid]/[base] is the same in both (2)

Total 12 marks

14.16

a **i** $4.9 = 4.8 - \lg\dfrac{[CH_3CO_2H]}{[CH_3CO_2^-]}$ (1)

$\lg\dfrac{[CH_3CO_2H]}{[CH_3CO_2^-]} = -0.1$ (1)

$\dfrac{[CH_3CO_2H]}{[CH_3CO_2^-]} = 0.79$ (2SF) (1)

ii $9.6 = 9.3 - \lg\dfrac{[NH_4^+]}{[NH_3]}$ (1)

$\lg\dfrac{[NH_4^+]}{[NH_3]} = -0.3$ (1)

$\dfrac{[NH_4^+]}{[NH_3]} = 0.505$ (2SF) (1)

b **i** $CH_3CO_2H : \dfrac{0.79}{1.79} \times 1000\ \text{cm}^3 = 441\ \text{cm}^3$ (1)

$CH_3CO_2Na : \dfrac{1}{1.79} \times 1000\ \text{cm}^3 = 559\ \text{cm}^3$ (1)

ii $NH_4Cl : \dfrac{0.5}{1.5} \times 1000\ \text{cm}^3 = 333\ \text{cm}^3$ (1)

$NH_3 : \dfrac{1.0}{1.5} \times 1000\ \text{cm}^3 = 667\ \text{cm}^3$ (1)

Total 10 marks

Examination questions

14.17

a No overall change in composition of system (1)
Reaction has same rate in both directions (1)

b **i** Weigh sealed syringe containing liquid, then expel required amount and re-weigh (OR suitable alternative – not conversion to volume). (1)

ii 1 mole weighs 100 g (1)
$\therefore$ 0.980 g = 0.0098 moles (1)

iii Moles Br_2 = moles of B = 38.7/1000 × 2 = 0.00774 mol (1)

iv Moles of A = 0.0098 − 0.00774 = 0.00206 or (0.0021) mol (1)

v $K_c = \frac{[B]_{eqm}}{[A]_{eqm}}$ (1)

$= \frac{0.00774}{0.00206} = 3.76$ (no units) (1)

(or 3.8 or 3.757)

Total 9 marks

14.18

a **i** Starch OR none (1)
Blue-black to colourless OR yellow to colourless (2)

ii $76 \times \frac{0.01}{1000} \times \frac{1}{2} \times \frac{1000}{5} = 0.076$ (mol dm^{-3}) (2)

iii $K_c = \frac{[I_2(\text{water})]}{[I_2(\text{hydrocarbon})]}$ (1)

$= \frac{8.9 \times 10^{-4}}{7.6 \times 10^{-2}} = 0.012$ (1)

iv Repeat titrations/record volume of $Na_2S_2O_3$ to 1 dec place
OR use more concentrated $Na_2S_2O_3$ to get lower titration value
OR use larger pipette than 5 cm^3
Any two sensible improvements (2)

v K_c unaffected (1)

b More iodine in aqueous layer if KI present so more $Na_2S_2O_3$ solution used because I_3^- formed, I_2 removed so more I_2 (from organic layer) will replace it. (2)

Total 12 marks

14.19

a $K_a = \frac{[H^+][H_2BO_3^-]}{[H_3BO_3]}$ (1)

b pH = −lg[H$^+$] (1)
[H$^+$] = 7.94 × 10^{-6} mol dm^{-3} (1)

$K_a = \frac{(7.94 \times 10^{-6})^2}{0.1} = 6.3 \times 10^{-10}$ mol dm^{-3} (1)

c
$$\left.\begin{array}{l} H_2BO_3^- = H^+ + HBO_3^{2-} \\ HBO_3^{2-} = H^+ + BO_3^{3-} \\ H_2O = H^+ + OH^- \end{array}\right\} \text{Any two}$$
(2)

d Boric acid is weaker than carbonic acid (1)
so unable to donate protons to CO_3^{2-} (1)

e $Na_3BO_3/Na_2HBO_3/NaH_2BO_3/NaOH$ (1)
(or K$^+$ or NH_4^+ salts or KOH)

Total 9 marks

14.20

a $K_a = \frac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]}$ (2)

b **i** pH = −lg[H$^+$] = 5.6 (1)
[H$^+$] = 2.5 × 10^{-6} mol dm^{-3} (1)

ii [NH_4^+] will increase (1)
so K_a can remain constant/H$^+$ combines with NH_3 (1)

c **i** Solution whose pH remains constant if small quantity of acid/alkali added. (2)

ii Added OH^- combines with H^+ in buffer (1)

H^+ replaced by dissociation of NH_4^+ (1)

d H_2O is accepting protons ∴ a base (1)

Total 11 marks

14.21 **a** **i** $K_p = \dfrac{p^2_{SO_3}}{p^2_{SO_2}p_{O_2}}$ (1)

atm^{-1} (1)

ii Reaction is exothermic so gases heat up in catalyst bed (1)

so heat is removed to maximise conversion (1)

iii Use excess oxygen/air (1)

Increase pressure (1)

iv SO_2 and SO_3 produce acid rain which damages plants/buildings (1)

b **i** Decrease because fewer product molecules (1)

ii $\Delta S_{surroundings} = \dfrac{-\Delta H}{T}$ (1)

$= -\dfrac{(-197\,000\ J\ mol^{-1})}{700\ K} = +281\ J\ mol^{-1}\ K^{-1}$ (1)

iii Negative but numerically less than 281 (1)

c **i** $[H^+] = 0.15\ mol\ dm^{-3}$ (1)

$pH = 0.82$ (1)

ii Curve starts at pH calculated in (i) (1)

Vertical part at $20\ cm^3$ (1)

Vertical part largely below pH 7 (1)

iii $[NH_3] = \dfrac{10.0\ cm^3}{1000\ cm^3} \times 0.00075\ mol\ dm^{-3} \times 2 \times \dfrac{1000\ cm^3}{20.0}$

$= 0.075\ mol\ dm^{-3}$ (2)

iv Unsuitable indicators change colour outside required range (1)

Total 19 marks

14.22 **a** $K_p = \dfrac{p_{C_2H_5OH(g)}}{p_{C_2H_4(g)} \times p_{H_2O(g)}}$ (1)

b Increasing the proportion of steam will increase the value of $p_{H_2O(g)}$, so for K_p to remain constant more C_2H_4 must be converted to C_2H_5OH. (1)

c **i**

	Ethene	**Steam**	**Ethanol**
initial moles	1.00	2.00	0
moles at equilibrium	0.54	1.54	0.46
partial pressures at equilibrium	$\frac{0.54}{2.54} \times 70$	$\frac{1.54}{2.54} \times 70$	$\frac{0.46}{2.54} \times 70$
	= 14.9 atm	= 42.4 atm	= 12.7 atm

(1 mark for each correct answer) (5)

ii $K_p = \dfrac{12.7}{14.9 \times 42.4} = 0.0201\ atm^{-1}$ (3SF) (2)

d Reaction would be too slow at lower temperatures. (1)

e Energy cost (for heating); energy to maintain high pressure; labour costs; capital depreciation; other sensible answers. 1 mark for each. (2)

Total 12 marks

TOPIC 15

Oxidation products of alcohols

Introduction

This topic of organic chemistry looks at the oxidation products of alcohols in the light of the principles of mechanistic classification, but also makes use of concepts such as K_a which have been introduced in more recent topics. The nucleophilic reactions of carbonyl compounds are studied before modifications of behaviour in carboxylic acids and their derivatives are considered. The importance of delocalisation in the ionisation of weak acids is stressed. Work on esters can be extended by a further preparation included here, but acid anhydrides and amides are no longer emphasised.

Background reading provides a brief introduction to enhance interest and support studies in *Biochemistry*, but again detailed knowledge is not expected. A study task shows some of the issues involved in the large scale manufacture of organic chemicals.

A knowledge of the subject matter is assumed in both the Special Studies *Biochemistry* and *Food science*. It is desirable that this topic is covered before either of these Special Studies is attempted.

Contents

Timing		**Students' Book**
15.1	2 hours	pages 357–61
15.2	4 hours	pages 361–6
15.3	2 hours	pages 367–70
15.4	Homework	pages 370–5
Total a little under 2 weeks		

15.1 Carbonyl compounds – carbonyl functional group; solubility; comparison with alkenes; experiments with carbonyl compounds; Benedict's solution and Brady's reagent; nucleophilic addition reactions and addition–elimination reactions.

15.2 Carboxylic acids – factors involved in the reactivity of the carboxylic group including delocalisation; experiments with ethanoic acid, solubility, pH, salt and ester formation; carboxylic acids, properties involving the O—H bond; infrared spectrum of ethanoic acid; nucleophilic reactions involving the C═O bond, esterification, reduction.

15.3 Carboxylic acid derivatives – esters; acyl chlorides; nucleophilic reactions and comparative ease of hydrolysis, reduction.

15.4 Background reading: the manufacture of citric acid.

Objectives

1. To apply the principles learnt in earlier topics to the reactions of carbonyl compounds, carboxylic acids, and their derivatives.
2. To learn about the reactions of carbonyl compounds, carboxylic acids and their derivatives.
3. To apply the principles learnt about hydrogen bonding and acid–base properties to the study of organic compounds.
4. To provide information about the industrial and social importance of selected compounds.

15.1 Carbonyl compounds

Timing About 2 hours

Suggested treatment

This section reviews the introduction to aldehydes and ketones as oxidation products of alcohols, given in Topic 2 and extends the study into the nucleophilic reactions of carbonyl compounds. These reactions are illustrated by the preparation of a hydrazone and this enables both nucleophilic reactions and addition–elimination reactions to be introduced before they are encountered in the more complex carboxylic acids and their derivatives.

Since aldehydes and ketones have unsaturated functional groups, the topic should start by comparing their properties with those of alkenes. Students should recall that the characteristic reactions of alkenes are electrophilic addition reactions on account of the relatively weak π bond (265 kJ mol^{-1}).

$E(C—C) = +347\,kJ\,mol^{-1}$ (σ bond)	$E(C—O) = +358\,kJ\,mol^{-1}$ (σ bond)
$E(C=C) = +612\,kJ\,mol^{-1}$ ($\sigma + \pi$ bonds)	$E(C=O) = +736\,kJ\,mol^{-1}$ ($\sigma + \pi$ bonds)
Therefore π bond is $+265$ kJ mol^{-1} in alkenes	Therefore π bond is $+378$ kJ mol^{-1} in aldehydes

Similar data for carbonyl compounds indicate that the carbon–oxygen π bond (378 kJ mol^{-1} in aldehydes) is about as strong as the carbon–oxygen σ bond, so nucleophilic addition to C=O bonds may not occur as readily as electrophilic addition to C=C.

The *Students' Book* mentions that a noticeable difference between the alkene and carbonyl groups is that the latter are strongly polarised; attention is also given to the infrared spectra of carbonyl compounds.

EXPERIMENT 15.1

An investigation of the reactions of aldehydes and ketones

HAZARD

Sodium dichromate(VI) may cause sensitisation by skin contact so gloves should always be worn when using the solid and preferably when using the solution.
The products are hazardous: propanoic acid is corrosive; propanal is highly flammable and irritant.
2,4-dinitrophenylhydrazine is explosive and toxic. Gloves and eye protection should be worn when making up the solution; students should not be allowed to handle the solid.

Each group of students will need:
Eye protection and protective gloves
Bunsen burner and heatproof mat
4 boiling tubes and racks
4 dropping pipettes
Propanal, a few drops HIGHLY FLAMMABLE, IRRITANT
Propanone, a few drops HIGHLY FLAMMABLE

Access to:
Benedict's solution
0.1 M sodium dichromate(VI) TOXIC
0.04 M sodium hydroxide IRRITANT
1 M sulphuric acid IRRITANT
Brady's reagent, 10 cm^3 (see below)

Brady's reagent

To prepare nearly 250 cm^3 of Brady's reagent, dissolve 10 g of 2,4-dinitrophenylhydrazine in 20 cm^3 of concentrated sulphuric acid (corrosive) and add carefully, with cooling, 150 cm^3 of methanol (toxic and highly flammable). Warm gently to dissolve any solid and then add 50 cm^3 of water. Crystals usually form at the bottom of the reagent bottle on standing.

An alternative is to dissolve 0.25 g of 2,4-dinitrophenylhydrazine in a mixture of 50 cm^3 concentrated hydrochloric acid and 50 cm^3 pure water; then dilute to 250 cm^3 with more water. This solution gives positive results with propanone and propanal, but the reaction may be slower. It does *not* give positive results with *all* aldehydes and ketones.

Procedure

Students should be advised to heat the solutions gently, otherwise the propanal or propanone will be volatilised rapidly and will not react with the reagents.

1 Solubility in water

The organic compounds will be found to dissolve in water; students should predict hydrogen bond formation between carbonyl groups and water molecules.

2 Oxidation with sodium dichromate(VI)

The propanal is oxidised to propanoic acid and the sodium dichromate(VI) is reduced to green Cr^{3+} ions. Students should already be familiar with the use of acidified sodium dichromate(VI) as an oxidising agent from Experiments 2.3a and 2.3b. No change is observed on boiling sodium dichromate(VI) with propanone.

3 Oxidation with Benedict's solution

With propanal, students should observe a yellow–green precipitate as soon as the solution boils and this may eventually turn red if boiling is continued. With propanone, a deep blue-violet colour is seen on adding Benedict's solution but no further change occurs on boiling.

Good results are usually obtained if the tubes are heated in a hot water bath, when the reaction with propanal can be seen to go through a series of colours, finally forming the characteristic red precipitate of copper(I) oxide.

4 Reaction with Brady's reagent

This reaction is included in order to provide a quick and colourful example of a nucleophilic addition reaction. It also allows the idea of a mechanism with more than one step to be introduced before addition–elimination reactions are encountered in carboxylic acids.

15.2 Carboxylic acids

Timing 4 hours

Suggested treatment

The behaviour of the hydroxyl group in alcohols was studied in Topic 2 and the modifications on account of delocalisation in phenol were considered in Topic 12. In this section the behaviour of the hydroxyl group in carboxylic acids is developed. Again some modifications are expected on account of the interaction of the lone pair of electrons of the hydroxyl group with the π bond of the carbonyl group. When the hydroxyl group ionises, the resulting anion is stabilised by delocalisation and carboxylic acids are more strongly acidic than phenols as seen in a comparison of K_a values.

The large dipole of the carbonyl group means that the carbon atom in the carboxyl group is electrophilic in nature and therefore should be susceptible to nucleophilic attack. The reactions could involve addition to the relatively strong π bond or substitution of the O—H group as in alcohols. The reactions are, of course, addition–elimination reactions, which usually require an acid catalyst, but as an *aide memoire* they can be regarded as 'overall nucleophilic substitution' of the hydroxyl group. The detailed mechanism of the nucleophilic formation of esters is potentially difficult. Students are expected to know and be able to interpret the evidence based on the use of the isotope ^{18}O but are not expected to learn the full theory of ester formation.

Solubility issues can be used to revise the work on intermolecular forces studied in Topic 9.

EXPERIMENT 15.2 The reactions of ethanoic acid

HAZARDS

The esters produced are flammable and irritant to the eyes.
The preparation of esters from methanoic acid is best avoided as it is corrosive and has a dangerous vapour.

Each group of students will need:
Eye protection
Test tubes and rack
Small beakers, 2
Dropping pipette
Measuring cylinder, 10 cm^3

Access to:
Ethanoic acid, pure (glacial), 2 cm^3 CORROSIVE, FLAMMABLE
0.1 M ethanoic acid, 10 cm^3
Ethanol HIGHLY FLAMMABLE
Full-range Indicator
0.1 M sodium hydroxide, 15 cm^3 IRRITANT
1 M sodium carbonate
0.1 M sodium ethanoate solution
Concentrated sulphuric acid, 1 cm^3 CORROSIVE

Optional formation of esters:
Benzyl alcohol (phenylmethanol) HARMFUL
Pentan-2-ol FLAMMABLE, HARMFUL
Propan-1-ol HIGHLY FLAMMABLE
Butanoic acid CORROSIVE

Procedure

Full instructions are given in the *Students' Book.* The following notes may be helpful.

1 Solubility with pH

The first K_a value of carbonic acid is 4.5×10^{-7} mol dm^{-3}, whereas the K_a values for the carboxylic acids are greater than 1×10^{-5} mol dm^{-3}. Consequently the carboxylic acids release CO_2 from carbonates.

2 Formation of salts

A gradual change of pH should be observed, characteristic of a weak acid forming a buffer solution with its salt. Sodium ethanoate is alkaline because of salt hydrolysis.

3 Formation of esters

Students can calculate the volumes of acid and alcohol required from the *Book of Data*, table 5.5.

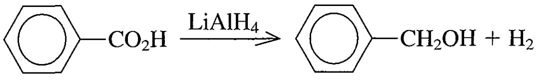
This reaction is discussed under the heading 'Nucleophilic reactions involving the C=O bond'. There is a set of optional ester preparations which can be attempted if the chemicals are available.

4 Structure of functional groups and delocalisation

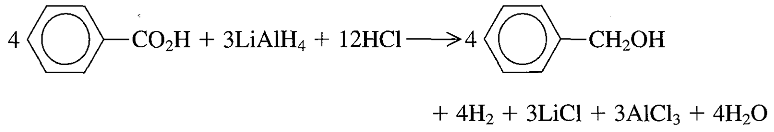
Evidence for delocalisation in methanoic acid and the methanoate ion is presented in the *Students' Book* by comparing observed and predicted bond lengths.

Reactions of carboxylic acids

A review of the reactions of the carboxylic acids is given in the *Students' Book.* In several of the more complicated cases full balanced equations are not used, a simplified version is all that is required. Reduction using lithium tetrahydridoaluminate(III), for example, is shown thus:



For the teacher's information the full balanced equation is:



An opportunity should be taken to test the students' knowledge of these reactions at a suitable point.

15.3 Carboxylic acid derivatives

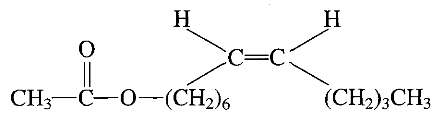
Timing 2 hours

Suggested treatment

Esters are emphasised in this section. The alkaline hydrolysis of methyl benzoate is proposed as a student experiment and details are included of an optional preparation of cholesteryl benzoate, 'liquid crystals'. Although the reagents are hazardous it does provide a context of interest and an opportunity to make an ester with an acyl chloride.

Acid anhydrides are no longer discussed in the context of acid derivatives, but ethanoic anhydride was used in the preparation of aspirin in Topic 12.

Students often have difficulty with the formulae of the acid derivatives. The building of ball-and-link models to help with the interpretation of the reactions is recommended. The formula of the pheromone of the cabbage looper moth, *cis*-7-dodecenyl ethanoate, mentioned in the comment, is given below.



cis-7-dodecenyl ethanoate

Students are not expected to know how to prepare acid anhydrides and acyl chlorides, but they are used in a number of preparations in the *Students' Book* so some familiarity with their properties is helpful.

The section concludes with a review of the reactions of carboxylic acid derivatives. These are seen as nucleophilic substitutions, and are considered in terms of the relative attracting powers of the various nucleophiles.

EXPERIMENT 15.3

Some reactions of carboxylic acid derivatives

HAZARDS

The experiments with ethanoyl chloride should be demonstrated. Ethanoyl chloride is both corrosive and has dangerous reactions with water. The teacher should use it with caution. It is volatile and forms corrosive fumes in moist air, and will react violently with anything containing water, and with alcohols.

The teacher will need:

Eye protection
Molecular model kit
3 small beakers
Dropping pipette
Reflux apparatus with 50 cm^3 pear-shaped flask
Suction filtration apparatus (optional)
Melting point apparatus
Ethanoyl chloride CORROSIVE, HIGHLY FLAMMABLE
Ethanol HIGHLY FLAMMABLE
Methyl benzoate, 2 cm^3 FLAMMABLE
8 M ammonia CORROSIVE
1 M sodium carbonate
2 M sodium hydroxide, 5 cm^3 CORROSIVE
Full-range Indicator paper
2 M hydrochloric acid IRRITANT

HAZARDS

Use only 15cm^3 of 2M sodium hydroxide solution. Check the apparatus before students begin refluxing, and keep a close eye on the procedure being followed, bearing in mind the factors which might lead to hazardous 'bumping'.

Procedure

Use the quantity of sodium hydroxide shown in the right hand Hazards box on P218, and not the larger quantity shown in the 2000 printing of the *Student's book.* This is to reduce the risk of alkali being ejected from the reflux condenser as a result of 'bumping'.

Full instructions are given in the *Students' Book.* The following notes may be helpful.

1 Esters

An ester hydrolysis is included in order that at least one student experiment is available in this section. Identification of the product by the melting point technique is an option if time is available.

2 Acyl chloride

The reactions are violent and hydrogen chloride fumes are evolved. The product with 8 M ammonia is mainly ethanamide and a solid residue is left on evaporation. The equations for the reactions are given in the *Students' Book.*

EXPERIMENT 15.3 (optional) Cholesteryl benzoate, 'liquid crystals'

This experiment is not included in the *Students' Book* see Sheet 15.1 on page 225 of this Teachers' guide.

HAZARDS

Because of the harmful vapours of the reagents this should be regarded as an optional experiment.
The safety precautions concerning the use of pyridine (harmful vapour; avoid contact with skin and eyes) and benzoyl chloride (lachrymatory) mentioned in the Students' Instruction (see Sheet 15.1 on page 225) should be rigidly adhered to.

Each group of students will need:
Eye protection
Protective gloves
Apparatus for suction filtration: 100 cm^3 Buchner flask and filter funnel
Bunsen burner and tongs
Conical flask, 50 cm^3
Measuring cylinder, 10 cm^3
Ice bath
Microscope slide
Steam bath
Access to:
Benzoyl chloride, 0.4 cm^3 CORROSIVE
Cholesterol, 1 g
Ethyl ethanoate, 20 cm^3 HIGHLY FLAMMABLE
Methanol, 20 cm^3 TOXIC, HIGHLY FLAMMABLE
Pyridine, 3 cm^3 HARMFUL, HIGHLY FLAMMABLE
Fume cupboard
Piece of polaroid
Balance, to weigh to ±0.1 g

Procedure

See the copiable instructions for students on page 225 of this book. The properties of liquid films can readily be seen, for example by looking at a digital watch display through a piece of polaroid film. Small mats impregnated with liquid crystal can be bought; they change colour dramatically when warmed.

15.4 Background reading: the manufacture of citric acid

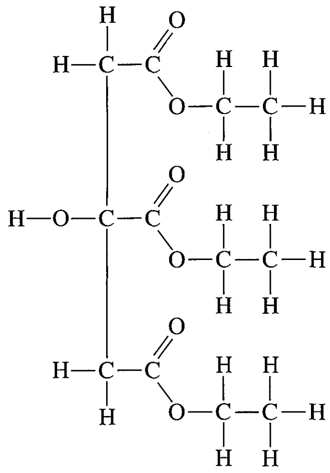
ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 370

1 Acidulant is a term for acid used in industry. Citric acid occurs widely in living things and, as an acid, it lowers the pH of solutions.

2

	Lime/sulphuric acid process	**Solvent extraction process**
Source of citric acid	Fermentation of renewable raw materials which need not be pure, such as molasses or glycose syrups from cereals	Source of carbohydrate for fermentation must be pure, such as sugar solution from hydrolysis of starch
Method of separation	Precipitation as insoluble calcium sulphate	Solvent extraction
Method of recovery and purification	Filter and wash precipitate, regenerate with sulphuric acid, filter to remove calcium sulphate	Release citric acid to give aqueous solution
Final stages	Recrystallise (by evaporation and cooling), centrifuge and air dry	Recrystallise (by evaporation and cooling), centrifuge and air dry
By-products	Mycelium, gypsum, biogas (from fermentation of organic waste)	Mycelium


Displayed formula of the triethyl ester of citric acid

3 Calcium hydroxide is more soluble so precipitation occurs in solution. Also no gas forms which avoids foaming.

4 Organic wastes increase the Biological Oxygen Demand of water courses. This lowers oxygen levels in rivers and streams which is a threat to life – especially fish.

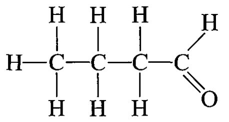
5 a food flavouring, buffer action in pharmaceuticals
b descaling, enhanced oil recovery, buffer action and food additives, anti-caking agent
c water softening, prevention of coagulation of blood products, addition of trace minerals to animal diets and plant fertilisers, anti-oxidant.

6 A plasticiser has molecules large enough to separate polymer chains in a plastic, thus weakening the effects of inter-chain forces so that they can move more freely. A plasticiser acts like an 'internal lubricant'. A desirable plasticiser is chemically relatively inert and non-toxic.

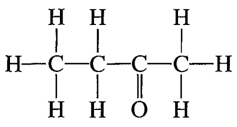
Answers to Topic 15 questions

Review questions

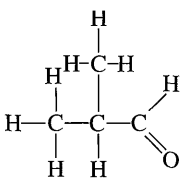
15.1


(1)

butanal (1)


(1)

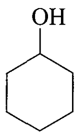
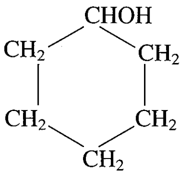
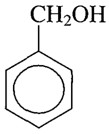
butanone (1)

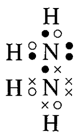
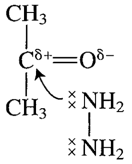

(1)

2-methylpropanal (1)

Total 6 marks

15.2		$CH_3CH_2CH_2COCH_3$	(1)
		pentan-2-one	(1)
		$CH_3CH_2COCH_2CH_3$	(1)
		pentan-3-one	(1)
		$(CH_3)_2CHCOCH_3$	(1)
		3-methylbutanone	(1)
			Total 6 marks

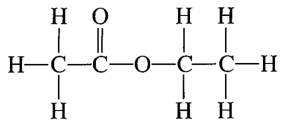
15.3	**a**	CH_3CH_2OH	(1)
		ethanol	(1)
	b	$CH_3CHOHCH_3$	(1)
		propan-2-ol	(1)
	c	$CH_3CH_2CH_2OH$	(1)
		propan-1-ol	(1)
	d	$CH_3(CH_2)_3CHOHCH_3$	(1)
		hexan-2-ol	(1)
	e	 or 	(1)
		cyclohexanol	(1)
	f		(1)
		phenylmethanol	(1)
			Total 12 marks

15.4	**a**		(2)
	b	Nucleophile	(1)
		it has lone pairs of electrons	(1)
	c		(1)
			Total 5 marks

15.5	**a**	**i** Oxidation (or redox)	(1)
		ii Oxidation (or redox)	(1)
		iii Nucleophilic attack (students will probably get no further)	(1)
	b	**i** $CH_3CH_2CH_2CO_2H$	(1)
		ii $CH_3CH_2CH_2CO_2H$	(1)
	c	Brady's reagent only: it reacts with aldehydes and ketones. Ketones cannot be oxidised and so do not react with dichromate or Benedict's solution.	(2)
			Total 7 marks

15.6	**a**	$2HCO_2H(l) + 2Na(s) \longrightarrow 2HCO_2^-Na^+(s) + H_2(g)$	(2)
	b	$HCO_2H(l) + NaOH(aq) \longrightarrow HCO_2^-Na^+(aq) + H_2O(l)$	(2)
	c	$2HCO_2H(l) + Na_2CO_3(aq) \longrightarrow 2HCO_2^-Na^+(aq) + CO_2(g) + H_2O(l)$	(2)
	d	$HCO_2H(l) + NaHCO_3(aq) \longrightarrow HCO_2^-Na^+(aq) + CO_2(g) + H_2O(l)$	(2)
			Total 8 marks

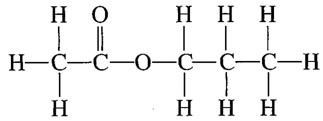
15.7 **a** **i**



$\mathrm{H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$

(2)

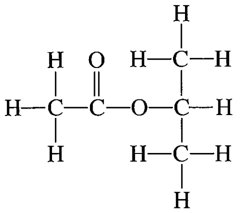
ii



$\mathrm{H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$

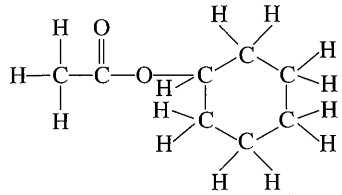
(2)

iii



(2)

iv



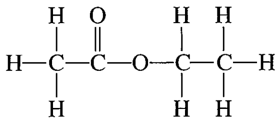
(2)

b

i Ethyl ethanoate (1)
ii Propyl ethanoate (1)
iii 2-propyl ethanoate (1)
iv Cyclohexyl ethanoate (1)

Total 12 marks

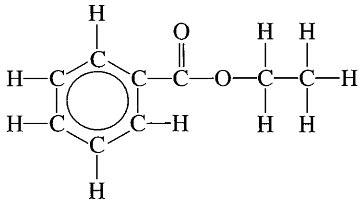
15.8 **a** **i**



$\mathrm{H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$

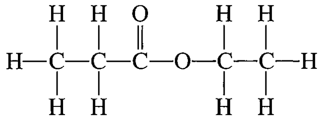
(2)

ii



(2)

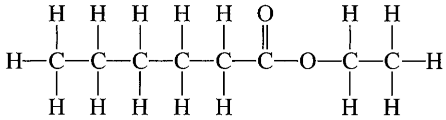
iii



$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$

(2)

iv



$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$

(2)

b

i Ethyl ethanoate (1)
ii Ethyl benzoate (1)
iii Ethyl propanoate (1)
iv Ethyl hexanoate (1)

Total 12 marks

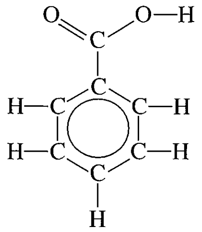
15.9

a	The C═O bond	(1)
b	Ethanoic acid	(1)
	because it is H-bonded	(1)
c	Yes: it contains a C═O bond	(1)
	but trough not broadened because no H-bonding	(1)

Total 5 marks

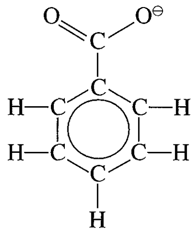
15.10

a (1)

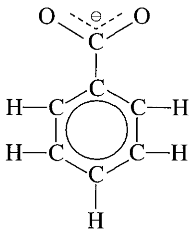


b	C—C in benzene ring 0.14 nm	(1)
	C—C (ring to carboxyl group) 0.154 nm	(1)
	C—H 0.108 nm	(1)
	C═O 0.122 nm (table 4.6 in the *Book of data*) or 0.125 nm (table 4.7)	(1)
	C—O 0.143 nm (table 4.6) or 0.131 nm (table 4.7)	(1)
	O—H 0.096 nm	(1)

c (1)



or



d	The two C to O bond lengths would be the same	(1)
	in between usual C—O and C═O	(1)
e	Two electrons delocalised over the two carbon to oxygen bonds	(2)

Total 12 marks

15.11

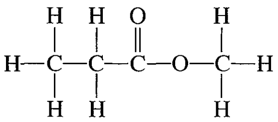
a	$HCO_2^- Na^+$	(1);	CH_3CH_2OH	(1)
b	$CH_3CO_2^- Na^+$	(1);	CH_3OH	(1)
c	$CH_3CH_2CH_2OH$	(1)		
d	$CH_3CO_2CH_2CH_2CH_3$	(1)		
e	$CH_3CH_2CONH_2$	(1)		

Total 7 marks

Examination questions

15.12

a	**i**	Sodium propanoate	(1)
	ii	Sodium, sodium oxide, sodium carbonate, sodium hydrogen carbonate (any two)	(2)
b	**i**		(2)

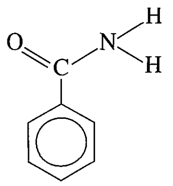


$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H}{\underset{H}{C}}-H}$$

	ii	Any specified mineral acid	(1)
		Heat/reflux	(1)
c	**i**	Reduction	(1)
	ii	Lithium tetrahydridoaluminate(III)	(1)
d	**i**	E	(1)
	ii	Nucleophile	(1)

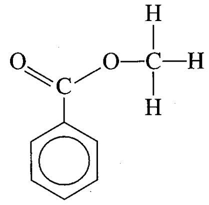
Total 11 marks

15.13 **a** **i** P =



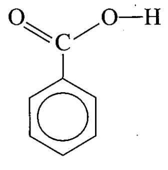
(1)

Q =



(1)

R =



(1)

ii Nucleophiles (1)

iii Ammonia has a lone pair of electrons but NH_4^+ does not. (1)

b Phenol (1)

dissolved in NaOH solution (1)

c **i** Impurities remain in solution when cooled (1)

because they are present in small quantities so solution is not saturated by them (1)

ii Measure melting point (1)

compare with literature value (1)

d Low solubility in water/volatile/soluble in solvent such as ethanol/not hydrolysed by water or other sensible answers (any two) (2)

Total 13 marks

15.14 **a** $2HCO_2H(aq) + CaCO_3(s) \longrightarrow Ca(HCO_2)_2(aq) + CO_2(g) + H_2O(l)$ (2)

b **i** $K_a = \frac{[H^+(aq)][HCO_2^-(aq)]}{[HCO_2H(aq)]}$ (2)

ii $K_a = \frac{[H^+]^2}{0.1}$ $(= 1.6 \times 10^{-4}\ \text{mol dm}^{-3})$ (1)

$[H^+] = \sqrt{}(1.6 \times 10^{-5}) = 4 \times 10^{-3}\ \text{mol dm}^{-3}$

$pH = -\lg[H^+] = 2.4$ (2SF) (1)

c **i** Sodium methanoate or sodium hydroxide (1)

ii $HCO_2H = H^+ + HCO_2^-$ (1)

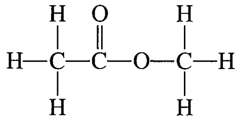
$H_2O = H^+ + OH^-$ (1)

iii Added OH^- combine with H^+ (1)

More HCO_2H ionises to restore $[H^+]$/equilibrium (1)

d **i** Ethanol (1)

ii Methyl ethanoate (1)



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{H}{\underset{H}{C}}{-}H}$$

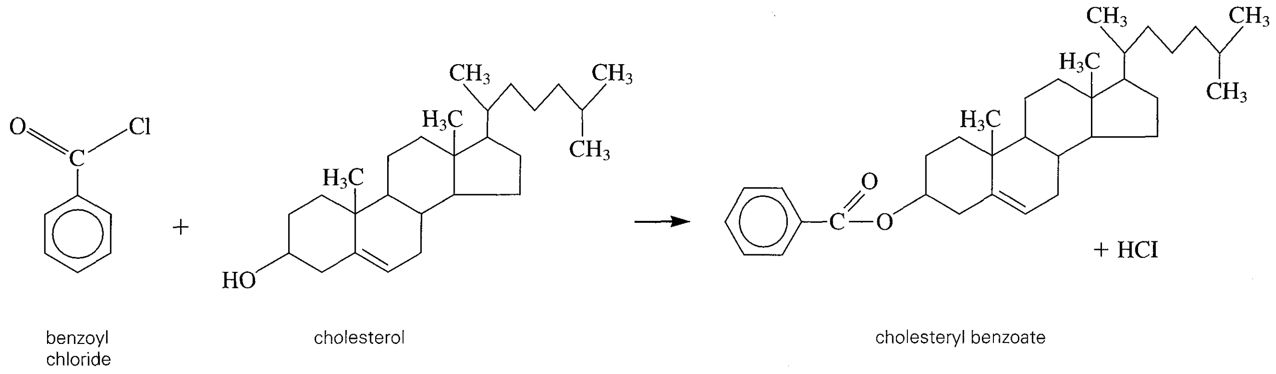
(1)

Total 14 marks

EXPERIMENT 15.3a

Cholesteryl benzoate, 'liquid crystals'

This experiment is an opportunity to prepare an example of a compound that has the particular properties of 'liquid crystals'.



Procedure

HAZARDS

Two of the reagents are very hazardous:
pyridine vapour is harmful, avoid contact with skin and eyes;
benzoyl chloride is corrosive and a lachrymator – that is, it will bring tears to your eyes. Only attempt this experiment in a fume cupboard. Wear gloves and remember to wear your eye protection properly.

Place 1 g of cholesterol in a 50 cm^3 conical flask. Add 3 cm^3 of pyridine (TAKE CARE) and swirl the mixture to dissolve the cholesterol. Then add 0.4 cm^3 of benzoyl chloride (TAKE CARE). Heat the resulting mixture on a steam bath for about 10 minutes. At the end of the heating period cool the mixture.

Dilute mixture with 15 cm^3 of methanol (toxic and highly flammable) and collect the solid cholesteryl benzoate by suction filtration, using a little methanol to rinse the flask and to wash the crystals. Recrystallise the cholesteryl benzoate by heating it in a conical flask with ethyl ethanoate (TAKE CARE highly flammable). Use the minimum volume, about 15–20 cm^3, which will completely dissolve the crystals. Cool in an ice bath, and collect the crystals by suction filtration. The yield should be 0.6 to 0.8 g.

The formation of the 'liquid crystal' phase of cholesteryl benzoate can be seen by placing 0.1 g of the compound on the end of a microscope slide and heating the sample by holding the slide with a pair of tongs well above a **small** Bunsen burner flame.

The solid will turn first to a cloudy liquid and then, with further heating, to a clear melt. On cooling, the cloudy liquid crystal phase will appear first, and then it will change to a hard, crystalline solid. With good lighting from the side, for example at a window, a band of colour should be seen at the boundary between the clear melt and the cloudy liquid on both heating and cooling. The more cautious the heating, the better you can see the changes.

You can repeat the heating and cooling many times with the same sample.

TOPIC 16

The Born–Haber cycle, structure and bonding

Introduction

In this topic the entropy ideas of Topic 13 are applied to the process of ion formation. We ask: 'Why is sodium so reactive?' but see that this is an improper question; sodium is not reactive in isolation, it is reactive in the context of each particular reaction. The question is re-cast in the form: 'Why is sodium reactive towards chlorine?' The Born–Haber cycle is introduced and, from it, the concept of lattice energy.

The mechanism by which ionic solids dissolve in polar solvents is discussed after a brief experiment. Lattice energies from the Born–Haber cycle and from purely theoretical calculation are compared and discussion of discrepancies leads to Fajans' rules.

The link with periodicity of physical and chemical properties of chlorides and oxides is established.

Content

Timing		Students' Book
16.1	$\frac{1}{2}$ hour	pages 381–3
16.2	1 hour	pages 383–6
16.3	2 hours	pages 386–9
16.4	2 hours	pages 390–2
16.5	Homework	pages 392–6
Total about 1 week		

16.1 The formation of ions and enthalpy changes – standard enthalpy changes of atomisation, electron affinity, ionisation energy.

16.2 The Born–Haber cycle: lattice energies – determination of experimental lattice energies from Born–Haber cycles.

16.3 Lattice energy values and reactivity – hydration of ions, comparison of theoretical and experimental lattice energies, the transition from ionic to covalent bonding, polarisation of ions, Fajans' rules.

16.4 Periodicity of the structures and properties of the chlorides and oxides of the Period 3 elements – behaviour of the chlorides and oxides towards water, trends in structure and bonding.

16.5 Background reading: the elements of Period 3

Objectives

1 To introduce the Born–Haber cycle and to show how to use it to calculate lattice energies.
2 To develop knowledge of the nature and behaviour of ionic substances.
3 To introduce Fajans' rules through a study of lattice energies.
4 To demonstrate the periodicity of the properties of chlorides and oxides and to relate these to their structures.

16.1 The formation of ions and enthalpy changes

Timing About $\frac{1}{2}$ hour will be required for this section

Suggested treatment

This is an excellent opportunity to practise what was learned in Topic 13 about entropy changes in the system and in the surroundings. The point to get over is that for the ionisation of metal atoms, the entropy change in the system is negligible compared with the entropy change in the surroundings. The controlling factor is, therefore, the enthalpy change of the reaction. Using the enthalpy change of atomisation plus the first ionisation energy to calculate the entropy change in the surroundings for the formation of gaseous sodium ions from elemental sodium results in a value which is highly negative. This seems a paradox since sodium is regarded as a very reactive metal. The resolution of this paradox is in the realisation that sodium ions do not stay in the gaseous state, nor are they in isolation – the sodium reacts with something to give either a solid or a solution. This leads on to the discussion of the Born–Haber cycle and to the nature of solutions of ionic substances.

The names and definitions of several enthalpy changes are introduced here. A possible teaching strategy is to involve the students by asking them what would have to be done to a piece of sodium and to a collection of chlorine molecules in order to make sodium chloride. Elicit answers of the type: 'You would have to separate the sodium atoms' to establish the need to find out how much energy that would take.

16.2 The Born–Haber cycle: lattice energies

Timing About 1 hour will be required for this section, plus homework time to do the examples

Suggested treatment

The teacher may find an expanded model of the sodium chloride lattice with detachable 'ions' useful when describing the meaning of lattice energy. Just as, for a molecular compound, it is often useful to know the enthalpy change of formation of the compound from atoms in the gaseous state, it is also useful to know the enthalpy change of formation of an ionic compound from ions in the gaseous state. This latter quantity is known as the *lattice energy* of the compound.

Strictly speaking, this quantity is the *lattice enthalpy*. The true lattice energy, U, is related to the lattice enthalpy by the equation

$$\Delta H_{\text{lattice}} = U + \Delta nRT$$

where Δn is the change in number of moles of gas for the process and is negative. The value of RT is only 2.5 kJ mol^{-1} and so the difference between the two terms is very small. In the *Students' Book*, the term lattice energy has been retained because these are the values given in the *Book of data* but the symbol $\Delta H^{\ominus}_{\text{lattice}}$ has been used in order to avoid a discussion of internal energy.

The direct determination of lattice energies is not possible but values can be obtained indirectly by means of an energy cycle known as the Born–Haber cycle. The method used for constructing such cycles is set out in detail in the *Students' Book.* At this stage, students should be given practice in calculating lattice energies for simple compounds. The examples should include cases involving successive ionisation energies as well as cases involving first and second electron affinities. The information required is given in the *Book of data* in tables 4.1, 5.2, 5.3 and 5.10. Students can check their calculations against the values given in table 5.9 and once they know how the calculations are made, can use the table for any further values they require.

16.3 Lattice energy values and reactivity

Timing About 2 hours will be required for this section, plus homework time for the study tasks

Suggested treatment

The seed is sown in this section for the discussion of theoretical lattice energies. Opportunity should be taken to get students to consider the trends in lattice energies in various parts of the Periodic Table.

ANSWERS

Questions, page 387

1 The lattice energies of Group 1 fluorides decrease down the group (due to increased size of the cation).

2 The lattice energies of the Group 2 chlorides are greater than those of Group 1 chlorides (reflecting the increased charge on the cation as well as the decreased cation size going across a period).

3 The oxides have a higher lattice energy than the corresponding chlorides (reflecting the higher charge on the oxide ion as well as its smaller ionic radius compared with the chloride ion).

The section then develops in the following way:

1 Students measure the temperature changes which accompany the dissolving of three ionic solids.

2 The ability of ionic solids to dissolve is discussed in terms of lattice energy and compensating enthalpy change of hydration. A mechanism for the process is proposed.

EXPERIMENT 16.3 Enthalpy changes of solution

HAZARDS

Students should be told to use anhydrous salts with care as they can cause burns on moist skin and in eyes.

Each group of students will need:
Eye protection
Test tubes and rack
Measuring cylinder, 5 cm^3
Dropping pipette
Spatulas
Thermometer, −10 to 110 °C
Access to anhydrous salts in stoppered containers:
Calcium chloride IRRITANT
Iron(III) chloride HARMFUL, IRRITATING TO SKIN
Potassium chloride

Procedure

Since the calcium chloride and iron(III) chloride are deliquescent, the main stock bottles should not be opened more than absolutely necessary. It would be advisable to put sufficient of each substance for the class in a stoppered bottle and let the students conduct their experiments from this source.

Even though students will probably not have compared equimolar quantities of the solutes, the differences in temperature change should be obvious.

Typical results are given, left, and some additional ones are included.

The experiment could be made quantitative by asking students to weigh out sufficient solid to produce 1 M solutions.

Anhydrous salt	Temperature change /°C
LiCl	+13
NaCl	−2
KCl	−7
$MgCl_2$	+45
$CaCl_2$	+30
$SrCl_2$	+16
$BaCl_2$	+4
$FeCl_3$	+42

The dissolving of ionic solids

An explanation for the changes involved in the dissolving of an ionic solid is given in the *Students' Book.* The discussion leads to an account of the attachment of solvent dipoles to ions and to the release of energy that occurs, the enthalpy change of hydration.

The attachment of solvent molecules to an ion on the surface of a crystal helps to lower the attraction of the rest of the ionic solid for that ion.

The following discussion is intended for teachers but may be of interest as extension work for some students. It is the attachment of the polar molecules to the ions that provides the principal energy to overcome the lattice energy. The relationship between lattice energy, enthalpy change of hydration and enthalpy change of solution is shown in figure 16.1 for potassium chloride.

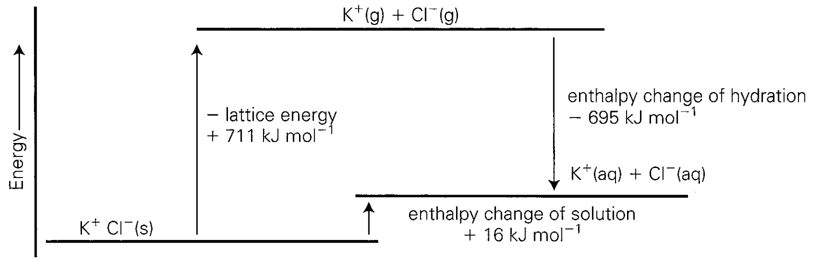


Figure 16.1 Principal energy relationships in the dissolving of an ionic solid, (aq) represents the full hydration of the ions

In the case of ionic compounds the enthalpy change of solution is the difference between two large quantities and can be either exothermic or endothermic.

The calculation of $\Delta H_{\text{hydration}}$ by such a cycle leads a value which is the sum of two enthalpy changes of hydration, so that the separate values, of K^+ and Cl^- for example, cannot be obtained by a single experiment.

In addition to the effects already described, there are entropy effects. The crystal lattice is broken down, leading to an increase in disorder. If the solvent is highly associated when in the pure state, and in particular if it has some structure by virtue of extensive hydrogen bonding as is the case with water, then the dissolving of a solid tends to destroy this solvent structure, and a further disordering results. On the other hand, the ordering of solvent molecules around the ions as they become solvated is an effect producing greater order. The relative importance of these effects is difficult to estimate; each is usually a few kilojoules per mole.

Theoretical values for lattice energies

In most cases all that will be required is for the teacher to explain that since a lattice energy is the energy change involved in bringing well-separated electrostatic charges together to form a lattice, it should be possible to make an estimate of the magnitude of this energy change using the principles of electrostatics. The work done in bringing the charges together from initial infinite separation can be calculated, and then the calculations extended to produce a row, a two-dimensional and finally a three-dimensional structure by calculating successive interactions. A full treatment is available in textbooks of physical chemistry.

Students should examine the values of the lattice energy for the alkali metal halides and compare the theoretical values and the Born–Haber cycle experimental values. The model on which the theoretical values are based assumes that an ionic crystal is composed of discrete spherical ions, each with its electrostatic charge distributed evenly around it. The excellent agreement between the experimental and theoretical values is strong evidence that this simple model of an ionic crystal is a good one, in the instances of the alkali metal halides.

Students then examine the corresponding data for the halides of magnesium where there is a much greater discrepancy between the theoretical and the experimental lattice energies. Discussion of the discrepancies leads to an explanation based on 'ion polarisation'. There is then a statement of Fajans' rules and a study task in which the validity of these rules can be investigated by the students. This then leads directly into the next section.

16.4 Periodicity of the structures and properties of the chlorides and oxides of the Period 3 elements

Timing About 2 hours will be required

Suggested treatment

In this section the link is made between bond type and physical properties for chlorides of the elements of the Third Period from sodium to phosphorus. The ionic radius for sulphur is 0.029 nm and not as given in the *Book of data*. In the table showing melting points, phosphorus trichloride is chosen rather than the pentachloride because the latter has an ionic structure in the solid state, $PCl_4^+PCl_6^-$. It is, therefore, unwise to attempt to demonstrate phosphorus pentachloride as an easily melted solid which will not conduct electricity (quite apart from any safety considerations)!

The behaviour of chlorides and oxides towards water

Not only do physical properties depend on bond-type, but so do some chemical properties. The ionic chlorides simply dissolve in water. There is some sign of hydrolysis with magnesium chloride which is consistent with its partial covalent character. Where the bond-type is essentially covalent, the chlorides hydrolyse. Whilst there is no intention that students should learn the equations given in the table by heart, they should at least realise that there is a pattern to the hydrolysis – hydrochloric acid is a product of the reaction and a second product is a hydroxide, hydrated oxide or acid containing the principal element concerned.

Non-metal chlorides are hazardous to use and very difficult to store because of their ready hydrolysis. It is recommended that these hydrolysis reactions should be watched only on a video or database.

The oxides and their behaviour towards water are familiar ground from more elementary courses but the opportunity should be taken to bring students' experience into line with the rest of the ideas of this Topic. In particular, students will probably be unaware until now that there is intermediate behaviour on the part of oxides in having both acidic and basic characteristics, exemplified here by aluminium oxide.

Again, the reactions should be watched using a video or database.

16.5 Background reading: the elements of Period 3

This is a reference section with information on the discovery of the elements, their uses and their functions in human metabolism.

ANSWERS TO THE BACKGROUND READING QUESTIONS

Questions, page 392

1 a Silicon and argon.
  b Aluminium and argon.
  c Silicon has a higher melting point than aluminium because silicon is held together by strong covalent bonds, while aluminium is held together by the electrostatic attraction between positive ions and mobile electrons. Once silicon has melted, the covalent bonds have been partially broken so it is relatively easier to boil. In aluminium, melting has very little effect on the forces of electrostatic attraction. The positive ions are still attracted to the mobile electrons.

2 **a** Sodium.

b Argon. It is useful when an unreactive atmosphere is needed. A good example is its use in light bulbs where it prevents the filament from burning.

3 Key points to include in the summary:

- Sodium is an essential element for humans.
- It is involved in the transmission of electrical impulses (in nerves) – and in the regulation of water content in tissue and blood.
- Silicon is found in connective tissue and skin.
- Phosphorus is essential to all forms of life since it is part of DNA.
- Phosphorus is also important in our bodies since our bones are mainly calcium phosphate.
- Magnesium, sulphur, and chlorine are also important in our diet.

Answers to Topic 16 questions

Review questions

16.1 **a** By using data for the conversions

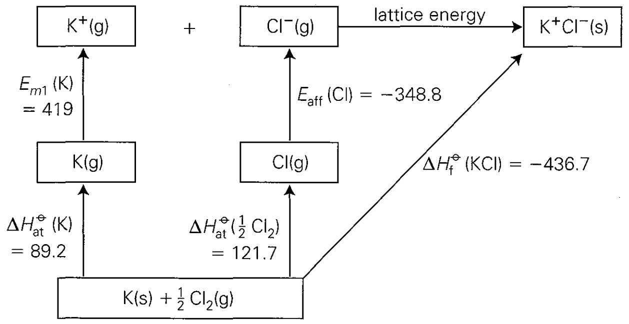
$K(s) \longrightarrow K(g)$ followed by $K(g) \longrightarrow K^+(g) + e^-$ (1)

i.e. enthalpy change of atomization + first ionization energy

and $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ followed by $Cl(g) + e^- \longrightarrow Cl^-(g)$ (1)

i.e. enthalpy change of atomization + electron affinity

b Fully correct cycle, including data (5)

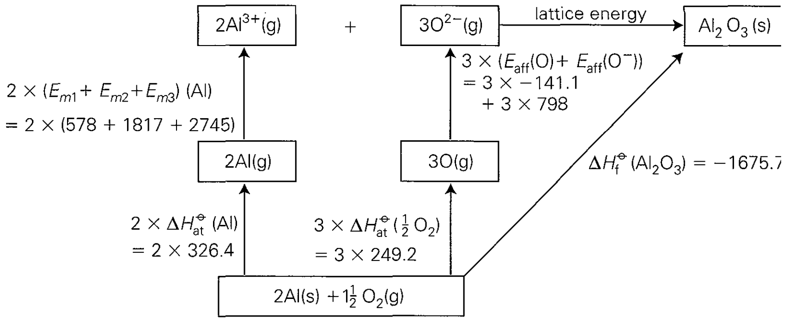


Lattice energy = $-436.7 - (89.2 + 419 + 121.7 - 348.8) = -718\ \text{kJ mol}^{-1}$ (2)

(*Book of data* gives $-711\ \text{kJ mol}^{-1}$) (1)

Total 10 marks

16.2 **a** Fully correct cycle, including data (6)



Lattice energy = $-1675.7 - (652.8 + 10\,280 + 747.6 + 1970.7)$

$= -15\,326.8\ \text{kJ mol}^{-1} = -15\,300\ \text{kJ mol}^{-1}$ (3SF) (2)

b Very high lattice energy has to be supplied to separate ions (1)

hydration energy of the ions is not likely to be large enough to provide this (1)

Total 10 marks

16.3

a Radius of Fe^{3+} = 0.055 nm; m.p. of $FeCl_3$ = 579 K (306 °C) (1)
Fairly low m.p. suggests some covalency; small radius (and high charge) of Fe^{3+} supports this (likelihood of polarisation of Cl^-). (1)

b Calculated lattice energy compared with experimental (Born–Haber) value. Significant difference suggests covalency. (3)

Total 5 marks

16.4

a Li^+ 0.074; Cs^+ 0.170; Be^{2+} 0.027; Ba^{2+} 0.136; Zn^{2+} 0.075; F^- 0.133; I^- 0.215; S^{2-} 0.185; N^{3-} 0.171 (all values in nm) (2)

b LiI: Small cation, large anion but no multiple charges. Covalent bonding probably not significant. (1)
CsF: Large cation, small anion, no multiple charges. Covalent bonding probably not significant. (1)
BeF_2: Small, doubly charged cation; small anion. Possibly slight tendency to covalency. (1)
BeI_2: Small, doubly charged cation, large anion. Some covalent bonding likely. (1)
BaI_2: Like BeI_2 but large cation. Covalency less likely. (1)
Li_2S: Small cation, large doubly charged anion. Some covalency likely. (1)
ZnI_2: Small, doubly charged cation, large anion. Some covalency likely. (1)
Li_3N: Small cation, large triply charged anion. Some covalency likely. (1)

Total 10 marks

16.5

a NaF 1266; MgF_2 1534; AlF_3 1564 (sublimes); SiF_4 183; PF_3 122 or PF_5 190 (all values in K) (2)

b NaF, MgF_2 and AlF_3 expected to be ionic. (1)
SiF_4 and PF_3 (or PF_5) expected to be covalent. (1)

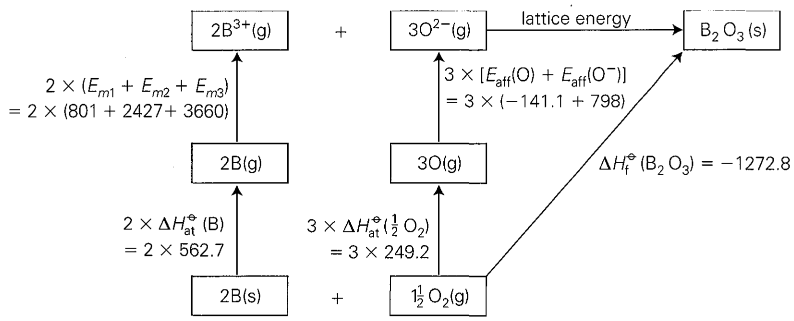
c Similar pattern shown by chlorides except $AlCl_3$ which has m.p. 463 (2.5 atm) and is predicted to be covalent. (2)

Total 6 marks

Examination questions

16.6

a **i**



Complete cycle, fully labelled (5)

ii Lattice energy = −1272.8 − (1125.4 + 13 776 + 747.6 + 1970.7)
= −18 892.5 = −18 900 kJ mol^{-1} (3SF) (2)

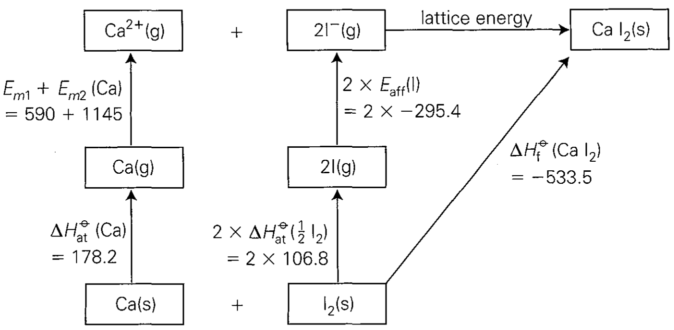
iii Probably poor agreement: B^{3+} is likely to be very small and is highly charged so will produce significant polarisation of the O^{2-} anion, i.e. significant covalent bonding. (2)

b $B_2O_3(s) + 3H_2O(l) \longrightarrow H_3BO_3(aq)$ (1)

c Melting point of chloride (BCl_3) is 166 K and boiling point 286 K (so likely to be gaseous at room temperature). (1)
Likely to be covalent and react with water, releasing HCl(g). (1)

Total 12 marks

16.7 **a** **i**



Complete cycle, fully labelled (5)

ii Lattice energy = −533.5 − (178.2 + 1735 + 213.6 − 590.8)
= −2070 kJ mol^{-1} (3SF) (2)

b Ionic
Calcium–iodine separation fits ionic or covalent bonding.
iodine–iodine suggests ionic bonding. (3)

c Compare experimental and theoretical lattice energies. (1)

Total 11 marks

TOPIC 17

Redox equilibria

Introduction

This topic sees the fulfilment of all the work that has been done on entropy. It begins with a study of redox equilibria so that electrode potentials can be drawn into the discussion. The relationship between total entropy changes, standard electrode potentials, and equilibrium constants is stated, and their value in determining the direction of chemical changes and the feasibility of chemical reactions is discussed.

This is an important topic which should not be hurried; there is much to be gained from a mastery of its contents. Students will go on to the study of the transition elements in Topic 19, putting their new-found experience to the test with confidence and understanding.

Content

Timing		Students' Book
17.1	4 hours	pages 400–7
17.2	2 hours	pages 407–11
17.3	1 hour	pages 411–4
17.4	1 hour	pages 414–6
17.5	1 hour	pages 417–8
17.6	Homework	pages 418–20
Total about 2 weeks		

17.1 Metal/metal ion systems – the reactivity series of the metals; oxidation and reduction by electron transfer, electrical energy from a redox reaction; measuring the tendency of a metal to form ions in solution; cell diagrams; contributions made by separate electrode systems to the e.m.f. of a cell, the hydrogen electrode; measuring the e.m.f. of some electrochemical cells; the quantitative effect of temperature and concentration on cell e.m.f.; standard electrode potentials.

17.2 Redox equilibria extended to other systems – the reaction between iron(III) ions and iodide ions, cell diagrams for systems involving metal ions; measuring electrode potentials for half reactions involved in the iron(III)/iron(II) and iodine/iodide equilibria.

17.3 The chemists' toolkit: some uses of $E^\ominus$ values – predicting whether a reaction is likely to take place; calculating the e.m.f. of electrochemical cells; writing equations from cell diagrams.

17.4 Entropy changes when metal ions go into solution – entropy changes are related to the number of ways of arranging the ions; entropy changes in redox reactions.

17.5 Predicting whether reactions will take place – ΔS_{total}, K_c and E_{cell}.

17.6 Background reading: cells and batteries.

Objectives

1 To develop an understanding of half-reactions and standard electrode potentials and use these to interpret reactions involving electron transfers and to calculate the e.m.f.s of electrochemical cells.

2 To interpret a wide range of redox reactions in electrochemical cells and to understand and be able to construct cell diagrams.

3 To provide practical experience in the measurement and use of electrode potentials.

4 To use standard electrode potentials to predict whether a reaction is likely to occur.

5 To study entropy changes when metal ions go into solutions and in redox reactions in general.

6 To demonstrate the relationship between total entropy changes, standard electrode potential and the equilibrium constant K_c, and to use these to predict the feasibility of reactions.

7 To develop an appreciation of some of the advantages and disadvantages of different types of electrochemical cell.

17.1 Metal/metal ion systems

Timing About 4 hours

Suggested treatment

Redox systems have been studied earlier in the course, especially in Topic 6, where a change of oxidation number was used as a criterion for redox processes. Here we deal with the electron transfers which take place in redox reactions, metal displacement reactions being used to provoke discussion.

EXPERIMENT 17.1a The reactivity series of the metals

Each group of students will need:
Full rack of test tubes
Copper powder, about 0.5 g
Iron powder, about 0.5 g
Lead powder, about .05 g TOXIC
Magnesium powder, about 0.5 g HIGHLY FLAMMABLE
Zinc powder, about 0.5 g HIGHLY FLAMMABLE
0.5 M copper(II) sulphate solution (solid is HARMFUL)
0.5 M zinc sulphate solution
Thermometer, −10 to +110 °C

Procedure

Details are given in the *Students' Book.* The results to be expected are as follows.

1 Zinc powder reacts fairly rapidly with copper sulphate solution and becomes coated with red metallic copper:

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

Energy is evolved and there is an increase in temperature. To observe the reaction products more clearly students could filter the mixture after 2 minutes.

2 Metals will react or not depending on their position in the reactivity series relative to copper, and the temperature increases will show a similar pattern.

3 Magnesium powder reacts readily with zinc sulphate solution with a temperature rise as energy is transferred to the surroundings.

The oxidation number of the metal powders is 0; most of the metal ions will be +2.

Oxidation and reduction by electron transfer

Discussion of the questions posed at the end of the experiment should lead to the establishment of the following points.

- Redox processes can involve transfer of electrons. Loss of electrons is oxidation, gain of electrons is reduction.
- The terms oxidising agent and reducing agent are relative only. Some chemical species are capable of acting in both senses.
- The equation for a redox process can be split into equations for 'half-reactions' so that the electron transfer is made plain, for example:

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

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

As these process are seen to be reversible, they can be treated as equilibria:

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

$$\text{and } 2e^- + Cu^{2+}(aq) \rightleftharpoons Cu(s)$$

Application of Le Chatelier's Principle to such equilibria tells us that the relative tendency of the two metals to form ions in solution determines the outcome of a given reaction.

- During a metal/metal ion reaction energy is transferred from system to surroundings.
- It is important at this stage to make it clear that the energy transfer during the change:

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

  shown above is *not* the same as that involved in the ionisation of zinc atoms:

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

  The formation of ions in solution is quite different from the conversion of gaseous atoms of a metal into gaseous ions.

Measuring the tendency of a metal to form ions in solution

The possibility of using metal/metal ion reactions as sources of electrical energy as in an electrochemical cell arises from the half-reactions considered in interpreting Experiment 17.1a. An electrochemical cell provides a means of comparing the relative tendencies of metal/metal ion couples to liberate electrons by forming ions in solution. Absolute electrode potentials cannot be measured, but cell e.m.f.s can be measured easily.

EXPERIMENT 17.1b

Electrical energy from a redox reaction

Each group of students will need:

Small glass food jar (baby food jar is best)
Stopper to fit the food jar
Visking tubing (about 15 cm long)
Dropping pipette
1 M ammonium sulphate (to fill the food jar)
Copper foil, 10 cm × $\frac{1}{2}$ cm
0.9 M copper sulphate (solid is HARMFUL)
Zinc foil, 10 cm × $\frac{1}{2}$ cm
Emery paper
3 connecting leads with crocodile clips
Digital voltmeter (pH meter with appropriate millivolt scale is suitable)
Bulb in holder, pea bulb, 1.5 V low current or LED

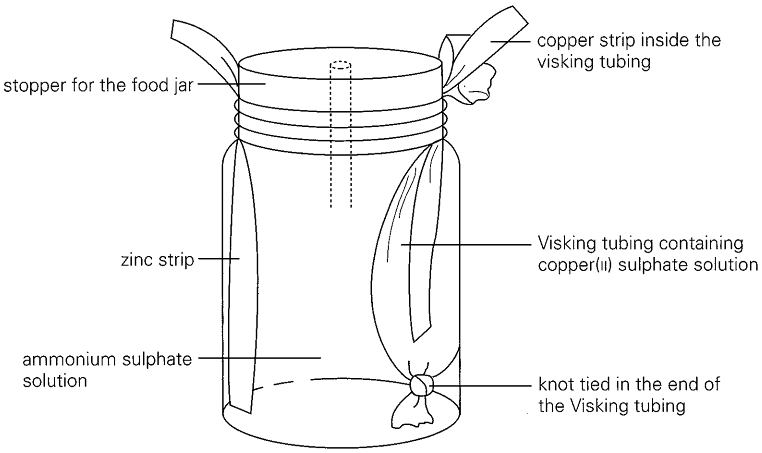


Figure 17.1 A simple cell made from a food jar

Procedure

The Visking tubing prevents rapid mixing of the solution and economises on the volume of copper sulphate solution needed. Similarly zinc sulphate, as in a Daniell cell, is not used because of the cost.

The voltage developed in this cell should be sufficient to power a low current lamp. Students should be able to work out the polarity of their cell by reference to the sign of the voltmeter reading.

Cell diagrams

In the IUPAC convention the sign before the *E* value gives the polarity of the **right-hand** electrode in the cell diagram. Of itself, of course, the e.m.f. always represents an energy loss to the system so the + or − sign has no connection with gain or loss of electrical energy. Thus for the Daniell cell, the appropriate method of representation can be either:

$$Zn(s)\,|\,Zn^{2+}(aq)\ \vdots\vdots\ Cu^{2+}(aq)\,|\,Cu(s) \qquad E = +1.1\ V$$

or

$$Cu(s)\,|\,Cu^{2+}(aq)\ \vdots\vdots\ Zn^{2+}(aq)\,|\,Zn(s) \qquad E = -1.1\ V$$

The two vertical broken lines represent the salt bridge.

Teachers might take the opportunity to demonstrate a Daniell cell at this point, measure the e.m.f. and draw attention to the function of the porous pot in preventing mixing of the solutions whilst allowing electrical contact. In this case the distinction between p.d. and e.m.f. is not necessary because in all instances we are dealing with the p.d. at very high resistances, that is the electromotive force of the cell, e.m.f.

Contributions made by separate electrode systems to the e.m.f. of a cell

Measurement of the potential of a single electrode system is impossible, because two such systems are needed to make a complete cell of which the e.m.f. can be measured. We can, however, assess the relative contributions of single electrode systems to cell e.m.f.s by choosing one system as a standard against which all other systems are measured. The standard system is then arbitrarily assigned zero potential and the potentials of all other systems referred to this value. By international agreement the hydrogen electrode has been chosen as the reference electrode for this purpose. It is worth emphasising that chemistry involves a number of arbitrary choices as students can confuse them with situations where a value really is zero.

The hydrogen electrode

The construction of a hydrogen electrode, and its role as a reference electrode, are described in the *Students' Book.* The potential of the standard hydrogen electrode is taken as zero at all temperatures. The students would no doubt be interested to see a hydrogen electrode and to satisfy themselves that a potential difference can actually be obtained from a cell having hydrogen gas as one of its electrodes. If desired, the following experiment may be done as a teacher demonstration.

TEACHER DEMONSTRATION

To measure the e.m.f. of simple cells using the hydrogen electrode as the common reference electrode

The teacher will need:

Hydrogen electrode consisting of a platinised Pt wire dipping into 1.0 M HCl(aq) in a squat-form beaker (50 or 100 cm^3)
Salt bridge cut from filter paper or from chromatography paper reel, 10 cm × 1 cm, wetted with a saturated solution of potassium nitrate, using a dropping pipette
Hydrogen supply (cylinder or gas preparation, see below) EXTREMELY FLAMMABLE
Copper foil, 5 cm × 1 cm
1 M copper(II) sulphate HARMFUL
1 M zinc sulphate
Zinc foil, 5 cm × 1 cm
Digital voltmeter
Connecting leads, fitted with suitable terminals, 2

Procedure

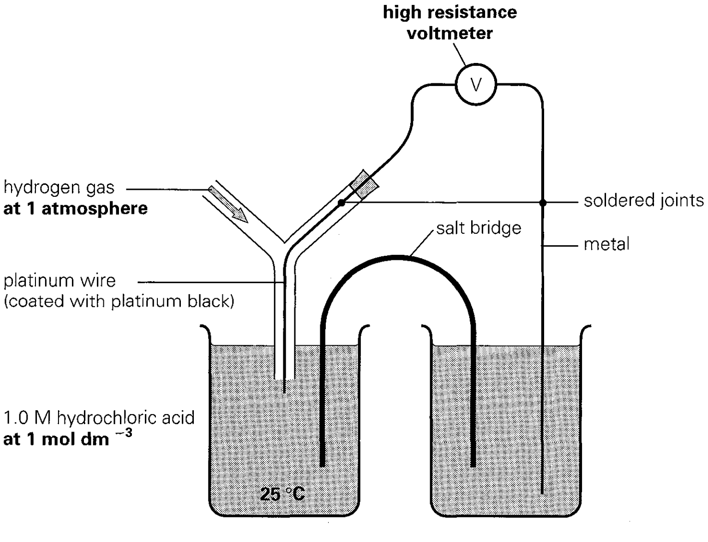


Figure 17.2 Arrangement for the hydrogen electrode

Set up apparatus as in figure 17.2. The electrodes should consist of about 5 cm × 1 cm strips of metal foil, cleaned with fine emery paper before use, dipping into solutions of 1 M copper(II) sulphate and 1 M zinc sulphate respectively in small squat-form beakers. Silver foil dipping into 0.1 M silver nitrate also gives reliable results if it is available.

Alternatively, the metal strips can be supported in small clamps between pieces of cork, and electrical connection made to them by leads with crocodile clips attached to one end. Or they can be bent over the sides of the beaker and held in place by the crocodile clips.

A potassium nitrate salt bridge consists of a single strip of filter paper, 10 cm × 1 cm, folded between the two beakers and then wetted with drops of saturated potassium nitrate solution.

Have the hydrogen electrode on the **left-hand side** as the class sees the apparatus. The end of the glass tube surrounding the platinised platinum wire should be immersed in the 1 M HCl(aq) as near to the surface as possible, so that the gas pressure is very nearly 1 atmosphere. Use the crocodile clips to connect the electrodes to the digital voltmeter.

COMMENT

If the platinum black has been exposed to the air, the hydrogen electrode will take a little time to reach equilibrium.

Adjust the flow of hydrogen to a rate of about one bubble every two seconds. Read the cell e.m.f. on the voltmeter. This e.m.f. will be the *E* value for the cell:

$$Pt[H_2(g)] \mid 2H^+(aq) \;\vdots\vdots\; Cu^{2+}(aq) \mid Cu(s) \qquad E = +0.32\,V$$

The experiment can then be repeated with zinc foil in place of the copper foil. The e.m.f. will be the *E* value for the cell:

$$Pt[H_2(g)] \mid 2H^+(aq) \;\vdots\vdots\; Zn^{2+}(aq) \mid Zn(s) \qquad E = -0.75\,V$$

Discussion

The *E* values obtained give no indication of the absolute potentials that can be attributed to an individual electrode. To do this by a method of this kind we should have to find an electrode with zero potential, in which case there would be no flow of electrons into or out of it.

The simplest way of assessing the relative contributions of single electrode systems to cell e.m.f. values is to choose one electrode system as a reference standard and measure the *E* values of all other systems against this. The standard chosen is, of course, the hydrogen electrode.

We can represent our *E* values on a linear chart, assuming silver foil was available:

$Zn^{2+}(aq) \mid Zn(s)$	$2H^+(aq) \mid [H_2(g)]Pt$	$Cu^{2+}(aq) \mid Cu(s)$	$Ag^+(aq) \mid Ag(s)$
−0.75	0.0	+0.32	+0.76 V

The electrode potential series given in table 6.1 in the *Book of data* can now be discussed briefly. The point should be made that these $E^\ominus$ values are obtained under carefully specified conditions (hence the superscript) which will be discussed in the next section. Therefore we should not expect exact comparison with the values that have been obtained experimentally in the teacher demonstration. The most important point to stress at this stage is that the $E^\ominus$ values given are the voltages of real and complete cells, of which the left-hand electrode is always

$Pt[H_2(g)] \mid 2H^+(aq) \;\vdots$ Hence its position on the bench during the demonstration.

Construction of a hydrogen electrode

A number of quite simple versions of this electrode can readily be constructed. One is shown below.

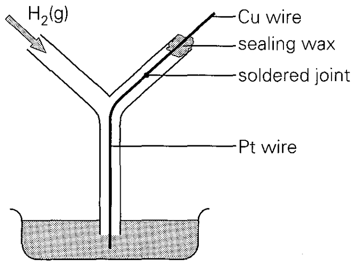


Figure 17.3 A hydrogen electrode

Expense is saved if copper wire is soldered to a short length of platinum wire (use zinc chloride/hydrochloric acid flux and ordinary soft solder). Beware the fumes! Use a fume cupboard.

The platinum wire must be covered with electrolytically-deposited platinum over the lower 2 cm or so. This is done by using another platinum wire as a second electrode, and immersing both in a 3% solution of platinum(IV) chloride (solid is very toxic) containing a small proportion (approximately 0.05%) of lead ethanoate (solid is toxic), connecting the electrodes to a dc supply (about 4 V), and reversing the current every half minute for 15 minutes. The electrodes are then washed with pure water, and occluded chlorine is removed by placing the electrodes in sodium ethanoate solution (approximately M) and again passing current for 15 minutes, reversing every half minute. The electrodes are then washed with pure water and stored in pure water when not in use.

HAZARDS

Hydrogen is extremely flammable.
Eye protection is needed for teacher and students.
No naked flames.

A cylinder is the safest and most convenient supply of hydrogen gas but must be fitted with a reducing valve, in order to provide a very slow stream of gas. The cylinder must be fixed securely to a bench or in a trolley. Alternatively, a filter flask can be used as an aspirator (see figure 17.4). This can be filled from a cylinder or from a suitable gas generating apparatus (in this case put dilute potassium manganate(VII) solution and a little dilute sulphuric acid in the aspirator flask to remove impurities liable to poison the platinum electrode).

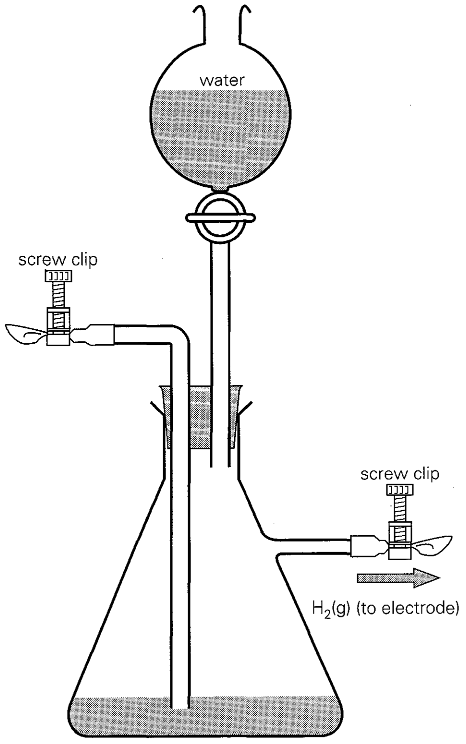


Figure 17.4 Aspirator for the hydrogen electrode

Experiment 17.1c which now follows is intended to give an opportunity for students to gain experience in constructing electrochemical cells and making e.m.f. measurements for themselves.

EXPERIMENT 17.1c To measure the e.m.f. of some electrochemical cells

Each group of students will need:
Copper foil, 5 cm × 1 cm
Zinc foil, 5 cm × 1 cm
Magnesium ribbon strip approx. 5 cm long
1.0 M copper(II) sulphate
0.1 M zinc sulphate
1.0 M magnesium sulphate
Salt bridges made from strips of filter paper, 10 cm × 1 cm wetted with a saturated solution of potassium nitrate
Digital high resistance voltmeter
Connecting leads, 2 lengths fitted with suitable terminals
Crocodile clips

Procedure

Full details are given in the *Students' Book.*

Parts 1 and 2

The average of results obtained by students in this experiment are given below.

$Cu(s)\,|\,Cu^{2+}(aq) \,\vdots\vdots\, Zn^{2+}(aq)\,|\,Zn(s) \qquad E = -1.03\text{ V}$ (1)

$Mg(s)\,|\,Mg^{2+}(aq) \,\vdots\vdots\, Cu^{2+}(aq)\,|\,Cu(s) \qquad E = +1.75\text{ V}$ (2)

$Mg(s)\,|\,Mg^{2+}(aq) \,\vdots\vdots\, Zn^{2+}(aq)\,|\,Zn(s) \qquad E = +0.72\text{ V}$ (3)

The magnesium half-cell values do not match the values expected from standard electrode potentials; if silver foil is available the silver half-cell gives better values.

ANSWERS

In your notes, page 406

1 Comparison of these results with the reactions in Experiment 17.1a on the reactivity series of the metals shows that the electrode system with the greater tendency to form ions is the negative pole in each cell.

2 The *E* value for cell 3 is very nearly that obtained by adding the *E* value for cell 1 to that for cell 2. This is reasonable because by connecting the cells together as written below

$$Mg(s)\,|\,Mg^{2+}(aq) \,\vdots\vdots\, Cu^{2+}(aq)\,|\,Cu(s) — Cu(s)\,|\,Cu^{2+}(aq) \,\vdots\vdots\, Zn^{2+}(aq)\,|\,Zn(s)$$

we should expect the effects of the two copper half-cells to cancel since they oppose each other and no electron flow should take place between them.

Question, page 406

Students use the *Book of data* to work out the e.m.f. of the cell:

$Ag(s)\,|\,Ag^{+}(aq) \,\vdots\vdots\, Cu^{2+}(aq)\,|\,Cu(s)$. For this cell $E^\ominus = -0.46\text{ V}$

Students should be given plenty of opportunity to calculate e.m.f. values for cells using table 6.1 in the *Book of data*, writing equations for the cell reactions and identifying + and − electrodes. The skill will be needed again in Topic 19.

Parts 3 and 4

The students examine the effects of change of concentration and temperature on the electrode potential values. Only the minimum data is collected: it is not intended that any mathematical relationship should be drawn from these experiments. Students should find that there are slight changes of electrode potential with change of temperature and concentration. They may not be significant enough to give convincing results. The extent of change depends on the electrode systems. The purpose is to introduce students to the necessity of using standard conditions if electrode potential measurements are to be compared.

Standard electrode potentials

A precise definition of *standard electrode potential* now becomes possible. For our purposes we shall define it as the e.m.f. of a cell in which one electrode is the standard hydrogen electrode and the other electrode consists of a metal in contact with a solution of its ions of concentration of 1 mol dm^{-3}, the e.m.f. being measured at 25 °C. A standard hydrogen electrode consists of hydrogen gas, at a pressure of one atmosphere, bubbling over a platinised surface in a solution which is of concentration 1 mol dm^{-3} with respect to hydrogen ions. This produces a system in which equilibrium has been established:

$$H_2(g) \rightleftharpoons 2H^+(aq)$$

Standard electrode potentials are denoted by the symbol $E^\ominus$ ('E standard' when spoken). A list is given in the *Book of data* in table 6.1.

A minute or two could be spent in pointing out that the concentration of free ions cannot strictly be equated with the solute concentration as calculated by number of moles of solute in a given volume of solution. Incomplete ionisation, inter-ion attraction, and 'crowding effects' in fairly concentrated solution result in the necessity of taking greater concentration of solute to achieve a given concentration of ions. Thus to obtain a 1.0 M solution of free hydrogen ions a concentration of 1.18 M hydrogen chloride must be used. No account will be taken of activities or activity coefficients in this topic but students should be aware that the treatment given here is simplified to some extent.

The information that has been collected so far can be summarised as follows:

- The standard electrode potential, $E^\ominus$, of an electrode has a specific value for each electrode system and does not depend on the size of the electrode or the volume of solution.
- $E^\ominus$ values are relative, the standard hydrogen electrode being given the arbitrary value of zero at all temperatures. The sign of $E^\ominus$ is the polarity of the metal/metal ion electrode when combined with the standard hydrogen electrode; if it forms the negative pole, the $E^\ominus$ value is given a negative sign, and vice versa.
- $E^\ominus$ values vary with concentration and temperature.

17.2 Redox equilibria extended to other systems

Timing About 2 hours

Suggested treatment

This section is developed as follows:

1. Students carry out an experiment to investigate qualitatively the reaction between iron(III) ions and iodide ions in aqueous solution and interpret the results in terms of the competing equilibria of the two half-reactions.
2. The electrode potential for the equilibrium set up in the previous experiment is measured and the conditions required for standard electrode potential involving equilibrium between ions discussed.
3. The conventions for writing cell diagrams are extended to reactions involving equilibria between ions or ions and molecules.
4. The uses of $E^\ominus$ values are summarised.

EXPERIMENT 17.2a

The reaction between iron(III) ions and iodide ions

Each group of students will need:
6 test tubes and rack
Access to:
0.1 M Fe^{3+}(aq), iron(III) sulphate or ammonium iron(III) sulphate (from alum) are suitable, 6 cm^3
0.1 M potassium iodide, 6 cm^3
1% potassium hexacyanoferrate(III), with dropping pipette
1% starch, with dropping pipette.

Procedure

Details of the procedure are given in the *Students' Book*. Formation of a deep blue colour with potassium hexacyanoferrate(III) solution and with starch solution indicates that iron(II) and iodine are formed when solutions of iron(III) and iodide ions are mixed.

The use of the iron(III)–iodide reaction in an electrochemical cell is studied in Experiment 17.2b. The electron transfer which occurs during the reaction can be seen from the half-reactions

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ reduction

and $2I^-(aq) \longrightarrow I_2(aq) + 2e^-$ oxidation

which arise from the competing equilibria

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

and $2I^-(aq) \rightleftharpoons I_2(aq) + 2e^-$

The qualitative study enables the equilibrium position for the complete reaction

$$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$$

to be established as lying towards the right-hand side of the equation.

EXPERIMENT 17.2b To measure some electrode potentials

Each group of students will need:

Copper reference electrode, as in Experiment 17.1c

Potassium nitrate salt bridges, as in Experiment 17.1c

2 smooth platinum electrodes

3 beakers, 100 cm³

Digital voltmeter, and connecting leads

Access to:

0.1 M iodine in aqueous KI, 50 cm³

A freshly made mixture of 0.1 M iron(II) and 0.1 M iron(III) salts, 50 cm³

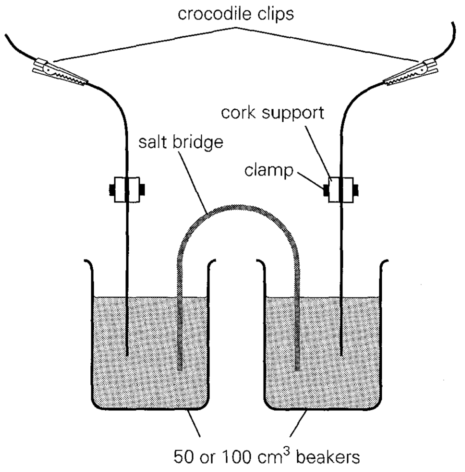


Figure 17.5 Details of the cell

Here are some sample results for the cell e.m.f.s which the students measure:

$Cu(s)\,|\,Cu^{2+}(aq)\;\vdots\vdots\;Fe^{3+}(aq), Fe^{2+}(aq)\,|\,Pt \qquad E_{cell} = +0.30\text{ V}$

and $Cu(s)\,|\,Cu^{2+}(aq)\;\vdots\vdots\;I_2(aq), 2I^-(aq)\,|\,Pt \qquad E_{cell} = +0.24\text{ V}$

Based on these results the e.m.f. of this cell is:

$$Pt\,|\,2I^-(aq), I_2(aq)\;\vdots\vdots\;Fe^{3+}(aq)\,|\,Pt \qquad E_{cell} = +0.06\text{ V}$$

They check their calculation by measuring the e.m.f. of this cell. A fresh potassium nitrate salt bridge should be used for each measurement. A typical value is $E_{cell} = +0.07$ V.

Students' attention should be drawn to the fact that it is necessary to have both the oxidised and reduced forms in each electrode system, to enable the half-cell reactions to proceed in either direction.

For this experiment the concentrations of the oxidised and reduced forms in each half-cell are not important as long as the ratio of concentrations is kept constant throughout.

The platinum electrode takes no part in the reactions but merely acts as an inert surface by means of which electrons can be transferred into or out of a half-cell.

The agreement between predicted and measured values for the third cell studied shows that ion/ion reactions and non-metal/non-metal ion reactions can be dealt with in the same way as metal/metal ion reactions studied earlier.

Students should appreciate by reference to Le Chatelier's Principle that for ion–ion systems the equilibrium position is affected by ion concentration. This is mentioned briefly in the *Students' Book.* Temperature also has an effect on the system so that for electrode systems of this kind it is necessary to specify concentration ratios and temperature.

Some further notes on standard potentials

To deal with cells of the kind studied in Experiment 17.2b an extension of the conventions for writing cell diagrams is necessary. The reduced form of the redox couple is always placed nearest to the inert electrode and separated from the oxidised form by a comma:

$$\underset{\text{oxidised form}}{Fe^{3+}(aq)},\ \underset{\text{reduced form}}{Fe^{2+}(aq)} \mid \underset{\text{non-reactive electrode}}{Pt}$$

Students should then examine more complex examples of cell diagrams, for example those including additional species such as H^+, OH^-, involving ions, water, oxygen, etc. The use of square brackets to link together oxidised or reduced forms is then introduced:

$$\underset{\text{oxidised form}}{[MnO_4^-(aq) + 8H^+(aq)]},\ \underset{\text{reduced form}}{[Mn^{2+}(aq) + 4H_2O]} \mid \underset{\text{non-reactive electrode}}{Pt}$$

Students should be given ample practice of writing such cell diagrams relating to specific equations. They may then check their answers by reference to table 6.1 in the *Book of data.*

ANSWERS

Study task, page 411

The cell diagram for the question is:

$$Pt \mid Fe^{2+}(aq), Fe^{3+}(aq) \ \vdots\vdots\ Ag^{+}(aq) \mid Ag(s)$$

17.3 The chemists' toolkit: some uses of $E^{\ominus}$ values

Timing About 1 hour will be needed

Suggested treatment

The *Students' Book* describes in some detail three uses for $E^{\ominus}$ values. They are:

1 Predicting whether a reaction is likely to take place. This is an extremely important subsection which should be gone through with care. It is important that the students can apply the 'anti-clockwise rule' correctly in preparation for work in Topic 19.

2 Calculating the e.m.f. of electrochemical cells. Students should be given practice in this, using some of the questions at the end of this topic.

3 Writing equations from cell diagrams. This subsection instructs students how to write complete equations by balancing electron loss and gain in two half-reactions.

ANSWERS

Study task, page 411

The diagram suggests that the oxidising agent shown as **Ox** reacts with the reducing agent shown as **Rd**.

Question, page 413

The e.m.f. of a lithium–silver cell is +3.83 V, with the Ag the + pole of the cell.

17.4 Entropy changes when metal ions go into solution

Timing About 1 hour

Suggested treatment

This section develops a simplified picture of the entropy changes which result when an atom in a solid metal changes into an ion in solution during the working of an electrochemical cell. The idea is introduced that the entropy increase which occurs when a metal atom changes into an ion varies with the concentration of the surrounding solution; being relatively larger when the solution is dilute than when it is concentrated.

The entropy changes in cells where the reactions taking place result in an overall change in the number of ions present are then compared with those in which the overall number of ions remains constant, using as examples cells in which the reactions are

$$2Ag^+(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$$

(loss of $2Ag^+(aq)$ ions for the gain of each $Cu^{2+}(aq)$ ion means that there is a relatively large decrease in $\Delta S^{\ominus}_{\text{system}}$)

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

(loss of a $Cu^{2+}(aq)$ ion is balanced by gain of a $Zn^{2+}(aq)$ ion and the change in $\Delta S^{\ominus}_{\text{system}}$ is relatively small).

17.5 Predicting whether reactions will take place: $\Delta S^{\ominus}_{\text{total}}$, K_c and E_{cell}

Timing About 1 hour

Suggested treatment

This section draws together the threads which have been running through the course. Teachers should make sure that students understand its importance as a summary, and also appreciate the limitations of any conclusions drawn from it about reaction possibilities. It could be linked profitably with the study of activation energy in Topic 11.

17.6 Background reading: cells and batteries

ANSWERS TO BACKGROUND READING

Questions, page 418

1 A wide range of cells is needed to match a wide range of applications. A hearing aid needs a very small, low power cell which need not be rechargeable. A vehicle needs a cell with larger capacity and power which can be recharged from the mains. Some cells are needed to supply power for a short time and can then be thrown away, other cells (for example in a computer or door bell) have to last a long time.

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

3 Simplified, unbalanced cell diagrams are acceptable here, such as

$Zn(s)\,|\,ZnO(s)\;\vdots\vdots\;Ag_2O(s)\,|\,Ag(s)$

$Li(s)\,|\,Li_2O(s)\;\vdots\vdots\;Mn_2O_3(s)\,|\,MnO_2(s)$

4 The Zn–HgO cell has the largest capacity of the cells quoted: 330 mA h cm^{-3}

5 Small devices needing significant power benefit from having a high energy output for a given volume. Examples include portable computers, cameras with flash lights and mobile phones.

6 Cells for use in aircraft and vehicles as well as in medical uses such as pacemakers and hearing aids all give benefits if the energy output per kilogram is high.

7 In static applications such as back-up electricity supplies in public buildings, the extra mass of secondary cells does not matter because they can be recharged when not supplying power. In vehicles their mass is a problem and much research is being devoted to developing cells with a higher ratio of capacity to mass. It seems likely that fuel cells will finally realise their potential as an alternative to rechargeable cells in the early part of the twenty-first century.

8 Here the answer depends on the point of view of the students. Answers might refer to developing cells for electric cars to improve air quality in cities, cells suitable for backing up the electricity supply from renewables as well as cells free of harmful chemicals to ease the disposal problems. Fuel cells are not mentioned in the passage but might legitimately crop up in answers to this question.

Answers to Topic 17 questions

Review questions

17.1

	Oxidising agents	Reducing agents	
a	$Cu^{2+}(aq)$	$Fe(s)$	(1)
b	$H^+(aq)$	$Al(s)$	(1)
c	$Pb^{2+}(aq)$	$Zn(s)$	(1)
d	$Fe^{3+}(aq)$	$Sn^{2+}(aq)$	(1)

Total 4 marks

17.2

a $E^\ominus = -0.44$ V: H_2 positive, Fe negative (2)

b $E^\ominus = +0.25$ V; H_2 positive, Ni negative (2)

c $E^\ominus = +0.51$ V; Ni positive, Zn negative (2)

d $E^\ominus = +0.92$ V; Cr positive, Al negative (2)

Total 8 marks

17.3 $E^\ominus = +0.34 - (-0.28) = +0.62$ V (2)

Total 2 marks

17.4 $E^\ominus = 1.61 - 0.76 = +0.85$ V (2)

Total 2 marks

17.5	**a**	$E^{\ominus}_{\mathrm{cell}} = +1.80\,\mathrm{V}$	(1)
		$\mathrm{Al(s)} \longrightarrow \mathrm{Al^{3+}(aq)} + 3\mathrm{e^-}$	
		$\mathrm{Al^{2+}(aq)} + 2\mathrm{e^-} \longrightarrow \mathrm{Sn(s)}$	(1)
		$\mathrm{2Al(s)} + \mathrm{3Sn^{2+}(aq)} \longrightarrow \mathrm{2Al^{3+}(aq)} + \mathrm{3Sn(s)}$	(1)
	b	$E^{\ominus}_{\mathrm{cell}} = -0.93\,\mathrm{V}$	(1)
		$\mathrm{Pb(s)} \longrightarrow \mathrm{Pb^{2+}(aq)} + 2\mathrm{e^-}$	
		$\mathrm{Ag^+(aq)} + \mathrm{e^-} \longrightarrow \mathrm{Ag(s)}$	(1)
		$\mathrm{Pb(s)} + \mathrm{2Ag^+(aq)} \longrightarrow \mathrm{2Ag(s)} + \mathrm{Pb^{2+}(aq)}$	(1)
	c	$E^{\ominus}_{\mathrm{cell}} = -2.37\,\mathrm{V}$	(1)
		$\mathrm{Mg(s)} \longrightarrow \mathrm{Mg^{2+}(aq)} + 2\mathrm{e^-}$	
		$\mathrm{2H^+(aq)} + 2\mathrm{e^-} \longrightarrow \mathrm{H_2(g)}$	(1)
		$\mathrm{Mg(s)} + \mathrm{2H^+(aq)} \longrightarrow \mathrm{Mg^{2+}(aq)} + \mathrm{H_2(g)}$	(1)
			Total 9 marks
17.6	**a**	$\mathrm{Ag^+(aq)}$, $\mathrm{Cu^{2+}(aq)}$, $\mathrm{Pb^{2+}(aq)}$, $\mathrm{Cr^{3+}(aq)}$	(2)
	b	$\mathrm{Fe^{3+}(aq)}$, $\mathrm{Sn^{2+}(aq)}$, $\mathrm{Zn^{2+}(aq)}$, $\mathrm{Mg^{2+}(aq)}$	(2)
			Total 4 marks
17.7	**a**	**ii** the value of K_c is not $>10^{10}$ or $<10^{-10}$	(2)
	b	No	(1)
	c	$\mathrm{Pt} \mid \mathrm{Fe^{2+}(aq), Fe^{3+}(aq)} \;\vdots\vdots\; \mathrm{Ag^+(aq)} \mid \mathrm{Ag(s)}$	(2)
	d	Diagram should show: beaker containing equimolar solution of $\mathrm{Fe^{2+}(aq)}$ and $\mathrm{Fe^{3+}(aq)}$; joined by salt bridge to second beaker containing 1.0 M $\mathrm{Ag^+(aq)}$; Pt electrode in $\mathrm{Fe^{2+}}$, $\mathrm{Fe^{3+}}$ solution; Ag electrode in second beaker; electrodes joined externally through high-resistance voltmeter.	(3)
			Total 8 marks
17.8	**a**	Correct 'anti-clockwise' diagram	(2)
		reaction should occur	(1)
	b	Correct 'anti-clockwise' diagram	(2)
		reaction not predicted	(1)
	c	Correct 'anti-clockwise' diagram	(2)
		reaction not predicted	(1)
			Total 9 marks
17.9	**a**	$\tfrac{1}{2}\mathrm{Br_2(aq)} + \mathrm{e^-} \longrightarrow \mathrm{Br^-(aq)}$	(1)
		$\mathrm{I^-(aq)} \longrightarrow \tfrac{1}{2}\mathrm{I_2(aq)} + \mathrm{e^-}$	(1)
	b	$\mathrm{Pt} \mid \mathrm{Br^-(aq)}, \tfrac{1}{2}\mathrm{Br_2(aq)} \;\vdots\vdots\; \tfrac{1}{2}\mathrm{I_2(aq)}, \mathrm{I^-(aq)} \mid \mathrm{Pt}$	(2)
	c	$E^{\ominus} = 0.54 - 1.09 = -0.55\,\mathrm{V}$	(2)
		(+0.55 V if cell **b** drawn the other way round)	
	d	$E^{\ominus}$ is very nearly 0.6 V, products predominate at equilibrium	(2)
			Total 8 marks
17.10	**a**	$\Delta S_{\mathrm{system}}$ positive	(1)
		gaseous product formed, solid reactant consumed	(1)
		$\Delta S_{\mathrm{surroundings}}$ positive	(1)
		ΔH negative, therefore $-\Delta H/T$ positive	(1)
		$\Delta S_{\mathrm{total}}$ positive	(1)
		both $\Delta S_{\mathrm{system}}$ and $\Delta S_{\mathrm{surroundings}}$ positive **or** spontaneous reaction occurs	(1)
	b	$\Delta S^{\ominus}_{\mathrm{system}} = -40.2\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta H^{\ominus}_{\mathrm{reaction}} = -466.9\,\mathrm{kJ\,mol^{-1}}$	(1)
		$\Delta S^{\ominus}_{\mathrm{surroundings}} = -(-466\,900/298)$	
		$= +1567\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^{\ominus}_{\mathrm{total}} = +1527\,\mathrm{J\,mol^{-1}\,K^{-1}}$	(1)
		$\Delta S^{\ominus}_{\mathrm{system}}$ differs from prediction but the others agree	(1)
	c	$\Delta S_{\mathrm{total}}$ is much greater than $+200\,\mathrm{J\,mol^{-1}\,K^{-1}}$, so reaction goes to completion and K_c is closest to 10^{20}.	(2)
			Total 13 marks

Examination questions

17.11
a **i** $Pt[H_2(g)] \,|\, 2H^+(aq) \;\vdots\vdots\; Fe^{3+}(aq), Fe^{2+}(aq) \,|\, Pt$ (2)
ii Fe^{3+}, Fe^{2+} electrode will be positive (1)
b **i** Fe(0) (1)
ii $2V^{3+}(aq) + Fe(s) \longrightarrow 2V^{2+}(aq) + Fe^{2+}(aq)$ (2)
iii 0.18 V (1)

Total 7 marks

17.12
a **i** +1 (1)
ii Reduce diffusion/prevent siphoning (1)
iii Calomel: danger of poisonous mercury but compact and portable (1)
Hydrogen: danger of explosion but absolute standard (1)
b **i** Diagram should show: calomel electrode connected through its own salt bridge to beaker containing 1.0 M $CuSO_4$ at 25 °C; Cu electrode in the $CuSO_4$ solution; Cu electrode connected through high-resistance voltmeter to Pt electrode of calomel half-cell (2)
ii $E^\ominus = 0.07$ V (2)

Total 8 marks

17.13
a **i** $Fe^{2+}(aq) \,|\, Fe(s)$ −0.44 V (1)
$Sn^{2+}(aq) \,|\, Sn(s)$ −0.14 V (1)
ii $E^\ominus = -0.44 - (-0.14) = -0.30$ V (2)
iii Iron is the better reducing agent. (1)
Electrons will flow from iron to tin (negative to positive) so iron is the better electron 'donor'. (1)
b Fe is oxidised (to $Fe^{2+}(aq)$). (1)
Fe has the stronger tendency to give away electrons or is the more negative. (1)

Total 8 marks

17.14
a **i** **A** −0.56 V; **B** −0.44 V; **C** +0.36 V; **D** −0.40 V; **E** +0.77 V (2)
ii **B** has iron as a solid electrode but the other cells have no metal to conduct electrons in or out (so Pt needed). (1)
iii Diagram should show: 2 beakers, one containing equimolar solutions of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, the other equimolar solutions of Fe^{2+} and Fe^{3+}; solutions connected by salt bridge; Pt electrodes in both solutions, connected through high-resistance voltmeter; temperature 298 K. (4)
iv +0.41 V (2)
v $Fe(CN)_6^{4-}(aq) + Fe^{3+}(aq) \longrightarrow Fe(CN)_6^{3-}(aq) + Fe^{2+}(aq)$ (2)
b **i** Half-cell **C**, CN^- not normally present (1)
ii Reactions from half-cells **B** and **D** produce $Fe^{2+}(aq)$ and $OH^-(aq)$ ($E^\ominus = +0.84$ V) which react to give a precipitate of $Fe(OH)_2$
Reactions from half-cells **A** and **D** produce $Fe(OH)_3(s)$ and $OH^-(aq)$ ($E^\ominus = +0.96$ V) (3)

Total 15 marks

TOPIC 18

Natural and synthetic polymers

Introduction

This topic is concerned with macromolecules which occur either naturally or are man-made for specific purposes. Proteins are studied as examples of natural polymers to provide links with biology courses and with the two Special Studies, *Biochemistry* and *Food science*, which are closely related to this topic. The nature and behaviour of amines and amino acids are considered first. The importance of the shape of molecules and the new concept of chirality is also considered here.

Students are expected to have a knowledge of the two types of polymerisation reaction and an understanding of the differences between polymers. The way in which the structure of polymer chains influence behaviour and lead to the design of particular polymers for specific functions is included as background reading.

Contents

Timing		Students' Book
18.1	2 hours	pages 425–8
18.2	1 hour	pages 428–31
18.3	4 hours	pages 431–4
18.4	Homework	pages 435–7
18.5	3 hours	pages 438–44
18.6	Homework	pages 444–6
Total about 2 weeks		

18.1 Amines – the reactions of amines, solubility, salt formation, reaction with transition metal ions and reactions as nucleophiles.

18.2 The shape of carbon compounds – chiral and achiral compounds.

18.3 Amino acids and proteins – chirality and amino acids, the peptide group; experiments with amino acids and proteins, acidity and basicity, chirality; chromatographic separation of amino acids, R_f values.

18.4 Background reading – the chemical and structural investigation of proteins.

18.5 Synthetic polymers – the nature of polymers; classification of polymers, thermoplastics, elastomers, thermosetting polymers; addition polymerisation, condensation polymerisation; polymerisation reaction experiments; *investigation of soluble laundry bags.*

18.6 Background reading – the structure and properties of synthetic polymers.

Objectives

1 To introduce the concepts of chirality and optical activity.

2 To develop knowledge of the reactions of amines and amino acids.

3 To develop skill in practical techniques such as chromatography.

4 To develop knowledge of addition and condensation polymerisation, the classification of polymers and an understanding of their properties as related to their structure.

5 To provide information about the industrial and social importance of selected compounds.

18.1 Amines

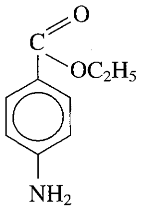
Timing 2 hours

Suggested treatment

The teacher will need:
Molecular model kit

The main objective is a comparison of ammonia, alkylamines and arylamines. It would be useful to review acid–base chemistry from Topic 4 at this point; the formation of dative bonds by ammonia is discussed in Topic 7. Phenylamine is not used because it is toxic and ethyl 4-aminobenzoate, benzocaine, is used instead, using procedures based on CLEAPSS Guide L195.

The difference in structure between primary, secondary, and tertiary amines and the parallel alcohols (Topic 2) and halogenoalkanes (Topic 10) should be pointed out by the use of models as well as the links with amides (ethanoylation reaction). Students should build models for themselves if sufficient kits are available.


Ethyl 4-aminobenzoate

EXPERIMENT 18.1 The reactions of amines

Each group of students will need:
Test tubes and rack
Dropping pipette

Access to:
2 M ammonia
Butylamine HIGHLY FLAMMABLE, CORROSIVE
0.1 M copper(II) sulphate
Ethyl 4-aminobenzoate
Ethanoyl chloride HIGHLY FLAMMABLE, CORROSIVE
Full-range Indicator solution
2 M hydrochloric acid

Access to fume cupboard

HAZARDS

Asthmatics should be warned to be cautious of smelling amines.
Butylamine needs to be used with care. The quantity available should be restricted and it should be dispensed in a fume cupboard.
Phenylamine (aniline) is toxic and it is better to avoid using it.
Ethanoyl chloride is hazardous and the teacher may prefer to demonstrate the reactions with it.

Procedure

Full instructions are given in the *Students' Book.* The following notes may be helpful.

1 Solubility and pH

If a pH meter is available, it is worthwhile comparing the pH of 0.1 M ammonia and 0.1 M butylamine. Students tend to assume that inorganic compounds are stronger acids and bases than organic compounds. The relevant K_a values are quoted in the *Students' Book.*

2 Formation of salts

The characteristic fishy odour of alkylamines disappears when they form salts. When students write out the equations, they should see that the pattern of the reactions is the same as for the familiar ammonium salts. The relevant K_a values are quoted in the *Students' Book.*

3 Reaction with transition metal ions

The amines are reacting as ligands and forming complex ions. The formation of complex ions is discussed in Topic 19 in more detail, but the reaction of ammonia with silver ions was covered in Topic 6.

4 Nucleophilic reactions of amines with acid derivatives

The teacher may prefer to demonstrate the reactions of amines with ethanoyl chloride.

Reactions of amines

The *Students' Book* contains a survey of the principal reactions of amines. An opportunity should be taken to test the students' knowledge of these reactions at a suitable point.

18.2 The shape of carbon compounds

Timing About 1 hour will be needed

Suggested treatment

The teacher will need:
Molecular model kit
Hand mirror (plastic)
Three opaque glass tubes with metal screw caps and their contents concealed under cotton wool:
Tube A, containing a small piece of spearmint chewing gum
Tube B, containing a quantity of caraway seeds
Tube C, containing a quantity of caraway seeds

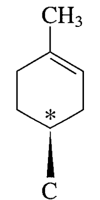
The introductory smell test is based on work by Gordon Woods, 'Illustrating optical isomerism'. (*School Science Review*, **73**(265), pages 107–109, 1992). The testing has been extended to Chile, The Gambia and Hong Kong. Chinese students were the most accurate in matching the smells, British students who are familiar with chewing gum and spearmint toothpaste were quite accurate and the overall accuracy is about 60%.

For the test to work well the metal caps to the tube should have any cork or plastic lining removed and should be labelled to avoid mixing up caps and tubes. To balance the smell intensity use a small piece of chewing gum to a rather larger amount of caraway seeds. It is important for students to have access to a set of molecular models, preferably of the ball-and-spoke type, so that they can build models of the molecules for themselves.

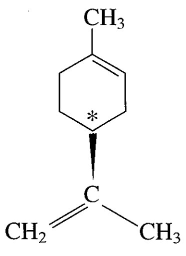
If teachers wish they could remind students of their extraction of limonene in Topic 8: the (+) form occurs in citrus fruits, the (−) form in pine needle oil and (±) in turpentine oil.

The word *chiral* (rather than asymmetric) is the preferred term for the type of molecular structure that leads to optical activity in compounds.

The use of a polarimeter for detecting chirality is introduced in Experiment 18.3.



(+) has an orange odour



(−) has a lemon odour

Figure 18.1 The chiral isomers of limonene. The chiral centre is marked*

18.3 Amino acids and proteins

Timing 4 hours

Suggested treatment

The section begins with a consideration of naturally occurring amino acids. The following points should be noted.

- The non-systematic names generally used by biochemists are used in the *Students' Book.*
- The attention of students should be directed to the existence of a chiral centre in the molecules of all of these compounds except for glycine. There is no intention of including L and D configurations.
- Amino acid 'residues' can be linked together through the —CO—NH— group. In this context this group is known as the *peptide* group. Two amino acid residues form a *dipeptide*; three a *tripeptide*; a number of amino acid residues form a *polypeptide* or *protein.*

  Protein molecules have very large numbers of amino acid residues linked together through peptide groups.
- All proteins are made up from about two dozen amino acids. Thirteen of them are listed in the *Students' Book* and a further seven in this *Teacher's Guide.*

The main objective of a discussion of proteins should be to establish their importance rather than to learn facts about specific proteins. Additional information is given in the Special Studies *Food science* and *Biochemistry*, and biology students should be able to make a valuable contribution to the discussion.

The teaching of this section can be merged with the teaching of the Special Studies *Food science* or *Biochemistry*, if either of these studies is being taken by the students.

EXPERIMENT 18.3a

Protein materials

Each group of students will need:
Eye protection
Protective gloves
Test tubes and rack
Dropping pipette
Chromatography paper ('lantern' type)

Access to:
Full-range Indicator
0.01 M hydrochloric acid
0.01 M L-glutamic acid
0.01 M glycine
0.01 M sodium hydroxide
0.02 M ninhydrin solution in propanone (store in refrigerator) HARMFUL, HIGHLY FLAMMABLE
Protein materials, e.g. casein, gelatin, fresh milk, egg, etc.
Fume cupboard
Oven at 110 °C
Polarimeter (optional)
Sodium glutamate, 50 cm^3 of concentrated solution for polarimetry (or sucrose – see Chirality below)

HAZARDS

Ninhydrin in propanone is harmful – the spray from an aerosol can is highly flammable. Only spray in a fume cupboard and wear gloves.

Procedure

Full instructions are given in the *Students' Book.* Because Experiment 18.3b 'The chromatographic separation of amino acids' is lengthy, students could start on it and then carry out Experiment 18.3a while their chromatograms develop. The following notes may be helpful.

1 Acidity and basicity

Glycine and L-glutamic acid are used for these experiments as they are the cheapest amino acids to purchase. The pH of other amino acids could be demonstrated to students. Students need not be introduced to the term 'zwitterion'.

2 Ninhydrin test

Students should be cautioned against getting ninhydrin spray on their hands. The reactions are complex and students are not expected to know them; for the teacher's information, they can be written as follows.

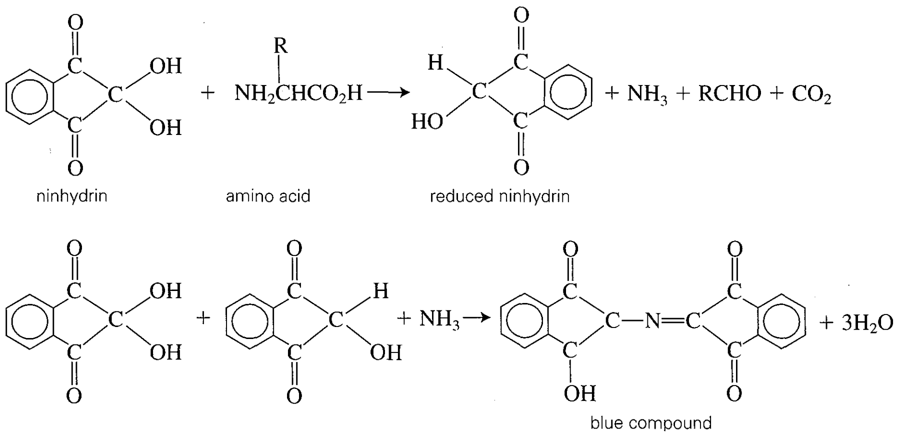


Figure 18.2 The development of ninhydrin blue

3 Chirality

Students should appreciate by the inspection of models that glycine is achiral while the other amino acids are chiral. A stock solution of sodium glutamate can be made sufficiently concentrated to display slight rotation in a simple polarimeter. If students use the stock solution to make their measurements, not much is needed and the experiment is quickly performed. A sucrose solution (100 g in 40 cm^3 water) is a cheaper alternative to illustrate the principle and that the extent of rotation is greater.

EXPERIMENT 18.3b The chromatographic separation of amino acids

Each group of students will need:
0.01% amino acid solutions (see procedure)

Apparatus for paper chromatography:
Beaker, 1 dm^3 and cover (cling film)
Capillary melting point tubes
Chromatography paper (No. 1 paper, 12.5 cm reel or 'lantern' type)
Measuring cylinder, 25 cm^3
Measuring cylinder, 5 cm^3
Paper clips
Gloves (for spraying)

Access to:
8 M ammonia in crystallising dish (*in a fume cupboard*) CORROSIVE
Butan-1-ol, 12 cm^3 HARMFUL, FLAMMABLE
Ethanoic acid, pure (glacial), 3 cm^3 CORROSIVE
Oven at 110 °C
Spray bottle containing methanol (19 cm^3), 1 M aqueous copper(II) nitrate (1 cm^3), and 2 M nitric acid (1 drop) TOXIC, HIGHLY FLAMMABLE
Spray bottle containing 0.02 M ninhydrin in propanone (store in refrigerator) HARMFUL, HIGHLY FLAMMABLE
Fume cupboard (for spraying)

Procedure

This experiment is lengthy and if convenient, students could start it and carry out the preceding Experiment 18.3a while their chromatograms develop. Full instructions are given in the *Students' Book*. The following notes may be helpful.

Reference solutions of 0.01% amino acids should be made up in a mixture of water (9 parts) and propan-2-ol (highly flammable) (1 part). Reference sets of amino acids can be purchased or about five of the cheaper amino acids could be selected to cover the range of polar (asparagine, tyrosine), non-polar (alanine, glycine, leucine, valine), acidic (aspartic acid, glutamic acid), and basic (arginine, lysine).

To reduce waste, 25 cm lengths of chromatography paper can be cut from the reel in advance. It is most important that each piece of paper is handled only at the extreme corners, because finger prints will yield blue colours when the paper is treated with ninhydrin.

Spraying of chromatography papers should be carried out in a fume cupboard with the paper **hung up and *not* held in an unprotected hand**. Ninhydrin aerosol sprays suitable for use in this experiment can be obtained from chemical supply companies.

When calculating their R_f values students should realise that the value varies with solvent and temperature, so comparison with the values quoted in the *Students' Book* is not strictly valid.

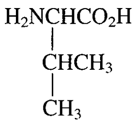
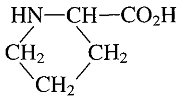
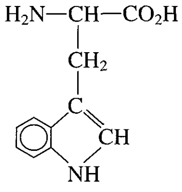
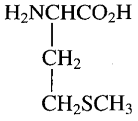
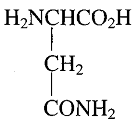
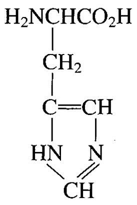
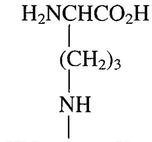
Formula	**Name**	**Abbreviation**	**Nature of side chain**	**R_f value in butan-1-ol/ ethanoic acid/ water**
 $\begin{array}{l}H_2NCHCO_2H\\ \quad\vert\\ \quad CHCH_3\\ \quad\vert\\ \quad CH_3\end{array}$	valine	val	non-polar	0.60
	proline	pro	non-polar	0.43
	tryptophan	try	non-polar	0.50
 $\begin{array}{l}H_2NCHCO_2H\\ \quad\vert\\ \quad CH_2\\ \quad\vert\\ \quad CH_2SCH_3\end{array}$	methionine	met	non-polar	0.55
 $\begin{array}{l}H_2NCHCO_2H\\ \quad\vert\\ \quad CH_2\\ \quad\vert\\ \quad CONH_2\end{array}$	asparagine	asn	polar	0.19
	histidine	his	basic	0.20
 $\begin{array}{l}H_2NCHCO_2H\\ \quad\vert\\ \quad(CH_2)_3\\ \quad\vert\\ \quad NH\\ \quad\vert\\ HN{=}C{-}NH_2\end{array}$	arginine	arg	basic	0.16

Figure 18.3 7 of the 20 'standard' amino acids and their R_f values – those not given in the *Students' Book*

18.4 Background reading: the chemical and structural investigation of proteins

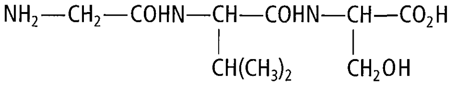
Timing Homework

The short passage introduces students to the classic work of Sanger and mentions briefly the use of mass spectrometry to determine the amino acid sequence in proteins.

ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 435

1 The structural formula of gly-val-ser is



$$NH_2{-}CH_2{-}COHN{-}\underset{CH(CH_3)_2}{\underset{|}{CH}}{-}COHN{-}\underset{CH_2OH}{\underset{|}{CH}}{-}CO_2H$$

2 The structures drawn should show hydrogen bonding between an NH group of one chain and a CO group of the other chain.

3 By chromatography.

18.5 Synthetic polymers

Timing 3 hours

Suggested treatment

It is suggested that students should review their prior knowledge through group work. As well as asking them to sort out ideas from their everyday knowledge of polymers they are expected to recall more specific knowledge of monomers and polymers from Topic 8.

Students should then be introduced to the distinction between addition and condensation polymerisation and there is a short study task for them to apply their understanding of polymerisation reactions. The experiments develop this theme with further examples.

EXPERIMENT 18.5 Polymerisation reactions

Each group of students will need:
Eye protection
Protective gloves

1 Poly(phenylethene)

Beaker, 250 cm^3
Test tube
Cotton wool
Phenyl(ethene) IRRITANT, HARMFUL, FLAMMABLE
Di(dodecanoyl) peroxide 0.2 g OXIDANT
Wooden splints
Fume cupboard

2 The 'nylon rope trick'

Beakers, 100 cm^3, 2
Measuring cylinders, 25 cm^3, 2
Crucible tongs or tweezers
Glass rods, 2
Decanedioyl chloride (0.5 cm^3) in petroleum spirit, 120–160 °C (15 cm^3) FLAMMABLE AND CORROSIVE
Hexane-1,6-diamine (0.7 g) CORROSIVE
Sodium carbonate-10-water (2 g) in water (15 cm^3)
50% aqueous ethanol, 20 cm^3

3 Polyester resin

Test tube
Thermometer, 0–360 °C
Oil bath
Dropping pipette
Benzene-1,2-dicarboxylic anhydride (phthalic anhydride), 3g IRRITANT
Propane-1,2,3-triol (glycerol), 2 cm^3

Access to:
Fume cupboard

4 Crosslinked polymer

Disposable container (plastic drinking cup)
Measuring cylinder, 50 cm^3
Measuring cylinder, 10 cm^3
Glass rod
4% aqueous poly(ethenol), 25 cm^3
4% aqueous sodium borate, 5 cm^3

Procedure

Full instructions are given in the *Students' Book.*

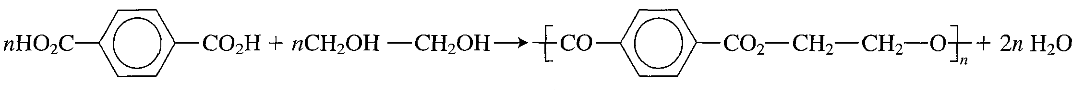
Students cannot be expected to perform more than one or two of the preparations. Alternatively, some of the experiments could be done as a teacher's demonstration. Note that phenylethene often contains a stabiliser which will slow down the polymerisation.

At the end of this section it is suggested that soluble laundry bags could be the subject of an investigation.

ANSWERS

Study task, page 442

1 The links in a nylon chain consist of amide groups.
2 The equation for the formation of Terylene fibre is



3 The carbonyl group enables methanol to react with the benzene ring in an electrophilic substitution reaction.

INVESTIGATION 18.5 Soluble laundry bags

While many students will be unfamiliar with soluble laundry bags, the exercise revolves around the general factors governing solubility in water with which all students should be conversant. It is important that the investigation is based around detailed and sound laboratory work and that at least two areas are covered. Students should be encouraged to process results quantitatively where possible, and be able to deal suitably with a consideration of errors. Risk assessments must be accurately and thoroughly prepared, and be rather more than a direct transfer from Hazcards.

The laundry bag material can be bought from Sigma Aldrich Chemicals, The Old Brickyard, New Road, Gillingham, Dorset SP8 4XT, telephone 0800 717181 or 01747 822211. They call it 'Hot water soluble PVA film', reference Z300381. In 2000 the price for 1 m^2 was £3.90 + VAT.

18.6 Background reading: the structure and properties of synthetic polymers

ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 444

1
- Amorphous polymers have linear chains in a disordered arrangement. There is limited movement as chains can twist and slide past each other in the solid state.
- Crystalline polymers contain some regions of chain alignment mixed with amorphous regions.
- Fibres consist of polymer chains aligned along the fibre axis.

2 If the polymer chain is regular and not branched, and includes polar groups, the intermolecular forces are increased which increases crystallinity.

3 Stretching involves only bond rotation rather than bond stretching in an elastomer.

4 There are strong covalent bonds cross-linking the polymer chains to each other in a thermosetting plastic.

Answers to Topic 18 questions

Review questions

18.1

a	C	(1)	**d**	E	(1)
b	D	(1)	**e**	B	(1)
c	A	(1)	**f**	D	(1)

Total 6 marks

18.2

a	$C_6H_5NH_2$	(1)	**c**	CH_3NH_2	(1)
	HCl	(1)		CH_3Cl	(1)
b	$CH_3CH_2CH_2NH_2$	(1)	**d**	$C_4H_9NH_2$	(1)
	$CuSO_4$(aq)	(1)		CH_3COCl	(1)

Total 8 marks

18.3

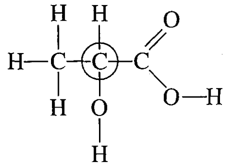
$CH_3CH_2CH_2CH_3$; $CH_3CH_2CH_2NH_2$; $CH_3CH_2CH_2OH$; CH_3CONH_2 (2)

Van der Waals forces are similar in all substances. Hydrogen bonding interactions in all cases except for butane, but —OH with two lone-pairs and greater polarity has stronger interactions than —NH_2. Amide has two electronegative atoms for hydrogen bonding or dipole–dipole attractions. (4)

Total 6 marks

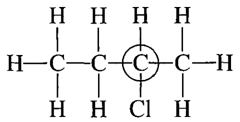
18.4

a



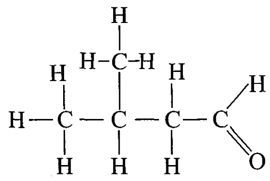
(2)

b



(2)

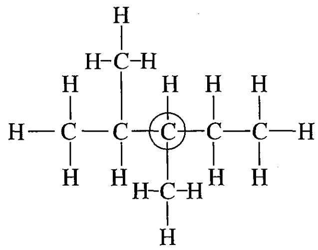
c



(no chiral centre)

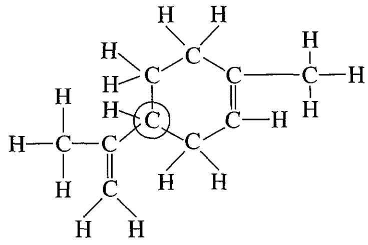
(2)

d



(2)

e



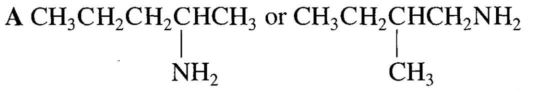
(2)

Total 10 marks

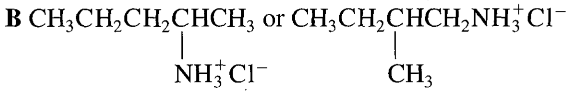
18.5

Alternative answers are possible for A, B and C in **a**

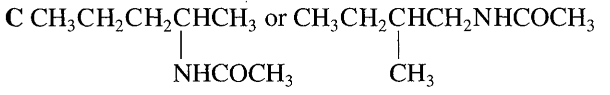
a



$\mathbf{A}\ CH_3CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCH_3$ or $CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2NH_2$ (2)



$\mathbf{B}\ CH_3CH_2CH_2\underset{NH_3^+Cl^-}{\underset{|}{C}}HCH_3$ or $CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2NH_3^+Cl^-$ (2)



$\mathbf{C}\ CH_3CH_2CH_2\underset{NHCOCH_3}{\underset{|}{C}}HCH_3$ or $CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2NHCOCH_3$ (2)

b $CH_3CH_2CH(NH_2)CH_2CH_3$ or $CH_3CH_2CH_2CH_2CH_2NH_2$ (2)

3-aminopentane 1-aminopentane

c

$$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[\text{KBr + conc. } H_2SO_4]{\text{HBr from}}$$

$$CH_3CH_2CH_2CH_2CH_2Br \xrightarrow[\text{ethanoic solution of ammonia}]{\text{Heat under pressure with}}$$

$$CH_3CH_2CH_2CH_2CH_2NH_2$$

(4)

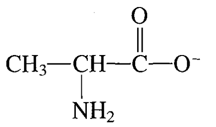
Total 12 marks

18.6

a **i** C—H bond (1)

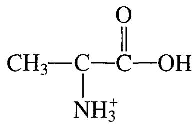
ii Stretching, 2962–2853; bending 1485–1365 (2)

b **i**



$CH_3-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O^-$

ii



$CH_3-\underset{\underset{NH_3^+}{|}}{C}-\overset{\overset{O}{\|}}{C}-OH$

(2)

c **i**, **ii** and **iii** No difference (3)

iv One will rotate the plane of plane polarised light in a clockwise sense and the other anti-clockwise by the same amount. (1)

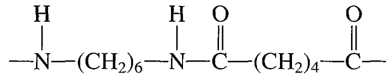
v Naturally occurring amino acids are all of the L form which, strictly speaking, could be either (+) or (−) in natural protein. It is reasonable for answers to suppose that either (+) or (−) would occur alone in any particular protein. (1)

Total 10 marks

18.7

a Condensation polymerisation (1)

b



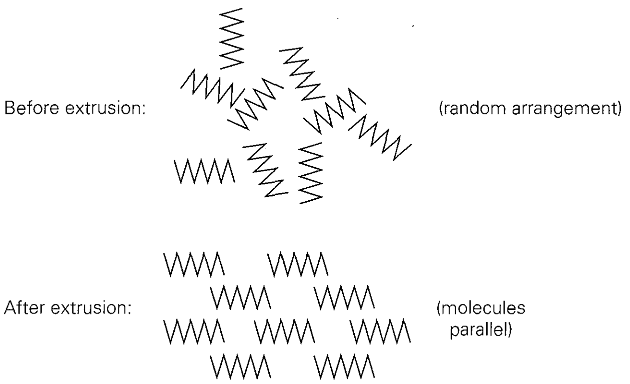
$-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-$

(3)

c Amide (or peptide) (1)

d Nylon (1)

e **i**



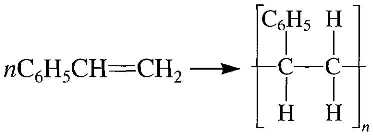
(2)

ii Molecules more closely aligned, parallel to one another so stronger van der Waals forces. Also, more opportunities for hydrogen bonding. (2)

Total 10 marks

18.8

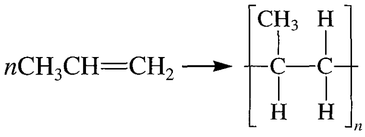
a



$nC_6H_5CH{=}CH_2 \longrightarrow \left[-\underset{\underset{H}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\right]_n$

(1)

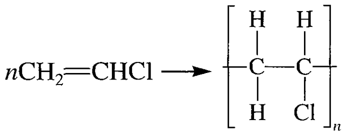
b



$nCH_3CH{=}CH_2 \longrightarrow \left[-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\right]_n$

(1)

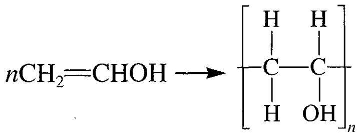
c



$nCH_2{=}CHCl \longrightarrow \left[-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-\right]_n$

(1)

d



$nCH_2{=}CHOH \longrightarrow \left[-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\right]_n$

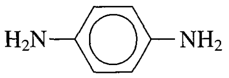
(1)

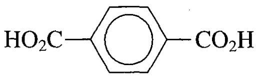
Total 4 marks

Examination questions

18.9 **a** Polymer with amide/peptide links between monomer units. (1)

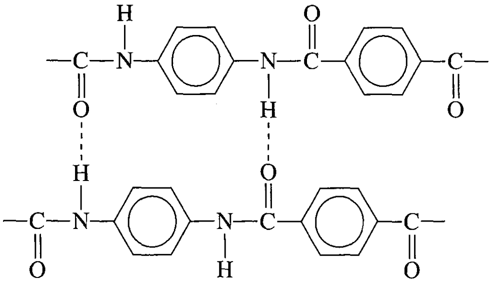
b (2)





c **i** Hydrogen bonding (1)

ii (2)

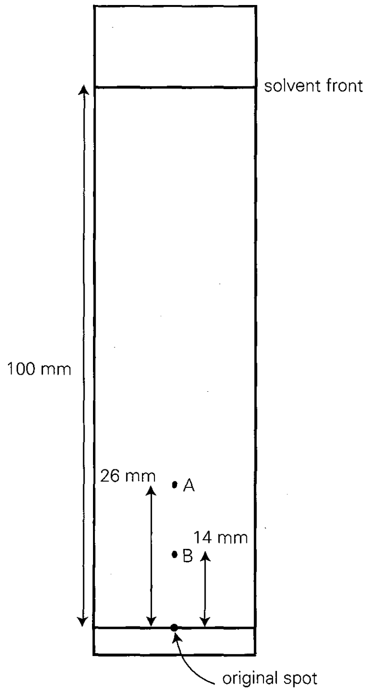


d **i** Molecules lined up in parallel in crystalline regions but more randomly in non-crystalline regions (or appropriate diagram). (1)

ii More hydrogen bonds/total intermolecular forces are stronger. (1)

Total 8 marks

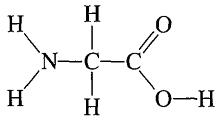
18.10 **a**



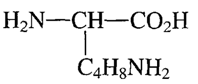
solvent front and origin correctly shown (1)
R_f values correct (1)
A and **B** (1)

b **i** Chiral centre (1)

ii (1)

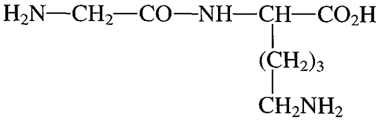


iii $C_6H_{14}N_2O_2$ (1)



$H_2N{-}CH(C_4H_8NH_2){-}CO_2H$ (1)

iv (2)



$H_2N{-}CH_2{-}CO{-}NH{-}CH((CH_2)_3CH_2NH_2){-}CO_2H$

c Alkaline (1)
Two basic groups but only one acidic group (1)

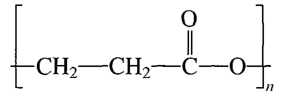
Total 11 marks

18.11

a $HOCH_2CH_2OH$ (1)

b In the polyether, van der Waals and dipole–dipole attractions (1)
In the polyurethane, hydrogen bonds as well (1)
which are stronger (1)

c



$$\left[-CH_2-CH_2-\overset{\overset{\large O}{\|}}{C}-O-\right]_n$$

(1)

Total 5 marks

18.12

a Van der Waals
Van der Waals (1)
Dipole–dipole (1)
Hydrogen bonds (1)

b **i** LD poly(ethene) has side chains branching from main chain so molecules do not pack as closely as those of HD poly(ethene) (must be a comparison). (1)
ii Stronger van der Waals forces in HD poly(ethene) because greater contact between molecules. (1)

c Bakelite is a thermoset so cross-links prevent melting/chars/decomposes on heating. (1)

d Possible properties include tensile strength, wet strength, water absorbance, elasticity/flexibility/density, glass temperature. Others should be assessed on their merits. Allow cost even though not a property (any four). (4)

Total 10 marks

TOPIC 19

The transition elements

Introduction

A transition element is defined as one which contains an incomplete d-shell in at least one of its *compounds*. It is *not* synonymous with a d-block element. The distinction between these two terms is addressed at the start of this topic in the *Students' Book*. The effect of this distinction is that scandium and zinc, two d-block elements which do not have the typical properties of transition elements, are not classified as such. Attention should be drawn to the electronic configurations given at the beginning of the topic; those for chromium and copper are seen to be anomalous – the 'stability' of the half-filled and of the filled sub-shells might be referred to at this point. Only the first row of the transition elements are considered in this topic, that is, the elements from titanium to copper inclusive.
To introduce the topic, the following points should be covered:

- the definition of a transition element
- the electronic configurations of the elements from scandium to zinc
- all are metals and possess many similarities in their physical properties
- all exhibit variable oxidation number – a discussion of this property is set out in section 19.1
- all form many complex ions (section 19.2)
- all have coloured ions
- all exhibit catalytic activity (section 19.3).

Content

19.1 Variable oxidation number – experimental study of redox reactions of iron and of vanadium; analysis of iron tablets.

19.2 Complex ion formation – ligands; experimental study of copper(II) complexes; stability constants; entropy considerations; preparations of compounds containing complex ions.

19.3 Transition elements as catalysts – kinetic study of an autocatalysed reaction; homogenous catalysis and electrode potentials.

19.4 The special properties of the transition elements – similarity of physical properties; variable oxidation number; ability to form complex ions; colour; catalytic activity.

Timing	Students' Book
19.1 4 hours	pages 454–9
19.2 3 hours	pages 459–66
19.3 2 hours	pages 466–8
19.4 1 hour	pages 469–71
Total about 2 weeks	

Objectives

1 To investigate the special characteristics of the transition elements.

2 To provide opportunities to use standard electrode potentials to predict reaction direction.

3 To apply equilibrium theory to complex formation.

19.1 Variable oxidation number

Timing About 4 hours will be needed

Suggested treatment

In the first experiment students apply the 'anti-clockwise rule', introduced in Topic 17, to the redox reactions of iron(II) and iron(III). The chart given in the *Students' Book* (figure 19.2) needs a little introduction, emphasising the unusual axes (negative to the right and upwards). It might be a good idea to do this introduction in advance of the practical session so as to give time for drawing up the chart as homework.

EXPERIMENT 19.1a The redox reactions of iron

HAZARDS

Silver nitrate solid is corrosive.
Sulphur dioxide should not be breathed by those who suffer from respiratory complaints such as asthma.

Each group of students will need:
Eye protection
Test tube rack
8 test tubes
Dropping pipette
Spatula

Access to:
Zinc powder HIGHLY FLAMMABLE
0.1 M iron(II) sulphate in 0.04 M sulphuric acid, about 40 cm^3
0.1 M iron(III) chloride in 0.8 M hydrochloric acid, about 40 cm^3
0.1 M bromine solution, 10 cm^3 TOXIC AND CORROSIVE
0.1 M potassium manganate(VII), 10 cm^3
0.1 M chlorine solution, 10 cm^3 HARMFUL AND IRRITANT WITH TOXIC VAPOUR
0.1 M sodium chloride, 10 cm^3
Sulphur dioxide solution, 10 cm^3 TOXIC, WITH CORROSIVE VAPOUR
Silver nitrate solution, 10 cm^3 (0.05 M or less is suitable)
0.1 M potassium iodide, 10 cm^3

Procedure

Full details of the procedure are given in the *Students' Book.* The outcome of the experiment is as follows:

a Iron(II) is oxidised to iron(III) by bromine water; the colour of bromine disappears.
b Iron(III) is reduced to iron(II) by zinc; slight colour change; the NaOH test gives the green colour of iron(II) hydroxide.
c Iron(II) reduces Ag^+ to silver metal; grey precipitate.
d No reaction.
e Iron(III) is reduced to iron(II) by sulphur dioxide; the reaction is quite slow; the NaOH test gives the green colour of iron(II) hydroxide.
f Iron(II) is oxidised by potassium manganate(VII); the purple colour disappears.
g Iron(III) oxidises iodide ions to iodine; 'iodine colour' is produced.
h Iron(II) is oxidised to iron(III) by chlorine water; the NaOH test gives the red-brown colour of iron(III) hydroxide.

EXPERIMENT 19.1b The reduction of vanadium(V)

HAZARDS

The bromine produced by oxidation of potassium bromide is toxic by inhalation.

Each group of students will need:
Eye protection
Test tube rack
8 test tubes
Dropping pipette
Spatula
Access to:
0.1 M ammonium vanadate(V) (solid is VERY TOXIC) in 1 M sulphuric acid, 20 cm^3 TOXIC AND IRRITANT
Zinc powder HIGHLY FLAMMABLE
Granulated tin
Copper powder
0.1 M potassium iodide, 10 cm^3
0.1 M iron(II) sulphate in dilute sulphuric acid, 10 cm^3 IRRITANT
0.1 M iron(III) chloride in dilute hydrochloric acid, 20 cm^3 IRRITANT
0.1 M potassium bromide, 10 cm^3
0.1 M copper(II) sulphate, 10 cm^3
0.5 M sodium thiosulphate, 10 cm^3
50% phosphoric(I) acid, H_3PO_3 (hypophosphorous acid), a few drops
Sulphur dioxide solution, 10 cm^3 TOXIC WITH CORROSIVE VAPOUR

Procedure

Full details are given in the *Students' Book*. The outcome of the experiment is as follows:

a VO^{2+} can be obtained using potassium iodide solution followed by just sufficient sodium thiosulphate solution to react with the iodine or by using tin and decanting the solution when the reaction has reached the appropriate stage. Students may need to have it pointed out to them that in going from a yellow colour to a blue colour, the solution passes through a stage of being green; this should not be confused with the green colour of V^{3+}. The use of phosphoric(I) acid provides the best way of getting VO^{2+}.

b V^{3+} can be obtained using granulated tin.

c V^{2+} can be obtained using powdered zinc; the intermediate oxidation numbers can be observed as the reaction proceeds.

EXPERIMENT 19.1c Analysis of 'iron tablets'

HAZARDS

Potassium manganate(VII) solid is an oxidising agent and is harmful.

Each group of students will need:
Eye protection
Access to balance, to weigh to 0.001 g
Filling funnel
Burette, 50 cm^3
Funnel
Pipette, 10 cm^3
Pipette filler
Volumetric flask, 100 cm^3
Conical flask, 250 cm^3
Pestle and mortar
2 iron tablets, for example, Boots 'ferrous sulphate', 200 mg tablets
1 M sulphuric acid, 100 cm^3 IRRITANT
0.005 M potassium manganate(VII) (standardised).

Procedure

Full details are given in the *Students' Book.*

There are some problems associated with the analysis of tablets because more than one reducing agent may be present. The most likely interference is from glucose but as glucose reacts only very slowly with acidified potassium manganate(VII) it is unlikely to affect the analysis significantly.

ANSWERS

In your notes, page 459

1 Excess 1 M sulphuric acid is added for two reasons:

- to suppress the hydrolysis of the iron(II) ions which would otherwise take place
- to supply the H^+(aq) ions needed for the reaction to proceed according to the equation.

2 The results appear to suggest that the 200 mg mentioned on the bottle label refers to the mass of *anhydrous* $FeSO_4$ in each tablet.
Iron tablets are taken medicinally to help combat anaemia, a condition in which the blood contains too little haemoglobin, a protein which contains iron in a complexed form.

19.2 Complex ion formation

Timing About 3 hours will be needed

Suggested treatment

By way of introduction the term 'ligand' should be explained and the basic structure of a complex ion presented as 'central metal ion surrounded by ligands in a variety of geometrical shapes'. The significance of 'monodentate', 'bidentate' and 'hexadentate' should be explained. Whilst some would question the use of the expression 'dative bond' to describe the bond between ligands and a central ion, it is at least within the scope of the students' present knowledge and does serve to emphasise the importance of the lone pair of electrons.

EXPERIMENT 19.2a Some copper(II) complexes

HAZARDS

Open stock bottles of ammonia with care.
Care should be taken when preparing 1,2-dihydroxybenzene (catechol) as the solid is an irritant.

Each group of students will need:
Eye protection
Test tube rack
8 test tubes
3 dropping pipettes
0.5 M copper(II) sulphate, 10 cm^3
Concentrated hydrochloric acid, 5 cm^3 CORROSIVE
8 M ammonia solution, 15 cm^3 CORROSIVE
0.2 M edta, 10 cm^3
0.1 M sodium 2-hydroxybenzoate (sodium salicylate), 20 cm^3
0.1 M 1,2-dihydroxbenzene (catechol) (solid is HARMFUL) in 0.4 M sodium hydroxide, 10 cm^3 IRRITANT

Procedure

Full details are given in the *Students' Book*. The results of the experiments in part 1 are as follows:

1 The complex ion present is $Cu(H_2O)_4^{2+}(aq)$. It is pale blue.
2 The solution turns green. The ligands in the complex ion are now Cl^-.
3 The solution is pale blue. The complex ion present is $Cu(H_2O)_4^{2+}(aq)$. The equilibrium has been reversed.
4 The solution is now dark blue. The ligands are now NH_3. $Cu(NH_3)_4^{2+} > CuCl_4^{2-} > Cu(H_2O)_4^{2+}$.
5 The edta–Cu(II) complex is pale blue, slightly darker than the aquo complex.
6 It turns pale blue.

The results of the experiments in part 2 are:

1 Blue, dark blue, green, green.
2 Blue ⟶ dark blue ⟶ green ⟶ pale blue ⟶ green.

After the experiment the idea of 'stability constant' should be introduced. This should be presented as the equilibrium constant for the formation of a complex *from the aquo ion*. Some time should then be spent in relating the values of the stability constant to the outcome of Experiment 19.2a.

The section on 'Entropy considerations' should be discussed carefully with the students; examination experience has shown that this is often not clearly understood and yet it is a logical use of the entropy change ideas of Topic 13.

EXPERIMENT 19.2b

Stabilising an unusual oxidation number: chromium(II) ethanoate, $Cr_2(CH_3CO_2)_4(H_2O)_2$

HAZARDS

Wear gloves when using sodium dichromate(VI), a category 2 carcinogen. In the past, the hazards of sodium dichromate have been underestimated. The chemicals and procedures used in this experiment are very hazardous, so it is important that care is taken to reduce the risk by suitable control measures.

Each group of students will need:
Eye protection
Gloves
Ground glass joint flask, 50 cm³ and apparatus as in figure 19.1
Measuring cylinder, 10 cm³
Beaker
2 boiling tubes in rack

Access to:
Rough balance
Concentrated hydrochloric acid, 20 cm³ CORROSIVE
Zinc granulated, 1.5 g
Zinc powder, 3 g HIGHLY FLAMMABLE
Sodium dichromate(VI), 1 g VERY TOXIC (Category 2 Carcinogen)
Sodium ethanoate, saturated solution, 10 cm³

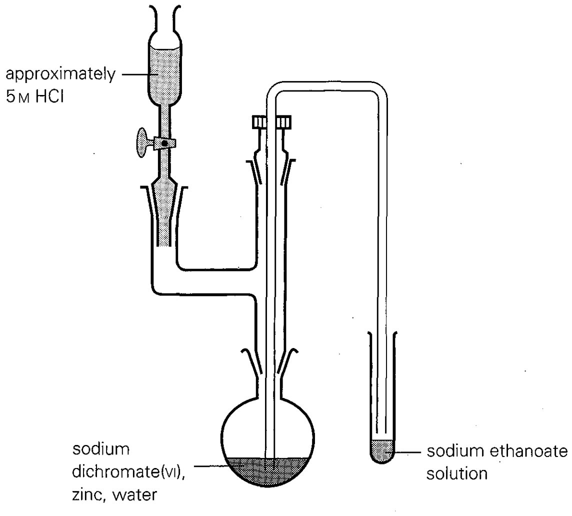


Figure 19.1 Apparatus for experiment 19.2b.

Procedure

Some tap funnels have long stems below the ground glass joints which prevent the funnels being fitted into the multiple adaptor as shown. In this case the excess length has to be cut off or some rubber tubing can be sleeved over the stem and the stem then carefully fitted in place as shown in figure 19.2.

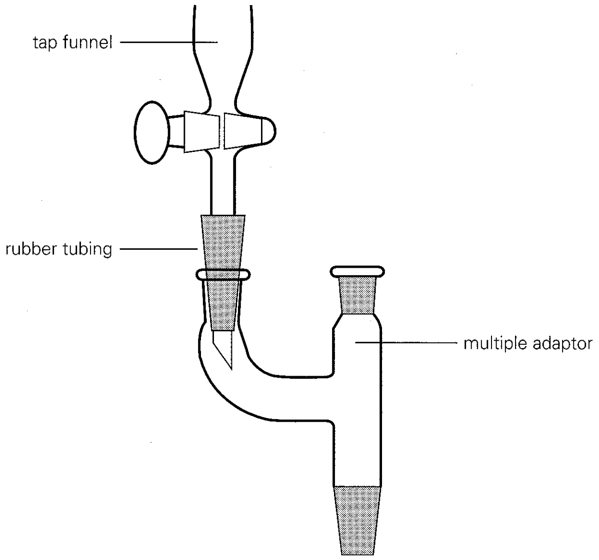


Figure 19.2 Rubber tubing in place of a glass joint fitting

Full details of the procedure are given in the *Students' Book.*

ANSWERS

In your notes, page 465

1 The relevant electrode potentials are:

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

$Cr^{3+}(aq), Cr^{2+}(aq) \mid Pt \quad E^{\ominus} = -0.41\ V$

$[Cr_2O_7^{2-}(aq) + 14H^+(aq)], [2Cr^{3+}(aq) + 7H_2O(l)] \mid Pt \quad E^{\ominus} = +1.33\ V$

Application of the anti-clockwise rule reveals that zinc, Zn, should reduce $Cr_2O_7^{2-}(aq)$ to $Cr^{3+}(aq)$ and Cr^{3+} to $Cr^{2+}(aq)$.

2 The blue colour of chromium(II) changes immediately on exposure to air to the green colour of chromium(III).

3 It takes *much* longer for any change to occur in the red colour of chromium(II) ethanoate.

EXPERIMENT 19.2c Preparation of a complex anion

Each group of students will need:
Eye protection
Bunsen burner and heatproof mat
2 test tubes and rack
Beaker, 100 cm^3, and cover
Dropping pipette
Measuring cylinder, 10 cm^3
Weighing bottles
Spatula
Iron(III) chloride-6-water, 2.7 g HARMFUL
Potassium ethanedioate (oxalate), 5.5 g HARMFUL

Access to:
Balance, to weigh to ±0.1 g
Bright light source (sunlight)

Procedure

Students calculate the amount of iron(III) chloride (2.7 g) and potassium ethanedioate (5.5 g) required to form 1/100 mole of the product. They then carry out the procedure as detailed in the *Students' Book*. Triethanedioatoferrate(III) salts are emerald green in colour and have associated water of crystallisation. The formula for the potassium salt is $K_3[Fe(C_2O_4)_3].3H_2O$.

The complex salts are sensitive to light, which reduces the Fe^{3+} to Fe^{2+} at the expense of the ethanedioate group, which is oxidised to carbon dioxide. The effect is quantitative and could be made the subject of an investigation. The Fe^{2+} ions can be detected using potassium hexacyanoferrate(III).

For the information of the teacher, triethanedioatoferrate(III) salts may give the expected reactions for Fe^{3+} ions, and precipitate calcium ethanedioate on addition of calcium chloride solution, due to a slight dissociation of the complex. Teachers should therefore not attempt to demonstrate that the components of this particular complex ion differ from the individual ions without explanation.

19.3 Transition elements as catalysts

Timing About 2 hours will be needed plus homework time for the study task

Suggested treatment

The section starts with a kinetic study providing a useful opportunity to revise aspects of Topic 11. Here we are concerned with homogeneous catalysis but there is a study task which expects a review of all aspects of the subject.

EXPERIMENT 19.3

A kinetic study of the reaction between manganate(VII) ions and ethanedioic acid

This reaction involves autocatalysis though there is no mention of this word in the *Students' Book*. The experiment can therefore be carried out in a spirit of investigation both to find out what happens and to try to explain the results.

Each group of students will need:
Eye protection
Flat-bottomed flask, 500 cm^3
Conical flask, 100 cm^3, for titration
2 measuring cylinders, 100 cm^3
Measuring cylinder, 10 cm^3
Burette, 50 cm^3, and burette stand
Pipette, 10 cm^3, and safety filler
Stopclock
0.2 M ethanedioic acid (oxalic acid), 100 cm^3 SOLID IS HARMFUL
0.2 M manganese(II) sulphate, 15 cm^3 (for about half the students)
1 M sulphuric acid, 5 cm^3 IRRITANT
0.02 M potassium manganate(VII), 50 cm^3
0.01 M sodium thiosulphate
1% starch solution, 15 cm^3
0.1 M potassium iodide, 100 cm^3

Procedure

Full details are given in the *Students' Book*. It is suggested that half the class should do experiment 1 and the other half experiment 2. Results should then be exchanged so that graphs from both experiments can be drawn by everyone. As a result of the experiments, the students should obtain graphs of the form shown in figure 19.3.

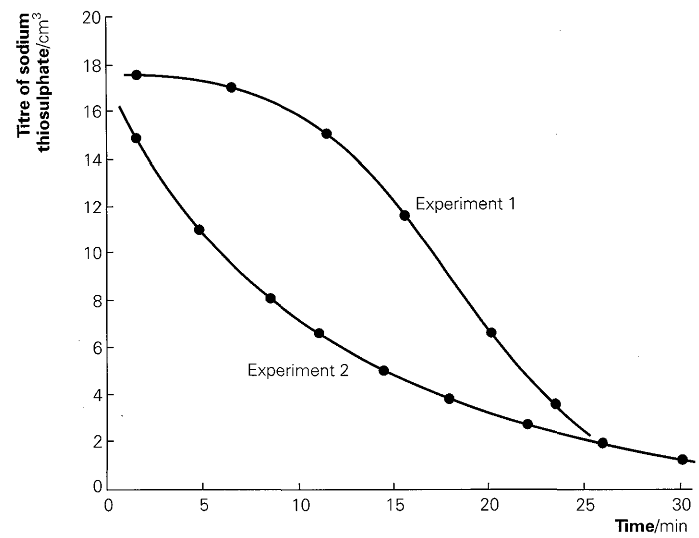


Figure 19.3 Results of kinetic study on Mn(VII)-ethanedioic acid reaction

ANSWERS

In your notes, page 467

1 A measure of the concentration of the manganate(VII) ion is given by the titre against sodium thiosulphate since the manganate(VII) ions react with iodide ions releasing iodine quantitatively, and this in turn reacts quantitatively with thiosulphate ions.

2 An appropriate form of graph is shown in figure 19.3.

3 The mixture for experiment 2 contains manganese(II) ions. Initially there are no such ions in the mixture for experiment 1, but manganese(II) ions are amongst the products of the reaction which takes place. Initially the rate of change of concentration of manganate(VII) ions is slow, but it accelerates when the manganese(II) ion concentration increases. Manganese(II) ions must be a catalyst for this reaction.

A possible way of testing this explanation would be to do the experiment several times with different concentrations of manganese(II) sulphate. The resulting graphs should show different rates of reaction.

19.4 The special properties of the transition elements

Timing About 1 hour will be needed

Suggested treatment

For this treatment the teacher will find the following items helpful:

- samples of transition elements
- samples of a selection of compounds of the transition elements in which these elements have as many different oxidation numbers as possible.

It will also be useful to have an oxidation number display board. The display board can be made of white surfaced chipboard, fitted with plastic coated clips to hold specimen tubes.

Guidelines are given in the *Students' Book*, and students are then expected to write their own account of this selection of special properties, expanding it by reference to the *Book of data* and textbooks of inorganic chemistry. The teacher can help in this process by drawing attention to sources of information.

The question of the electronic configuration of the transition elements needs extra discussion along the lines of these notes. In Topic 3 it was found that the 2,3,3 grouping of first ionisation energies was broken after calcium, and that the ten

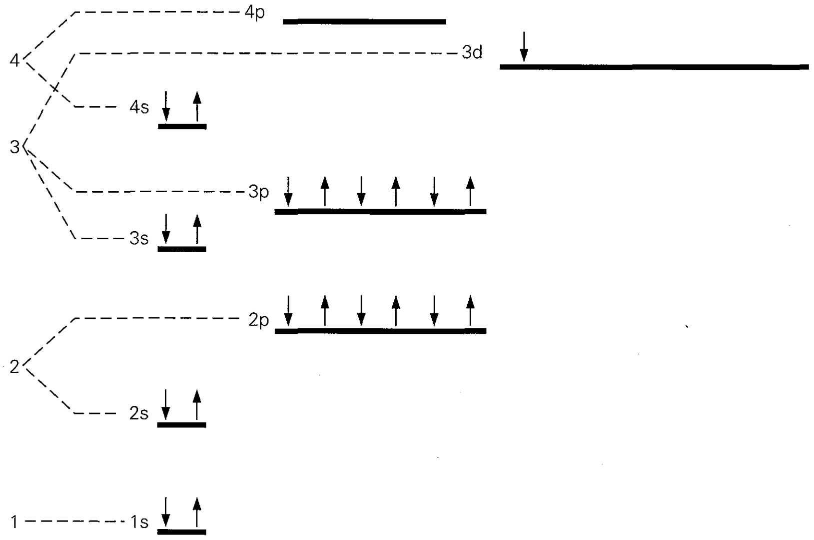


Figure 19.4 Electronic structure of scandium

d-block elements produced this break. Furthermore, a new energy level, the d level, belonging to the $n = 3$ quantum level, became occupied after calcium. This level comes just above the 4s level and below the 4p level, as indicated in figure 19.4.

As the atomic number increases from 21 to 30, each element has one more electron in the 3d level than the previous elements, until the d level is full (10 electrons); then gallium has a full 3d level and one electron in the 4p level.

The teacher may wish to point out that the electrons do not fill the 3d level in a straightforward manner, as in some cases an arrangement with only one electron in the 4s level and an extra one in the 3d level may be more stable. In fact the 3d level is below the 4s from scandium onwards but the two levels are very close in energy.

The teacher should use as much of this information as seems appropriate. All students should realise that the 3d and 4s levels are very close and that therefore the most stable arrangement of electrons may not necessarily have two electrons in the 4s level.

Answers to Topic 19 questions

Review questions

19.1

a $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ (1)
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$ (1)
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$ (1)
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$ (1)
e $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$ (1)

Total 5 marks

19.2

a **i** +7; **ii** +6; **iii** +4; **iv** +5; **v** +6; **vi** +1; **vii** +8; **viii** +6; **ix** +6; **x** +4 (10)
b **vi** mercury; **vii** osmium; **viii** rhenium; **ix** molybdenum; **x** iridium (1 mark each)

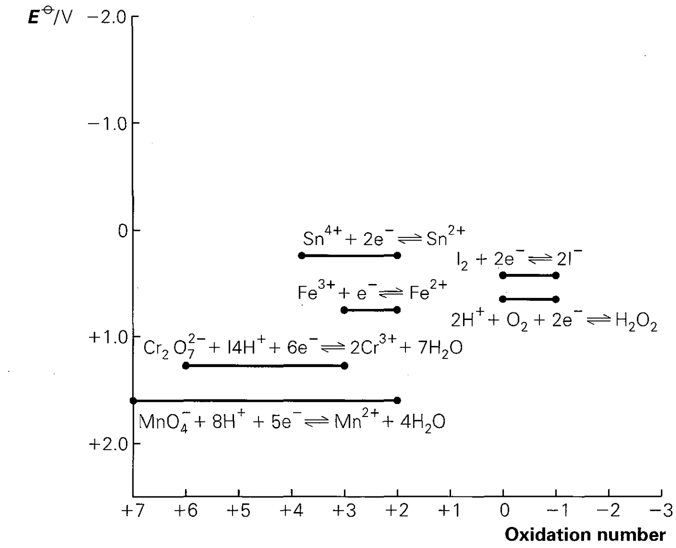
Total 15 marks

19.3

a $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^\ominus = +0.77\ V$ (2)
b $Sn^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2e^-$ $E^\ominus = +0.15\ V$ (2)
c $2I^-(aq) \rightleftharpoons I_2(aq) + 2e^-$ $E^\ominus = +0.54\ V$ (2)
d $H_2O_2(aq) \rightleftharpoons 2H^+(aq) + O_2(g) + 2e^-$ $E^\ominus = +0.68\ V$ (2)
e $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ $E^\ominus = +1.51\ V$ (2)
f $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ $E^\ominus = +1.33\ V$ (2)

Total 12 marks

19.4



Axes correct way round (1); scales (1); each system entered correctly (6)

Total 8 marks

19.5

a	Reaction should go to completion:	(1)
	$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$	(1)
b	Reaction should go to completion:	(1)
	$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$	(1)
c	Reaction should go to completion:	(1)
	$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$	(1)
d	Reaction will not occur.	(2)
e	Reaction will not occur.	(2)

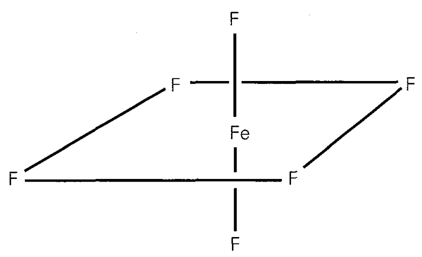
Total 10 marks

19.6

a	$E^\ominus$ for $Zn^{2+} + 2e^- \rightleftharpoons Zn$ is −0.76 V	(1)
	$E^\ominus$ for $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ is +0.77 V	(1)
	so anti-clockwise rule predicts that Zn will reduce Fe^{3+} to Fe^{2+}	(1)
b	Sulphuric acid prevents hydrolysis of Fe^{2+} ions	(1)
c	Equation: $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$	(1)
	Moles of MnO_4^- in each titration = 2×10^{-4}	
	Moles of Fe^{2+} in 10 cm³ = 1×10^{-3}	(1)
	Moles of Fe^{2+} in 100 cm³ = 1×10^{-2}	(1)
	Mass of Fe = $1 \times 10^{-2} \times 56 = 0.56$ g	(1)
	$\%Fe = \frac{0.56}{2.41} \times 100 = 23.2\%$ (3SF)	(1)

Total 9 marks

19.7

a	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$	(1)
b		(2)
c	+2	(1)
d	Electrode potential for $I_2(aq) + 2e^- \rightleftharpoons 2I^-$ is +0.54 V	
	Electrode potential for $Fe^{3+} + e^- \rightleftharpoons Fe^2$ is +0.77 V	(1)
	so anti-clockwise rule predicts reaction will occur between Fe^{3+} and I^- to give Fe^{2+} and I_2	(1)
	but will not go to completion	(1)

Total 7 marks

19.8

a From pink to green (2)

b Green to pink (1)
the acid reacts with ammonia to give ammonium ions which are not ligands (1)
so H_2O ligands would be complexed to Co^{2+}. (1)

c Not much colour change (1)
although edta ligands would displace H_2O (1)
both complexes are pink. (1)

d One edta ligand replaces six H_2O ligands (1)
so there is a positive entropy change (of the system). (1)

Total 10 marks

19.9

a **i** 13.08 (1)
ii 4.39 (1)
iii 8.01 (1)
iv 7.23 (1)

b **i** Cu^{2+} (1)
ii Co^{2+} (1)

c **i** Yes; edta would displace NH_3 (1)
lg K for the Ni^{2+}/edta complex is 18.6, compared with 8.01 for Ni^{2+}/ammonia complex. (1)
ii The two stability constants have very similar values, 7.23 and 7.3, so the two complexes would both be present in comparable concentrations at equilibrium. (2)

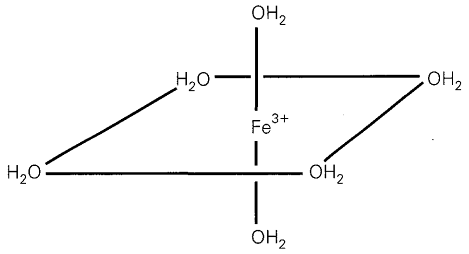
Total 10 marks

Examination questions

19.10

a **i** $Fe(s)\,|\,Fe^{2+}(aq)\;\vdots\vdots\;4OH^-(aq)[O_2(g) + 2H_2O(l)]\,|\,Pt$ (2)
(or the other way round)
ii +0.84 V (or −0.84 V) value, sign and units (2)
iii $2Fe(s) + O_2(g) + 2H_2O(l) \longrightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$ (2)
iv Any two from: temperature not 298 K; pressure of O_2 not 1 atm; NaCl may be present; solutions not 1.0 M (2)

b **i**



(1)

ii $Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Fe(H_2O)_5OH^{2+}$ (2)

Total 11 marks

19.11

a **i** $[Ar]3d^{10}$ and $[Ar]3d^9$ (1)
ii Zn always has a complete 3d shell in its compounds but Cu^{2+} compounds do not. (1)

b Tetradentate (1)

c **i** When edta is added the solution changes from green to pale blue. (1)
ii When NaCl is added the solution remains green. (1)
iii Edta ligands displace 2-hydroxybenzoate because the Cu^{2+}/edta complex has a higher stability constant. The Cu^{2+}/Cl^- has a lower stability constant so Cl^- will not displace 2-hydroxybenzoate. (1)

d **i** Cu^{2+} gains an electron to form Cu^+; some I^- lose electrons becoming I_2. (2)
ii Cu(I) compounds have a complete 3d shell but Cu(II) compounds do not. (2)

Total 10 marks

19.12

a $Co(NO_2)_6^{3-}$ (2)
(1 for correct charge)
b mono (1)
c $2H^+$ (1)
and H_2O (1)
d 3 (1)
e Effervescence/gas produced/brown fumes (1)
NO(g) shown in equation or NO_2 produced (1)
colour change (1)
different oxidation state/liquid/complex. (1)
f Octahedral (1)
g **i** Co(edta) or $Co^{2+}(edta)^{2-}$ (1)
ii When edta complex is formed the number of particles increases so ΔS_{system} is positive. (1)
When the ammonia complex forms there is no change in number of particles so ΔS_{system} does not change significantly. (1)

Total 14 marks

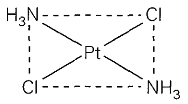
19.13

a $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$ (2)
b **i** The $KMnO_4$ pink colour persists at the end point (1)
ii Moles of $KMnO_4 = 1.18 \times 10^{-4}$ (1)
Moles of $Fe^{2+} = 5.9 \times 10^{-4}$ (1)
Mass of Fe in sample = 0.3304 g (1)
%Fe = 94.9% (1)

Total 7 marks

19.14

a **i** Dative covalent (1)
ii Lone pair of electrons on N atom (1)
iii Ligand (1)
b **i** 90° (1)
ii (1)



c **i** Nitrogen (1)
ii Chloride (1)
iii Adenine can act as a bidentate ligand, displacing both chlorides from cis-diplatin, but in trans-diplatin the Cl atoms are too far apart/on opposite sides of the Pt atom. (2)

Total 9 marks

TOPIC 20

Organic synthesis

Introduction

This synoptic topic provides an opportunity for students to integrate their studies of organic chemistry by learning how to link the individual functional groups in synthetic routes. In this mapping activity they should achieve an important synthesis of their knowledge.

Students are no longer expected to know the reactions of nitriles and this means that the Friedel–Crafts reaction is the only carbon–carbon bond forming reaction that remains in the course. However, a piece of background information emphasises the importance of being able to change the length of a carbon chain in synthetic procedures. This is of particular significance in the synthesis of new drugs where computer assisted design has become a most powerful tool.

Content

Timing		Students' Book
20.1	4 hours	pages 479–87
20.2	4 hours	pages 487–9
20.3	2 hours	pages 489–95
20.4	Homework	pages 496–9
Total about 2 weeks		

20.1 Devising a synthesis – The approach to synthesis; study task on synthetic routes; study task on mapping synthetic routes; study task on planning synthetic routes.

20.2 A two-step synthesis – formation, and then nitration, of the ester methyl benzoate (including optional microscale procedure).

20.3 The identification of organic compounds – combustion analysis of organic compounds; calculation of empirical formulae; identification of organic compounds from mass spectra, infrared spectra, nmr spectra, and chemical tests.

20.4 Background reading: drugs

Objectives

1 To map synthetic routes between functional groups and use the maps to solve significant synthetic problems.

2 To carry out a two-step synthesis and develop experimental skills.

3 To develop an understanding of how organic molecular formulae are determined by calculation from combustion data, analysis of mass spectra, nmr and infrared spectra, and chemical tests.

20.1 Devising a synthesis

Timing 4 hours plus homework

Suggested treatment

The material presented in the *Students' Book* has been kept simple so that the pattern of synthetic pathways can be identified without being obscured by detail.

Students should, however, go back over the earlier topics on organic chemistry and add the details of reagents and reaction conditions.

Students are then introduced to the idea of **intermediate** and **target molecules**. The strategy of **working backwards** is emphasised as the procedure to use when constructing synthetic routes.

ANSWERS

Study task, page 481

Students are presented with two problems and they are led through them in simple steps.

Using the strategy of working backwards, the overall answers are:

1 $CH_3CH_2CHBrCH_2Br \xleftarrow{\text{addition}} CH_3CH_2CH{=}CH_2 \xleftarrow{\text{dehydration}} CH_3CH_2CH_2CH_2OH$

2 $CH_3CH_2CH_2CO_2H \xleftarrow{\text{oxidation}} CH_3CH_2CH_2CH_2OH \xleftarrow{\text{substitution}} CH_3CH_2CH_2CH_2Br$

Study task, page 482

After an example showing the importance of the yield from each step in a multi-stage synthesis students are asked to prepare three large flow sheets. Three standard flow diagrams are provided in the *Students' Book* for students to copy onto A4 paper or even larger.

Students are not expected to learn how to synthesise different isomers. Teachers may like to add the additional information that the first enantioselective synthesis of strychnine took 20 steps with an overall yield of 3% (Overman *et al., Journal of the American Chemical Society,* **115**, page 9293, 1993).

Study task, page 484

A set of synthetic problems are provided for students to appreciate something of the range of syntheses that organic chemists are asked to solve. Students should be asked to solve a selection of these problems, matched to their ability, using the flow sheets they designed for the 'Mapping synthetic routes' study task.

The should be able to produce the following answers to the problems:

1 a $CH_3CH_2OH \xrightarrow{Al_2O_3} CH_2{=}CH_2 \xrightarrow{H_2/Ni} CH_3CH_3$

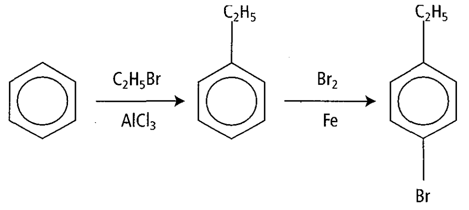
b $CH_3CH_2OH \xrightarrow{Na_2Cr_2O_7/\text{acid}} CH_3CO_2H \xrightarrow{\text{ethanol/acid}} CH_3CO_2CH_2CH_3$

c $CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br \xrightarrow{NH_3} CH_3CH_2NH_2$

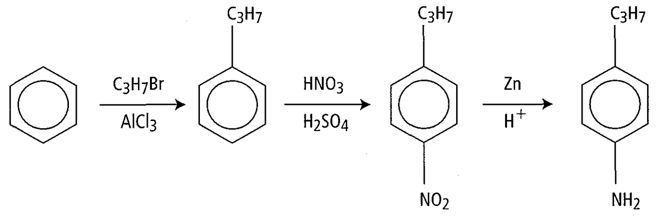
COMMENT

In this question students are told to assume that substitution occurs in the 4-position. They may also need help with the reduction of the nitro group to the amine group in 2b.

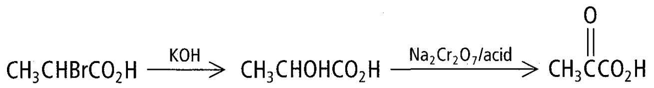
2 a



b

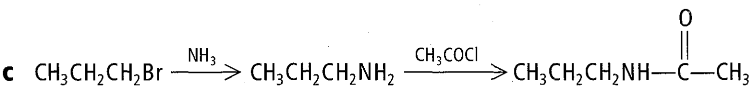


3 a



$$CH_3CHBrCO_2H \xrightarrow{KOH} CH_3CHOHCO_2H \xrightarrow{Na_2Cr_2O_7/\text{acid}} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CO_2H$$

b $CH_3CHOHCO_2H \xrightarrow{HBr} CH_3CHBrCO_2H \xrightarrow{NH_3} CH_3CHNH_2CO_2H$

c 

$CH_3CH_2CH_2Br \xrightarrow{NH_3} CH_3CH_2CH_2NH_2 \xrightarrow{CH_3COCl} CH_3CH_2CH_2NH{-}\overset{\overset{O}{\|}}{C}{-}CH_3$

d $CH_3CH_2CH_2OH \xrightarrow{Al_2O_3} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3CHBrCH_3 \xrightarrow{KOH} CH_3CH(OH)CH_3$

4 This set of questions deals with more complex molecules but the substances are all of interest because they are pheromones.

a $CH_3CH_2CH{=}C(CH_3)CH_2CH_2CH_3 \xrightarrow{HBr}$

$CH_3CH_2CHBrCH(CH_3)CH_2CH_2CH_3 \xrightarrow{KOH(aq)}$

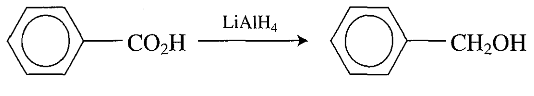
$CH_3CH_2CH(OH)CH(CH_3)CH_2CH_2CH_3$

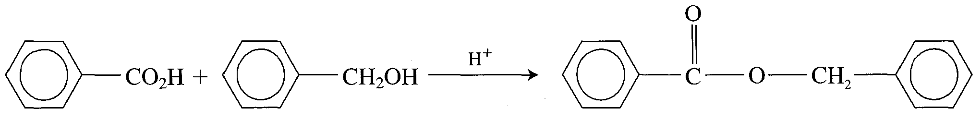
b i $CH_3CO_2H + HOCH_2CH_2CH(CH_3)CH_3$

ethanoic acid 3-methylbutan-1-ol

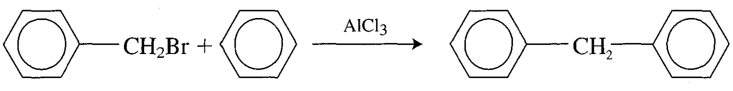
ii $CH_3CH_2CH_2CO_2H + CH_3(CH_2)_5CH_2OH$

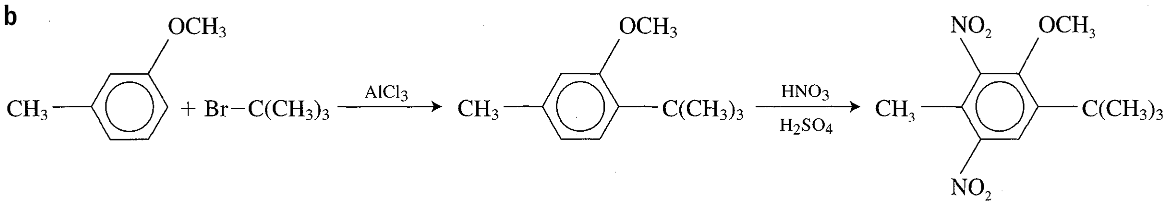
butanoic acid heptan-1-ol

iii 

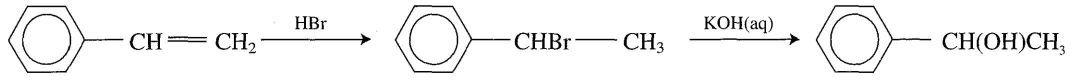


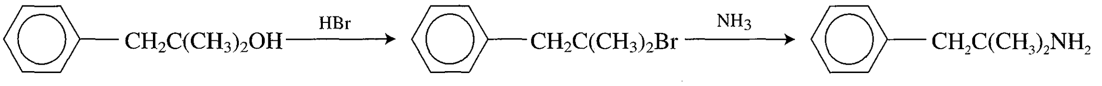
5 This set of questions deals with compounds that are used in perfumes.

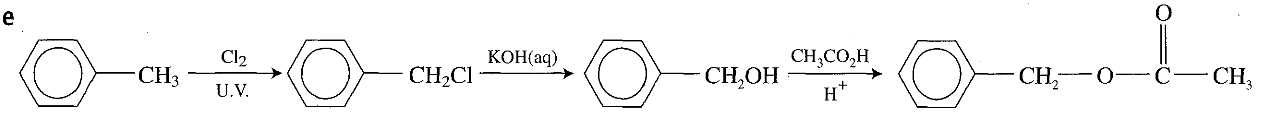
a 

b 

Nitration followed by alkylation is equally acceptable. Students are not expected to be familiar with the position of substitution on the benzene ring or oxidation problems.

c 

d 

e 

20.2 A two-step synthesis

Timing About 4 hours

Suggested treatment

These experiments provide students with an opportunity to explore a short synthetic route to review their knowledge of some important functional group chemistry and improve their experimental skills.

EXPERIMENT 20.2

The synthesis of methyl 3-nitrobenzoate in two steps

This is a microscale alternative to the experiment (see pages 297 and 305 (M8))

Step 1 Formation of the ester, methyl benzoate

Each group of students will need:
Eye protection
Apparatus for reflux and distillation, consisting of a 50 cm^3 pear-shaped flask, still head fitted with thermometer, 0–250 °C, and Liebig condenser
Separating funnel, 100 cm^3
Benzoic acid, 8 g
Hydrocarbon solvent, petroleum spirit (boiling range 120–160 °C) FLAMMABLE
Methanol, 15 cm^3 HIGHLY FLAMMABLE AND TOXIC
0.5 M sodium carbonate, 15 cm^3
Sodium sulphate, anhydrous
Concentrated sulphuric acid, 2 cm^3 CORROSIVE
Measuring cylinder, 25 cm^3
Balance, ± 0.01 g
Conical flask, 50 cm^3, for drying.

Procedure

Full instructions are given in the *Students' Book*

Step 2 The nitration of methyl benzoate

HAZARDS

The ultraviolet lamp should be arranged so that students cannot look directly at the light source.
Ethoxyethane (ether) is extremely flammable and can ignite. Its vapour is dense and can travel long distances across benches before being ignited.

Each group of students will need:
Eye protection
4 conical flasks, 100 cm^3
Measuring cylinder, 10 cm^3
Balance to weigh ± 0.01 g
Beaker, 600 cm^3, to act as a water bath
Dropping pipette
Ice bath
Apparatus for suction filtration with an extra small Büchner flask
Evaporating basin
Thermometer, 0–100 °C
Apparatus for thin layer chromatography on silica
Ultraviolet lamp, or a few crystals of iodine HARMFUL
Melting point apparatus
Ice, crushed, 40 g
Ethanol, 30 cm^3 HIGHLY FLAMMABLE
Ethoxyethane (ether, diethyl ether), 1 cm^3 EXTREMELY FLAMMABLE
Hexane, 9 cm^3 HIGHLY FLAMMABLE AND HARMFUL
Methyl benzoate, 4 cm^3
Concentrated nitric acid, 3 cm^3 CORROSIVE AND OXIDISING
Concentrated sulphuric acid, 12 cm^3 CORROSIVE

Procedure

Full instructions for this preparation are given in the *Students' Book*. Students should use whatever melting point apparatus is available.

Ether is dangerously flammable; there should be no naked flames anywhere in the laboratory when it is being used.

If an ultraviolet lamp is used it should be correctly shielded, and students must be warned not to look directly at the source of the light.

The infrared absorption spectrum of methyl 3-nitrobenzoate is given in figure 20.4.

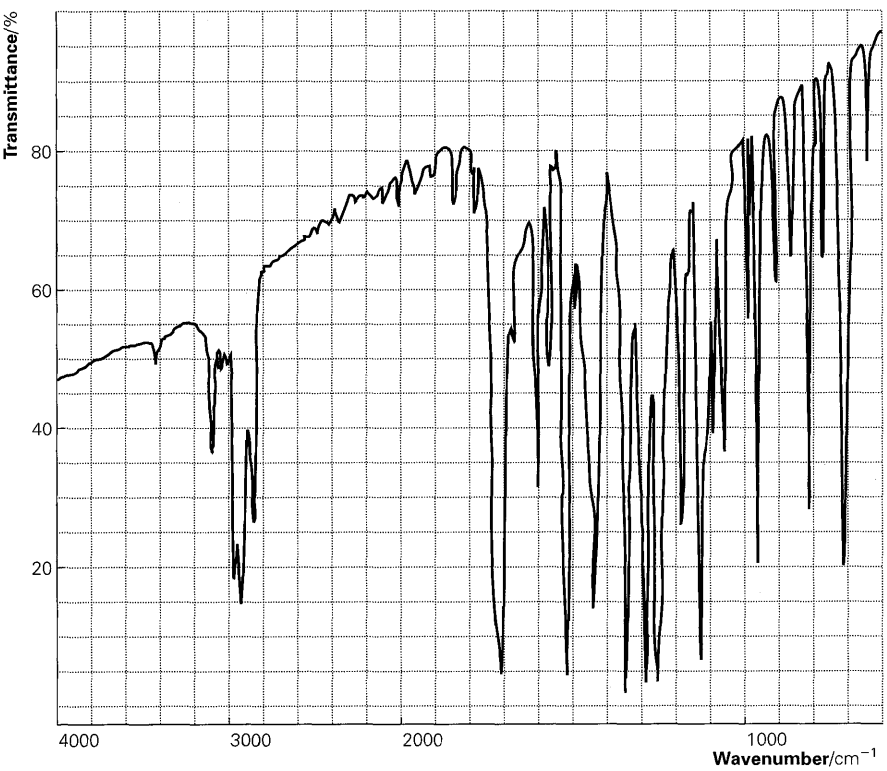


Figure 20.4 The infrared spectrum of methyl-3-nitrobenzoate

20.3 The identification of organic compounds

Timing About 2 hours

Suggested treatment

The *Students' Book* starts with a description of the combustion analysis of an organic compound to determine the empirical formula, and the conversion of a molecular formula. Two sample problems are given, one is worked out and the answer is given in the other case.

The determination of the molecular formula of an organic compound is rarely sufficient to identify the compound unambiguously. In the next experiment students learn about the use of mass spectra, nuclear magnetic resonance spectra and infrared spectra together with chemical tests as an approach to the full determination of structural formulae, and hence identity of the compound in question.

Before beginning the next experiment, students should read or re-read sections 21.1, 21.2 and 21.3 and carry out the study tasks in these sections.

EXPERIMENT 20.3 The identification of organic compounds

Each group of students will need:
Eye protection
Combustion spoon
Test tubes and rack

Access to:
0.05 M bromine water HARMFUL, IRRITANT
1 M sodium carbonate solution
0.1 M sodium dichromate(VI) solution IRRITANT, TOXIC
1 M sulphuric acid IRRITANT
Unknown A (benzoic acid) HARMFUL
Unknown B (propan-2-ol) HIGHLY FLAMMABLE

Unknown C (*N*-phenylethanamide, acetanilide) HIGHLY FLAMMABLE, HARMFUL
Melting point apparatus
Full-range Indicator
Book of data
Calculator

Procedure

Full details of the procedure are given in the *Students' Book.*

The three investigations have been kept quite simple as they are intended only as elementary exercises and not as an introduction to a systematic scheme for the identification of organic functional groups. The investigations can be shortened by providing students with the results to some parts of the investigations, for example, the molecular formulae or the melting points.

Unknown A

1 Empirical formula: $C_7H_6O_2$
2 Mass spectrum and infrared spectrum – see page 492 in the *Students' Book*
3 nmr spectra: chemical shift at 8 ppm confirms carboxyl group and at 7.6 ppm arene ring protons.
4 Melting point 121 °C
5 Unknown is benzoic acid.

m/e	Groups commonly associated with the mass	Possible inference
39	$C_3H_3^+$	
50	$C_4H_2^+$	aromatic compound
51	$C_4H_3^+$	C_6H_5—
77	$C_6H_5^+$	C_6H_5—
78	$C_6H_6^+$	C_6H_5—
105	$C_6H_5CO^+$	C_6H_5CO—
105	$C_8H_9^+$	
122	$C_6H_5CO_2H^+$	molecular ion peak

Wavenumber	Possible inference
3300–2500	carboxylic acid, hydrogen bonded
1725	carboxylic acid
700	arene

Unknown B

1 Empirical formula C_3H_8O
2 Mass spectrum and infrared spectrum – see pages 493–4 in *Students' Book.*
3 nmr spectrum chemical shifts at 1.2, 1.6 and 4.00 ppm are consistent with CH_3—, CH— and —OH in propan-2-ol
4 Unknown is propan-2-ol.

m/e	Groups commonly associated with the mass	Possible inference
27	$C_2H_3^+$	
29	CHO^+, $C_2H_5^+$	
39	$C_3H_3^+$	
41	$C_3H_5^+$	
43	CH_3CO^+	CH_3CO—
43	$C_3H_7^+$	C_3H_7—
45	$CH_2{=}^+OCH_3$ $CH_3CH{=}^+OH$	some ethers and alcohols
60	$C_3H_7OH^+$	molecular ion peak

Wavenumber	Possible inference
3300	alcohol, hydrogen bonded
2960	alkane

Unknown C

1 Empirical formula C_8H_9NO

2 Mass spectrum and infrared spectrum – see page 495 in the *Students' Book.*

3 Unknown is *N*-phenylethanamide (acetanilide), melting point 114 °C.

m/e	Groups commonly associated with the mass	Possible inference
39	$C_3H_3^+$	
43	CH_3CO^+	CH_3CO^-
66	$C_5H_6^+$	loss of HCN
93	$C_6H_5NH_2^+$	phenylamine derivative
135	$C_8H_9NO^+$	molecular ion peak

Wavenumber	Possible inference
3300	N—H amide
2960	C—H alkane
1640	Carbonyl of an amide
770, 730	C—H arene

20.4 Background reading: drugs

ANSWERS TO BACKGROUND READING QUESTIONS

Questions, page 496

1 All three molecules have an identical ring structure of five fused rings with a methyl group on a nitrogen.
Where morphine has two attached —OH groups, cocaine has only one, the other replaced by an O—CH_3 group. In heroin both —OH groups are reacted to produce ethanoate esters.

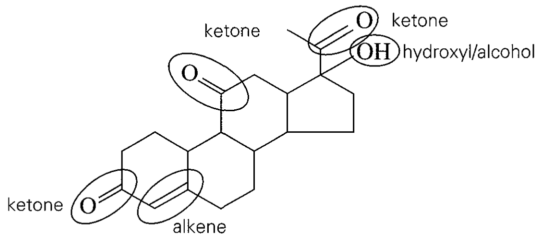
2 All the local anaesthetics have a substituted benzene ring.
Cocaine, novocaine, xylocaine and 2-chloronovocaine all have an intermediate chain or ring connecting the benzene ring to a tertiary amine.
All five compounds contain the ester or the amide functional group.

3 Answers to this question should be limited to about two sides of A4.
Look for points **for** and **against** the legal sale of alcohol and nicotine products.
Look also for points **for** and **against** the legislation of cannabis, cocaine and heroin.
It should be possible to come up with at least one scientific and one social point in each category.
Look for ten sensible, well argued points in total.

Answers to Topic 20 questions

Review questions

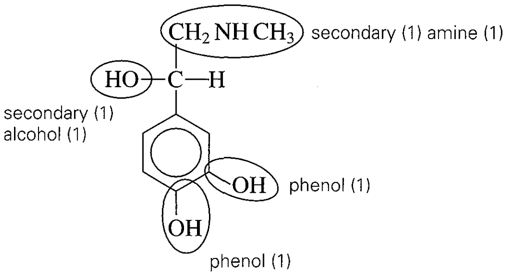
20.1 **a** (5)



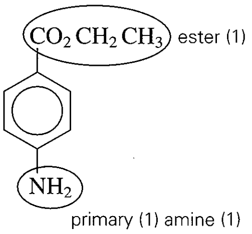
b $C_{19}H_{24}O_4$ (2)

Total 7 marks

20.2 **a** (6)



b (3)



Total 9 marks

20.3 **a** 1 mole phenol gives 1 mole aspirin (in theory)
i.e. 94 g gives 180 g

50 g gives $\frac{180}{94} \times 50$ g (1)

so mass obtained $= \frac{95}{100} \times \frac{90}{100} \times \frac{180}{94} \times 50$ (1)

$= 81.9$ g (3SF) (1)

b Overall yield $= 95 \times \frac{90}{100} = 85.5\%$ (2)

c 81.9 g from 50 g phenol

$\therefore \frac{50 \times 1000}{81.9}$ from 1000 kg

$= 611$ kg (3SF) (2)

Total 7 marks

20.4 **a** Mass of carbon in 0.200 g of **Q** $= \frac{11}{44} \times 0.455 = 0.124$ g

Mass of hydrogen in 0.200 g of **Q** $= \frac{1}{9} \times 0.186 = 0.021$ g

Mass of oxygen in 0.200 g of **Q** $= 0.200 - (0.124 + 0.021) = 0.055$ g (1)

Moles of C atoms $= \frac{0.124}{12} = 0.0103$

Moles of H atoms $= 0.021$

Moles of O atoms $= \frac{0.055}{16} = 0.0034$ (1)

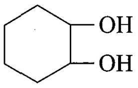
Ratio C : H : O $= \frac{0.0103}{0.0034} : \frac{0.021}{0.0034} : \frac{0.0034}{0.0034}$

$= 3 : 6 : 1$ (1)

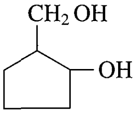
Empirical formula $= C_3H_6O$ (1)

b From mass spectrum, molar mass = 116
$C_3H_6O = 58$
$\therefore$ Molecular formula $= C_6H_{12}O_2$ (2)

c Many isomers are possible so this is not a complete list
The Aldrich catalogue lists 22 compounds!
e.g.



(positional isomers as well)



(more positional isomers)

$CH_2{=}CHCH_2CH_2CHOHCH_2OH$ (more structural isomers)

$CH_3(CH_2)_4CO_2H$
$CH_3CO_2(CH_2)_3CH_3$

Any 2 isomers of $C_6H_{12}O_2$ (2)

d Infrared spectroscopy (1)
would differentiate isomers having different bonds/functional groups (1)
which absorb it at different frequencies/wavenumbers. (1)
or
nmr (1)
would differentiate isomers having H atoms in different molecular environments (1)
producing peaks at different chemical shifts. (1)
Suitability of method is dependent on isomers suggested.

Total 11 marks

20.5 **a** **i** Moles of C atoms $= \frac{70.5}{12} = 5.88$

Moles of H atoms $= 5.9$

Moles of O atoms $= \frac{23.6}{16} = 1.48$

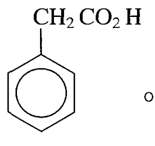
Ratio C : H : O $= \frac{5.88}{1.48} : \frac{5.9}{1.48} : \frac{1.48}{1.48}$

Empirical formula $= C_4H_4O$ (2)

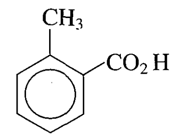
ii From mass spectra, molar masses are 136
$C_4H_4O = 68$
so molecular formula is $C_8H_8O_2$ (2)

b 136 $C_8H_8O_2^+$ (1)
105 $C_7H_5O^+$ (1)
91 $C_7H_7^+$ (1)
77 $C_6H_5^+$ (1)

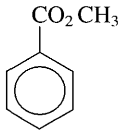
c A =



or



B =



Benzene ring suggested (3)

d pH test; hydrolysis by acid or alkali; acylation of A
(any two sensible suggestions) (2)

e A: phenylethanoic acid 5 peaks: 4 at around 7–8 ppm from TMS; 1 at 10–12 ppm.
B: methylbenzoate 5 peaks. (4)

Total 17 marks

20.6

a Infrared spectroscopy, **or** nmr (1)
Appropriate chemical test, e.g. Brady's reagent (1)

b Reducing agent e.g. $LiAlH_4$ (1)

c Reduction with hydrogen (1)
using Ni catalyst (1)

d **i** Both can be esterified under appropriate conditions. (1)
ii Appropriate chemical difference, e.g. phenolic —OH shows acidity but alcoholic —OH does not. (2)

Total 8 marks

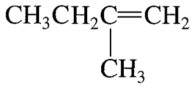
20.7

a $$\text{Moles of C atoms} = \frac{85.7}{12} = 7.14$$

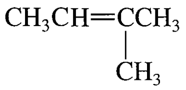
$$\text{Moles of H atoms} = \frac{14.3}{1} = 14.3$$

∴ empirical formula = CH_2 (1)
Molar mass = 70; CH_2 = 14
∴ Molecular formula = C_5H_{10} (1)

b Peaks at 3085 cm^{-1} and 1650 cm^{-1} suggest alkene
Possible isomers include
$CH_3CH_2CH_2CH{=}CH_2$
$CH_3CH_2CH{=}CHCH_3$



$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

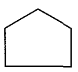


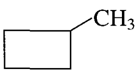
$CH_3CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_3$

$CH_3CH(CH_3)CH{=}CH_2$

and also *cis-* and *trans-*isomers
1 mark for each correct isomer (5)

c Would have to be a cycloalkane: (1)





d Sensible suggestions would include

- addition of $H_2/Br_2/H_2O$
- oxidation by MnO_4^-/H^+
- polymerisation

Any 3 with equations/conditions (6)

e Differences in physical properties (e.g. boiling point) expected but not chemical differences (1)

Total 15 marks

Examination questions

20.8 **a** **i** Mass of C in 2.20 g $= \frac{12}{44} \times 2.20 = 1.10\,\text{g}$

Mass of H $= \frac{2}{18} \times 1.10 = 0.122\,\text{g}$

Mass of O $= 2.20 - (1.10 + 0.122) = 0.98\,\text{g}$ (1)

Moles of C atoms $= \frac{1.10}{12} = 0.0916$

Moles of H atoms $= 0.122$

Moles of O atoms $= \frac{0.98}{16} = 0.0612$

$$\text{Mole ratio C : H : O} = \frac{0.0916}{0.0612} : \frac{0.122}{0.0612} : \frac{0.0612}{0.0612}$$

$$= 1.5 : 2 : 1$$ (1)

Empirical formula = $C_3H_4O_2$
Molar mass (from mass spectrum) = 72
$C_3H_4O_2 = 72$
∴ Molecular formula = $C_3H_4O_2$ (1)

ii Compound will contain $—CO_2H$ (reaction with Na_2CO_3) and $C{=}C$ (reaction with Br_2)
so structural formula is $CH_2{=}CHCO_2H$ (1)

iii $2CH_2{=}CHCO_2H + Na_2CO_3 \longrightarrow$
$2CH_2{=}CHCO_2^-Na^+ + CO_2 + H_2O$ (1)

$CH_2{=}CHCO_2H + Br_2 \longrightarrow CH_2BrCHBrCO_2H$ (1)

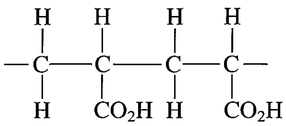
iv 27 $C_2H_3^+$
44 CO_2^+
45 CO_2H^+ (all three) (1)
55 loss of OH
71 loss of H proton (both) (1)

b **i** With methanol, forms ester $CH_2{=}CHCO_2CH_3$; acid catalyst + heat needed. (1)

ii With HCl, addition to $C{=}C$ giving $CH_3CHClCO_2H$ (1)

iii Reduction by H_2 will give $CH_3CH_2CO_2H$ (Ni catalyst needed). (1)
Reduction by $LiAlH_4$ would give $CH_2{=}CHCH_2OH$. (1)
(no specific conditions expected)

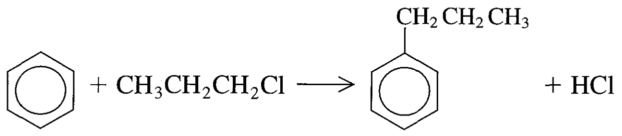
c Addition polymerisation (1)



$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ —C— & C— & C— & C— \\ | & | & | & | \\ H & CO_2H & H & CO_2H \end{array}$$ (1)

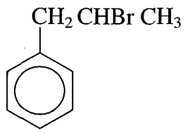
Total 14 marks

20.9 **a** **i** 1-chloropropane + anhydrous $AlCl_3$ (1)



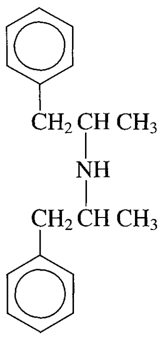
(1)

ii (1)

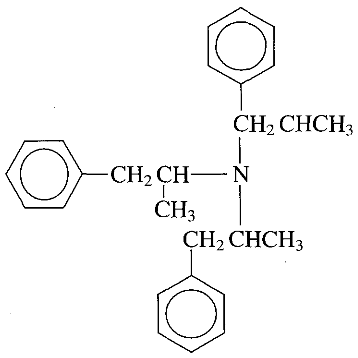


Heat under pressure with ammonia in ethanol (1)

b



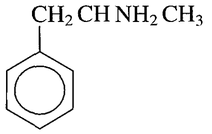
(1)



(1)

Produced by replacement of 2nd and 3rd H atoms in ammonia (1)
by the ammonia acting as a nucleophile (can be shown using formula). (1)

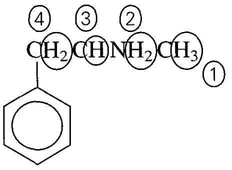
c



Infrared spectroscopy would produce peaks due to:

- C—H stretching 3030 and 2900 cm^{-1}
- C—H bending 750 and 700 cm^{-1}
- N—H stretching 3500–3300 cm^{-1} (2)

nmr would produce a fairly complex spectrum.
Predicted peaks



plus 3 more from benzene ring H atoms (2)

Total 12 marks

TOPIC 21

Instrumental methods

Introduction

This topic is designed to support the teaching of the other topics in this course and to serve as a reference section rather than a topic to be taught as a separate entity. Instrumental methods are described here rather than in the sections where the uses of the various techniques are first met. Most attention is given to mass spectrometry and infrared spectrometry as students will be interpreting spectra, mainly in the organic topics.

Content

Timing

No allocation is suggested for this topic as the time required has been allocated to the sections of the other topics in which the instruments are first met. The linked study tasks in 20.3 will require 1 to 2 hours.

21.1 The mass spectrometer – calculation of molar masses from mass spectra; interpretation of mass spectra of organic compounds.

21.2 Infrared spectrometry – interpretation of infrared spectra (see *Book of data*, table 3.3)

21.3 Nuclear magnetic resonance spectroscopy – interpretation of nmr spectra (see the *Book of data*, table 3.4)

21.4 X-ray diffraction – electron density maps.

21.5 Ultraviolet and visible spectroscopy – uses in analytical laboratories.

21.6 Using a pH meter – the glass electrode.

Objectives

1. To provide information about instruments such as the mass spectrometer, which produce data that students will be expected to interpret.
2. To provide examples of the use of the various techniques considered to assist students in their understanding of the data they are required to interpret.
3. To provide information about the pH meter which students are likely to meet during their practical work.

21.1 The mass spectrometer

The *Students' Book* shows a simplified diagram (figure 21.1b) of a mass spectrometer, a description of its principles, a simplified mass spectrometer trace, and a worked example of the calculation of the molar mass of naturally-occurring lead. There are also two study tasks (page 509), the first of which could be set during section 3.1.

ANSWERS

Study tasks, pages 509–10

1 Students are asked to work out the molar masses of naturally-occurring lithium and iron. Table 2.1 in the *Book of data* gives the mass number of nuclides and percentage abundances (in brackets).
Lithium: 6.0 (7.42); 7.0 (92.58)
Iron: 54.0 (5.84); 56.0 (91.68); 57.0 (2.17); 58.0 (0.31)
giving molar masses Li = 0.4352 + 6.4806 = 6.92 g mol^{-1} (to 3 significant figures)
Fe = 3.1536 + 51.3408 + 1.2369 + 0.1798 = 55.9 g mol^{-1} (to 3 significant figures)
The conversion factor from atomic mass units (amu) to molar mass units is ×1.

COMMENT

amu are defined in the *Book of data*, but students are not expected to recall the meanings of the different units in this calculation.

2 The comparison of the molar masses of I, Te, Ar and K relative to their position in the Periodic Table also needs data from table 2.1 in the *Book of data*.
Table 2.1 uses mass numbers, rather than the exact mass of the nuclides used in table 2.2. Consequently the answers obtained in g mol^{-1}: Te 127.7; I 127; Ar 39.99; K 39.18; do not match exactly the molar masses given in table 2.1. It will be seen that the sequence of the elements in the Periodic Table follows their atomic numbers and only coincidentally their molar masses. The relatively high abundances of the relatively heavy isotopes $^{128}_{52}\text{Te}$, $^{130}_{52}\text{Te}$, and $^{40}_{14}\text{Ar}$, are responsible for the breakdown of the molar mass pattern.

The second study task could be done before Experiment 20.3. It asks the students to interpret the mass spectrum of an unknown compound **V**, C_8H_8O, that is actually phenylethanone (acetophenone). Isomers with the formula C_8H_8O include phenylethanal, $C_6H_5CH_2CHO$, and methylbenzaldehyde, $CH_3C_6H_4CHO$.
The molecule breaks up giving fragments:

Molar mass/g mol^{-1}	**Possible fragment**	**Atoms lost**
105	$C_6H_5CO^+$	loss of CH_3
77	$C_6H_5^+$	further loss of CO

Phenylethanal is unlikely to produce a fragment with molar mass of 105 g mol^{-1}.
Methylbenzaldehyde is unlikely to produce a fragment with molar mass of 77 g mol^{-1}.
Phenylethanone, having the structure $C_6H_5COCH_3$, could produce fragments with molar masses of both 105 and 77 g mol^{-1}.
Students are then asked to compare their deductions with those that can be made from the infrared spectrum of compound **V** in the next study task.

21.2 Infrared spectrometry

Students should be aware that absorptions are often referred to as ‘peaks’ although they are actually troughs in the spectra and that the positions are referred to by their wavenumber, the reciprocal of the wavelength.

The study task (page 512) ask students to identify the bonds responsible for the peaks in the spectrum of an unknown compound **V**, C_8H_8O, that is actually phenylethanone (acetophenone).

The major peaks which can be identified using table 3.3 in the *Book of data* are:

Wavenumber range/cm^{-1}	**Group**
3030	arene
1700	ketone, aryl, alkyl
1600 and 1450	arene
750, 700	arene, 5 adjacent H

Students are asked to compare their deductions with those that can be made using the mass spectrum in the preceding study task.

21.3 Nuclear magnetic resonance spectroscopy

This important method is described briefly and there are examples in Topic 20 in the *Students' Book.*

21.4 X-ray diffraction

X-ray diffraction is also described briefly. It is the source of valuable structural information; in particular, electron density maps provide compelling visual support for our ideas about ionic, covalent and metallic structures as well as the symmetrical nature of the benzene ring, see figures 7.1 and 7.2 in Topic 7 and figure 12.2 in Topic 12 in the *Students' Book.* It should be stressed that X-ray diffraction patterns and electrons density maps are two different things, and that one is deduced from the other.

As well as the achievements of Professor Dorothy Hodgkin in X-ray crystallography, the work of Rosalind Franklin on DNA deserves to be mentioned. Rosalind Franklin died in 1958 aged 37 before any Nobel prizes were awarded for the elucidation of the structure of DNA. (Crick and Watson were awarded a Nobel prize in 1962.)

21.5 Ultraviolet and visible spectroscopy

These techniques are particularly valuable in industry for routine testing of the concentration of solutions and the purity of products, but they do not generate useful problem-solving activities for the course and are not mentioned elsewhere in the *Students' Book.*

21.6 Using a pH meter

The pH meter is probably the most versatile and therefore the most useful instrument available at a reasonable cost for use in sixth-form chemistry courses. The 'dipstick' pH meter is particularly useful being robust and suitable for field work, although meters that can be interfaced to a computer are valuable for the laboratory demonstrations.

A wide range of challenging observations and interesting investigations can be studied quantitatively by the use of a pH meter in ways that are not really possible with Full-range Indicator. Simple examples include strong and weak acids and bases, hydrolysis of salts, change of pH during reaction and the pH of biological materials. One example is the pH of the cell sap of poppies and cornflowers – the same compound is red in poppies but blue in cornflowers due to a difference in pH.

pH electrodes need to be stored with care. Electrodes usually need to be stored in a buffer solution rather than in water; the manufacturer's advice should be noted and the functioning of the electrodes checked at least once a term. See also CLEAPSS, 'pH measurement' (R35), 1993.

Appendix 1

Microscale chemistry

Introduction

Microscale technology is widely used in industry and has been described in science education for some years. This section begins with an introduction and then includes photocopiable guides to microscale techniques followed by alternatives to a range of the experiments in the *Students' Book.*

This section draws heavily on the work of others. The Royal Society of Chemistry has distributed to all schools and colleges in the UK a book of microscale chemistry experiments compiled by John Skinner (RSC, 1997). Teachers who decide to make use of microscale techniques will find that the RSC book is a rich source of tried and tested ideas which can be adapted for this course. The guidance on techniques is also very helpful. Stephen Breuer of Lancaster University has written a comprehensive guide to microscale organic chemistry (Lancaster University, 1996). The CLEAPSS School Science Service has also published a guide to microscale organic chemistry written by Bob Worley (CLEAPSS, L215, 1996).

Some teachers of Nuffield Chemistry have already embraced microscale chemistry with enthusiasm and we are grateful to Malcolm Evetts for his advice. There is a section on the Nuffield Advanced Chemistry website to supplement the information in this book www.nuffieldfoundation.org/curriculum.

The examinations will be set in such a way that those who use microscale techniques are not disadvantaged: descriptions of microscale procedures will be accepted where appropriate. However basic laboratory techniques must also be known.

The main benefits of microscale chemistry are:

- cost-effective practical sessions which make better use of time
- enhanced value of practicals
- use of up-to-date laboratory technology
- reduced environmental hazard
- greatly reduced chemical costs
- reduced waste disposal problems.

Microscale chemistry in schools and colleges can be carried out with small items of plastic apparatus, much of which is familiar, including laminated worksheets, pipettes, Petri dishes and well plates.

HAZARD

Microscale chemistry sometimes presents different health and safety hazards from conventional scale activities. For example, microscale chemistry sometimes requires more concentrated solutions and often dispenses these using teat pipettes, with the risk of dangerously squirting concentrated liquids. On the other hand, microscale chemistry may mean that the scale of working is so small that reactions normally carried out in a fume cupboard can be carried out in the open laboratory. The different hazards of microscale and conventional scale chemistry must be weighed up.

It is the duty of the teacher to consult his/her employer's risk assessments before any hazardous procedure is undertaken, or any hazardous chemicals are used or made. Most education employers have adopted various nationally available publications (such as CLEAPSS *Hazcards*, SSERC *Hazardous Chemicals. A Manual for Science Education*) as model (general) risk assessments. Teachers should therefore consult these and consider whether any adaptation is necessary to deal with their particular circumstances.

Sources of equipment and/or publications

Stephen Breuer, School of Physics and Chemistry, Lancaster University, Lancaster LA1 4YB www.lancaster.ac.uk (for *Microscale practical organic chemistry*)

Paul Priest, Academy Equipment, PO Box 53, Cheadle, Cheshire SK8 4GZ

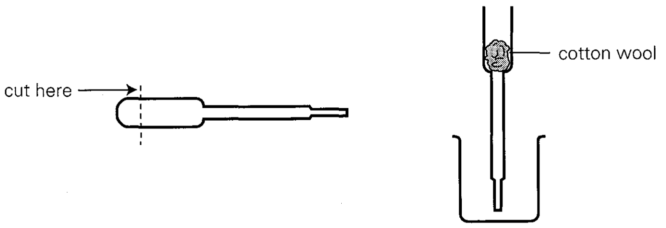
Royal Society of Chemistry Customer Services, Turpin Distribution Services Ltd, Blackhorse Road, Letchworth, Herts SG6 1HN (for their *Microscale chemistry* book)

CLEAPSS School Science Service *at* Brunel University, Uxbridge, UB8 3PH
www.cleapss.org.uk
(available to members, which at the time of writing include all LEAs in England and Wales – and hence their schools – and the majority of independent schools, incorporated colleges and teacher training establishments)

Microscale procedures

Microscale filtration

This is a simple but effective method for constructing a filter funnel from a plastic pipette.



Microscale filtration

The efficiency of the filter funnel depends mainly on how compact the cotton wool is in the funnel. For coarse particles the cotton wool need not be packed very tightly. However, if very fine particles are to be separated from the liquid, tight packaging is essential for effective separation.

Note that in microscale filtration, transfer of liquids is always by dropping pipette never by pouring.

Extraction

At the microscale level, a separating funnel is not used.

Instead, the reaction mixture is transferred by a plastic pipette into a specimen tube and the extracting solvent is added. The tube is capped and agitated gently to mix the two phases. The cap is loosened to release any pressure increase from the solvent and time is allowed to let the phases separate.

If the lower phase is the one required for further purification, a plastic pipette is inserted vertically into the specimen tube which is tilted slightly. The teat is squeezed gently to remove any liquid in the pipette. The lower phase is slowly drawn up and transferred to another specimen tube. The process may be repeated to obtain further extractions.

If the upper phase is required (as in an ethoxyethane extraction), both layers should be withdrawn into the pipette, trying not to suck in any air as this causes some mixing. The lower phase is returned into the specimen tube and the upper phase that is wanted, is put into a clean specimen tube.

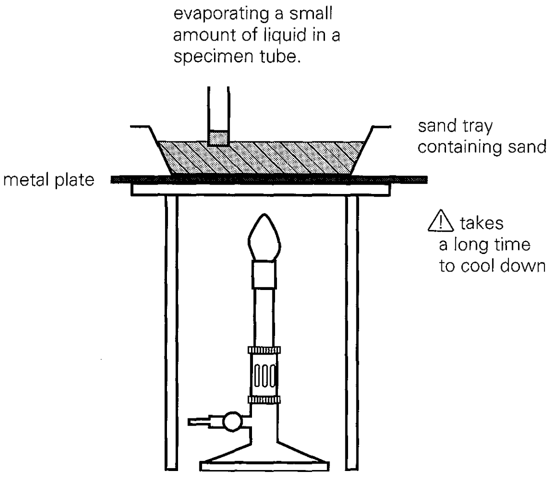
Heating

In microscale work, vessels are heated using a sand bath.

For class work, a Bunsen burner or, better still, a semi-micro burner or electric hotplate, is used for heating. A tripod supports a metal plate which, as well as providing a support for the sand bath, also protects the hands from the heat when manipulating a clamp holding the apparatus.

It takes some time for the sand to reach working temperature so the burner should be lit as soon as practical work starts. The sand also takes time to cool and this is a potential hazard.

The depth of sand should be about 10–15 mm. The temperature gradient through the sand is large. Specimen tubes can be placed on the top of the sand to evaporate solvents. To obtain the higher temperatures for refluxing or distillation, the reaction vessel should be buried deeper in the sand. A thermometer can be supported to the same depth in the sand as the apparatus being heated; it should read about 20 °C more than the temperature required in the specimen tube or reaction vessel.



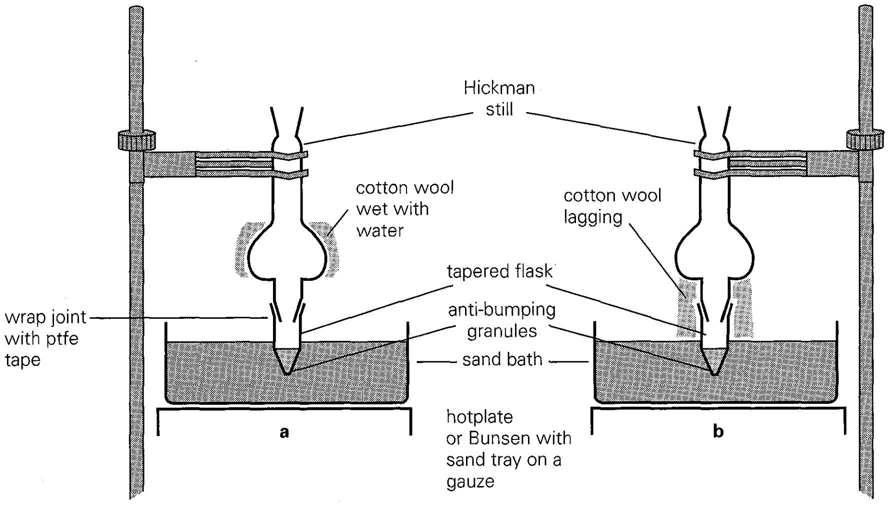
Microscale heating

This arrangement is safe for heating highly flammable liquids because the amounts used are very small. If the vessel breaks, the liquid spreads out over the sand and evaporates.

An alternative to the sand bath is a small brass or copper tube just a little larger in diameter than the reaction vessel and packed with a little aluminium foil at the base to ensure conduction of heat. Some schools and colleges may still have the aluminium heating blocks that were used in the days of semi-micro qualitative analysis.

Distillation

The Hickman still is essential for microscale preparations. It fits onto a reaction vessel via the ground glass connector. Teachers experienced in this technique strongly recommend that students bind the male socket of the still with ptfe tape to ensure a close fit and to avoid the joint jamming. It has been found useful to place a small plug of cotton wool into the male socket of the still to stop splashes of boiling liquid entering it. As the vapour condenses on the side of the still, the liquid runs back into the depression and can be removed by a pipette to a specimen tube. For more efficient cooling, a ‘scarf’ of cotton wool soaked in water can be wrapped around the upper part of the still. An example of the arrangement is shown in the following diagram. Anti-bumping granules are essential.



Microscale distillation

Typical procedure

With the sand bath at 180–200 °C, weigh 0.5 g of the liquid to be distilled into a tapered flask and add an anti-bumping granule. Fit the Hickman still on the top and place the flask into the sand bath, clamping it loosely to ensure that it does not topple over. Lag the region between the top of the sand and the collector part of the still. Allow the distillation to proceed until there is no more liquid left in the tapered flask (about 10–15 minutes) and then lift the assembly out of the sand bath. Pipette the distillate out of the still into a weighed specimen tube, weigh it and determine its boiling point. Compare the appearance of the distillate with the original liquid and calculate the percentage recovery of the liquid on distillation.

Refluxing

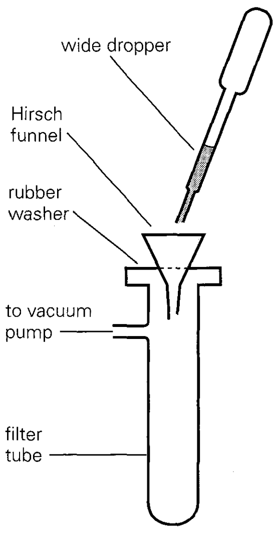
Although it is possible to use an expensive microscale reflux condenser attached to the reaction vessel, refluxing can be carried out in a test tube, supported vertically on the sand bath by a clamp. Wet cotton wool is placed around the upper part of the test tube just above the clamp to help with the condensation. Once refluxing starts, the test tube can be gradually lifted from the hot sand until the refluxing is steady. Anti-bumping granules are essential. Trials using liquids such as methanol have showed that, although not as efficient as a reflux condenser, very little material is in fact lost.

Recrystallisation

To recrystallise a solid sample place 50–100 mg of the solid in a 4 cm^3 specimen tube and add 0.5–2 cm^3 of the chosen solvent. Add an anti-bumping granule and place the tube into a hot sand bath to boil the solvent gently. Once the solid has dissolved to produce a clear solution, set the tube aside to cool and crystallise.

When crystallisation is complete, separate the solid from the solvent by vacuum filtration using a small Hirsch funnel. Transfer the crystals and solution to the funnel using a wide dropper. After filtering use the filtrate to help to transfer any crystals remaining in the specimen tube to the funnel.

Wash the solid on the filter paper with just a drop or two of cold solvent and then suck dry.



Microscale recrystallisation

Teachers' guide to the microscale photocopiable sheets

The numbering of the experiments and parts of experiments corresponds to the numbers for the equivalent activities in the *Students' Book*.

• Plastic pipettes	Sheet M1
• Experiment 1.1b Further precipitation reactions	Sheet M2
• Experiment 2.2b Preparations using propan-1-ol	Sheet M3
• Experiment 2.3 Cyclohexene from cyclohexanol and phosphoric acid	Sheet M4
• Experiment 12.4 The reactions of the phenolic functional group	Sheet M5
• Experiment 12.5 The microscale synthesis of aspirin	Sheet M6
• Experiment 14.2 Measurement of an equilibrium constant K_c	Sheet M7
• Experiment 20.2 Nitration of methyl benzoate	Sheet M8

Plastic pipettes

Teachers' notes for Sheet M1

It enhances efficiency and reduces risks if students get in the habit of setting up a workstation and working methodically. A workstation is based on a set of about seven labelled screw-capped specimen tubes supported in a drilled block. Each specimen tube contains one of the reagents needed and has its own dropping pipette.

Risks are much reduced if the pipettes always point downwards, whether in a specimen tube or when adding a liquid to a reaction vessel.

EXPERIMENT 1.1b

Further precipitation reactions

HAZARDS

Note that the NaOH used here is more concentrated than in the conventional technique and so more hazardous.

Teachers' notes for Sheet M2

This microscale experiment illustrates a quick and easy alternative to test tube experiments. The reactions take place on the surface of a plastic sheet. Well-defined drops form on the surface of the plastic.

The plastic sheets are reasonably resilient. They may be wiped clean with tissues and reused many times. The plastic may be attacked by concentrated acids. Iodine solution stains the sheets if left on the surface for more than a minute or two.

The RSC *Microscale Chemistry* book includes a range of experiments of this kind several of which could be adopted as alternatives to procedures in the *Students' Book*.

The RSC book also describes how to make shortened pipettes for storing reagents in a ready to use dropper container (see pages 1–2).

Each group of students will need:

Plastic pipettes, specimen tubes, microscale block (= work station)

A laminated copy of Sheet M2 (or a clear A4 plastic wallet to protect a paper copy)

Eye protection

Access to:

Solutions of the following in small dropper bottles:

0.5 M sodium chloride
0.5 M sodium sulphate
0.2 M sodium carbonate
0.2 M copper(II) sulphate
0.5 M lead nitrate TOXIC
1.0 M sodium hydroxide CORROSIVE

Tissues

Procedure

Full details are given on the students' copiable sheet.

EXPERIMENT 2.2b Preparations using propan-1-ol

HAZARDS

Students must wear eye protection.
Take special care with steps 4 and 5.
The addition and transference of liquids always requires the use of a pipette; use separate pipettes for each liquid.
Sodium dichromate(VI) may cause sensitisation by skin contact so gloves should always be worn when using the solid and preferably when using the solution.
The products are hazardous: propanoic acid is corrosive; propanal is highly flammable and irritant.
Refer to Hazcards 30, 40, 78, 83, 84 and 98 (1995 or later).

Teachers' notes for Sheet M3

This is an alternative to parts 2 and 3 of the experiment in the *Students' Book.* On this scale the time taken adding the alcohol to the oxidising agent is much shorter than in larger-scale preparations.

Each group of students will need:
Sheet M3
Eye protection
Beaker, 250 cm^3
Beaker, 100 cm^3
3 plastic pipettes
Long test tube
Tapered reaction vessel
Hickman still
Sandbath
Hotplate, or burner with tripod and metal plate
Stand and clamp
Sodium dichromate(VI), up to 1 g VERY TOXIC, SKIN SENSITISER
Propan-1-ol, up to 1 g HIGHLY FLAMMABLE
Concentrated sulphuric acid, up to 1 cm^3 CORROSIVE
Spatula

Access to:
Anti-bumping granules
Cotton wool
Balance
Graduated pipettes with teats (secured with rubber bands) to dispense liquid reagents

Procedure

Full details are given on the students' copiable sheet.

EXPERIMENT 2.3 Cyclohexene from cyclohexanol and phosphoric acid

HAZARDS

Students must wear eye protection.
The product is highly flammable.

Teachers' notes for Sheet M4

A widely used method of forming alkenes is the elimination of a small molecule from a substituted alkane. This can be, for example, the dehydration of an alcohol. The reaction has to be carried out with the aid of an acid catalyst which serves to turn the hydroxyl group into a better leaving group. The formation of the alkene is confirmed by its characteristic reaction on addition of bromine water. Unlike the full-scale preparation, the microscale version is not quantitative.

Each group of students will need:
Sheet M4
Eye protection
3 plastic pipettes
Tapered reaction vessel
Hickman still
Sand bath
Hotplate, or burner with tripod and metal plate
Stand and clamp
Cyclohexanol, 0.5 cm^3 HARMFUL
85% Phosphoric acid, 0.5 cm^3 CORROSIVE

Access to
Anti-bumping granules
Cotton wool
Bromine water, HARMFUL, IRRITANT
Graduated pipettes with teats (secured with rubber bands) to disperse liquid reagents

Procedure

Full details are given on the students' copiable sheet.

EXPERIMENT 12.4 The reactions of the phenolic functional group

HAZARDS

Phenol is corrosive and causes painful blisters, and it is toxic by skin absorption. This microscale alternative provides a procedure which allows students to work with phenol with minimal risk. Students must wear eye protection and gloves.

Teachers' notes for Sheet M5

Each group of students will need:

Laminated copy of Sheet M5 (or a clear A4 plastic wallet to protect a paper copy)
Eye protection
Gloves
Plastic petri dish (9 cm diameter)
Solutions contained in plastic pipettes
  Distilled water
  Full-range indicator solution, diluted 1:1 with distilled water
  1 M nitric acid CORROSIVE
  0.05 M bromine water HARMFUL, IRRITANT
  1 M sodium carbonate
  1 M sodium hydroxide CORROSIVE
  1 M hydrochloric acid
  Phenol TOXIC, CORROSIVE

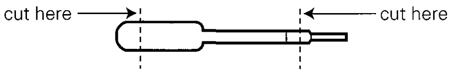
Procedure

Full details are given on the students' copiable sheet except for the sampling procedure for phenol.

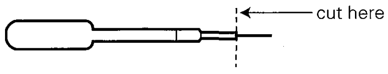
Phenol is a hazardous substance and sampling a bottle of phenol using a spatula is usually difficult. Difficulties include the need to wear gloves to ensure that crystals of phenol do not touch the skin, and the fact that phenol is hygroscopic so that the crystals stick together.

The following procedure using two plastic pipettes reduces safety hazards and allows students to gain in confidence and practical skills. Students must still wear eye protection and gloves.

1 Take a standard form plastic pipette and cut off the ends as shown.

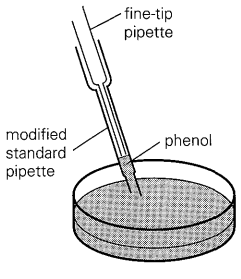


2 Cut the tip off the end of a fine-tip pipette as shown.



3 Taking the modified standard pipette, press it gently down into the crystals in the phenol bottle and withdraw. A small column of solid phenol should be held on the inside of the bevelled end.

4 Place the pipette over the Petri dish and insert the fine-tipped pipette to press out a small quantity of phenol. Repeat at other places on the dish (as shown on the worksheet) to give the 5 samples needed for the experiment.



Clean the pipettes by placing the ends of both pipettes into a 100 cm^3 beaker about half full of 1 M sodium hydroxide solution. This dissolves any solid phenol. The pipettes can then be washed with distilled water, dried on tissue paper and stored for re-use.

EXPERIMENT 12.5 The microscale synthesis of aspirin

HAZARDS

Students must wear eye protection. This experiment should preferably be done in a fume cupboard.

Phosphoric acid is corrosive.

Ethanoic anhydride is corrosive and flammable.

Ethanol is highly flammable.

2-hydroxybenzoic acid (salicylic acid) is harmful.

Teachers' notes for Sheet M6

In this experiment students make aspirin using a microscale esterification reaction between 2-hydroxybenzoic acid (salicylic acid) and ethanoic anhydride with phosphoric acid as a catalyst. In practice teachers have found this particularly successful.

The reaction, which uses reactive ethanoic anhydride and phosphoric acid catalyst, is quite fast at microscale. A good yield of white crystals should be formed.

Each group of students will need:
Sheet M6
Eye protection
Beaker, 10 cm^3
Hot plate
Measuring cylinder, 5 cm^3
Beaker, 50 cm^3
Test tube
Small filter funnel.
2-hydroxybenzoic acid (salicylic acid), 0.23 g HARMFUL
Ethanoic anhydride, 25 drops CORROSIVE, FLAMMABLE
Phosphoric acid (85%), 1 drop CORROSIVE
Ethanol HIGHLY FLAMMABLE

Procedure

Full details are given on the students' copiable sheet.

EXPERIMENT 14.3 Measurement of an equilibrium constant K_c

HAZARDS

Students must wear eye protection.

Teachers' notes for Sheet M7

This experiment uses microscale titration apparatus to measure the equilibrium constant of the redox reaction between silver(I) and iron(II).

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

An advantage of this microscale version is that it uses less silver nitrate solution than the existing method and is therefore more economical.

Each group of students will need:
Microscale titration apparatus (see diagram on Sheet M7)
Eye protection
Stoppered flask, 5–10 cm^3
2 2-cm^3 pipettes
Beaker, 10 cm^3
0.10 M Iron(II) sulphate solution
  (Dissolve 2.780 g of Analar grade $FeSO_4.7H_2O$ [HARMFUL SOLID] in 50 cm^3 of 0.5 M sulphuric acid [IRRITANT] and make up to 100 cm^3 with distilled water in a volumetric flask.)
0.10 M Silver nitrate solution
  (Dissolve 0.849 g of $AgNO_3$ [CORROSIVE SOLID] in distilled water and make up to 50 cm^3 in a volumetric flask. Store in the dark if this solution is not be used immediately; it will be usable for several days. This is sufficient solution for 20–25 pairs of students to do the experiment. The amounts may be scaled down if appropriate.)
0.020 M Potassium thiocyanate solution
  (Dissolve 0.194 g of potassium thiocyanate [HARMFUL SOLID] in distilled water and make up to 100 cm^3 in a volumetric flask.)

Procedure

Full details are given on the students' copiable sheet.

EXPERIMENT 20.2
(alternative)

Nitration of methyl benzoate and the hydrolysis of the product

HAZARDS

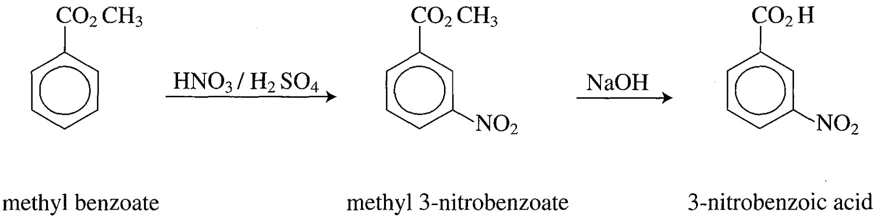
Students should wear eye protection.
Methanol is toxic and highly flammable.
Concentrated sulphuric acid is corrosive.
Methyl benzoate is harmful.
2 M sodium hydroxide is corrosive.
Concentrated hydrochloric acid is corrosive.

Teachers' notes for Sheet M8

This is an alternative, but related, two-step synthesis to the one in the *Students' Book*.

One of the most important reactions of arenes is nitration, because of the large numbers of other functional groups that can be formed from the nitro group by fairly simple transformations. Nitration is usually carried out by reacting the arene with a mixture of nitric and sulphuric acids; in those arenes which already contain a functional group attached to the benzene ring the incoming nitro group becomes attached to specific positions, depending on the orienting effect of the first substituent.

Methyl nitrobenzoate can be readily hydrolysed to the carboxylic acid. The reaction between an ester and water can be catalysed by either acid or base, but the latter is more effective in driving the reaction to completion.

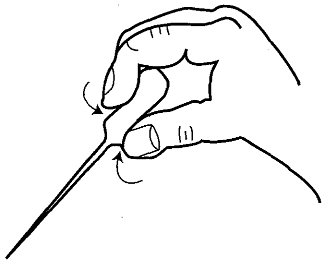


Each group of students will need:
Sheet M8
Eye protection
Specimen tube, 4 cm^3
Beaker, 100 cm^3
2 test tubes
Specimen tube with cap, 6 cm^3
Hirsch funnel, rubber washer and side-arm filter tube
Methyl benzoate, 0.2 cm^3 HARMFUL
Concentrated sulphuric acid, 0.55 cm^3 CORROSIVE
Concentrated nitric acid, 0.15 cm^3 CORROSIVE, OXIDISING
Methanol, 0.8 cm^3 TOXIC, HIGHLY FLAMMABLE LIQUID
2 M Sodium hydroxide, 1 cm^3 CORROSIVE
Concentrated hydrochloric acid, a few drops CORROSIVE

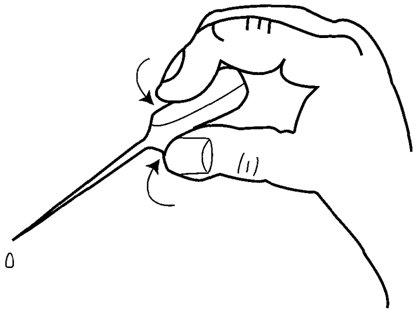
Access to:
Ice
Anti-bumping granules
Melting point apparatus
Water pump for vacuum filtration

NUFFIELD ADVANCED CHEMISTRY Microscale Chemistry **M1**

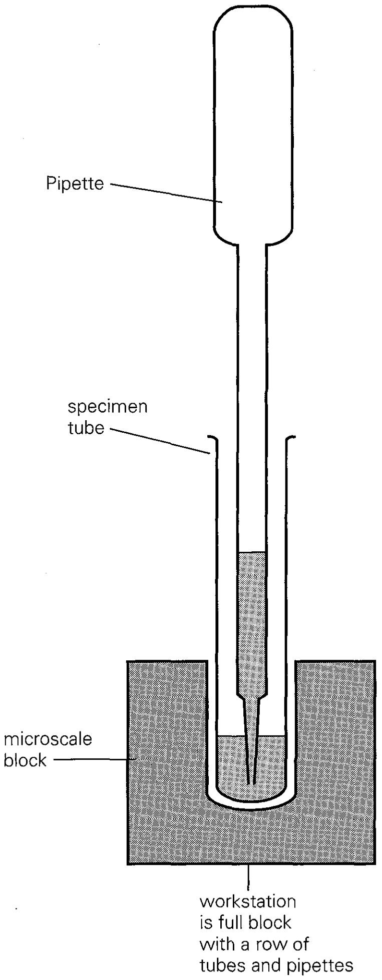
Plastic pipettes



Squeeze the air out of the bulb of the plastic pipette and insert it into the solution



Squeeze the pipette bulb very gently to deliver drops



Put the pipette into a specimen tube and keep the two together to avoid cross-contamination

SAFETY

Never point a filled pipette upwards. Similarly, never use pipettes to squirt solutions at one another. Both these actions may injury the eye or skin of another student. Solutions used for microscale reactions are often more concentrated than normal.

The thin-stemmed plastic pipette is used to deliver drops of liquids and solutions.

How to use a plastic pipette

1 Squeeze the bulb of the pipette between your thumb and forefinger to force out the air.

2 Hold the pipette with the bulb pressed in, and place the stem of the pipette into the desired solution.

3 Release the bulb of the pipette and allow it to slowly fill with the solution. The bulb of the pipette should be at least half filled with solution. If there is too little solution in the bulb, air bubbles may accumulate in the stem of the pipette and affect the drop size delivered by the pipette.

4 When the bulb has filled with solution, remove the pipette from the solution. Press gently on the bulb of the pipette to allow the solution to flow down the stem and form a drop at the end. The pressure on the bulb of the pipette must be carefully controlled to ensure that each drop delivered is of the same size. This may require some practice.

EXPERIMENT 1.1b Further precipitation reactions

Procedure

1 Check that the worksheet is protected with clear plastic.

2 For each pair of solutions put 2 drops of the solution listed in the left-hand column in the empty box in the middle column; then add 2 drops of the solution listed in the right hand column.

3 Look carefully to see if a precipitate forms. Note any colour changes. Identify the precipitate by considering the solubilities of ionic compounds

SAFETY

Wear eye protection.
Aqueous sodium hydroxide is corrosive.
Aqueous lead(II) nitrate is toxic.

$Pb(NO_3)_2$(aq)	Put solutions in this column	NaOH(aq)
NaCl(aq)		NaOH(aq)
$CuSO_4$(aq)		NaOH(aq)
$Pb(NO_3)_2$(aq)		Na_2SO_4(aq)
$Pb(NO_3)_2$(aq)		Na_2CO_3(aq)
$Pb(NO_3)_2$(aq)		NaCl(aq)
$CuSO_4$(aq)		Na_2CO_3(aq)
$CuSO_4$(aq)		NaCl(aq)
$CuSO_4$(aq)		$Pb(NO_3)_2$(aq)

NUFFIELD ADVANCED CHEMISTRY Microscale Chemistry **M3**

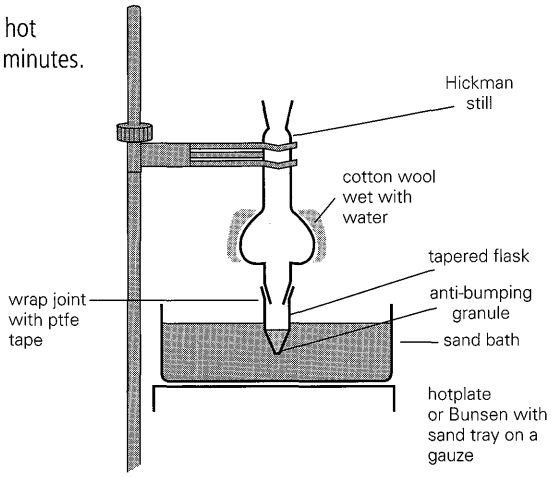
EXPERIMENT 2.2b Preparations using propan-1-ol

2 The oxidation of propan-1-ol to propanoic acid

Oxidation by refluxing with more concentrated reagents produces propanoic acid, the yield of which can be determined by titration.

Procedure

1 Start heating a sand bath. (It should be 170–180 °C.)
2 Place 0.6 g of sodium dichromate(VI) in a long test tube. Clamp the test tube, surrounding it with cold water.
3 Add 1 cm^3 of water, anti-bumping granule, and 0.4 cm^3 of concentrated sulphuric acid IN THAT ORDER and stir the mixture with a glass rod until all the solid has dissolved.
4 Tare on a balance, a 250 cm^3 beaker complete with plastic pipette. Measure out 0.3 g of propan-1-ol by sucking the liquid into the pipette. Now add the liquid drop by drop to the reaction vessel with stirring. (This reaction is violent at first and great care should be taken.)
5 Place the equipment on the hot sand bath and reflux for 30 minutes.



6 Transfer the liquid to a reaction vessel and add some anti-bumping granules. Place a little cotton wool in the cone of the Hickman still and connect it to the reaction vessel. Make sure the connection is tight. Place the equipment on the hot sand bath and distil off about 0.5 cm^3 of liquid.

SAFETY

Wear eye protection. Take special care with steps 3, 4 and 5. The addition and transference of liquids always require the use of a pipette. Use separate pipettes for each liquid and keep it standing in the labelled container for that liquid.

Sodium dichromate(VI) is very toxic and a skin sensitiser.

Propan-1-ol is highly flammable.

Concentrated sulphuric acid is corrosive and so is the reaction mixture.

Refer to Hazcards 32, 38, 78, 84, 91 and 98 (1995 or later).

3 The oxidation of propan-1-ol to propanal

Procedure

1 Start heating a sand bath. (It should be 80–90 °C.)
2 Place 0.3 g of sodium dichromate(VI) in a reaction vessel. Clamp the reaction vessel and surround it with cold water in a beaker.
3 Add 1 cm^3 of water, an anti-bumping granule, and 0.2 cm^3 of concentrated sulphuric acid IN THAT ORDER and stir the mixture until all the solid has dissolved.
4 Tare on a balance, a 250 cm^3 beaker complete with plastic pipette. Measure out 0.3 g of propan-1-ol by sucking the liquid into the pipette. Now add the liquid drop by drop to the reaction vessel with stirring. (This reaction is violent at first and great care should be taken.)
5 Place a little cotton wool in the cone of the Hickman still, wrap the joint with PTFE tape and connect it to the reaction vessel. Make sure the connection is tight. Place the apparatus on the hot sand bath. Collect the liquid that forms in the Hickman still; about 0.5 cm^3 should be adequate. Remove the reaction vessel from the sand bath, cool it in water and disconnect as soon as possible to avoid the joints sticking. Place the glassware in a bowl of water.

SAFETY

Wear eye protection. Take special care with steps 4 and 5. The addition and transference of liquids always require the use of a pipette. Use separate pipettes for each liquid.

Sodium dichromate(VI) is very toxic and a skin sensitiser.

Concentrated sulphuric acid is corrosive and so is the reaction mixture. The product is highly flammable and an irritant.

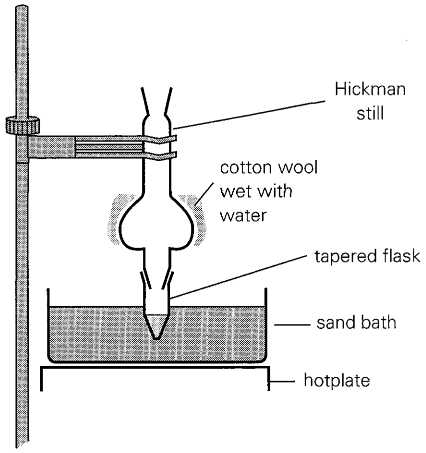
EXPERIMENT 2.3 Cyclohexene from cyclohexanol and phosphoric acid

SAFETY

Wear eye protection.
Cyclohexanol is harmful.
Phosphoric acid is corrosive.

Procedure

1 Add 0.5 cm^3 cyclohexanol to 1 cm^3 85% phosphoric acid in a tapered flask containing an anti-bumping granule and mix them to ensure a homogeneous liquid phase. Attach a Hickman still and cool it by wrapping it with cotton wool wet with water (see diagram).



Making cyclohexane

2 Heat the reaction mixture in a sand bath at 150 °C for 10–15 minutes.

3 Two immiscible liquids may collect in the still: the product and water. Where does the water come from? How can you decide which is which? Pipette out the product into a specimen tube and test it for the presence of unsaturation with bromine water.

Based on *Microscale practical organic chemistry* by Stephen Brewer, Lancaster University, 1996

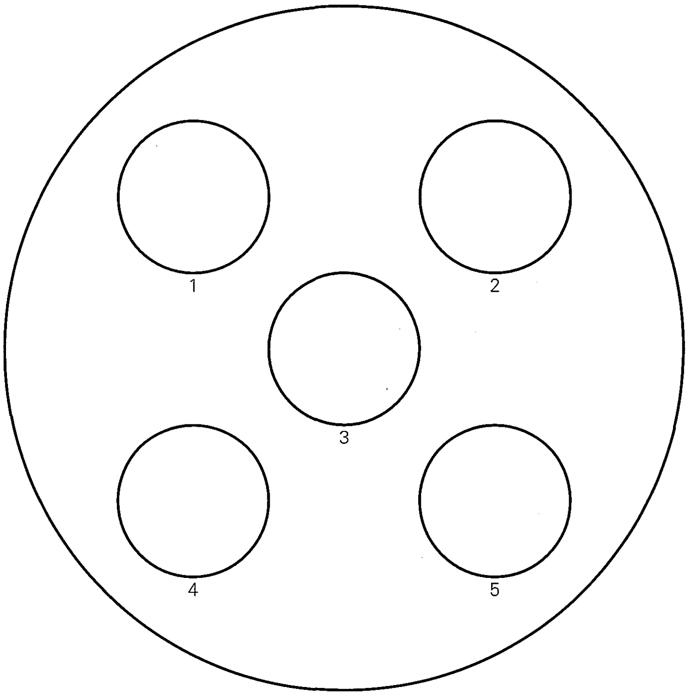
EXPERIMENT 12.4 The reactions of the phenolic functional group

SAFETY

Wear eye protection.
1 M nitric acid is corrosive.
1 M sodium hydroxide is corrosive.
Phenol is toxic by skin absorption and corrosive – it causes painful blisters.
In this experiment you will be observing and interpreting some of the chemical reactions of phenol inside a plastic Petri dish.

Procedure

1. Check that the worksheet is protected with clear plastic.
2. Place the base of the Petri dish over the circle below. Using the phenol sampling procedure (ask your teacher), place small quantities of phenol in the Petri dish over each of the five small circles.
3. In circle 1, add 2 drops of water, leave for 1 minute, then add 1 drop of Full-range Indicator solution.



Circle template

4. In circle 2, add 2 drops of sodium hydroxide solution. Observe closely over the next minute. Add one drop of hydrochloric acid and observe closely.
5. In circle 3, add 2 drops of sodium carbonate solution.
6. In circle 4, add 2 drops of 1 M nitric acid. Observe any changes over the next 5 minutes.
7. In circle 5, add 2 drops of aqueous bromine.
8. When you have finished, add drops of sodium hydroxide to the Petri dish to dissolve the phenol, and then mop up with tissue.

Based on *Microscale chemistry* Royal Society of Chemistry, 1997

EXPERIMENT 12.5 The microscale synthesis of aspirin

In this experiment you will be preparing aspirin from the reaction between 2-hydroxybenzoic acid (salicylic acid) and ethanoic anhydride.

SAFETY

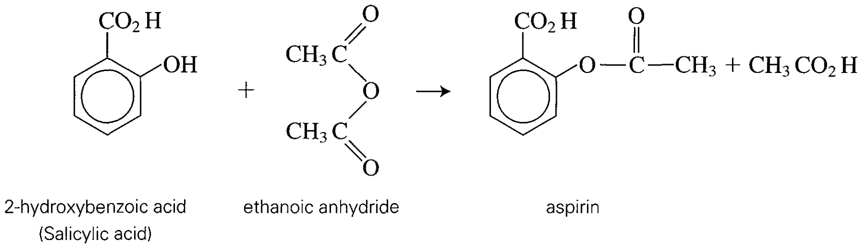
Wear eye protection.
Transfer the ethanoic anhydride to the test tube in a fume cupboard if possible.

Phosphoric acid is corrosive.

Ethanoic anhydride is corrosive and flammable.

Ethanol is highly flammable.

2-hydroxybenzoic acid (salicylic acid) is harmful.



The reaction to form aspirin

Procedure

1. Half fill a 50 cm^3 beaker with distilled water, and heat to 70–80 °C.
2. Weigh 0.23 g of 2-hydroxybenzoic acid (salicylic acid) into a test tube.
3. Add 25 drops of ethanoic anhydride followed by one drop of 85% phosphoric acid.
4. Place in the water bath and leave at 70–80 °C for 15 minutes.
5. While still warm add 1.5 cm^3 of distilled water (use a measuring cylinder) and cool to room temperature until crystallisation begins, then cool in an ice bath.
6. Filter through a small filter funnel and recrystallise in a test tube using a mixture of 0.7 cm^3 ethanol and 2 cm^3 of distilled water.

Based on *Microscale chemistry* Royal Society of Chemistry, 1997

NUFFIELD ADVANCED CHEMISTRY Microscale Chemistry **M7**

EXPERIMENT 14.3 Measurement of an equilibrium constant K_c

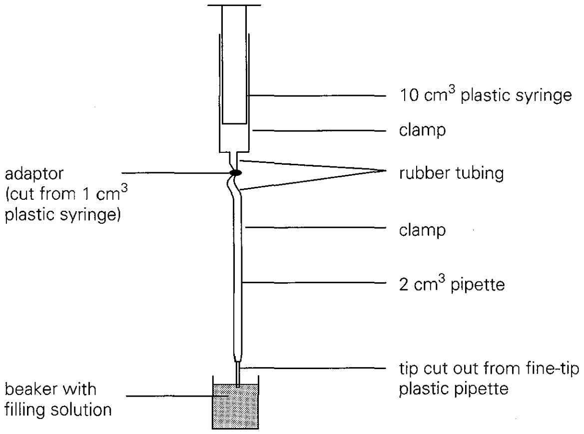
SAFETY

Wear eye protection.

Procedure

1 Using a 2 cm^3 pipette, transfer 2 cm^3 each of the 0.01 M silver nitrate solution and 0.10 M iron(II) sulphate solution to the flask and stopper it so that it is air-tight. Shake the flask and leave undisturbed overnight.

2 Set up the microscale titration apparatus.



Microscale burette made from a 2 cm^3 pipette and a 10 cm^3 plastic syringe

The burette tip is made by cutting the end off a fine-tip plastic pipette and pushing it over the end of the graduated pipette. The syringe is attached to the upper end of the pipette with two short lengths of rubber tubing. Cut the length off a 1 cm^3 plastic syringe to make the adaptor.

3 Fill the graduated part of the titration apparatus with potassium thiocyanate solution by dipping the tip of the burette into a small beaker of the solution and slowly raising the plunger of the syringe. (If you trap any air bubbles expel them by raising and lowering the syringe plunger a few times.) Draw the liquid up to a suitable level. Check for air leaks by making sure that the liquid level does not fall until you are ready to titrate.

4 Using a 1 cm^3 pipette, transfer 1 cm^3 of the equilibrium solution from the flask to a 10 cm^3 beaker, trying not to disturb the silver precipitate.

5 Using the microscale titration apparatus, titrate with 0.020 M potassium thiocyanate solution. A permanent red colour marks the end-point.

6 Repeat the titration and calculate the average of your titres.

Calculations

1 Write the expression for the equilibrium constant K_c for the reversible reaction.

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

2 Work out the initial concentrations of the silver(I) and iron(II) ions in the reaction vessel (bearing in mind that you mixed equal volumes of the two solutions).

3 Write the equation for the titration reaction and use it to calculate the equilibrium concentration of silver(I) ions.

4 Refer to the equation for the reversible reaction and your answer to **3** to work out the equilibrium concentration of iron(II) ions.

5 Use your answers to **2** and **4**, together with the equation, to work out the equilibrium concentration of iron(III) ions.

6 Work out the value and the units of K_c.

Based on *Microscale chemistry* Royal Society of Chemistry, 1997 © In this format Nuffield Foundation 2000

EXPERIMENT 20.2 Nitration of methyl benzoate and the hydrolysis of the product

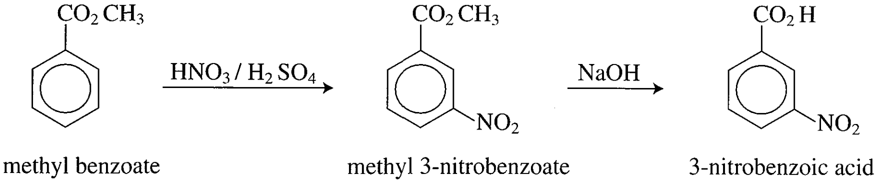
SAFETY

Wear eye protection.
Methanol is toxic and highly flammable.
Concentrated sulphuric acid is corrosive.
Methyl benzoate is harmful.
2 M sodium hydroxide is corrosive.
Concentrated hydrochloric acid is corrosive.

This is a microscale alternative to the two-step synthesis in the *Students' Book*.

One of the most important reactions of arenes is nitration, because of the large numbers of other functional groups that can be formed from the nitro group by fairly simple transformations. Nitration is usually carried out by reacting the arene with a mixture of concentrated nitric and concentrated sulphuric acids.

Methyl nitrobenzoate can be readily hydrolysed to the carboxylic acid. The reaction between an ester and water can be catalysed by either acid or base, but the latter is more effective in driving the reaction to completion.



Nitration

1 First prepare 0.3 cm^3 of the nitrating mixture by mixing equal volumes of concentrated nitric and sulphuric acids and cooling the resulting mixture.

2 Dissolve 0.2 cm^3 methyl benzoate in 0.4 cm^3 concentrated sulphuric acid in a 4 cm^3 specimen tube and cool the warm solution in an ice bath. When cool, add to it 0.3 cm^3 of a previously cooled nitrating mixture. The reaction mixture gets warm and darkens. Cool the mixture to room temperature and allow it to stand for 15–20 minutes.

Work-up and isolation of the product

3 Place 3 cm^3 of ice and water in a 6 cm^3 specimen tube and add the reaction mixture to it, cap the tube and shake it well until an off-white solid separates out. Filter this under suction with a Hirsch funnel, wash it with a little water and dry it by sucking air through it on the funnel. Divide the solid product roughly in half.

Purification and characterisation

Take half the product and recrystallise it by dissolving it with boiling in about 0.6–0.8 cm^3 methanol in the fume cupboard (add an anti-bumping granule). When it has all gone into solution, set it aside to cool and to crystallise. Filter the crystalline product with the Hirsch funnel under suction, dry it and determine its melting point. It should be 78 °C.

Hydrolysis

Take the other half of the product and add it to 1 cm^3 of 2 M sodium hydroxide. Add an anti-bumping granule and heat to boiling. Continue heating until all the oily product goes into solution and then for a minute or two longer. The process should be complete in about 5 minutes. Set the solution aside to cool.

Work-up, purification and characterisation

To the cooled solution add concentrated hydrochloric acid dropwise until it is acidic. Filter the white precipitate with a Hirsch funnel with suction. Suck it dry and then recrystallise it by dissolving it in about 2 cm^3 boiling water (add an anti-bumping granule). (If it is very slow to dissolve add a drop or two of methanol until it does.)

Set the solution aside to cool. When crystallisation is complete, filter the solid with the Hirsch funnel with suction, dry it and determine its melting point. It should be 142 °C.

Based on Microscale Organic Chemistry, CLEAPSS, 1996

Appendix 2

Hazardous laboratory chemicals

The aim of this list of chemicals is to provide information on the more hazardous substances used during the course. It does not claim to be exhaustive or authoritative.

It is hoped that teachers and technicians will find here most of the information they need when making Risk Assessments for operations involving solids and pure liquids. The most frequent dangerous operation is the *preparation* of dilute solutions, and risks are much greater than those involved when students *use* dilute solutions in the various experiments.

When students are preparing for an investigation they will need sources of information to help them make their Risk Assessments. They will need access to the sources listed in the bibliography and it is acceptable to photocopy the list of hazardous substances included in this section. Students and teachers should remember that this list is *incomplete* as it only aims to cover chemicals needed in the *standard experiments*.

The warning 'Keep out of reach of children' has been omitted in every case listed, as it is unhelpful in a school or college context.

In the list the standard terms used have the following meanings.

- **Toxic:** substances which if inhaled, swallowed, or allowed to penetrate the skin, may involve serious health risks.
- **Harmful:** substances which if inhaled, swallowed or allowed to penetrate the skin, may involve limited health risks.
- **Corrosive:** substances which on contact may destroy living tissue.
- **Irritant:** substances which on contact with the skin may cause inflammation.
- **Extremely flammable:** substances with a flash point below 0 °C.
- **Highly flammable:** substances with a flash point between 0 °C and 21 °C.
- **Flammable:** substances with a flash point between 21 °C and 55 °C.
- **Carcinogenic substances** are divided into three categories; **category 1** are known to be carcinogenic to humans; **category 2** should be regarded as carcinogenic, generally on the basis of animal studies; **category 3** cause concern but a satisfactory assessment is not possible at present.

Please note

Whilst every care has been taken in the preparation of this information and it is believed to be correct and based upon the best advice currently available, no guarantee can be given as to its accuracy, and no liability is accepted for any loss, damage or injury arising from the use of the information.

Occupational Exposure Limits

The limits of exposure to chemicals are described in **Occupational Exposure Limits** (OELs). There are two sorts of OEL:

1 **Occupational Exposure Standards** (OES): these are concentrations to which it is believed that normal healthy adults can be exposed day after day with no ill effect.

2 **Maximum Exposure Limits** (MEL): these are for the most dangerous substances. It is believed that no level of exposure is completely safe, but in any case the MEL must never be exceeded and every effort must be made to keep exposure well below the MEL.

For both OESs and MELs both short-term exposure limits (STELs) and long-term exposure limits (LTEL) may be defined.

- LTEL corresponds to an 8-hour working day.
- STEL corresponds to a 15-minute exposure.

For many students activities, the STEL is the more relevant figure, but for technicians working in ill-ventilated prep rooms LTELs may be more relevant.

Risk phrases and safety phrases are denoted R and S respectively.

Hazardous substances used in the Nuffield Advanced Chemistry experiments

Extracts from the pages may be photocopied for use by students.

- Acetamide
  see Ethanamide
- Acetic acid
  see Ethanoic acid
- Acetic anhydride
  see Ethanoic anhydride
- Acetone
  see Propanone
- Acrylamide
  see Propenamide
- Adipic acid
  see Hexanedioic acid
- Aluminium powder
  Highly flammable
  OES: 10 mg m^{-3} (LTEL)
  R15 Contact with water liberates extremely flammable gases
  R17 Spontaneously flammable in air
  S7/8 Keep container tightly closed and dry
- Aluminium chloride (anhydrous)
  Corrosive
  OES: 2 mg m^{-3} (LTEL)
  R34 Causes burns
  S7/8 Keep container tightly closed and dry
  S28 After contact with skin, wash immediately with plenty of water
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)

- Ammonia gas
  Toxic, Corrosive, Flammable, Dangerous to the environment
  OES: 18 mg m^{-3} (LTEL), 25 mg m^{-3} (STEL)
  R10 Flammable
  R23 Toxic by inhalation
  R34 Causes burns
  R50 Very toxic to aquatic organisms
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  S61 Avoid release to the environment
- Ammonia solution
  Corrosive when >6 M or more
  Irritant when 3–5.9 M
  Dangerous to the environment
  $\geqslant 25\%$ R34 Causes burns
  $\geqslant 25\%$ R50 Very toxic to aquatic organisms
  $\geqslant 10\%$ R34 Causes burns
  $\geqslant 5\%$ R36/37/38 Irritating to eyes, respiratory system and skin
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear protective clothing, gloves and eye, face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  S61 Avoid release to the environment
  Refer to special instructions/safety data sheet
- Ammonium chloride
  Harmful, Irritant
  OES: 20 mg m^{-3} (STEL), 10 mg m^{-3} (LTEL)
  R22 harmful if swallowed
  R36 Irritating to the eyes
  S22 Do not breathe dust
- Ammonium dichromate(VI)
  Explosive, Very Toxic
  OES: 0.05 mg cm^{-3} (LTEL)
  R49 May cause cancer by inhalation
  R46 May cause heritable genetic damage
  R1 Explosive when dry
  R8 Contact with combustible material may cause fire
  R21 Harmful in contact with skin
  R25 Toxic if swallowed
  R26 Very toxic by inhalation
  R37/38 Irritating to respiratory system and skin
  R41 Risk of serious damage to eyes
  R43 May cause sensitisation by skin contact
  R50/53 Very toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment
  S53 Avoid exposure
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  S60 This material and its container must be disposed of as hazardous waste
  S61 Avoid release to the environment.
- Ammonium nitrate
  Oxidising
  R8 Contact with combustible material may cause fire
  S15 Keep away from heat
  S17 Keep away from combustible material

- Aniline
  see Phenylamine
- Anisole
  see Methoxybenzene
- Barium compounds
  Harmful
  OES: 0.5 mg m^{-3} (LTEL)
  Some Ba compounds (e.g. nitrate, peroxide) are oxidising
- $BaCl_2$
  Toxic solid or
  Harmful $\geqslant 0.02$ M <0.2 M
  R20 Harmful by inhalation
  R25 Toxic if swallowed
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Other Ba salts (not sulphate)
  Harmful $\geqslant 0.05$ M
  R20/22 Harmful by inhalation and if swallowed
  S28 After contact with skin, wash immediately with plenty of water
- Benedict's reagent
  Harmful product
- Benzene
  Toxic, Highly flammable
  All educational use is illegal
  MEL: 16 mg m^{-3} (LTEL)
  R45 May cause cancer. Category 1 carcinogen
  R11 Highly flammable
  R48/23/24/25 Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
  S53 Avoid exposure
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Benzene-1,2-dicarboxylic anhydride (phthalic anhydride)
  Irritant
  MEL: 4 mg m^{-3} (LTEL) 12 mg m^{-3} (STEL)
  R36/37/38 Irritating to eyes, respiratory system and skin
- Benzene-1,2-diol or 1,2-dihydroxybenzene (catechol)
  Harmful
  OES: 23 mg m^{-3} (LTEL)
  R21/22 Harmful in contact with skin and if swallowed
  R36/38 Irritating to eyes and skin
  S22 Do not breathe dust
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S37 Wear suitable gloves
- Benzene-1,3-diol (Resorcinol)
  Harmful, Dangerous to the environment
  OES: 46 mg m^{-3} (LTEL), 92 mg m^{-3} (STEL)
  R22 Harmful if swallowed
  R36/38 Irritating to eyes and skin
  R50 Very toxic to aquatic organisms
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S61 Avoid release to the environment
- Benzoyl chloride (benzenecarbonyl chloride)
  Corrosive
  R34 Causes burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)

- Benzyl alcohol (phenylmethanol)
  Harmful
  R20/22 Harmful by inhalation, in contact with skin and if swallowed
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

- **Boric acid**
  none

- Bromine
  Very toxic, Corrosive
  OES: 2 mg m^{-3} (STEL), 0.7 mg m^{-3} (LTEL)
  R26 Very toxic by inhalation
  R35 Causes severe burns
  S7/9 Keep container tightly closed and in a well ventilated place
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)

- Bromine water
  0.4 M or more **Very toxic and Corrosive**
  0.06 M to 0.4 M **Toxic and Corrosive**
  0.006 to 0.06 M **Harmful and Irritant**
  OES: 2 mg m^{-3} (STEL), 0.7 mg m^{-3} (LTEL)

- Bromoethane
  Harmful
  R20/21/22 Harmful by inhalation, in contact with skin and if swallowed
  S28 After contact with skin, wash immediately with plenty of water

- Butanoic acid
  pure or $\geqslant$4 M **Corrosive**
  $\geqslant$1.5 M <4 M **Irritant**
  R34 Causes burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36 Wear suitable protective clothing
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)

- Butan-1-ol
  Harmful, Flammable
  OES: 154 mg m^{-3} (STEL)
  R10 Flammable
  R20 Harmful by inhalation
  S16 Keep away from sources of ignition. No smoking

- Butan-2-ol
  Harmful, Flammable
  OES: 462 mg m^{-3} (STEL), 308 mg m^{-3} (LTEL)
  R10 Flammable
  R20 Harmful by inhalation
  S16 Keep away from sources of ignition. No smoking

- Butanone
  Highly flammable, Irritant
  OES: 899 mg m^{-3} (STEL) 600 mg m^{-3} (LTEL)
  R11 Highly flammable
  R36/37 Irritating to eyes and respiratory system
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S25 Avoid contact with eyes
  S33 Take precautionary measures against static discharges

- Tertiary butyl alcohol
  see 2-methylpropan-2-ol
- Butylamine
  Highly flammable, Corrosive
  OES: 15 mg m^{-3} (STEL)
  R11 Highly flammable
  R20/21/22 Harmful by inhalation, in contact with skin and if swallowed
  R35 Causes severe burns
  S3 Keep in a cool place
  S16 Keep away from sources of ignition. No smoking
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S29 Do not empty into drains
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Calcium chlorate(I) (calcium hypochlorite)
  Corrosive, Oxidising
  R8 Contact with combustible material may cause fire
  R31 Contact with acids liberates toxic gas
  R34 Causes burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Calcium chloride
  Irritant
  R36 Irritating to the eyes
  S22 Do not breathe dust
  S24 Avoid contact with skin
- Chlorine
  Toxic, Dangerous to the environment
  OES: 2.9 mg m^{-3} (STEL), 1.5 mg m^{-3} (LTEL)
  R23 Toxic by inhalation
  R36/37/38 Irritating to eyes, respiratory system and skin
  R50 Very toxic to aquatic organisms
  S9 Keep container in a well-ventilated place
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  S61 Avoid release to the environment.
  Refer to special instructions/safety data sheet
- 1-chlorobutane
  Highly flammable
  R11 Highly flammable
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S29 Do not empty into drains
- Chloroethanoic acid
  Toxic, Corrosive, Dangerous to environment
  Solid and its solution cause severe skin burns that may only be apparent several hours after contact; toxic if swallowed; *see* also dichloroethanoic and trichloroethanoic acids
  R25 Toxic if swallowed
  R34 Causes burns
  R50 Very toxic to aquatic organisms
  S23 Do not breathe gas/fumes/vapour/spray
  S37 Wear suitable gloves
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  S61 Avoid release to the environment.
  Refer to special instructions/safety data sheet

- Copper compounds
  Solid and >1 M **Harmful**
  OES: 2 mg m^{-3} (STEL), 1 mg m^{-3} (LTEL) dusts and mists (as Cu)
- $CuCl_2$, $CuCrO_4$
  Solid and solutions >1.4 M **Toxic**
  Solutions >0.15 M **Harmful**
- $CuSO_4$
  R22 Harmful if swallowed
  R36/38 Irritating to eyes and skin
  S22 Do not breathe dust
- CuCl
  R22 Harmful if swallowed
  S22 Do not breathe dust
- $CuCl_2$
  R25 Toxic if swallowed
  R36/37/38 Irritating to eyes, respiratory system and skin
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Copper(I) oxide
  Harmful
  R22 Harmful if swallowed
  S22 Do not breathe dust
- Cyclohexane
  Highly flammable
  OES: 350 mg m^{-3} (LTEL), 1050 mg m^{-3} (STEL)
  R11 Highly flammable
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S33 Take precautionary measures against static discharges
- Cyclohexanol
  Harmful
  OES: 200 mg m^{-3} (LTEL)
  R20/22 Harmful by inhalation and if swallowed
  R36/38 Irritating to respiratory system and skin
  S24/25 Avoid contact with skin and eyes
- Cyclohexanone
  Harmful, Flammable
  OES: 408 mg m^{-3} (STEL), 102 mg m^{-3} (LTEL)
  R10 Flammable
  R20 Harmful by inhalation
  S25 Avoid contact with eyes
- Cyclohexene
  Highly flammable, Irritant
  OES: 1020 mg m^{-3} (LTEL)
  R11 Highly flammable
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S33 Take precautionary measures against static discharges
- Decanedioyl dichloride (sebacoyl dichloride)
  Corrosive
  Irritant to tissue; harmful by inhalation or skin absorption
  R34 Causes burns
  R37 Irritating to the respiratory system
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)

- Dibutyl phthalate
  Harmful, Dangerous to the environment
  OES: 10 mg m^{-3} (STEL), 5 mg m^{-3} (LTEL)
  R62 Possible risk of impaired fertility
  R63 Possible risk of harm to the unborn child
  R50/53 Very toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment
  S36/37 Wear suitable protective clothing and gloves
  S61 Avoid release to the environment.
- Dichloroethanoic acid
  Corrosive
  R35 Causes severe burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- di(dodecanoyl) peroxide (lauroyl peroxide)
  Oxidising
  R7 May cause fire
  S3/7 Keep container tightly closed in a cool place
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
- Ethanamide (acetamide)
  Harmful
  Category 3 carcinogen
  R40 Possible risk of irreversible effects
  S36/37 Wear suitable protective clothing and gloves
- Ethanedioic acid (oxalic acid)
  Harmful
  Harmful solid and solution $\geqslant 5\%$
  OES: 2 mg m^{-3} (STEL) 1 mg m^{-3} (LTEL)
  R21/22 Harmful in contact with skin and if swallowed
  S24/25 Avoid contact with skin and eyes
- Ethane-1,2-diol (ethylene glycol)
  Harmful
  OES: 125 mg m^{-3} (STEL) 60 mg m^{-3} (LTEL) (as vapour)
  R22 Harmful if swallowed
- Ethanoic acid (acetic acid)
  Corrosive, Flammable
  4 M or more is **Corrosive**
  1.5 M to 3.9 M is **Irritant**
  OES: 37 mg m^{-3} (STEL) 25mg m^{-3} (LTEL)
  R10 Flammable
  R35 Causes severe burns
  S23 Do not breathe gas/fumes/vapour/spray
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Ethanoic anhydride (acetic anhydride)
  Corrosive, Flammable
  OES: 21 mg m^{-3} (STEL)
  R10 Flammable
  R34 Causes burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Ethanol
  Highly flammable
  Schools rarely use (pure) ethanol. Mostly i.m.s. is used – **toxic** (due to presence of CH_3OH) *(Continued)*

OES: 1920 mg m^{-3} (LTEL)
R11 Highly flammable
S7 Keep container tightly closed
S16 Keep away from sources of ignition. No smoking

- Ethanoyl chloride
  Highly flammable, Corrosive
  R11 Highly flammable
  R14 Reacts violently with water
  R34 Causes burns
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Ethoxyethane (diethyl ether, ether)
  Extremely flammable
  OES: 1540 mg m^{-3} (STEL) 1230 mg m^{-3} (LTEL)
  R12 Extremely flammable
  R19 May form explosive peroxides
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S29 Do not empty into drains
  S33 Take precautionary measures against static discharges
- Ethyl ethanoate (ethyl acetate)
  Highly flammable
  OES: 1460 mg m^{-3} (LTEL)
  R11 Highly flammable
  S16 Keep away from sources of ignition. No smoking
  S23 Do not breathe gas/fumes/vapour spray
  S29 Do not empty into drains
  S33 Take precautionary measures against static discharges
- Formaldehyde
  see Methanal
- *n*-hexane
  Highly flammable, Harmful
  OES: *n*-hexane 72 mg m^{-3} (LTEL)
  R11 Highly flammable
  R48/20 Harmful: danger of serious damage to health by prolonged exposure through inhalation
  S9 Keep container in a well-ventilated place
  S16 keep away from sources of ignition. No smoking
  S24/S25 Avoid contact with skin and eyes
  S29 Do not empty into drains
  S51 Use only in well-ventilated areas
- Hexane-1,6-diamine (diaminohexane)
  Corrosive
  R21/22 Harmful in contact with skin and if swallowed
  R34 Causes burns
  R37 Irritating to the respiratory system
  S22 Do not breathe dust
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Hexanol
  Harmful
  R22 Harmful if swallowed
  S24/25 Avoid contact with skin and eyes

- Hexanedioic acid
  Irritant
  R36 Irritating to the eyes
- Hydrochloric acid
  Corrosive
  6.5 M or more is **Corrosive**
  2.0 to 6.4 M is **Irritant**
  R34 Causes burns
  R37 Irritating to the respiratory system
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Hydrogen
  Extremely flammable
  R12 Extremely flammable
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S33 Take precautionary measures against static discharges
- Hydrogen chloride gas
  Toxic, Corrosive
  OES: 2 mg m^{-3} (LTEL), 8 mg m^{-3} (STEL)
  R23 Toxic by inhalation
  R35 Causes severe burns
  S9 Keep container in a well-ventilated place
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Hydrogen peroxide
  Oxidising, Corrosive
  OES: 2.8 mg m^{-3} (STEL), 1.4 mg m^{-3} (LTEL)
  R8 Contact with combustible material may cause fire
  R34 Causes burns
  S3 Keep in a cool place
  S28 After contact with skin, wash immediately with plenty of water
  S36/39 Wear suitable protective clothing and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  $\geqslant$60% R8 Contact with combustible material may cause fire
  $\geqslant$20% R34 Causes burns
  $<$20%, $\geqslant$5% R36/38 Irritating to eyes and skin
- 2-hydroxybenzoic acid (2-hydroxybenzenecarboxylic acid, or salicylic acid)
  Harmful
  R22 Harmful if swallowed
  R36/37/38 Irritating to eyes, respiratory system and skin
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36 Wear suitable protective clothing
- Iodine
  Harmful
  OES: 1.1 mg m^{-3} (STEL)
  R20/21 Harmful by inhalation and in contact with skin
  S23 Do not breathe gas/fumes, vapour/spray
  S25 Avoid contact with eyes
- Indicators
  Highly flammable, if made up in ethanol etc.
  The solutes from which indicator solutions are made are often harmful or even toxic, but at the concentrations used in indicators the hazard is low.

- Iron(III) chloride (anhydrous)
  Harmful, Irritant
  R22 Harmful if swallowed
  R38 Irritating to the skin
  R41 Risk of serious damage to eyes
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S39 Wear eye/face protection
- Iron(II) salts
  Harmful
  Harmful solid or in solution 1 M or more
- Iron(III) salts
  Irritant
  Irritant solid or in solution 0.75 M or more.
  OES: 2 mg m^{-3} (STEL) 1 mg m^{-3} (LTEL).
- Lauroyl peroxide
  see di(dodecanoyl) peroxide.
- Lead (powder)
  Irritant
  Irritant when inhaled
  OEL 0.15mg m^{-3} (LTEL)
  R20/22 Harmful by inhalation, in contact with skin and if swallowed
  R33 Danger of cumulative effects
  R61 May cause harm to the unborn child
  R62 Possible risk of impaired fertility
  S53 Avoid exposure. Obtain special instructions before use
  S37 Wear suitable gloves
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Lead compounds (in general)
  Toxic for reproduction in categories 1 and 3
  OEL: 0.15 mg m^{-3} (LTEL)
  R61 May cause harm to the unborn child
  R62 Possible risk of impaired fertility
  R20/22 Harmful by inhalation and if swallowed
  R33 Danger of cumulative effects
  S53 Avoid exposure. Obtain special instructions before use
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Lead ethanoate
  Category 3 carcinogen
  Toxic for reproduction in categories 1 and 3
  Toxic solid or $\geqslant 0.01$ M
  Harmful $\geqslant 0.001$ M
  R61 May cause harm to the unborn child
  R62 Possible risk of impaired fertility
  R33 Danger of cumulative effects
  R40 Possible risk of irreversible effects
  R48/22 Harmful: danger of serious damage to health by prolonged exposure if swallowed
  S53 Avoid exposure. Obtain special instructions before use
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Magnesium powder
  Highly flammable
  R11 Highly flammable
  R15 Contact with water liberates extremely flammable gases
  S7/8 Keep container tightly closed and dry
- Manganese(IV) oxide (manganese dioxide)
  Harmful
  OES: 5 mg m^{-3} (LTEL)

R20/22 Harmful by inhalation and if swallowed
S25 Avoid contact with eyes

- Methanal (formaldehyde)
  Corrosive, Toxic Category 3 carcinogen
  $\geqslant$25% **Toxic and corrosive**
  $\geqslant$5% **Harmful**
  $\geqslant$0.2% **Irritant**
  MEL 2.5 mg m^{-3} (STEL and LTEL)
  R23/24/25 Toxic by inhalation, in contact with skin and if swallowed
  R34 Causes burns
  R40 Possible risk of irreversible effects
  R43 May cause sensitisation by skin contact
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  S51 Use only in well-ventilated areas
- Methanoic acid
  Corrosive
  Corrosive >2 M
  Irritant >0.5 M
  OES: 9.6 mg m^{-3} (LTEL)
  R35 Causes severe burns
  S23 Do not breathe gas/fumes/vapour/spray
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Methanol
  Highly flammable, Toxic
  OES: 266 mg m^{-3} (LTEL) 333 mg m^{-3} (STEL)
  R11 Highly flammable
  R23/25 Toxic by inhalation and if swallowed
  S7 Keep container tightly closed
  S16 Keep away from sources of ignition. No smoking
  S24 Avoid contact with skin
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Methoxybenzene (anisole)
  Flammable
  R10 Flammable
  S16 Keep away from sources of ignition. No smoking
  S24 Avoid contact with skin
- Methylbenzene (toluene)
  Highly flammable, Harmful
  OES: 574 mg m^{-3} (STEL) 191 mg m^{-3} (LTEL)
  R11 Highly flammable
  R20 Harmful by inhalation
  S16 Keep away from sources of ignition. No smoking
  S25 Avoid contact with eyes
  S29 Do not empty into drains
  S33 Take precautionary measures against static discharges
- Methyl 2-methylpropenoate (methyl methacrylate)
  Highly flammable, Irritant
  OES: 416 mg m^{-3} (STEL) 208 mg m^{-3} (LTEL)
  R11 Highly flammable
  R36/37/38 Irritating to eyes, respiratory system and skin
  R43 May cause sensitisation by skin contact
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S29 Do not empty into drains
  S33 Take precautionary measures against static discharges

- 2-methylpropan-2-ol
  Highly flammable, Harmful
  OES: 308 mg m^{-3} (LTEL), 462 mg m^{-3} (STEL)
  R11 Highly flammable
  R20 Harmful by inhalation
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
- Naphthalen-2-ol
  Harmful
  R20/22 Harmful by inhalation and if swallowed
  S24/25 Avoid contact with skin and eyes
- Nickel salts
  Harmful
  Some compounds Category 3 carcinogen
  Harmful in solution 0.5 M or more
  MEL: 0.1 mg m^{-3} (LTEL)
  R22 Harmful if swallowed
  R40 Possible risk of irreversible effects
  R42/43 May cause sensitisation by inhalation and skin contact
  S22 Do not breathe dust
  S36/37 Wear suitable protective clothing and gloves
- Nitric acid
  Oxidising, Corrosive
  0.5 M or more is **Corrosive**
  0.1 M to 0.4 M is **Irritant**
  OES: 5.2 mg m^{-3} (LTEL) 10 mg m^{-3} (STEL)
  R8 Contact with combustible material may cause fire
  R35 Causes severe burns
  S23 Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer)
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36 Wear suitable protective clothing
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Nitrogen dioxide
  Very toxic, Corrosive
  OES: 5.7 mg m^{-3} (LTEL) 9.6 mg m^{-3} (STEL)
  R26 Very toxic by inhalation
  R34 Causes burns
  S9 Keep container in a well-ventilated place
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S28 After contact with skin, wash immediately with plenty of water
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Nitrophenols
  Harmful
  R20/21/22 Harmful by inhalation, in contact with skin and if swallowed
  R33 Danger of cumulative effects
- Oxalic acid and oxalates
  see ethanedioic acid
- Pentanols (amyl alcohol)
  Harmful, Flammable
  R10 Flammable
  R20 Harmful by inhalation
  S24/25 Avoid contact with skin and eyes
- Petroleum spirit
  Highly flammable (80 °C and above)
  R11 Highly flammable

S9 Keep container in a well-ventilated place
S16 Keep away from sources of ignition. No smoking
S24/25 Avoid contact with skin and eyes
S29 Do not empty into drains
S33 Take precautionary measures against static discharges

- Phenol
  Toxic, Corrosive
  Avoid using this compound whenever possible.
  OES: 39 mg m^{-3} (STEL) 20 mg m^{-3} (LTEL)
  R24/25 Toxic in contact with skin and if swallowed
  R34 Causes burns
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Phenylamine (aniline)
  Toxic, Dangerous to the environment
  Category 3 carcinogen
  Avoid using this compound whenever possible.
  MEL: under review (April 1999)
  R20/21/22 Harmful by inhalation, in contact with skin and if swallowed
  R40 Possible risk of irreversible effects
  R48/23/24/25 Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
  R50 Very toxic to aquatic organisms
  S36/37 Wear suitable protective clothing and gloves
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  S61 Avoid release to the environment.
- Phosphoric(V) acid
  Corrosive
  2.5 M or more is **Corrosive**
  1 M or more **Irritant**
  OES: 2 mg m^{-3} (STEL)
  R34 Causes burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Phosphorus, red
  Highly flammable
  Explosive when mixed with oxidising substances; relatively harmless when free of white allotrope
  R11 Highly flammable
  R16 Explosive when mixed with oxidising substances
  S7 Keep container tightly closed
- Phosphorus pentachloride
  Corrosive
  OES: 0.87 mg m^{-3} (LTEL)
  R34 Causes burns
  R37 Irritating to the respiratory system
  S7/8 Keep container tightly closed and dry
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Phosphorus pentoxide
  Corrosive
  R35 Causes severe burns
  S22 Do not breathe dust
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)

- Phthalic anhydride
  see Benzene-1,2 dicarboxylic acid
- Potassium bromate(V)
  Toxic, Oxidising
  Category 2 carcinogen
  R45 May cause cancer
  R9 Explosive when mixed with combustible material
  R25 Toxic if swallowed
  S53 Avoid exposure
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Potassium chlorate(V)
  Oxidising, Harmful
  R9 Explosive when mixed with combustible material
  R20/22 Harmful by inhalation and if swallowed
  S13 Keep away from food, drink and animal feeding stuffs
  S16 Keep away from sources of ignition. No smoking
  S27 Take off immediately all contaminated clothing
- Potassium hexacyanoferrate(III) (ferricyanide)
  R32 Contact with acids liberates very toxic gas
  S22 Do not breathe dust
  S24/25 Avoid contact with skin and eyes
- Potassium hexacyanoferrate(II)
  R32 Contact with acids liberates very toxic gas
  S22 Do not breathe dust
  S24/25 Avoid contact with skin and eyes
- Potassium hydroxide (caustic potash)
  Corrosive
  0.4 M or more is **Corrosive**
  0.1 M to 0.39 M is **Irritant**
  OES: $2\,\text{mg m}^{-3}$ (STEL)
  R35 causes severe burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S37/39 Wear suitable gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Potassium iodate(V)
  Oxidising
  R9 Explosive when mixed with combustible material
  S35 This material and its container must be disposed of in a safe way
- Potassium manganate(VII) (permanganate)
  Harmful, Oxidising
  R8 Contact with combustible material may cause fire
  R22 Harmful if swallowed
- Potassium nitrate
  Oxidising
  R8 Contact with combustible material may cause fire
  S16 Keep away from sources of ignition. No smoking
  S41 In case of fire and/or explosion do not breathe fumes
- Potassium peroxodisulphate (persulphate)
  Oxidising, Harmful
  R8 Contact with combustible material may cause fire
  R22 Harmful if swallowed
  R42/43 May cause sensitisation by inhalation and skin contact
  S17 Keep away from combustible material
  S22 Do not breathe dust
  S24 Avoid contact with skin
  S37 Wear suitable gloves

- Propanal (propionaldehyde)
  Highly flammable, Irritant
  R11 Highly flammable
  R36/37/38 Irritating to eyes, respiratory system and skin
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S29 Do not empty into drains
- Propanoic acid
  Corrosive
  >4 M is **Corrosive**
  >1.5 M **Irritant**
  R34 Causes burns
  S23 Do not breathe gas/fumes/vapour/spray
  S36 Wear suitable protective clothing
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Propan-1-ol
  Highly flammable
  OES: 625 mg m^{-3} (STEL) 500 mg m^{-3} (LTEL)
  R11 Highly flammable
  S7 Keep container tightly closed
  S16 Keep away from sources of ignition. No smoking
- Propan-2-ol
  Highly flammable
  OES: 1250 mg m^{-3} (STEL) 999 mg m^{-3} (LTEL)
  R11 Highly flammable
  S7 Keep container tightly closed
  S16 Keep away from sources of ignition. No smoking
- Propanone (acetone)
  Highly flammable
  OES: value 3620 mg m^{-3}, (STEL) 1810 mg m^{-3} (LTEL)
  R11 Highly flammable
  S9 Keep container in a well-ventilated place
  S16 Keep away from sources of ignition. No smoking
  S23 Do not breathe gas/fumes/vapour/spray
  S33 Take precautionary measures against static discharges
- Propenamide (acrylamide)
  Toxic
  Category 2 carcinogen, Category 2 mutagen
  Not recommended for use in schools.
  MEL: 0.3mg m^{-3} (LTEL)
  R45 May cause cancer
  R46 May cause heritable genetic damage
  R24/25 Toxic in contact with skin and if swallowed
  R48/23/24/25 Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
  S53 Avoid exposure
  S45 In case of accident of if you feel unwell seek medical advice immediately (show the label where possible)
- Pyridine
  Highly flammable, Harmful
  OES: 16 mg m^{-3} (LTEL) 33 mg m^{-3} (STEL)
  R11 Highly flammable
  R20/21/22 Harmful by inhalation, in contact with skin and if swallowed
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
- Salicylic acid
  see 2-hydroxybenzoic acid
- Sebacoyl dichloride
  see Decanedioyl dichloride

- Silver nitrate
  Corrosive
  OES: 0.01 mg m^{-3} (LTEL)
  ⩾0.5 M is **Corrosive**
  ⩾0.2 M is **Irritant**
  R34 Causes burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Sodium
  Highly flammable, Corrosive
  R14/15 Reacts violently with water, liberating extremely flammable gases
  R34 Causes burns
  S8 Keep container dry
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Sodium borate (*di*-sodium tetraborate, decahydrate, borax)
  OES: 5mg m^{-3} (LTEL) decahydrate
  S24/25 Avoid contact with skin and eyes
- Sodium carbonate
  Irritant
  R36 Irritating to the eyes
  S22 Do not breathe dust
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
- Sodium chlorate(I) (hypochlorite)
  Corrosive
  10% available chlorine is **Corrosive**, causes burns; 5–10% available chlorine is **Irritant**, painful to skin and eyes
  R31 Contact with acids liberates toxic gas
  R34 Causes burns
  S28 After contact with skin, wash immediately with plenty of water
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Sodium chromate(VI)
  See Sodium dichromate(VI)
- Sodium dichromate(VI)
  Very toxic, Oxidising, Dangerous to the environment
  Category 2 carcinogen, Category 2 mutagen
  MEL: 0.05 mg m^{-3} (LTEL)
  R49 May cause cancer by inhalation
  R46 May cause heritable genetic damage
  R8 Contact with combustible material may cause fire
  R21 Harmful in contact with skin
  R25 Toxic if swallowed
  R26 Very toxic by inhalation
  R37/38 Irritating to respiratory system and skin
  R41 Risk of serious damage to eyes
  R43 May cause sensitisation by skin contact
  R50/53 Very toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment
  S53 Avoid exposure
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
  S60 This material and its container must be disposed of as hazardous waste
  S61 Avoid release to the environment
- Sodium ethanedioate (sodium oxalate)
  Harmful
- R21/22 Harmful in contact with skin and if swallowed
  S24/25 Avoid contact with skin and eyes

- Sodium hydrogensulphite
  Harmful
  OES: 5 mg m^{-3} (LTEL) (sulphur dioxide)
  R22 Harmful if swallowed
  R36/37/38 Irritating to eyes, respiratory system and skin
- Sodium hydroxide (caustic soda)
  Corrosive
  0.5 M or more is **Corrosive**
  0.05 M to 0.49 M is **Irritant**
  OES: 2 mg m^{-3} (STEL)
  R35 causes severe burns
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S37/39 Wear suitable gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Sodium nitrite
  Oxidising, Toxic
  R8 Contact with combustible material may cause fire
  R25 Toxic if swallowed
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Tri-Sodium phosphate(v)
  Irritant
  R36/38 Irritating to eyes and skin
- Sodium vanadate
  Toxic
  R25 Toxic if swallowed
  R36/37/38 Irritating to eyes, respiratory system and skin
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- Styrene
  Harmful
  R10 Flammable
  R20 Harmful by inhalation
  R36/38 Irritating to eyes and skin
  S23 Do not breathe gas/fumes/vapour/spray
- Sulphamic acid
  Irritant
  R36/38 Irritating to eyes and skin
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S28 After contact with skin, wash immediately with plenty of water
- Sulphur dioxide
  Toxic, Corrosive
  OES: 5.3 mg m^{-3} (LTEL) 13 mg m^{-3} (STEL)
  R23 Toxic by inhalation
  R34 Causes burns
  S9 Keep container in a well-ventilated place
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S36/37/39 Wear suitable protective clothing, gloves and eye/face protection
  S45 In case of accident or if you feel unwell seek medical advice immediately (show label where possible)
- Sulphuric acid
  Corrosive
  1.5 M or more **corrosive**
  0.5 to 1.49 M is **irritant** *(Continued)*

OES: 1 mg m^{-3} (LTEL)
R35 Causes severe burns
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S30 Never add water to this product
S45 In case of accident or if you feel unwell seek medical advice immediately (show label where possible)

- Toluene
  see Methylbenzene
- Trichloroethanoic acid
  Corrosive
  R35 Causes severe burns
  S24/25 Avoid contact with skin and eyes
  S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
  S45 In case of accident or if you feel unwell seek medical advice immediately (show label where possible)
- Zinc powder
  Highly flammable
  R10 Flammable
  R15 Contact with water liberates extremely flammable gases
  S7/8 Keep container tightly closed and dry

Appendix 3

Laboratory health and safety

You are more likely to suffer a minor injury – a cut, burn or scald – in a kitchen than in a laboratory. The reason is quite simple; we know there are hazards involved in working in a laboratory so risk assessments are made for every experiment and protective measures are taken to control those risks. In chemistry lessons most risks arise from the use of chemicals, but some other practical activities have associated hazards (for example, micro-organisms or electricity).

HAZARDS

In boxes like this you will find important safety instructions.

Laboratory safety is about minimising exposure to risk as well as protecting yourself from the results of mishaps. When you do an experiment that involves the production of an unpleasant gas like nitrogen dioxide, you should think about using small quantities of reagents and containing the gas in a fume cupboard, as well as thinking about what you might need to do if the gas is produced unexpectedly fast.

You will be healthy, safe and successful in your laboratory work provided:

- you plan your work, taking note of the health and safety information provided
- you wear eye protection and take other recommended precautions
- you carry out all instructions thoughtfully and correctly.

All experiments in this course have been checked for health and safety implications, but when you are going to do an investigation of your own you will be expected to carry out a Risk Assessment (and have it checked by your teacher before starting any practical work).

Risk Assessment

Risk Assessments are most conveniently made on a standard form and an example is given on sheet S2. The procedure is straightforward when you realise that the intention is to protect you from any risks. The steps in making an assessment are:

1. **Write down the procedures** you will be using (chemicals used or made, quantities, concentrations, techniques; any non-chemical hazards).
2. Use reference sources to **identify any hazardous chemicals** you are planning to use or make. The appropriate warning symbols should be on reagent bottles and in suppliers' catalogues.
3. **Record the nature of the hazards** involved and the way you might be exposed to the hazard. There are standard reference sources with this information such as the 'Hazcards' published by CLEAPSS.
4. **Decide what protective or control measure to take** so that you can carry out your practical work healthily and in safety.
5. Find out how to **dispose** of any hazardous residues from your practical work.

The protective measures you need to take will depend on your laboratory as well as your experiment. The experiments in this course have been assessed for use in a well-lit, well-ventilated and uncrowded laboratory. Where conditions are different additional protective measures may be necessary.

Risk Assessment form

Title of the experiment			
Outline of the procedures			
Hazardous substances being used or made	**Nature of the hazards (e.g. toxic, flammable)**	**Quantities and concentrations being used or made**	**Control measures (precautions)**
Any non-chemical hazards and precautions to be taken			Signed (student) …………………………………… Signed (teacher) ……………………………………
Disposal of residues			Date:

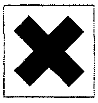
Good laboratory practice

As well as the specific protective measures to be taken when hazardous chemicals are being used, there are also general procedures to be observed in all laboratories at all times.

- **Long hair should be tied back**, and you should not wear 'wet look' hair preparations, which can make hair unusually flammable. **Do not let ties, scarves or cardigans hang freely**, where they could be a fire hazard. We strongly recommend the wearing of laboratory coats to avoid damage to clothing.
- **Eating, drinking and chewing are not permitted in laboratories.** It is in fact contrary to the COSHH Regulations to permit eating, drinking or indeed smoking or the application of cosmetics in any area which could be contaminated with hazardous chemicals.
- **Eye protection should be worn whenever a Risk Assessment requires it**, or whenever there is any risk to your eyes. This includes, for example, washing up at the end of the lesson and even when you have finished practical work, as long as other students are still working.
- You should find that the chemicals that you are going to use are in **clearly labelled stock bottles**, with the name of the chemical, any hazards, and the date of acquisition or preparation. In taking liquids from a bottle, remove the stopper with one hand, and keep the stopper in your hand whilst pouring from the bottle. This way, the stopper is likely to be replaced at once, and remain uncontaminated. Pour liquids from the opposite side to the label, so that it does not become damaged by corrosive chemicals.
- Study carefully the best **techniques for safely heating chemicals**. Small quantities of solid can be heated in test tubes; liquids present greater problems, because of the risk of 'bumping' and 'spitting'. Boiling tubes are safer than test-tubes (because of their greater volume), but should be **less than one-fifth full**. You are fairly likely to point test tubes away from your own face, but do remember the need to do the same for your neighbours. **Use a water bath to heat flammable liquids; NEVER use a naked flame**.
- When testing for the odour of gases the gas should be contained in a test tube (not a larger vessel) and the test tube held about 10–15 cm from your face, pointing away. Fill your lungs with air by breathing in, and then cautiously sniff the contents of the test tube, by using a hand to waft the vapours cautiously to your nose. Slowly bring the test tube nearer, if necessary. **If you are asthmatic you should not smell gases** without checking with other students because gases such as chlorine are harmful.
- **You must always clear up chemical spillages straight away**. Whilst a few spills may need chemical neutralisation or similar treatment, most minor spills can be dealt with by a damp cloth. (Don't forget to rinse it afterwards.)
- In the event of getting a chemical in your eye, or on your skin, **flood the area with large quantities of water at once**. Keep the water running for at least 10 minutes (20 minutes for alkalis in the eye). Rubber tubing on a tap is the most convenient way of doing this. Even if the chemical reacts exothermically with water, provided a large quantity of water is used, the heating effect will be negligible.
- A heat burn from apparatus, scalding liquids or steam is treated by **immersing the area in cool water** for at least 10 minutes. Preferably use running water from rubber tubing, fixed to a tap.
- **Report all accidents at once**.

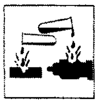
SAFETY

The most common mishaps in the laboratory involve splashes from liquids (especially in the eye) and burns from hot apparatus.



HARMFUL
or IRRITANT

HIGHLY
FLAMMABLE



CORROSIVE

OXIDISING

TOXIC

EXPLOSIVE

DANGER

EYE PROTECTION
MUST BE WORN

DANGEROUS FOR
THE ENVIRONMENT

Appendix 4

Help with mathematics

1 Direct proportion

Some calculations in chemistry involve *direct proportion*. For example, the number of moles of a substance used in an experiment is directly proportional to the mass that was used. If you want to *double* the number of moles you have to *double* the mass you use. If you want to *treble* the number of moles used you have to *treble* the mass you use. This is an example of direct proportionality and the symbol $\propto$ has the meaning 'is proportional to', so:

number of moles $\propto$ mass of substance

Whatever factor we increase or decrease the number of moles by, the mass will increase or decrease by the same factor.

Example 1

2 mol calcium has a mass of 80 g, then
6 mol (= **3** × 2 mol) has a mass of **3** × 80 g = 240 g (scale factor 3);
or 0.4 mol (= **0.2** × 2 mol) has a mass of **0.2** × 80 g = 16 g (scale factor 0.2).

You can do calculations involving direct proportion by the following method.

Example 2

If 1.8 cm^3 of mercury has a mass of 24.5 g; you can work out the mass of 1 cm^3 of mercury as a first stage because the mass is directly proportional to its volume. Then you can work out the mass of mercury in any other volume, such as 500 cm^3.

1.8 cm^3 of mercury has a mass of 24.5 g
you divide both quantities by 1.8 to find the mass of 1 cm^3 of mercury:
1 cm^3 has a mass of 13.61 g (24.5 g ÷ 1.8)
To find the mass of 500 cm^3 multiply both by 500.

500 cm^3 has a mass of 6800 g, to 2 significant figures (13.61 × 500)

COMMENT

Significant figures (SF) are explained in the next section.

To get a feel for the answer to a calculation you can do it with easier numbers first.

Example 3

You can find a rough estimate of the answer to the mercury problem by working out the mass of 500 cm^3 using the approximation that there are 25 g in 2 cm^3. The volume has increased by a factor of 250, so the mass will also increase by a factor of 250. The mass will be approximately 25 × 250 = 6250 g.

Approximating like this with easier values may help you to see the method to use. For example, here the multiplying factor was found to be dividing 500 cm^3 by 2 cm^3. Using the actual values the multiplying factor is 500 cm^3 ÷ 1.8 cm^3 = 277.78.

2 Inverse proportion

Other calculations involve inverse proportionality. An example involving inverse proportion is the time taken for sulphur to precipitate from sodium thiosulphate solution when acid is added. When the concentration of thiosulphate is increased, the time for precipitation decreases.

Increasing the thiosulphate concentration by a factor of 3 reduces the time by $\frac{1}{3}$. For this reaction, time is inversely proportional to concentration. This is written as

$$\text{time} \propto \frac{1}{\text{concentration}}$$

Example 4

If a concentration of 2 M gives a time of 50 seconds then a concentration of 6 mol (= **3** × 2 M) gives a time of $\frac{1}{3} \times 50$ seconds (= 16.67 s) a concentration of 0.4 M (**0.2** × 2 M) gives a time of $\frac{1}{0.2} \times 50$ seconds (= 250 s)

QUESTIONS

1 4.63 g of copper are precipitated by 4.07 g of iron.
  a What mass would be precipitated by 55.85 g of iron (1 mol)?
  b Are the masses directly or inversely proportional to each other?
  c What is your first estimate of the answer?

2 100.2 g of cyclohexanol (1 mol) should form 82.1 g of cyclohexane (1 mol). How much cyclohexane should you obtain from 15.0 g of cyclohexanol?

3 The density of cyclohexanol is 0.962 g cm^{-3}. What is the volume of 100.2 g (1 mol)?
  [density = mass ÷ volume ∴ volume = mass/density]

4 The mass of 1 mol of sodium hydroxide is 40 g. What is the mass of:
  a 2 mol
  b 0.1 mol
  c 0.02 mol
  d 0.17 mol?

5 What is the mass of sodium hydroxide dissolved in
  a 1 dm^3 of a 2 M solution
  b 100 cm^3 of a 0.1 M solution
  c 35 cm^3 of a 0.02 M solution
  d 182 cm^3 of a 0.02 M solution?

ANSWERS TO QUESTIONS

1 a 63.5 g to 3 significant figures
  b directly proportional

2 12.3 g to 3 significant figures

3 104 cm^3 to 3 significant figures

4 a 80 g b 4 g c 0.8 g d 6.8 g

5 a 80 g b 0.4 g c 0.028 g d 0.15 g (to 2 SF)

3 Significant figures

The most accurate value we have for the molar mass of iodine, I, is 126.9045.

The first figure **1**26.9045 occupies the highest place value and is called the most significant figure, abbreviated to SF, or the first significant figure, 1SF.
the second most significant figure is 1**2**6.9045
the third most significant figure is 12**6**.9045, and so on.

When you do not need the value as accurately as 126.9045 you can quote it to a number of significant figures.

$126.9045 \xrightarrow{\text{is}}$ **100** to one significant figure (1SF)

$126.9045 \xrightarrow{\text{is}}$ **130** to two significant figures (2SF)

$126.9045 \xrightarrow{\text{is}}$ **127** to three significant figures (3SF)

Notice that 126.9045 to two significant figures is 130 because 126 is nearer to 130 than 120.

The rule is that when the next significant figure is less than five (4, 3, 2, 1 or 0) round down, when it is five or more (5, 6, 7, 8 or 9) round up.

However you will often use molar masses as exact numbers and should not adjust your answers for their apparent number of significant figures. Thus molar masses are usually quoted as H = 1, C = 12 g mol^{-1} but these are exact values and should not be treated as having only 1SF and 2SF.

In chemistry, another rule you will need is:

Zeros at the end of a number are significant figures when they occur after a decimal point.

130	130.0
↑	↑
This number has 2SF; chemists would not normally consider the zero a significant figure	This number has 4SF; the zero after the decimal point is a significant figure

You are most likely to need this rule when doing calculations involving the concentrations of solutions. The zeros are used to describe the accuracy with which the solution was prepared.

Example 5

5.844 g of sodium chloride (4SF) in 100.0 cm^3 of solution (4SF) would be described as 1.00 M (4SF).
0.02 M is only accurate to 1SF
0.020 M is accurate to 2SF
0.0200 M is accurate to 3SF

When reporting the results of calculations you need to think about how many significant figures there should be in the answer. You need to identify the quantity used in the calculation with the **least number** of significant figures; your final answer should have the **same number** of significant figures.

After a titration you might need to calculate the mass of dissolved reactant. If you used a pipette to measure 25.0 cm^3 of 0.0200 M acid and found that the end-point was 21.3 cm^3 your numbers all have 3SF so you should state your answer to 3SF.

But if the concentration of acid was 0.020 M your answer can only have 2SF. And if you used a measuring cylinder rather than a pipette you would have to decide how to record the volume of acid: 25 cm^3 to 2SF would probably be appropriate, with your answer restricted to the same number of significant figures.

You should only adjust your **final** answer to an appropriate number of significant figures and not the starting quantities or intermediate answers. Otherwise you may not arrive at the best answer.

For example:

$$27 \times 16 \times 2 = 858$$
$$= 900 \text{ to 1SF}$$

but adjusting the starting number to 1SF gives

$$30 \times 20 \times 2 = 1200$$

COMMENT

NAUTE

No approximation until the end.

QUESTIONS

1 Round the molar mass of iron 55.847 g mol^{-1} to:
a 1SF b 2SF c 3SF d 4SF

2 Round the Faraday constant 96 484.6 C mol^{-1} to:
a 1SF b 2SF c 3SF d 4SF

3 Round the solubility of nickel bromide 0.516 mol/100 g to:
a 1SF b 2SF

4 Round the solubility of iron(II) sulphate 0.103 mol/100 g to:
a 1SF b 2SF

5 Round the Avogadro constant $6.02204531 \times 10^{23}$ mol^{-1} to:
a 1SF b 2SF c 3SF d 4SF
e 5SF f 6SF g 7SF

ANSWERS TO QUESTIONS

1 a 60 g mol^{-1} b 56 g mol^{-1} c 55.8 g mol^{-1} d 55.85 g mol^{-1}

2 a 100 000 C mol^{-1} b 96 000 C mol^{-1} c 96 500 C mol^{-1} d 96 480 C mol^{-1}

3 a 0.5 mol/100 g b 0.52 mol/100 g

4 a 0.1 mol/100 g b 0.10 mol/100 g

5 a 6×10^{23} mol^{-1} b 6.0×10^{23} mol^{-1}
c 6.02×10^{23} mol^{-1} d 6.022×10^{23} mol^{-1}
e $6.022\,0 \times 10^{23}$ mol^{-1} f $6.022\,05 \times 10^{23}$ mol^{-1}
g $6.022\,045 \times 10^{23}$ mol^{-1}

4 Indices

A common method of writing down very large and very small numbers is to use indices (singular: index).

Numbers can be written down as 'powers of a base number' such as 1×10^{23}.

When the base number is 10 the form of expression is called standard form with the number in front of the powers of 10 always being between 1 and 10 [or equal to 1].

Example 6

The molar mass of iodine 126.904 5 becomes $1.269\,045 \times 10^2$ in standard form and the number of cubic metres in a pint is 0.000 568 2 which in standard form is 5.682×10^{-4}.

There are four rules that you need to learn in order to deal with indices correctly when you meet them in calculations:

Rule 1 A positive index means $n^3 = n \times n \times n$

Rule 2 A negative index means $n^{-3} = 1/n^3 = \dfrac{1}{n \times n \times n}$

Rule 3 A fractional index means $n^{1/3} = \sqrt[3]{n}$

Rule 4 A zero index means $n^0 = 1$

From these rules we can derive some guidelines for working out the answers to problems involving indices:

1 To multiply add the indices
$$10^5 \times 10^3 = (10 \times 10 \times 10 \times 10 \times 10) \times (10 \times 10 \times 10) = 10^8$$

2 To divide subtract the indices
$$10^5 \div 10^3 = \frac{(10 \times 10 \times 10 \times 10 \times 10)}{(10 \times 10 \times 10)} = 10^2$$

To work out the value of fractional indices take the root: $10^{1/3} = \sqrt[3]{10} = 2.15$ (3SF)

QUESTIONS

1 Write down the following numbers in standard form:

a 1 250 **b** 145 623 **c** 57

d 1000 **e** 0.56 **f** 0.0070

2 Work out the answers to these problems, using the values in the *Book of data* (page 15).

- **a** Multiply the elementary charge on the electron by the Avogadro constant. Which other constant have you calculated?
- **b** Multiply the Boltzmann constant by the Avogadro constant. Which other constant have you calculated?
- **c** Divide the rest mass of the proton by the rest mass of the electron.

ANSWERS TO QUESTIONS

1 **a** 1.25×10^3 **b** 1.45623×10^5 **c** 5.7×10^1

d 1×10^3 **e** 5.6×10^{-1} **f** 7×10^{-3}

2 **a** $1.602\,189\,246 \times 10^{-19} \times 6.022\,045\,31 \times 10^{23}$
$= 96484.56235 = 9.65 \times 10^4\ \text{C mol}^{-1} = 1$ Faraday

b $1.380\,662\,44 \times 10^{-23} \times 6.022\,045\,31 \times 10^{23}$
$= 8.314411771 = 8.31 =$ Gas constant R

c $1.672\,648\,586 \times 10^{-27} \div 9.109\,534\,47 \times 10^{-31}$
$= 1836 = 1.84 \times 10^3$

---

5 Logarithms

Logarithms are a special case of indices, called common logarithms, abbreviated to log, when the base number is 10.

$10^2 = 100 \longrightarrow \log_{10}100 = 2$

All numbers can be expressed as ten raised to a power, e.g.

$100 = 10^2$
$3 = 10^{0.477}$

The power is the common logarithm (or base 10 logarithm) of the number so

$\log_{10}100 = 2$
$\log_{10} 3 = 0.477$

Some more examples

$10^4 = 10\,000 \longrightarrow \log 10\,000 = 4$

$10^{-2} = 0.01 \longrightarrow \log 0.01 = -2$

$10^{-4} = 0.0001 \longrightarrow \log 0.0001 = -4$

Converting numbers to their common logarithms

To find the logarithm of 123.4 on most calculators use the log button, to give the answer 2.091315.

$\log(123.4) = 2.091$ to 4SF

which is the equivalent of

$123.4 = 10^{2.091}$

Notice that the logarithm of fractional values are negative.

$\log(0.009876) = -2.005$ to 4SF

Converting logarithms to their numbers

To find the value that has a logarithm of 3.5 use the 10^x button.

$\log x = 3.5$
so $x = 10^{3.5}$
$= 3200$ (2SF)

If $\log x = -1.5$, $x = 10^{-15}$ and $x = -0.032$

QUESTIONS

1 Convert these numbers to logarithms

75, 7.5, 0.75, 0.00075, 7.5×10^4, 7.5×10^{-4}

2 Convert your answers to **1** back to numbers.

3 Write down the exact procedure you used on your calculator to get the correct answers to 1 and 2.

4 Use the relationship pH = $-\log[H^+(aq)]$ to calculate the pH of solutions in which $[H^+(aq)]$ is

a 0.5 mol dm^{-3} **b** 0.0005 mol dm^{-3}
c 5×10^{-6} mol dm^{-3} **d** 5×10^{-12} mol dm^{-3}.

5 Convert your answers to **4** back to $[H^+(aq)]$.

ANSWERS TO QUESTIONS

1 1.875, 0.875, −0.125, −3.125, 4.875, −3.125

2 74.99, 7.499, 0.750, 7.50×10^{-4}, 7.499×10^4, 7.499×10^{-4}

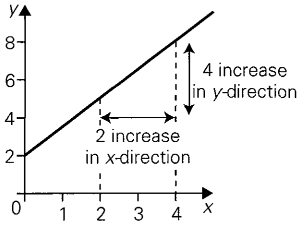
3 (1) Press 'log' button log
then input number log 75
then press EXE or ENTER 1.87506 1263
(2) Press shift log button 10^x
then input number 10^x 1.875
then press EXE or ENTER 74.98942093

4 **a** 0.301 **b** 3.301 **c** 5.301 **d** 11.301

5 **a** 0.500 **b** 0.0005 **c** 5×10^{-6} **d** 5×10^{-12}

6 Graphs

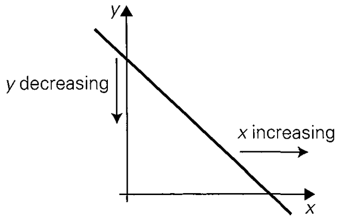
Measuring gradients



Gradient is given by increase in y-direction divided by increase in x-direction.

Gradient $m = \frac{4}{2} = 2$

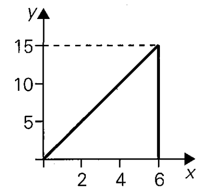
Note that if y decreases as x increases, the gradient is negative.



QUESTIONS

What are the gradients of the following lines?

1



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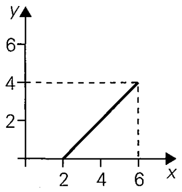

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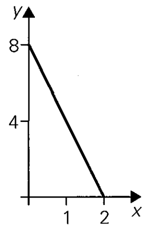

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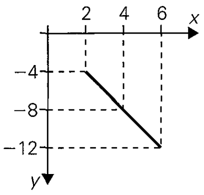


ANSWERS TO QUESTIONS

1 $\frac{15}{6} = 2.5$

2 $\frac{4}{4} = 1$

3 $\frac{-8}{2} = -4$

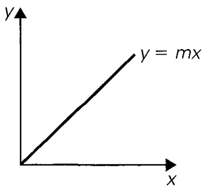
4 $\frac{-8}{4} = -2$

Recognizing graphs

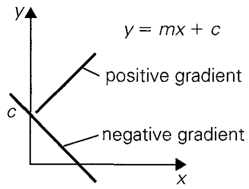
It is useful to be able to recognize certain shapes of graph. Where appropriate, the examples below show how to change the quantities on the axes to produce a straight line graph.

A y is directly proportional to x ($y \propto x$)
m = gradient
$y = mx$

Note that this is a straight line passing through the origin.



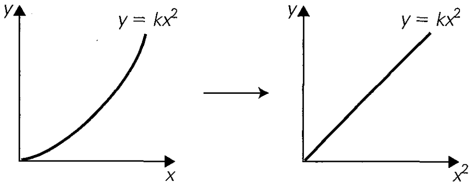
B Linear relationship between y and x
m = gradient
c = intercept on y-axis
$y = mx + c$



C y is proportional to x^2 ($y \propto x^2$)
$y = kx^2$

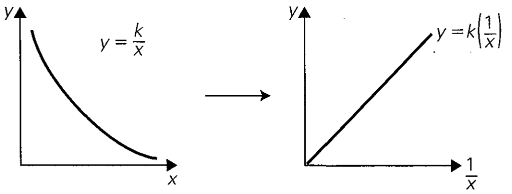
Note that this curve passes through the origin. $y = 0$ when $x = 0$.

If $y = kx^2$, plotting y against x^2 will give a straight line passing through the origin with gradient k.



D y is inversely proportional to x ($y \propto \frac{1}{x}$)

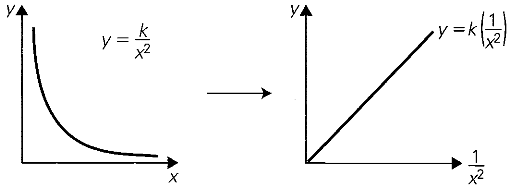
$$y = \frac{k}{x}$$



If $y \propto \frac{1}{x}$, plotting y against $\frac{1}{x}$ will give a straight line passing through the origin with gradient k.

E y is inversely proportional to x^2 ($y \propto \frac{1}{x^2}$)

$$y = \frac{k}{x^2}$$



If $y = k/x^2$, plotting y against $1/x^2$ will give a straight line passing through the origin with gradient k.

Index

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