NUFFIELD ADVANCED SCIENCE

CHEMISTRY

TEACHERS GUIDE

Third Edition

LONGMAN

Nuffield Advanced Science

Chemistry
Teachers' guide

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Note
All references to the *Book of data* are to the **revised** edition which is part of the present series.

Contents

Foreword

The first Nuffield Advanced Science series appeared in 1970, nearly twenty-five years ago. They, and their successors, were devised by experienced teachers, working with university teachers and the examination boards, and subjected to extensive trials in school classrooms. They were quickly credited with introducing a new element of intellectual excitement into the work of A-level students. Later editions, in 1984 and now in 1994, have held firm to the original Nuffield principles.

All three editions of the Chemistry materials have been based in a common philosophy: that the science teacher must transmit an understanding of what 'being scientific' means to the scientist; that science is process; and that knowledge best grows within these two concepts.

Much has changed in schools since 1984. The National Curriculum for Science has been introduced, and the GCE has been replaced by the GCSE. Many students begin A-level courses with a 'Double Science' qualification, and syllabuses have become subject to central accreditation and to a specified core content. These are all challenges, to which this far-reaching revision responds, to offer the same Nuffield principles to another generation of teachers and students.

In 1961, the Nuffield Foundation made a far-sighted decision to support the initiative of science teachers for curriculum development in the debates of their professional association, now the Association for Science Education.

The first editions were a fruit of this support, and the second editions were written under the aegis of the Nuffield–Chelsea Curriculum Trust. This new edition will once again be supported by the Nuffield Foundation.

The debt of this new edition to the pioneers of the 1960s – especially, in the case of the Chemistry project, to the late Frank Halliwell, Ernest Coulson and Gordon van Praagh – is apparent on almost every page. Much of their original planning was done walking through the lovely gardens of Nuffield Lodge in London, in a quiet search for excellence. Today we may envy them for the atmosphere in which they worked, but we must be grateful that they were given that opportunity.

The editors' response to the new specifications has been twofold. First, some new material has been added so as to guarantee full coverage of the new core, at the same time shortening or omitting other material that is not now required. Secondly, one entirely new unit has been added which aims to help students through the transition from their experience in 'Double Science' to the more specialized intellectual world of A-level Chemistry.

I should like to express the gratitude of the Trust to all those who have created this new edition: to the General Editor, Michael Vokins, to his colleague Bryan Stokes and to their dedicated team of writers; to the staff of the Trust's publications unit; and to our publishers, Longmans, for their professional and intellectual support.

Kevin Keohane
Chairman, Nuffield–Chelsea Curriculum Trust

Introduction

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

The core publications of the third edition are one *Students' book* and one *Teachers' guide* for the two years of the course. They are supported by a *Book of data* that 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.

Publications

The complete list of publications is as follows.

For the student
Students' book:
Topics 1 to 18 of the basic course in one volume, with two appendices 'Help with mathematics' and 'Laboratory safety'.
Book of data.
The Special Studies:
Biochemistry, Chemical engineering, Food science (revised edition, 1994), *Materials science* (new edition, 1994), *Mineral process chemistry.*

For the teacher
Teachers' guide:
A guide for teachers and technicians to Topics 1 to 18 of the basic course. There is a section on 'Hazardous laboratory chemicals'.
The Special Studies:
Teachers' guides: individual *Teachers' guides* are published for each of the Special Studies.

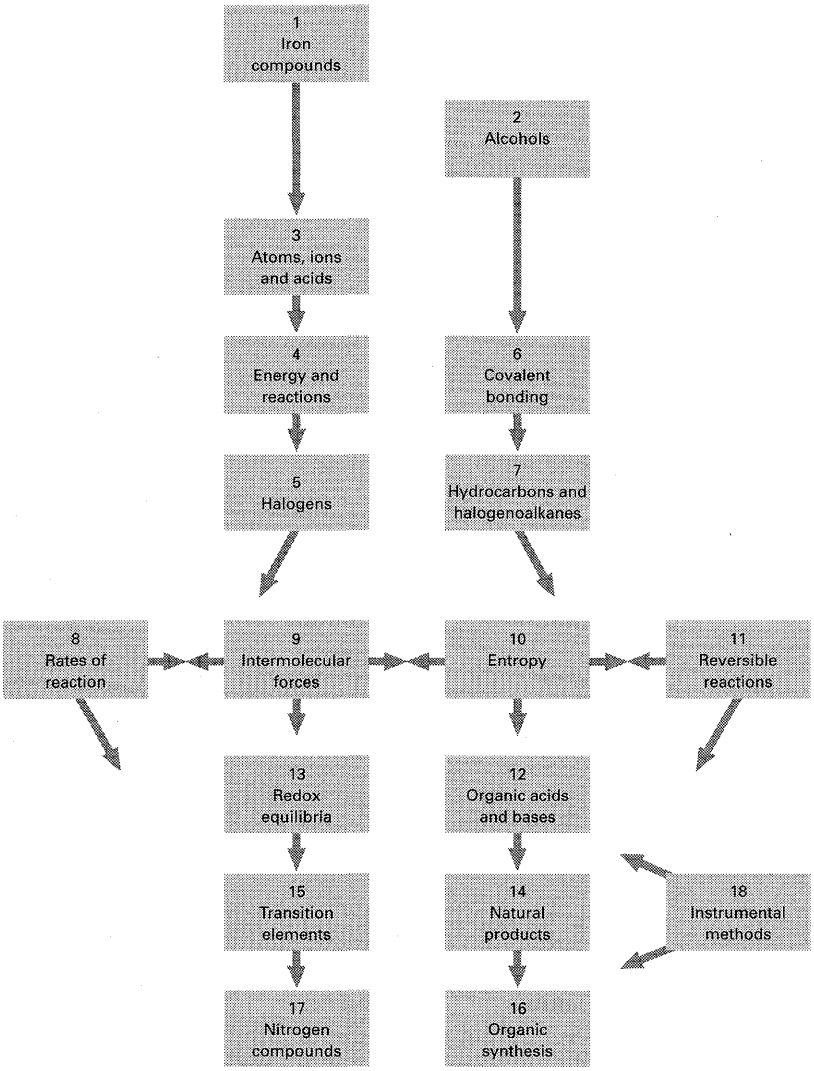
The timing of the course

In planning the course we have assumed that 5 hours of contact time are available per week for teaching the main content of the Topics and a Special Study. On that basis we estimate that the course requires 55 weeks, with the remaining time from two academic years used for investigations, tests, revision, group work and reviewing homework, including answers to questions and Study Tasks. A student will be occupied for 300 hours in total, including homework.

Topic	Title	Timing/weeks
1	Iron compounds: an introduction to inorganic chemistry	4
2	Alcohols: an introduction to organic chemistry	3
	Reading task 1: The carbon cycle	–
3	Atoms, ions and acids	3
4	Energy and reactions	3
5	The halogens and redox reactions	4
	Reading task 2: Origin of the chemical elements	–
6	Covalent bonding	2
7	Hydrocarbons and halogenoalkanes	4
8	How fast? Rates of reaction	3
	Reading task 3: Photochemistry	–
9	Intermolecular forces and solubility	3
10	Entropy	1
11	How far? Reversible reactions	4
12	Carbon compounds with acidic and basic properties	3
13	Redox equilibria and electrochemical cells	2
14	Natural products and polymers	3
	Reading task 4: Diabetes	–
15	The transition elements	4
16	Organic synthesis	2
	Reading task 5: Drugs	–
17	Nitrogen compounds	3
	Reading task 6: Nitrates in agriculture	–
18	Instrumental methods	–
A Special Study		4
	Total	55 weeks

Alternative routes through the course

The subject matter of this course could have been arranged in many different ways and the order in which the Topics are taught is a matter for the teachers involved. The sequence adopted in this edition is based on the views of experienced teachers of the course. It is a logical and workable order and provides students with variation between Topics that are based on extensive experimental work and those that are inevitably more book based. However, the division of Topics into sections makes the course sufficiently flexible for a variety of rearrangements to be adopted relatively easily. Such rearrangements can be within Topics or between Topics. Much will depend on the local situation and the pre-A-level background of the students. When two teachers are sharing the teaching of a group of students an alternative pathway is often adopted.



After the two introductory Topics, there are two strands which could be taught in parallel – an ionic strand followed through Topics 3, 4 and 5 and a covalent strand developed through Topics 6 and 7.

The central phase of the course introduces a variety of new ideas and these could be taught in any order with some adjustments to the content: rates of reaction, intermolecular forces, entropy and reversible reactions are covered in Topics 8 to 11.

The final phase of the course aims to increase students' knowledge and develop their understanding by the application of theories in new contexts. The course again has two strands which could be taught in parallel: organic in Topics 12, 14 and 16; inorganic in Topics 13, 15 and 17. The final Topic on instrumental techniques is support material to be consulted whenever necessary.

A further factor which needs to be borne in mind is the choice of Special Study.

The *Students' book*

Like its predecessors, the *Students' book* contains instructions for practical work, interpretations of the experiments, reading tasks, and questions to help students develop their understanding of chemical ideas. The content of the course is divided into 18 Topics; each Topic has several features in common which are used repeatedly during the course to help students organize their learning.

There are **Review Tasks** in which we suggest that students work in small groups when asked to recall facts and ideas they should have met already. Learning can be a co-operative activity; sharing ideas will help the students to learn.

Sometimes there is a short **comment**. These comments will be extra information: sometimes curious facts, and sometimes more advanced explanations that students may find helpful but are not part of the main development of the course; students are not normally expected to memorize the information in the comments.

There are **questions** and **Study Tasks** in each Topic. Questions are usually short and planned to guide students through the interpretation of their experimental results or other parts of the work. Study Tasks are more extensive and are designed to develop and also test students' understanding, particularly their ability to extract appropriate information from their reading and report their findings clearly in well-expressed English. A number of the Study Tasks will be useful as homework.

There are also 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 organized this book on that 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 improve their understanding.

⚠ At the beginning of most experiments there is information about **safety**, listing the specific hazards involved in that experiment. There is an appendix on 'Laboratory safety' which provides general guidelines for safe working in laboratories and notes on how to carry out risk assessments.

In most Topics there is an **investigation**. 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 get 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 and we recommend that students carry out brief trial tests before attempting to plan the details of their work.

Topics end with a **summary** which lists the facts and ideas students should know when they have learnt the Topic fully. Sometimes we suggest ways in which they might try to organize an outline of a Topic so that they concentrate on learning the main ideas before adding the detail. They should be encouraged to add some fun – cartoons, verses, coloured charts can all help them learn chemistry.

After each Topic there are **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 examination papers set in the past. Good answers to the examination questions will require a broad understanding of the Topic, so they may be rather difficult if attempted without a period for review and revision of the whole Topic.

Reading Tasks are provided as background material to demonstrate the great range of activities in which chemists are involved. We hope they will be read for interest rather than as work. The information that they contain is not necessary for the study of the course, but we have included questions at the end of each reading task to encourage close and thoughtful reading. There is usually one question about the social implications of chemistry: these questions could be used for debating the issues involved.

The naming of chemicals and the use of units in this course follows the recommendations of the Association for Science Education, which are published in *Chemical nomenclature, symbols, and terminology* (third edition 1985). Short non-systematic names have been used in a few cases of natural products 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 endanger 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 section on 'Hazardous laboratory chemicals' is cross-referenced with both systematic and non-systematic names.

The *Teachers' guide*

This book is designed to guide you and your laboratory technician through the 18 Topics in the *Students' book.*

Each Topic starts with a summary of content, estimates of the teaching time needed, and teaching objectives. Most sections of Topics include a **suggested treatment** which is a guide to teaching the material, and there are answers to questions and answers to study tasks, corresponding to tasks set to the students during the Topic. At the end of each Topic there are answers to the review questions and examination questions in the *Students' book.* Answers are provided to all these questions, but those provided for the examination questions should be taken as only a guide to what would be an acceptable answer in an operational A-level examination. In a number of cases an examination question has 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 for each experiment there is information about the **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 include alternative experiments not given in the *Students' book.* The instructions for these experiments can be photocopied for use in your laboratory if you want to use them.

Although all experiments are, of course, investigative in nature, some have been written in the *Students' book* without experimental detail so that they can be set as **investigations**. These are listed in the contents summary of each Topic in this book in *italics*. In some instances you will find more detailed alternatives to the investigations in this book, which you may prefer to use instead.

Hazardous laboratory chemicals is a section at the end of this book which gives further information about the nature of the 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.

Special Studies

Towards the end of the course, provision is made for a four-week study of a science which is based on chemical principles. The principal purpose of this section of the course is to enable students to see something of the scope of a related subject, and to appreciate its dependence upon chemical principles. In doing this, students automatically revise several of the basic concepts of chemistry: structure and its relation to physical and chemical properties; equilibria; rates; and energy changes. The Studies therefore also provide a valuable means of recapitulation, not by going over the old ground again but by revising the ideas in a new context. The Studies are also designed to show something of the applications of the subjects, and of their social and economic effects. We regard this as important because students should come to regard chemistry as *useful* knowledge – useful in the mining industry, 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*.

Each student has to complete one Special Study. There is a list of the Special Studies available at the beginning of this introduction. A centre can also be examined in a Special Study of its own devising; details of the procedure to be followed can be obtained from the University of London Examinations and Assessment Council.

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 timetabled 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 individualized 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 the selected Special Study is to occupy in the teaching sequence: *Biochemistry* and *Food science* are probably best taught after Topic 14, while *Mineral process chemistry* can be taught after Topic 13.

The Topics

There have been significant, but not drastic, changes in the content and presentation of the course from the revised edition. One of the aims was to start at the level of knowledge and understanding of Chemistry that can be expected from students who have studied Double Award Science in the National Curriculum, and not a full Chemistry course. Standards on entry are bound to vary greatly from student to student – some may need an extended treatment of the new introductory Topics 1 and 2, while others may find much of the material is straightforward revision. For all students we have aimed to provide a framework of interesting practical work at the start of their sixth-form studies.

Topic 1 is a completely new Topic designed to revisit and reinforce essential chemical ideas from the National Curriculum through the study of some reactions of iron compounds. Iron was chosen as its compounds have varied and colourful reactions: opportunities are provided to teach about molar quantities, oxidation–reduction, energy, and bonding. We have provided an outline that should be sufficient for revision, but some students may need a more detailed programme to match their specific needs.

In the second introductory Topic the reactions of alcohols are used to introduce basic ideas about organic compounds. Alcohols were selected for this introduction because, unlike alkanes, their chemistry is rewarding in terms of the variety of changes that can be observed. Substitution and esterification are left to later Topics, so the reactions studied are essentially a continuation of the oxidation–reduction theme of Topic 1.

The next three Topics introduce ideas about atomic structure, ionic bonding, acids and bases, enthalpy changes, and oxidation numbers. This stage of the course closes with a review of all these ideas in Topic 5, in the context of halogen chemistry.

Topic 6 aims to develop students' understanding of the covalent bond; in Topic 7 students' knowledge of organic compounds is extended to hydrocarbons and halogenoalkanes in a treatment that is very little changed from the previous edition.

Topics 8 to 11 introduce an important range of ideas that will be used to interpret the reactions that are studied later in the course – rates of reaction (which takes us to about the mid-point of the course), intermolecular forces and solubility, entropy and equilibria. Intermolecular forces are presented in the logical order of van der Waals, dipole–dipole and lastly hydrogen bonding. The previous approach to teaching entropy was to 'drip-feed' the ideas, and parts of the story were included in several Topics. A number of schools have been teaching entropy as a coherent Topic and that approach has been adopted. The ideas are introduced using some experiments involving endothermic reactions and the development is less mathematical than previously. The link between entropy changes and equilibrium includes an experimental study of the nitrogen dioxide/dinitrogen tetroxide system.

The development of carbon chemistry is continued in Topics 12, 14 and 16 in a way that will be familiar from previous editions, except for a new treatment of polymers and a fuller discussion of organic synthetic routes.

More ideas useful to the understanding of inorganic reactions are introduced in Topic 13. After a straightforward treatment of electrode potentials, the link to free energy is made in a non-mathematical approach. The value of these ideas is then demonstrated in the context of the chemistry of transition elements in Topic 15 and non-metals, taking nitrogen as our example, in Topic 17.

The nature of investigations

There is general agreement that practical work rests on the skills of planning, carrying out and processing results from experiments. The ordinary experiments in the course aim to develop the later two skills, but planning is an artificial exercise unless conducted in the context of feedback from results obtained by carrying out the plan. This dynamic relationship can only be experienced and the appropriate skill developed by getting students to conduct small scale investigations.

We have therefore included in the course a variety of suggestions for investigations. Some have definite outcomes which teachers will know about, in a few a variety of conclusions are possible, but all can be studied by a variety of procedures – and students are likely to surprise us with ingenious routes to their answers.

Two approaches are possible to investigations: either conducting a series of mini-investigations as opportunities arise during the early topics, leading to a full investigation later in the course, or setting aside two periods of time for investigations – the first for a 'trial' investigation towards the end of the first year of the course, and the second for one full investigation based on ideas from any of the main topics in the course.

Conducting an investigation is likely to involve some preliminary study involving the *Students' book* or other books (for which a laboratory reference collection will be helpful), followed by a few tentative trial experiments to establish the nature and range of the variables worthy of full investigation. Such experiments may involve no more than mixing solutions at room temperature and, when warm, at molar and tenth molar concentrations, or checking the colour change of an indicator. But without fuel for the imagination planning an investigation is likely to be both difficult and unsound. Indeed an investigation, might need a series of modifications as it proceeds. When a student cannot see how to proceed we have suggested the provision of 'cue cards' to provide help with specific difficulties.

⚠ For purposes of risk assessment, teachers will need to know what each student intends to do before any experimental work is undertaken.

A complete investigation need occupy no more than two hours of laboratory time, although some may be spread out over a longer period and all will require time for preliminary research, for trial experiments, and for writing a report.

A student's report of an investigation should show how the student has approached the investigation, give records of procedures, observations and measurements, details of secondary sources consulted, and conclusions and summaries based on the evidence collected. A report should also include a justification of the practical procedures adopted and the conclusions drawn. These justifications will need to be based on information from the *Book of data* and theory from the *Students' book*. Collaborative or co-operative work can be very supportive when students are attempting investigations, but each student should produce his or her own individual report.

The quality of an investigation should be judged on the work as finally executed, using the student's report and (where necessary) any additional evidence such as observation of the student at work, or questioning related to the work or the report.

Teaching the course

The philosophy behind the Nuffield Science courses is now well-known. They are written in the belief that courses should not only be based on the principles of the subject which are regarded as of fundamental importance at the present time, but must also seek to develop imaginative thinking on the part of the student. 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 mechanical reproduction of factual material. This must not be taken as implying that factual information is considered unimportant, but rather that facts should be given their proper place in the study of the subject – indispensable as the basis for speculation about possible explanations of the behaviour of matter, and playing a crucial role in disciplining such speculation. Theory which outruns facts can have no lasting place in science, but it is proper and permissible to make imaginative leaps forward, provided these are checked against known facts, or are used to guide the search for further factual information against which they can be tested. There is, of course, nothing new or revolutionary about this approach. It has been the basis of good chemistry teaching for many years.

An Advanced 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; and those who will subsequently embark on a career in which the methods of science are not of prime importance and for whom this will probably be a terminal course. In order to provide for the varying needs of students, a course must be provided which has some degree of flexibility, can be used with students of a fairly wide range of abilities, and is satisfying and complete in itself, whilst 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.

In order to achieve these aims a greater degree of discussion will be needed than is sometimes customary. This is, however, a decided advantage in that it will result in students gaining confidence in their ability to convey ideas and arguments clearly to others. Both class discussion and written work must provide opportunities for self-expression.

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:

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

These principles will be applied to the experimental study of both organic and inorganic systems, but in a manner 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. Always the evolution of a major concept is accompanied by the collection of factual information, leading to the emergence of an underlying principle which is then tested and often modified by appeal to further facts. Time and school laboratory resources do not always permit the necessary factual information 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 school chemistry from related subjects such as metallurgy, biochemistry, and chemical engineering. The essential unity of these and similar disciplines demands that this be attempted; in addition, it is obviously 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 realized 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. It is, however, often advisable to deal specifically with certain elements or groups of elements at certain points during the course, the obvious example being carbon. We have therefore proposed that some time shall be devoted to a concentrated investigation of the carbon compounds, but here the concepts developed earlier in the course are used freely.

Information on, and in some cases experience of, the contribution of chemistry in a variety of activities are included in the course. This is done in two 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 a Study Task or a Reading Task. Secondly, towards the end of the course each student undertakes one Special Study, during which the basic principles studied earlier can be applied in new contexts of a technological nature. The Special Studies have already been discussed in more detail in this Introduction.

In dealing with technological and other applications in the ways described above, the social and economic results of advances in chemistry are discussed, as are the moral and ethical implications.

Teaching method

Teaching method is very much an individual affair and it would be presumptuous to pretend that it can be communicated by a few written words. 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. This being said, there are a few matters to which the attention of teachers should be directed.

The course relies heavily on class discussion if it is to be taught successfully.

Such discussion may be relatively lengthy, involving the whole class, or occupy a few minutes only and a small number of students. It is most important that these discussions should be held at the precise time when they are relevant. Questions which will lead to discussion are included at frequent intervals in both the *Students' book* and the *Teachers' guide*. When such questions arise in connection with practical work they should be discussed *as the experiment proceeds*, that is, at frequent intervals in the laboratory. It is unwise to ask a class to do all the practical work and then 'answer the questions for homework'.

Homework and written work in general can pose problems in a course of this nature. Many teachers have found it helpful for their students to have a notebook in which to keep their own record of their experimental work, and their answers to the questions that appear in the text, and the *Students' book* has been written with this practice in mind. Phrases such as 'copy the following table into your notes and enter your experimental results in it' and 'write the answers to the following questions in your notes' occur in a number of places. Although some of the burden of this type of reporting can be eased by reference to pages in the *Students' book*, some 'writing up' of experimental procedures is important for good scientific training, and it helps to have the notebook reasonably self-contained.

The questions at the ends of the Topics in the *Students' book* provide useful tests of understanding and application. In addition to these, there is a need for students to be given lengthier pieces of written work which require them to select facts, marshal evidence, and present ideas in a lucid and not too wordy form. Examples are provided in some of the Study Tasks. Students should also be encouraged to read as widely as possible, and opportunity to discuss what they have read should be provided in class time: the Reading Tasks are provided with the aim of stimulating this type of reading. We hope that students' interest will take their reading well beyond their *Students' book.*

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. In addition to ensuring that the apparatus and chemicals needed are readily available, the use to be made of visual aids and other learning resources must be given careful consideration. The overhead projector is a valuable piece of teaching equipment in this connection. Transparencies prepared in advance, either by using a copier or by hand, make a considerable contribution to easing the task of the teacher during class time.

Although careful planning is essential if each lesson is to make its full impact, the teacher must be prepared to depart from the set scheme when occasion arises. Students who have been encouraged to become involved in what is being done at any time will expect their contributions to be treated seriously and they should be given reasonable opportunities to implement any suggestions that they make. As a consequence the course of a lesson may be quite different from that envisaged by teachers in their preliminary planning. These 'excursions off the beaten track' are most valuable in promoting enthusiasm amongst students. They can be time-consuming so should be kept under reasonable control; teachers will know how much time they can afford to spend in this way and will be able to compensate by speeding up the treatment of one or more later Topics.

Pre-examination revision is not such an important factor for success or failure in the type of A-level examination that is set on this course. Study and consistent application throughout the course are much more profitable. It is, however, valuable for students to be in a position to survey the essentials of what they have done during their two years in the sixth form. The *Students' book* is of some assistance, especially the final three Topics which are synoptic in nature, but their own notes will be required to supplement this source. Careful note-making is thus necessary throughout the course, and in any case facility in making usable notes needs to be cultivated for reasons other than examination success. Note-making can easily get out of hand, and advice and guidance will need to be provided by the teacher. Outline summaries are given at the end of each Topic in the *Students' book*, and these can be used as a basis for compiling a more detailed version as a joint exercise by teacher and students.

Examinations

Nuffield Advanced Chemistry is examined at both A- and S-levels by the University of London Examinations and Assessment Council, on behalf of all the GCE examining boards. There is also an AS examination. The London board issues a syllabus, a guide to practical assessment, including the criteria for the assessment of Investigations, notes for guidance and, each year, an examination report to examination centres. The syllabus 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.

Special Studies which are out of print will only be available for examination by special application to ULEAC. The Studies available by this route are *Ion exchange*, *Metallurgy*, and *Surface chemistry*.

Contributors

Many people have contributed to this new third edition. The books have been the responsibility of a working group meeting mainly over many weekends at the Cecil Powell Centre, University of Bristol. The members were:

John Apsey, David Craggs, Alastair Fleming, Alan Furse, Frances Hawkesford, Brian Hitchen, Andrew Hunt, Glyn James, Roger Norris, Bill Price, Bryan Stokes, and Michael Vokins. Additional material was provided by Peter Higgens.

Advice on safety matters has been given by Dr Peter Borrows, Chairman of the Safeguards in Science Committee, an ASE service group.

This edition has benefited greatly from the valuable help and advice that have been given by teachers using the revised course, particularly through contributions at the summer meetings and by filling in a very detailed questionnaire.

The first edition was the responsibility of a Headquarters team, who assembled and wrote the material for the several draft versions that were used in school trials. The Headquarters team consisted of Ernest Coulson (organizer), Aylmer Aylmer-Kelly, Dr Erica Glynn, Bob Jones, Tony Malpas, Dr Tony Mansell, John Mathews, Dr Gordon Van Praagh, Gordon Raitt, Bryan Stokes, Roy Tremlett, and Michael Vokins.

The revised edition was undertaken largely by three working groups, whose members were: Alan Furse (chairman), Keith Badman, Michael Cane, Colin Nicholls, and Dennis Russell (inorganic chemistry); Michael Vokins (chairman), Jim Eggleton, Glyn James, and Professor David Waddington (organic chemistry); Professor Malcolm Frazer (chairman), Professor Paul Black, Dr Peter Borrows, John Holman, David Mansfield, Professor Jim Millen, and Jon Ogborn (physical chemistry). Bryan Stokes directed the work and edited the books.

Finally, as writer of this introduction I should like to record our thanks to the Longman Group Limited and the Nuffield–Chelsea Curriculum Trust: particularly to Hendrina Ellis for her calm cheerfulness as she guided our work from manuscript to publication, and to her colleagues, Catherine Blackie, Sarah Codrington, Donna Evans, Dieter Pevsner, Deborah Williams and Jean and Keith Macqueen.

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Introduction to the *Students' book:* Faraday's candle

Michael Faraday's 'The Chemical History of a Candle' is available as a reprint (see 'Reference sources and bibliography' at the end of this book).

A twentieth century account of a burning candle can be found in P.W. Atkins *Chemical change*, Scientific American Books, 1984.

The Introduction in the *Students' book* is more than an introduction to be read, since a number of questions are posed about Faraday's classic account of the chemical history of a candle. It is suggested that students observe a candle burning and attempt to produce forty observations! This exercise was introduced as part of the American *CHEM Study* curriculum project and this list of possible observations is based on their description of a burning candle.

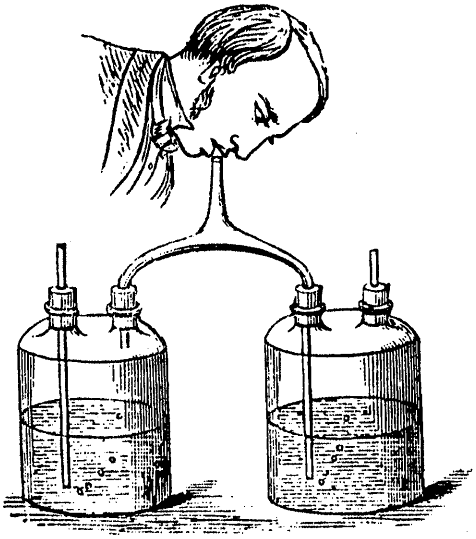
- A candle is cylindrical in shape.
- The diameter is about [3] cm.
- The length was about [15] cm.
- A candle is easily broken in half.
- The break is rough, non-crystalline.
- Candle wax is [white].
- The wax has a faint odour.
- The wax is moderately soft.
- The wax is translucent.
- A wick extends from top to bottom.
- The wick consists of twisted strands.
- The unburnt wick is white.
- A flame is needed to light a candle.
- A candle continues to burn once lit.
- The candle length decreases about [2] cm per hour.
- The flame is hot.
- A finger is uncomfortably hot 10 cm above the flame.
- A finger is uncomfortably hot 0.5 cm to the side of the flame.
- The burning candle is only warm near the top.
- The warm wax is easily moulded.
- The flame is always moving.
- The flame flickers in draughts.
- The flame is sometimes smoky.
- The flame is silent.
- The base of the flame is blue.
- The centre of the flame is dark.
- The top of the flame is yellow.
- Light is emitted mostly from the yellow top.
- The flame has an oval base.
- The sides of the flame are smooth.
- The top of the flame comes to a point.
- The top of the flame is ragged.
- The wick is burnt away.
- The wick turns black when it enters the flame.
- The wick curls over in the flame.

- At the edge of the flame the wick glows red.
- A liquid forms in a bowl at the base of the wick.
- The liquid is colourless.
- The pool of liquid remains constant in size.
- The liquid rises slightly round the wick.
- In a draught the sides of the bowl may melt, allowing the liquid to drain down the side of the candle.
- The liquid that escapes solidifies.
- The drips look like the original wax.
- In the absence of draughts drips do not form.

This is a total of 44 observations.

Students are also invited to propose experiments that would support Faraday's account of what is happening as a candle burns. They are likely to be familiar with most of these experiments.

- Invert a jar over a candle to cut off the air supply; the candle is soon extinguished and the period of time for which the candle continues to burn is proportional to the volume of the jar.
- Use a cold surface to condense moisture from candle fumes; testing with cobalt chloride paper suggests the liquid is water.
- Bubble candle fumes through limewater to show carbon dioxide is present.
- Hold a wooden splint across the flame just above the wick; it will scorch at the outer edges of the flame but not in the centre.
- Hold a test-tube containing water in the luminous part of the flame; a deposit of soot particles will be formed.
- When one end of a glass tube is held in the dark part of the flame, a flammable gas can be lit at the other end of the tube; a cold surface will cause wax to condense.
- Blow out a candle and hold a light in the gas still rising from the wick; the candle will relight.
- Connect two wash bottles, both containing limewater, so that when you breathe in, air bubbles through one bottle, and when you breathe out, the exhaled air bubbles through the other; this demonstrates that we breathe out more carbon dioxide than we breathe in.



TOPIC 1

Iron compounds: an introduction to inorganic chemistry

Introduction

This introductory Topic is designed to revise and reinforce basic chemical concepts from students' pre-A-level science courses as well as extending students' knowledge in a practical context. The time taken over this Topic will depend largely on the students' previous experience, for example, single subject sciences or dual award courses.

A study of the properties of iron and its compounds to a greater depth than was possible in GCSE courses provides an introduction to basic chemical concepts such as the mole, balancing equations, the reactivity series, and exothermic and endothermic reactions. A range of chemical reactions (oxidation, reduction, thermal decomposition, formation of salts) is studied and students are asked to consider practical techniques for making iron salts.

With the advent of the National Curriculum, it has been assumed that students have studied the Periodic Table and know the difference between ionic and covalent compounds. These ideas are revised by means of a Review Task and a Study Task. Teachers could discuss these in more detail in order to bring all their students to an equivalent state of knowledge. It is important at this early stage to emphasize the need for precise knowledge and a clear understanding of basic concepts.

Content

1.1 The chemistry of iron. Chemical reactions revised: oxidation, reduction, precipitation, thermal decomposition, complex ions, tests for iron(II) and iron(III) compounds; interpretation of the experiments.

1.2 Introduction to the chemists' toolkit. Amount of substance, the mole, molar mass, Avogadro constant; Thermit reaction, reactivity series, oxidation and reduction.

	Timing	*Students' book*
1.1	5 hours	Pages 5–8
1.2	3 hours	Pages 9–12
1.3	3 hours	Pages 13–15
1.4	5 hours	Pages 15–18
1.5	2 hours	Pages 19–21
1.6	Homework	Pages 22–25

Total about 4 weeks

1.3 More about the chemists' toolkit. Writing formulae, charges on ions; balancing equations; *an investigation of the reaction of iron with copper(II) sulphate solution.*
1.4 Preparation of some iron compounds. Preparation of ammonium iron(II) sulphate and ammonium iron(III) sulphate; preparation of a 'complex ion'; the corrosion of iron.
1.5 Iron in the Periodic Table. Groups and periods, simple model of the atom, isotopes; periodicity of physical properties, atomic volume; properties of iron compounds; revision of properties of metals and non-metals, and ionic and covalent compounds.
1.6 Study Task. History of the Periodic Table.

Objectives

1. To define a distinct chemical quantity, amount of substance, and its unit, the mole.
2. To give students an opportunity to perform simple calculations using moles and molar masses.
3. To study the properties of iron and iron compounds and their different oxidation states.
4. To give students an understanding of oxidation and reduction in terms of change in ionic charge, and through practical work to introduce a variety of oxidants and reductants.
5. To review the periodic recurrence of certain physical properties of the elements when arranged in the Periodic Table.
6. To revise basic chemical concepts such as the structure of the atom, isotopes, the reactivity series, oxidation-reduction, thermal decomposition, salt formation and the use of symbolic equations.

1.1 The chemistry of iron

Timing

About 5 hours will be required.

Suggested treatment

The time taken in introducing this Topic will depend on the students' previous experience of chemistry. Following a brief discussion of reaction types and an introduction to oxidation states in terms of Roman numerals, students should be reminded of hazard symbols and their meanings, and the need for safe working practices. Students then carry out a variety of reactions with iron(II) and iron(III) compounds. The interpretation of these reactions is given in the *Students' book.*

At this stage, the intention is to introduce students to the main types of inorganic reaction and the use of specific chemical tests to identify particular compounds. It is *not* the intention that students write or memorize equations for these reactions but merely that they use them to follow the oxidation or reduction of iron compounds by critical observation, and become conversant with a variety of oxidants and reductants. The equations given in the *Students' book* should only be used for referring to the formulae of the iron compounds and the number of moles of substances which react. Details of what constitutes a complex ion are not required at this stage – complex ions are simply introduced as compounds that are formed or involved in specific tests for iron compounds.

EXPERIMENT 1.1

Iron compounds

Each group of students will need:
Eye protection
Full rack of test-tubes
Bunsen burner and heatproof mat
Ignition tubes, 2
Test-tube holder
Full-range Indicator paper or solution
Access to:
A selection of iron compounds as solids, each with a spatula
Iron, polished sample
0.1 M ammonium iron(II) sulphate, labelled 'iron(II) sulphate in water'
0.1 M ammonium iron(III) sulphate, labelled 'iron(III) sulphate in water'
0.1 M barium chloride HARMFUL
20 volume hydrogen peroxide IRRITANT
Iron(III) nitrate-9-water
Iron(II) sulphate-7-water
Concentrated nitric acid CORROSIVE
2 M sodium hydroxide CORROSIVE
0.1 M sodium sulphite (or solution of sulphur dioxide) TOXIC
1 M sulphuric acid IRRITANT
1% potassium hexacyanoferrate(III), w/v solution
0.1 M potassium manganate(VII)
1% potassium thiocyanate, w/v solution
Zinc, foil or granulated

⚠ Hazards

Students attention should be drawn to Appendix 2 on *Laboratory safety* in their books.

There are a few hazards that might need to be pointed out to students: sulphur dioxide may cause difficulties to students with respiratory conditions; protective gloves could be issued as protection against the dangers of concentrated nitric acid and students should be warned about the toxic nature of the oxides of nitrogen produced in its reactions; heating iron(III) nitrate and iron(II) sulphate might need to be done in a fume cupboard because of the gases produced.

The appendix on *Hazardous laboratory chemicals* in this book should be consulted for further information.

Teachers may prefer to make solutions available only in dropping bottles.

Procedure

Full details of the procedure are given in the *Students' book*. As this is the first experiment, teachers should take the opportunity to explain to students the method they prefer for recording accounts of practical work.

4 Oxidation

Students will need to use very small volumes of iron(II) sulphate solution: too much will lead to incomplete conversion to products unless a large amount of oxidant is added and this masks the expected result on adding sodium hydroxide. Students may notice effervescence when sodium hydroxide is added to the solution. This is due to decomposition of the peroxide to oxygen in the presence of the alkali. Oxidation with potassium manganate(VII) is best carried out by adding the oxidant until there is a slight purple coloration and then adding a drop of iron(II) sulphate to remove the colour. When Fe^{2+} solutions are warmed with concentrated nitric acid, a dark brown coloration due to the $Fe(NO)^{2+}$ ion should be noticed. This then turns yellow as it decomposes to release nitrogen monoxide on further warming. This is the basis of the 'brown ring' test for nitrates.

For the benefit of the teacher, the equations for the reactions, which are not given in the *Students' book*, are as follows.

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

$$2NO_3^-(aq) + 6Fe^{2+}(aq) + 8H^+(aq) \rightarrow 2NO(g) + 6Fe^{3+}(aq) + 4H_2O(l)$$

5 Reduction

Students may sometimes see a reddish tinge during the reaction with sulphite solution. This is caused by the formation of a complex with sulphur dioxide but will only occur if there is an excess of this reductant.

$$SO_3^{2-}(aq) + 2Fe^{3+}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2Fe^{2+}(aq) + 2H^+(aq)$$

On addition of sodium hydroxide, a dark green precipitate is formed. The precipitate obtained on reduction of Fe^{3+} ions with zinc followed by addition of sodium hydroxide may appear a light green colour if left too long before observations are made. This is due to a white precipitate of zinc hydroxide obscuring the colour of the iron(II) hydroxide.

The solutions of iron(II) and iron(III) sulphate used in experiments 4 and 5 are acidified not only to suppress hydrolysis but also to supply the hydrogen ions needed for the reactions to occur.

6 Thermal decomposition

When iron(III) nitrate is heated, students should observe the crystals dissolving in their water of crystallization followed by the liberation of steam and the evolution of brown nitrogen dioxide gas. Iron(II) sulphate gives off steam on heating and a white solid remains, which on strong heating gives off an acidic gas and leaves a blackish red solid, iron(III) oxide.

7 Tests for the presence of iron compounds

No colour should be observed on testing Fe^{2+} ions with potassium thiocyanate, but because of the sensitivity of this test, even small amounts of impurities will cause a slight red coloration. It is important therefore, that reagents of the highest purity should be used. When potassium hexacyanoferrate(III) is added to a solution of Fe^{3+} ions, a brownish green coloration may be seen but there is no precipitate. Small quantities of contaminating Fe^{2+} ions may cause a light blue coloration. The reaction with Fe^{2+} ions gives a dark blue precipitate (Turnbull's Blue). The simplified equation is:

$$3Fe^{2+}(aq) + 2Fe(CN)_6^{3-}(aq) \rightarrow Fe_3[Fe(CN)_6]_2(s)$$

Interpretation of the experiments

This section discusses the reactions the students have just performed in terms of reaction type, mainly focusing on oxidation and reduction.

ANSWERS TO THE QUESTIONS

Iron(III) oxide is known as jewellers' rouge because it is a brick-red powder used by jewellers for polishing glass and jewellery.

The iron(II) compounds have been oxidized in the presence of water and air to form iron(III) compounds.

1.2 Introduction to the chemists' toolkit

Timing About 3 hours will be required.

Suggested treatment

The time taken over this section will depend on the extent to which students are already familiar with the use of the mole. Most students should have been introduced to the mole in their pre-A-level courses and consequently the teacher may only need to remind them of the essential points in this section. The mole is placed in the practical context of its value for calculating reacting masses of substances. Students should realize the importance of precise definitions and understand the principal terms used and the units in which they are expressed. In the *Students' book* review questions 1.1 to 1.3 provide some practice in the use of these ideas. The main points to be covered can be summarized 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 one gram of hydrogen, or the number of hydrogen molecules, H_2, in two grams 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.

The term relative atomic mass is not used in the course, molar mass being preferred for all entities.

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 grams (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:

$$\underset{\text{in mol}}{\text{amount of substance}} \times \underset{L\,(\text{mol}^{-1})}{\text{Avogadro constant}} = \text{number of specified entities}$$

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:

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

Experiment 1.2 The Thermit reaction

Before this experiment is begun, the reacting masses needed are worked out from the equation, to give practice in the use of mole calculations. The meanings of the terms exothermic and endothermic are revised, and the reactivity series used to predict whether a reaction is likely to take place or not. The experiment then shows that a more reactive metal will take the non-metal part of a compound from a less reactive metal.

Each student will need:
Eye protection

The teacher will need:
Eye protection
Safety screen
Small fireclay pot or other disposable container
Bucket nearly full of **dry** sand
Iron(III) oxide, **dry**, three portions of 8.0 g (0.05 mol)
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 boats

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.

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). The fireclay pot will 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. 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.

1.3 More about the chemists' toolkit

Timing About 3 hours.

Suggested treatment

The first part of this section is largely revision of the use of chemical symbols, the magnitude of charges on cations and anions, and balancing simple equations. It may be set for reading homework but it is important that students have a thorough grasp of the formulae of elements and ions before proceeding with section 1.4. The section is completed by an investigation involving the reaction of iron with copper(II) sulphate. Students are asked to verify which of two equations gives the observed stoichiometry and products. Students are asked to suggest their own experiments and to make an assessment of the risks involved, both of which must be checked by the teacher before the experiment is begun.

Investigation 1.3 The reaction of iron with copper(II) sulphate

The students plan and carry out their own experiments to find out which of the two equations is correct when iron reacts with copper(II) sulphate.

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

$$2Fe(s) + 3Cu^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 3Cu(s)$$

Students should appreciate that a quantitative experiment is required. Teachers may wish to do this investigation as an alternative experiment, in which case the procedure described below may be photocopied for use by the students.

Alternative Experiment 1.3

The reaction of iron with copper(II) sulphate

Each student will need:
Eye protection
Bunsen burner, tripod, gauze and heatproof mat
Beaker, 100 cm^3
Test-tubes and rack
0.1 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 boat
Oven or hot-water bath

Procedure

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 the washing with more pure water.

Add about 20 cm^3 of propanone and stir the mixture. Allow the precipitate to settle and pour off the propanone (CARE flammable). Allow the beaker to stand for 5 minutes so that most of the propanone clinging to the precipitate can evaporate. Drive off the remainder by heating the beaker in an oven at 100 °C for 5 minutes. Allow it to cool and find the mass of beaker plus copper.

1.4 Preparation of some iron compounds

Timing About 5 hours will be needed for this section.

Suggested treatment

This section gives students the opportunity to use moles in a practical context during the preparation of a number of iron compounds. The experiments which follow give the students an opportunity to carry out neutralization reactions and prepare double salts.

Experiment 1.4a Preparation of ammonium iron(II) sulphate (Mohr's salt), $(NH_4)_2SO_4.FeSO_4.6H_2O$

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
Crystallizing dish and cover
Weighing boat
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 crystallizing 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 realize 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.

Experiment 1.4b

Preparation of ammonium iron(III) sulphate (iron alum), $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$

Each group of students will need:
Eye protection and protective gloves
Bunsen burner, tripod, gauze and heatproof mat
Beaker, 100 cm^3
Boiling tube and rack
Crystallizing dish and cover
Dropping pipette
Measuring cylinder, 25 cm^3
2 weighing boats
Ammonium sulphate, 0.66 g
Iron(II) sulphate-7-water, 2.8 g
Access to:
Concentrated nitric acid CORROSIVE
1 M sulphuric acid IRRITANT
Balance, to weigh to ±0.1 g
Fume cupboard

Procedure

The procedure is detailed in the *Students' book.* Students calculate the amount of ammonium sulphate (0.66 g) required to make $\frac{1}{200}$ mol iron alum. They then carry out the preparation by oxidizing iron(II) sulphate to iron(III) sulphate using concentrated nitric acid then adding the calculated quantity of ammonium sulphate and crystallizing. The equations for the preparation may appear rather daunting to some students, but they do not need to be learnt and teachers should only use them to refer to the stoicheiometry. Dilute sulphuric acid is added to the iron(II) sulphate to prevent hydrolysis.

Light-violet, octahedral crystals of iron alum are obtained which are stable for a time in the air. If too much acid is used a white powder may be formed rather than the crystals. When the crystals are not properly dried students may observe that, after a time, they may change into a brown, gummy deliquescent mass caused by the partial hydrolysis of the iron(III) sulphate component to form iron(III) hydroxide. Students should note that during the oxidation of iron(II) sulphate, the nitric acid has been reduced and also that the double salt behaves in solution as if it were a mixture of its component sulphates.

Ammonium iron(II) sulphate is an example of a group of double salts of formula $(M^+)_2SO_4.(M^{3+})_2(SO_4)_3.24H_2O$ where M^{3+} may be Al, V, Cr, Mn, Fe, Co etc. in the +3 oxidation state and M^+ may be NH_4^+, Na^+, K^+ etc. Students may wonder why the compound is called an alum: the term originates with potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$ which was the first of this type of double salt of similar formula and structure to be discovered.

Experiment 1.4c Preparation of a 'complex ion'

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 boats
Iron(III) chloride-6-water, 2.7 g
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 crystallization. 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 oxidized to carbon dioxide. The effect is quantitative and could be made the subject of an investigation later in the course. The Fe^{2+} ions can be detected using potassium hexacyanoferrate(III).

Students should appreciate the difference between a complex ion and a double salt but a full understanding of complex ions should be left until Topic 15. 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.

Experiment 1.4d The corrosion of iron

Each group of students will need:
8 Petri dishes or other suitable containers
Other apparatus as requested by the students
Access to:
Iron, nails or narrow strips
Other metals in narrow strips (Al, Cu, Mg, Ni, Pb, Sn, Zn)

Students design an experiment to study the corrosion of iron under a variety of conditions. Students should show their plans to their teacher, together with any assessment of risks, before commencing the experiment.

Procedure

The corrosion indicator is best made up in bulk in advance. The recipe is provided for the students' information and is repeated here on a larger scale. The corrosion indicator can be placed in drops on the surface of iron; the results are visible within an hour. Iron in contact with another metal can be immersed in the corrosion indicator. When the gel sets the results are easy to examine.

Disperse 20 g of powdered agar in 1000 cm^3 of boiling water and add 20 cm^3 of 5% potassium hexacyanoferrate(III) solution, 4 cm^3 of 1% phenolphthalein solution and 30 g of sodium chloride. Keep at 80 °C until required.

The corrosion indicator detects Fe^{2+} ions. With the suggested concentration of potassium hexacyanoferrate(III) and in the absence of sodium chloride, it may take up to 15 minutes before signs of corrosion are visible. The results are more rapid if sodium chloride is added to the indicator. Phenolphthalein indicates regions where OH^- ions are being formed.

It is not intended that students study the process of corrosion in great detail – this experiment merely gives students the opportunity to use some of the knowledge they have gained during their study of various iron compounds earlier in this Topic.

1.5 Iron in the Periodic Table

Timing About 2 hours.

Suggested treatment

This section can be started by reminding students of their study of related elements in their pre-A-level work. During this time they will probably have met the halogens, the alkali metals and the transition elements of period 4. The various regions of the Periodic Table can then be pointed out, indicating where metals, non-metals, transition elements and other named groups are placed. A demonstration chart of the Periodic Table in which the different regions are coloured differently can be useful here. The term 'atomic number' should be explained to the students and can be described at this stage as the number of protons in an atom.

In section 1.2 molar masses were defined and were then put to use to find the amounts of chemical substances in moles. Their use in building up the Periodic Table may now be mentioned briefly – this historical perspective is developed further in section 1.6. The use of the mass spectrometer for determining the molar mass can be discussed if wished by reference to section 18.5. Students need not learn the details of how a mass spectrometer works but should be able to appreciate its use.

Students should also be able to calculate the composition of the nucleus of a particular atom in terms of protons and neutrons, given the mass number and atomic number. Students should also be able to demonstrate an understanding of isotopes.

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 refer to the variation of atomic volumes of the elements with atomic number (figure 1.11 in the *Students' book*). 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:

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

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 atomic volumes of the Group 1 and 2 elements, in $\text{cm}^3\ \text{mol}^{-1}$, are:

Li = 13.2	Na = 23.7	K = 45.3	Rb = 56.1	Cs = 70.7
Be = 4.9	Mg = 14.0	Ca = 26.0	Sr = 33.7	Ba = 39.1

The graphs of atomic volume are important in an 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 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 radon and francium are not sufficiently accurate). The elements at the troughs belong to Group 3, if the transition metals are ignored. The atomic volumes increase down each group within which the structures are generally the same owing to the increase in atomic radius. In other cases comparisons are made difficult because atomic volume is a function of both atomic radius and factors such as structure, the presence of allotropes etc.

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 vaporization, and the melting and boiling points. Tables and graphs illustrating these features of periodicity could be drawn for homework or plotted using a computer database. The relevant information for all the elements is given in the *Book of data*. 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.

The properties of iron compounds

This is largely a summary exercise which brings together the various strands in this Topic and revises a number of areas (metals and non-metals, ionic and covalent compounds, reactivity series) which students have met in their previous science courses. In answering question 2, students may need access to standard chemistry texts to compare the reactivity of iron with that of other elements. This question could be set for homework as an information retrieval task. In their pre-A-level courses, some students may have studied oxidation and reduction in terms of electron transfers. It is not the intention to go this far in answering question 4; all that is required at this stage is an understanding of oxidation and reduction in terms of changing the charge on a metal ion, or the addition or removal of oxygen or hydrogen. Redox reactions in terms of electron transfer will be dealt with in Topic 5.

1.6 Study Task: History of the Periodic Table

Timing This Study Task may be set as homework, with a brief discussion in class.

Suggested treatment

This is a good point at which to refer back to Lothar Meyer and thence to others, including Lavoisier, Newlands and Mendeleev, who noticed relationships among the elements and attempted to classify them. The Study Task should be set for homework and the questions answered with the aid of the *Book of data* and other reference sources.

Teachers could refer students to one of the many computer databases on the Periodic Table, such as the CD-ROM *Interactive Periodic Table,* which includes Roger McGough's poems on the elements.

ANSWERS TO THE STUDY TASK QUESTIONS

1 Light, caloric, the radicals, e.g. boracic radical, and the earthy substances.

2 Calcium hydroxide, magnesium hydroxide, barium hydroxide, sodium aluminosilicate, sodium silicate.

3 Muriatic = chloride, fluoric = fluoride, boracic = borax.

4 Phlogisticated air (from the Greek – to set on fire) is unreactive. Phlogiston was supposed to exist in combination with all combustible bodies and disengaged itself in the process of combustion. Azote is nitrogen.

5 Light is electromagnetic radiation of visible wavelengths, caloric is equivalent to the energy transferred during a chemical reaction. According to the caloric theory, a fluid passed from one body to another when energy was transferred.

6 Iodine (53) and tellurium (52), argon (39.9) and potassium (39.1), cobalt (58.9) and nickel (58.7), thorium (232) and protactinium (231).

7 Students should attempt this question graphically. Extrapolation of the curves gives a boiling point for astatine of about 600 K and a density of about 7 g cm^{-3}. The melting point of sodium astatide will be about 850–880 K with a solubility of perhaps 1.5×10^{-1} mol/100 cm^3.

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

1.1

a	6.54 g	(1)
b	0.08 g	(1)
c	117.4 g	(1)
d	124.0 g	(1)
e	29.25 g	(1)
f	111.0 g	(2)
g	171.0 g	(2)

Total 9 marks

1.2

a	2.0 g	(1)
b	1.0 g	(1)
c	60.1 g	(2)
d	22.0 g	(2)
e	71.5 g	(2)

Total 8 marks

1.3

a	1	(1)
b	2	(1)
c	$\frac{1}{4}$	(2)
d	$\frac{1}{8}$	(2)
e	$\frac{1}{2}$	(2)

Total 8 marks

1.4

a	$BaCl_2$	(1)
b	$Cu(NO_3)_2$	(1)
c	Na_2CO_3	(1)
d	KOH	(1)
e	$Al_2(SO_4)_3$	(1)

Total 5 marks

1.5

a	$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$	(2)
b	$2NaOH(aq) + CuSO_4(aq) \rightarrow CuO(s) + Na_2SO_4(aq) + H_2O(l)$	(2)
c	$Na_2CO_3(s \text{ or } aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$	(2)
d	$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$	(2)

Total 8 marks

1.6

a	$Fe(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Fe(OH)_2(s) + 2NaNO_3(aq)$	(3)
b	$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g)$	(2)
c	$Na_2CO_3(aq) + ZnSO_4(aq) \rightarrow ZnCO_3(s) + Na_2SO_4(aq)$	(2)
d	$CuO(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + H_2O(l)$	(2)

Total 9 marks

1.7

a	A: 14	(1)
	B: 15	(1)
	C: 16	(1)
b	28.1	(1)
	$(28 \times 0.922) + (29 \times 0.047) + (30 \times 0.031)$	(2)

Total 6 marks

Examination questions

1.8

a (27 + 113) ÷ 2 = 70 (1)
Gallium makes a triad with Al and In, therefore molar mass is average (2)

b **i** $Ga(OH)_3$ (1)
ii gallium(III) nitrate and water;
$Ga(OH)_3(s) + 3HNO_3(aq) \rightarrow Ga(NO_3)_3(aq) + 3H_2O(l)$ (3)

c Add gallium to dilute sulphuric acid to form gallium(III) sulphate, add an equimolar amount of potassium sulphate dissolved in water, and evaporate the mixture until crystals start to form. (3)

Total 10 marks

1.9

a **i** electrons 29, protons 29, neutrons 34 (2)
ii (63 x 0.691) + (65 x 0.309) = 63.6 (2)

b 24 g of alloy contain $\frac{18}{197}$ mol Au = 0.091,
$\frac{6}{63.6}$ mol Cu = 0.094 (1)
∴ Molar ratio 1:1 (1)

Total 6 marks

1.10

Mark by impression

A good answer would be based on two metals with contrasting uses and would include examples of uses of compounds. The alternative materials should have specific properties described; an imaginative alternative might do away with the present use (e.g. telephone wires).

Total 15 marks

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.

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 groups chosen for study, alcoholic —OH and carbonyl, 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 7. Wherever possible, the Topic is developed in the context of the chemistry of natural products, for example, the extraction of limonene from oranges, the importance of alcohols in insects, fermentation.

Content

	Timing	*Students' book*
2.1	3 hours	Pages 30–33
2.2	3 hours	Pages 33–36
2.3	4 hours	Pages 36–42
2.4	3 hours	Pages 42–44
2.5	2 hours	Pages 45–46
2.6	Homework	Pages 46–48

Total about 3 weeks

2.1 Extraction of a natural product. Extraction of limonene by steam distillation, distinction between saturated and unsaturated hydrocarbons, interpretation of the experiments.

2.2 Naming carbon compounds. Bonding in alkanes; molecular, structural and displayed formulae, structural isomers; names for compounds containing carbon atom chains; naming primary alcohols.

2.3 Reactions of alcohols. Experiments with alcohols: solubility, reaction with sodium, oxidation, dehydration; preparation of propene and propanoic acid from propan-1-ol; interpretation of reactions of alcohols; naming more complicated alcohols: primary, secondary and tertiary alcohols.

2.4 How much? Molar masses of organic compounds; stages in a laboratory preparation; laboratory preparation of cyclohexene from cyclohexanol.

2.5 Oxidation products from alcohols. Carbonyl functional group; oxidation of carbonyl compounds by sodium dichromate(VI) and Benedict's solution; oxidation products from alcohols.
2.6. Fermentation. The requirements for fermentation; making ginger beer.

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 how extraction procedures are used to obtain purified preparations of natural products and the importance of fermentation reactions.

2.1 Extraction of a natural product

Timing About 3 hours will be required.

Suggested treatment

Before students embark on a study of alcohols it is necessary for them to gain some knowledge of the simpler compounds of carbon and hydrogen. This introductory section is set in the context of the economic importance of plant products and shows how chemists have developed methods for extracting individual compounds from plants. Introducing a study of organic chemistry in this way also places it in its correct historical context; it was Lavoisier who first suggested in 1784 that all compounds extracted from vegetables and animals always contain carbon and hydrogen. The experiments in this section not only follow on naturally from these ideas but also introduce students to specific chemical tests for distinguishing unsaturated from saturated compounds.

Experiment 2.1a 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 2.1)
Measuring cylinder, 50 cm^3
Dropping pipette
Test-tube with stopper or specimen bottle
Kitchen grater (or sharp knife)
2 oranges, or their zest

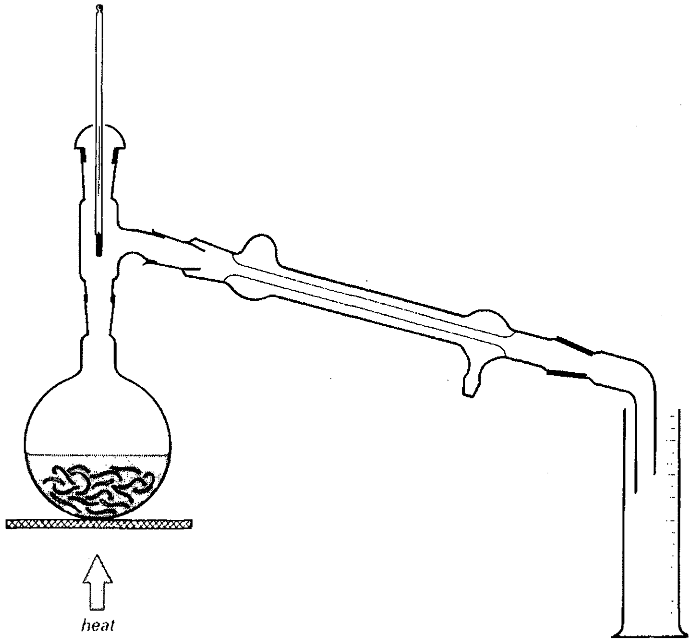


Figure 2.1 Steam distillation apparatus.

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 2.1b. If there is not sufficient time to do this straight away, the product should be stored in a closed container to prevent evaporation.

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 14.

Experiment 2.1b Testing limonene

Each group of students will need:
6 test-tubes and rack
Dropping pipettes, 5
Cyclohexane, 1 cm^3 HIGHLY FLAMMABLE
Cyclohexene, 1 cm^3 HIGHLY FLAMMABLE

Limonene, 1 cm^3
Access to:
Bromine water CORROSIVE
0.01 M potassium manganate(VII)
1 M sulphuric acid IRRITANT

Procedure

1 Odour

Students should be advised of the correct way of smelling liquids such as cyclohexane and cyclohexene. Teachers may prefer to arrange matters so that the cyclohexane and cyclohexene are available in small quantities in several closed containers, for example, glass specimen bottles, so that the stock bottles are not used for the smell test. Cyclohexane and cyclohexene have typical 'organic solvent' odours and the limonene has a sweet aromatic citrus smell.

2 Action of bromine

The bromine water should be decolorized by limonene and cyclohexene but not by cyclohexane. Some shaking will be necessary to ensure that the organic and aqueous layers become mixed for a little while.

3 Oxidation

It is suggested that the hydrocarbon is added dropwise to 1 cm^3 of potassium manganate(VII) to which a few drops of dilute sulphuric acid have been previously added. Rapid decolorization of the potassium manganate(VII) should be observed on gentle shaking with limonene or cyclohexene.

Students may also test the samples of limonene they have made. Following the experiment, teachers should discuss the difference between saturated and unsaturated compounds and may introduce reactions 2 and 3 as tests for unsaturation. Details of addition reactions are left until Topic 7.

2.2 Naming carbon compounds

Timing About 3 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 National Curriculum 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 TO SELECTED QUESTIONS

Questions, page 36

1 The boiling points are: methanol, 338.1 K, ethanol 351.6 K, propan-1-ol, 370.5 K and butan-1-ol, 390.3 K. Students should notice a difference of approximately 20 K between successive alcohols. They could try to work out the boiling point of other alcohols by extrapolation to see if the pattern continues.

3 Students should see the similarity of the ethanolic —OH group with the —OH in water and compare

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

with

$2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2$

2.3 Reactions of alcohols

Timing 4 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 Topic 7 as part of halogenoalkane behaviour and esterification is studied in Topic 12 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 2.3a Experiments with alcohols

Each group of students will need:
Eye protection
Bunsen burner and heatproof mat
Full rack of test-tubes and boiling tubes
Test-tube holder
Penknife
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, small pieces FLAMMABLE, CORROSIVE
0.1 M sodium dichromate(VI) IRRITANT
1.0 M sulphuric acid IRRITANT
Full-range Indicator paper

Hazards

Teachers will probably prefer to provide freshly cut pieces of sodium; otherwise extra suitable apparatus will be needed. 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 irritants.

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

Procedure

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

1 Solubility

The longer the carbon chains, the less soluble the alcohol. After pentan-1-ol, the solubility of the alcohols is less than 1 g 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 realize 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 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 2.3b Preparations using propan-1-ol

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 2.2)
Ceramic fibre
3 test-tubes with corks
Apparatus for refluxing and distillation with pear-shaped flask, 50 cm^3 (see figures 2.3 and 2.4)
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 IRRITANT
Concentrated sulphuric acid, 2 cm^3 CORROSIVE
1 M sulphuric acid, 15 cm^3 IRRITANT
Access to:
Benedict's solution HARMFUL
Bromine water CORROSIVE
0.01 M potassium manganate(VII)
0.1 M sodium carbonate
Balance, to weigh to ±0.1 g

⚠ Hazards

Sodium dichromate(VI) may cause sensitization 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.

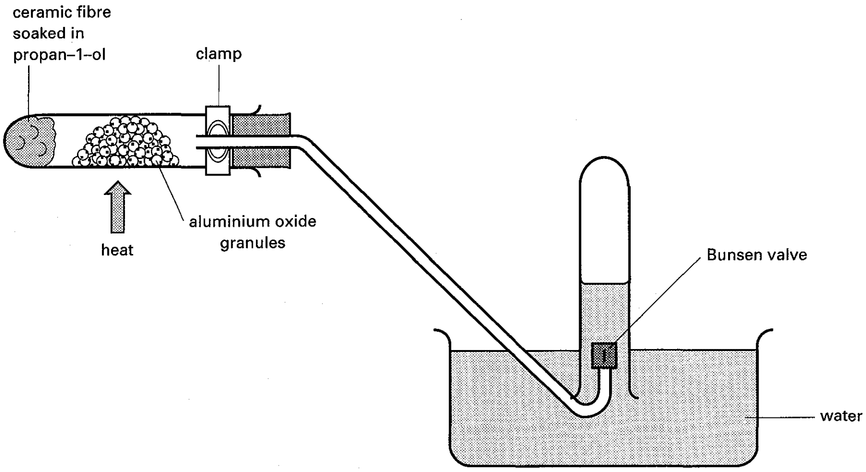


Figure 2.2 Apparatus for gas collection.

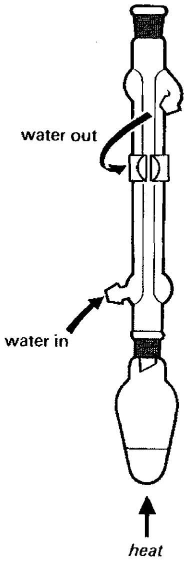


Figure 2.3 Apparatus for refluxing.

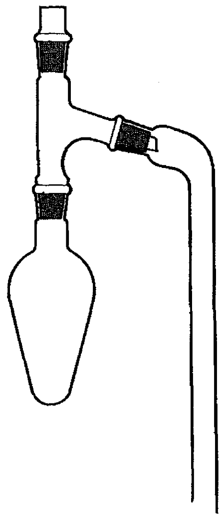


Figure 2.4 Apparatus for distillation.

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 harmful and gives more consistent results.

1 The dehydration of propan-1-ol

Bromine water and acidified potassium manganate(VII) are decolorized. The product is therefore unsaturated. This is an elimination reaction producing a good yield of propene.

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 neutralizes a relatively large volume of sodium carbonate solution. It should not give an orange precipitate with Benedict's solution.

3 Partial oxidation of propan-1-ol

The propanal produced in this reaction should only neutralize 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 to make models of propan-1-ol, propanal and propanoic acid.

This section summarizes the reactions which the students have just carried out. The simplified equations are all that is necessary at this stage.

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 TO THE QUESTIONS

1 $2C_4H_9OH + 2Na \rightarrow 2C_4H_9O^-Na^+ + H_2$

3 a ethene b ethanol c ethanoic acid

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 7.

2.4 How much?

Timing About 3 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 TO THE QUESTIONS

1 Molar masses are: limonene, 136; citric acid, 192; insulin, 5727 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 2.4

How much cyclohexene can you get from cyclohexanol?

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 2.5)
Beaker, 100 cm^3
Conical flask, 50 cm^3
2 measuring cylinders, 10 cm^3
2 dropping pipettes
Thermometer, 0–110 °C
Separating funnel, 50 cm^3
Sample tube or weighing bottle
Access to:
Cyclohexanol, 15 cm^3 FLAMMABLE, HARMFUL
Concentrated phosphoric(V) acid (85% syrupy), 4 cm^3 CORROSIVE
Calcium chloride, anhydrous granular IRRITANT
Bromine water CORROSIVE
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 product, cyclohexene, is flammable 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. 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.

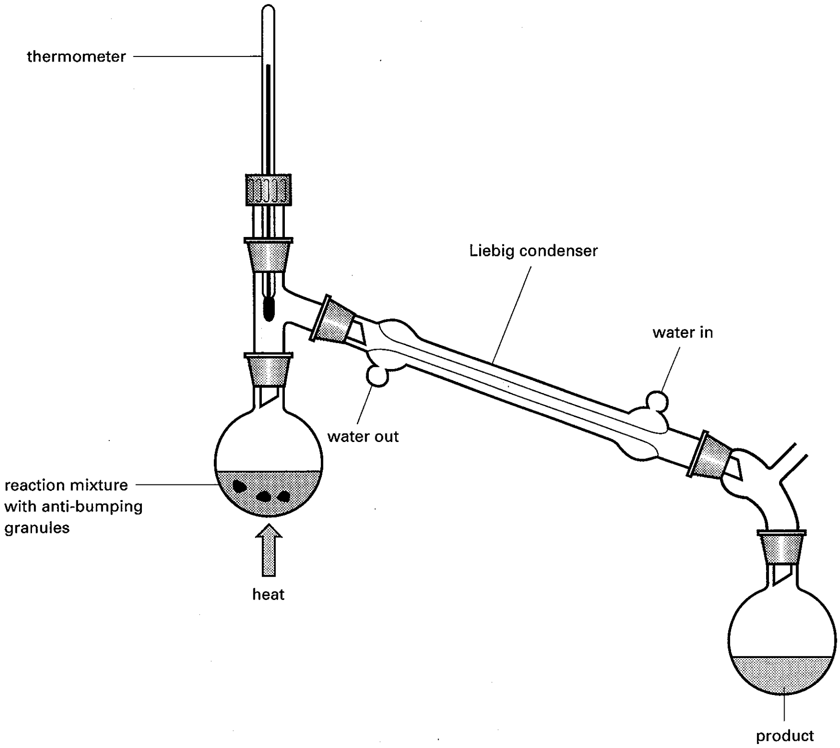


Figure 2.5 Apparatus for distillation with vent.

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. The receiver adaptor has a vent to lead off flammable vapours to below bench level 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:

(i) separation of cyclohexene from water-soluble contaminants using a separating funnel;
(ii) removing water from the organic layer using anhydrous calcium chloride;
(iii) 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.

2.5 Oxidation products from alcohols

Timing About 2 hours.

Suggested treatment

This section introduces aldehydes and ketones as oxidation products of alcohols. The study of carbonyl compounds is limited to distinguishing aldehydes from ketones using Benedict's solution and acidified sodium dichromate(VI) solution. If there is time, students could be asked to make models, either open type or space-filling, of different aldehydes and ketones.

Experiment 2.5 Oxidation of carbonyl compounds

Each group of students will need:
Eye protection and protective gloves
Bunsen burner and heatproof mat
4 boiling-tubes and rack
Dropping pipettes, 4
Propanal, a few drops HIGHLY FLAMMABLE, IRRITANT
Propanone, a few drops HIGHLY FLAMMABLE
Access to:
Benedict's solution HARMFUL
0.1 M sodium dichromate(VI) IRRITANT
1 M sulphuric acid IRRITANT

Procedure

Students should be advised to heat the solutions gently, otherwise the propanal or propanone will be volatilized rapidly and not react with the reagents.

1 Oxidation with sodium dichromate(VI)

The propanal is oxidized 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 oxidizing agent from experiments 2.3a and 2.3b. No change is observed on boiling sodium dichromate(VI) with propanone.

2 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.

Oxidation products from alcohols

The oxidation of primary and secondary alcohols is discussed briefly and simplified equations given. The further oxidation of aldehydes to carboxylic acids is contrasted with the inability of ketones to be oxidized easily.

2.6 Fermentation

Timing This section may be set as homework, with a brief discussion in class.

Suggested treatment

The final section of this Topic introduces students to the biochemical basis of fermentation and provides a further example of the use of mole calculations as well as giving a recipe for ginger beer that students might try at home. Fermentations are not only commercially important in the production of alcoholic beverages but are also used in the dairy industry, in the initial stages of making vinegar and in the treatment of sewage. The word fermentation was formerly applied to cases in which a liquid mass was seen to become 'puffed up' and release gas. In the 19th century, Schwann was the first to recognize that yeast was necessary to convert sugar to alcohol and carbon dioxide.

Fermentations may also involve fungi or bacteria and produce a wide range of alcohols, carboxylic acids etc., but most function in the absence of oxygen. In this section, it is alcoholic (ethanolic) fermentation which is considered. At one time, fermentation was a major source of organic chemicals, but ethanol is now produced by the cheaper process of reacting ethene with steam.

The flow chart showing the conversion of glucose to ethanol is introduced mainly for the interest of students who are studying biology as well as chemistry. Students do not have to remember details of the flow chart, but they should appreciate that the reaction involves a number of specific enzyme-catalysed steps which take place in the absence of oxygen. Although the flow chart starts with glucose, sucrose or other carbohydrates are the usual feedstocks for fermentations. The sequence glucose → pyruvic acid is called glycolysis. The students' attention should be drawn to the step ethanal → ethanol which is a reduction reaction.

Experiment 2.6a Making ginger beer

The details are described in the *Students' book.* This optional experiment may be done at home with materials provided by the students themselves. Students should ensure that the fermentation vessel is thoroughly clean before use and should take care with the corked bottles. The experiment must *not* be done in a science laboratory because of general hygiene requirements.

ANSWERS TO THE QUESTIONS

1 a 9.1 dm^3 water, 680 g sugar, 28.4 g ginger, 14.2 g cream of tartar, 14.2 g yeast.
b Sucrose is a sufficient answer. Cream of tartar is potassium hydrogen tartrate (monopotassium salt of 2,3-dihydroxybutanedioic acid).

2 a The maximum concentration of ethanol is 0.87 mol dm^{-3}.
b 40.3 g ethanol has a volume of 51.1 cm^3. This converts to a concentration of 5.1 g per 100 cm^3 of solution. 2 per cent ethanol by volume is about 1.6 g per 100 cm^3.

Experiment 2.6b The flavour of ginger beer

This optional experiment, a variant on experiment 2.6a, could be done at home with materials provided by the students themselves. Satisfactory ginger beers can be obtained from recipes, for 1.2 dm^3 of water, that range from

175 g to 56 g sugar
22 g to 2 g root ginger
7 g to 3 g cream of tartar.

The experiment must *not* be done in a science laboratory because of general hygiene requirements. Students should take care to point the corked bottles away from their face when opening.

Summary

Students should produce a summary chart of the reactions they have studied in this Topic, showing the reactions of alcohols and the conditions necessary for the reactions to proceed.

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

2.1

a $CH_3CH(OH)CH_3$ (1)
b $CH_3CH_2CH_2CH_2CH_2CH_2OH$ (1)
c CH_3CH_2CHO (1)
d $CH_3CH_2COCH_2CH_3$ (1)
Total 4 marks

2.2

a Hydrocarbons containing single bonds only. (2)
b Reactive group with characteristic properties. (2)
c Formula showing all atoms and bonds. (2)
d Reaction which removes a simple molecule. (2)
Total 8 marks

2.3

a 102 (1)
b 120.5 (1)
c 72 (1)
d 86 (1)
Total 4 marks

2.4

a **D** (1)
b **B, C, D** (1)
c **B** (1)
d **A** (1)
e **A** (1)
Total 5 marks

2.5

a But-1-ene (1)
$CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH = CH_2 + H_2O$ (1)
b Molar masses are
butan-1-ol = 74 g, butene = 56 g (1)
so percentage yield = $\frac{1.8 \times 74}{3.7 \times 56} \times 100 = 64\%$ (to 2 SF) (1)
c Dehydrating agent (1)
Total 5 marks

2.6

a Hexan-3-ol (1)
b $CH_3CH_2CH = CHCH_2CH_3$ *and*
$CH_3CH = CHCH_2CH_2CH_3$ (2)
c $CH_3CH_2CHBrCHBrCH_2CH_3$ *and*
$CH_3CHBrCHBrCH_2CH_2CH_3$ (2)
Total 5 marks

Examination questions

2.7

Formulae of reagents added to ethanol	**Reaction type**	**Formula of organic product**	**Name of organic product**
Na	substitution or replacement	$CH_3CH_2O^-Na^+$	*sodium ethoxide*
H_3PO_4	elimination or dehydration	$CH_2{=}CH_2$	ethene
$Na_2Cr_2O_7/H_2SO_4$	*mild oxidation*	CH_3CHO	ethanal

Total 9 marks

2.8

a Flask containing water plus dried blooms. (1)
Condenser in distillation position. (1)
Container 'open' and able to collect product. (1)
Well labelled diagram which would work. (1)
b **i** To dissolve organic product or to extract the oil (1)
ii Dry or remove water (1)
c **i** $C—O^-Na^+$ or $C—O^-$ (1)
ii Addition to both double bonds (2)

iii Double bond in any of the 3 possible positions (2)

d Any three from: non-toxic, economical to produce, accessible starting materials, high yield at each stage, similar physical properties, stable. (3)

Total 14 marks

2.9

a $2CH_2H_5SH + 2Na \rightarrow 2C_2H_5SNa + H_2$ (2)

b $C_2H_5S^-$ (1)

c carbon dioxide, water (steam), sulphur dioxide (3)

Total 6 marks

TOPIC 3

Atoms, ions and acids

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 shell. It is assumed that students have already gained some knowledge of atomic structure and electron arrangements from their previous courses.

The Topic starts by considering how the evidence obtained from emission spectra has been used to determine electron arrangements. This leads to a consideration of the properties of ionic compounds and an appreciation of the size and shape of simple ions.

The final section focuses on the hydrogen ion and develops the Brønsted–Lowry theory of acidity and the concept of weak and strong acids in terms of extent of ionization. Solution concentration is then introduced in the context of acid–base reactions to enable students to tackle problems involving molarities.

Content

	Timing	*Students' book*
3.1	1 hour	Pages 56–58
3.2	2 hours	Pages 58–60
3.3	2 hours	Pages 61–66
3.4	3 hours	Pages 66–71
3.5	3 hours	Pages 72–74
3.6	3 hours	Pages 75–77
3.7	Homework	Pages 78–79
Total about 3 weeks		

3.1 The story of the atom. Evidence for the atom, development of the model of the atom.

3.2 Flame colours and emission spectra. Flame colours of elements of Group 1 and 2; interpretation of line emission spectra, evidence for the existence of electron energy levels, ionization energies.

3.3 The arrangement of electrons in atoms. Patterns of ionization energies, the arrangement of electrons in quantum shells and subshells; periodic trends in atomic radii, ionic radii and ionization energies.

3.4 Evidence for the ionic model. Electrical conductivity, migration of ions, crystal structure; the shape of ions; electron arrangements in ions.

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

3.6 The chemists' toolkit: solution concentration. Preparing molar solutions, calculations using molarities; finding the solubility of calcium hydroxide in water by titration.

3.7 Study Task. The role of calcium in agriculture.

Objectives

1. To indicate some of the evidence for the pattern of electron distribution in atoms.
2. To appreciate how the pattern of electron distribution in atoms influences the properties of the elements.
3. To study the trends in ionic radii and ionization energy in the Periodic Table in terms of electronic structure.
4. To consider the formation of ions in terms of electron transfer.
5. To review the properties of ionic compounds and the evidence for the ionic model.
6. To extend the concept of acids and bases by considering the Brønsted–Lowry theory of acid–base behaviour.
7. To consider the strengths of different acids and bases and the effect of strength on the pH of the solution.
8. To provide an opportunity to perform simple calculations using molar masses and concentrations in mol dm^{-3}.

3.1 The story of the atom

Timing

About 1 hour will be required.

Suggested treatment

In Topic 1, students revised the structure of the atom. The introductory section to the present Topic, 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.

The analogy of the development of chemical theory with the development of maps can be extended by pointing out the existence of errors in both cases.

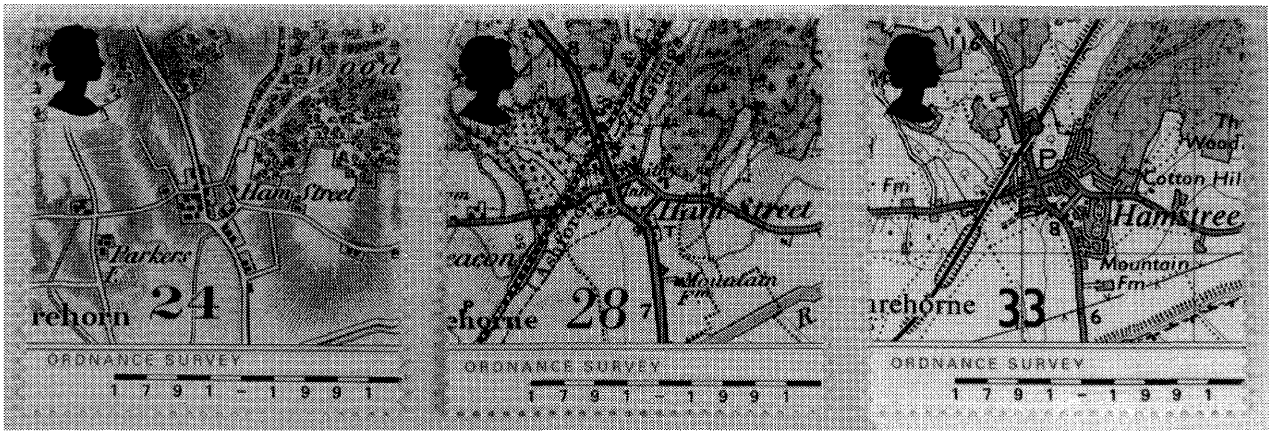


Figure 3.1 Only 20 copies of this stamp have been found.

3.2 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 ionization energies is then developed.

Experiment 3.2 Flame colours and emission spectra

Each group of students will need:
Eye protection
Diffraction grating or direct vision spectroscope
Cobalt blue glass
Each station will need:
Bunsen burner and heatproof mat
Nichrome wire in insulating handle
Concentrated hydrochloric acid in a small beaker CORROSIVE
Sample of a salt on a watchglass, one for each station, chosen from the chlorides of Li to Cs and Mg to Ba
Darkened room

⚠ Hazards

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 oxidizing 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. Only small amounts of concentrated hydrochloric acid should be used in the bottom of a small beaker and the acid should be changed if a wire from another station is dipped in it.

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 detailed below together with details of what the students should observe from both experiments.

Experiment 3.2a (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 characterized by its own particular set of lines.

Interpretation of the emission spectra of elements

The relationship between atomic spectra and ionization energies is now developed. The atomic emission spectrum of hydrogen may be examined more closely by reference to figure 3.4 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 3.5 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 ionization results. By finding the convergence limit, it is possible to obtain a value for the ionization energy. Figure 3.4 in the *Students' book* indicates the existence of several series of lines other than those observed in the visible region. As the ultra-violet series represents transitions back to the $n = 1$ or ground state, the convergence limit for this series of lines gives a measure of the ionization energy for a ground state atom of hydrogen.

As optional extension work, students might be asked to calculate the convergence limit and thus the ionization energy for hydrogen. They can do this by plotting the difference in frequency between successive lines against the frequency and extrapolating the curve to the point where $\Delta\nu = 0$. The values for the various lines in the Lyman series are:

line number	1	2	3	4	5	6	7	8
frequency/10^{15} Hz	4.568	6.167	6.907	7.309	7.551	7.709	7.817	7.894

A graphical representation of the results is shown in figure 3.2 which shows the difference in frequency plotted against the higher and lower frequencies of the pairs of frequencies taken. When the convergence limit is multiplied by the Planck constant, 6.6×10^{-34} J s, it is converted into the value in joules. This value must then be multiplied by the Avogadro constant to give the value in joules per mole.

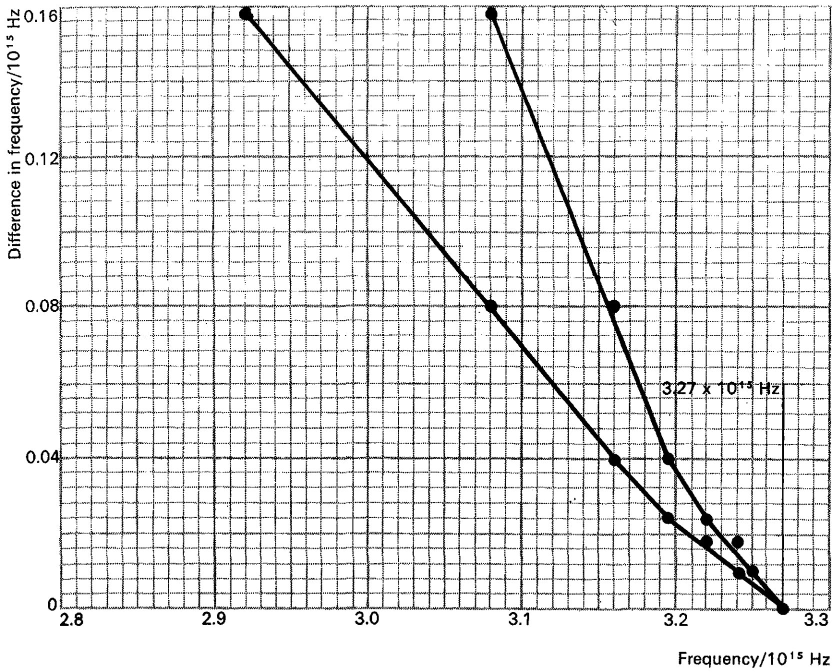


Figure 3.2 Difference in frequency, plotted against frequency for the ultra-violet spectrum of hydrogen.

The ultra-violet convergence limits for the alkali metals and the corresponding ionization energies obtained from these are shown in the table.

Element	**Series limit/10^{15} Hz**	**Ionization energy/kJ mol^{-1}**
Li	1.30	520
Na	1.24	495
K	1.05	419
Rb	1.01	403
Cs	0.94	376

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

3.3 The arrangement of electrons in atoms

Timing About 2 hours, together with a homework for the Study Task.

Suggested treatment

The introductory work is presented as a Study Task.

ANSWERS TO THE STUDY TASK QUESTIONS

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

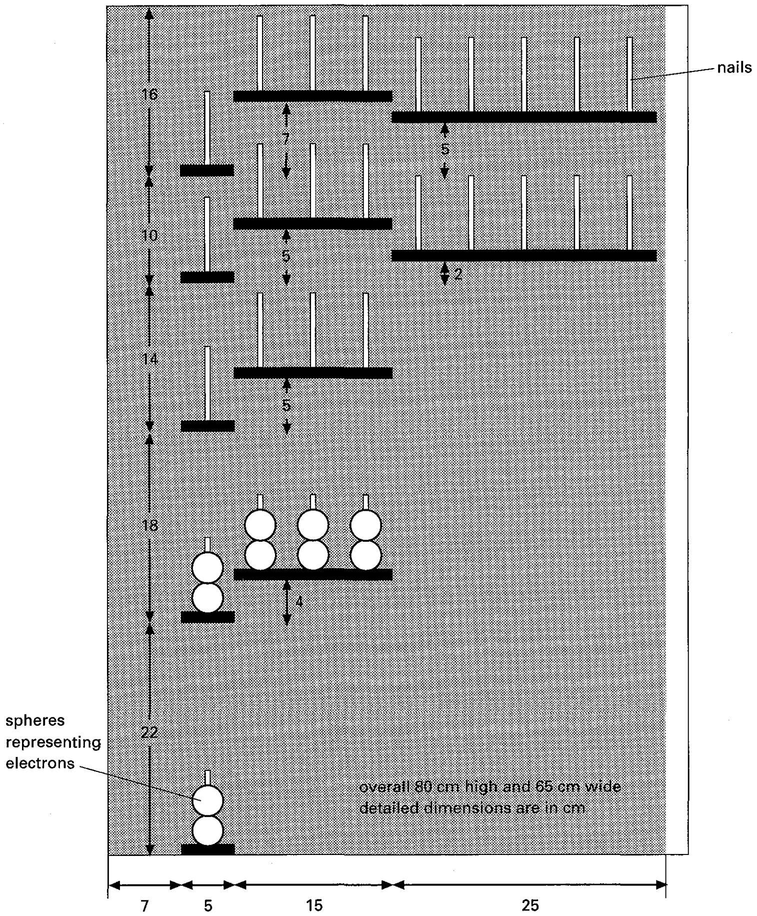
2 The logarithm (to the base 10) of the ionization energy is then plotted and the pattern noted; one electron in the $n = 3$ level is relatively easy to remove, 8 electrons in the $n = 2$ level are removed with difficulty and 2 electrons in the $n = 1$ level are extremely difficult to remove.

Students might also plot the values of successive ionization 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.

3 Students are then asked to plot a graph of the first ionization energies of the first 20 elements in the Periodic Table against the atomic number and comment on the pattern through answering a number of questions.

Interpretation of the patterns in the ionization 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 a useful aid for this section.



overall 80 cm high and 65 cm wide
detailed dimensions are in cm

Figure 3.3 Suitable dimensions for a display board.

For sodium, successive ionization energies show that two electrons in the $n = 1$ level spend most of their time closer to the nucleus than do the other electrons and are said to be in the first quantum shell. The 8 electrons in the $n = 2$ level spend most of their time 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. 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 spend most of their time.

In the plot of the first ionization 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 8 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 ionization energy for each of the elements in the Periodic Table (figure 3.9 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 3.10 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 of 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 cloud charges are only revealed by wave mechanics and it is not possible at this level to provide evidence for such shapes.

The section is completed by a Study Task, which asks students to extract information from the *Book of data* concerning atomic and ionic radii and first ionization energies. They then use these data to draw out patterns of relationships in the Periodic Table.

The atomic radius decreases across a period as a result of the increasing nuclear charge acting on the electrons in quantum shells, including the outer one which 'fixes' the boundary of the atom. The atomic radius increases down a group because the outer electrons are successively one shell further out and the inner electrons screen the outer ones from the attraction of the nucleus.

Students should also realise that the chemical similarities existing among members of a group of elements arise because of the similiar configurations of the outer electron shells of their atoms.

ANSWERS TO THE STUDY TASK QUESTIONS

1 Trends in ionization energies

Ionization energies increase across a period with minor irregularities, reaching a maximum with a noble gas. This is a result of the increasing nuclear charge acting on electrons in the same quantum shell. Down a group, the first ionization 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 is larger as the group is descended, the increased attraction is not sufficient to overcome the effect of the increased atomic radius.

2 Trends in ionic radii

Ionic radii increase down a group for much the same reasons as atomic radii except that ions, unlike atoms, have outer quantum shells in a noble gas configuration. For metals, the ionic radii are always smaller than the corresponding atomic radii because, in attaining the nearest noble gas configuration, the electrons in the outer quantum shell of the atoms have been removed. For Groups 5 to 7, the ionic radii are greater than the atomic radii. For Group 1 metals, the percentage increase in the ionic radius as the group is descended is much greater than that for the atoms. This may be partly explained by the increased shielding effect of inner electrons.

3.4 Evidence for the ionic model

Timing About 3 hours will be required, together with a homework for the Study Task.

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 Review 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 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 organized as a circus and the requirements are listed in that form.

Experiment 3.4 Properties of ionic compounds

Each station will need:

1 The electrical resistance of solutions

Conductivity meter
6 or 8 clean beakers, 100 cm^3
The following 0.1 M solutions:
Ethanoic acid
Hydrochloric acid
Sodium chloride
Sodium ethanoate
Sodium hydroxide

Procedure

Conductivity meters are expensive and therefore this experiment may be performed as a teacher demonstration. Students should read section 2 of Topic 18, 'Using a conductivity meter', before doing the experiment. Although it is not the intention to measure the absolute conductivity values, deionized water should be used to wash the conductivity probe and to make up the solutions. The beakers to be used in the work should be very thoroughly washed and dried.

Further information about measuring conductivity is given in Topic 18. Students should appreciate the need for careful washing of the conductivity probe between each measurement. Teachers may like to include solutions of glucose and ethanol for conductivity testing to make the point that molecular substances do not contain ions. It should be pointed out that water itself has a very low conductivity.

A comparison of the conductivity values of the ionic solutions with that of water, shows that ionic solutions have a high conductivity. The value for hydrochloric acid should be highest (reflecting the high mobility of the hydrogen ion), sodium hydroxide, sodium ethanoate and sodium chloride will be intermediate in value while ethanoic acid has a low conductivity due to incomplete ionization.

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
Agar
Saturated potassium nitrate solution
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, OXIDIZING
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 the 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.

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 3.17 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 3.17. 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.

3.5 Acids and bases

Timing About 3 hours will be required.

Suggested treatment

The section is introduced by means of a Review Task. Students are asked to work in groups to pool their knowledge of properties which typify acids and bases. After a brief revision of neutralization 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 3.5 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 0.1 M solutions of acids and alkalis, including orthophosphoric(V) acid, urea and saturated calcium hydroxide
A selection of indicators
8 M ammonia IRRITANT
Hydrogen chloride in hydrocarbon solvent* FLAMMABLE, IRRITANT
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
Box with circular hole in the side
The teacher or technician will need:
Eye protection and protective gloves
Apparatus for generating hydrogen chloride
Anhydrous calcium chloride
Methylbenzene (toluene) or petroleum spirit, boiling range 120–160 °C
Rock salt or sodium chloride
Concentrated sulphuric acid CORROSIVE

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.

Procedure

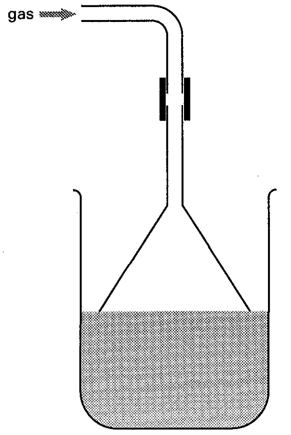


Figure 3.4 Apparatus for dissolving hydrogen chloride gas in hydrocarbon solvent.

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 neutralization 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 3.6. 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.

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 about 5 cm diameter: on tapping the lid attractive smoke rings can be produced.

4 This may be this first time that students have used a pH meter, so some explanation of the apparatus may be necessary. It is not yet appropriate to refer the students to the relevant text in Topic 18. '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 realize 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 11.

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 hydroxonium ion has been used throughout because this name can be identified clearly with the formula for this species. The terms oxonium and hydronium ions are also acceptable.

Strong 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.

3.6 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 neutralization 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 solutions is expressed more helpfully as moles per cubic decimetre (abbreviated mol dm^{-3}) and these units are used in the *Students' book* in the questions. In laboratories the convenient system of labelling solutions as 'M', '2 M' is usual; students should be familiar with both practices. Dilute acids and alkalis are expected to be 2 M except for H_2SO_4 and Na_2CO_3 which are 1 M in most experiments.

As a preliminary to the practical work in experiment 3.6, 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 neutralize 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

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

in a variety of types of calculation. Questions 3.6–3.9 will provide useful practice.

ANSWERS TO THE STUDY TASK QUESTIONS

1 H^+ is 3 mol dm^{-3}, PO_4^{3-} is 1 mol dm^{-3}; and one-tenth of these values.

2 a 5 mol b 0.1 mol c 0.01 mol.

3 15 cm^3

Experiment 3.6 To find the solubility of calcium hydroxide in water by titration

Each group of students will need 24 hours in advance:
Conical flasks, 250 cm^3, with stopper
Calcium hydroxide IRRITANT
For the titration:
Filter funnel and filter paper
Titration apparatus with 10 cm^3 pipette
0.050 M hydrochloric acid
Indicator, methyl orange or bromphenol blue

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 the pipette and burette before starting the experiment and revise other points 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.

3.7 Study Task: The role of calcium in agriculture

Timing

This Study 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 STUDY TASK QUESTIONS

1 Calcium compounds are added as lime or calcium carbonate. Liming not only neutralizes 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 Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

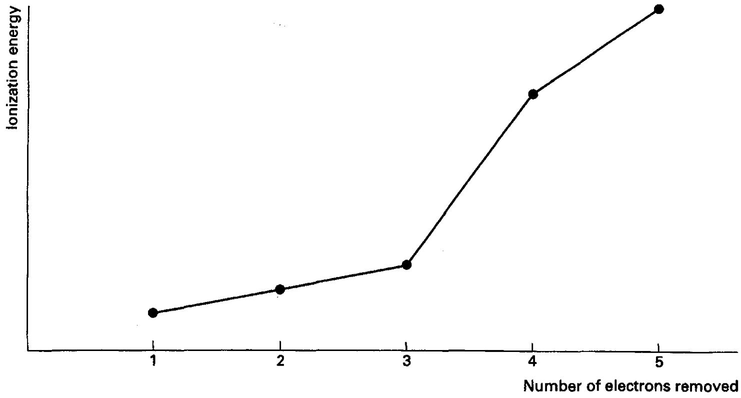
Review questions

3.1

a **A** and **I** (1)
b **H** (1)
c **K** (1)
d *Mark by impression*
Look for the idea that ionization energy is a periodic function and that within a short period it rises irregularly with atomic number. (5)
Total 8 marks

3.2

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 ionization energy, and fairly regular, but smaller, rises between the first and second, and the second and third. (5)
Total 5 marks



3.3

a 38 (1)
b Group 2 (1)
c 2+ (1)
Total 3 marks

3.4

a **A.** *Mark by impression*
Look for awareness of the shielding effect of the inner electrons, which decreases the ionization energy despite the increase in nuclear charge. (5)
b Group 1. *Mark by impression*
Look for awareness of the significance of a big increase between the first and second ionization energies. (5)
Total 10 marks

3.5

a **B** (aluminium) (1)
b **A** and **D** (lithium and sodium) (1)
c **C** (1)
d **A** (1)
Total 4 marks

3.6

a 0.912 g (2)
b 2.45 g (2)
c 1.00 g (2)
d 3.95 g (2)
e 6.20 g (2)
Total 10 marks

3.7

a 0.100 mol dm^{-3} (2)
b 0.400 mol dm^{-3} (2)
c 0.010 mol dm^{-3} (2)
d 0.100 mol dm^{-3} (2)
Total 8 marks

a 0.0025 (2)
b 0.0200 (2)
c 0.0190 (2)
d 0.0190 (2)
Total 8 marks

3.8

a 0.100 mol dm^{-3} (2)
b 0.200 mol dm^{-3} (2)
c 0.3 mol dm^{-3} (2)
d 0.2 mol dm^{-3} (2)
Total 8 marks

3.10

3.9

a Methyl orange, yellow to red (2)
b $Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$ (2)

c $\frac{0.2}{1000} \times 24$ mol of hydrochloric acid

$\equiv \frac{1}{2} \times (0.0048)$ mol barium hydroxide in 10 cm^3, $\equiv 0.24$ mol dm^{-3} (2)

d Solubility = 171 × 0.24 g dm^{-3} (1)

Total 7 marks

Examination questions

3.11

a Use a fume cupboard; CO is poisonous
or wear eye protection; rock may shatter (2)

b Filter, wash, dry at room temperature (2)

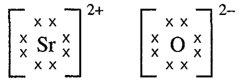
c i $Sr(OH)_2(s) \rightarrow SrO(s) + H_2O(g)$ (2)

ii 184 g → 104 g

so $4.6 \rightarrow \frac{104}{184} \times 4.6$

% yield $= \frac{1.3 \times 184}{104 \times 4.6} = 50\%$ (3)

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

ii 

(2)

or 4p shell

e i Clean wire in hydrochloric acid, dip in solid, view in colourless flame (2)

ii Red (1)

iii Electrons falling back to lower energy levels in atoms (2)

Total 17 marks

3.12

a i Be $1s^2\,2s^2$ (1)

ii Ba $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^2$ (1)

b i Group 2 (1)

ii +2 (1)

iii Breaking into full shells (1)

c i Be, electron closer to nucleus or Ba electron shielded by inner shell (2)

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

Total 9 marks

3.13

a **K** 1600 ± 1000 (less than **C**) (1)

L 400 ± 100 (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**, $\mathbf{E_3H_2}$ (2)

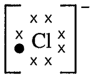
c Increasing positive charge on the nucleus, a quantum shell is filling (2)

Total 10 marks

3.14

a $1s^2 2s^2 2p^6 3s^2 3p^5$ (2)

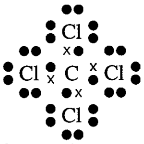
b **i** Na^+



charges (1)

ii Argon (1)

c



d **i** Ionic, covalent (1)

ii Transfer of electrons, sharing of electrons (2)

Total 9 marks

3.15

i *Book of data:* $Ca(OH)_2$, $m_{sat} = 1.53 \times 10^{-3}$ mol/100 g

molar mass = 74.1 g mol^{-1}

so $(1.53 \times 10^{-3} \times 74.1)$ g dissolve = 0.11 g

some solid dissolves forming saturated solution/white suspension

ii *Book of data:* $CaSO_4{\cdot}2H_2O$, $m_{sat} = 7.00 \times 10^{-2}$ mol/100 g

moles of H_2SO_4 added = $\frac{10}{1000} \times 2 = 2.00 \times 10^{-2}$ mol

moles of $Ca(OH)_2$ available = $\frac{1}{74.1}$ = 1.35×10^{-2} mol

all the $Ca(OH)_2$ dissolves to form a solution of $CaSO_4$ in excess sulphuric acid

iii Moles of sulphuric acid remaining = $(2.0 - 1.35) \times 10^{-2}$ mol

= 0.65×10^{-2} mol in 100 cm^3

so concentration $[H^+] = 2 \times 0.65 \times 10^{-2} \times 10$ mol dm^{-3}

= 0.13 mol dm^{-3}

so Full-range Indicator will be red.

Total 10 marks

TOPIC 4

Energy 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 10, when the need to consider the system as well as the surroundings is introduced. In Topic 11 our ideas about entropy are applied to equilibrium reactions and finally in Topic 13 the effect of temperature change is included with the introduction of Gibbs free energy. The development of these ideas is mainly qualitative and the only calculations are straightforward.

When the story is well told 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. The energy changes involved in Born–Haber cycles are introduced and the stability of the crystal lattice discussed in terms of the ionization energies and lattice energies. Ion polarization is discussed in relation to theoretical and experimental lattice energies. The emphasis is on the study of enthalpy changes involving ionic compounds.

Content

	Timing	*Students' book*
4.1	4 hours	Pages 85–88
4.2	3 hours	Pages 89–90
4.3	3 hours	Pages 91–93
4.4	4 hours	Pages 94–98

Total about 3 weeks

4.1 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.
4.2 Hess's Law. Determining standard enthalpy changes of reaction; *an investigation of an enthalpy change that cannot be measured directly.*
4.3 Uses of standard enthalpy changes of formation. Range of values of standard enthalpy changes; the value of Hess's Law, standard enthalpy change of atomization, electron affinity, ionization energy.
4.4 The Born–Haber cycle: lattice energies. Definition of lattice energy, determination of lattice energy from Born–Haber cycle; lattice stability and formation of ions; comparison of theoretical and experimental lattice energies; polarization of ions.

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 atomization, and electron affinity and lattice energy.
3. To examine the evidence for Hess's Law and use this Law to evaluate enthalpy changes that cannot be measured directly.
4. To introduce Born–Haber cycles and use them to calculate experimental lattice energies.
5. To compare experimental and theoretical values for lattice energies and to interpret the differences in terms of structure and bonding.
6. To discuss ion polarization in terms of a transition from ionic to covalent bonding.

4.1 Energy from chemical reactions

Timing About 4 hours will be needed.

Suggested treatment

It is suggested that students are introduced to energy changes through experiments involving exothermic and endothermic reactions.

Experiment 4.1 Measuring some energy changes

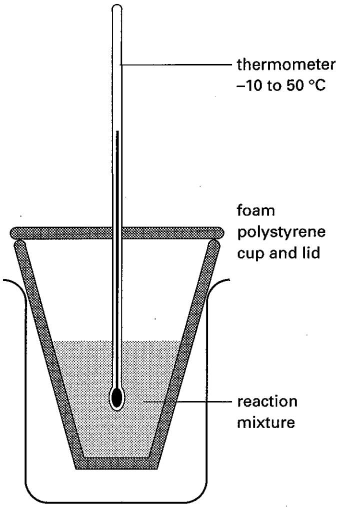


Figure 4.1 Apparatus for measuring energy changes.

Each group of students will need:
Apparatus as in figure 4.1
Thermometer, –10 to 50 °C in 0.1 °C intervals
2 measuring cylinders, 25 cm^3
Dropping pipettes, 2
2 weighing boats
1 M citric acid, 25 cm^3
0.2 M copper(II) sulphate, 25 cm^3 HARMFUL
Sodium hydrogencarbonate, 10 g
Zinc powder, 1 g
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 oxidized 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.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq) \qquad \Delta H^{\ominus} = -219 \text{ kJ mol}^{-1}$$

$$C_6H_8O_7(aq) + 3NaHCO_3(s) \rightarrow C_6H_5O_7{}^{3-}(aq) + 3Na^+(aq) + 3CO_2(g) + 3H_2O(l) \qquad \Delta H^{\ominus} = +70 \text{ kJ mol}^{-1}$$

Using a joulemeter

Teachers might prefer to take the option of using the electrical compensation calorimeter to measure the energy changes in experiment 4.1 and discuss the advantages of this method.

The method using an electrical compensation calorimeter has the advantage of greater accuracy and of measuring the number of joules directly, without calculation or assumption about the value of specific heat capacity. However, it has the disadvantage of greater expense.

Details of the apparatus are given in the *Students' book* in Topic 18.4, which students should read. If this method is used, the quantities of materials used may need to be doubled so that the heater is fully immersed.

The electrical compensation calorimeter consists of a vacuum flask equipped with a small electric immersion heater or lamp and a thermometer reading to 0.1 °C. Each reaction is carried out in the vacuum flask and the temperature change is noted.

Electrical energy is then supplied via a joulemeter

- in exothermic reactions to produce a further rise in temperature by the same number of degrees;
- in endothermic reactions to bring the temperature back to its original value.

The energy supplied is measured directly by the joulemeter.

A possible source of error lies in the fact that the heater may continue to transfer energy to the solution in the calorimeter even after it has been switched off and thus the number of joules that is recorded is too high.

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 heat of formation or the enthalpy change 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 4.2.

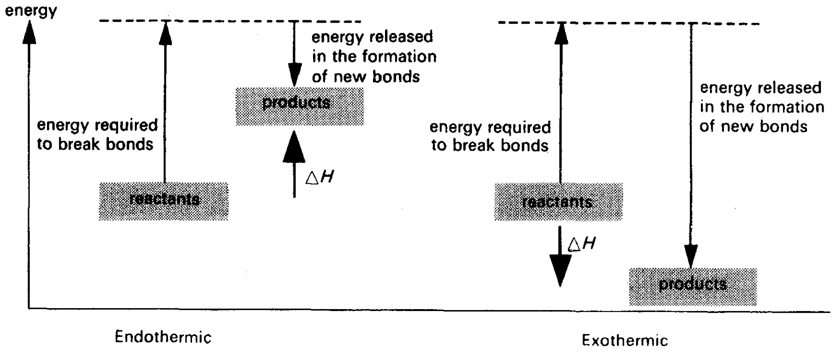


Figure 4.2 Energy diagram for exothermic and endothermic changes.

- 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.

4.2 Hess's Law

Timing About 3 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:

$$Fe_2O_3(s) + 3Cu(s) \rightarrow 2Fe(s) + 3CuO(s)$$

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 4.3). This gives students the necessary practice required before they attempt investigation 4.2.

Investigation 4.2 Determining an enthalpy change that cannot be measured directly

Students are asked to carry out an investigation to determine the enthalpy change for the thermal decomposition of potassium hydrogencarbonate. The planning stage will require time for library research and trial experiments and must include an assessment of risks. A suitable procedure involves measuring the enthalpy change for the reaction of potassium carbonate and potassium hydrogencarbonate with excess dilute acid.

When students have completed their plans, they should be shown to the teacher for checking before they carry out their experiments.

A good report will include a full justification of the method used, based on Hess's Law.

4.3 Uses of standard enthalpy changes of formation

Timing About 3 hours will be needed.

Suggested treatment

	$\Delta H_f^\ominus$/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
NO_2	+33.2
H_2O	−285.8

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 the table opposite.

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 anion size increases).

An explanation of these patterns should not be attempted at present although it might form extension work after discussion of section 4.4. The $\Delta H_f^\ominus$ values for the decomposition of hydrogen halides is relevant to the experiment on these gases in Topic 5.4.

This section is completed by giving further examples of the use of Hess cycles. The example of this type of calculation given in the *Students' book* is the reaction between ammonia gas and hydrogen chloride gas to form ammonium chloride solid. An additional example which might be used is the hydrolysis of silicon tetrachloride:

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$$

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.

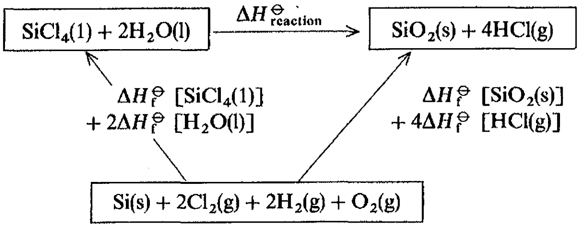


Figure 4.3 Energy cycle for the reaction of silicon tetrachloride with water.

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

$$-910.9 + 4(-92.3) = -687.0 + 2(-285.8) + \Delta H^\ominus_{reaction}$$

So $\Delta H^\ominus_{reaction} = -21.5$ kJ

More enthalpy changes

This section is completed by considering enthalpy change of atomization, electron affinity and revision of the meaning of ionization energy. It is important that students have a precise understanding of these terms. The symbol used for ionization energy in the *Students' book* is E_{mj} ,which is used for successive molar ionization energies, that is, the energy needed to remove the jth successive electron from the atoms or ions.

The symbol E_{aff} has been used for the electron affinity. Strictly speaking the values quoted for the electron affinity refer to the molar internal energy change ΔU for the process

$$X^{n-}(g) + e^- \rightarrow X^{(n+1)-}(g)$$

but since internal energy is not a part of the present course, the difference has been ignored. In any case, the values for the electron affinities are only approximate in many instances and there is considerable variation in the values given by different workers. The determination is difficult but some values have been obtained directly. That of chlorine has been found by a study of the equilibrium

$$Cl(g) + e^- \rightleftharpoons Cl^-(g)$$

set up when a hot tungsten filament is surrounded by chlorine at low pressure.

The teacher should be aware that some books define electron affinity in terms of the energy required to remove an electron from an ion, for example:

$$Cl^-(g) \rightarrow Cl(g) + e^- \qquad E_{aff} = 348.8 \text{ kJ mol}^{-1}$$

The most recent practice is however, to use the definition given above. Provided an ionic equation is always given no confusion should result.

4.4 The Born–Haber cycle: lattice energies

Timing 4 hours will be needed for this section.

Suggested treatment

The sequence followed is:

1 The meaning of lattice energy and the stages in building up a Born–Haber cycle.
2 Lattice stability in terms of the relative values of lattice energy and ionization energies.
3 Theoretical values for lattice energy.
4 Polarization of ions as a transition between ionic and covalent bonding.

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 ionization 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.

Lattice stability and ion formation

The stability of a crystal lattice of a compound is discussed in terms of the relative values of the lattice energy compared with the energy required in forming the anion and cation. The fact that magnesium(III) chloride is unknown, whereas magnesium(II) chloride is a stable compound is mentioned in the *Students' book.* The reasons for this could be discussed in the context of the balance between ionization energies and lattice energy. All the students need to realize is that the successful formation of a compound depends on whether the energy needed for forming the cation and anion is recovered in the energy released as lattice energy.

The following is mainly for the benefit of the teacher when comparing Born–Haber cycles for MgCl, $MgCl_2$ and $MgCl_3$.

We should expect that the compound which has the most negative standard enthalpy change of formation would be most stable. If it is assumed that MgCl would have a sodium chloride lattice structure and $MgCl_3$ a similar structure to $AlCl_3$, then a reasonable estimate of the lattice energies for the hypothetical crystals MgCl and $MgCl_3$ can be made. Born–Haber cycles can then be constructed and values obtained for the standard enthalpy changes of formation of these hypothetical crystals. These cycles are shown in figure 4.4.

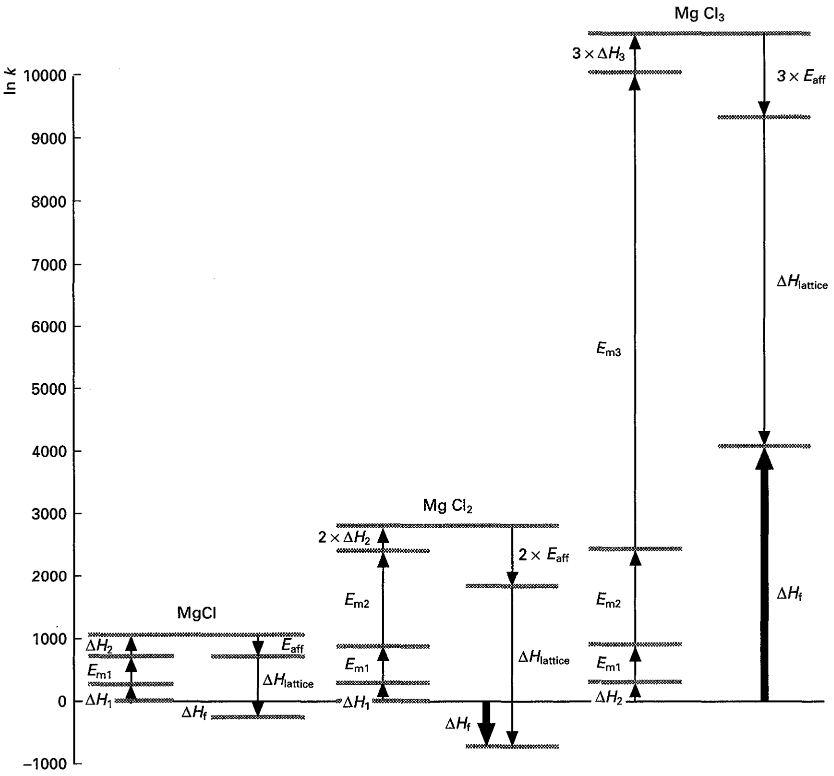


Figure 4.4 Born–Haber cycles for MgCl, $MgCl_2$ and $MgCl_3$ /kJ mol^{-1}

Key	ΔH_1 = enthalpy change of atomization of magnesium	+148
	ΔH_2 = enthalpy change of atomization of chlorine	+122
	E_{m1} = first ionization energy of magnesium	+738
	E_{m2} = second ionization energy of magnesium	+1451
	E_{m3} = third ionization energy of magnesium	+7733
	E_{aff} = electron affinity of chlorine	−349

The enthalpy changes of formation obtained from these cycles are:

$$\Delta H_f^{\ominus}\,[MgCl(s)] = -94 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\ominus}\,[MgCl_2(s)] = -643 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\ominus}\,[MgCl_3(s)] = +3949 \text{ kJ mol}^{-1}$$

From these, it can be seen that the formation of MgCl is just exothermic and the compound is energetically stable with respect to its elements but *not* with respect to $MgCl_2$. The formation of $MgCl_2$ is is even more exothermic and so would be energetically stable with respect to its elements. The formation of $MgCl_3$ is highly endothermic and so it would be extremely unstable with respect to its elements.

The scale diagram in figure 4.4 shows that the largest single contributions in each cycle are made by the ionization energies and the lattice energy, and that these two are always opposite in sign.

Broadly speaking, therefore, the magnitude of the standard enthalpy change of formation depends on the competition between the ionization energy and lattice energy. If it requires more energy to ionize the metal than is returned as lattice energy, then the compound will probably not be formed.

Calculations of this type can be done for many classes of compound. For instance, it can be shown that the formation of NaO would not be energetically favoured, while the formation of Na_2O would be energetically favoured.

Teachers should note that while change in the surrounding $\Delta H_f^\ominus$ has been used as a measure of stability in this discussion, care should be taken not to overemphasize the argument as the change in the system, entropy change, has been neglected. For this reason, students have *not* been introduced to $\Delta H_f^\ominus$ as a criterion for the energetic stability of a compound. The thermodynamic meaning of stability will be discussed later in Topic 10.

ANSWERS TO THE QUESTIONS

1 The lattice energy of Group 1 fluorides decreases down the group (due to increased size of the cation).

2 The lattice energy of the Group 2 chlorides are greater than those of the 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 the smaller ionic radius compared with the chloride ion).

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 values for silver halides, calculating the approximate percentage difference between the theoretical and the experimental values. They will find that there is a considerable percentage discrepancy between these values. Students should be asked whether they think that the ionic model accurately represents the bonding situation in the silver halides. If not, some other model is required.

Polarization of ions

The agreement of the values of theoretical and experimental lattice energies for the sodium and potassium halides was within 1% but similar comparisons for silver halides and zinc oxide showed considerable discrepancies. These discrepancies are due to the presence of an appreciable proportion of covalent bonding.

The internuclear distance in the diatomic molecules MX, for the alkali metal halides, are less than in the solid and this implies a stronger bonding. The stronger bonding implies a higher concentration of electrons between the nuclei than in the crystal and hence some distortion of the electron cloud from a spherical distribution. Figure 4.9 in the *Students' book* shows the increasing polarization of negative ions with increasing ionic radius. Polarization of an ion represents a transition from ionic bonding to covalent bonding.

The Study Task asks students to suggest what factors influence the degree of distortion of the ions. The following ideas which are not in the *Students' book* might be suggested. These statements constitute Fajans' Rules.

- A small positive ion should be more effective than a large one. (With a small ion the positive nuclear charge will be able to approach close to the negative ion.)
- A double positive charge will be more effective than a single one, for similar ionic radii, and a triple positive charge will be even more effective.
- A large negative ion will be more readily distorted than a small negative ion. (The further the electrons are from the nucleus, the less control the nucleus has over them.)
- An ion with a double negative charge will be more readily distorted than one with a single negative charge. (The increased mutual repulsion of the electrons in a doubly charged ion assists transfer; and there is a greater quantity of negative charge available for transfer.)

An examination of the trends in the discrepancies between calculated and experimental lattice energies is illuminating. It is seen that the discrepancies due to the contributions of covalent bonding increase from fluoride to iodide as predicted on the basis of the likely polarizabilities of small and large negative ions. A decrease in the discrepancies for the series BeF_2 to SrF_2 may be interpreted in terms of the effect of the size of the polarizing ion.

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

4.1

a $\frac{100}{1000} \times 0.02 = 0.002$ mole (1)

b 0.002 mole evolved 1052 joules

1 mole would evolve $\frac{1052}{0.002} = 526\,000$ joules = 526 kJ

$\Delta H^\ominus = -526\ \text{kJ mol}^{-1}$ (2)

c Evolved (1)

d $Mg(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Mg^{2+}(aq)$ $\Delta H = -526\ \text{kJ mol}^{-1}$ (2)

Total 6 marks

4.2

a $\frac{50}{1000} \times 0.05 = 0.0025$ mole (1)

b 0.0025 mole silver evolved 184 joules

1 mole would evolve $\frac{184}{0.0025} = 73\,600$ joules = 73.6 kJ

$\Delta H^\ominus = -73.6\ \text{kJ mol}^{-1}$ of silver atoms, or
$-147.2\ \text{kJ mol}^{-1}$ of copper atoms (3)

c $Cu(s) + 2Ag^{+}(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$ $\Delta H = -147.2\ \text{kJ mol}^{-1}$ (2)

Total 6 marks

4.3

$(-526) + (-147.2) = -673.2\ \text{kJ mol}^{-1}$ of magnesium atoms (2)
$Mg(s) + 2Ag^{+}(aq) \rightarrow 2Ag(s) + Mg^{2+}(aq)$ $\Delta H = -673.2\ \text{kJ mol}^{-1}$ (2)
Hess's Law has been assumed (1)

Total 5 marks

4.4

all answers in kJ mol^{-1}

a –234 (3)
b –239 (3)
c +176 (3)
d –602 (3)
e –20.6 (3)
f –810 (3)
g –411 (3)

Total 21 marks

4.5

a None (2)
b $\Delta H_f\ [CuO(s)]$ (2)
c $\Delta H_f\ [CuO(s)]$ (2)

Total 6 marks

4.6

Lattice energy of CaO is –3454 kJ mol^{-1} (although the question does not require the calculation to be carried out) Total 2 marks

4.7

Lattice energy of Na_2O by Born–Haber cycle is 2527 kJ mol^{-1}

Total 4 marks

Examination questions

4.8

a 0–100 °C, 0.1 °C or smaller range with greater sensitivity (2)
b **i** 1.1 °C (or the same) (1)
  ii 0.4 °C (1)
c Second, large volume minimize errors (2)
d Third, small temperature change maximizes errors (2)
Total 8 marks

4.9

Mark by impression

Apparatus may be temperature measurement or electrical compensation method. Look for determination of solution concentrations, a specified method of measuring volumes (cylinders should do), type of thermometer selected, stirring well, sample calculation. (10)

The data should be identified as strong acid/strong base, weak/strong, strong/weak, weak/weak. This answer stretches the student's knowledge of Topic 3. (5)

Total 15 marks

4.10

Mark by impression

Any diagram should be well drawn and labelled, quantities should be specified and a method for treating the results. (10)

'Correct' or 'incorrect' are acceptable but the answer must be explained for any marks to be awarded; further reaction with water and difficulty of energy transfer are problems that could be mentioned. (4)

The student is correct, as the reaction between calcium and water is much more rapid. (1)

Total 15 marks

4.11

a B_2O_3 (1)
b **i** Labelled cycle (2)
  ii Lattice energy

$$= -1270 - [(2 \times 590) + (3 \times 250) + 2\,(+800 + 2400 + 3700) + 3\,(-140 + 790)]$$

$$= -18\,950 \text{ kJ mol}^{-1}$$ (2)

(or $B_2O = -4950$, $BO = -5960$, $BO_3 = -9090$)

c **i** $B_2O_3(s) + 3H_2O(l) \rightarrow 2H_3BO_3(aq)$ (1)
  and appropriate ionic product e.g. $H_2BO_3^-$ (1)
  ii Poor agreement
  Covalent oxide because polarization by charge, acidic (2)
Total 9 marks

4.12

a Definite amounts, enthalpy change, substances in standard states at 298 K (3)

b Calcium(II) iodide, much greater enthalpy change of formation (2)

c Fully labelled clear diagram (7)

d Lattice energy = –534 – (2127 – 590)

= –2071 kJ mol^{-1} (3)

e Ionic

Calcium–iodine separation fits ionic or covalent, iodine–iodine suggests ionic. (3)

f Compare experimental and theoretical lattice energies (1)

Total 19 marks

4.13

Mark by impression

Explanation of lattice energy with list of data needed for a Born–Haber cycle (3)

Lattice energy for CdO

$$= \Delta H_f^\ominus[\text{CdO}] - \Delta H_{at}^\ominus[\text{Cd}] - E_1[\text{Cd}] - E_2[\text{Cd}] - \Delta H_{at}^\ominus\left[\tfrac{1}{2}\text{O}_2\right] - E_{\text{aff }1}[\text{O}] - E_{\text{aff }2}[\text{O}]$$

= –258.1 –112.0 –868 –1631 –249.2 +141.1 –798

= –3775 = –3780 kJ mol^{-1} (to 3 SF) (8)

Theoretical value is –3806 kJ mol^{-1}

Values within 1% suggests ionic model for CdO is accurate

Theoretical values are based on electrostatic forces of attraction between spherical ions in a regular lattice. (4)

Total 15 marks

TOPIC 5

The halogens and redox reactions

Introduction

Students are likely to be aware from their pre-A-level courses, that there are trends in the physical and chemical properties in Group 1 and Group 7 elements. This Topic extends students' knowledge of Group 7 elements by introducing a range of halogens and halogen compounds and considering their redox reactions, their sources and uses.

In Topic 1, oxidation and reduction was related to changes in the oxidation state of simple ionic compounds. This is expanded in the present topic where redox reactions are first studied in terms of electron transfer and then in terms of oxidation number. The use of oxidation numbers in balancing equations and the Stock notation is also introduced.

Content

	Timing	*Students' book*
5.1	2 hours	Pages 104–106
5.2	3 hours	Pages 106–109
5.3	6 hours	Pages 110–114
5.4	3 hours	Pages 114–115
5.5	3 hours	Pages 116–117
5.6	1 hours	Page 118
5.7	2 hours	Pages 119–121
5.8	Homework	Pages 121–122

Total about 4 weeks

5.1 Sources of the halogens. Method of extraction of halogens from their sources; the extraction of iodine from seaweed.

5.2 Redox reactions and oxidation numbers. Reactions between halogens and halide ions; oxidation and reduction by electron transfer; the meaning of oxidation number; rules for assigning oxidation numbers; oxidation-reduction and oxidation number change; oxidation numbers and the Stock notation.

5.3 The range of halogen compounds. Oxidation numbers of halogens and halogen compounds; oxidation number 0, reactions of the halogens with alkalis; preparation of potassium iodate(V); estimation of iodine using sodium thiosulphate solution; determination of the purity of samples of potassium iodate(V).

5.4 Oxidation number –1: the properties of the halides. Reaction of halides with silver nitrate solution, action of sulphuric acid and phosphoric acid on solid halides, properties of hydrogen halides.

5.5 Oxidation number +1: the reactions of sodium chlorate(I). Sodium chlorate(I) as an oxidizing agent; balancing redox equations using oxidation numbers; *an investigation of the reaction of bromine with sodium thiosulphate.*

5.6 Oxidation number +5: the reactions of the potassium halates(V). Thermal decomposition of potassium halates(V), potassium halates(V) as oxidizing agents.

5.7 The properties of the halogens. Trends in the physical and chemical properties of the halogens, electronic structure of halide ions, relative reactivity of halogen compounds, reactivity and structure of chlorides across a period, sources and uses of the halogens.

5.8 **Study Task.** The halogens in human metabolism.

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 extend students' knowledge of periodic trends by reference to the properties of the chlorides across a period of the Periodic Table.
7. To evaluate information concerning the sources of the halogens and their uses.

5.1 Sources of the halogens

Timing

About 2 hours.

Suggested treatment

This introductory section summarizes 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 TO THE STUDY TASK QUESTION

1 1.27×10^{-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 crystallization 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 5.1 The extraction of iodine from seaweed

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 cork
Spatula
Access to:
Dried seaweed, preferably from a _Laminaria_ seaweed*, 2 g
1 M sulphuric acid, 5 cm^3 IRRITANT
20 volume hydrogen peroxide, 10 cm^3 OXIDIZING, CORROSIVE
Petroleum spirit, boiling range 120–160 °C, 10 cm^3 labelled
'Hydrocarbon solvent' FLAMMABLE

Hazards

If 100 volume hydrogen peroxide is purchased it must be handled with great care. 100 volume hydrogen peroxide causes burns, is irritant and caustic. Gloves should be worn when diluting the solution to 20 volume for laboratory use.

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 Laminariaceae 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 volatilizing the solute.

Students should observe the purple colouration 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 results, however, will not be convincing unless the hydrocarbon solvent is allowed to evaporate with the minimum of heating.

5.2 Redox reactions and oxidation numbers

Timing

About 3 hours.

Suggested treatment

This section is developed in the following way:

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 5.2

The reactions between halogens and halide ions

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 CORROSIVE
0.05 M aqueous iodine*, 5 cm^3 HARMFUL
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' FLAMMABLE
Fume cupboard (for the aqueous chlorine and bromine)

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 with three times its own volume of pure water.
- Dissolve 12 g of iodine and 10 g of potassium iodide in 1 dm^3 of water.

Store the aqueous chlorine and bromine solutions in a fume cupboard.

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 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 (oxidizing agents) are substances which gain electrons and 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:

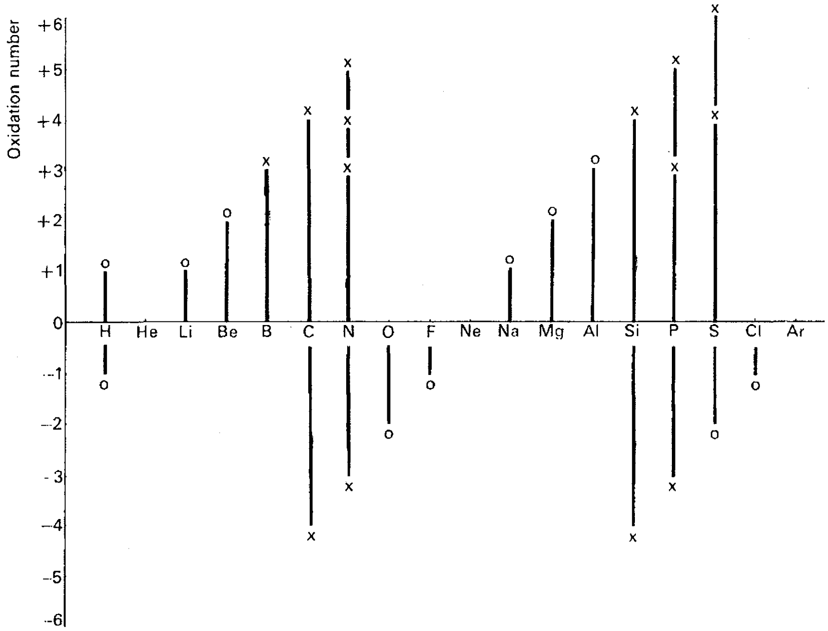


Figure 5.1 Oxidation number chart.

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 realize 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 difficulty 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. Some examples of reactions involving change of oxidation number should be provided for students to identify oxidants and reductants.

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). This conforms with the system of nomenclature suggested by the ASE. Plenty of practice at naming inorganic compounds should be given; review question 5.2 is suitable.

5.3 The range of halogen compounds

Timing About 6 hours will be needed.

Suggested treatment

This section extends the students' knowledge of the halogens in a practical context by considering their reactions with alkalis. It is developed as follows:

1. The range of oxidation numbers of halogen compounds is discussed using an oxidation number chart.
2. The reaction of halogens with concentrated alkali is studied.
3. Students prepare a sample of potassium iodate(V) from iodine and potassium hydroxide.
4. The use of sodium thiosulphate for estimating iodine is introduced.
5. Students determine the purity of the sample of potassium iodate(V) they have prepared by an experiment involving titration with sodium thiosulphate.

The range of halogen compounds

Once the idea of oxidation number has been established, it can be applied to the compounds of the halogens. A convenient way is to construct an oxidation number chart. This is done by numbering a vertical axis as shown in figure 5.2 and writing against each number the formulae of the compounds in which the chosen element has an oxidation number of that value.

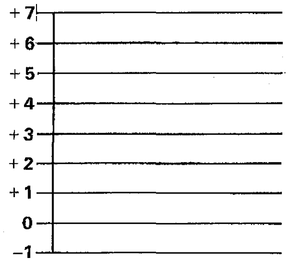


Figure 5.2

Such a chart can show clearly the range of compounds formed by an element and allows likely reactions to be considered. Using such a chart, redox reactions are clearly seen as reactions involving a change in oxidation number. Discussing these reactions in terms of change in oxidation number has the advantage of not prejudging either bond type or reaction mechanism. This approach therefore avoids the possibility of having to correct false ideas at a later stage.

As an example, the students should construct an oxidation number chart for chlorine. Once they have done this, the students can draw similar charts whenever they study a new element. If it is convenient, a large board can be kept permanently for this purpose. The vertical, oxidation number axis could be painted down one side and Terry clips of a suitable size to hold specimen bottles could be fitted at each level so that samples of the various compounds could be exhibited.

Experiment 5.3a Oxidation number 0: the reactions of the halogens with alkalis

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:
1 M sodium hydroxide, 10 cm^3 IRRITANT
Aqueous chlorine, saturated solution, 2 cm^3 TOXIC
0.05 M aqueous bromine, 2 cm^3 CORROSIVE
0.05 M aqueous iodine, 2 cm^3 HARMFUL
Fume cupboard (for the aqueous chlorine and bromine)

⚠ 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 5.2.

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 also introduced to disproportionation by answering the question 'What changes of oxidation number does the chlorine undergo?' for the reaction

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

The chlorine undergoes two changes; part of it changes from 0 to –1 and part from 0 to +1.

The *Students' book* then gives the equation for the action of chlorine with hot alkali.

ANSWERS TO THE QUESTIONS

1 Chlorine changes in oxidation number from 0 to +5 and from 0 to –1
2 $3I_2(aq) + 6KOH(aq) \rightarrow 5KI(aq) + KIO_3(aq) + 3H_2O(l)$

Experiment 5.3b

The preparation of potassium iodate(v)

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
Access to:
4 M potassium hydroxide, 10 cm^3 CORROSIVE
Iodine, solid HARMFUL

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 advisable to wear face masks if available.

The potassium iodate(v) formed in this reaction is oxidizing 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.

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 5.3d.

Experiment 5.3c

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:

$$2Na_2S_2O_3(aq) + I_2(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$$

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 5.3d To determine the purity of samples of potassium iodate(v)

Each group of students will need:
Eye protection
2 weighing boats
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 5.3b
Access to:
0.1 M potassium iodide, 60 cm^3
1 M sulphuric acid, 60 cm^3 IRRITANT
0.1 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 5.3b. Results are likely to be variable but percentages in the high nineties are to be expected.

Part 2 utilizes the same method but this time, the percentage of potassium iodate(v) remaining in the potassium iodide is found. Figures of around 15% 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.

5.4 Oxidation number -1: the properties of 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 5.4 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

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 CORROSIVE
Lamp or brightly lit windowsill

⚠ 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.

Silver nitrate is severely irritant to the eyes.

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.

Experiment 2a and 2b

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 IRRITANT
Concentrated sulphuric acid with pipette CORROSIVE
Full-range Indicator paper
Fume cupboard
Lead ethanoate paper HARMFUL

Hazards

85% (ortho)phosphoric acid can be used instead of 100% orthophosphoric acid and is nearly as effective. Alternatively add phosphorus pentoxide to about double its volume of 85% orthophosphoric acid. Wear gloves and a face shield for this procedure. Lead ethanoate is a harmful 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 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.

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 pH paper (optional). Students should hold the test papers using tweezers or gloves.

Sulphur dioxide 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 vaporization 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 oxidizes 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 oxidized 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 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

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 5.3)
Beaker, 250 cm^3 or ice cream tub (for the gas solubility experiment)
Length of nichrome wire in holder or 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

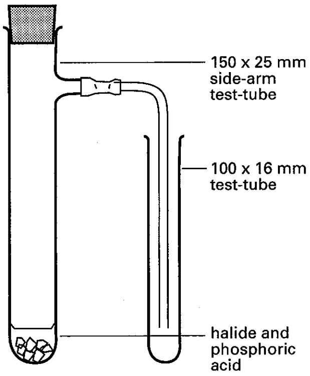


Figure 5.3 Apparatus for making hydrogen halides.

Hazards

See the notes for experiment 2.

Procedure for experiment 3

A wide ice-cream tub or plastic food box 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 pH 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 for the hydrogen halides in Topic 4.3. The values of the bond energies of the hydrogen halides are considered further in Topic 6.

5.5 Oxidation number +1: the reactions of sodium chlorate(I)

Timing About 3 hours.

Suggested treatment

This section is developed to include a discussion of the use of oxidation numbers in balancing equations.

The sequence is:

1 examining some reactions of sodium chlorate(I);
2 balancing redox equations;
3 determining the equation for the reaction of bromine with sodium thiosulphate.

Experiment 5.5a

Some reactions of sodium chlorate(I)

Each group of students will need:
Eye protection
4 test-tubes and rack
0.1 M iron(II) sulphate, 3 cm^3
0.1 M potassium iodide, 3 cm^3
Sodium chlorate(I) solution, with dropping pipette, 4 cm^3 CORROSIVE
1% potassium thiocyanate, 1 cm^3

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.

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 oxidizing 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

Students could use a solution of potassium thiocyanate to test for the presence of Fe^{3+} ions. The relevant equation is:

$$2Fe^{2+}(aq) + ClO^{-}(aq) + H_2O(l) \rightarrow 2Fe^{3+}(aq) + Cl^{-}(aq) + 2OH^{-}(aq)$$

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 (see experiment 5.3a). The equation for the reaction is:

$$2I^{-}(aq) + ClO^{-}(aq) + H_2O(l) \rightarrow I_2(aq) + Cl^{-}(aq) + 2OH^{-}(aq)$$

The chemists' toolkit: balancing redox equations

Attention should be drawn to the use of oxidation numbers in balancing redox equations. The *Students' book* discusses this fully and provides an example. Students may practise using the method by doing problem 5.3.

Investigation 5.5b The reaction of bromine with sodium thiosulphate

Students are asked to carry out an investigation to determine the equation of the reaction of bromine with sodium thiosulphate in dilute solutions. The planning stage will need to include trial experiments and must include an assessment of risks. When students have completed their plan, it should be checked by the teacher before they carry out their experiments.

Students should realise that a quantitative investigation is expected. The *Book of data* quotes the solubility of bromine in water as 0.0224 mol/100 g at 293 K. For a simplified investigation students can be provided with diluted bromine water of a stated concentration. Alternatively it is a problem they will have to solve by addition of excess potassium iodide solution and titration of the liberated iodine with a standard sodium thiosulphate solution.

Adding sodium thiosulphate solution to bromine water solution is colourless produces sulphate ions (barium chloride test in Topic 1.1) and bromide ions (silver nitrate–ammonia test in Topic 5.4).

A successful titration with standard sodium thiosulphate will need to use starch–iodine as an indicator for the end-point. Using the guidelines for balancing a redox equation should produce the equation

$$4Br_2 + Na_2S_2O_3 + 5H_2O \rightarrow Na_2SO_4 + H_2SO_4 + 8HBr$$

A set of cue cards could be prepared to help students who have difficulty devising a procedure on their own.

This investigation is based on the article by Bolton, C. 'The chemistry of the bromine–thiosulphate reaction', *School Science Review*, **73**, *265*, pages 101–2, 1992.

5.6 Oxidation number +5: the reactions of the potassium halates(v)

Timing

About 1 hour.

Suggested treatment

The action of potassium halates as oxidizing agents is discussed by reference to thermal decomposition and by experiments involving their reaction with Fe^{2+} and I^- ions.

Experiment 5.6 Some reactions of the potassium halates(v)

Each group of students will need:

Eye protection and protective gloves
3 hard glass test-tubes
Additional test-tubes and rack
Bunsen burner and heatproof mat
Test-tube holder
Access to:
Potassium chlorate(v) OXIDIZING, HARMFUL

Potassium bromate(v) TOXIC, OXIDIZING
Potassium iodate(v) IRRITANT
1 M sulphuric acid, 5 cm^3
0.1 M iron(II) sulphate, 5 cm^3
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 5.4) should 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.

Particular care should be taken when testing for oxygen; students should not let the glowing splint fall into the tube otherwise a violent reaction will take place. Students should be advised to use small amounts of the halates(v).

Procedure

Instructions for the experiment are given in the *Students' book.* Students should identify the species which have been oxidized 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 Action of heat

On heating, potassium chlorate(v) disproportionates

$$4KClO_3(s) \rightarrow KCl(s) + 3KClO_4(s)$$

The chlorate(VII) produced then decomposes

$$KClO_4(s) \rightarrow KCl(s) + 2O_2(g)$$

The bromate and iodate decompose directly to give bromide or iodide and oxygen. The decomposition temperatures in the *Book of data* follow the order

$$KIO_3 > KBrO_3 > KClO_3$$

However, the melting point of the iodates are higher and iodates are generally not so easily decomposed compared with the chlorates and bromates.

2 Reaction with iron(II) ions

All the halates(v) are good oxidants. They all oxidize Fe^{2+} to Fe^{3+} in a similar manner, for example,

$$6Fe^{2+}(aq) + ClO_3^-(aq) + 6H^+(aq) \rightarrow 6Fe^{3+}(aq) + Cl^-(aq) + 3H_2O(l)$$

3 Reaction with iodide ions

Chlorates and bromates oxidize iodide to iodine, the halates(v) being reduced to halide. The reaction of iodide with iodate produces iodine and water.

$$6I^-(aq) + ClO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + Cl^-(aq) + 3H_2O(l)$$

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

5.7 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 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 ion

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 Relative reactivity of the compounds

Students should use the results of their experiments as well as reference books to elucidate trends in reactivity of halogen compounds. The following general trends down the group might be noted:

- The ease of oxidation of the hydrogen halides increases.
- The ease of oxidation of the halide ions increases.
- The temperature at which the halates(v) decompose decreases

As oxidation number increases, the following trends might be noted:

- The oxidizing ability of the salts of the oxoacids increases; for example, potassium chlorate(v) is a better oxidant that potassium chlorate(I).
- The oxidizing ability of the oxoacids decreases, that is $HOCl > HClO_2 > HClO_3 > HClO_4$.

5 Reactivity and structure across a period of the Periodic Table

A table showing the reactivity and structure of the chlorides in Period 3 is given in the *Students' book*. This material will be studied again as part of Topic 6.6.

The students are not expected to learn the detailed equations by heart but having considered the tables, they should know in outline what patterns exist in the physical and chemical properties across a period. It is necessary to make sure that the students understand properly the meanings of the words *trend* and *periodicity*. Samples of the chlorides of the Period 3 elements could be provided for students to observe or an optional experiment to illustrate the formation of some of these chlorides could first be demonstrated if teachers feel this will be of help. Details are given below.

The following points may be brought out.

- The proportion of chlorine in the 'characteristic' chlorides increases as far as Group 5 in Period 3 and then falls again.
- The chlorides of non-metals appear to have several oxidation states. Phosphorus has a pentachloride, PCl_5 as well as a trichloride, PCl_3. The chloride of sulphur with the highest proportion of chlorine is SCl_2 whilst silicon has numerous chlorides (of general formula Si_nCl_{2n+2}).
- The chlorides with giant lattice structures are those of metals on the left of the Periodic Table. Molecular chlorides are formed from the elements to be found on the right of the Periodic Table.
- The standard enthalpy change of formation shows a maximum at Group 3 but if plotted per mole of chlorine atoms, it gets less negative in an approximately linear manner with atomic number.
- Broadly, the chlorides of the metals show the least tendency to be hydrolysed.

Experiment 5.7 Optional teacher demonstration of the action of chlorine on the elements of the third period of the Periodic Table

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 FLAMMABLE
Magnesium ribbon
Aluminium powder FLAMMABLE
Silicon powder
RED phosphorus HIGHLY FLAMMABLE, TOXIC
Sulphur
Chlorine, 6 gas jars TOXIC
Fume cupboard
Each student will need:
Eye protection

SAFETY

On no account must white phosphorus be used. In some areas the use of phosphorus may be restricted.

Sulphur should be kept away from aluminium powder. The products of some of the reactions are corrosive and should be treated with care.

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.

6 Sources and uses

This may be omitted if students have covered the material in section 5.1.

5.8 Study Task: The halogens in human metabolism

Timing This Study Task may be set for homework.

Suggested treatment

Part of this task, which is suitable for homework, requires students to summarize the important points of a passage. This may be the first time that students have been asked to do such a summary exercise and some suggestions on how to go about the task might be given beforehand.

ANSWERS TO THE STUDY TASK QUESTIONS

1 The answer should relate to the oxidizing action of halogens on the tissues.
2 Bones, especially teeth.
3 Fluoride ion causes teeth to become mottled and at high concentrations is toxic.
4 Chlorine solution kills bacteria.
5 1.03×10^{-3} mol dm^{-3}.
6 Iodide. Iodine can be metabolized in the body. The other halide ions are required for specific functions but there are no natural mechanisms to oxidize 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 oxidized to iodine in the thyroid and are then involved in the synthesis of thyroxine. (55 words)

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

5.1

a	B	(1)	**h**	A	(1)
b	A	(1)	**i**	B	(1)
c	A	(1)	**j**	C	(1)
d	A	(1)	**k**	B	(1)
e	B	(1)	**l**	A	(1)
f	A	(1)	**m**	C	(1)
g	A	(1)			Total 13 marks

5.2

a	Copper(II) sulphate-5-water	(1)
b	Copper(I) oxide	(1)
c	Iron(III) hydroxide	(1)
d	Iron(II) sulphide	(1)

e Lead(II) carbonate (1)
f Lead(IV) chloride (1)
g Chromium(II) bromide (1)
h Cobalt(III) oxide (1)
i Manganese(III) oxide (1)
j Manganese(VI) oxide (1)
k Manganese(VII) oxide (1)
l Uranium(VI) fluoride (1)
m Thallium(III) fluoride (1)
n Thallium(I) chlorate (1)
o Titanium(IV) iodide (1)
p Strontium(II) nitrate (1)

Total 16 marks

5.3

a $Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$ (3)
b $2Al(s) + 6H^{+}(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$ (3)

or

$Al(s) + 3H^{+}(aq) \rightarrow Al^{3+}(aq) + 1\frac{1}{2}H_2(g)$

c $Cu^{2+}(aq) + 2I^{-}(aq) \rightarrow CuI(s) + \frac{1}{2}I_2$ (or doubled) (3)
d $Fe(s) + 2Fe^{3+}(aq) \rightarrow 3Fe^{2+}(aq)$ (3)
e $Sn(s) + 4HNO_3(l) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$ (3)
f $Cl_2(aq) + 2OH^{-}(aq) \rightarrow Cl^{-}(aq) + ClO^{-}(aq) + H_2O(l)$ (3)
g $SO_2(aq) + Br_2(aq) + 2H_2O(l) \rightarrow 4H^{+}(aq) + SO_4^{2-}(aq) + 2Br^{-}(aq)$ (3)
h $As_2O_3(s) + 2I_2(aq) + 2H_2O(l) \rightarrow As_2O_5(aq) + 4H^{+}(aq) + 4I^{-}(aq)$ (3)
i $MnO^{-}_4(aq) + 8H^{+}(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$(3)
j $[Fe(CN)_6]^{4-}(aq) + \frac{1}{2}Cl_2(aq) \rightarrow [Fe(CN)_6]^{3-}(aq) + Cl^{-}(aq)$ (3)

Total 30 marks

5.4

a $0.100\ mol\ dm^{-3}$ (2)
b $\frac{0.100}{2} \times \frac{23.6}{25}$ (2)
$= 0.0472\ mol\ dm^{-3}$ (1)
c 0.0472×254 (2)
$= 12.0\ g\ dm^{-3}$ (1)

Total 8 marks

5.5

$10\,000\ cm^3\ 0.100\ M\ S_2O_3^{2-} \equiv \frac{1}{2}I_2 \equiv \frac{1}{2}Cl_2$ (2)
$\equiv 35.5$ g chlorine (1)
$45\ cm^3\ 0.100\ M\ S_2O_3^{2-} \equiv \frac{45}{10\,000} \times 35.5\ g$ (2)
$\equiv 0.16$ g chlorine (1)

Total 6 marks

5.6

a A reducing agent is a substance which can change the oxidation number of another element to some less positive or more negative value. (2)
b Tin(II) chloride (or tin(II) ions). (1)
c **i** 6 (1)

ii 2 (1)
iii 3 (1)
iv 6 (1)
v $3Sn^{2+}(aq) + ClO_3^-(aq) + 6H^+(aq) \rightarrow 3Sn^{4+}(aq) + Cl^-(aq) + 3H_2O(l)$ (3)

Total 10 marks

Examination questions

5.7

a $\frac{100}{1000} \times 4$ moles of KOH
React with 0.4×127 g iodine (suitable I_2/KOH ratio)
= 50.8 g (3)

b Disappearance of iodine colour (1)

c KIO_3: 6 moles → 1 mole

$$0.4 \rightarrow \frac{0.4 \times 214 \text{ g}}{6}$$

= 14.3 g

KI: 6 moles → 5 moles

$$0.4 \rightarrow \frac{0.4 \times 5 \times 166 \text{ g}}{6}$$

= 55.3 g (4)

(no mark for first number with more than 4 SF)

d about 35 °C (1)

e (pure) KIO_3 (1)

Total 10 marks

5.8

a **i** Sodium chlorate(I). (2)
ii Bubble chlorine through cold sodium hydroxide solution. (2)
iii Disinfectant/swimming pool/oxidizing agent. (1)

b **i** $\frac{15}{74.4} = 0.20$ mol (1)

ii $\frac{15}{74.4} \times \frac{1000}{100} = 2.0 \text{ mol dm}^{-3}$ (1)

c **i** Harmful/irritant. (1)
ii Acid produces free chlorine gas. (2)
iii Store securely (away from children). (1)

d **i** Oxygen, –2 to 0 (2)
ii Dark cupboard/out of sunlight. (1)

Total 14 marks

5.9

a **i** $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2S_4O_6^{2-}(aq) + 2I^-(aq)$ (or formal equation)
Balanced equation (1)
State symbols (1)
ii Procedure: only one titration carried out – no check on accuracy (1)
Recording: initial reading of burette is only recorded as whole number of cm^3 (1)

iii Concentration of chlorine molecules, Cl_2:
Number of moles of thiosulphate ions used
$= 2 \times$ moles of iodine molecules liberated
$= \frac{9.3}{1000} \times 0.00500 = 4.65 \times 10^{-5}$ mol
$= 2 \times$ moles of chlorine molecules in 1000 cm^3 of water
$\therefore$ Concentration of chlorine molecules in pool water
$= \frac{1}{2} \times 4.65 \times 10^{-5} = 2.3 \times 10^{-5}$ mol dm^{-3} (3)
iv Indicator: starch (1)
Colour change at end-point: from blue-black to colourless. (1)
b i Chlorine gas is poisonous/highly toxic etc. (1)
ii $Ca(ClO)_2$ (1)
iii Any reasonable variation on:
$4ClO_2 + 2H_2O \rightarrow HClO + 3HClO_3$
$2ClO_2 + H_2O \rightarrow HClO + HClO_4$
Reasonable prediction of an oxidation product (1)
Balanced equation (1)
Total 13 marks

5.10
Mark by impression
An answer should deal with compounds, not the elements;
useful data (tables 5.3, 6.1, 6.5) for making comparisons. data (5)
Equations and explanations (redox, precipitation, complex ions). (10)
Total 15 marks

5.11
Mark by impression
An answer should be well balanced with substantial chemical detail and expressed in the student's own words, not copied verbatim from the *Students' book.*
Total 15 marks

5.12
Mark by impression
An answer should cover all the standard oxidation states
(–1, 0, +1, +5, +7) with well organized examples. (10)
$Sn^{2+}(aq) + I_2(aq) \rightarrow Sn^{2+}(aq) + 2^{-}(aq)$
so 10.0 cm^3 of 0.050 M $I_2 = 0.0005$ mol I_2
$\equiv 0.0005$ mol Sn^{2+} in 25.0 cm^3
so mass of Sn $= 0.0005 \times 10 \times 119 = 0.595$ g
and percentage of tin in the alloy = 59.5 = 60%
Nitric acid is not used as it will interfere with titration by oxidation. (5)
Total 15 marks

TOPIC 6

Covalent bonding

Introduction

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 stoicheiometry. The distribution of bonds in space is then considered. 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.

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. This complements the idea, first introduced in Topic 4, that ionic and covalent bonding are considered as extreme types and in reality there is a range of intermediate situations. The topic ends with a discussion of electron delocalization.

Content

	Timing	*Students' book*
6.1	3 hours	Pages 133–136
6.2	4 hours	Pages 136–143
6.3	1 hour	Pages 143–144
6.4	1 hour	Pages 145–146
6.5	1 hour	Pages 147–149
6.6	1 hour	Page 149

Total about 2 weeks

Introduction. Electron density maps of covalent compounds.
6.1 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.
6.2 Bond energies. Standard enthalpy change of combustion and its use in calculating enthalpy change of formation; determination of enthalpy changes of combustion of alcohols, contributions of specific groups of atoms to enthalpy changes; bond lengths and bond energies.
6.3 Dative covalency. The hydroxonium ion, the ammonium ion, carbon monoxide and nitric acid.
6.4 The chemists' toolkit: electronegativity. Definition of electronegativity, bond polarization, intermediate types of bonding; electronegativity and polar molecules.
6.5 Delocalization of electrons. Evidence for delocalization, nitric acid and nitrate ion, methanoic acid and methanoate ion, effect of delocalization on bond angles and bond lengths.
6.6 Bonding, structure and chemical behaviour. Behaviour of chlorides and oxides towards water related to their structure and bonding.

Objectives

1. To discuss 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 use Hess cycles and enthalpy changes of combustion to calculate the enthalpy change of formation of compounds.
5. To introduce bond energies.
6. To introduce the idea of electronegativity.
7. To interpret some properties of polar molecules in terms of electron distribution.
8. To introduce the idea of electron delocalization.

Introductory section

In this Topic, we consider the nature of the bonds which may exist in a representative range of materials. It is emphasized that questions concerning geometry may be answered experimentally, but questions concerning bonding can only be discussed in terms of simplified mathematical 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. Nor do they seem to be necessary concepts at this level.

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.

The students should study the electron density maps for the simplest diatomic molecule of all, the H_2^+ molecule ion, and for the molecule of 4-methoxybenzoic acid, given in the *Students' book* as figures 6.1 and 6.2. Students should recognize at once that the electron distribution is significantly different from that described for ionic structures in Topic 3. In figures 6.1 and 6.2, there is a substantial electron density at all points between the two bonded nuclei. The electrons are being shared by those nuclei.

In the H_2^+ molecule there is very much more negative charge-cloud in a position to exert a net attractive force than there is to exert a net disruptive force, so there is a strong net attractive force holding the nuclei together.

The sharing of an electron cloud leads to a lower potential energy than if the cloud were not shared, and a lower potential energy results in greater stability.

The effect is even greater with the neutral H_2 molecule, where two electrons are available for bonding; and this is revealed in the internuclear distances and the bond dissociation energies. The internuclear distances for the H_2^+ and the H_2 species are 0.104 nm and 0.074 nm respectively, and the bond dissociation energies are 257 kJ mol^{-1} and 435 kJ mol^{-1} respectively.

The shape of ions and distortion of their electron clouds has been mentioned in earlier topics and reference should now be made to this with the aid of figure 6.3 in the *Students' book.*

At this point it would be appropriate to recall the aspects of ion formation which can be accounted for in terms of electron transfer. This accounts for the stoicheiometry of the compounds. It also accounts for the charges on the ions, and hence for the forces which hold the compounds together. The agreement between lattice energies calculated from the electron transfer model and those determined experimentally is also strong support for the model. Since a noble gas structure corresponds to a complete electron shell it is reasonable to suppose that there might be a spherical symmetry in the distribution of these electrons.

6.1 Electron sharing in covalent molecules

Timing About 3 hours will be required.

Suggested treatment

The teacher will need:
Molecular model kit, with orbitals, to make models of the molecules of $BeCl_2$, BF_3, CH_4, NH_3, H_2O, HCl; C_2H_6, $CH_2 = CH_2$, $HC \equiv CH$; CH_3OH, C_2H_5OH; 4–methoxybenzoic acid, H_2.

The distribution of bonds in space is considered through the Sidgwick–Powell and Nyholm–Gillespie 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 stoicheiometry, 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 first short period of the Periodic Table. PCl_5, SF_6 and SF_4 are examples of exceptions to the rule, and their stoicheiometry can be interpreted on the basis of the number of half-filled atomic orbitals available. But this is beyond the ideas covered in this course.

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 stoicheiometry.

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 emphasizing 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 diagrams give a proper indication of the shapes of the molecules, for they are two-dimensional representations of three-dimensional structures.

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. The class should make dot-and-cross diagrams for the electronic structures of several simple molecules. The *Students' book* gives an example (methane) in figure 6.5. 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 and O_2. A number of other examples could also be given. Students then consider the shapes of molecules in terms of bonding pairs of lone pairs of electrons. This may be developed as follows.

Single bonds

The teacher will need:
Models of $BeCl_2$, BF_3, CH_4, NH_3, H_2O and HCl, together with pear-shaped lobes representing lone pairs of electrons.

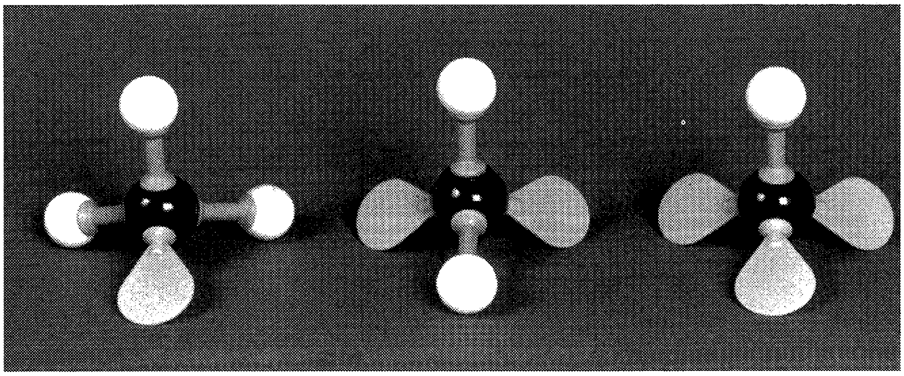


Figure 6.1 Molecular models showing bonds and lone pairs.

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 molecules $BeCl_2$, BF_3 and 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 $BeCl_2$, BF_3 and CH_4, the bonds attempt to arrange themselves as far apart from each other as possible, then 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 placed on the bench and discussed.

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?

Each is made up of regions of 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?

The bond angles for methane, ammonia, and water may be examined and interpreted.

	Bond angle	**Change in bond angle from methane**
CH_4	109.5°	–
NH_3	107.0°	2.5°
H_2O	104.5°	5°

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.

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, C_2H_4, and C_2H_2.

The stereochemistry of some molecules containing multiple bonds should now be considered on an electron charge-cloud basis.

The *Students' book* introduces the terms 'sigma bond' and 'pi bond' at this point.

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) which consists of two electron clouds which are not symmetrical about this axis. This statement is intended as a foundation for further development in Topic 7, where alkenes are considered.

Ethene, C_2H_4, is used in the *Students' book* as 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.

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.

6.2 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.

Standard enthalpy change of combustion

In Topic 4, students were introduced to a number of specific enthalpy changes and to calculations using Hess's Law. The first part of section 6.2 extends their knowledge of enthalpy changes by defining the standard enthalpy change of combustion, and showing how values for standard enthalpy change 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.

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 6.2.

Experiment 6.2 To find the enthalpy changes of combustion of some alcohols

Each group of students will need:
Eye protection
Combustion calorimeter, with facility for electrical ignition; the filament for electrical ignition should be replaced by 35 cm of 28 s.w.g. nichrome wire to act as heater (see figure 6.9 in the *Students' book*)
Joulemeter and power supply
Water pump, and sufficient tubing to reach the calorimeter without strain
Thermometer, 10–50 °C in 0.1 °C intervals
Graph paper
Measuring cylinder 500 cm^3, or 1000 cm^3

Access to:
Balance, to weigh to ±0.001 g
Series of primary alcohols from propan-1-ol to octan-1-ol in separate spirit burners
Bunsen burner, heatproof mat and splint (for lighting spirit burner)
Molecular models of each of the alcohols should be available for inspection

Hazards

All the alcohols used, propan-1-ol to octan-1-ol, are flammable and butan-1-ol is particularly harmful.

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 lamps supplied with some commercial calorimeters may cause some inaccuracy if the wicks are 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. A rise in temperature is obtained from a chemical reaction, and then the amount of electrical energy required to bring about the same temperature rise in the same apparatus found. The teacher will need to find out beforehand, by trial, the best operating techniques for the various models of apparatus available.

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 the electrical method that is used minimizes their effect.

If it is not possible to use an electrical method, then rather than try to calculate heat capacities and to estimate heat losses, it is better to calibrate the apparatus. This can be done by burning an alcohol, the enthalpy change of combustion of which is known accurately, and noting the temperature rise. The heat capacity of the calorimeter and its contents, which includes a cooling correction *for that particular temperature rise under those particular conditions,* is then calculated. The experiment is then repeated with an alcohol, the enthalpy change of combustion of which is not known, in such a way that the temperature rise is as nearly as possible the same as in the first experiment. The cooling correction in each experiment is then about the same, and the unknown enthalpy change of combustion can be calculated, using the heat capacity just determined. Propan-1-ol, for which $\Delta H_c^{\ominus} = -2021 \text{ kJ mol}^{-1}$, is a suitable alcohol for calibration.

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.

Whichever way the experiment is conducted, however, it 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. If a combustion calorimeter is not available an alternative apparatus is described in the article by Reed, N.V. and Tordoff, V.J. 'A simplified apparatus for the determination of the combustion of alcohols', *School Science Review*, **70**, *250*, page 77, 1988.

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}
$CH_4(g) \rightarrow CH_3(g) + H(g)$	$\Delta H^\ominus = 423$
$CH_3(g) \rightarrow CH_2(g) + H(g)$	$\Delta H^\ominus = 364$
$CH_2(g) \rightarrow CH(g) + H(g)$	$\Delta H^\ominus = 385$
$CH(g) \rightarrow C(g) + H(g)$	$\Delta H^\ominus = 335$

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 TO THE QUESTIONS

1 To work out the approximate value for the energy needed to atomize 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

$$7E(\mathrm{C-H}) + 2E(\mathrm{C-C}) + E(\mathrm{C-O}) + E(\mathrm{O-H})$$
$$= 7\times413 + 2\times347 + 358 + 464$$
$$= 4407\ \mathrm{kJ\ mol^{-1}}$$

2 The bond energies of the hydrides required are:

C — H	N — H	O — H	F — H
413	391	464	568
and 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 5.4.

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	598
C ≡ C	0.121	837

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 251 kJ mol^{-1} and 239 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 7 where the reactivity of alkenes and alkanes is compared.

6.3 Dative covalency

Timing About 1 hour.

Suggested treatment

The two electrons which form a covalent bond do not necessarily have to come 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. They have also considered the formation of a hydroxonium 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.

Students are asked whether it would be possible in terms of electron availability, to form the ion H_4O^{2+}.

As extension work teachers might include the formation of a covalent bond when NH_3BF_3 is formed from BF_3 and NH_3. However, since electron deficient molecules such as BF_3 have not been discussed, this example may complicate the idea of the stable octet of electrons which was introduced at the beginning of this topic.

6.4 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.

Ion polarization has been discussed in Topic 3. In the present section students focus their attention on bond polarization. The intention is to reinforce the idea that truly ionic and truly covalent bonds are extreme types, and 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 polarization 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 was seen in the study of bond energies earlier 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 yet available.

Mulliken derives his set of values from ionization energies and electron affinities. The latter are difficult to measure with accuracy, and in some instances values had to be assumed. More recently Allred and Rochow have proposed that the electrostatic force acting on an electron at the periphery of an atom is a measure of the atom's electronegativity. Their values have a good linear relationship to Pauling's values.

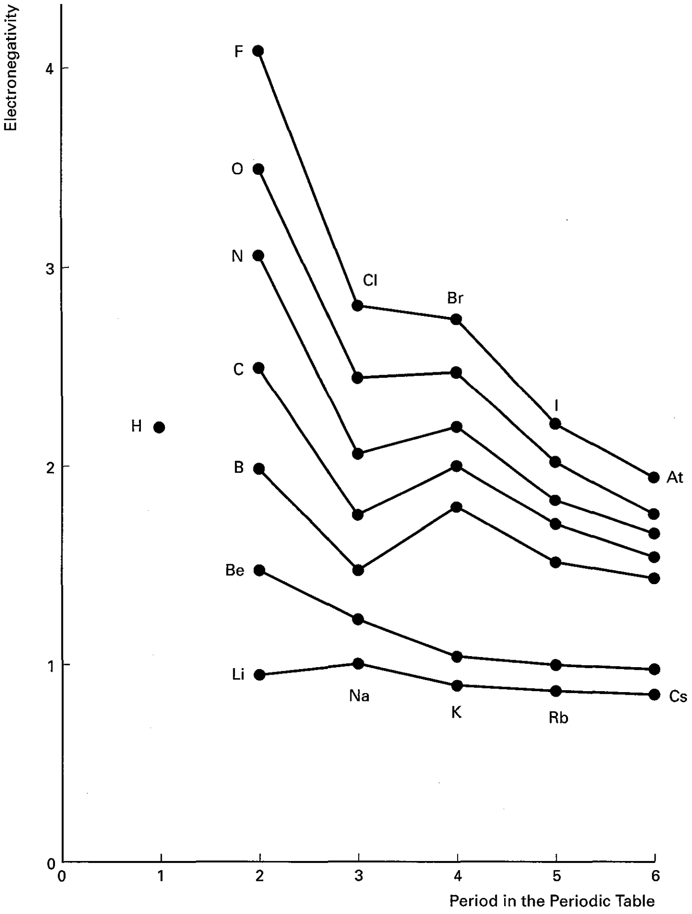


Figure 6.2 Allred–Rochow electronegativities.

Whatever the situation may be concerning individual values, the trends are clear. The safe approach, and one which is wholly adequate at this level, 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; and 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 polarization of ions.

Fajans's Rules as discussed in Topic 3 indicate that the beryllium–fluorine bond, for example, will be more polarized (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's Rules indicates that the beryllium–iodine bond will be more polarized (that is more covalent) than the beryllium–chlorine bond, and the trend in electronegativities of the halogens indicates the same.

The two discussions were conducted from opposite extremes towards an intermediate position, from ions towards polarization 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.

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 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 polarization and the final dipole includes both of these factors.

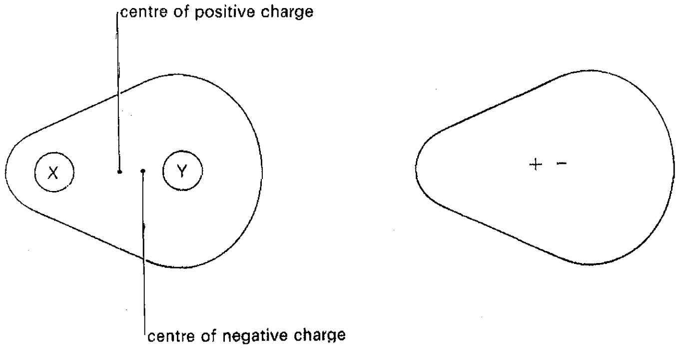


Figure 6.3 The origin of a dipole in a molecule.

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. The situation is an electrostatic parallel of a bar magnet.

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 6.4 in the *Students' book*. Students should appreciate the 3-dimensional structure of these molecules.

6.5 Delocalization of electrons

Timing

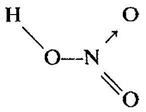
About 1 hour.

Suggested treatment

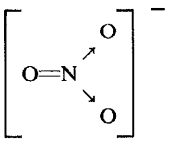
The concept of delocalization of electrons is developed by posing a series of leading questions concerning the structures of nitric acid, the nitrate ion, methanoic acid, and the methanoate ion. These are designed to bring out the inadequacy of single and double covalent bonds as a way of accounting for the experimentally determined structures. When the inadequacy has been fully brought out, it is intended that the teacher should discuss delocalization of electrons as a means of accounting for the observed structures as well as the thermochemical observations in Topic 7.

Nitric acid, and the nitrate ion

Students are asked to draw bond structures for these. They should, from dot-and-cross diagrams, reach the structures.

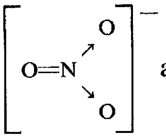


and

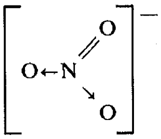


Questions are then asked about the expected bond lengths and possible alternative bond arrangements. Experimentally determined bond lengths are given.

The conclusion should again be that the suggested bond structure is inadequate. By now students should begin to suspect that where two or more alternative equivalent bond structures seem possible, as in



and



then the actual structure is neither of these, and the bond lengths are between those for single and double bonds.

Methanoic acid, and the methanoate ion

The students are next given the structure of methanoic acid and the bond lengths, and are asked to predict what the structure and bond lengths of the methanoate ion might be.

Conclusions

One conclusion from these studies is that single and double bonds cannot account for the known structure of the compounds. Where equivalent alternative bond structures can be drawn, the actual situation is neither of these; the bond lengths in these situations always prove to be equal, and the available electrons must therefore be distributed equally among the atoms concerned. It seems unlikely that double and single bonds should be rapidly switching round. Instead, it is believed that each atom is bonded to the next by two electrons between the nuclei, forming a single covalent bond, and that the remaining available electrons are distributed as charge-clouds above and below all the atoms concerned. These electron charge-clouds are not associated with any particular atom but are mobile over the whole atomic system; they are thus known as *delocalized electrons.* Representations of the situation in nitric acid and the nitrate ion are given in the *Students' book.*

The delocalization of electrons in the benzene molecule has important implications for the chemistry of benzene and this is developed further in Topic 7.

Thermochemical data may provide some evidence for delocalization of electrons. A comparison of theoretically calculated enthalpy changes of hydrogenation for a number of organic compounds with values obtained experimentally, indicates that some compounds are more stable than expected. This can be linked to the presence of delocalized electrons. Although this is considered in more detail in Topic 7 in relation to benzene, some teachers may prefer to discuss the thermochemical evidence at this point.

6.6 Bonding, structure and chemical behaviour

Timing

About 1 hour plus homework.

Suggested treatment

This section provides an opportunity to review what has been learnt about bonding by getting students to apply their knowledge to the behaviour of chlorides and oxides towards water and to review the behaviour of the Period 3 elements with chlorine, oxygen and water.

The work is presented as a Study Task involving library research, but the combustion of Period 3 elements in oxygen could be presented as a teacher demonstration parallel to optional experiment 5.7 (*Teachers' guide*, page 83).

ANSWERS TO THE STUDY TASK QUESTIONS

1 The information in figure 5.13 shows that the ionic chlorides of the Period 3 elements dissolve in water and the covalent chlorides are hydrolysed forming acidic solutions.

2 The oxides of the Period 3 elements show the same transition from ionic to covalent structure as the chlorides, the ionic oxides producing alkaline solutions with water and the covalent oxides producing acidic solutions.
The oxides of the Group 1 elements are ionic (table 5.9 of lattice energies) and produce hydroxides when they react with water; the peroxides form hydrogen peroxide and oxygen as well as hydroxides.

3 Students should use the *Book of data* to collect quantitative information about the enthalpy changes of formation for the chlorides and oxides of the Period 3 and Group 1 elements. The data are more informative when presented as histograms per mole of oxygen and per mole of chlorine.

Students should also record which elements react with water and note that it is mainly a property of metals.

For the convenience of teachers the appropriate data are listed here.

Element	$\Delta H_f^\ominus$/kJ mol^{-1}	
	oxide	chloride
Na	−414.2	−411.2
Mg	−601.7	−641.3
Al	−1675.7	−704.2
Si	−910.9 (quartz)	−687.0
P	−1640.1 (P_4O_6)	−319.7 (PCl_3)
S	−296.8 (SO_2)	−19.7 (SCl_2)
Cl	+80.3 (Cl_2O)	–
Li	−597.9	−408.6
K	−361.4	−436.7
Rb	–	−435.3
Cs	−345.8	−443.0

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

6.1

$$\begin{tikzcd}
C_2H_5OH(l) + 3O_2(g) \arrow[rr] & & 2CO_2(g) + 3H_2O(l) \\
& 2C(\text{graphite}) + 3H_2(g) + 3\tfrac{1}{2}O_2(g) \arrow[ul, "-277.1"] \arrow[ur, "{2(-393.5) + 3(-285.8) = -1644.4\ \text{kJ mol}^{-1}}"'] &
\end{tikzcd}$$

$\Delta H_c = -1644.4 + 277.1 = -1367$ kJ mol^{-1} (4 SF)

Total 6 marks

6.2

Methanol $22.34 \times 32.0 = 714.9$ $\Delta H_c = -715$ kJ mol^{-1}

Ethanol $29.80 \times 46.1 = 1374$ $\Delta H_c = -1374$ kJ mol^{-1}

Propanol $33.50 \times 60.1 = 2013$ $\Delta H_c = -2013$ kJ mol^{-1}

Butanol $36.12 \times 74.1 = 2676$ $\Delta H_c = -2676$ kJ mol^{-1} (4)

There is a fairly uniform rise from one alcohol to the next (1)

Graph (2)

will show a value for pentanol of about −3320 kJ mol^{-1} (1)

Total 8 marks

6.3

a –638 kJ mol^{-1} (3)

b –890.3 kJ mol^{-1} (3)

c –1663 kJ mol^{-1} (3)

Total 9 marks

6.4

a 568 kJ (2)

b 432 kJ (2)

c 366 kJ (2)

d 298 kJ (2)

The energies of the X — H bonds get less with increasing atomic number of X (1)

Total 9 marks

6.5

a 1173 kJ (2)

b 981 kJ (2)

c 890 kJ (2)

d 771 kJ (2)

The energies of the X — H bonds get less with increasing atomic number of X. (1)

Total 9 marks

6.6

a $983 \div 3 = 327\frac{2}{3}$ kJ (2)

b $958 \div 3 = 319\frac{1}{3}$ kJ (2)

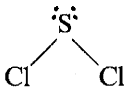
c $364 \times \frac{2}{3} = 242\frac{2}{3}$ kJ (2)

d $636 \times \frac{2}{3} = 424$ kJ (2)

Total 8 marks

6.7

S has six valency electrons and two are used for bonding so there are two lone pairs.



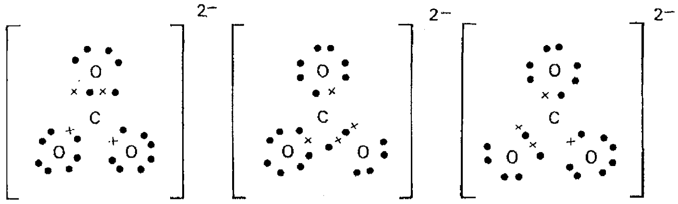
(2)

Since lone pair/lone pair repulsion > lone pair/bond pair repulsion > bond pair/bond pair repulsion, one would expect the Cl — S — Cl angle to be less than tetrahedral, say about 100°. (2)
Answers in the range 95° to 100° are acceptable. (1)

Total 5 marks

6.8

a



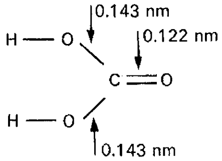
(2)

b One bond (double) of length 0.122 nm. Two bonds (single) of length 0.143 nm. (1)

No, they do not agree with observed values. (1)
They are not all the same, whereas observed values are. Observed values are intermediate between single and double bond lengths. (2)

c Delocalization of one pair of electrons distributed around the three oxygen atoms and the carbon atom equally. The ion is thus symmetrical and the bonds are intermediate. (2)

d The expected structure of the H_2CO_3 molecule is shown below. The expected C — O bond lengths are as shown, that is, the molecule is not symmetrical and it includes single and double bonds. (2)



Total 10 marks

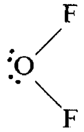
6.9

a Hydrogen is sufficiently more electronegative than sodium to be able to form the negative ion H^- in relation with sodium. (2)

b The electronegativities of C and H are very similar so that there is no appreciable polarity in the C — H bonds. (2)

c Chlorine, being more strongly electronegative than hydrogen, exerts a stronger attraction on the electron pair in the HCl bond, so a dipole results with the chlorine end negatively charged. (Note that the lone pairs of electrons on the chlorine atom contribute as much as, and probably more than, bond polarization to this dipole.) (3)

d The electronegativity of fluorine is very much more than that of sodium, so that the fluoride ion has sole charge of the pair of electrons which were available for bonding and is F^-, and sodium is Na^+. The electronegativities of oxygen and fluorine do not differ greatly so the electrons in the resulting covalent bond between O and F atoms are fairly evenly shared. One would expect OF_2 to have an electric dipole but to see this it is necessary to appreciate that the molecule is non-linear:



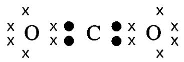
(3)

Total 10 marks

Examination questions

6.10

a C $1s^2 2s^2 2p^2$
Si $1s^2 2s^2 2p^6 3s^2 3p^2$ (1)

b  bonding electrons (1)

non-bonding electrons (1)

c **i** $SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(g)$ (2)

ii Si — H bond easier to break than C — H bond (1)

d Enthalpy change of combustion is bond making–bond breaking, and forming four Si — O bonds produces more energy than two C ═ O bonds, and less energy is needed for bond breaking in Si — H than C — H so overall more energy from combustion of SiH_4 than CH_4 (4)

e **i** SiO_3^{2-} (2)

ii Precipitate formed (1)

Silicon dioxide, SiO_2 (1)

Total 14 marks

6.11

a 4 (1)

b 50 (1)

c **i** Tin(II) chloride (1)

ii Sn $(1s^2 \ldots 4d^{10})\ 5s^2$ (1)

iii $Sn(s) + Cl_2(g) \rightarrow SnCl_2(s)$ (1)

d **i** mol of I $= \dfrac{6.35}{127} = 0.05$ (1)

mol of Sn $= \dfrac{2.00}{119} = 0.0168$ (1)

mol of I required $= 0.0168 \times 4 = 0.067$

so tin present in excess (1)

ii Recrystallization in organic solvent (2)

iii Maximum yield $= \dfrac{0.05}{4} \times [119 + 4(127)] = 7.84$ g (2)

% yield $= \dfrac{5.6}{7.84} \times 100 = 71.8 = 72\%$ (1)

e **i** Low melting point, soluble in tetrachloromethane (2)

ii SnI_4 large charge on cation and large anion

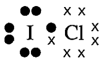
SnF_2 small charge on cation and small anion (2)

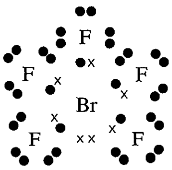
iii Tetrahedral (1)

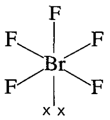
Total 18 marks

6.12

a

i  (1)

ii  (1)

b Distorted octahedral  (2)

c Small size of atom, highest electronegativity, fluorine most reactive (1)

Total 5 marks

6.13

Mark by impression

The data available are

		T_m/K	T_b/K	m_{sat}	
Li	LiH	953	–	dec	
	Li_3H_4 – not needed				
Be	$(BeH_2)_n$ – not in *Book of data*				
B	B_2H_6	108	181	dec	
C	CH_4	91.1	109.1	–	
	C_2H_6 etc. – not needed				
N	NH_3	195	240	3.11 (1.79 mol/100 cm^3)	
O	H_2O	273	373	–	
F	HF	190	293	4.33×10^{-2}	(3)

Ionic and covalent structures (9)

Only LiH is ionic; NH_3, H_2O and HF should be described as hydrogen-bonded and students are expected to remember this rather than make a full data search. (3)

Total 15 marks

TOPIC 7

Hydrocarbons and halogenoalkanes

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, halogenoalkanes, alkenes and arenes is discussed in an experimental context. The scope of organic reactions is widened to include addition, substitution and polymerization 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, nucleophilic substitution of halogenoalkanes and electrophilic addition to alkenes. The evidence for delocalized electrons in benzene is discussed as well as the electrophilic substitution reactions of arenes.

Content

	Timing	*Students' book*
7.1	2 hours	Pages 155–160
7.2	3 hours	Pages 160–171
7.3	Homework	Pages 172–173
7.4	6 hours	Pages 174–184
7.5	3 hours	Pages 184–192
7.6	Homework	Pages 193–194
7.7	3 hours	Pages 194–203
7.8	Homework	Pages 203–204

Total about 4 weeks

7.1 The variety of molecular structure in organic compounds. Properties of C — C bonds; rules for naming organic compounds; names and structures of functional groups.
7.2 The alkanes. The importance of alkanes in the petroleum industry. The chemical and physical properties of the alkanes; the infra-red spectra of the alkanes; photochemical reaction of alkanes; free radical substitution; homolytic and heterolytic fission; chain reactions.
7.3 Study Task. Octane number of petrol hydrocarbons.
7.4 The halogenoalkanes. Occurrence and uses of halogenoalkanes; factors influencing reactivity of halogenoalkanes, bond strength and bond polarity; infra-red and mass spectra of halogenoalkanes; preparation of halogenoalkanes from primary and tertiary alcohols, reactions of halogenoalkanes; substitution reactions, attacking groups and leaving groups, nucleophiles, elimination reactions.
7.5 The alkenes. The uses of alkenes; geometric isomerism; nomenclature of alkenes; the chemical and physical properties of alkenes, addition reactions of alkenes; electrophiles.
7.6 Study Task. Polymerization.
7.7 Benzene and some substituted benzene compounds. The structure of benzene, thermochemical and X-ray diffraction evidence; infra-red spectrum of

benzene; experiments with arenes; electrophilic substitution reactions; reactions of the benzene ring.

7.8 Survey of reactions and reagents in Topic 7. Bond breaking, homolytic and heterolytic; types of reaction; types of reagent.

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, elimination, addition, polymerization and free radical reactions.
4 To develop knowledge of the reactions of alkanes, halogenoalkanes, alkenes and arenes.
5 To develop an appreciation of practical procedures used in the preparation of halogenoalkanes from alcohols.
6 To develop knowledge of how information from infra-red spectra and simple correlation tables may be used to deduce the functional groups present in organic compounds.
7 To show how bond energies and bond polarization can be used in a discussion of reaction mechanisms in organic chemistry.
8 To provide information about the economic and social importance of alkanes, alkenes and halogenoalkanes.

7.1 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 visualize the three-dimensional structure but allows ideas such as free rotation about a C—C single bond and *cis–trans* isomerism (see section 7.5) to be explained more readily.

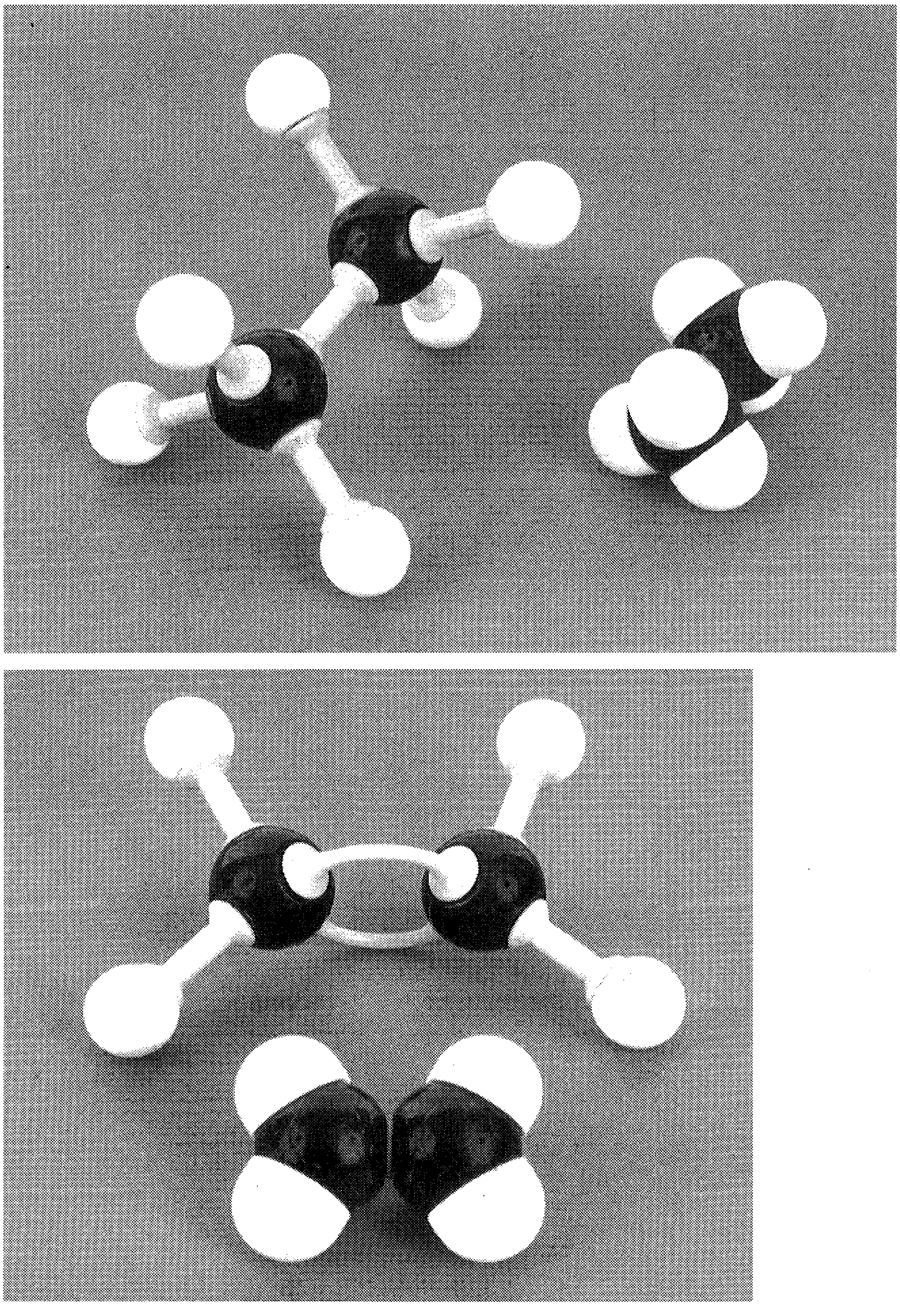


Figure 7.1 Open and semispace-filling models (**MOLYMOD**^{R} models).

As part of this section 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:

$CH_3CH_2CH_2CH_2CH_2CH_3$
$CH_3CH_2CH_2CH(CH_3)CH_3$
$CH_3CH(CH_3)CH_2CH_3$
$CH_3CH(CH_3)CH(CH_3)CH_3$
$CH_3CH_2C(CH_3)_2CH_3$

7.2 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 leads into a study of the infra-red spectra of the alkanes.
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 the alkane.
4 The reactions of the alkanes are discussed in more detail.

Following a brief introduction to the petroleum industry, students are asked to study the infra-red spectrum of decane. Before doing this they should familiarize themselves with the method of infra-red absorption spectroscopy which is described in Topic 18 of the *Students' book*. Students are not required to memorize details of the procedure, but should be able to interpret infra-red 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 then use it to identify both stretching and bending modes of vibration.

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 7.2 The properties of alkanes

Each group of students will need:
Eye protection
Test-tubes and rack
Combustion spoon or equivalent
Small trough (ice-cream tubs are suitable)
Delivery tube for gas collection (see figure 7.2)
Dropping pipettes
Metal spatula
Access to:
Aluminium oxide, 4–8 mesh granules, 5 g
2 M ammonia, 2 cm^3
Bromine water, 2 cm^3 CORROSIVE
2% bromine in inert solvent, 2 cm^3
Hexane, free from aromatics, 12 cm^3 HIGHLY FLAMMABLE, HARMFUL
Paraffin, light, laboratory grade, 5 cm^3
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. The appendix on *Laboratory safety* in the *Students' book* should be useful as well as the section in this book starting on page 342.

The following additional notes may be helpful.

When preparing solutions technicians should note that:

- Bromine can cause burns, and is 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 irritates the respiratory system.
- Potassium hydroxide can cause severe burns.
- Potassium manganate(VII) is HARMFUL and OXIDIZING; the solid is destructive to all tissue.

The photoflood light should be in a suitable holder so that it cannot shine directly into the students' eyes.

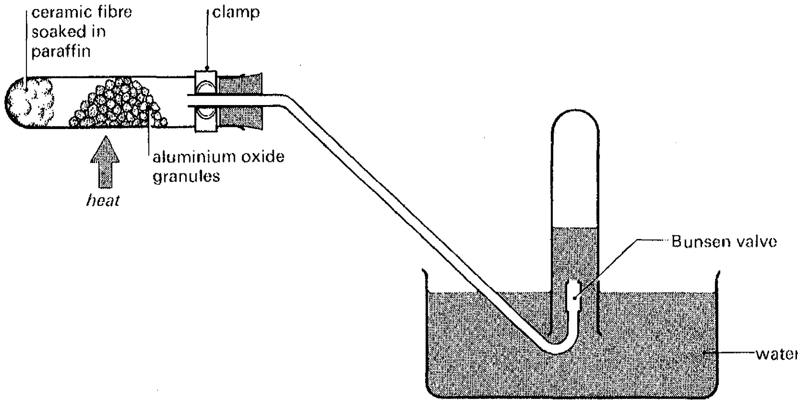


Figure 7.2 Apparatus for the catalytic cracking of an alkane.

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.

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. 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 (see section 7.7).

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 7.2).

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 memorize the discussion but there is an advantage in letting them see something of the way chemists organize 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 reactions of the class of compounds that has been discussed in the section. It is expected that students will learn these reactions; opportunities should be taken from time to time to test their knowledge.

Summary

Students should draw up a flow chart to summarize the reactions they have studied.

7.3 Study Task: Octane number of petrol hydrocarbons

Timing This Study Task may be set for homework.

Students are asked to read a passage which introduces the processes of catalytic cracking, catalytic reforming, alkylation and isomerization of hydrocarbons and answer questions based on the passage.

ANSWERS TO THE QUESTIONS

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 for *unbranched hydrocarbon → branched hydrocarbon* should have correct structural formulae and should balance.
5 The simplest equation is:
$CH_3(CH_2)_{18}CH_3 \rightarrow CH_2{=}CH_2 + CH_3(CH_2)_{16}CH_3$
6 A simple example is:
$CH_2{=}CH_2 + H^+ \rightarrow {}^+CH_2{-}CH_3$
$(CH_3)_3CH + {}^+CH_2{-}CH_3 \rightarrow (CH_3)_3C{-}CH_2{-}CH_3 + H^+$
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 less reactive free radicals.

7.4 The halogenoalkanes

Timing About 6 hours will be needed.

Suggested treatment

This section is developed in the following way:

1 The structure and nomenclature of the halogenoalkanes are introduced, followed by a consideration of the factors responsible for their reactivity.
2 Halogenoalkanes are prepared from a primary or a tertiary alcohol.
3 The reactions of the halogenoalkanes are studied experimentally.
4 The reactions of the halogenoalkanes are summarized.

Teaching notes

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, infra-red absorption spectra, and mass spectra. The infra-red absorption spectrum of 1-chlorobutane is given in the *Students' book* in figure 7.18 and its mass spectrum in figure 7.19.

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

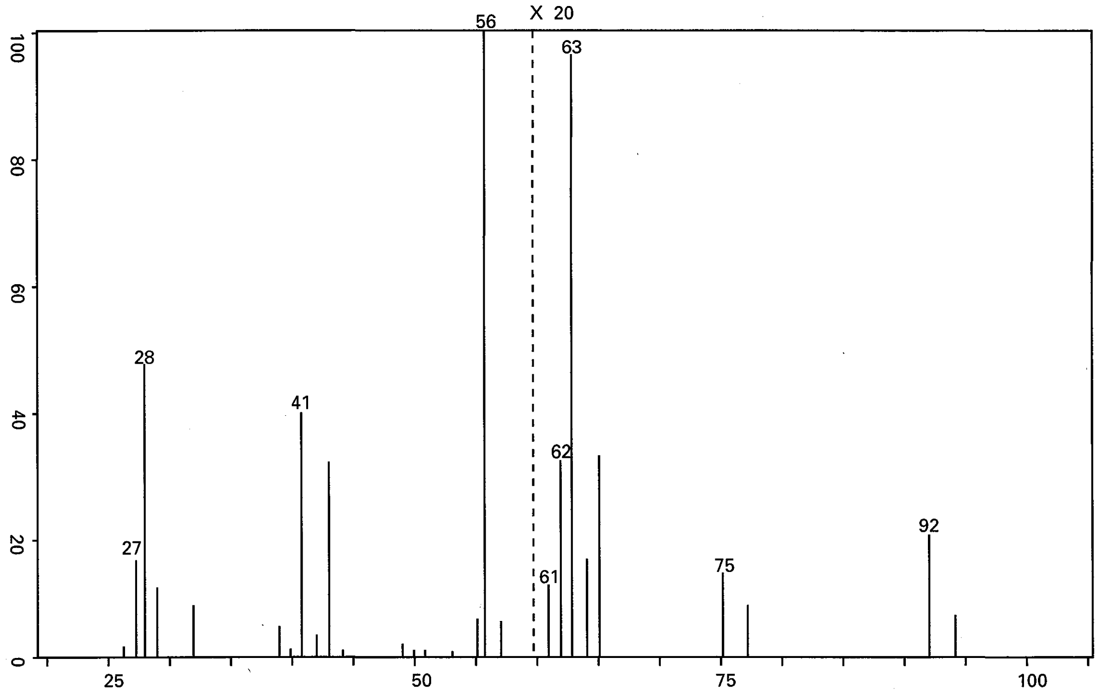


Figure 7.3 The mass spectrum of 1-chlorobutane.

Experiment 7.4a Preparation of halogenoalkanes

Students should carry out one of the two experiments.

1 A halogenoalkane from a primary alcohol

Each group of students will need:
Eye protection
Apparatus for distillation with a pear shaped flask, 50 cm^3 (see figure 7.4)
Dropping pipette
Measuring cylinder, 5 cm^3
Weighing boat
Balance, to weigh to ±0.1 g
Access to:
Ethanol, 5 cm^3 HIGHLY FLAMMABLE

Potassium bromide, 6 g
Concentrated sulphuric acid, 5 cm^3 CORROSIVE

Hazards

Several of the products have associated hazards:
Bromoethane is flammable and irritant; bromine (by-product) is corrosive; ethoxyethane and ethene (by-product) are both highly flammable.

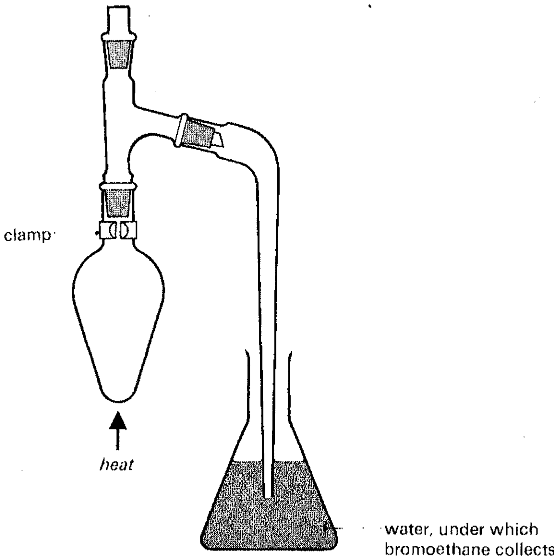


Figure 7.4 Apparatus for the preparation of a halogenoalkane.

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.

2 A halogenoalkane from a tertiary alcohol

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 7.5)
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 FLAMMABLE

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

⚠ Hazards

2-Chloro-2-methylpropane (product) is flammable and all halogenoalkanes should be treated as harmful.

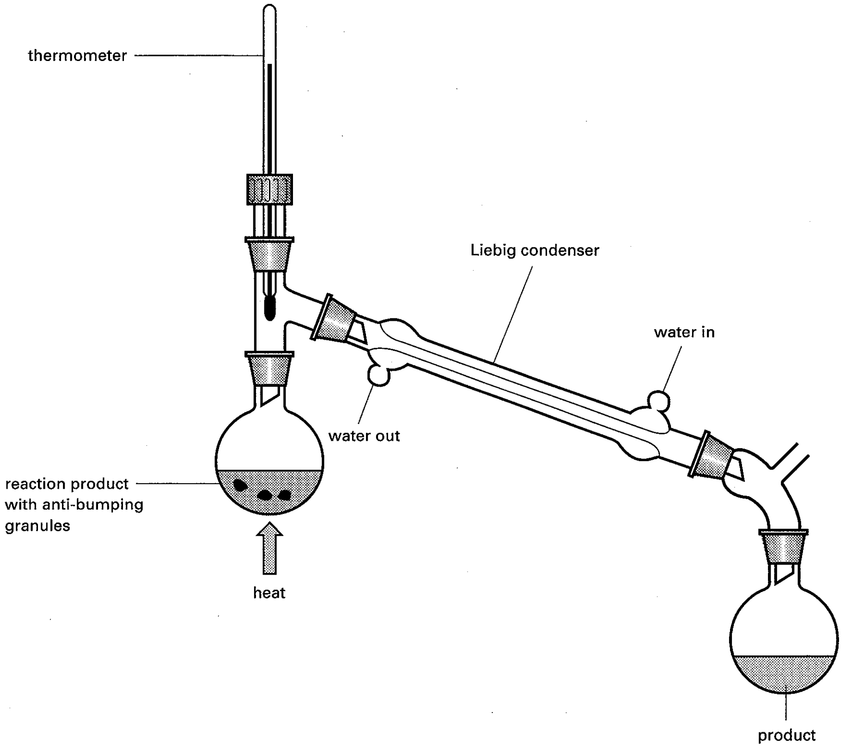


Figure 7.5 Apparatus for distillation.

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 7.4b, parts 2 and 4.

Experiment 7.4b The reactions of the halogenoalkanes

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
Small trough (ice-cream tubs are suitable)
Dropping pipette
Access to:
1-bromobutane, a few drops SEE NOTE BELOW
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 CORROSIVE
2 M nitric acid, 2 cm^3 IRRITANT
Full-range Indicator
Ceramic fibre, a small tuft
Ethanol, 12 cm^3 HIGHLY FLAMMABLE

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.

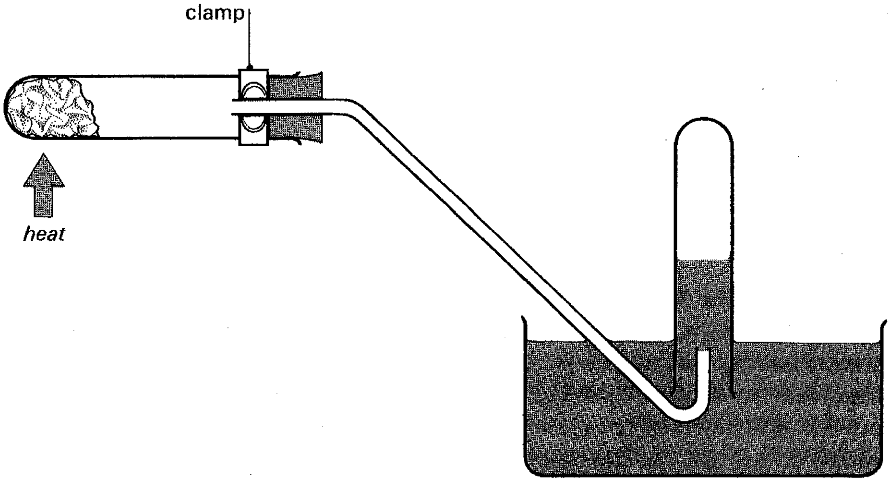


Figure 7.6 Apparatus for part 4.

COMMENT
3YE
1992

The meaning of the hazard warning in figure 7.21 in the *Students' book* is:

- 3 refers to the method to be used for extinguishing the fire.
- Y refers to the type of protective clothing to be worn.
- E refers to any need to evacuate the area.
- 1992 is the code for further information.

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 8 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.

7.5 The alkenes

Timing About 3 hours will be needed.

Suggested treatment

This section is developed in the following way:

1 The structure and bonding in alkenes is discussed.
2 The reactions of alkenes are studied experimentally.
3 The reaction between an alkene and bromine is considered in mechanistic terms.
4 The reactions of the alkenes are summarized.

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.

Attention is then drawn to the differences between the infra-red absorption spectra of the alkenes and alkanes. The infra-red absorption spectrum of oct-1-ene is given in the *Students' book* as figure 7.26.

Rules for naming alkenes are briefly reviewed; students should be given some practice in putting them into effect.

Experiment 7.5 The reactions of the alkenes

Each group of students will need:
Eye protection
Test-tubes and rack
Combustion spoon, or equivalent
Beaker, 250 cm^3 (as a waterbath)
Dropping pipettes
Access to:
Bromine water, 1 cm^3 CORROSIVE
Cyclohexene, 2 cm^3 FLAMMABLE, IRRITANT
Di(dodecanoyl) peroxide (lauroyl peroxide), 0.1 g IRRITANT
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

Hazards

Cyclohexene is an irritant to the respiratory system.

Di(dodecanoyl) peroxide (lauroyl peroxide) is oxidizing as well as being irritant.

Methyl 2-methylpropenoate (methyl methacrylate) is poisonous and inhalation of the vapour can be dangerous. It should be restricted to use in a fume cupboard under strict supervision.

Procedure

Full instructions are given in the *Student's book.*

Students repeat experiment 7.2 this time using alkenes instead of alkanes, and are thus able to compare the properties of these two classes of hydrocarbons. The following notes may be helpful.

1 Combustion

The flame should be yellow (luminous) and slightly sooty.

2 Oxidation

The alkenes should readily decolorize the 0.01 M potassium manganate(VII) solution.

3 Action of bromine

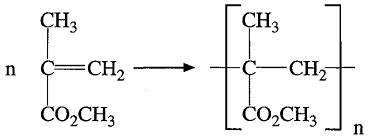
The bromine solution should be decolorized instantly. Reactions 2 and 3 should be introduced to students as indications of unsaturation. Students should be reminded that they have previously used these tests in connection with the experiment with limonene in Topic 2.

4 Action of sulphuric acid

Some charring occurs and the reaction mixture becomes hot. If water is added, a cloudy solution is obtained, with most of the material water-soluble.

5 Polymerization

The use of methyl 2-methylpropenoate must be carefully controlled as the vapour is irritating and poisonous. The reaction should be carried out only in a fume cupboard. The equation for the reaction is



$$n\ \overset{\displaystyle CH_3}{\underset{\displaystyle CO_2CH_3}{C}}{=}CH_2 \longrightarrow \left[\overset{\displaystyle CH_3}{\underset{\displaystyle CO_2CH_3}{C}}—CH_2\right]_n$$

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 and it may be helpful to students to point out that types of reagent tend to occur in pairs: acid and base, oxidizing and reducing, and now electrophile and nucleophile.

The experiments of Francis should be interpreted as

$$CH_2{=}CH_2 \xrightarrow{\overset{\delta+}{Br}—\overset{\delta-}{Br}} CH_2Br—\overset{+}{C}H_2 \xrightarrow{:NO_3^-} CH_2Br—CH_2—NO_2$$

Polarization 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 polarized.

The original interpretation given by Francis postulated the intervention of 'nascent bromine' (Francis, A.W. *Journal of the American Chemical Society* **47**, pages 2340–7, 1925).

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:

$$CH_3 - CH = CH_2 + H^+ \rightarrow CH_3 - {}^+CH - CH_3$$

The positive charge appears on the carbon atom with fewest hydrogen atoms, rather than having $CH_3 - CHBr - CH_2{}^+$ as the intermediate.

If the reaction mixture is illuminated, a different product is obtained

$$CH_3 - CH = CH_2 + HBr \xrightarrow{h\nu} \underset{\text{1-bromopropane}}{CH_3 - CH_2 - CH_2Br}$$

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

$$CH_3 - \dot{C}H - CH_2Br$$

as the intermediate in the reaction.

The odd electron appears on the carbon atom with the fewest hydrogen atoms, rather than having $CH_3 - CHBr - CH_2\cdot$ 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 ultra-violet light.

To summarize:

$$CH_3{-}CH{=}CH_2 \xrightarrow{H^+} CH_3{-}\overset{+}{C}H{-}CH_3 \xrightarrow{Br^-} \underset{\text{Markovnikov addition}}{CH_3{-}CHBr{-}CH_3}$$

$$CH_3{-}CH{=}CH_2 \xrightarrow{Br\cdot} CH_3{-}\dot{C}H{-}CH_2Br$$

$$\xrightarrow{HBr} \underset{\text{anti-Markovnikov addition}}{CH_3{-}CH_2{-}CH_2Br + Br\cdot}$$

At the end of this section students should draw up a chart to record the reactions they have studied. A detailed study of polymerization can be left until Topic 14.

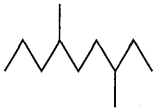
7.6 Study Task: Polymerization

Timing This Study Task may be set for homework.

Students are asked to read a passage which introduces addition and condensation polymerization 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 THE STUDY TASK QUESTIONS

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 A successful manufacturing process would have to be continuous or react material in large batches; the explosive carbonization would have to be prevented, for example by careful temperature control.

7.7 Benzene and some substituted benzene compounds

Timing About 3 hours will be needed.

Suggested treatment

This section is developed in the following way:

1 The structure of benzene is considered using electron density and thermochemical evidence.

2 Students study the reactions of arenes using methylbenzene and methoxybenzene.

3 An interpretation of the substitution reactions of the benzene ring is discussed.

4 The reactions of the benzene ring are summarized.

The teacher will find it helpful to have a model of the benzene molecule available throughout this section.

The *Students' book* describes how Kekulé came to propose the cyclic structure of benzene, and gives some modern evidence in support of delocalized 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.

2 The appearance of the electron density diagram of benzene (which is given in the *Students' book* as figure 7.30).

3 Thermochemical data: these call for a comparison of the enthalpy changes of hydrogenation of benzene and cyclohexene.

The infra-red absorption spectrum of benzene is shown in figure 7.31 in the *Students' book* and students are asked to identify the origin of the main absorption bands by reference to the *Book of data.*

The significance of the Loschmidt structure is debated in Noe C. and Bader A., 'Facts are better than dreams', *Chem. Br.*, **29**(2), pages 126–8, 1993 and Rocke A., 'Waking up to the facts', *Chem. Br.*, **29**(5), pages 401–402, 1993.

Experiments with arenes

Benzene is considered to be carcinogenic, and experiments with it should not be performed in a school. In experiment 7.7 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 7.7 The reactions of the 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)
Spatula
Beaker to act as a water-bath, 250 cm^3
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
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
(prepared just before use)
2-chloro-2-methylpropane, 1 cm^3
1 M sulphuric acid, 1 cm^3 IRRITANT
Dropping pipettes, 4
Full-range Indicator paper

Hazards

Methylbenzene (toluene) is poisonous by skin absorption.
2% bromine in hydrocarbon solvent should be prepared in a fume cupboard; a

suitable solvent is hexane (free from aromatics) but the solution has to be freshly prepared as the colour fades within an hour in bright daylight.

Procedure

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

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.

Interpretation of the substitution reaction of the benzene ring

In the *Students' book* students are asked a series of questions about the possible mode of attack of iodine monochloride on methoxybenzene. On the basis of the relative electronegativities of iodine and chlorine, the expected polarization is

$$\overset{\delta+}{\mathrm{I}}\text{—}\overset{\delta-}{\mathrm{Cl}}$$

which means that the attacking group is positively charged. 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 polarized.

This work was originally published in an article by Lambourne, L.J. and Robertson, P.W. in *Journal of the Chemical Society*, pages 1167–8, 1947 (part II).

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 summarized in the *Students' book*. Students are asked to draw up a chart summarizing the reactions of benzene.

7.8 Survey of reactions and reagents in Topic 7

Timing This summary may be studied for homework.

This is a summary which draws together the various types of reactions and reagents which students have encountered during this Topic. The student's knowledge of these should be tested with specific reference to the reactions they have met in Topic 7.

Answers to Questions in the *Students' book*

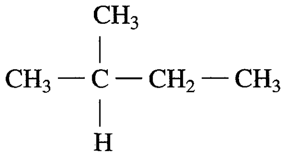
A suggested mark allocation is given in brackets after each answer.

Review questions

Alkanes

7.1

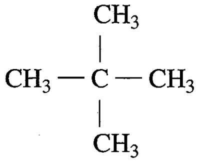
a



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-CH_3$$

(1)

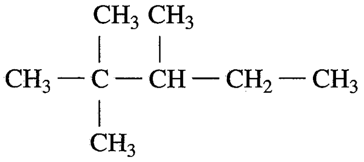
b



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

(1)

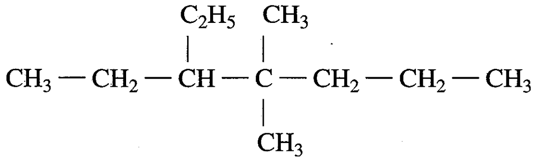
c



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$$

(1)

d



$$CH_3-CH_2-\overset{\overset{\displaystyle C_2H_5}{|}}{CH}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-CH_3$$

(1)

Total 4 marks

7.2

a $\Delta H_f^{\ominus}[CH_4(g)] = -74.8\ \text{kJ mol}^{-1}$

$\Delta H_{at}^{\ominus}$ [C(graphite)] $= 716.7\ \text{kJ mol}^{-1}$

$\Delta H_{at}^{\ominus}[\frac{1}{2}H_2(g)] = 218.0\ \text{kJ mol}^{-1}$

$\Delta H_f^{\ominus}[CH_4(g)]$ from free atoms $= -1663.5\ \text{kJ mol}^{-1}$

$E(C - H) = 415.9\ \text{kJ mol}^{-1}$ (5)

b $\Delta H_f[C_2H_6(g)]$ from free atoms $= 2826.1\ \text{kJ mol}^{-1}$ (3)

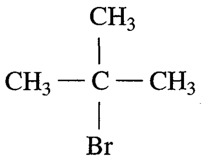
$E(C - C) = 330.7\ \text{kJ mol}^{-1}$

Total 8 marks

Halogenoalkanes

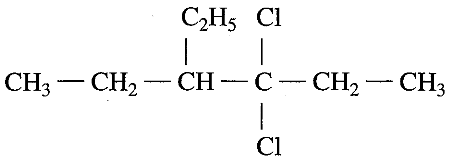
7.3

a (1)



$$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3$$

b (1)



$$CH_3-CH_2-\overset{C_2H_5}{CH}-\underset{Cl}{\overset{Cl}{C}}-CH_2-CH_3$$

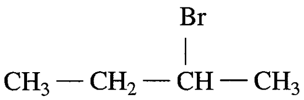
Total 2 marks

7.4

$CH_3 - CH_2 - CH_2 - CH_2Br$ (1)

1-bromobutane

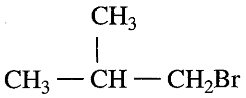
(1)



$$CH_3-CH_2-\overset{Br}{CH}-CH_3$$

2-bromobutane

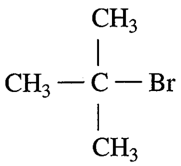
(1)



$$CH_3-\overset{CH_3}{CH}-CH_2Br$$

1-bromo-2-methylpropane

(1)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$$

2-bromo-2-methylpropane

Total 4 marks

7.5

a $CH_3CHBrCH_3 \xrightarrow{\text{reflux, aqueous NaOH}} CH_3CHOHCH_3$ (2)

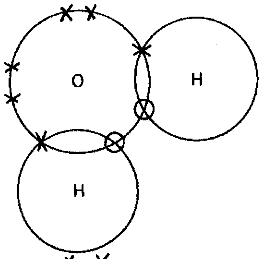
b $Br(CH_2)_6Br \xrightarrow[\text{under pressure}]{\text{heat, ethanolic } NH_3} H_2N(CH_2)_6NH_2$ (3)

c $CH_3CH_2CH_2 - CH_2Br \xrightarrow[\text{ethanolic KOH}]{\text{hot, concentrated}} CH_3CH_2CH = CH_2$ (3)

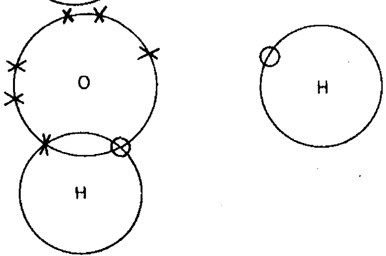
Total 8 marks

7.6

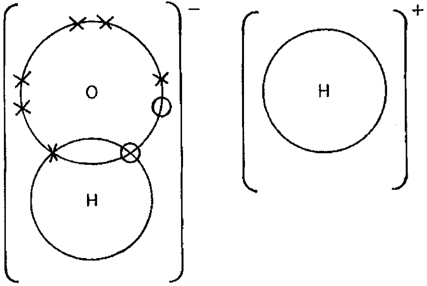
a (2)



b (2)



c (2)



d It is an attacking group with a lone pair of electrons which attacks a positive centre. (1)

e Electrophilic. (1)

Total 8 marks

7.7

CN^-, OH^-, H_2O, NH_3, Br^-, CH_3NH_2 (1 mark each)

Total 6 marks

Alkenes

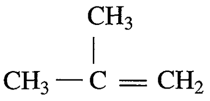
7.8

$CH_3—CH_2—CH=CH_2$ (1)

but-1-ene

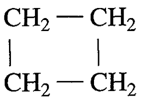
$CH_3—CH=CH—CH_3$ (2)

but-2-ene (*cis*- and *trans*-)



$CH_3—\overset{\overset{CH_3}{|}}{C}=CH_2$ (1)

2-methylpropene



(1)

cyclobutane

Total 5 marks

7.9

B and **D**.

Total 2 marks

7.10

$Br_2(l)$, $H_2(g)$, $HBr(g)$

Total 3 marks

7.11

a $CH_3CH_2Br \xrightarrow[\text{of KOH in ethanol}]{\text{hot concentrated solution}} CH_2=CH_2 \xrightarrow{\text{bromine}} CH_2BrCH_2Br$ (5)

b $CH_2=CH_2 \xrightarrow{\text{bromine}} CH_2BrCH_2Br \xrightarrow[\text{aqueous KOH}]{\text{reflux with}} CH_2OH—CH_2OH$ (5)

Total 10 marks

7.12

Free radicals (unpaired electron; seven electrons in outer shell)

$CH_3\cdot$, $Cl\cdot$. (2)

Electrophiles (electron deficient; six electrons in outer shell)

Br^+, CH_3^+, and H^+ (no electrons in outer shell). (3)

Nucleophiles (electron rich; eight electrons in outer shell)

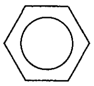
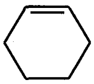
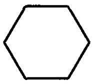
OH^-, H_2O, I^-, CH_3NH_2. (3)

It is unusual for metal atoms to form covalent bonds to carbon. (2)

Total 10 marks

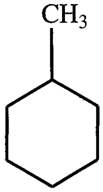
Arenes

7.13

Formulae				(3)
Conditions	Br_2 and Fe filings	Br_2 alone	Br_2 and ultra-violet light	(3)
Reaction type	Substitution	Addition	Substitution	(3)
Reagent type	Electrophile	Electrophile	Free radical	(3)

Total 12 marks

7.14

a 

methylcyclohexane (1)

b I Reduction and/or addition. (1)
  II Oxidation. (1)
  III Substitution. (1)
  IV Substitution. (1)
  V Reduction. (1)

c Large volumes of gaseous products available from combustion of 1 mole of substance, including highly stable $N_2(g)$. (2)

d Look for O — H stretch 3000–3500 cm^{-1}
C ═ O stretch 1500–1800 cm^{-1}
Also typical C — H and C — C absorption of arenes. (3)

Total 11 marks

7.15

a Addition reaction involving free radicals. (2)

b Delocalization stability results in energetic preference for substitution rather than addition reactions. (3)

c Geometric isomers are possible in ring structure which lacks free rotation. (3)

Total 8 marks

7.16

$\Delta H_f^\ominus [C_6H_6(l)] = +49.0 \text{ kJ mol}^{-1}$
$\Delta H_b [C_6H_6(l)] = +39.4 \text{ kJ mol}^{-1}$
$\Delta H_{at}^\ominus [C(\text{graphite})] = +716.7 \text{ kJ mol}^{-1}$
$\Delta H_{at}^\ominus [\tfrac{1}{2}H_2(l)] = +218.0 \text{ kJ mol}^{-1}$

This gives
$\Delta H_{at}^\ominus [C_6H_6(g)] = +5525.3 \text{ kJ mol}^{-1}$ (5)

Average bond energies C–C = 347 kJ mol^{-1}
C ═ C = 612 kJ mol^{-1}
C — H = 413 kJ mol^{-1}

This gives
$\Delta H_{at}^\ominus [C_6H_6(g)] = +5360 \text{ kJ mol}^{-1}$(3 SF) (3)

Comment on difference in terms of delocalization stabilization (2)

Total 10 marks

Examination questions

7.17

a Any primary alcohol, $C_5H_{11}OH$, is acceptable. (2)

b **i** Apparatus for reflux with addition, well drawn. (2)

ii Bromine formed by oxidation with sulphuric acid. (2)

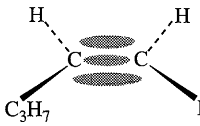
iii $C_5H_{11}OH \rightarrow C_5H_{11}Br$

molar masses 88 g 151 g

yield 88 g $\frac{60}{100} \times 151$ g

to produce 15 g $\frac{88 \times 100}{60 \times 151} \times 15 = 15$ g (to 2 SF) (2)

c (2)



d Reflux with aqueous sodium dichromate(VI) and sulphuric acid. (2)

Total 12 marks

7.18

a **i** Free radical, substitution. (2)

ii To produce Cl•/to break Cl — Cl bonds. (1)

iii 1,2-dichloropropane (1)

$CH_2Cl — CHCl — CH_3$ (1)

b Electron pair available from the double bond. (2)

c Elimination involves the removal of atoms, in this case those making HCl. (2)

Total 9 marks

7.19

a **i** O — H (1)

ii C — H (1)

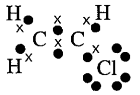
b **i** Potassium hydroxide, aqueous and reflux. (2)

ii Potassium hydroxide, ethanolic and reflux. (2)

iii Ammonia, ethanolic and heat under pressure. (2)

c Both nucleophilic. (2)

d **i** (3)



ii H — C — H 120–115° C = C — H 125–120° (2)

iii Addition of chlorine. (1)

Elimination of HCl by ethanolic KOH. (1)

iv Manufacture of poly(chloroethene), PVC. (1)

Total 18 marks

7.20

a Bromine with iron catalyst. (3)

b Nitrobenzene, $C_6H_5—NO_2$. (2)

c Benzenesulphonic acid, $C_6H_5—SO_3H$. (2)

Total 7 marks

7.21

Mark by impression

A full description of reactions with comments on the mechanisms is expected. (12)

A good chemical test should be described (combustion is not very useful). (3)

Total 15 marks

7.22

Mark by impression

Listing reactions should attract little credit, pointing out and explaining similarities and differences is expected. (10)

Reference to bond energies (quoting data) is expected. (5)

Total 15 marks

7.23

Mark by impression

Brief explanation expected. (2)

Energy cycle for C — C bond is described in detail in Topic 6. (4)

Disilane:

From table 4.6	$kJ\ mol^{-1}$
E(Si — Si)	226
E(Si — H)	318
E(H — H)	435.9

From table 5.2

$\Delta H_{at}[Si] = +455.6\ kJ\ mol^{-1}$

$\Delta H_{at}[\frac{1}{2}H_2] = +218.0\ kJ\ mol^{-1}$

$\Delta H_f\,[Si_2H_6] = 2\Delta H_{at}[Si] + 6\Delta H_{at}[\frac{1}{2}H_2] - E(Si - Si) - 6E(Si - H)$

$= +2219 - 2134 = +85\ kJ\ mol^{-1}$ (6)

Formation of ethane is exothermic ($-85\ kJ\ mol^{-1}$), so decomposition is endothermic and unlikely.

Decomposition of disilane is exothermic so likely, and three simple gas molecules are produced from one large molecule (needs knowledge of Topic 10). (3)

Total 15 marks

TOPIC 8

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*
8.1	1 hours	Pages 212–214
8.2	5 hours	Pages 214–219
8.3	2 hours	Pages 219–224
8.4	3 hours	Pages 224–226
8.5	4 hours	Pages 227–232

Total about 3 weeks

8.1 Why we study rates of reactions. Factors which may influence rates of reaction, measurement of rate by rate of change of concentration, rate equations, order of reaction, the rate constant.

8.2 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.

8.3 Kinetics and reaction mechanism. Rate determining steps; hydrolysis of primary and tertiary halogenoalkanes, S_N1 and S_N2 mechanisms.

8.4 The effect of temperature on the rate of reaction. Measurement of activation energy by experiment; collision theory of reaction kinetics; the Arrhenius equation.

8.5 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.*

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 simple treatment of the collision theory of reaction kinetics.
5 To gather information on catalysts and to introduce a theoretical understanding of catalysis.

8.1 Why we study rates of reactions

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 concentrations 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 *not* be used in a quantitative sense, at any rate at this level, so that any possible ambiguity is avoided (see *Chemical nomenclature, symbols, and terminology for use in schools,* Association for Science Education, third edition, 1985). 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 realize 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 8.4.

Students should be given practice in working out for themselves the units of rate constants for particular reactions as they progress through the Topic.

8.2 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 8.2a 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
Stop clock
Balance, to weigh to ± 0.01 g

METHOD 2

Test-tube with side-arm, 150 × 25 mm, or equivalent
Glass gas syringe, 100 cm^3
Rubber stopper to fit test-tube
Rubber connection tubing
Marble, as for Method 1
1 M hydrochloric acid, 10 cm^3
Stop clock

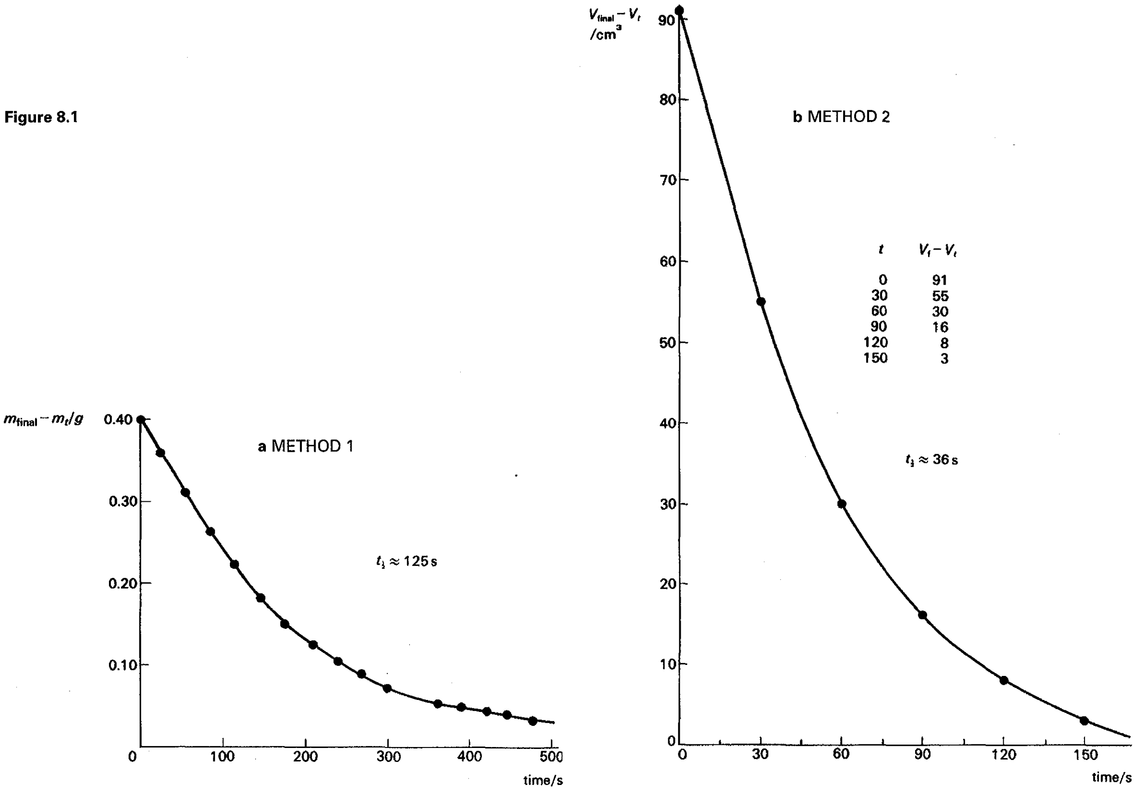
Procedure

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. Sample results are shown in the graphs in figure 8.1.

Figure 8.1



Students are asked to plot this graph, and compare it with types of graphs that would be expected from zero, first, and second order reactions (see figure 8.5 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.

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 8.2b The kinetics of the reaction between iodine and propanone in acid solution

Each group of students will need:

METHOD 1

5 conical flasks
Burette, 50 cm^3, and burette stand
White tile
Pipette, 10 cm^3, and safety filler
4 measuring cylinders, 50 cm^3, 2 × 25 cm^3, 10 cm^3
0.02 M iodine in potassium iodide solution, labelled A, 50 cm^3 HARMFUL
1 M propanone solution (in water), labelled B, 25 cm^3

1 M sulphuric acid, labelled C, 25 cm^3 IRRITANT
0.5 M sodium hydrogencarbonate, labelled D, 150 cm^3
0.01 M sodium thiosulphate, labelled E, 200 cm^3
1% starch solution, 10 cm^3
Stop clock

METHOD 2

Conical flask, 100 cm^3
Test-tube
Stop clock
Access to communal burettes with 'drip trays' containing:
2 M hydrochloric acid, 100 cm^3 per group of students
2 M propanone, 40 cm^3 per group of students
0.01 M iodine in potassium iodide solution, 20 cm^3 per group of students 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 8.2a, 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 emphasized, and the need for 'quenching' the reaction before titration, in this case by neutralizing 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

	Run 1	**Run 2**	**Run 3**	**Run 4**
Time for colour to disappear/s	115	264	243	58
Rate	4/115	4/264	4/243	2/58
	= 0.035	= 0.015	= 0.016	= 0.034

ANSWERS TO QUESTIONS

1 Water is added to some of the mixtures to ensure that the total volumes 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.

8.3 Kinetics and reaction mechanism

Timing About 2 hours will be needed.

Suggested treatment

The mechanistic implications of experiment 8.2b 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 TO THE QUESTIONS

CASE A

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

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

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

1 With 0.5 mole 2-chloro-2-methylpropane in 15 cm^3 of solvent the rate of reaction is

proportional to 35 microsiemens min^{-1}.
With 0.1 mole 2-chloro-2-methylpropane in 15 cm^3 of solvent the rate is 21 microsiemens min^{-1}. Students may find it difficult to estimate the initial rate as the graphs have slight curvature.

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

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.

8.4 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 8.4 The effect of temperature on the rate of the reaction between sodium thiosulphate and hydrochloric acid

Each group of students will need:
Beaker, 400 cm^3
2 boiling tubes, 150 × 25 mm
Labels
Thermometer, 0–110 °C
2 measuring cylinders, 10 cm^3
Stop clock
0.1 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 emphasized 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 *Appendix* on mathematical help should be useful here.

Sample results are shown on the graph, figure 8.2. This experiment is adapted from Turner, J.W. 'The activation energy of the thiosulphate–acid reaction', *School Science Review* **53**, *185*, page 751, 1972.

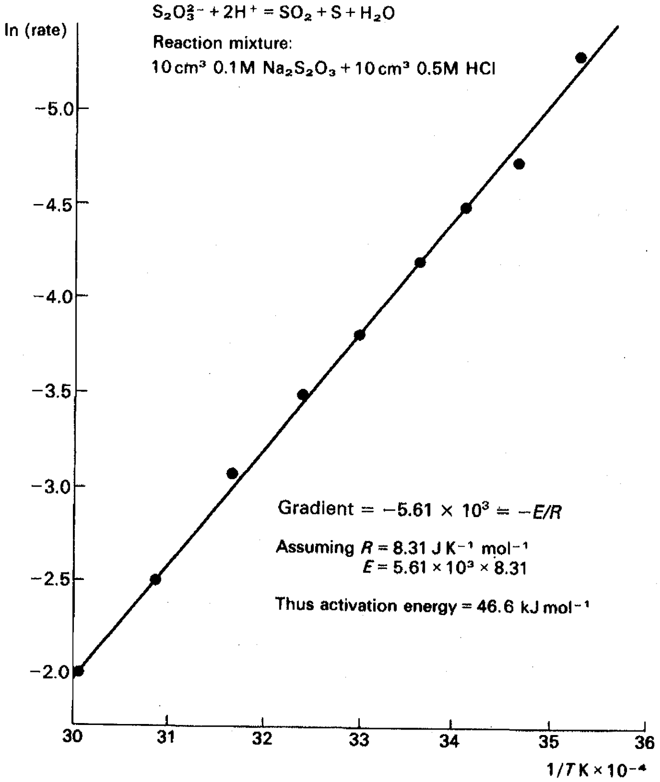


Figure 8.2 Activation energy of the thiosulphate–acid reaction.

Teachers should note that when completing the table, students enter the time, units seconds, s, and then work out the rate by taking the reciprocal of the time, units seconds^{-1}, 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.

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 8.2 by measuring the gradient of the graph. 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, for example, the textbook by P.W. Atkins.

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 is explained by reference to a graph showing the distribution of energy amongst molecules at different temperatures (figure 8.13 in the *Students' book).*

8.5 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 in the course where the subject is discussed.

The principal 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 8.15 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 always a true intermediate. A true intermediate is relatively more stable 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 8.5a

A study of some catalysts

Each group of students will need:
Test-tubes and rack
Dropping pipettes
Beaker, 250 cm^3 as a water bath
Access to:
0.1 M cobalt chloride (or similar salt), 1 cm^3
0.1 M barium chloride, 2 cm^3
2 M ethanoic acid
2 M hydrochloric acid
2 M hydrogen peroxide, 20 cm^3 IRRITANT
0.5 M potassium sodium tartrate
2 M sodium hydroxide CORROSIVE
Sulphamic acid, 3 g IRRITANT
2 M urea, 3 cm^3
Liver, small piece of calf or pig
1% urease-active meal
Selection of metal oxides (Cu_2O, MnO_2, ZnO, MgO) SEVERAL ARE HARMFUL
Red litmus paper

Hazards

Biological materials should be treated as irritant and disposed of in an approved manner.

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 sulphite solution is oxidized by oxygen gas, the reaction is inhibited by a variety of alcohols. It is thought that inhibitors work by preventing the formation or propagation of reaction chains.

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; CuO: slight 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 electron shells in their ions.

Liver contains the enzyme catalase which catalyses the breakdown of hydrogen peroxide.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

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 oxidize 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 oxidized form.

3 The barium sulphate precipitate appears in the order: first, HCl; second, CH_3CO_2H; last, H_2O alone. The reaction is

$$NH_2SO_2OH + H_2O \rightarrow NH_4^+ + HSO_4^-$$

This suggests that the hydrogen ion is responsible for the catalysis. The point could be brought out that increasing the concentration of catalyst increases the catalytic effect.

4 The enzyme urease in the jack bean meal catalyses the hydrolysis of urea:

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$

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 localized alkaline conditions when ammonia is produced.

Study Task: Heterogeneous catalysis

Students are asked to read a passage which describes heterogeneous catalysis in terms of adsorption and desorption. It is placed in the context of choosing the best catalyst for ammonia synthesis.

For teachers' information some additional notes are included here.

Chemisorption is characterized by a high enthalpy change of adsorption, −80 kJ to −800 kJ, which is comparable to the energy evolved in chemical changes. This is because no energy has to be expended in breaking the metal lattice when forming a surface layer. Another striking feature of chemisorption is that it can occur at temperatures far above the boiling point of the adsorbed substance, for example ammonia on tungsten at 800 °C, which points to strong bonding between the surface of the metal and the gas molecules.

ANSWERS TO THE STUDY TASK QUESTIONS

1 The students should explain the difference in terms of chemisorption involving directional bonds and physical adsorption involving non-directional bonding.
2 Students should realize that physical adsorption involves weak, non-directional forces. These are discussed further in Topic 9.
3 Students should suggest that there is a need for a balance between fairly good absorption to promote the alignment of reactants whilst being not too strong to prevent the formation of new bonds during ammonia synthesis and/or desorption.

Investigation 8.5b The rate of reaction of magnesium with acid

Students are asked to carry out an investigation on the rate of reaction of magnesium with acid. The planning stage should include trial experiments and an assessment of risks. When students have completed their plan it should be shown to the teacher before they carry out their experiments.

The reaction is fully discussed by Iolo Williams and Roger Hacker in *Education in Chemistry*, **7**, *1*, pages 20–24, 1970. They found that the reaction has some interesting variants, the rate relationships being different in hydrochloric and sulphuric acids and the reaction time being affected by the degree of agitation of the solution. Zinc can be used instead of magnesium.

A good account of this investigation would consider the theory related to the procedures used, using some of the mathematical concepts that have been learnt during this Topic.

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

8.1

a Dilatometry – the very small change of volume of the reaction mixture with time. (2)

b Measure the volume of gas produced with time, keeping the temperature constant. (2)

c Withdraw samples of the reaction mixture, quench by cooling, and titrate with alkali of known concentration. (3)

d Withdraw samples of reaction mixture, quench by cooling, and titrate with alkali of known concentration; a 'final' titration is necessary. (4)

e Withdraw samples of reaction mixture, quench by neutralizing the acid with sodium hydrogencarbonate, and titrate with sodium thiosulphate solution; a 'final' titration is necessary. (5)

f Withdraw samples, quench by neutralizing the acid with sodium hydrogencarbonate, add excess potassium iodide, and titrate the iodine with sodium thiosulphate; a 'final' titration is necessary. The use of a colorimeter, correctly described, would be an acceptable alternative answer. (6)

Total 22 marks

8.2

a **i** Rate of formation of iodine = $k[H_2O_2]^1[I^-]^1[H^+]^0$ (3)

ii 1.75×10^{-2} (2)

iii $dm^3\ mol^{-1}\ s^{-1}$ (2)

b Both H_2O_2 and I^- are reactants in the rate-determining step and in such numbers of particles that the reaction should be first order with respect to each of these. H^+ is involved in the mechanism after the rate-determining step so the reaction should be zero order with respect to H^+. This mechanism is therefore consistent with the results. (5)

Total 12 marks

8.3

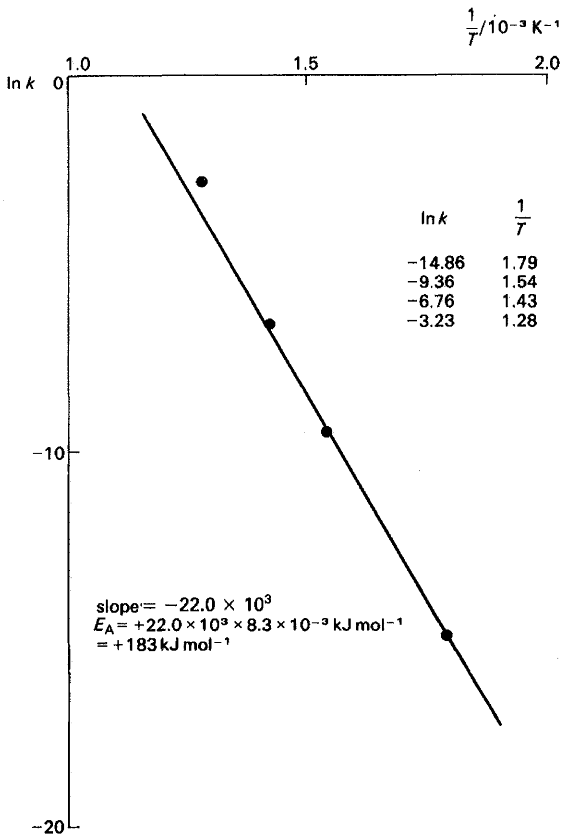
a **i** Rate of formation of bromine = $k[BrO_3^-]^1[Br^-]^1[H^+]^2$ (3)

ii The units of rate constant here would be $dm^9\ mol^{-3}\ s^{-1}$ (2)

b Considering the rate-determining step,
$[HBr]$ depends on the concentrations of Br^- and H^+;
$[HBrO_3]$ depends on the concentrations of BrO_3^- and H^+.
The rate of the reaction should therefore depend on the concentrations of Br^- and BrO_3^- and on the square of the concentration of H^+. This is consistent with the rate equation. (5)

Total 10 marks

8.4

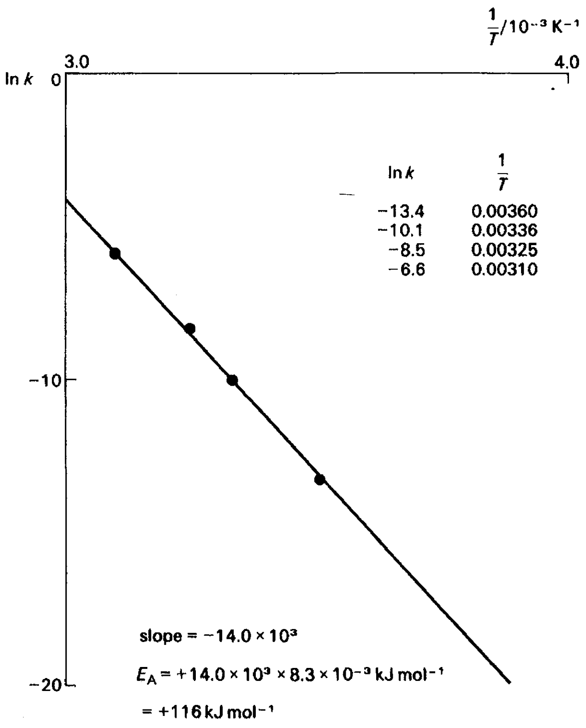


ln k	$\frac{1}{T}$
−14.86	1.79
−9.36	1.54
−6.76	1.43
−3.23	1.28

slope = -22.0×10^3
$E_A = +22.0 \times 10^3 \times 8.3 \times 10^{-3}$ kJ mol^{-1}
= +183 kJ mol^{-1}

Total 10 marks

8.5



ln k	$\frac{1}{T}$
−13.4	0.00360
−10.1	0.00336
−8.5	0.00325
−6.6	0.00310

slope = -14.0×10^3

$E_A = +14.0 \times 10^3 \times 8.3 \times 10^{-3}$ kJ mol^{-1}

= +116 kJ mol^{-1}

Total 10 marks

Examination questions

8.6

a Method based on gas collection or titration: suitable apparatus/reagents; measurements over a period of time; suitable graph of results. (6)

b **i** $rH_2O_2 = k[H_2O_2]$ (1)

ii Units of k are s^{-1} (or any time^{-1}) (1)

Total 8 marks

8.7

Either: Measurement of volume of carbon dioxide at suitable time intervals in suitable apparatus. (4)

Or: Samples taken at suitable time intervals, quenched by chilling or dilution, titrated with NaOH using weak acid–strong base indicator. (4)

Plot volume against time. (1)

Measure half-lives, first order if constant. (2)

Total 7 marks

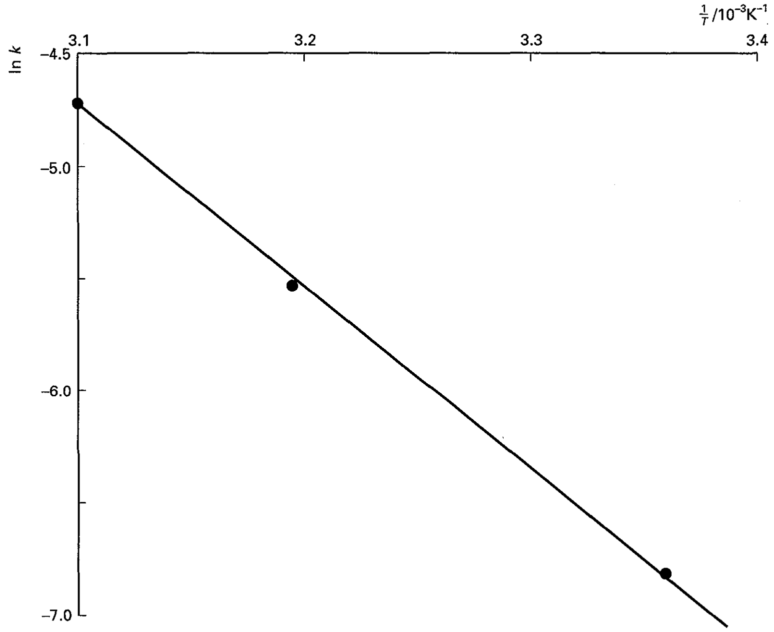
8.8

Mark by impression

a Method based on quenching and titration (with use of an acid catalyst). Alternatively, variation of pH or electrical conductivity.
Details of any titration procedures should be given. (6)

b Rate = $k[HCO_2CH_3][H^+]$
Rate constant = 1.12×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$
Figures for graph:

1/T	**ln** ***k***
3.360×10^{-3}	–6.794
3.195×10^{-3}	–5.534
3.096×10^{-3}	–4.753

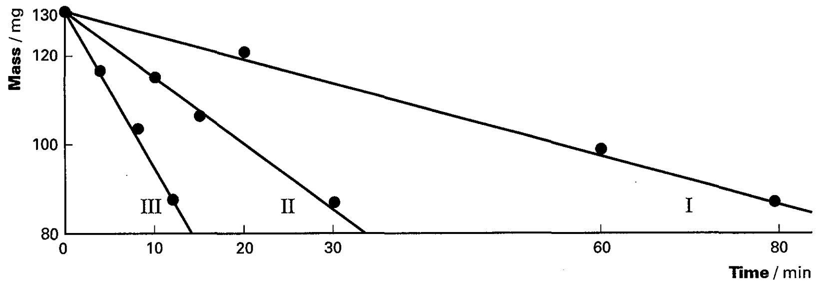


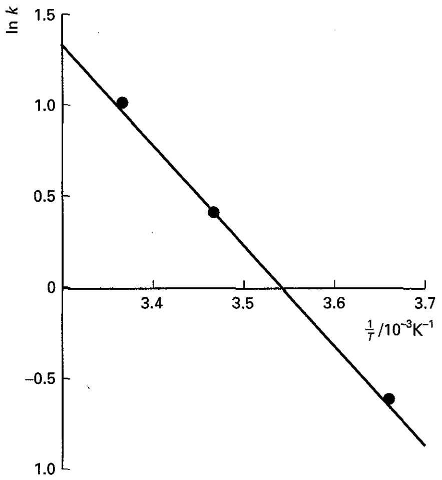
Gradient = 7800
$E_A = 8.31 \times 7.8 = 65$ kJ mol^{-1} (9)

Total 15 marks

8.9

Mark by impression





Graphical determination of k (data are real experimental results).

I 0.55 **II** 1.5 **III** 3.6 (8)

Graphical determination of E 12 kJ (6)

Non-rotation would reduce rate due to localized reduction of solution concentration. (1)

Total 15 marks

8.10

a **i** 2-bromo-2-methylpropane. (1)

ii Alcohols. (1)

iii HBr produces an increase in the number of ions present, and hence in the conductivity, as the reaction proceeds. (2)

iv For a viable method:

1 mark for property to be monitored; 1 mark for how it will be monitored, for example, use pH meter to measure acidity due to HBr. (2)

b **i** Correct derivation of initial rate data; correct plotting of points; acceptable 'best-fit' line. (3)

ii Straight line graph, hence first order with respect to formation of HBr;

each molecule of HBr derives from 1 molecule of **A**;

hence rate of disappearance of **A** is first order. (3)

iii Rate = $k[C_3H_7Br]$ (1)

Total 13 marks

8.11

a **i** Temperature. (1)

ii Any constant temperature device. (1)

b **i** Rates do not vary with time. (1)

ii Zero order. (1)

iii Rate = $k[HNO_3]$ (1)

iv Minimum number is 2 steps. (1)

Slow step can only involve HNO_3, so there must be a second fast step involving the arene. (1)

c Electrophile, substitution. (2)

Total 9 marks

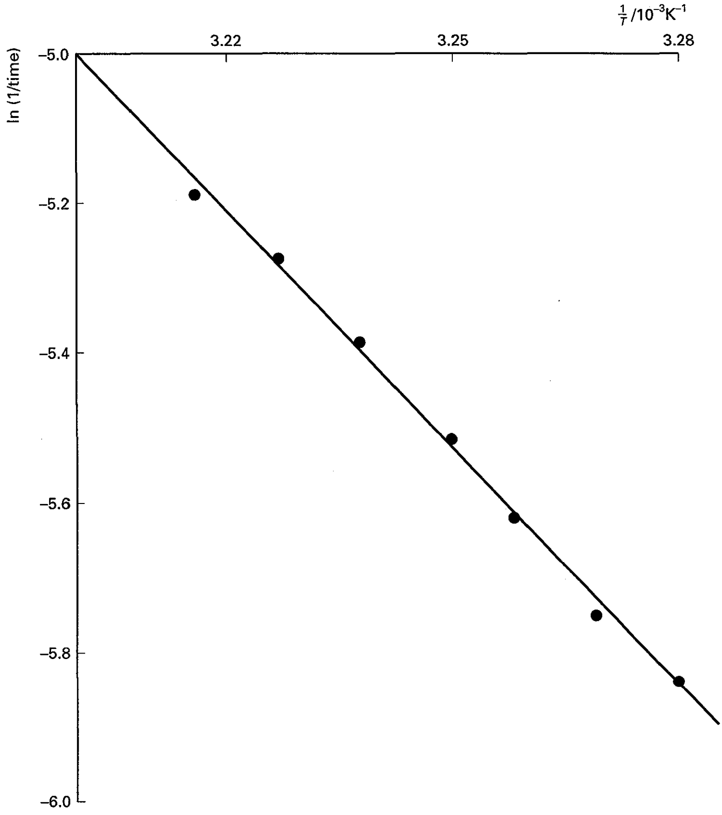
8.12

a **i** Total time is longer (slower reaction), so any time error is a smaller proportion of the total time. (1)

ii $K^{-1} = 3.279 \times 10^{-3}$ (1)

ln (1/development time) = –5.84 (1)

iii (2)



iv Gradient of graph –10 300 to –10 840 (1)

$E = -8.31 \times$ gradient = 85.6 to 90.1 kJ mol^{-1} (1)

b **i** Hexacyanoferrate(II)/ferrocyanide (1)

ii $Fe(CN)_6^{3-} + Ag \rightarrow Fe(CN)_6^{4-} + Ag^+$ (2)

Total 10 marks

TOPIC 9

Intermolecular forces and solubility

Introduction

In their pre-A-level courses students may have studied solubility in terms of the generalization that many ionic substances are soluble in water but that molecular substances are often insoluble. This generalization has been further refined by the study of ionic compounds in Topic 3 and by an appreciation of the range of solubilities of the organic compounds studied in Topics 2 and 7. The present Topic extends the student's understanding of solubility through a study of a wide range of solvent–solute interactions.

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. The Topic is concluded by a consideration of the enthalpy changes occurring when ionic substances dissolve.

Content

	Timing	*Students' book*
Introduction	1 hour	Pages 245–246
9.1	3 hours	Pages 246–249
9.2	2 hours	Pages 249–251
9.3	3 hours	Pages 251–258
9.4	3 hours	Pages 259–262
9.5	3 hours	Pages 263–265
Total about 3 weeks		

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; polarization 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 vaporization; the importance of hydrogen bonding.

9.4 The solubility of molecular compounds. Solubility in polar and non-polar liquids; the dissolving of organic compounds in water; *an investigation of soluble laundry bags.*

9.5 The solubility of ionic compounds. Enthalpy changes of solution; solvation; *an investigation of enthalpy changes of hydration.*

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.
6 To interpret solubility patterns of molecular and ionic compounds in terms of possible interactions between solute and solvent.
7 To interpret solvation of ions in terms of the enthalpy changes of solution and lattice energy.

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 ionization energy have been discussed in Topic 3 and covalent bond energies in Topic 6.

Experiment 9.0 Evidence for intermolecular forces

Each group of students will need:
10 wine bottle corks (preferably parallel sided)
Steel sewing needle (clean and blunt)
Razor blade (clean and blunt, use an oil stone)
Access to:
Large shallow container
Petri dish (optional)
Hexane or similar hydrocarbon (optional) HIGHLY FLAMMABLE, HARMFUL

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 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 merely to show that there are greater intermolecular forces in water than in hexane, and that the total force increases when the contact area increases.

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.

When students look at figure 7.7, they should notice that the boiling point of the alkanes does not increase in a linear manner. This is because as the molecule becomes larger the percentage increase of the forces caused by each consecutive CH_2 group becomes smaller, so the difference in boiling point between consecutive members of the series decreases.

ANSWER TO THE STUDY TASK QUESTION

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.

For a detailed discussion of boiling point trends for isomeric hydrocarbons see Perkins, R. 'Hydrocarbon boiling point trends' *School Science Review*, 68, *244*, pages 510–512, 1987.

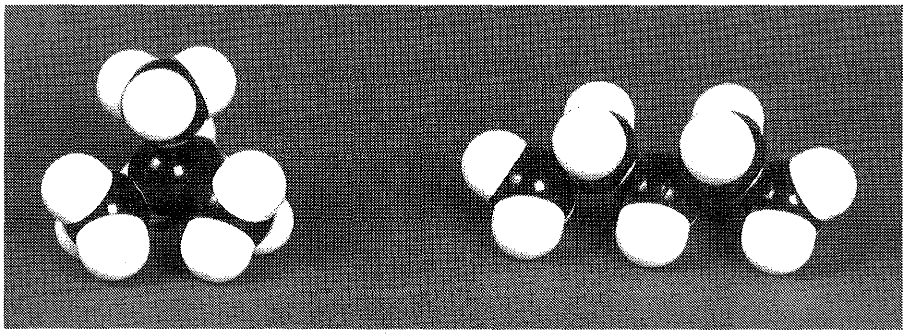


Figure 9.1 Two isomers of formula C_5H_{12}.

Van der Waals radii

Van der Waals radii were referred to in Topic 3, where students used them to compare patterns in atomic 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 14.

STUDY TASK

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 9.2)
Beaker, 600 cm^3, or large diameter container
Access to:
A range of organic hydrocarbons, alcohols and ketones, 50 cm^3 each
Water

Hazards

A risk assessment will be necessary so that appropriate precautions are taken for the liquids selected for testing.

Procedure

This experiment is intended to be operated as a circus. The students circulate repeating the experiment with a different liquid at each station.

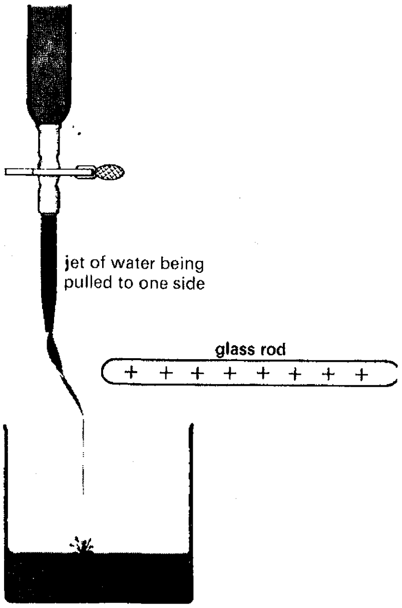


Figure 9.2 Apparatus for experiment 9.2.

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. Hexane shows no, or almost no deflection while alcohols such as hexan-1-ol show marked deflections. The degree of polarization 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 and the possibility of measuring their dipole moments, 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)

$$\mu = qd = (1.6 \times 10^{-19}) \times (1 \times 10^{-10}) \text{ C m} \approx 5 \text{ D}$$

Molecules which do not possess a permanent dipole moment are nevertheless polarized 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 polarization may therefore be made up of three parts: the orientation polarization, P_O, due to a permanent dipole; the electron polarization, P_E; and the atom polarization, 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 polarization is mentioned in the *Students' book*, polarizability and induced dipoles need not be discussed with the students in any depth.

STUDY TASK

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	36 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.

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 vaporization 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 requirement 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 emphasized to students that very few elements can take part in hydrogen bonding. Such bonds can form in the following situations:

$\mathrm{N{-}H\cdots O}$
$\mathrm{N{-}H\cdots N}$
$\mathrm{O{-}H\cdots O}$
$\mathrm{F{-}H\cdots F}$ but *not* $\mathrm{C{-}H\cdots C}$

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.

Carbon is not normally sufficiently electronegative for attached hydrogen atoms to participate in hydrogen bonding. Carbon can, however, be made sufficiently electronegative to form a hydrogen bond by the presence of three chlorine atoms as, for example, in trichloromethane. Teachers should introduce this example at their discretion as students may find it a source of confusion.

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.

STUDY TASK

1 Students are asked to predict from a graph the boiling point of water without its hydrogen bonding. A reasonable estimate is 150 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 one hundred hydrogen fluoride molecules, although there are three hundred non-bonded electron pairs, there are only one hundred hydrogen atoms. Therefore, only one hundred 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 vaporization, and melting point, using values of these constants from the *Book of data*.

The next experiment can be done in a variety of ways depending on the apparatus available.

Experiment 9.3 Measuring enthalpy changes of vaporization

Each group of students will need:

Procedure 1

Electric kettle (free of scale)
Balance weighing to 2 kg
Stop clock

Procedure 2

Apparatus as shown in figure 9.3. The immersion heater can be made from a loosely-coiled length of resistance wire. Its resistance must be chosen to suit the low voltage supply and joulemeter that are used. Alternatively, a 'heat of

vaporization of liquids apparatus' may be borrowed from the physics department.
2 beakers, 100 cm^3
Access to:
Balance to weigh to ±0.1 g

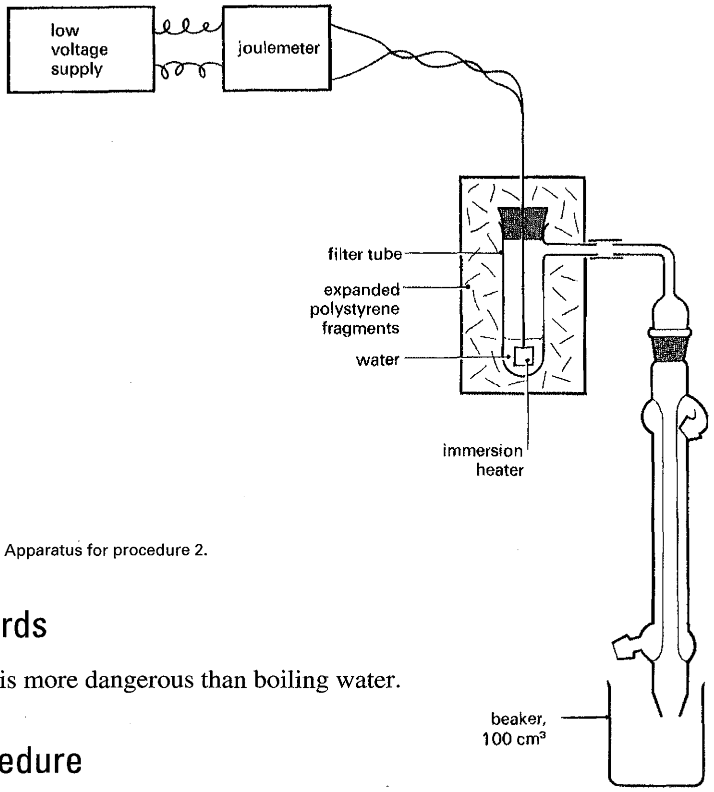


Figure 9.3 Apparatus for procedure 2.

Hazards

Steam is more dangerous than boiling water.

Procedure

Full details for *procedure 1* are given in the *Students' book.* Using *procedure 1*, 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 3*, detailed below.

Procedure 3

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 overleaf and may be photocopied if teachers wish to use this method.

Each group of students will need;
Apparatus as shown in figure 9.4
Measuring cylinder, 250 cm^3
Dropping pipette
Stop clock
Stirrer

Alternative experiment 9.3

Measuring enthalpy changes of vaporization

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.

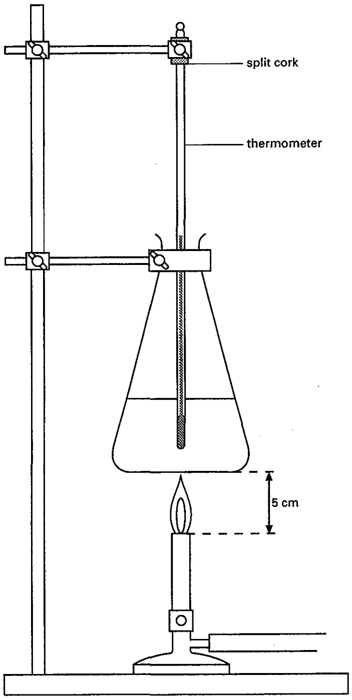


Figure 9.4 Apparatus for experiment 9.3.

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?

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 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 TO THE STUDY TASK QUESTIONS

1 Students are asked to estimate the hydrogen bonding contribution to the enthalpy change of vaporization of water. When a smooth line is drawn between the points students will arrive at a value of about 18.5 kJ mol^{-1} for the estimate if there were no hydrogen bonding, leading to about 11.1 kJ mol^{-1} for the strength of 1 mole of hydrogen bonds in water.

2 For ammonia a value of 12 kJ mol^{-1} should be obtained.
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

This section is set as a *Study Task* which students could do for homework.

ANSWERS TO THE STUDY TASK QUESTIONS

1 Students should appreciate that there is an overall decrease in density of water with increase in temperature, due to the commonly observed thermal expansion of materials. The increase in density at the melting point which continues until 4 °C is due to the gradual collapse of the three-dimensional hydrogen bonded structure of ice. Above 4 °C water molecules are still extensively hydrogen bonded but the density of water is now more influenced by temperature change than by change in hydrogen bonding.

During discussion of students' answers a model of an ice crystal (wurtzite type) might be useful.

2 Hydrogen bonds give water a skin effect (figure 9.5) 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.

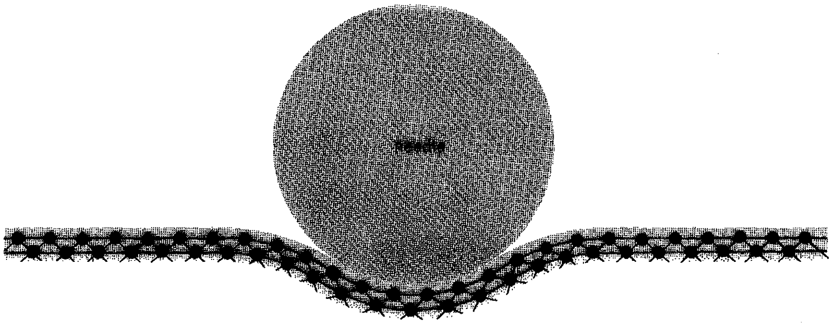


Figure 9.5 A water surface, showing how the surface tension is increased by intermolecular hydrogen bonding (not to scale).

Liquid	Surface tension at 20 °C /N m^{-1}
Water	0.072
Propane-1,2,3-triol	0.063
Methanoic acid	0.037
Benzene	0.029
Ethanoic acid	0.028
Methanol	0.023

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.

Optional experiment

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. (See Healey, J.A.D. 'An open-ended problem in liquid flow', *School Science Review,* **49**, *169*, pages 884–885, 1968.

Optional experiment

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 bond is 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.

Hydrogen bonds are responsible for stabilizing the α-helical regions of proteins. The hydrogen bonds run more or less parallel with the long axis of the helix with the amino acid side chains projecting from the sides. Each oxygen atom from the carbonyl group is hydrogen bonded to the N — H hydrogen, three amino acid residues distant from it.

In contrast, in DNA, the hydrogen bonds link the nitrogenous bases at right angles to the axis of the helix.

Although hydrogen bonding may help stabilize the three-dimensional structure of proteins, van der Waals forces are also of great importance in maintaining the tertiary structure of proteins.

ANSWER TO THE STUDY TASK QUESTIONS

The ability of some natural substances to absorb moisture is due to the presence of atoms able to become involved in hydrogen bonding with water.

When all the material in this section has been discussed with students it is desirable to summarize the basic information about the hydrogen bond, concerning participating groups, bond energy, bond length, and bond angle.

9.4 The solubility of molecular compounds

Timing About 3 hours.

Suggested treatment

This section is developed in the following way:

1 Students examine the solubility of molecular compounds in a variety of solvents.

2 A generalization relating solubility to the polarity of the solvent and the solute is introduced.

3 The dissolving of organic compounds in water is related to the polarity of the organic solute.

4 Students conduct an investigation into the behaviour of soluble laundry bags using the ideas they have been introduced to in this and the preceding Topic.

Experiment 9.4a The solubility of molecular compounds

Each group of students will need:

Eye protection

10 test-tubes and rack

Dropping pipettes, 3

Access to:
Glucose
Hexane HIGHLY FLAMMABLE
Iodine HARMFUL
Methanol TOXIC, HIGHLY FLAMMABLE
Methylbenzene HIGHLY FLAMMABLE, HARMFUL
Fume cupboard
Solvent residues container

Procedure

Students should be advised to use only small volumes (1–2 cm^3) of solvent and very small amounts of solid. Iodine is relatively soluble in hexane and methylbenzene, slightly less soluble in methanol and insoluble in water. Glucose is soluble only in solvents of high polarity such as water. The suggested criterion for solubility in these experiments is the disappearance of the solid but students may also realize that energy changes are associated with the solution process.

The pattern of solubility

The conclusion which is drawn from experiment 9.4a is that as a general guide, non-polar substances dissolve in non-polar solvents and polar substances dissolve in polar solvents.

The point should be made that, for liquids of moderate polarity such as methanol, the solubility effects cannot be predicted with confidence.

A more extended discussion is given here which teachers may wish to use with students.

Only van der Waals forces are involved when non-polar solutes dissolve in non-polar solvents. In these cases, the solvent molecules can readily penetrate the crystal structure of the solid, and since solute–solute, solvent–solvent and solute–solvent attractions are approximately the same, the solid dissolves.

With polar solvents, however, the dipole–dipole interactions cause the solvent–solvent attractions to be greater than either solute–solute or solute–solvent attractions, and the associated solvent structure is not readily broken down. The result is insolubility or poor solubility of non-polar substances. If the polar solvent is also hydrogen bonded as is the case with water, the situation is accentuated.

The dissolving of organic compounds in water

The basic idea which students should grasp here, as in the last section, is that for solubility, the new solute–solvent interactions must outweigh the existing solute–solute and solvent–solvent interactions.

Polarity conferred upon an organic molecule by the presence of a nitrogen or an oxygen atom also confers the property of water solubility if the molecule is reasonably small. This is because hydrogen bonding may take place with the water molecules. Solvation therefore occurs and the compound dissolves. Thus the lower alcohols, aldehydes, ketones and the low molar mass peptides are water soluble. This is a particularly important effect in living organisms, since the solvent for plant and body fluids is water.

Some data are given opposite for the information of teachers.

Compound	Solubility at 20 °C /g in 100 cm^3 water
hexadecanol	nil
heptanol	0.1
hexanol	0.6
butanol	8
ethanol	mixes in all proportions
hexane	0.01
hexane-2,3-diol	8

ANSWERS TO THE STUDY TASK QUESTIONS

Answers to the questions should be based on:

3a Glucose and blood are both polar.
b Iodine and decane are both non-polar.
c Ethanol and water are both polar, cyclohexanol is only moderately polar.

Investigation 9.4b An investigation of soluble laundry bags

Students are asked to carry out an experiment to investigate the factors affecting the rate at which soluble laundry bags dissolve in water. The planning stage is likely to need library research and should include trial experiments and an assessment of risks involved. A good report would include a full use of theoretical ideas.

When students have completed their plans they should be shown to the teacher before they carry out their experiments.

Soluble laundry bags are widely used in hospitals. The material can be bought from the Aldrich Chemical Co.

9.5 The solubility of ionic compounds

Timing About 3 hours.

Suggested treatment

The section is developed in the following way:

1. Students measure the enthalpy changes of solution for a number of ionic compounds.
2. The ability of ionic solids to dissolve is discussed in terms of lattice energies and solvation energies.
3. The structure of some complex ions is introduced.
4. Students investigate the enthalpy change of hydration of an anhydrous ionic salt.

Experiment 9.5a Enthalpy changes of solution

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
Potassium chloride

Hazards

Students should be told to use anhydrous salts with care as they can cause burns on moist skin and in eyes.

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.

The experiment could be made quantitative by asking students to weigh out sufficient solid to produce 2 M solutions.

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 opposite, and some additional ones are included.

Anhydrous salt	Temperature change /°C
LiCl	+13
NaCl	–1
KCl	–7
$MgCl_2$	+45
$CaCl_2$	+30
$SrCl_2$	+15
$BaCl_2$	+4
$FeCl_3$	+4

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 solvation energy. The term solvation energy is not however given to the students. The emphasis is on the process of solvation itself.

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, solvation energy and enthalpy change of solution is shown in figure 9.6 for potassium chloride.

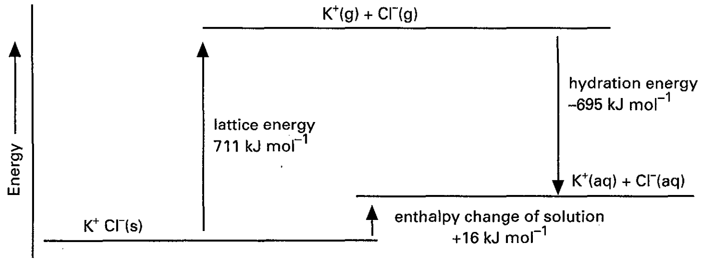


Figure 9.6 Principal energy relationships in the dissolving of an ionic solid. (aq) represents the full hydration of the ions.

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 $\Delta H_{\text{solvation}}$ by such a cycle leads to a value which is the sum of two solvation energies, so that the separate solvation energies, 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.

Energy changes and solution

This section is introduced by definitions of enthalpy change of *formation* of an aqueous solution (table 5.6 in the *Book of data*) and hydration energy (which are not listed in the *Book of data*). The term hydration energy is used rather than solvation energy as students will normally only be expected to consider problems involving aqueous solution.

A Study Task asks students to calculate the standard enthalpy change of solution of potassium chloride and calcium chloride, matching experiment 9.5a (data for iron(III) chloride are not available). The second question asks the students to construct a Hess cycle to determine the hydration energy of the two salts. An appropriate cycle is shown in figure 9.6, page 165. Lattice energies are listed in table 5.9 in the *Book of data.*

Ion	Approximate solvation number in water
Li^+	5
Na^+	5
K^+	4
Cl^-	1
Br–	1
I^-	1
Mg^{2+}	15
Al^{3+}	25

ANSWERS TO THE STUDY TASK QUESTIONS

1 KCl + 17.1; $CaCl_2$ – 81.4 kJ mol^{-1}

2 KCl – 694; $CaCl_2$ – 2340 kJ mol^{-1} (to 3 SF)

	$\Delta H^{\ominus}_{\text{solvation}}$/kJ mol^{-1}
H^+	(–1090)
Li^+	–520
Na^+	–405
K^+	–321
Rb^+	–300
Cs^+	–277
Mg^{2+}	–1920
Ca^{2+}	–1650
Sr^{2+}	–1480
Ba^{2+}	–1360
Fe^{2+}	–1950
Fe^{3+}	–4430
Cu^{2+}	–2100
Zn^{2+}	–2050
Al^{3+}	–4690
F^-	–581
Cl^-	–425
Br^-	–380
I^-	–314
OH^-	–460

Some hydration energies at infinite dilution are tabulated opposite to 3 SF.

The trends can be discussed in terms of the ionic charge and ionic radius. On descending Group 1, the hydration energy decreases as the size of the ion increases. Ions of the same charge have hydration energies of a similar magnitude but 2+ or 3+ ions have much greater hydration energies.

The ordering of polar molecules around ions and an appreciation that the different ions have different hydration energies leads to a discussion of how many solvent molecules may be associated with an ion in a crystal.

It is not intended that the discussion should go as far as mentioning total solvation numbers and solvation shells – these at best are only known approximately. Some examples are given opposite.

However teachers might like to introduce the fact that ions in solution do not exist as free ions but are surrounded by a sheath of solvent molecules, firmly or loosely attached. Solvated ions are therefore very much larger than ions in anhydrous crystals. They diffuse more slowly in solution, and move slowly under a potential gradient because of the extra drag created by the attached solvent molecules.

Students could extend their study to include the pattern of hydration energy across a period. In traversing a period there is an increase in the hydration energy of cations with decrease in ionic radius and increases in charge, that is, the greater the charge/radius ratio, the greater the hydration energy.

Teachers could mention that the hydrogen ion has a large hydration energy due to its very small size. The hydration energy for individual ions cannot be measured directly. One attempt to assign particular values is based on the hydrogen ion as a standard and, based on indirect evidence, assigns a value of 1090 kJ mol^{-1}. The hydration energy of the H^+ ion serves as a fixed value from which the hydration energy of individual ions can be calculated.

Investigation 9.5b An investigation of an enthalpy change of hydration

Students are asked to plan, trial, and carry out an experiment to measure the enthalpy change of hydration of sodium thiosulphate, or a similar anhydrous salt. The planning stage will need to include an assessment of risks involved, and trial experiments. When students have completed their plan it should be shown to the teacher before they carry out their experiment.

Students are expected to use their knowledge of the material in Topic 4 on Hess's Law to do the experiment. A good report of an investigation should include a full account of the theory related to the experimental method adopted, and suggestions about the nature of the hydrated ions.

Teachers may prefer to carry out a standard experiment on the measurement of an enthalpy change of hydration. These instructions may be photocopied for the students to use.

Alternative experiment 9.5b Measuring an enthalpy change of hydration

When anhydrous sodium thiosulphate is left in the atmosphere it slowly absorbs water vapour, giving the hydrated solid.

$$\underset{\text{anhydrous}}{Na_2S_2O_3(s)} + 5H_2O(g) \rightarrow \underset{\text{hydrated}}{Na_2S_2O_3{\cdot}5H_2O(s)}$$

Consider how the enthalpy change of this reaction might be measured directly, using either water vapour or liquid water. Either way presents difficulties.

We can, however, measure the enthalpy changes that take place when both anhydrous and hydrated sodium thiosulphate are dissolved in water, and we can use Hess's Law to calculate the enthalpy change that we require.

The equations for these changes are

1 $Na_2S_2O_3(s) + aq \rightarrow Na_2S_2O_3(aq, \text{M})$ enthalpy change ΔH_1

2 $Na_2S_2O_3{\cdot}5H_2O(s) + aq \rightarrow Na_2S_2O_3(aq, \text{M})$ enthalpy change ΔH_2

Measure 100 cm^3 of water into the electrical compensation calorimeter and note its temperature. Add 15.8 g (0.1 mole) of finely powdered anhydrous sodium thiosulphate, swirling the flask continuously, and record the final steady temperature that is reached. Find the electrical energy required to compensate for this change and so calculate the value of ΔH_1.

Repeat using 24.8 g (0.1 mole) of finely powdered hydrated sodium thiosulphate. You must use less water this time because of the quantity of water that will come from the hydrated salt; you should measure 100 cm^3 less (5×1.8) cm^3, that is, 91 cm^3. Find the electrical energy required to compensate for this change, and calculate ΔH_2.

Now use Hess's Law to calculate the enthalpy change that is required.

Teachers' guide to Alternative experiment 9.5b

Measuring an enthalpy change of hydration

Each group of students will need:

Electrical compensation calorimeter as described in Topic 18, with associated electrical meters; or the non-electrical calorimeter equivalent (plastic drinking cups, etc.)
Thermometer reading –10 to 50 °C in 0.1 °C intervals
Measuring cylinder, 100 cm^3
Weighing boat
Spatula

Sodium thiosulphate-5-water (24.8 g) and anhydrous sodium thiosulphate (15.8 g); both compounds should be finely powdered. Anhydrous sodium thiosulphate can be prepared by grinding the hydrated crystals to a powder and then heating them in an oven at 250 °C for 3 hours. The product should then be allowed to cool in a desiccator.

When calculating the required enthalpy change, the students should draw a cycle as follows

$$\begin{tikzcd}
Na_2S_2O_3(s) + 5H_2O(l) \arrow[rr, "\Delta H_{\text{hydration}}"] \arrow[dr, "\Delta H_1"'] & & Na_2S_2O_3{\cdot}5H_2O(s) \arrow[dl, "\Delta H_2"] \\
& Na_2S_2O_3(aq) &
\end{tikzcd}$$

Applying Hess's Law to the cycle, we have

$$\Delta H_{\text{hydration}} = \Delta H_1 - \Delta H_2$$

The accepted value for the enthalpy change of hydration of sodium thiosulphate is $-55\ kJ\ mol^{-1}$.

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

9.1

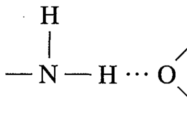
a Ethanol. (1)
b **i** $CCl_4 < C_2H_5OH < C_8H_{18}$ (1)

ii Tetrachloromethane and ethanol have similar boiling points (350 and 352 K) so van der Waals forces in tetrachloromethane and hydrogen bonding in ethanol are about the same strength; octane has the highest boiling point (399 K) and about the same number of electrons as tetrachloromethane (66 compared to 74) and so has relatively strong van der Waals forces. (5)

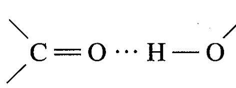
Total 7 marks

9.2

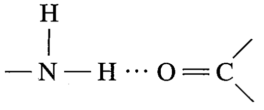
a **i**



(2) **ii**



(2) **iii**



(2)

b More opportunities for hydrogen bonding between urea molecules than between those of propan-1-ol. (2)

Stronger dipole–dipole interaction between molecules of urea than between those of propan-1-ol (dipole moments: urea 4.56 D, propan-1-ol 1.66 D)

Total 8 marks

9.3

C D B A (2)

C and **D** are polar, van der Waals forces in **C** greater than those in **D** because of its shape. (3)

A and **B** are non-polar, shape again decides the order. (3)

Total 8 marks

9.4

a Octane. Van der Waals forces greater because of linear shape. (3)

b No. Neither could form intermolecular forces with water which would be stronger than water's hydrogen bonding. (2)

c Yes. New intermolecular forces very similar to those in individual substances. (2)

Total 7 marks

9.5

a	iii	(1)	**d**	ii	(1)
b	iii	(1)	**e**	i	(1)
c	i	(1)	**f**	ii	(1)

Total 6 marks

9.6

a Argon, neon, helium (decreasing numbers of electrons in atoms). (2)

b Pentane, butane, propane (decreasing numbers of electrons). (2)

c Sodium bromide (ionic), hydrogen fluoride (H-bonded), hydrogen chloride (dipole–dipole). (2)

d Hydrazine (H-bonded), disilane, diborane (number of electrons decreases). (2)

e 4-hydroxybenzoic acid (many H-bonds), benzoic acid (fewer H-bonds), benzene (only van der Waals forces). (2)

Total 10 marks

9.7

a Water forms average of 2 hydrogen bonds per molecule. (2)

b Greater van der Waals forces. (2)

c Hydrogen bonding in ethanol, not in thioethanol. (2)

d Hydrogen bonds in water, van der Waals forces in cyclohexane would not be overcome by intermolecular forces between the two. (2)

e In the ice structure the water molecules are held in an open arrangement with 'holes', in liquid water these holes are less in evidence. (2)

Total 10 marks

Examination questions

9.8

a Water: hydrogen bonding.
Propanone: dipole–dipole.
Pentane: van der Waals. (3)

b Hydrogen bonding > dipole–dipole > van der Waals. (2)

Decreases in enthalpy of vaporization and boiling point correspond to decrease in energy needed for bond breaking. (2)

c **i** Water and pentane. (1)
ii Water–water attractions greater than pentane–water. (2)

d Pentane–propanone: endothermic.
Propanone–water: endothermic or exothermic acceptable.
Endothermic (exothermic): stronger (weaker) bonds being broken than being formed.
Answer must have matching reason. (2)

Total 12 marks

9.9

a **i** No; **ii** Yes; **iii** Yes; **iv** Yes. (2)

b Mpt, bpt abnormally high with hydrogen bonding compared to normal Group trend. (2)

c Any two: mpt/bpt/density/surface tension/ice structure (but not a solvent property). (2)

d Easier to break hydrogen bonded structure than 3-D ionic structure. (2)

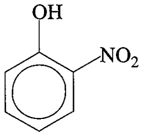
Total 8 marks

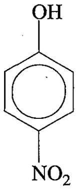
9.10

a Increasing number of electrons/surface area causing increasing van der Waals forces. (2)

b Because of its strong hydrogen bonds (relative to size). (1)

c **i**





correct groups (1)

correct positions (2)

ii 4-nitrophenol forms hydrogen bonds between molecules (forms dimers). (1)
2-nitrophenol forms hydrogen bonds within molecules. (1)
iii 4-nitrophenol forms hydrogen bonds from water to both groups. (2)

Total 10 marks

9.11

a Three sets of state symbols (s, g, aq). (3)

b **i** Smaller the ions the greater the lattice energy. (2)
ii Larger the change the greater the lattice energy. (2)

c **i** Copper(II) ion smaller than calcium ion, charge density is greater. (2)
ii Iron(III) ion has greater charge than copper(II) ion. (2)

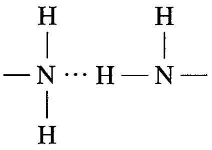
d Propanone is polar so attracted to ions, cyclohexane is non-polar and therefore not attracted. (3)

Total 14 marks

9.12

a **i** 1-aminobutane (1)

ii



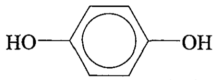
$$-\underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle H}{|}}{N}}\cdots H-\overset{\overset{\textstyle H}{|}}{N}-$$

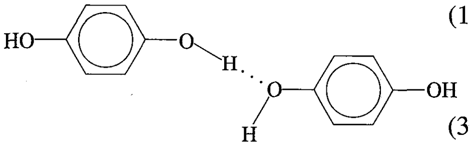
(2)

b Butanone is polar and has strong dipole–dipole attractions; pentane is non-polar and has only weak van der Waals forces. (3)

Total 6 marks

9.13

a **i**  (1)



ii O — H ··· O 180°
H — O — H 109°
H — O — C 109 to 95° (3)

iii Each water molecule has 2 lone pairs and 2 hydrogen atoms so can form 2 hydrogen bonds per molecule, making rings and cages. (2)

iv Same pattern as water with lone pairs, hydrogen atoms suitable for hydrogen bonding at both ends of the molecules. (1)

b **i** van der Waals forces. (1)

ii Only two electrons so van der Waals forces too weak; or atom so small it can escape from the cage. (2)

Total 10 marks

9.14

Mark by impression

Strong forces of attraction between the ions and solvent should be described with examples (and probably diagrams). (5)

Data:

Substance	**Enthalpy change of formation of solid** /kJ mol^{-1}	**Enthalpy change formation of solution** /kJ mol^{-1}
LiF	–616.0	(–278.5) + (–332.6) = –611.1
NaF	–573.6	(–240.1) + (–332.6) = –572.7
KF	–567.3	(–252.4) + (–332.6) = –585.0
RbF	–557.7	(–251.2) + (–332.6) = –583.8
CsF	–553.5	(–258.3) + (–332.6) = –590.9
		(3)

Calculated enthalpies of solution:

LiF	+616.0 –611.1 = +4.9
NaF	+573.6 –572.7 = +0.9
KF	+567.3 –585.0 = –17.7
RbF	+557.7 –583.8 = –26.1
CsF	+553.5 –590.9 = –37.4
	(3)

Comments on trends in data and calculated enthalpies: solubility is related to a 'trade-off' between lattice energy and enthalpy of hydration of cation, linked to increasing cation size. (4)

Total 15 marks

9.15

Mark by impression

The general principle should be established that for a substance to be soluble, the new solute–solvent interactions should outweigh the previously existing solute–solute and solvent–solvent interactions. Discussion of individual examples should examine the presence/absence/extent of ion–dipole interaction, hydrogen bonding, etc.

Total 15 marks

9.16

Mark by impression

Maximum of 9 for one aspect.

Total 15 marks

9.17

Mark by impression

Answers need to demonstrate skills of selection, collation and synthesis into succinct descriptions.

Selection of relevant information (3)
Linking information to basic information about bonding and structure (3)
Reasonable development of ideas (3)
Sound and full discussion of each substance. (6)

Total 15 marks

TOPIC 10

Entropy

Introduction

The concept of entropy is an important part of the Nuffield A-level chemistry course. Entropy helps us 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 11 and 13. 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 balance between ΔS_{system} and $\Delta S_{\text{surroundings}}$.

Teachers who wish to take the discussion further could consult a book such as P.W. Atkins *The second law*, Scientific American Books, 1984.

Content

	Timing	*Students' book*
10.1	3 hours	Pages 273–279
10.2	3 hours	Pages 279–284
Total about 1 week		

10.1 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.

10.2 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 $\Delta S_{\text{surroundings}}$.

10.1 How does chance operate in chemistry?

Timing About 3 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 quantization 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 *Mathematical comment* 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).

Translational entropy	156 J mol^{-1} K^{-1}
Rotational entropy	54 J mol^{-1} K^{-1}
Vibrational entropy	10 J mol^{-1} K^{-1}
Total entropy	220 J mol^{-1} 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 quantization of vibrational energy in iodine molecules.

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
Ceramic fibre
Access to:
Fume cupboard

Hazards

Iodine vapour is corrosive and harmful to skin and eyes so this experiment should be done in a fume cupboard. When students are observing the effect they should wear eye protection.

Procedure

The test-tube containing the iodine should be clean and loosely plugged to minimize 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 vaporizes.

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.

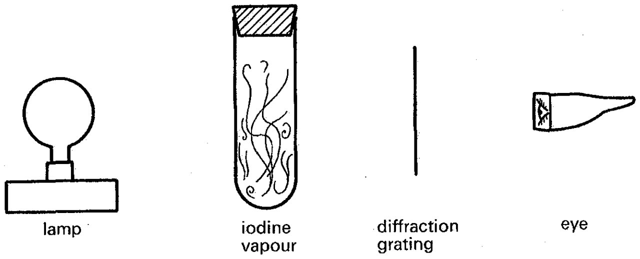


Figure 10.1 Arrangement of the apparatus for the optional experiment.

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 quantized vibrations of iodine molecules. Students should not be allowed to get the impression that the absorption is responsible for the colour of the iodine.

Experiment 10.1 Chance in chemical reactions

Each group of students will need:
Eye protection
Test-tubes and rack
Test-tube holder
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
Ammonium chloride, 3 g plus 1 g
Ammonium nitrate, 5 g
Barium hydroxide, $Ba(OH)_2{\cdot}8H_2O$, 3 g HARMFUL
Ethanoic acid, pure (glacial acetic acid), 5 cm^3 CORROSIVE
Lime water
Magnesium ribbon, 5 cm length
Sodium nitrite, 3 g OXIDIZING, TOXIC
Zinc carbonate
Weighing boats
Balance, to weigh to ±0.1 g

Hazards

Ammonium nitrate should not be heated or ground up since it is explosive.
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).

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
$$\underset{\text{ordered}}{NH_4^+\,NO_3^-(s)} + \underset{\text{disordered}}{aq} \rightarrow \underset{\text{disordered}}{NH_4^+(aq)} + \underset{\text{disordered}}{NO_3^-(aq)}$$

The reaction is endothermic and spontaneous.

2
$$\underset{\text{disordered}}{2CH_3CO_2H(l)} + \underset{\text{ordered}}{(NH_4^+)_2CO_3^{2-}(s)} \rightarrow \underset{\text{disordered}}{2CH_3CO_2^-NH_4^+(aq)} + \underset{\text{very disordered}}{CO_2(g)} + \underset{\text{disordered}}{H_2O(l)}$$

The reaction is endothermic and spontaneous.

3 $\underset{\text{ordered}}{2Mg(s)} + \underset{\text{very disordered}}{O_2(g)} \rightarrow \underset{\text{ordered}}{2MgO(s)}$

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 10.2.

4 $\underset{\text{ordered}}{NH_4Cl(s)} + \underset{\text{ordered}}{NaNO_2(s)} \xrightarrow{aq} \underset{\text{disordered}}{NaCl(aq)} + \underset{\text{disordered}}{2H_2O(l)} + \underset{\text{very disordered}}{N_2(g)}$

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 endothermic.

5 $\underset{\text{ordered}}{Ba(OH)_2(s)} + \underset{\text{ordered}}{2NH_4Cl(s)} \rightarrow \underset{\text{ordered}}{BaCl_2{\cdot}2H_2O(s)} + \underset{\text{very disordered}}{2NH_3(g)}$

This is an endothermic reaction which occurs spontaneously. The entropy change of this reaction is calculated in 10.2 and the equation has been written to match the available data.

6 $\underset{\text{ordered}}{ZnCO_3(s)} \rightarrow \underset{\text{ordered}}{ZnO(s)} + \underset{\text{very disordered}}{CO_2(g)}$

This reaction is endothermic and not spontaneous. The entropy change of this reaction is calculated in 10.2 and 11.8.

Study Task

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**, **4** 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**, **4** and **5**, a gas is released and in reaction **1** a solution is formed.

A similar 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 so important here, as 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 and
- 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 10.1 can now be discussed in terms of entropy changes. Students should be able to recognize 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.

10.2 Measuring entropy

Timing About 3 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 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 vaporizing can be seen in figure 10.10.

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

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{reversible}}}{T}$$

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

$$S_{\mathrm{T}}^{\ominus} = \int_0^T \frac{C_p}{T}\mathrm{d}T$$

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.

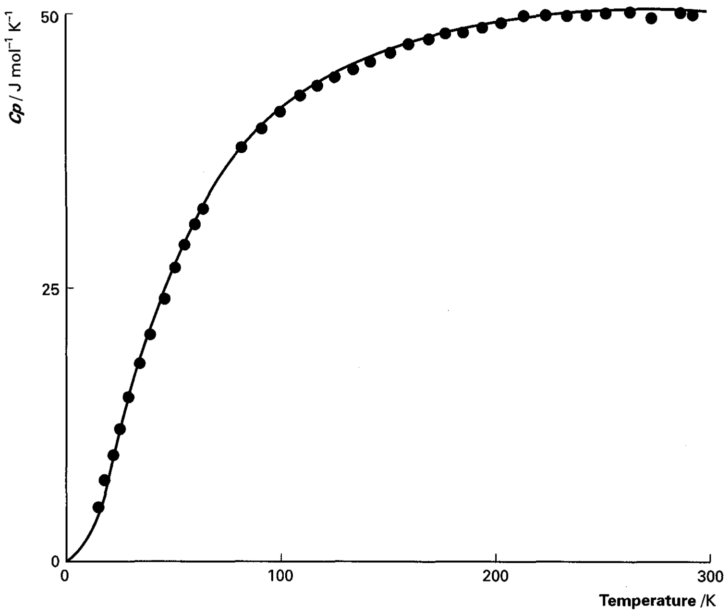


Figure 10.2 Graph of C_p against *T* for silver chloride.

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.

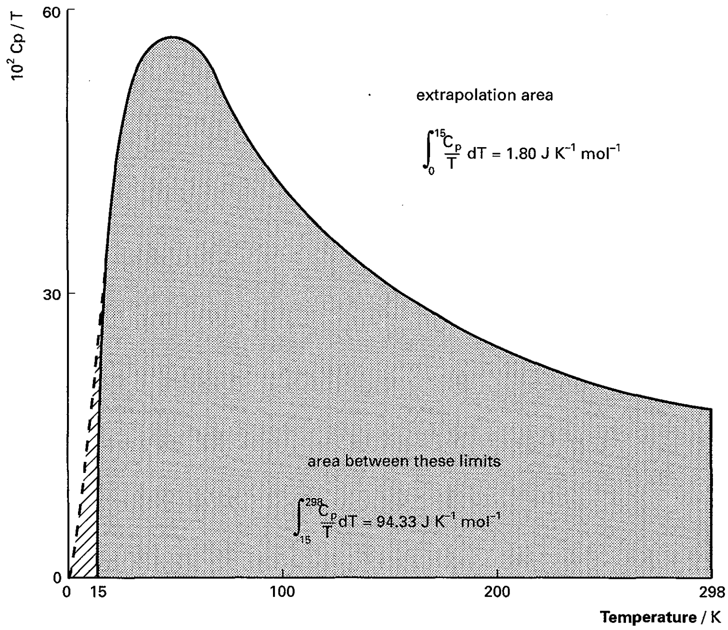


Figure 10.3 Graph of $\frac{C_p}{T}$ against *T* for silver chloride.

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 TO THE QUESTIONS

1 Students are asked to calculate the entropy change for the reaction

$Ba(OH)_2(s) + 2NH_4Cl(s) \rightarrow BaCl_2{\cdot}2H_2O(s) + 2NH_3(g)$

The calculation is set out below in a form that can be photocopied for use by students.

You should now be able to calculate the entropy change at 298 K for another reaction you carried out in experiment 10.1.

$2NH_4Cl(s) + Ba(OH)_2(s) \rightarrow BaCl_2{\cdot}\,2H_2O(s) + 2NH_3(g)$

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

$S^{\ominus}[NH_4Cl(s)] = +94.6\ \text{J mol}^{-1}\ \text{K}^{-1}$
$S^{\ominus}[Ba(OH)_2(s)] = +99.7\ \text{J mol}^{-1}\ \text{K}^{-1}$
$S^{\ominus}[BaCl_2{\cdot}2H_2O(s)] = +202.9\ \text{J mol}^{-1}\ \text{K}^{-1}$
$S^{\ominus}[NH_3(g)] = +192.3\ \text{J mol}^{-1}\ \text{K}^{-1}$
$\Delta H_f^{\ominus}[NH_4Cl(s)] = -314.4\ \text{kJ mol}^{-1}$
$\Delta H_f^{\ominus}[Ba(OH)_2(s)] = -944.7\ \text{kJ mol}^{-1}$
$\Delta H_f^{\ominus}[BaCl_2{\cdot}2H_2O(s)] = -1460.1\ \text{kJ mol}^{-1}$
$\Delta H_f^{\ominus}[NH_3(g)] = -46.1\ \text{kJ mol}^{-1}$

You then have to work out $\Delta S^{\ominus}_{\text{system}}$ for the reaction using an energy cycle

$$\Delta S^{\ominus}_{\text{system}} = \Delta S^{\ominus}_{\text{products}} - \Delta S^{\ominus}_{\text{reactants}}$$
$$= +587.5 - (+288.9)$$

therefore $\Delta S^{\ominus}_{\text{system}} = +298.6\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta H^{\ominus}_{\text{reaction}}$ is calculated using a similar energy cycle

$$\Delta H^{\ominus}_{\text{reaction}} = \Delta H^{\ominus}_{\text{products}} - \Delta H^{\ominus}_{\text{reactants}}$$
$$= -1552.3 - (-1573.5)$$

therefore $\Delta H^{\ominus}_{\text{reaction}} = +21.2\ \text{kJ mol}^{-1}$

and from $\Delta H^{\ominus}_{\text{reaction}}$ you can calculate

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H^{\ominus}_{\text{reaction}}}{T} = -(+21.2 \times 1000 \div 298)\ \text{J mol}^{-1}\ \text{K}^{-1}$$
$$= -71.1\ \text{J mol}^{-1}\ \text{K}^{-1}$$

Finally you obtain a value for ΔS_{total} by using the relationship

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

with the values you have already calculated

$\Delta S_{\text{system}} = +298.6\ \text{J mol}^{-1}\ \text{K}^{-1}$
$\Delta S_{\text{surroundings}} = -71.1\ \text{J mol}^{-1}\ \text{K}^{-1}$

therefore $\Delta S_{\text{total}} = +\ 298.6 - 71.1\ \text{J mol}^{-1}\ \text{K}^{-1}$
$= +227.5\ \text{J mol}^{-1}\ \text{K}^{-1}$

and the reaction will go spontaneously at 298 K.

The experiment you did matches this theoretical prediction. We have 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 Students are asked to calculate the entropy change for the decomposition of zinc carbonate at 298 K. The calculation is set out below in a form that can be photocopied for use by students.

As an example we will consider the decomposition of zinc carbonate, which you looked at in experiment 10.1:

$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

The standard entropy values at 298 K are

$S^\ominus[ZnCO_3(s)] = +82.4 \text{ J mol}^{-1} \text{ K}^{-1}$

$S^\ominus[ZnO(s)] = +43.6 \text{ J mol}^{-1} \text{ K}^{-1}$

$S^\ominus[CO_2(g)] = +213.6 \text{ J mol}^{-1} \text{ K}^{-1}$

so $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

$+82.4 \quad +43.6 \quad +213.6$

and $\Delta S^\ominus_{system} = \Delta S^\ominus_{product} - \Delta S^\ominus_{reactants}$

therefore $\Delta S^\ominus_{system} = +257.2 - 82.4$

$= +174.8 \text{ J mol}^{-1} \text{ K}^{-1}$

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

$\Delta H_f^\ominus[ZnCO_3] = -812.8 \text{ kJ mol}^{-1}$

$\Delta H_f^\ominus[ZnO] = -348.3 \text{ kJ mol}^{-1}$

$\Delta H_f^\ominus[CO_2] = -393.5 \text{ kJ mol}^{-1}$

so $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

$-812.8 \quad -348.3 \quad -393.5$

and $\Delta H^\ominus_{reaction} = \Delta H^\ominus_{products} - \Delta H^\ominus_{reactant}$

therefore $\Delta H^\ominus_{reaction} = -348.3 - 393.5 - (-812.8)$

$= +71.0 \text{ kJ mol}^{-1}$

and $\Delta S_{surroundings} = \dfrac{-\Delta H^\ominus_{reaction}}{T} = -(+71.0 \times 1000 \div 298)$

$= -238 \text{ J mol}^{-1} \text{ K}^{-1}$

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

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

with the values we have already calculated

$\Delta S_{total} = +174.8 - 238$

$= -63 \text{ J mol}^{-1} \text{ K}^{-1}$

So our 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 we next consider entropy in Topic 11.

3 In Topic 1 students studied the thermal decomposition of iron(II) sulphate and in Topic 4 they calculated the standard enthalpy of reaction for:

$2FeSO_4{\cdot}7H_2O(s) \rightarrow Fe_2O_3(s) + SO_2(g) + SO_3(l) + 14H_2O(l)$

$\Delta H^\ominus_{reaction} = +194.8 \text{ kJ mol}^{-1}$

Here they are asked which entropy values are mainly responsible for this reaction being spontaneous when heated and what are the differences between the molecules that might account for this entropy effect.

The *standard* entropy values from the *Book of data* are:

$S^{\ominus}[\mathrm{FeSO_4.7H_2O(s)}] = +409.2\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$S^{\ominus}[\mathrm{Fe_2O_3(s)}] = +87.4\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$S^{\ominus}[\mathrm{SO_2(g)}] = +248.1\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$S^{\ominus}[\mathrm{SO_3(l)}] = +95.6\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$S^{\ominus}[\mathrm{H_2O(l)}] = +69.9\ \mathrm{J\ mol^{-1}\ K^{-1}}$

Using the relationship

$$\Delta S_{\mathrm{total}} = \Delta S_{\mathrm{system}} + \Delta S_{\mathrm{surroundings}}$$

students will find

$$\begin{aligned}\Delta S_{\mathrm{total}} &= +591.3 - 653.7\\ &= -62.4\ \mathrm{J\ mol^{-1}\ K^{-1}}\end{aligned}$$

If students notice the entropy value

$S^{\ominus}[\mathrm{H_2O(g)}] = +188.7\ \mathrm{J\ mol^{-1}\ K^{-1}}$

and use it to calculate $\Delta S_{\mathrm{total}}$ the answer becomes $+1600\ \mathrm{J\ mol^{-1}\ K^{-1}}$. So 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.

Summary

The Topic concludes with a table that summarizes what students need to remember about the relative effect of the different entropy changes:

$\Delta S_{\mathrm{surroundings}}$	$\Delta S_{\mathrm{system}}$	$\Delta S_{\mathrm{total}}$
+	+	+
+	–	probably +
–	+	probably –
–	–	–

So $\Delta S_{\mathrm{surroundings}}$ is the most important factor in determining whether a reaction will 'go' or not. This is why so many reactions that 'go' are exothermic, and endothermic reactions that 'go' are rare.

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

10.1

From the *Book of data:*

a $S^{\ominus}[\mathrm{C\ (graphite)}] = 5.7\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$S^{\ominus}[\tfrac{1}{2}\mathrm{O_2(g)}] = 102.5$

$S^{\ominus}[\mathrm{CO_2(g)}] = 213.6$

therefore $\Delta S^{\ominus}_{\mathrm{reaction}} = 213.6 - (2 \times 102.5) - 5.7$

$= +2.9\ \mathrm{J\ mol^{-1}\ K^{-1}}$ (3)

b $\Delta H_f^{\ominus}[CO_2(g)] = -393\ \mathrm{kJ\ mol^{-1}}$
$\Delta S^{\ominus}_{surroundings} = -(-393\ 500/298)$
$= 1320.5\ \mathrm{J\ mol^{-1}\ K^{-1}}$ (3)
c and $\Delta S^{\ominus}_{total} = +2.9 + 1320.5$
$= +1323\ \mathrm{J\ mol^{-1}\ K^{-1}}$ (2)
d Yes (1)
Total 8 marks

10.2

All $\mathrm{J\ mol^{-1}\ K^{-1}}$ to 3 SF
a $-(-234 \times 1000/298) = +785$ (1)
b $-(-239 \times 3.356) = +802$ (1)
c $-(+176 \times 3.356) = -591$ (1)
d $-(-602 \times 3.356) = +2020$ (1)
e $-(-20.6 \times 3.356) = +69.1$ (1)
f $-(-810 \times 3.356) = +2720$ (1)
g $-(-411 \times 3.356) = +1380$ (1)
Total 7 marks

10.3

All $\mathrm{J\ mol^{-1}\ K^{-1}}$ to 3 SF
a $S^{\ominus}[SO_2(g)] = +248.1$
$S^{\ominus}[H_2S(g)] = +205.7$
$S^{\ominus}[S(s)] = +31.8$ (monoclinic 32.6)
$S^{\ominus}[H_2O(l)] = +69.9$ $\Delta S^{\ominus}_{system} = -424$ (2)
b $S^{\ominus}[N_2O(g)] = +219.7$
$S^{\ominus}[Cu(s)] = +33.2$
$S^{\ominus}[CuO(s)] = +42.6$
$S^{\ominus}[\frac{1}{2}N_2(g)] = +95.8$ $\Delta S^{\ominus}_{system} = -18.7$ (2)
c $S^{\ominus}[NH_4Cl(s)] = +94.6$
$S^{\ominus}[NH_3(g)] = +192.3$
$S^{\ominus}[HCl(g)] = +186.8$ $\Delta S^{\ominus}_{system} = +285$ (2)
d $S^{\ominus}[Mg(s)] = +32.7$
$S^{\ominus}[\frac{1}{2}O_2(g)] = +102.5$
$S^{\ominus}[MgO(s)] = +26.9$ $\Delta S^{\ominus}_{system} = -108$ (2)
e $S^{\ominus}[\frac{1}{2}H_2(g)] = +65.3$
$S^{\ominus}[S(s)] = +31.8$
$S^{\ominus}[H_2S(g)] = +205.7$ $\Delta S^{\ominus}_{system} = +43.3$ (2)
f $S^{\ominus}[CO_2(g)] = +213.6$
$S^{\ominus}[C(graphite)] = +5.7$
$S^{\ominus}[Mg(s)] = +32.7$ $\Delta S^{\ominus}_{system} = -220$ (2)
$S^{\ominus}[MgO(s)] = +26.9$
g $S^{\ominus}[Na(s)] = +51.2$
$S^{\ominus}[\frac{1}{2}Cl_2(g)] = +82.5$
$S^{\ominus}[NaCl(s)] = +72.1$ $\Delta S^{\ominus}_{system} = -61.6$ (2)
Total 14 marks

10.4

All $\mathrm{J\ mol^{-1}\ K^{-1}}$, to 3 SF,
a +361 (1)
b +783 (1)

c −306 (1)

d +1910 (1)

e +112 (1)

f +2500 (2 SF) (1)

g +1320 (1)

b All except **c.** (1)

Total 8 marks

10.5

a None. (1)

b $\Delta S^{\ominus}_{\text{total}}$ for $2Cu(s) + O_2(g) \rightarrow CuO(s)$ (1)

c Same as **c.** (1)

Total 3 marks

Examination questions

10.6

a Moles of $NiSO_4 = \frac{100}{1000} \times 0.200 = 0.020$ mol (1)

b Mass of Zn = 0.022 × 65.4 = 1.44 g (1)

c Enthalpy change $= \frac{1700}{0.02} = -85\,000 \text{ J mol}^{-1}$ (1)

d i $\Delta S^{\ominus}_{\text{surroundings}} = -\left(\frac{-85\,000}{298}\right) = +285 \text{ J mol}^{-1} \text{ K}^{-1}$ (1)

ii $\Delta S^{\ominus}_{\text{system}} = S^{\ominus}[\text{Ni}] + S^{\ominus}[\text{Zn}^{2+}] - S^{\ominus}[\text{Zn}] - S^{\ominus}[\text{Ni}^{2+}]$

$= +29.9 - 112.1 - 41.6 + 128.9$

$= +5.1 \text{ J mol}^{-1} \text{ K}^{-1}$ (1)

iii No significant changes in the structure of the solids or the solution. (1)

iv $\Delta S^{\ominus}_{\text{total}} = +285 + 5.1 = +290 \text{ J mol}^{-1} \text{ K}^{-1}$ (to 3 SF)

Process is spontaneous and goes to completion. (2)

Total 8 marks

10.7

a $\Delta S^{\ominus}_{\text{surroundings}} = -\,\Delta H^{\ominus}/T = -19\,000/298 = -64 \text{ J mol}^{-1} \text{ K}^{-1}$ (to 2 SF)

method (1)
answer (1)

b $\Delta H^{\ominus}_{\text{system}} = -S^{\ominus}_{\text{product}} - S^{\ominus}_{\text{reactants}}$

$= +121.5 + 56.5 - (+95.9) = +82.1 \text{ J mol}^{-1} \text{ K}^{-1}$

method (1)
answer (1)

c Although the entropy change in the surroundings is –ve, the greater +ve entropy change in the system means that the total entropy change for the process is +ve and therefore spontaneous. (2)

Total 6 marks

10.8

a i substances in standard states, values related to 298 K (2)

ii Enthalpy change of formation of 1 mole of liquid ethanol from graphite, hydrogen molecules, oxygen molecules (2)

iii $\Delta H_1 = 2\,\Delta H^{\ominus}_{\text{at}}[\text{C, graphite}] + 6\,\Delta H^{\ominus}_{\text{at}}[\tfrac{1}{2}\text{H}_2] + \Delta H^{\ominus}_{\text{at}}[\tfrac{1}{2}\text{O}_2]$
$= (2 \times 716.7) + (6 \times 218) + 249.2$
$= 2990.6\ \text{kJ mol}^{-1}$ (2)

iv By Hess's Law or similar statement (1)

v $\Delta H^{\ominus}_{\text{at}} = 2990.6 - (-277.1) = 3267.7\ \text{kJ mol}^{-1}$ (1)

b i $\Delta S^{\ominus}_{\text{surroundings}} = \dfrac{-\Delta H_{\text{at}}}{T} = \dfrac{-3267.7}{298} = -10.97\ \text{J mol}^{-1}\ \text{K}^{-1}$ (2)

ii Formation of a large number of atoms from one large molecule should mean $\Delta S^{\ominus}_{\text{system}}$ is positive. (2)

iii At high temperature when $\Delta S_{\text{surroundings}} < \Delta S_{\text{system}}$. (2)

Total 14 marks

10.9

a i $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^2$ (or just $4s^2\,3d^2$) (1)

ii Yes because it has an incompletely filled d sublevel or because it is a transition (or d-block) element. (1)

b i $\Delta H = 2 \times \Delta H_f[\text{CO(g)}] - \Delta H_f[\text{TiO}_2\text{(s)}]$
$= (2 \times -110) - (-940)$
$= +720\ \text{kJ mol}^{-1}$ *or* $720\,000\ \text{J mol}^{-1}\ \text{K}^{-1}$ for value (1)
for sign and units (1)

ii $\Delta S_{\text{surroundings}} = \dfrac{-(+720 \times 1000)}{2200}$
$= -327\ \text{J mol}^{-1}\ \text{K}^{-1}$ for value (1)
for sign and units (1)

iii $\Delta S_{\text{total}} = +365 - 327 = +38\ \text{J mol}^{-1}\ \text{K}^{-1}$ (1)

iv ΔS_{total} is positive therefore reaction is feasible. (1)

c CO given off which is poisonous (2)
or CO forms CO_2 adding to global warming. (1)

Total 10 marks

10.10

a i One mole undergoing complete combustion at standard conditions. (3)

ii $\text{C}_4\text{H}_{10}\text{(g)} + 6\tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)} + 5\text{H}_2\text{O(l)}$ (2)

iii Amount $= \dfrac{2500}{58.1} = 43$ mol (2)

iv Enthalpy change $= -2877 \times 43 = -124$ MJ (2)

v Heat losses, incomplete combustion, residue in cylinder. (2)

vi Propane, ethanol, wood
one advantage, one disadvantage. (3)

b i Large molecule → small molecules. (1)

ii $\Delta S_{\text{surroundings}} = \dfrac{-(-2877 \times 1000)}{298} = +9654\ \text{J mol}^{-1}\ \text{K}^{-1}$ (2)

iii ΔS_{total} is positive (1)

Total 18 marks

Topic 11

How far? Reversible reactions

Introduction

This is the first Topic in this course to deal with the principles governing equilibrium reactions, although examples of such reactions have been met on a number of previous occasions. In this Topic, the Equilibrium Law is introduced as the result of experiments, and its implications are considered for a number of equilibria, including acid–base reactions. In the final section the position of equilibrium is related to the total entropy change of a reaction.

Redox equilibria are not considered until Topic 13 but basic ideas could be introduced in this Topic if that approach is preferred.

The pH meter and its use is described in Topic 18.

Content

	Timing	*Students' book*
11.1	2 hours	Pages 290–294
11.2	3 hours	Pages 294–298
11.3	3 hours	Pages 299–303
11.4	3 hours	Pages 303–306
11.5	3 hours	Pages 307–308
11.6	3 hours	Pages 309–310
11.7	Homework	Pages 311–314
11.8	2 hours	Pages 314–318

Total about 4 weeks

11.1 Reversible reactions. Experiments and interpretation of reversible processes; characteristics of the equilibrium state.
11.2 The Equilibrium Law. Equilibrium constant, K_c, units of K_c; relative concentrations at equilibrium; measurement of an equilibrium constant by experiment.
11.3 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 ionization of water, calculation of pH from hydrogen ion concentration and *vice versa.*
11.4 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.
11.5 Acid–base titrations. Change of pH during acid–base titrations; theory of indicators.
11.6 Buffer solutions. Composition of buffer solutions; interpretation of buffer behaviour; *investigation of vinegar.*
11.7 Study Task. Acid–base reactions in living materials.
11.8 Entropy and equilibrium reactions. The effect of product concentration on entropy change, a study of the nitrogen dioxide-dinitrogen tetroxide equilibrium; relationship between entropy change and K_c; at equilibrium $\Delta S_{\text{total}} = 0$; effect of temperature and pressure on entropy change; how to make reactions go the way you want, Le Châtelier's Principle.

Objectives

1 To consider the properties which characterise the equilibrium state.
2 To consider the application of the Brønsted–Lowry theory to acid–base equilibria.
3 To develop a quantitative understanding of pH.
4 To consider entropy changes in an equilibrium reaction.

11.1 Reversible reactions

Timing

About 2 hours.

Suggested treatment

The Topic starts by asking students to review their previous knowledge of reversible reactions. This is likely to be rather scanty but will serve to set the scene for the introductory experiments.

Experiment 11.1 Reversible processes

Each group of students will need:
Test-tubes and rack
Dropping pipettes
Spatula or tweezers (for iodine)
Hydrocarbon solvent (petroleum spirit, 120–160 °C) FLAMMABLE
Iodine HARMFUL
0.1 M iodine in potassium iodide solution
0.02 M iron(III) chloride
Saturated potassium nitrate solution (with solid present)
0.02 M potassium thiocyanate
0.1 M sodium chloride
0.1 M sodium chromate(VI) HARMFUL
0.1 M sodium dichromate(VI) HARMFUL
0.1 M sodium ethanedioate (oxalate) HARMFUL
0.1 M sodium dihydrogenphosphate(V)
2 M sodium hydroxide CORROSIVE
M sulphuric acid IRRITANT

⚠ Hazards

Iodine solid burns the skin and students should be warned not to touch their crystals.

Procedure

Full instructions are given in the *Students' book*. At the end of 11.2 students are set a Study Task to write the K_c expressions and work out the units of K_c for their reactions.

The following notes may be helpful.

1 For both **a** and **b**

$$K_c = \frac{[\mathrm{I_2(hydrocarbon)}]_{eq}}{[\mathrm{I_2(aq)}]_{eq}} \quad \text{no units}$$

2 $$K_c = \frac{[\mathrm{I^-(aq)}]_{eq}[\mathrm{IO^-(aq)}]_{eq}}{[\mathrm{I_2(aq)}]_{eq}[\mathrm{OH^-(aq)}]_{eq}^2} \quad \text{units are mol}^{-1}\text{ dm}^3$$

A common mistake is to include water in the equilibrium expression; it is worthwhile stressing the difference between equilibria in aqueous solution where $[H_2O]$ is constant and equilibria such as the ester equilibrium in which $[H_2O]$ is a variable.

3 $$K_c = \frac{[\mathrm{Cr_2O_7^{2-}(aq)}]_{eq}}{[\mathrm{CrO_4^{2-}(aq)}]_{eq}^2[\mathrm{H^+(aq)}]_{eq}^2} \quad \text{units are mol}^{-3}\text{ dm}^9$$

4 $$K_c = \frac{[\mathrm{Fe(CNS)^{2+}(aq)}]_{eq}}{[\mathrm{Fe(H_2O)^{3+}(aq)}]_{eq}[\mathrm{CNS^-(aq)}]_{eq}} \quad \text{units are mol}^{-1}\text{ dm}^3$$

5 $K_c = [K^+(aq)]_{eq}\,[NO_3^-(aq)]_{eq}$ units are mol^2 dm^{-6}

Equilibrium constants are not quoted for soluble salts because the equilibrium law does not apply satisfactorily to concentrated solutions.

Using the results of the experiment, the *Students' book* then discusses what is meant by a state of equilibrium; its dynamic nature; and the expressions forward reaction and reverse reaction.

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). Stable equilibrium cannot be attained in an open system, that is, one that can exchange both matter and energy with its surroundings.
- If allowed to stand long enough systems 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. Changes of this kind are called *reversible reactions*. Equilibrium may be attained very rapidly, or very slowly. The possibility that a system may appear to be in the equilibrium state when it is, in fact, changing at a very slow rate, makes the criterion that equilibrium is approachable from either direction important.
- 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 *Students' book* does not introduce the terms intensive and extensive 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 characterized by constancy of intensive properties in a closed or isolated system.

Finally in this section students are asked to apply their new knowledge to an unfamiliar equilibrium, the hydrolysis of bismuth(III) chloride. It would be an advantage if teachers could demonstrate the equilibrium to their students.

ANSWERS TO THE QUESTIONS

1 Concentrated hydrochloric acid will redissolve the precipitate.
2 Adding more bismuth(III) chloride or more water will re-form the precipitate.
3 A faint suspension.
4 The larger the volume of water the more difficult it becomes to raise the concentration of hydrochloric acid; adding hydrogen chloride gas would be one approach.

11.2 The Equilibrium Law

Timing About 3 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 with 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.

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 12.

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 and 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* mole) in the equilibrium mixture is calculated. As the original mixture contained *b* mole ethyl ethanoate and *c* mole water, there must be *d* mole ethanoic acid, *d* mole ethanol, $(b - d)$ mole ethyl ethanoate, and $(c - d)$ mole 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 need to be well sealed (ground glass joint apparatus). Hydrogen ions from the hydrochloric acid act catalytically in enabling equilibrium to be attained in a week.

ANSWERS TO THE QUESTIONS

Students are asked to calculate K_c from data about the ester equilibrium

$CH_3CO_2C_2H_5(l) + H_2O(l) \rightleftharpoons CH_3CO_2H(l) + C_2H_5OH(l)$

Teachers are reminded that students will not have met esters before unless this Topic is being taught in parallel with Topic 12.

The calculated values for K_c, to 3 SF, are opposite. Students could be told that the experimental work was carried out in a school.

A second question introduces data on the equilibrium:

$2NO_2(\text{solvent}) \rightleftharpoons N_2O_4(\text{solvent})$

This equilibrium will be used to introduce Le Châtelier's Principle and discussed in 11.8 in the context of the entropy change of equilibrium reactions.

The calculated values for K_c are opposite.

Mixture	K_c
1	0.231
2	0.280
3	0.282
4	0.272
Mean	0.266 (to 3 SF)

Mixture	$K_c/10^4\ \text{mol}^{-1}\ \text{dm}^3$
1	9.0
2	11.0
3	8.9
4	9.5
5	9.9
Mean	9.9 (to 2 SF)

The equilibrium between hydrogen, iodine, and hydrogen iodide, all in the gas phase

The equilibrium

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

has been extensively investigated. Information about the equilibrium is provided here for teachers who wish to discuss another or an alternative equilibrium to the ester equilibrium. This section may be photocopied for use by students.

Investigating the equilibrium between hydrogen, iodine and hydrogen iodide, all in the gas phase

The equilibrium between hydrogen, iodine and hydrogen iodide is established very slowly indeed at room temperature but is attained in a day or so at higher temperatures. The method of investigation is to seal mixtures of hydrogen and iodine (or pure hydrogen iodide, so that equilibrium can be established from both directions) in glass or silica vessels. The vessels are then heated at a known temperature until equilibrium is attained. (How could this be checked?) After this, the vessels are rapidly cooled to 'freeze' the equilibrium, that is, to preserve the concentrations of reactants and products as they were at high temperature by taking advantage of the fact that any changes at low temperatures will be very slow. The contents of the vessels are then analysed.

One method of doing this is to open the tubes which initially contained hydrogen and iodine, under potassium iodide solution when the iodine and hydrogen iodide dissolve. The solution is then titrated with sodium thiosulphate solution to estimate the iodine. The resulting solution (from which the iodine has now been removed) is titrated with alkali to find the amount of hydrogen iodide present. (Why is it necessary to remove the iodine first?) The hydrogen can be estimated from the fact that conversion of 1 mole of iodine molecules to hydrogen iodide is accompanied by similar conversion of 1 mole of hydrogen molecules.

The tubes which contained hydrogen iodide initially, are opened similarly under potassium iodide solution and the iodine estimated by titration with sodium thiosulphate solution. If the initial mass of hydrogen iodide in the tube is known, the composition of the equilibrium mixture can be calculated. From the known volume of the sealed vessel, equilibrium concentrations of hydrogen, iodine, and hydrogen iodide can be calculated.

Concentrations at equilibrium for the system (temperature 425 °C)

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

a *Results obtained by heating hydrogen and iodine in sealed vessels*

$[H_2(g)]_{eq}$ /mol dm^{-3}	**$[I_2(g)]_{eq}$** /mol dm^{-3}	**$[HI(g)]_{eq}$** /mol dm^{-3}
4.56×10^{-3}	0.74×10^{-3}	13.54×10^{-3}
3.56×10^{-3}	1.25×10^{-3}	15.59×10^{-3}
2.25×10^{-3}	2.34×10^{-3}	16.85×10^{-3}

Can you find a constant numerical relationship between the equilibrium concentrations of the reactants and products? Try

$$\frac{[HI(g)]_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}} \quad \text{and} \quad \frac{[HI(g)]_{eq}^2}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$$

Which gives the better constant? Check your conclusion by using the results given in **b.** These were obtained by approaching the equilibrium from the reverse direction, that is starting from hydrogen iodide.

Investigation continued

b *Results obtained by heating hydrogen iodide in sealed vessels*

$[H_2(g)]_{eq}$ /mol dm^{-3}	$[I_2(g)]_{eq}$ /mol dm^{-3}	$[HI(g)]_{eq}$ /mol dm^{-3}
0.48×10^{-3}	0.48×10^{-3}	3.53×10^{-3}
0.50×10^{-3}	0.50×10^{-3}	3.66×10^{-3}
1.14×10^{-3}	1.14×10^{-3}	8.41×10^{-3}

Questions

1 The symbol K_c is used to represent the constant obtained. Hence

$$K_c = \frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$$

when this equilibrium is represented by

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

The equilibrium can also be represented by

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

What expression must be used to calculate K_c from this equation?
Will the values be the same as those obtained from **a** and **b**?
If not, how will the two sets of values be related?

2 Find the average value of K_c from the calculations that you have done on the results in **a** and **b**, correct to 3 significant figures. If an equilibrium mixture of hydrogen, iodine, and hydrogen iodide at 425 °C contains 0.5 mole of hydrogen molecules and 5.42 moles of hydrogen iodide molecules, how much iodine is present? Why do you not need to know the volume of the system in order to obtain an answer?

3 Why are the concentrations of hydrogen and iodine the same in each of the first two columns of **b**?

ANSWERS TO THE QUESTIONS

The results of the calculations suggested in a and b are printed below.

	$\frac{[HI(g)]_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$ /dm^3 mol^{-1}	$\frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$
a	4.01×10^3	54.3
	3.50×10^3	54.6
	3.20×10^3	53.9
b	15.3×10^{-3}	54.1
	14.6×10^{-3}	53.6
	6.47×10^{-3}	54.4

The expression

$$\frac{\left[HI(g)\right]_{eq}^{2}}{\left[H_2(g)\right]_{eq}\left[I_2(g)\right]_{eq}}$$

gives the better constant in all the cases quoted above. The relationship to the stoicheiometric equation for the reaction should be emphasised.

1 Values of K_c can be based on the equation

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

that is $K_c = \dfrac{\left[HI(g)\right]_{eq}}{\left[H_2(g)\right]_{eq}^{\frac{1}{2}}\left[I_2(g)\right]_{eq}^{\frac{1}{2}}}$

The values will be the square roots of those given above, that is about 7.3. This means that *whenever a value for an equilibrium constant is quoted the equation on which it is based must be indicated.*

2 The average value of K_c correct to 3 significant figures for the results in a and b is 54.2. If an equilibrium mixture of hydrogen, iodine, and hydrogen iodide at 698 K contains 0.5 mole of hydrogen and 5.42 moles of hydrogen iodide, the amount of iodine present can be determined from the above value of the equilibrium constant. If the total volume of the mixture is V cubic decimetres, the equilibrium expression is

$$\frac{(5.42)^2/(V)^2}{(0.5)/(V)\left(I_2(g)_{eq}\right)/(V)} = 54.2$$

and V cancels out, giving $I_2(g)_{eq} = 1.08$ mol.

3 The concentrations of hydrogen and iodine are the same in b because the hydrogen iodide was heated in a sealed vessel and its decomposition produces equimolar amounts of hydrogen and iodine.

Experiment 11.2 Measurement of an equilibrium constant K_c

Each group of students will need:
Titration apparatus
25.0 cm^3 pipette
10.0 cm^3 pipette
Conical flask, 100 cm^3, stoppered and dry
Access to:
0.10 M iron(II) sulphate (freshly made from Analar grade), 25 cm^3
0.10 M silver nitrate, 25 cm^3
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, due in part to the difficulty of maintaining a pure solution of iron(II) sulphate.

11.3 Acid–base equilibria

Timing

About 3 hours.

Suggested treatment

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 3 as an extension of the work on ionic structure. 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 ionization 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.

Experiment 11.3 What is an acid?

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
Benzoic acid
Boric acid
Ethanoic acid
Chloroethanoic acid
Dichloroethanoic acid
Trichloroethanoic acid
Phosphoric(V) acid
Sodium carbonate
Sodium ethanoate
Disodium hydrogenphosphate(V)
Sodium dihydrogenphosphate(V)
Trisodium phosphate(V)
Sodium hydrogen sulphate
Sodium sulphate
Sulphuric acid
and in addition:
M sodium carbonate
M sulphuric acid IRRITANT

2 M sodium hydroxide CORROSIVE
Indicator solutions such as
  bromophenol blue
  bromothymol blue
  methyl orange
  phenolphthalein FLAMMABLE

Hazards

All three chloroethanoic acids are corrosive and can cause severe skin burns; wear gloves when preparing the dilute solutions.

Indicator solutions are flammable when prepared in ethanolic solution.

Procedure

Full instructions are given in the *Students' book*. 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 18. The solutions should have 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	Na_2CO_3	10		
	NH_4Cl	5		
	$NaCH_3CO_2$	8		
3	CH_3CO_2H	2.9		
	CH_2ClCO_2H	2.1		
	$CHCl_2CO_2H$	1.9		
	CCl_3CO_2H	1.8		

4 Carbon dioxide is produced from sodium carbonate by ethanoic and benzoic acids but not by boric acid.

11.4 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.

Teacher demonstration

To distinguish strong and weak acids by pH measurements

The teacher will need:
pH meter and pH electrode
1.0 M, 0.1 M, 0.01 M, and 0.001 M solutions of ethanoic and hydrochloric acids
Further solutions of ethanoic acid of molarity 0.5 M, 0.2 M, 0.05 M, and 0.02 M, to enable a total of eight measurements to be made with this acid

Procedure

Measure the pH of the first set of solutions. Wash the electrodes between measurements and start from the most dilute solution to minimize the effect of contamination.

The pH of the purest available water could be measured at some convenient stage. Discussion of the deviation from the expected value of 7 can be useful.

The values obtained can be discussed in terms of dilution and possible increased ionization on dilution, as in the *Students' book.*

Now measure the pH of the second set of solutions and use the results to calculate values of K_a. For all but the highest and lowest concentrations, K_a should lie between 1.5 and 2.5×10^{-5} mol dm^{-3}, and at the extremes of the concentration range studied it should not be far outside these limits.

ANSWERS TO THE QUESTIONS

The following are acceptable answers to the questions.

Name of acid	Equilibrium equation	K_a/mol dm^{-3}
Ethanoic	$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO^-_2$	1.7×10^{-5}
Chloroethanoic	$CH_2ClCO_2H \rightleftharpoons H^+ + CH_2ClCO_2^-$	1.3×10^{-3}
Dichloroethanoic	$CHCl_2CO_2H \rightleftharpoons H^+ + CHCl_2CO_2^-$	5.0×10^{-2}
Trichloroethanoic	$CCl_3CO_2H \rightleftharpoons H^+ + CCl_3CO_2^-$	2.3×10^{-1}
Boric	$H_3BO_3 \rightleftharpoons H^+ + H_2BO^-_3$	5.8×10^{-10}
Benzoic	$C_6H_5CO_2H \rightleftharpoons H^+ + C_6H_5CO^-_2$	6.3×10^{-5}
Carbonic	$H_2O + CO_2 \rightleftharpoons H^+ + HCO^-_3$	4.5×10^{-7}

1 In order of acid strength:

Benzoic > ethanoic > carbonic > boric acid.

2 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 stabilize the anion.

3 The results from experiment 11.3 should match predictions based on the K_a values.

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 $[H^+(aq)]_{eq} \ll [HCO_2^-(aq)]_{eq}$.

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.

$$HCO_2H(aq) \rightleftharpoons HCO_2^-(aq) + H^+(aq)$$

$$K_a = \frac{[HCO_2^-(aq)]_{eq}[H^+(aq)]_{eq}}{[HCO_2H(aq)]_{eq}}$$

Neglecting the hydrogen ions which arise from ionization 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

$$[H^+(aq)]_{eq} = [HCO_2^-(aq)]_{eq}$$

and $[HCO_2H(aq)]_{eq} = 0.01 - [H^+(aq)]_{eq}$

$$\therefore \quad 1.6 \times 10^{-4} = \frac{[H^+(aq)]_{eq}^2}{10^{-2} - [H^+(aq)]_{eq}}$$

At this point, a quadratic has to be worked out:

$$[H^+(aq)]_{eq}^2 + (1.6 \times 10^{-4}[H^+(aq)]_{eq}) - (1.6 \times 10^{-4} \times 10^{-2}) = 0$$

giving a value for $[H^+(aq)]_{eq} = 1.35 \times 10^{-3}$ and pH = 2.87.

COMMENT

The general solution to a quadratic equation of the form $ax^2 + bx + c = 0$ is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Alternatively as in the *Students' book*, making the approximation that $[H^+(aq)]_{eq}$ will be very small for weak acids, we can omit the $1.6 \times 10^{-4}[H^+(aq)]_{eq}$ term and simplify the calculation to

$$[H^+(aq)]_{eq}^2 - 1.6 \times 10^{-4} \times 10^{-2} = 0$$

so that $[H^+(aq)]^2_{eq} = 1.6 \times 10^{-6}$

and $[H^+(aq)]_{eq} = 1.26 \times 10^{-3}$

from which pH = 2.9

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 TO THE QUESTION

The solution is as follows:

For 0.001 M HClO with $K_a = 3.7 \times 10^{-8}$ mol dm^{-3}

$$K_a = \frac{[H^+(aq)]^2}{0.001} = 3.7 \times 10^{-8}$$

$$[H^+(aq)]^2 = 3.7 \times 10^{-11}$$

and pH = 5.22

Experiment 11.4 Determination of K_a for a weak acid

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)
Balance, to weigh to ±0.01 g
pH meter, calibrated to ±0.1
or
Full-range Indicator
Narrow-range Indicator papers

Hazards

Ethanoic acid is corrosive and flammable; propanoic acid is corrosive.

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 2 SF and their K_a should also have no more than 2 SF.

11.5 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 11.5 The change of pH during an acid–base titration

Each group of students will need:
Burette, 50 cm^3
Pipette, 25 cm^3, and filler or second burette
Beaker, 100 cm^3
Magnetic stirrer, if possible
Access to:
pH meter
Computer
1.0 M ammonia, 40 cm^3
1.0 M ethanoic acid, 25 cm^3
1.0 M hydrochloric acid, 25 cm^3
1.0 M sodium hydroxide, 40 cm^3 IRRITANT

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 different combinations of acid and base possible, namely

- 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.

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 3 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 3–7. This is also the case in the weak acid/strong base titration but here the pH range of rapid change is approximately 7–11. 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.

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 end-point therefore means the *equivalence-point* 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 we have a means of detecting the end-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 3–7, and for phenolphthalein somewhere in the pH range 7–11.

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

$$H^+(aq) \text{ ions per } 50\ cm^3 = \frac{0.05 \times 1.0}{1000} \text{ mol}$$

$$\therefore [H^+(aq)] = \frac{0.05 \times 1.0 \times 1000}{1000 \times 50} \text{ mol dm}^{-3}$$

$$= 10^{-3} \text{ mol dm}^{-3}$$

$$\therefore \text{pH value} = 3$$

One drop after equivalence-point we have 0.05 cm^3 1.0 M $NaOH(aq)$ in excess

$$OH^-(aq) \text{ ions per } 50\ cm^3 = \frac{0.05 \times 1.0}{1000} \text{ mol}$$

$$\therefore [OH^-(aq)] = \frac{0.05 \times 1.0 \times 1000}{1000} \times 50 = 10^{-3} \text{ mol dm}^{-3}$$

but $[H^+(aq)][OH^-(aq)] = K_w = 10^{-14}$

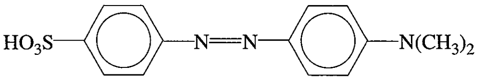
$$\therefore [H^+(aq)] = \frac{10^{-14}}{10^{-3}} = 10^{-11}$$

$$\therefore \text{pH value} = 11$$

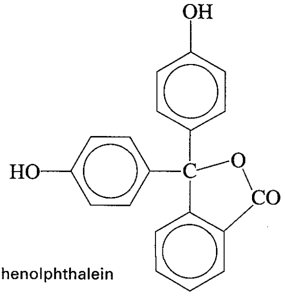
Thus there is a change in pH value of 8 units during the addition of two drops of 1.0 M $NaOH(aq)$ at the end-point of this titration.

Formulae for indicators

The formulae of two indicators are given in the student's book after Experiment 11.3 and are repeated here.



methyle orange



phenolphthalein

Enquiries about litmus should be answered by referring to an article by H.G. Andrew on the subject in *School Science Review*, **44**, *153*, page 338, 1963.

11.6 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. After the experimental study of buffer action, there is an opportunity to carry out an investigation which will test students' ability to apply what they have learnt in this Topic about acid–base chemistry. The problem suggested is the concentration of ethanoic acid in vinegar but there are many other acid–base problems which could be investigated. Students could be challenged to identify their own problem.

Experiment 11.6a Buffer solutions

Each group of students will need:
2 beakers, 100 cm^3
Spatula
Dropping pipette
Labels
Full-range Indicator, and colour chart
0.1 M ethanoic acid, 50 cm^3
0.1 M hydrochloric acid, 5 cm^3
1 M hydrochloric acid, 1 drop
Sodium ethanoate (acetate), 2 g
0.1 M sodium hydroxide, 5 cm^3
Access to:
pH meter
or
Full-range Indicator, and colour chart

Procedure

Full instructions are given in the *Students' book.* After doing the experiments students should reread the passage on the interpretation of buffer behaviour in order to interpret their results. They are likely to need help with this task.

Investigation 11.6b Vinegar

Students are asked to plan, trial and then carry out an investigation with the aim of measuring the concentration of ethanoic acid in white wine vinegar.

A good report would give a full account of the theory underlying the method adopted and consider the possibility of other acids, such as citric acid, being present at a significant concentration.

11.7 Study Task: Acid–base reactions in living materials

Timing

Homework.

Students are asked to read a passage on acid–base chemistry in animals and plants and then answer two questions to test their understanding of the text.
These are possible answers to the questions.

1 Most of the following key points should be included in a 150 word summary. The summary should be well organized.

1 Cells obtain their energy from tissue fuels in a process that eventually produces carbon dioxide.
2 Sulphuric acid is produced by oxidation of the sulphur in proteins.
3 Some amino acids from proteins are not wanted for the synthesis of new compounds.
4 Hydrochloric acid is produced in the stomach to digest food.
5 Bacteria and moulds obtain their energy by processes that produce acids such as lactic, citric and ethanoic.
6 The acids produced by bacteria and moulds accumulate outside the cells.
7 Unicellular animals lose carbon dioxide by diffusion through the cell membrane.
8 In small animals the carbon dioxide is lost via tubes which reach all the cells.
9 In larger animals circulating blood carries the carbon dioxide to the diffusion surface of the lungs or gills.
10 An enzyme releases carbon dioxide from carbonic acid.
11 The carbon dioxide is removed from lungs as expired air.
12 Strong acids such as sulphuric are secreted by the kidney into the urine.
(152 words)

2 Plants have problems with acids in their external environment rather than internal. Soils exist with a very wide pH range and only specially adapted plants can survive in soils of unusually high or low pH. The absorption of minerals from the soil may alter its pH.

The atmosphere can contain nitric acid formed by lightning and plants can be stunted or killed by sulphurous and sulphuric acids from the sulphur in fuels.

11.8 Entropy and equilibrium reactions

Timing About 2 hours.

Suggested treatment

The aim of this section is to provide a molecular basis for Le Châtelier's Principle in terms of entropy changes. Students should be aware from their work in Topic 10 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 tetroxide 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 10) can now be calculated.
6. Le Châtelier's Principle is introduced as a generalization about the direction of change in a system at equilibrium.

Experiment 11.8 The $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium

The teacher will need:
Lead nitrate, dried and powdered, 20 g HARMFUL
Sand, fine dried, 10 g
Apparatus for preparation and collection of dinitrogen tetroxide (see figure 11.1)
Glass syringe, 100 cm^3 (the plunger must be lubricated with a thin film of a light lubricating oil)

Hazards

The dinitrogen tetroxide 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.

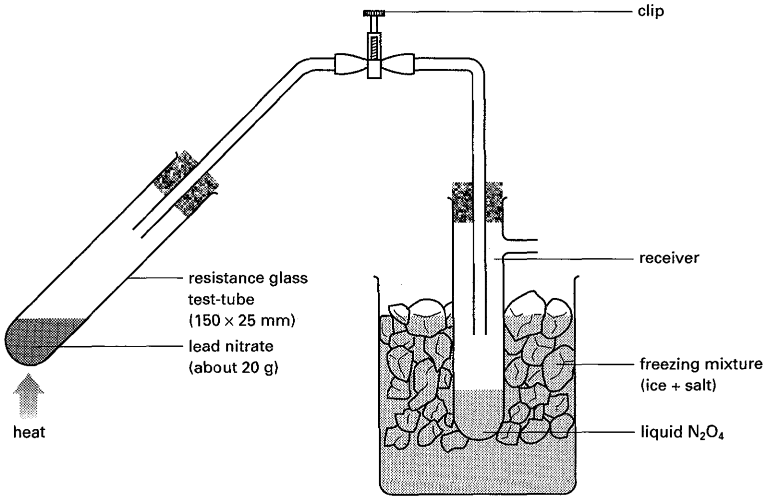


Figure 11.1 a Gas preparation

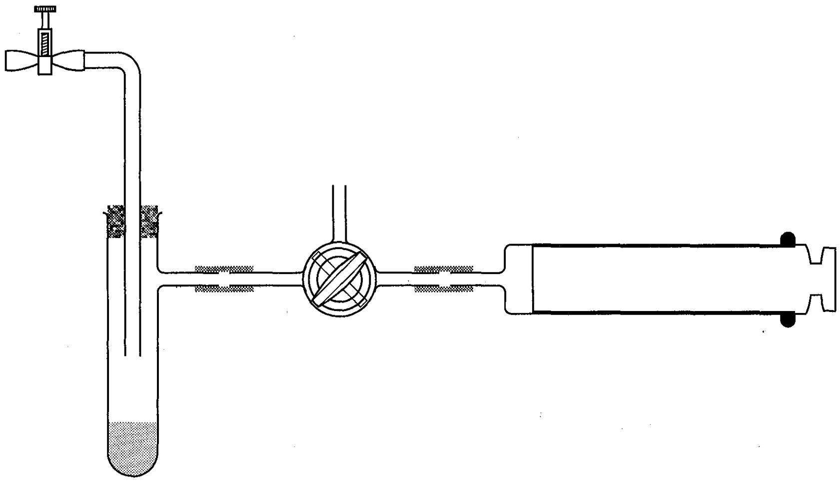


Figure 11.1b Method of filling the syringe

Procedure

Set up the apparatus shown in figure 11.1a in a fume cupboard to collect a few cm^3 of liquid dinitrogen tetroxide. 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 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 11.1b.

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.

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.

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 $\Delta S_{\text{total}} \propto \ln K_c$ 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 temperature on entropy change

This section follows on from the discussion in Topic 10 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.

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. The application of entropy ideas to the synthesis of ammonia will be developed in Topic 17.

Further examples should be given to consolidate these ideas.

How to make reactions go the way you want

The *Students' book* introduces Le Châtelier's Principle as a summary of the effects discussed.

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

11.1

11 g of ethyl ethanoate = $\frac{1}{8}$ mol (1)

18 g of water = 1 mol (1)

Ethanoic acid formed = (106 – 18) cm^3 M NaOH (1)

= 0.088 mol (1)

Ethanol formed = 0.088 mol (1)

$[CH_3CO_2C_2H_5(l)]_{eq} = 0.125 - 0.088$ (1)

$[H_2O(l)]_{eq} = 1 - 0.088$ (1)

$$K_c = \frac{[CH_3CO_2H(l)]_{eq}[C_2H_5OH(l)]_{eq}}{[CH_3CO_2C_2H_5(l)]_{eq}[H_2O(l)]_{eq}} \quad (2)$$

$$= \frac{(0.088)^2}{0.037 \times 0.912}$$

$$= 0.23 \quad (2)$$

Total 11 marks

11.2

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \quad (1)$$

$$= \frac{0.0014^2}{0.19} \text{ mol dm}^{-3} \quad (2)$$

$$= 1.03 \times 10^{-5} \text{ mol dm}^{-3} \quad (1)$$

Total 4 marks

11.3

Initial concentration of propanone = 0.05 mol dm^{-3} (1)
Initial concentration of HCN = 0.1 mol dm^{-3} (1)

Let $[\text{product}]_{eq} = x$ mol dm^{-3}

$$\frac{x}{(0.05 - x)(0.1 - x)} = 32.8 \quad (2)$$

$$x = 0.034 \text{ mol dm}^{-3} \quad (1)$$

Final volume of solution = 200 cm^3 (1)

containing $\frac{200 \times 0.034}{1000}$ mole product (1)

The molar mass of the product = 85 g mol^{-1} (1)

therefore mass of product = $\frac{200 \times 0.034 \times 85}{1000}$ g (1)

= 0.58 g (1)

Total 10 marks

11.4

The molar mass of $C_2H_5CO_2C_2H_5$ = 102 g mol^{-1} (1)

therefore $\frac{80}{102}$ g = 0.78 mol $C_2H_5CO_2C_2H_5(l)$ is present at equilibrium (1)

The molar mass of $C_2H_5CO_2H$ = 74 g mol^{-1} (1)

therefore $\frac{60}{74}$ g = 0.81 mol

so 0.81 – 0.78 = 0.03 mol of $C_2H_5CO_2H(l)$ is present at equilibrium (2)

Let *x* g be the mass of $C_2H_5OH(l)$ needed

The molar mass of C_2H_5OH = 46 g mol^{-1} (1)

therefore $\frac{x}{46} - 0.78$ mol $C_2H_5OH(l)$ is present at equilibrium (2)

$$K_c = \frac{0.78^2}{0.03(x/46 - 0.78)} = 7.5 \qquad (2)$$

x = 160 g (1)

Total 11 marks

11.5

a $[H^+(aq)]_{eq} = 2 \times 10^{-1}$ mol dm^{-3} (1)
pH = $-\lg 2 \times 10^{-1}$
pH = 0.7 (1)

Total 2 marks

b $[OH^-(aq)]_{eq} = 2 \times 10^{-1}$ mol dm^{-3} (1)
$[H^+(aq)]_{eq} = 10^{-14} \div (2 \times 10^{-1})$ (1)
pH = $-\lg 5 \times 10^{-14}$
pH = 13.30 (1)

Total 3 marks

c $[H^+(aq)]_{eq} = 1.25 \times 10^{-1}$ mol dm^{-3} (1)
pH = $-\lg 1.25 \times 10^{-1}$
pH = 0.90 (1)

Total 2 marks

d Excess of acid ≡ 50 cm^3 0.1 M in a total volume of 100 cm^3 (1)
Concentration of acid = 0.05 m (1)
$[H^+(aq)]_{eq} = 5 \times 10^{-2}$ mol dm^{-3} (1)
pH = $-\lg 5 \times 10^{-2}$
pH = 1.30 (1)

Total 4 marks

e $CH_2BrCO_2H(aq) \rightleftharpoons CH_2BrCO^-_2(aq) + H^+(aq)$ (1)

$$K_a = \frac{[CH_2BrCO_2^-(aq)]_{eq}[H^+(aq)]_{eq}}{[CH_2BrCO_2H(aq)]_{eq}} \qquad (1)$$

$= 1.35 \times 10^{-3}$

Let $[H^+(aq)]_{eq} = x$

Then $\dfrac{x^2}{0.1 - x} = 1.35 \times 10^{-3}$ (2)

If x is small $0.1 - x \approx 0.1$

$\therefore x^2 = 1.35 \times 10^{-3} \times 10^{-1}$

$= 1.35 \times 10^{-4}$

$\therefore x = 1.16 \times 10^{-2}$ mol dm^{-3} (1)

$\therefore$ pH $= -\lg 1.16 \times 10^{-2} = 1.94$ (1)

Total 6 marks

11.6

From the *Book of data:*

$K_a = 1.6 \times 10^{-4}$

Neglecting the hydrogen ions which arise from ionization of the water,

$[HCO^-_2(aq)]_{eq} = [H^+(aq)]_{eq}$

$[HCO_2H(aq)]_{eq} = 0.01 - [HCO_2^-(aq)]_{eq}$

$\therefore \dfrac{[HCO_2^-(aq)]^2_{eq}}{0.01 - [HCO_2^-(aq)]_{eq}} = 2 \times 10^{-4}$ (1)

Ignoring $[HCO_2^-(aq)]_{eq}$ with respect to 0.01:

$\dfrac{[HCO_2^-(aq)]^2_{eq}}{0.01} = 1.6 \times 10^{-4}$ (1)

$[HCO_2^-(aq)]_{eq} = 1.3 \times 10^{-3}$ mol dm^{-3} (1)

Total 3 marks

11.7

For $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$$K_a = \frac{[H^+(aq)]_{eq}[A^-(aq)]_{eq}}{[HA(aq)]_{eq}}$$

and $[A^-(aq)]_{eq} = [H^+(aq)]_{eq} = 1.3 \times 10^{-3}$ mol dm^{-3}

$\therefore [HA(aq)]_{eq} = [0.1 - (1.3 \times 10^{-3})]$ mol dm^{-3}

$\therefore K_a = \dfrac{(1.3 \times 10^{-3})^2}{0.1 - (1.3 \times 10^{-3})}$ (1)

Ignoring 1.3×10^{-3} with respect to 0.1,

$K_a = \dfrac{(1.3 \times 10^{-3})^2}{0.1}$ (1)

$= 1.7 \times 10^{-5}$ (1)

Total 3 marks

11.8

pH $= -\lg[H^+(aq)]_{eq} = 5.1$

therefore $[H^+(aq)]_{eq} = 7.94 \times 10^{-6}$ (1)

For $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$[H+(aq)]_{eq} = [A^-(aq)]_{eq} = 7.94 \times 10^{-6}$ mol dm^{-3}

$[HA(aq)]_{eq} = [0.1 - (7.94 \times 10^{-6})]$ mol dm^{-3}

therefore $K_a = \dfrac{[H^+(aq)]_{eq}[A^-(aq)]_{eq}}{[HA(aq)]_{eq}}$

$= \dfrac{(7.94 \times 10^{-6})^2}{0.1 - (7.94 \times 10^{-6})}$ (1)

Ignoring 7.94×10^{-6} with respect to 0.1

$K_a = \dfrac{(7.94 \times 10^{-6})^2}{0.1}$ (1)

$= 6.3 \times 10^{-10}$ (1)

Total 4 marks

11.9

From the *Book of data:*

$K_a = 2 \times 10^{-5}$

$[C_6H_5NH_2(aq)]_{eq} = [H^+(aq)]_{eq}$

$[C_6H_5NH_3^+(aq)]_{eq} = 0.001 - [H^+(aq)]_{eq}$

therefore $\dfrac{[H^+(aq)]^2_{eq}}{0.001 - [H^+(aq)]_{eq}} = 2 \times 10^{-5}$ (1)

Ignoring $[H^+(aq)]_{eq}$ with respect to 0.001

$[H^+(aq)]_{eq} = 1.41 \times 10^{-4}$ mol dm^{-3} (1)

pH = 3.9 (1)

Total 3 marks

11.10

From the *Book of data:*

$S^\ominus[SO_2(g)] = 248.1$ J mol^{-1} K^{-1}

$S^\ominus[\frac{1}{2}O_2(g)] = 102.5$ J mol^{-1} K^{-1} (1)

and, (quoted) $S^\ominus[SO_3(g)] = 256.1$ J mol^{-1} K^{-1}

$\Delta S^\ominus_{system}(298) = -189$ J mol^{-1} K^{-1} (1)

$\Delta S^\ominus_{surroundings}(298) = -197\,000/298 = +661$ J mol^{-1} K^{-1} (1)

therefore $\Delta S^\ominus_{total}(298) = +472$ J mol^{-1} K^{-1} (1)

Equilibrium is well to the right. (1)

At 750 K, $\Delta S^\ominus_{total} = -189 + \dfrac{197\,000}{750} = +73.6$ J mol^{-1} K^{-1} (1)

At 1250 K, $\Delta S^\ominus_{total} = -189 + \dfrac{197\,000}{1250} = -31.4$ J mol^{-1} K^{-1} (1)

$\Delta S^{\ominus}_{\text{total}} = 0$ at 1042 K (1)

Method $\left(-1894 + \frac{197\,000}{T} = 0\right)$ (1)

Total 9 marks

Examination questions

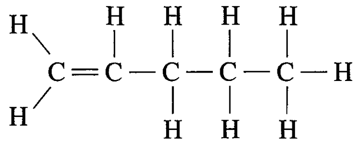
11.11

a i By volume. (1)

ii Densities of the liquid. (1)

iii Chill/dilute to freeze the equilibrium, titrate measured volumes with standard NaOH solution using weak acid – strong base indicator (phenolphthalein) (3)

b i



(1)

ii Esters. (1)

c i $K_c = \frac{[CHCl_2CO_2C_5H_{11}(l)]_{eq}}{[CHCl_2CO_2H(l)]_{eq}[C_5H_{10}(l)]_{eq}}$ (2)

ii $[CHCl_2CO_2C_5H_{11}(l)]_{eq} = 0.50 - 0.20 = 0.30$ mol (1)

iii $[C_5H_{10}(l)]_{eq} = 1.15 - 0.30 = 0.85$ mol (1)

iv $K_c = \frac{0.30/0.15}{0.20/0.15 \times 0.85/0.15} = 0.26 \text{ mol}^{-1} \text{ dm}^3$ (3)

Total 14 marks

11.12

a i To freeze the equilibrium. (1)

ii Solid iodine would appear/black solid. (1)

iii Make up to a standard volume, titrate measured volumes with standard $Na_2S_2O_3$ solution using starch indicator; indicator from blue to colourless. (3)

b i $K_c = \frac{[H_2(g)]_{eq}[I_2(g)]_{eq}}{[HI(g)]^2_{eq}}$ (2)

ii The same, 4.8×10^{-4} mol dm^{-3} (1)

iii $0.019 = \frac{(4.8 \times 10^{-4})^2}{[HI(g)]^2_{eq}}$

so $[HI(g)]_{eq} = 3.48 \times 10^{-3}$

$= 3.5 \times 10^{-3}$ mol dm^{-3} (to 2 SF) (2)

Total 10 marks

11.13

a i Acids: HCl and H_3O^+.
Bases: H_2O and Cl^-. (2)

ii An acid is a proton donor and its conjugate base accepts the proton; HCl and Cl^-. (2)

iii Strong acid is fully ionized producing protons. (2)

iv pH = 1 (1)

b **i** $K_a = \dfrac{[H_3O^+(aq)]_{eq}[CH_3CO_2^-(aq)]_{eq}}{[CH_3CO_2H(aq)]_{eq}}$ (2)

ii **I** The hydrogen ions and ethanoate ions are produced in equal numbers by the ionization of ethanoic acid; the contribution from the ionization of water is insignificant.

II The proportion of ethanoic acid molecules that have ionized has a negligible effect on the total concentration. (3)

iii $1.7 \times 10^{-5} = \dfrac{[H^+]^2}{0.1}$

$\text{pH} = 1.9$ (2)

c $\Delta S^{\ominus}_{\text{total}} = +137.5 + 51.0 = +188.5\ \text{J mol}^{-1}\ \text{K}^{-1}$

This is positive so the reaction takes place spontaneously. (2)

Total 16 marks

11.14

a **i** Donates a proton to water. (1)

ii Only partially ionized so a weak acid. (2)

iii $K_a = \dfrac{[H_3O^+(aq)]_{eq}[HCO_3^-(aq)]_{eq}}{[H_2CO_3H(aq)]_{eq}}$ (2)

assuming $[HCO_3^-]_{eq} = [H^+]_{eq}$

and $[H_2CO_3]_{eq} \approx 0.1$ (2)

$2 \times 10^{-4} = \dfrac{[H^+]^2}{0.1}$

$[H^+] = 0.0044$

$\text{pH} = 2.4$ (2)

v Buffer solution. (1)

vi Citrate ions react with most of the added hydrogen ions so pH change is minimal. (2)

b ΔS_{system} is positive because of the production of CO_2 gas. (2)

ΔS_{total} is positive because the change takes place spontaneously. (2)

Total 16 marks

TOPIC 12

Carbon compounds with acidic and basic properties

Introduction

This Topic on organic chemistry continues the interpretation of reactions in terms of nucleophilic or electrophilic reagents but also makes extensive use of concepts such as K_a and hydrogen bonding. The substances studied include the carboxylic acids, their main derivatives plus phenols and amines. The behaviour of nitriles is not described until Topic 16 when their importance in synthetic organic chemistry is emphasised.

A knowledge of the subject matter of this topic is assumed in both the Special Studies *Biochemistry* and *Food science*. It is desirable, therefore, that this topic is covered before either of these Special Studies is attempted.

Content

Timing		*Students' book*
12.1	4 hours	Pages 324–329
12.2	2 hours	Pages 329–332
12.3	6 hours	Pages 332–343
12.4	2 hours	Pages 343–347
12.5	Homework	Pages 347–350
	Homework	Pages 350–351
Total about 3 weeks		

12.1 Carboxylic acids. Factors involved in the reactivity of the carboxylic group; experiments with ethanoic acid, solubility, pH, salt and ester formation; carboxylic acids, properties involving the O — H bond; infra-red spectrum of ethanoic acid; nucleophilic reactions involving the C = O bond, esterification, reduction; the oxidation of cyclohexanone.

12.2 Carboxylic acid derivatives. Acid anhydrides; acyl chlorides; acid amides; reactions of carboxylic acid derivatives, nucleophilic reactions and comparative ease of hydrolysis, reduction.

12.3 Phenols. Reactions of the phenolic functional group, solubility in water, acidic properties, ester formation, properties of the benzene ring; comparison of phenol with ethanoic acid and ethanol; preparation of aspirin and oil of wintergreen from 2-hydroxybenzoic acid; aspirin: from herbal remedy to modern drug; disadvantages of aspirin.

12.4 Amines. Experiments with of amines, solubility, salt formation, reaction with transition metal ions; preparation of 2-ethanoylaminobenzoic acid; reactions of amines, basic properties, complex ion formation, reaction with electrophiles.

12.5 Study Task. The manufacture of citric acid.

Survey of reactions in Topic 12. Summary of the reactions of carboxylic acids and their derivatives, and amines.

Objectives

1. To apply the principles learnt in Topic 7 to the reactions of carboxylic acids, their derivatives, and amines.
2. To learn about the reactions of carboxylic acids, their derivatives, and amines.
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.

12.1 Carboxylic acids

Timing 4 hours

Suggested treatment

This is a short section, introduced in the *Students' book* by a discussion of possible reaction mechanisms, and the infra-red absorption spectrum of ethanoic acid.

The theory 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.

Experiment 12.1 The reactions of ethanoic acid

Each group of students will need:
Eye protection
Test-tubes and rack
Small beaker
Dropping pipette
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
1 M sodium carbonate
0.1 M sodium ethanoate solution
Concentrated sulphuric acid, 1 cm^3 CORROSIVE
Optional formation of esters
Benzyl alcohol IRRITANT
Pentan-2-ol
Propan-1-ol HIGHLY FLAMMABLE
Butanoic acid TOXIC; burns the eyes severely

⚠ Hazards

The esters produced are also flammable and irritant to the eyes.

The preparation of esters from methanoic acid is is best avoided as it is Corrosive and has a dangerous vapour.

Procedure

Full instructions are given in the *Students' book.* The laboratory preparation of methyl benzoate is an optional experiment. The following notes may be helpful.

1 Solubility and 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

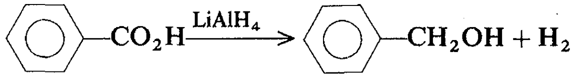
A gradual change of pH should be observed, characteristic of a weak acid forming a buffer solution with its salt. Sodium ethanoate is alkaline because of salt hydrolysis.

3 Formation of esters

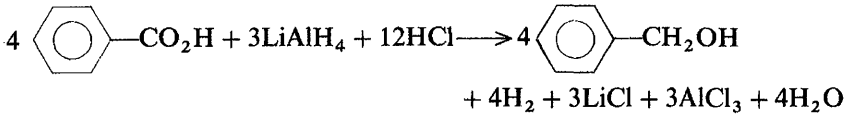
This reaction is discussed under the heading Nucleophilic reactions involving the $C=O$ bond. There is a set of optional ester preparations which can be attempted if the chemicals are available.

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.

Experiment 12.1b

Oxidation of cyclohexanone

Each group of students will need:
Eye protection
Conical flask, 500 cm^3
Beaker, 500 cm^3 and 100 cm^3
Measuring cylinders, 250 cm^3 and 10 cm^3

Apparatus for suction filtration
Access to:
Cyclohexanone, 6 cm^3 FLAMMABLE, HARMFUL
Decolorizing charcoal, small amount
Concentrated hydrochloric acid, 15 cm^3 CORROSIVE
0.4 M potassium manganate(VII), 63.2 g dm^{-3}, an almost saturated solution OXIDIZING, HARMFUL
2 M sodium hydroxide solution, 10 cm^3 CORROSIVE ·
Full-range Indicator paper

Hazards

Cyclohexanone should be dispensed in a fume cupboard as the vapour is harmful.

Procedure

There are no instructions in the *Students' book* on the procedure for obtaining the product from the reaction mixture. They are directed to table 5.6 in the *Book of data* where they will find that hexanedioic acid is a solid of melting point 153 °C; they should be able to predict that it will be only moderately soluble in water so the procedure of experiment 5.3b The preparation of potassium iodate(v) should be helpful.

The following cues could be given, one at a time, to students who get stuck:

- The product is in solution. Use suction filtration to remove the precipitate of manganese(IV) dioxide, decanting the bulk of the solution, and wash the residue to recover all the product.
- Concentrate the solution by evaporation to about 70 cm^3.
- To remove coloured impurities boil briefly with decolorizing charcoal; filter carefully.
- Acidify the solution to obtain the product as an acid instead of the sodium salt. Add concentrated hydrochloric acid until the pH is 1–2. Then add a further 10 cm^3 of concentrated acid.
- Leave the solution to cool when the product should crystallize out. Collect by suction filtration, wash with a little ice-cold water and leave to dry.
- Well done!

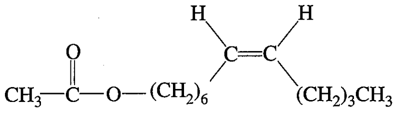
The yield from this slow oxidation can be 50% whereas when the reaction mixture is heated the yield will only be 40%.

12.2 Carboxylic acid derivatives

Timing 2 hours

Suggested treatment

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 overleaf.



cis-7-dodecenyl acetate

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 necessary.

Although the students can do the experiment with ethanamide, it is a short experiment and it is probably easier for teachers to demonstrate all the reactions, with the students noting down the results.

Experiment 12.2 Some reactions of carboxylic acid derivatives

The teacher will need:
Eye protection
Molecular model kit
3 small beakers
Dropping pipette
Ethanamide, small portion HARMFUL
Ethanoic anhydride CORROSIVE, FLAMMABLE
Ethanoyl chloride CORROSIVE, HIGHLY FLAMMABLE
Ethanol HIGHLY FLAMMABLE
8 M ammonia CORROSIVE
1 M sodium carbonate
2 M sodium hydroxide, 5 cm^3 CORROSIVE
Full-range Indicator paper

⚠ Hazards

The experiments with ethanoyl chloride and ethanoic anhydride should be demonstrated. Ethanoyl chloride and ethanoic anhydride are both corrosive and have dangerous reactions with water. In particular the teacher should use ethanoyl chloride with caution. It is volatile and forms pungent fumes in moist air, and will react violently with anything containing water, and with alcohols. Ethanamide is a category 3 carcinogen and should be used with extra care.

Procedure

Full instructions are given in the *Students' book.* The following notes may be helpful.

1 Acid anhydride

The reactions are vigorous. The product with 8 M ammonia is mainly ammonium ethanoate which vaporizes during evaporation. They are nucleophilic reactions.

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.*

3 Acid amides

Amides are hydrolysed by both acid and alkali catalysts, the alkali being more effective. The reaction with sodium hydroxide can be used to distinguish between ammonium salts which give off ammonia in the cold, amides which need to be warmed, and amines which do not react.

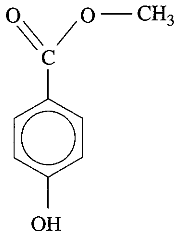
12.3 Phenols

Timing 6 hours

Suggested treatment

One aim of this section is to show students how the properties of the — OH group are modified when it occurs in different environments. The phenolic group is discussed at this stage of the course in order to make a comparison with ethanoic acid and ethanol, but it also affords an opportunity to remind students of the main features of arene electrophilic substitution.

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 delocalization 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 delocalization in phenol, accounting for 21 kJ mol^{-1}.



Methyl 4-hydroxybenzoate

Because of the corrosive nature of many phenols it is suggested that methyl 4-hydroxybenzoate is used instead, using procedures based on 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.

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 12.3a The reactions of the phenolic functional group

Each group of students will need:
Eye protection
Test-tubes and rack
Combustion spoon, or equivalent CORROSIVE
Dropping pipettes
Access to:
Bromine water, 5 cm^3
Concentrated hydrochloric acid, 2 cm^3 CORROSIVE
2 M ethanoic acid, 2 cm^3
Ethanoic anhydride, 1 cm^3 CORROSIVE, FLAMMABLE
Ethanol, 2 cm^3 HIGHLY FLAMMABLE
Full-range Indicator
Iron(III) chloride, a few crystals
Methyl 4-hydroxybenzoate
2 M nitric acid, 5 cm^3 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

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 as it reacts dangerously with water.

Procedure

Full instructions are given in the *Students' book*.
The following notes may be helpful.

1 Solubility

The phenolic compound in water should have a pH of about 6.

2 Phenolic compounds as acids

a *Action of sodium* Clean pieces of sodium should be used to avoid unwanted effects.
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 Formation of an ester

This experiment is less impressive but more pleasant to carry out than the alternative benzoylation using benzoyl chloride. In experiment 12.1a, part **3**, by contrast, an acid catalyst was used in the formation of an ester.

4 Properties of the benzene ring

a *Combustion* The phenolic compound should burn with a typical arene smoky flame.
b *Action of iron(III) chloride* The intense violet colour is due to complex ion formation.
c *Bromine* and **d** *Nitric acid* Typical electrophilic substitution reactions occur, similar to those already observed with methoxybenzene.

Experiment 12.3b 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
Beaker, 100 cm^3
Dropping pipette
Ice bath
Measuring cylinder, 5 cm^3
Stirring rod
Access to:
Ethanoic anhydride, 4 cm^3 CORROSIVE, FLAMMABLE
2-hydroxybenzoic acid (salicylic acid), 2 g
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 cylinder, 25 cm^3
Separating funnel
Access to:
Ethyl ethanoate, 15 cm^3 HIGHLY FLAMMABLE
2-hydroxybenzoic acid (salicylic acid), 9 g
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 autoignition temperature of 426 °C so 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 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 neutralization.

Reference to section 12.1 will remind students that esterification is an addition–elimination reaction 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. The opportunity can be taken to revise the chemistry of carboxylic acid derivatives and the general methods of preparing esters, including the equilibrium nature of the reaction.

A possible extension to the work on aspirin is described in the article by Gale, S.E. *et al* Copper(II) co-ordination of aspirin, *School Science Review*, **74**, *269*, pages 88-89, 1993.

Aspirin, from herbal remedy to modern drug

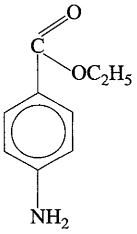
The passage on aspirin could be set as homework and used as the basis for a discussion on the use and abuse of drugs in society today. It is instructive to compare the cost of different brands of aspirin tablets based on their aspirin content.

12.4 Amines

Timing 2 hours

Suggested treatment

The teacher will need:
Molecular model kit



Ethyl 4-aminobenzoate

The main objective is a comparison of ammonia, alkylamines and arylamine. Phenylamine is not used because it is toxic and ethyl 4-aminobenzoate, benzocaine, is used instead, using procedures based on CLEAPSS Guide L195.

The diazotization reaction is studied in Topic 17 as part of a section on dyestuffs, but it could be taken now if wished.

The difference in structure between primary, secondary, and tertiary amines and the parallel alcohols (Topic 2) and halogenoalkanes (Topic 7) 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.

Experiment 12.4 The reactions of amines

Each group of students will need:
Test-tubes and rack
Dropping pipette
Access to:
2 M ammonia
Butylamine HIGHLY FLAMMABLE, HARMFUL
0.1 M copper(II) sulphate
Ethyl 4-aminobenzoate
Full-range Indicator
2 M hydrochloric acid

Optional preparation of 2-ethanoylaminobenzoic acid:
Apparatus for reflux, consisting of 50 cm^3 pear-shaped flask and Liebig condenser
Apparatus for suction filtration (100 cm^3 Buchner flask and funnel)

Measuring cylinder, 10 cm^3
Access to darkened room
2 watchglasses
2-aminobenzoic acid, 3.5 g
Ethanoic anhydride, 10 cm^3 CORROSIVE, FLAMMABLE
Methanol (chilled) TOXIC, HIGHLY FLAMMABLE

Hazards

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.

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 worth while comparing the pH of 0.1M ammonia and 0.1M butylamine. Students tend to assume that inorganic compounds are stronger acids or 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 relevent 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.

4 Preparation of 2-ethanoylaminobenzoic acid

This is an optional experiment; the crystals of the product are fluorescent.

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.

12.5 Study Task: The manufacture of citric acid

Students are asked to read a passage on the manufacture and uses of citric acid and then to answer questions to test their understanding of the text. Students who ask about the formula and structure of citric acid should be referred to figure 2.1.

These are possible answers to the questions.

1 The passage is just over 1100 words long, of which about 650 are about the manufacturing process. The students are asked to write an account in 150 words suitable for visitors to the factory, so technical terms should be avoided as much as possible.

Most of the following points should be referred to:

1 A selected strain of mould is used.
2 For the first stage the fermenter is sterilized.
3 A medium of molasses and nutrients is sterilized.
4 The medium is treated with air and some mould spores added.
5 The mould is allowed to grow for about 24 hours.
6 The mould is transferred to a large fermenter containing molasses solution.
7 The sugar is converted to citric acid over about 7 days.
8 The mould is removed by filtration.
9 Addition of lime forms an insoluble salt of the citric acid.
10 The insoluble salt is collected by filtration and washed.
11 The citric acid is redissolved by adding an acid.
12 The solution is decolorized by charcoal.
13 The solution is concentrated and citric acids crystals form on cooling.
14 The crystals are dried and sieved to produce a range of sizes.
15 The product is sampled, and analysed to ensure it is suitable for use in foods.

(144 words)

2 Sodium citrate is used in soft drinks, as a flavour enhancer; sodium citrate is used as an anticoagulant for blood; zinc citrate is added to toothpaste, to inhibit plaque formation; sodium citrate can replace phosphates in detergents.

3 Citric acid is added to soft drinks and wine as a flavour enhancer; in effervescing drinks; in the manufacture of soluble aspirin; in sweets and jams; in jams and jellies to help set them; as an antioxidant in foods; to prevent loss of vitamin C; to remove traces of metals; as a descaling agent.

Survey of reactions in Topic 12

As in Topics 2 and 7, the chart provided in the *Students' book* is intended as a base from which students can develop their own more elaborate charts.

It is suggested that a set of charts each with different information such as formulae, reagents or type of reaction, is more valuable for revision purposes than a single chart containing all the information.

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

Carboxylic acids

12.1

a 1-iodo-4-methylpentane. (1)

b Reflux with an aqueous solution of sodium hydroxide; nucleophilic substitution reaction. (2)

c Hot, concentrated, alcoholic solution of sodium hydroxide; elimination reaction. (2)

d $CH_3CH(CH_3)CH_2CH(Br)CH_3$ 2-bromo-4-methylpentane (2)
Electrophilic addition reaction (1)

e $CH_3CH(CH_3)CH_2CH_2CHO$ (1)

f PCl_3 or PCl_5 (1)

g $CH_3CH(CH_3)CH_2CH_2CO_2CH_3$ (1)

h $CH_3CH(CH_3)CH_2CH_2CH_2OH$ (1)

i $CH_3CH(CH_3)CH_2CH_2COCl$ (1)

Total 13 marks

12.2

Butane	Van der Waals forces only.	(2)
Propanal	Dipole–dipole interactions.	(2)
Propan-1-ol	Hydrogen bonding.	(2)
Ethanoic acid	Hydrogen bonding and 2 polar atoms in same molecule.	(2)

Van der Waals forces are of similar magnitude in each compound: hydrogen bond interactions are larger than dipole–dipole attractions. (2)

Total 10 marks

12.3

a A; B; C; D. (2)

b A; E; D; C; B. (2)

Total 4 marks

Amines

12.4

a **i** A; **ii** B; **iii** D; **iv** E. 1 mark each (4)

b A, B, D. (2)

c A. (1)

d E. (1)

e A, B, D (E is a reasonable suggestion). (2)

f A and B. (2)

Total 12 marks

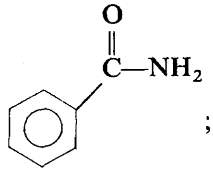
12.5

$CH_3CH_2CH_2CH_3$; $CH_3CH_2CH_2NH_2$; $CH_3CH_2CH_2OH$; 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 2 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

12.6



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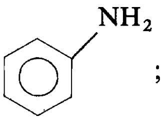
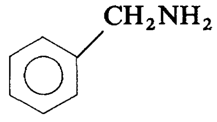


; NH_3;



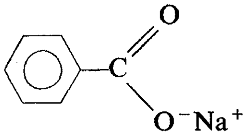
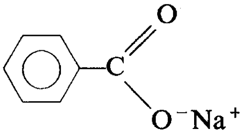
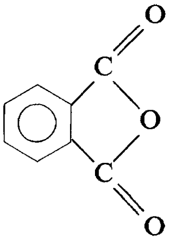
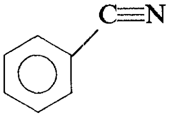
(2)

Discuss in terms of the availability of the electron lone pair for donation to protons. In the amide the lone pair is delocalized with the highly polar carbonyl group; in phenylamine it is delocalized into the ring. CH_3— or —CH_2— groups are weakly electron-releasing facilitating lone-pair donation in the strongest base. (4)

Total 6 marks

Acid derivatives

12.7

a D. (1)
b C. (1)
c B. (1)
d  (1)
e CH_3OH plus acid catalyst. (2)
f CH_3OH. (1)
g NH_3. (1)
h CH_3OH and  (2)
i B and E. (2)
j  and  (2)

Total 14 marks

12.8

Any suitable reactions (2 marks each)

Total 10 marks

12.9

Any appropriate series of reactions

Total 10 marks

Examination questions

12.10

a **i** Catalyst. (1)
ii To avoid excess acid reacting with either of the organic reagents. (1)
iii Methanol is an alcohol, methyl benzoate is an ester. (2)
iv Diagram of standard reflux apparatus. (2)
v Volatile materials would be lost, flammable vapours. (2)
b **i** To remove water soluble materials. (1)
ii To neutralize and remove acid. Invert the separating funnel and open the tap (to release CO_2). (2)
iii Anhydrous sodium sulphate, and others. (1)
iv Use apparatus for distillation with a thermometer;
collect and discard material boiling below 190 °C;
collect fraction boiling 190–210°C (or similar temperatures). (2)

c 8/122.1 mol benzoic acid should give 8/122.1 = 0.0655 mol ester
yield of ester = 4/136.1 = 0.294 mol

% yield of ester = $\frac{4}{136.1} \times \frac{122.1}{8} \times 100 = 44.8 = 45\%$ (to 2 SF) (2)

d **i** Break O — H bond in methanol and C — O bond in benzoic acid (2)

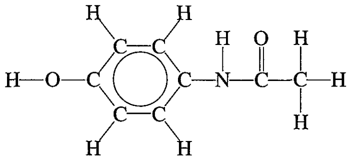
ii Use methanol with heavy isotope of oxygen and find out if it appears in the ester or the water from the reaction (or equivalent) (2)

e Sodium benzoate, benzamide, benzoyl chloride plus reagents and conditions. (3)

Total 23 marks

12.11

a **i** Delocalized electrons over the whole ring (or equivalent). (2)

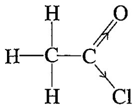
ii  (2)

b Electrophilic substitution. (2)

c Dissolve sample in solvent and spot onto a chromatographic plate with sample of 2-nitrophenol. Develop and look for spot with same R_f value as 2-nitrophenol. (3)

d **i** Reaction forms sodium 4-aminophenoxide. (2)

ii Reaction forms the phenylammonium chloride. (2)

e **i**  formula (1)

dipoles (1)

ii Lone pair of electrons on the N atom attacks the partially positively charged C in the polar molecule (2)

f Phenol is corrosive so wear gloves; hydrogen chloride/ethanoyl chloride fumes are corrosive so use a fume cupboard (4)

Total 21 marks

12.12

a **i** Substitution. (1)

ii Electrophile. (1)

iii NO_2^+ (1)

iv To control the reaction, and prevent polysubstitution. (1)

b **i** Washed with water and sodium (hydrogen) carbonate solution. (2)

ii Stood with anhydrous sodium sulphate (or similar). (1)

c Any three structural formulae showing mono, di or tri substitution in the 2-, 4-, or 6-position. (3)

d Chromatography. (1)

e **i** No change. (1)

ii Dilute nitric acid alone. (1)

Total 13 marks

12.13

Mark by impression

This is a two-stage synthesis.

Stage 1: $2CH_3CO_2H + PCl_5 \rightarrow 2CH_3COCl + POCl_3 + H_2O$

Stage 2: $CH_3COCl + C_4H_9OH \rightarrow CH_3CO_2C_4H_9 + HCl$

The data required:

	molar mass /g mol^{-1}	**density** /g cm^{-3}	**boiling point** /K
ethanoic acid	60.1	1.049	391.0
phosphorus pentachloride	208.2	–	–
ethanoyl chloride	78.5	1.104	324.0
butan-1-ol	74.1	0.810	390.3

Calculation of starting quantities:

10 g of butyl ethanoate = $\frac{10}{116}$ = 0.086 mol

Theoretical yield for Stage 2 = $\frac{0.086}{60} \times 100 = 0.143$ mol

0.143 mol butan-1-ol = $0.143 \times 74 = 10.6$ g (≈ 13 cm^3 to 2 SF)

0.143 mol ethanoyl chloride = $0.143 \times 78.5 = 11.2$ g (≈ 10 cm^3 to 2 SF)

Theoretical yield for Stage 1 = $\frac{0.143}{60} \times 100 = 0.24$

0.24 mol ethanoic acid = $0.24 \times 60.1 = 14.4$ g (≈ 14 cm^3 to 2 SF)

0.12 mol phosphorus pentachloride = $0.12 \times 208.2 = 25$ g

For Stage 1 the apparatus suggested should be suitable for the gradual addition of ethanoic acid to the required quantity of PCl_5, or *vice versa*, with due provision for safe handling. This should be followed by distillation of the product over a suitable temperature range.

For Stage 2 the apparatus suggested should be suitable for the gradual addition of (excess) butan-1-ol to the required quantity of ethanoyl chloride, or *vice versa*, with due provision for safe handling and exclusion of water vapour. The separation of the ester from the reaction mixture by distillation over a suitable temperature range, noting the small difference in boiling point between the product and butan-1-ol, should be followed by redistillation to obtain a pure product.

Some indications of levels of marking are:

3 Interprets the generalized reaction scheme correctly in terms of ethanoic acid and butan-1-ol, but only gives details of apparatus and procedure at a generalized 'mix, heat and distil' level of description; also fails to make any substantial progress in writing down the equations and calculating the quantities of reagents.

6 The reaction scheme is given as specific equations, and an attempt is made to calculate quantities, but without much success. Apparatus and procedure given in limited outline manner only, and may well be incomplete.

9 The equations are accompanied by an attempt to calculate quantities on the basis of the stoichiometric quantities, but without taking account of the 60% yield in each stage. Apparatus and procedure are basically on the right lines, but lack detail.

12 An answer, with a suitable level of detail and explanation which could be followed safely, but from which two or three important points, or a larger number of minor points, are missing or incorrect.

15 Correct and complete in respect of all the major points, with only minor errors or omissions.

Total 15 marks

TOPIC 13

Redox equilibria and electrochemical cells

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. Next, the value and use of standard Gibbs free energy changes are explained and the procedure for performing straightforward calculations is demonstrated. The relationship between standard free energy 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 then go on to the study of the transition elements, in Topic 15, putting their new-found experience to the test with confidence and understanding.

Content

	Timing	*Students' book*
13.1	4 hours	Pages 359–367
13.2	4 hours	Pages 367–374
13.3	1 hour	Pages 375–377
13.4	1 hour	Pages 377–380
13.5	1 hour	Pages 380–381
13.6	Homework	Pages 382–385
Total about 2 weeks		

Introduction. Revision of redox reactions.
13.1 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 qualitative effect of temperature and concentration on cell e.m.f.; standard electrode potentials.
13.2 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; some uses of $E^{\ominus}$ values: predicting whether reactions are likely to take place, balancing equations, calculating the e.m.f. of cells.
13.3 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.
13.4 Gibbs free energy. Total entropy change and e.m.f. of an electrochemical cell; Gibbs free energy change must be negative for a spontaneous chemical change; Gibbs free energy change and cell e.m.f; Gibbs free energy calculations using energy cycles.

13.5 Predicting whether reactions will take place: using ΔS_{total}, ΔG, E_{cell} and K_c as indicators of reaction feasibility.
13.6 Study Task. 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 solution and in redox reactions in general.
6. To demonstrate that free energy is related to the total entropy change for a reaction and be able to perform calculations involving free energy changes.
7. To demonstrate the relationship between standard free energy change, standard electrode potential and the equilibrium constant K_c, and to use these to predict the feasibility of reactions.
8. To develop an appreciation of some of the advantages and disadvantages of different types of electrochemical cell.

13.1 Metal/metal ion systems

Timing About 4 hours.

Suggested treatment

Redox systems have been studied earlier in the course, especially in Topic 5, 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 13.1a 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 0.5 g
Magnesium powder, about 0.5 g HIGHLY FLAMMABLE
Zinc powder, about 0.5 g FLAMMABLE
0.5 M copper(II) sulphate solution
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

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

Energy is evolved and there is an increase in temperature. To observe the reaction products more clearly students could filter the mixture after two 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 oxidizing agent and reducing agent are relative only. In the experiment zinc is seen to be capable of acting in both senses.
- The equation for a redox process can be split into 'half-equations' so that the electron transfer is made plain, for example:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad \text{oxidation}$$

$$2e^- + Cu^{2+}(aq) \rightarrow Cu(s) \quad \text{reduction}$$

As these processes 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 Châtelier'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:

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

shown above is *not* the same as the ionization energy of zinc:

$$Zn(g) \rightarrow Zn^{2+}(g) + 2e^-$$

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 in an electrochemical cell arises from the half-equations considered in interpreting experiment 13.1a. 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 13.1b Electrical energy from a redox reaction

Each group of students will need:
Small glass food jar (baby food or yogurt)
Cork to fit the food jar
Dialysis tubing (about 15 cm long)
Dropping pipette
1 M ammonium sulphate (to fill the food jar)
Copper foil, 10 cm × $\frac{1}{2}$ cm
1 M copper sulphate HARMFUL
Zinc foil, 10 cm × $\frac{1}{2}$ cm
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

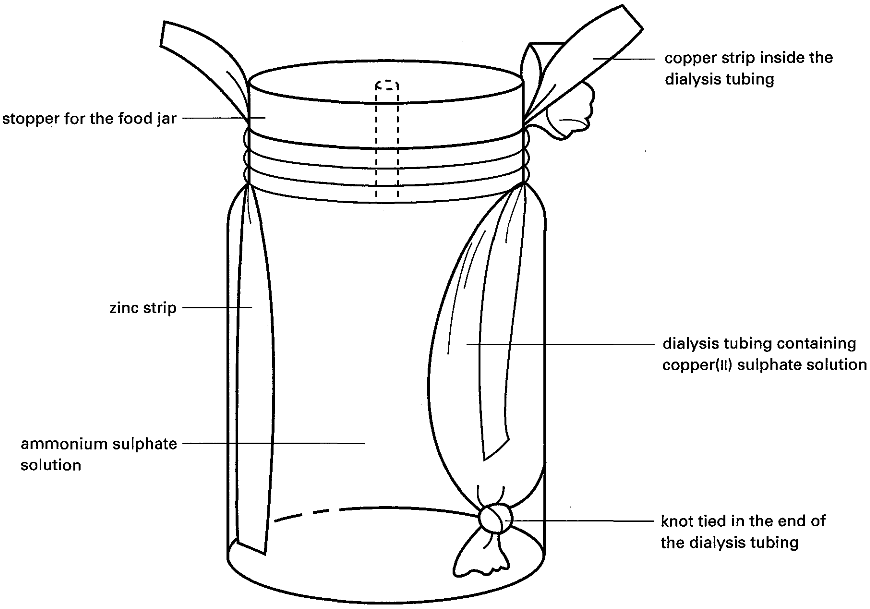


Figure 13.1 A simple cell made from a food jar.

Procedure

Some students may have made electrochemical cells in their pre-A-level courses. The dialysis tubing prevents rapid mixing of the solution and economizes 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

$$Zn(s)\,|\,Zn^{2+}(aq)\,\vdots\vdots\,Cu^{2+}(aq)\,|\,Cu(s) \quad E = +1.1\ V$$

or

$$Cu(s)\,|\,Cu^{2+}(aq)\,\vdots\vdots\,Zn^{2+}(aq)\,|\,Zn(s) \quad E = -1.1\ V$$

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 emphasizing that chemistry involves a number of arbitary 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 platinized Pt wire dipping into 1.0 M HCl(aq) in a squat-form beaker (50 or 100 cm^3)
Salt bridge cut 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 sulphate HARMFUL
1 M zinc sulphate
Zinc foil, 5 cm × 1 cm
Digital voltmeter
Connecting leads, fitted with suitable terminals, 2

Procedure

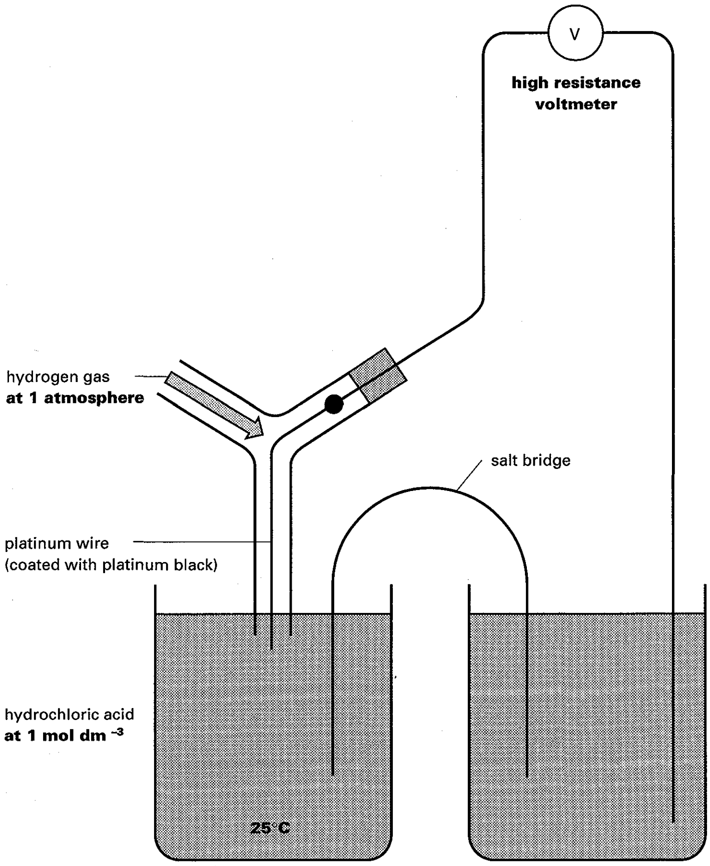


Figure 13.2 Arrangement for the hydrogen electrode.

Set up apparatus as in figure 13.2. The electrodes should consist of about 6 × 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.

The metal strips can be supported in small clamps between pieces of cork, and electrical connection made to them by leads with a crocodile clip 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 platinized 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. Note that the hydrogen electrode should be connected to the common terminal of the 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:

$$\text{Pt}[\text{H}_2(\text{g})] \mid 2\text{H}^+(\text{aq}) \;\vdots\vdots\; \text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)} \qquad E = +0.32\ \text{V}$$

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:

$$\text{Pt}[\text{H}_2(\text{g})] \mid 2\text{H}^+(\text{aq}) \;\vdots\vdots\; \text{Zn}^{2+}(\text{aq}) \mid \text{Zn(s)} \qquad E = -0.75\ \text{V}$$

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:

$\text{Zn}^{2+}(\text{aq}) \mid \text{Zn(s)}$	$2\text{H}^+(\text{aq}) \mid [\text{H}_2(\text{g})]\text{Pt}$	$\text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)}$	$\text{Ag}^+(\text{aq}) \mid \text{Ag(s)}$
–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

$Pt[H_2(g)]\ 2H^+(aq)$ ⁞⁞	Hence its position on the bench during the demonstration.

The order of oxidizing and reducing agents is important in the above chart; it is the order given in the tables of electrode potentials framed according to the IUPAC convention.

Construction of a hydrogen electrode

A number of quite simple versions of this electrode can readily be constructed. Three possible designs are shown in figure 13.3.

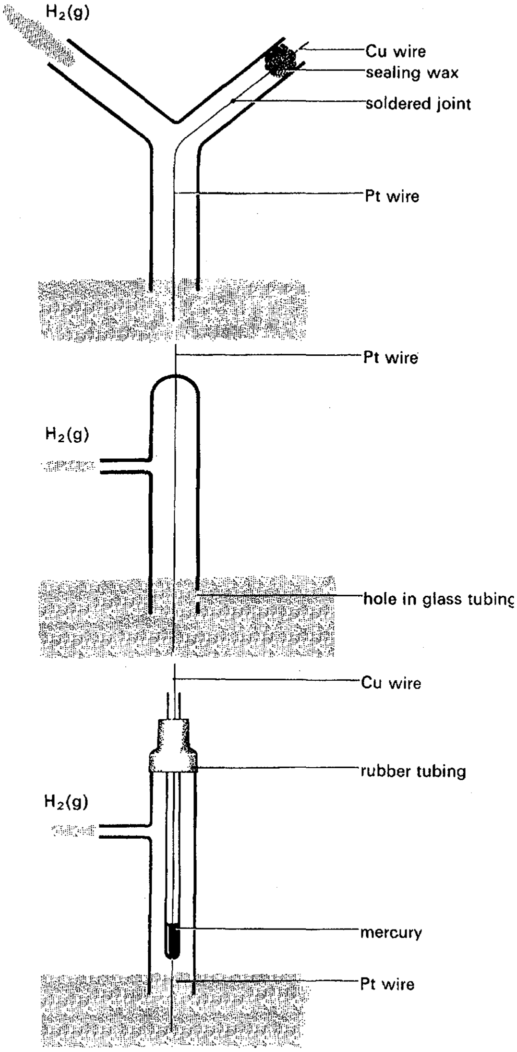


Figure 13.3 Types of hydrogen electrode.

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).

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 containing a small proportion (approximately 0.05%) of lead ethanoate, 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.

A cylinder is the most convenient supply of hydrogen gas but must be fitted with a reducing valve, in order to provide a very slow stream of gas. Alternatively, a filter flask can be used as an aspirator (see figure 13.4). 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).

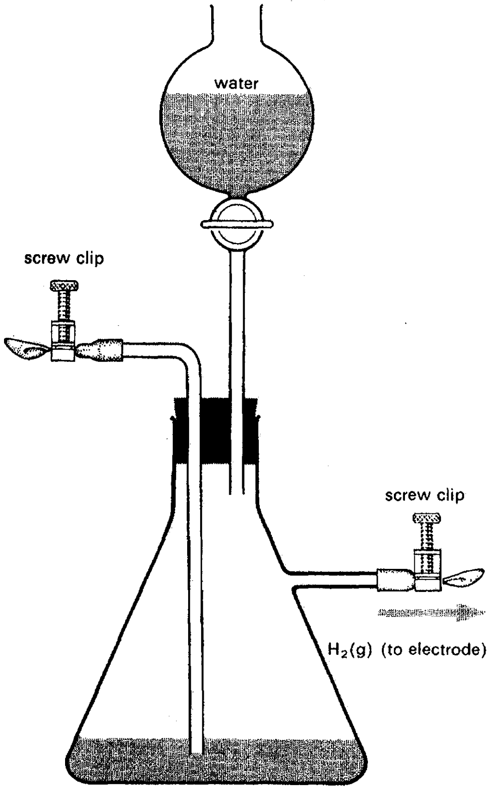


Figure 13.4 Aspirator for the hydrogen electrode.

Experiment 13.1c 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 13.1c To measure the e.m.f. of some electrochemical cells

Each group of students will need:
Copper, zinc, and magnesium half cells
Potassium nitrate salt bridges
Digital voltmeter

Connecting leads, 2 lengths
Details of the apparatus are given in the list of apparatus needed for the teacher demonstration.

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.

$Cu(s) | Cu^{2+}(aq) ⁞⁞ Zn^{2+}(aq) | Zn(s)$ $E = -1.03$ V   **(1)**

$Mg(s) | Mg^{2+}(aq) ⁞⁞ Cu^{2+}(aq) | Cu(s)$ $E = +1.75$ V   **(2)**

$Mg(s) | Mg^{2+}(aq) ⁞⁞ Zn^{2+}(aq) | Zn(s)$ $E = +0.72$ 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 TO THE QUESTIONS

Answers to the questions posed in the *Students' book* should be along the following lines.

1 Comparison of these results with the reactions in experiment 13.1a 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

$Mg(s) | Mg^{2+}(aq) ⁞⁞ Cu^{2+}(aq) | Cu(s)$ — $Cu(s) | Cu^{2+}(aq) ⁞⁞ Zn^{2+}(aq) | Zn(s)$

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.

The *Comment* suggests that students use the *Book of data* to work out the e.m.f. of the cell

$Ag(s) | Ag^{+}(aq) ⁞⁞ Cu^{2+}(aq) | Cu(s)$. For this cell $E = -0.46$ V

Students should be given plenty of opportunities 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 the + and – electrodes. The skill will be needed again in Topic 15.

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 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 platinized 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 ionization, inter-ion attraction, and 'crowding effects' in fairly concentrated solution result in the necessity of taking a greater concentration of solute to achieve a given concentration of ions. Thus to obtained 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 summarized 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 (it is an intensive property).
- $E^\ominus$ 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.

13.2 Redox equilibria extended to other systems

Timing About 4 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 summarized.

Experiment 13.2a 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 (iron 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 13.2b. The electron transfer which occurs during the reaction can be seen from the half-reactions

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad \text{reduction}$$

$$\text{and } 2I^-(aq) \rightarrow I_2(aq) + 2e^- \qquad \text{oxidation}$$

which arise from the competing equilibria

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$

$$\text{and } 2I^-(aq) \rightleftharpoons I_2(aq) + 2e^-$$

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 13.2b To measure the electrode potentials for the $Fe^{3+}(aq)/Fe^{2+}(aq)$ equilibrium and the $2I^-(aq)/I_2(aq)$ equilibrium

Each group of students will need:
Copper reference electrode, as in experiment 13.1c
Potassium nitrate salt bridges, as in experiment 13.1c
2 smooth platinum electrodes
3 beakers, 100 cm^3
Digital voltmeter, and connecting leads

Access to:
0.1 M iodine in aqueous KI, 50 cm^3
A mixture of 0.1 M iron(II) and 0.1 M iron(III) salts, 50 cm^3

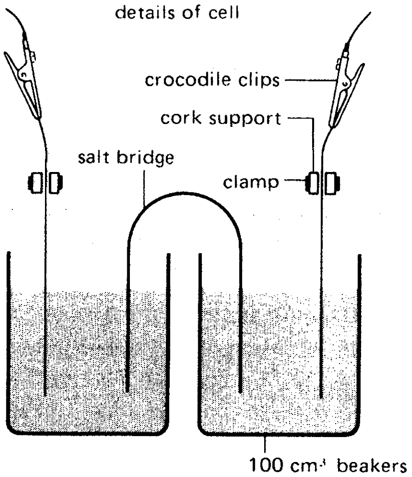


Figure 13.5 Details of the cell.

Students measure the e.m.f.s of the cells:

$$\text{Cu(s)} \mid \text{Cu}^{2+}\text{(aq)} \vdots\vdots \text{Fe}^{3+}\text{(aq)}, \text{Fe}^{2+}\text{(aq)} \mid \text{Pt}$$

$$\text{and Cu(s)} \mid \text{Cu}^{2+}\text{(aq)} \vdots\vdots \text{I}_2\text{(aq)}, 2\text{I}^-\text{(aq)} \mid \text{Pt}$$

and from the results calculate the e.m.f. of the cell

$$\text{Pt} \mid 2\text{I}^-\text{(aq)}, \text{I}_2\text{(aq)} \vdots\vdots \text{Fe}^{3+}\text{(aq)}, \text{Fe}^{2+}\text{(aq)} \mid \text{Pt}$$

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.

Students' attention should be drawn to the fact that it is necessary to have both the oxidized 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 oxidized 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 Châtelier'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 13.2b 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 oxidized form by a comma

Fe^{3+}(aq),Fe^{2+}(aq) | Pt
oxidized reduced non-reactive
form form electrode

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 oxidized or reduced forms is then introduced

[MnO_4^-(aq) + $8H^+$(aq)],[Mn^{2+}(aq) + $4H_2O$] | Pt
oxidized form reduced form non-reactive electrode

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 TO THE QUESTIONS

The cell diagrams for the questions given in the *Students' book* are:

¦¦ [$2IO_3^-$(aq) + $12H^+$(aq)], [I_2(aq) + $6H_2O$(l)] | Pt
Pt | Fe^{2+}(aq), Fe^{3+}(aq) ¦¦ Ag^+(aq) | Ag(s)

The chemists' toolkit: some uses of $E^{\ominus}$ values

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 15.

2 Balancing the equations of the predicted reactions.

This subsection instructs students how to write complete equations by balancing electron loss and gain in two half-equations. It also introduces the idea that $E^{\ominus}$ values are related to the position of equilibrium for a given change. This is taken further in the next section.

3 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 in the *Students' book.*

ANSWER TO THE QUESTION

The e.m.f. of a lithium–silver cell is +3.83 V, with the Ag the + pole of the cell.

13.3 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

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

(loss of $Ag^+(aq)$ ions is greater than gain of $Cu^{2+}(aq)$ ions so there is a relatively large decrease in $\Delta S^{\ominus}_{system}$)

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

(loss of $Cu^{2+}(aq)$ ions equals gain of $Zn^{2+}(aq)$ ions and the change in $\Delta S^{\ominus}_{system}$ is relatively small).

13.4 Gibbs free energy

Timing About 1 hour.

Suggested treatment

The *Students' book* uses an empirical approach to the relationship of E_{cell} to entropy change as students are only expected to link them qualitatively. It is more important that they appreciate that for a spontaneous change ΔG must be negative and learn how to calculate ΔG for a reaction from data.

Gibbs free energy calculations

The treatment can be parallel to that in Topic 4 *Energy and reactions* where standard enthalpy change of formation of compounds was introduced. This is in fact a good moment for students to revise that part of Topic 4.

The following points, which are treated more fully in the *Students' book*, could be brought out during discussion.

- Just as in the case of enthalpies absolute values of free energies are not known, so it is convenient to choose some base-line, or arbitrary zero, from which to measure the standard free energies of substances. The convention chosen for Gibbs free energies is the same as that for enthalpies, namely that
  at 1 atmosphere
  and 298 K
  with the elements in the physical states normal under these conditions, the standard free energies of the elements are zero.
- The standard Gibbs free energy of formation of any compound, $\Delta G^{\ominus}$ (298)(298) is the standard free energy change when one mole of the compound at 298 K is formed from its elements in physical states normal at 1 atmosphere and 298 K.
- It follows necessarily from this convention that $\Delta G_f^{\ominus}$ (298) [elements in physical states normal at 1 atmosphere and 298 K] = 0.
- It is possible therefore, using this convention, to tabulate standard free energies of formation of compounds rather than standard free energies relating to specific reactions. In fact, of course, the standard free energy of a compound does really refer to a reaction, namely the formation of one mole of a compound from its elements in standard conditions.

The tabulation of standard free energy data relating to compounds rather than reactions, however, makes for very general and flexible use of such tables. Because most reactions that the students meet will be at 298 K the style adopted in the *Students' book* is to indicate the temperature only when it is not 298 K.

- In dealing with ions, the standard free energy of the hydrogen ion is taken as zero, that is

$$\Delta G_f^{\ominus} (298)\ [\mathrm{H^+(aq)}] = 0$$

This corresponds to the convention of regarding the standard potential of the hydrogen electrode as zero volts.

The examples of calculations in the *Students' book* are intended to show how the Gibbs free energy change for a reaction can be calculated from tabulated values of standard free energies of formation. The examples chosen are for reactions familiar from Topic 10. The teacher can invent many other examples using table 5.3 in the *Book of data*.

13.5 Predicting whether reactions will take place: ΔS_{total}, ΔG, E_{cell} and K_c

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 8.

13.6 Study Task: Cells and batteries

Timing The Study task is suitable for homework.

Students are asked to read a passage about the structure and chemical reactions of common commercial cells, and then answer some questions on it.

ANSWERS TO THE QUESTIONS

For related experimental work see Smith, M.J., 'Practical electrochemistry for sixthformers', *Education in Chemistry*, 29, pages 12–14, 1992.

1 Miniature cells, e.g. the $Zn–Ag_2O$ cell, have the most constant voltage; the most variable are the $Zn–MnO_2$, standard dry cell and heavy duty types.

2 The Zn–HgO has the largest capacity of the cells quoted, 330 mA h cm^{-3}.

3 Equations for the reaction in the Leclanché cell include

$$Zn + MnO_2 + 2NH_4Cl \rightarrow Zn(NH_3)_2Cl_2 + 2MnO(OH)$$

$$Zn + 2MnO_2 + 2H_2O \rightarrow Zn(OH)_2 + 2MnO(OH)$$

4 Cell diagrams for button cells include

$$Zn(s)\,|\,ZnO(s)\,\vdots\vdots\,Ag_2O(s)\,|\,Ag(s)$$

and $Li(s)\,|\,Li_2O(s)\,\vdots\vdots\,Mn_2O_3(s)\,|\,MnO_2(s)$

5 The Gibbs free energy change for the lithium–manganese(IV) oxide cell is

$$\Delta G^{\ominus}_{reaction} = -561.2 - 881.2 - (-465.2)$$

$$= -977.2 \text{ kJ mol}^{-1}$$

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

13.1

Platinum black electrode, hydrogen gas at 1 atmosphere pressure, H^+ at 1.0 M, temperature of 25 °C, tidy drawing.

Total 5 marks

13.2

a Fe(s) reducing agent, $Cu^{2+}(aq)$ oxidizing agent. (1)
b Al(s) reducing agent, $H^+(aq)$ oxidizing agent. (1)
c Zn(s) reducing agent, $Pb^{2+}(aq)$ oxidizing agent. (1)
d $Fe^{3+}(aq)$ oxidizing agent, $Sn^{2+}(aq)$ reducing agent. (1)

Total 4 marks

13.3

a H_2 positive, Fe negative. (1)

$E^{\ominus} = -0.44$ volt (1)

b Ni negative, H_2 positive. (1)

$E^{\ominus} = +0.25$ volt (1)

c Zn negative, Ni positive. (1)

$E^{\ominus} = +0.76 - 0.25 = +0.51$ volt (1)

d Al negative, Cr positive. (1)

$E^{\ominus} = +1.66 - 0.74 = +0.92$ volt (1)

Total 8 marks

13.4

Standard electrode potential = +0.34 – 0.62 = –0.28 volt

Total 2 marks

13.5

Standard electrode potential = +1.61– 0.76 = +0.85 volt

Total 2 marks

13.6

a $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

$2Al(s) + 3Sn^{2+}(aq) \rightarrow 3Sn(s) + 2Al^{3+}(aq)$ (3)

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

$Ag^+(aq) + e^- \rightarrow Ag(s)$

$Pb(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Pb^{2+}(aq)$ (3)

c $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$ (3)

Total 9 marks

13.7

a $Ag^+(aq)$ $Cu^{2+}(aq)$ $Pb^{2+}(aq)$ $Cr^{3+}(aq)$ (2)

b $Fe^{3+}(aq)$ $Sn^{2+}(aq)$ $Zn^{2+}(aq)$ $Mg^{2+}(aq)$ (2)

Total 4 marks

13.8

a +0.03 V (2)

b –2.8 kJ mol^{-1} (3)

c Slight excess of products; ΔG is small and negative, E is small and positive, K_c is small and greater than 1. (4)

Total 9 marks

13.9

a $I^-(aq) \rightarrow \frac{1}{2}I_2(aq) + e^-$; $\frac{1}{2}Br_2(aq) + e^- \rightarrow Br^-(aq)$ (2)

b $Pt \mid I^-(aq), I_2(aq) \mid Br_2(aq), Br^-(aq) \mid Pt$ (1)

c +0.53 V (1)

d Products; e.m.f. large and positive. (3)

Total 7 marks

13.10

a –50.8 kJ (1)

b Yes (1)

c No (1)

d Answer should refer to distinction between kinetic and energetic factors. (2)

Total 5 marks

13.11

a $\Delta G_f^{\ominus}$ [FeO] $= -245.4$ kJ mol^{-1}
$\Delta G_f^{\ominus}$ [Fe_2O_3] $= -742.2$ kJ mol^{-1} (1)

b For the reaction
$2FeO(s) + \frac{1}{2}O_2(g) \rightarrow Fe_2O_3(s)$
$\Delta G^{\ominus} = -252$ kJ mol^{-1} (1)

c Iron(III) oxide. (1)

Total 3 marks

13.12

a i $\Delta G^{\ominus} = -394.4$ kJ mol^{-1}; $\Delta H^{\ominus} = -393.5$ kJ mol^{-1} (2)
ii $\Delta G^{\ominus} = -33.0$ kJ mol^{-1}; $\Delta H^{\ominus} = -92.2$ kJ mol^{-1} (2)
iii $\Delta G^{\ominus} = +130.4$ kJ mol^{-1}; $\Delta H^{\ominus} = +178.3$ kJ mol^{-1} (2)
iv $\Delta G^{\ominus} = -212.5$ kJ mol^{-1}; $\Delta H^{\ominus} = -218.7$ kJ mol^{-1} (2)

b Reactions **i** and **iv** above agree closely; the others differ significantly (1)

c ΔG and ΔH are most likely to show close agreement in reactions that involve the same numbers of particles on both sides of the equation, and have reactants and products in the same state. (2)

d ΔH is a good guide to the feasibility of a reaction because entropy changes of the surroundings (measured by $\Delta H/T$) at room temperature are usually much larger than those of the system, and thus usually outweigh them. ΔG is a better guide because it takes account of both entropy changes. (3)

Total 14 marks

Examination questions

13.13

a i $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightleftharpoons 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
Correct balancing (1)
Correct formulae/state symbols (1)

ii 25 cm^3 of MnO_4^- at end point (1)

From equation: 5 Fe^{2+} react with 1 MnO_4^- (1)

As same volume of Fe^{2+} and MnO_4^- solutions are used then the molarity of the MnO_4^- must be $\frac{1}{5}$of the Fe^{2+}
that is: $[MnO_4^-] = 0.02$ M (1)

b i Pt | Fe^{2+}, Fe^{3+} ¦¦ [$MnO_4^- + 8H^+$], [$Mn^{2+} + 4H_2O$] | Pt
One mark each half cell, either way round. (2)
ii Manganese electrode, right hand (as written above). (1)
iii 0.74 V (1)

Total 9 marks

13.14

a i Any simple diagram is acceptable. (1)
ii 25 °C. (1)
iii Pt black electrode. (1)
iv Hydrogen gas at one atmosphere, H^+ at 1 M. (1)
v Filter paper soaked in KNO_3. (1)
vi Pt[$H_2(g)$] | $2H^+$ ¦¦ $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ | Pt
1 mark for rd | ox ¦¦ ox | rd, 1 mark for the rest (2)

vii The Fe^{3+}/Fe^{2+} electrode. (1)

b **i** Fe(0) (1)

ii $Fe(s) + 2V^{3+}(aq) \rightleftharpoons Fe^{2+}(aq) + 2V^{2+}(aq)$ (2)

iii 0.18 V (1)

Total 12 marks

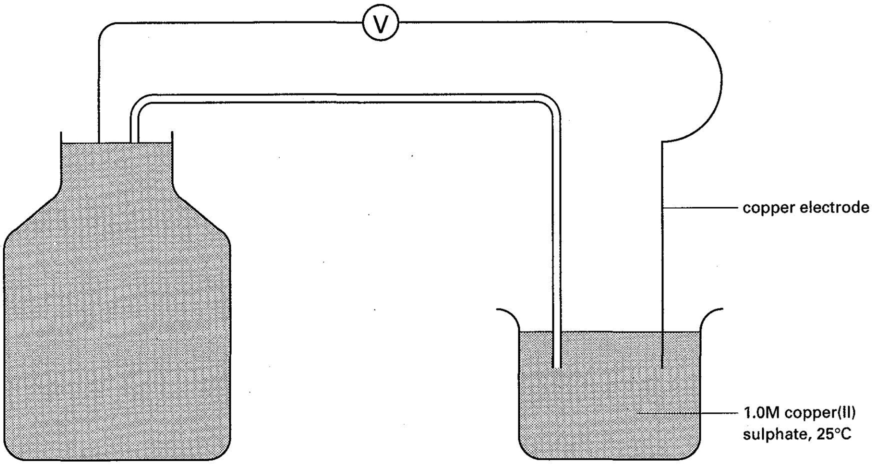
13.15

a **i** +1 (1)

ii To prevent siphoning or to slow solution diffusion. (1)

iii Any three good points: danger with Hg/H_2; compact/cumbersome apparatus; robust/unreliable. (3)

b **i**



(4)

ii 0.07 V (1)

Total 10 marks

13.16

Mark by impression

From the *Book of data*

1	$I_2(aq), 2I^-(aq) \mid Pt$	+0.54 V	
	$Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt$	+0.77 V	$E_{cell} = 0.23$ V
2	$Br_2(aq), 2Br^-(aq) \mid Pt$	+1.09	
	$[MnO_2(s) + 4H^+(aq)], [Mn^{2+}(aq) + 2H_2O(l)] \mid Pt$	+1.23	$E_{cell} = 0.14$ V
3	$[Sn^{4+}(aq)\ (1.0\ \text{M}HCl)], [Sn^{2+}(aq)\ (1.0\ \text{M}\ HCl)] \mid Pt$	+0.15 V	
	$Hg_2Cl_2(s), [2Hg(s) + 2Cl^-(aq)] \mid Pt$	+0.27	
	$\frac{1}{2}\ Hg_2^{2+}(aq) \mid Hg(s)$	+0.79	
	$2Hg^{2+}(aq),\ Hg_2^{2+}(aq) \mid Pt$	+0.92	$E_{cell} = 0.77$ V

(4)

In **3** the reaction will go to completion, in **1** and **2** products will predominate. (2)

The expected products are iron(II) ions and iodine, black precipitate; manganese(II) ions and bromine, red colour; tin(IV) ions and mercury, black (silver) solid. (9)

Total 15 marks

13.17

Mark by impression

Statement of meaning of oxidation and reduction with examples from both inorganic and organic chemistry.	(7)
Choice of oxidizing and reducing agent.	(3)
Example with explanation of compound acting as both oxidizing and reducing agent.	(5)
	Total 10 marks

TOPIC 14

Natural products and polymers

Introduction

This Topic introduces an important new concept, chirality, and goes on to develop students understanding in the context of carbohydrates and amino acids. Lipids are included as an important component of foods, and to complete the link to biology courses and the two Special Studies, *Biochemistry* and *Food science,* which are closely related to this Topic.

The last section on polymers is concerned with their properties as materials rather than their chemistry, except for the two types of polymerization reaction.

Content

	Timing	*Students' book*
14.1	2 hours	Pages 391–396
14.2	2 hours	Pages 397–400
14.3	2 hours	Pages 400–403
14.4	5 hours	Pages 403–410
14.5	Homework	Pages 410–413
14.6	4 hours, plus homework	Pages 413–423
Total about 3 weeks		

14.1 The shape of carbon compounds. Chiral and achiral compounds; preparation of cholesteryl benzoate; liquid crystal displays.

14.2 Carbohydrates. Some experiments with sugars, dehydration, reaction with Benedict's solution, hydrolysis, effect on polarized light, use of a polarimeter; reactions of carbohydrates.

14.3 Naturally occurring carboxylic acids. Lipids; hydrolysis of a lipid; uses of lipids.

14.4 Amino acids and proteins. Chirality and amino acids, the peptide group; experiments with amino acids and proteins, acidity and basicity, biuret test, reaction with ninhydrin, chirality; chromatographic separation of amino acids, R_f values; enzyme-catalysed hydrolysis of urea; properties of enzymes, enzyme-catalysed reactions; *investigation of the pH of amino acid solutions.*

14.5 Study Task. The chemical and structural investigation of proteins.

14.6 Polymers. Revision task, useful properties of polymers; the nature of polymers; addition polymerization, condensation polymerization; polymerization reaction experiments, making poly(propenamide), nylon, polyester, poly(ethenol); classification of polymers, thermoplastics, elastomers, thermosetting polymers, physical properties of polymers related to their structure; *investigation of the properties of 'slime'.*

Objectives

1. To introduce the concept of chirality and optical activity.
2. To develop knowledge of the reactions of carbohydrates, lipids and amino acids.
3. To develop skill in practical techniques such as chromatography.
4. To develop knowledge of addition and condensation polymerization, the classification of polymers and their properties as related to their structure.
5. To provide information about the industrial and social importance of selected compounds.

14.1 The shape of carbon compounds

Timing

About 2 hours 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

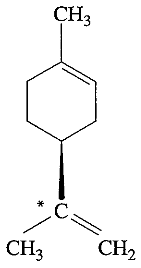
The introductory smell test is based on work by Gordon Woods 'Illustrating optical isomerism', *School Science Review,* **73**, *265*, pages 107–109, 1992). The testing has been extended to Chile, The Gambia and Hong Kong. Chinese students were the most accurate in matching the smells, British students 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.

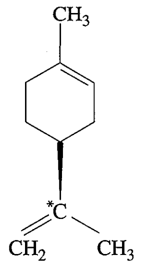
If teachers wish they could remind students of their extraction of limonene in Topic 2: the (+) form occurs in citrus fruits, the (–) form in pine needle oil and (±) in turpentine oil.

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 14.2.



(+) has an orange odour



(–) has a lemon odour

Figure 41.1 The chiral isomers of limonene. The chiral centre is marked *.

Experiment 14.1 Cholesteryl benzoate, 'liquid crystals'

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 IRRITANT, HIGHLY FLAMMABLE
Fume cupboard
Piece of polaroid
Balance, to weigh to ±0.1 g

Hazards

Because of the harmful vapours of the reagents this should be regarded as an optional experiment, perhaps carried out by only a few students.

The safety precautions concerning the use of pyridine (harmful vapour; avoid contact with skin and eyes) and benzoyl chloride (lachrymatory) mentioned in the *Students' book* should be rigidly adhered to.

Procedure

Full instructions are given in the *Students' 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.

The section in the *Students' book* on liquid crystal displays may be set for a reading homework.

14.2 Carbohydrates

Timing 2 hours.

Suggested treatment

Students should have the opportunity of building or inspecting ball-and-spoke models of simple carbohydrates and should be able to discuss the ring structures without needing to memorize the details of the individual structures.

When discussing this section with students, teachers have an opportunity to build links with biology, and should consider extending the treatment of carbohydrates to give appropriate support to the biology courses that their students may be following.

Experiment 14.2 Some reactions of carbohydrates

Each group of students will need:
Eye protection
Test-tubes and racks
Wide-bore test-tube (or disposable bottle tops)
Access to:
2 M ammonia, 5 cm^3
Benedict's solution, 10 cm^3
Fructose, 1 g
Glucose, 1 g
2 M hydrochloric acid, 5 cm^3
Starch (any), 1 g
Sucrose, 1 g
Concentrated sulphuric acid, 1 cm^3 CORROSIVE
Molecular model kit
Polarimeter
Solutions of carbohydrates (15 g in 100 cm^3 water)
Optional:
Clock
Concentrated hydrochloric acid, 5 cm^3 CORROSIVE
Sucrose solution (100 g in 40 cm^3 water)

Procedure

Full instructions are given in the *Students' book.* To allow students to have access to polarimeters, it will probably be necessary to arrange the experiments as a 'circus': experiments **1, 2,** and **3** form a group, which can be carried out in parallel with the polarimeter experiment. If solutions are available, the polarimeter experiment is actually quite brief, apart from the optional kinetic study.

Before starting this experiment, ensure that the students understand what is meant by 'polarized light', and know how to use the polarimeter.

The hydrolysis of (+) sucrose produces an equimolar mixture of (+) glucose and (–) fructose, but because the specific rotation of fructose is greater than that of glucose, the mixture of products is (–). It is because of this overall change from (+) to (–) that this reaction is called the *inversion* of sucrose, and the course of the reaction can be followed using the polarimeter.

The following notes may be helpful.

1 Dehydration

This is a complex reaction. The foaming is due to steam, but CO, CO_2, and SO_2 are also formed and the black residue contains carbonyl compounds as revealed by Fehling's solution and chromatography (Meek, E.G. 'The action of concentrated sulphuric acid on sucrose', *School Science Review,* **61**, *215*, page 281, 1979).

2 Benedict's solution

This is a test for aldoses, giving a precipitate of copper(I) oxide, but a positive result is also given by some ketoses, including fructose.

3 Hydrolysis

The hydrolysis is only partial under these conditions but the Benedict's solution should be partially reduced at least.

4 Polarized light

This is an important experiment as it gives students experience of chiral molecules. The experiment can be repeated with amino acids but the degree of rotation is much less and the compounds are more expensive. The kinetic study is optional but would be a useful extension to Topic 8.

14.3 Naturally occurring carboxylic acids

Timing

About 2 hours

This is a short section, included to complete the trio of food components – fats, carbohydrates and proteins – in the Topic. The experiment involves simple techniques but a very corrosive solution of sodium hydroxide. It provides an opportunity to revise the hydrolysis of esters, and their structure (a structure that students find difficult to grasp).

The passage on the uses of lipids describes some of their sources, including the relative proportions of saturated and unsaturated fatty acids. This is an opportunity to point out how chemical knowledge contributes to good health.

Experiment 14.3 Hydrolysis of a lipid

Each group of students will need:
Eye protection (face shields if available)
Protective gloves
Beaker, 250 cm^3 (as a water bath)
Evaporating basin
Conical flask
Test-tubes and rack
Glass rod
Access to:
Castor oil, 2 cm^3
Sodium chloride
Sodium hydroxide, 2 g CORROSIVE
A calcium salt solution
2 M hydrochloric acid

Hazards

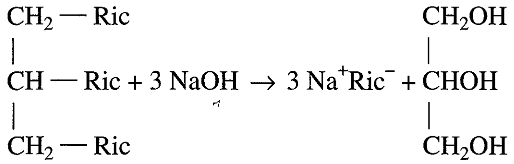
Face shields are advised if they are available because hot concentrated NaOH solution is used in this experiment.

Procedure

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

The product should lather well, and give a precipitate with both calcium salts (calcium ricinoleate) and hydrochloric acid (ricinoleic acid).

Students should write an equation for the hydrolysis in the form:



$$\begin{array}{lcl} CH_2 - Ric & & CH_2OH \\ | & & | \\ CH - Ric + 3\,NaOH & \rightarrow & 3\,Na^+Ric^- + CHOH \\ | & & | \\ CH_2 - Ric & & CH_2OH \end{array}$$

14.4 Amino acids and proteins

Timing 5 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.
- 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. Twenty of them are listed in the *Students' book.*

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 14.4a Protein materials

Each group of students will need:

Eye protection
Protective gloves
Test-tubes and rack
Dropping pipette
Chromatography paper ('lantern' type)
Access to:
0.1 M copper(II) sulphate solution
Full-range Indicator
0.01 M hydrochloric acid
0.01 M L-glutamic acid

0.01 M glycine
2 M sodium hydroxide CORROSIVE
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
Polarimeter (optional)

Hazards

Ninhydrin in propanone is an irritant and poisonous; the spray from an aerosol can is very flammable.

Procedure

Full instructions are given in the *Students' book.* Because experiment 14.4b 'The chromatographic separation of amino acids' is lengthy, students could start on it and then carry out experiment 14.4a 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 Biuret test

This test depends on the formation of a complex ion between copper(II) ions and peptide groups.

3 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.

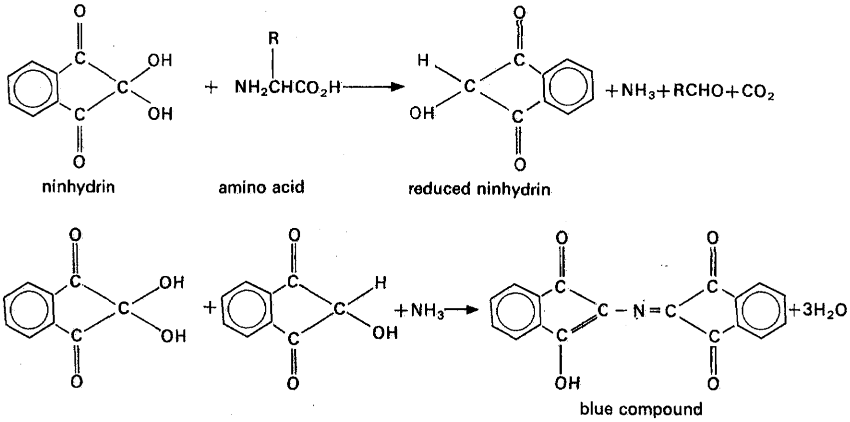


Figure 14.2 The development of ninhydrin blue.

4 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.

Experiment 14.4b

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
Access to:
8 M ammonia in crystallizing dish (*in a fume cupboard*)
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

Procedure

This experiment is lengthy and if convenient, students could start it and carry out the preceding experiment 14.4a 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 (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 realize that the value varies with solvent and temperature so comparison with the values quoted in the *Students' book* is not strictly valid.

Experiment 14.4c The enzyme-catalysed hydrolysis of urea

Each group of students will need:
Test-tubes and rack
Dropping pipette
Bunsen burner
Stopclock
Full-range Indicator
0.25 M ethanamide, 5 cm^3 HARMFUL
0.01 M hydrochloric acid, 10 cm^3
0.25 M methylurea, 5 cm^3
0.25 M urea, 5 cm^3
1% urease-active meal solution (a cloudy suspension), 5 cm^3

Hazards

Ethanamide is a category 3 carcinogen and should be used with extra care.

Procedure

Full instructions are given in the *Students' book*. Students should find that urease will only hydrolyse urea. The boiling of enzymes causes a loss of structure due to hydrogen bonds breaking and is known as 'denaturing'.

Students should note the specific nature of enzyme catalysis. In further discussion the sensitivity of enzyme activity to temperature and pH of solution is introduced.

These characteristics of enzyme catalysis can be compared with the characteristic features of inorganic catalysts (Topics 8 and 15). Urease is the only enzyme in higher organisms that is known to use nickel.

Investigation 14.4d The pH of amino acid solutions

Students will need time for library research as well as laboratory time for trial experiments before starting their investigation. Their risk assessment will need to be checked before they start experimental work. A good report would discuss the theory of titration as developed in Topic 11.

If teachers wish to use the investigation as an alternative experiment, the following notes will be helpful.

A standard procedure for the titration of glycine by strong acid and strong base uses the following solutions:
0.1 M glycine, 100 cm^3
0.25 M sulphuric acid, 100 cm^3
0.5 M sodium hydroxide, 100 cm^3

Titrate 20.0 cm^3 portions of glycine solution against sulphuric acid and a second 20.0 cm^3 portion against sodium hydroxide. Add the acid and alkali dropwise for the first 1 cm^3 and then increase the volume added until the pH reaches about 1.5 and 11 respectively.

Measure the pH change with a recently calibrated pH meter and stir the titration mixture continuously. A typical result is shown in figure 14.3. At the isoelectric point [acid] = [base].

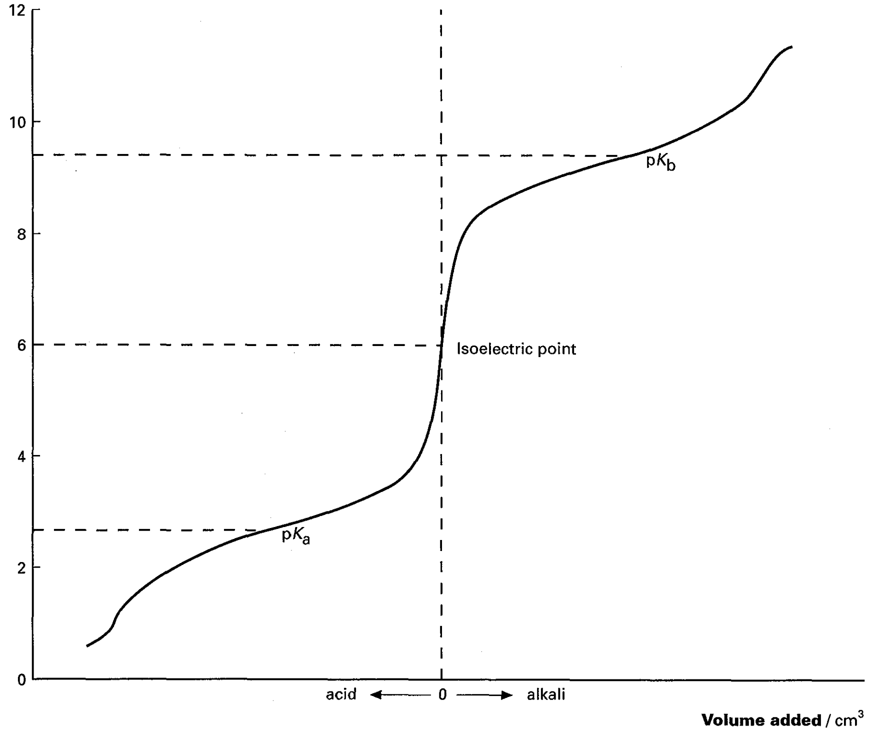


Figure 14.3 A typical titration curve for glycine and similar amino acids.

14.5 Study Task: The chemical and structural investigation of proteins

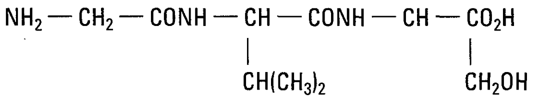
Timing Homework.

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 THE STUDY TASK

There are three questions that students could be told to answer as a homework task.

1 The structural formula of gly-val-ser is



$$\begin{array}{l} NH_2 - CH_2 - CONH - \underset{\displaystyle CH(CH_3)_2}{\underset{|}{CH}} - CONH - \underset{\displaystyle CH_2OH}{\underset{|}{CH}} - CO_2H \end{array}$$

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.

14.6 Polymers

Timing 4 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 7.

Students should then be introduced to the distinction between addition and condensation polymerization and there is a short Study Task for them to apply their understanding of polymerization reactions. The experiments develop this theme with further examples.

The final section on the classification of polymers is organized for individual learning through a set of Study Tasks which test students understanding of their reading.

There is additional information of interest in the article by Kauffman, G.B. 'Teflon – 50 slippery years', *Education in Chemistry*, **25**, pages173-5, 1988.

Experiment 14.6 Polymerization reactions

Each group of students will need:
Eye protection
Protective gloves

1 Poly(propenamide)

Beaker, 250 cm^3
Measuring cylinder, 50 cm^3
Thermometer, 0–100 °C
Tin can (throw-away container), larger than 50 cm^3
Propenamide, 10 g TOXIC
Potassium peroxodisulphate, 0.1 g
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 (see figure 14.3)
Decanedioyl chloride (0.5 cm^3) in petroleum spirit,
120–160 °C (15 cm^3) FLAMMABLE
Hexane-1,6-diamine (0.7 g), FLAMMABLE AND HARMFUL and
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), 3 g 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

Hazards

Propenamide is a category 2 carcinogen and should be used under close supervision.

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.

An arrangement of the apparatus for the 'nylon rope trick' is shown in figure 14.4.

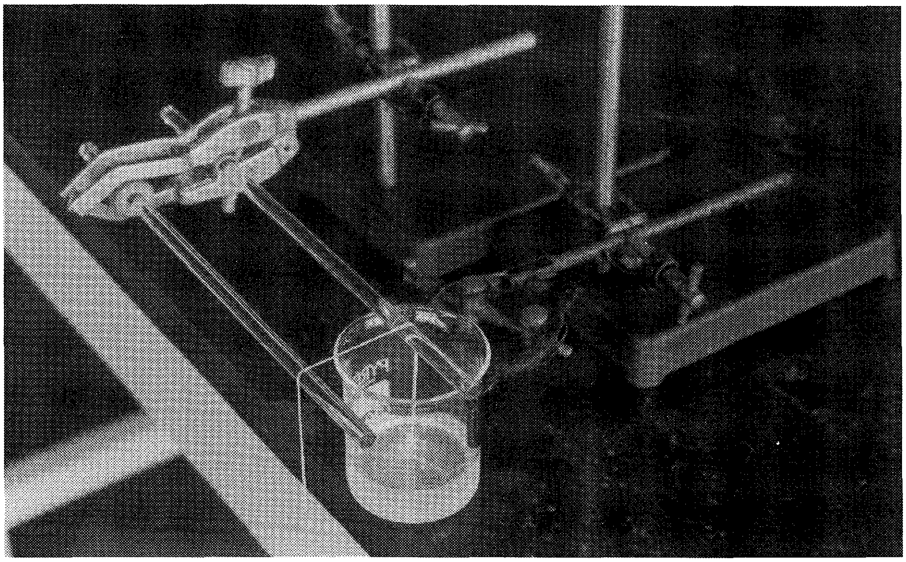


Figure 14.4 The 'nylon rope trick'.

At the end of this section it is suggested that the preparation of 'slime' could be the subject of an investigation. The appropriate poly(ethenol) is available from Aldrich Chemical Co as poly(vinyl alcohol), 96% hydrolysed, molar mass 85 000–146 000 g mol^{-1}. The details on which this experiment is based were kindly supplied by The Salters' Advanced Chemistry Project.

The 4% aqueous solution of poly(ethenol) needs to be prepared in batches on a hotplate with continuous stirring. Heat 200 cm^3 of pure water to 90 °C and add 8 g of poly(ethenol) in small portions while stirring. Maintain the temperature at 90 °C (do not boil) and continue to stir while the poly(ethenol) dissolves. This should take no more than 15 minutes. A hotplate with a magnetic stirrer is useful for this operation.

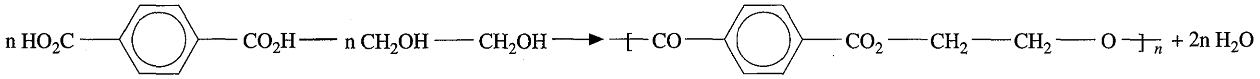
Classification of polymers

This section could be used for extended self-directed study, either in groups or individually as homework.

ANSWERS TO THE STUDY TASK QUESTIONS

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 methanal to react with the benzene ring in an electrophilic substitution reaction.

Study Task on glass temperatures

1 The movement of the polymer chains is restricted by either bulky methyl side chains or bulky rigid phenyl groups, resulting in higher glass temperatures than that of poly(chloroethene).

2 The bulky rigid benzene ring and the relatively rigid amide link result in a more rigid chain than $—CH_2—CH_2—$.

3 **a** Students should suggest that plasticizers work by reducing intermolecular forces between chains.

b Window frames need to be made of rigid polymer with a glass temperature high enough to withstand hot weather.

c uPVC has a glass temperature of 85 °C so it becomes rubbery in hot water.

Study Task on stretching poly(ethene)

Each group of students will need:
Poly(ethene) film, in strips 2 cm × 10 cm
Carothers' original description of 'cold drawing' is still valid:

> In connection with the formation of fibres the polymers exhibit a rather spectacular phenomenon which we call cold drawing. If stress is gently applied to a cylindrical sample of the opaque, unoriented polymer at

> room temperature or at a slightly elevated temperature, instead of breaking apart, it separates into two sections joined by a thinner section of the transparent, oriented fibre. As pulling is continued this transparent section grows at the expense of the unoriented sections until the latter are completely exhausted. A remarkable feature of this phenomenon is the sharpness of the boundary at the junction between the transparent and the opaque sections of the filament. During the drawing operation the shape of this boundary does not change; it merely advances through the opaque sections until the latter are exhausted. This operation can be carried out very rapidly and smoothly, and it leads to oriented fibres of uniform cross section. The oriented and unoriented forms of the polymer are different crystalline states, and in the cold drawing operation one crystalline form is instantly transformed into the other merely by the action of very slight mechanical stress.

Poly(ethene) made into a gel and spun into fibres is strong enough to be used to make bullet-proof vests.

Study Task on Terylene

1. Students should predict that the forces between Terylene chains are dipole–dipole attractions due to the polar carbonyl groups, and the forces are therefore weaker than the hydrogen bonding between nylon chains.
2. The benzene rings constitute a large inflexible unit in the Terylene chains making them less flexible, and contributing to a high glass temperature.
3. Nylon 6 has a glass temperature of 50 °C (table 7.7 in the *Book of data*) so a warm wash will allow the chains to move and ironed-in pleats to disappear.
4. A polymer with a poor elastic recovery will not regain its original shape after being stretched.

Investigation 14.6b The properties of 'slime'

Each group of students will need:
Poly(vinyl alcohol), 96% hydrolysed, molar mass 85 000–146 000 g mol^{-1}
Sodium borate

Procedure

The solution of poly(vinyl alcohol) should be prepared in small batches on a hot plate with continuous stirring.

Students will already know the basic procedure using 4% solutions of poly(ethenol) and sodium borate from experiment 14.6a.

An investigation could consider the variables of concentration, temperature of mixing and pH. Table 6.7 in the *Book of data* lists the composition of borate buffers. 'Slime' can be coloured by water-soluble food dyes.

Poly(vinyl alcohol) can be bought with alternative molar mass ranges and different percentage hydrolysed but this would be an expensive extension to the investigation.

The students' risk assessment should report that sodium borate is an irritant and boric acid is poisonous if swallowed, but their use is not restricted.

An alternative mixture to investigate is:
Sodium silicate solution (water glass), 20 cm^3
Ethanol, 5 cm^3
This crosslinked polymer can be moulded into a 'super ball'. The ball will need moistening if it shows signs of crumbling.

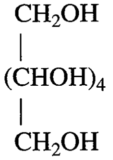
Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

14.1

a 1 (1)
b Primary hydroxyl group, 6. (1)
Secondary hydroxyl groups, 1, 2, 3, 4. (2)
Tertiary hydroxyl group, none. (1)
c 1 and 4. (2)
d Presence of an aldehyde group in open chain structure. (1)
e



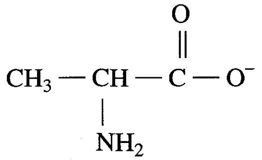
$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

(1)

Total 9 marks

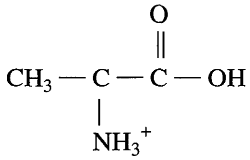
14.2

a C — H bond (2)
b **i**



$$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-O^-$$

ii



$$CH_3-\underset{\displaystyle NH_3^+}{\underset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

(2)

c **i, ii** and **iii** No difference. (3)
iv One will rotate the plane of plane polarized light in a clockwise sense and the other anti-clockwise by the same amount. (2)
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. (2)

Total 11 marks

14.3

a Protein. (1)
b Polymeric material with high tensile strength. Probably insoluble in water since there is hydrogen bonding between the chains. Material likely to be 'denatured' by heat as secondary and tertiary structure breaks down. (2)
c Hydrolysis of peptide linkage. (2)
d Reflux with 6 M HCl for 24 hours. (2)
e Method of paper chromatography. (2)
f X-ray diffraction. (1)

Total 10 marks

14.4

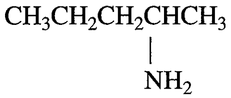
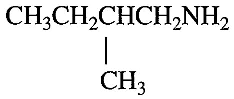
Charges on the molecule vary with pH

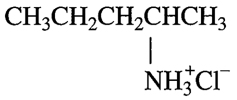
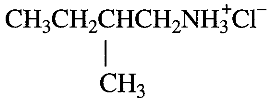
$H_3\overset{+}{N}CH_2CO_2^-$ pH 7 $H_3\overset{+}{N}CH_2CO_2H$ pH 2 $H_2NCH_2CO_2^-$ pH 12 (6)

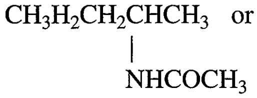
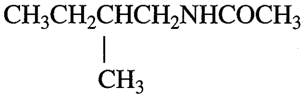
Total 6 marks

14.5

Alternative answers are possible for A, B and C in **a**

a A 
$CH_3CH_2CH_2\underset{NH_2}{CH}CH_3$ or 
$CH_3CH_2\underset{CH_3}{CH}CH_2NH_2$ (2)

B 
$CH_3CH_2CH_2\underset{NH_3^+Cl^-}{CH}CH_3$ or 
$CH_3CH_2\underset{CH_3}{CH}CH_2NH_3^+Cl^-$ (2)

C 
$CH_3H_2CH_2\underset{NHCOCH_3}{CH}CH_3$ or 
$CH_3CH_2\underset{CH_3}{CH}CH_2NHCOCH_3$ (2)

b $CH_3CH_2CH(NH_2)CH_2CH_3$ and $CH_3CH_2CH_2CH_2CH_2NH_2$ (2)

c $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[\text{KBr + conc. } H_2SO_4]{\text{HBr from}}$

$CH_3CH_2CH_2CH_2CH_2Br \xrightarrow[\text{ethanolic solution of ammonia}]{\text{Heat under pressure with}}$

$CH_3CH_2CH_2CH_2CH_2NH_2$ (4)

Total 12 marks

14.6

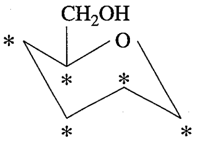
a H_2 and Ni catalyst. (2)
b addition. (1)
c Condensation polymerization. (1)
d Nylon. (1)
e $H_2N — (CH_2)_6 — NH_2 + ClOC — (CH_2)_4 — COCl \rightarrow$
$H_2N(CH_2)_6 — NHCO — (CH_2)_4 — COCOCl + HCl$ (2)
f Warm to soften and then draw or extrude material; or 'cold drawing'. (2)
g **i** The crystalline form has the higher elasticity.
ii The crystalline form has a higher tensile strength. (2)

Total 11 marks

Examination questions

14.7

a **i** Two monosaccharide molecules joined together/dimers. (1)
ii By boiling with dilute acid; hydrolysis. (2)
iii Benedict's solution with glucose produces a red precipitate of copper(I) oxide by reduction. No reaction with sucrose. (3)
b **i** Four different groups attached to a carbon atom/asymmetric carbon atom. (1)

ii 

(2)

iii By their ability to rotate the plane of plane-polarized light. (1)

c **i** Hydrolysis followed by chromatography. (1)

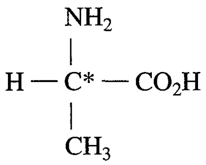
ii Partial hydrolysis, separation and chromatography or mass spectrometry. (1)

iii X-ray diffraction. (1)

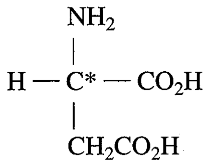
Total 13 marks

14.8

a



$$\begin{array}{c} NH_2 \\ | \\ H-C^*-CO_2H \\ | \\ CH_3 \end{array}$$

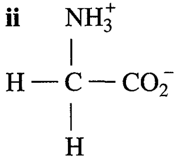


$$\begin{array}{c} NH_2 \\ | \\ H-C^*-CO_2H \\ | \\ CH_2CO_2H \end{array}$$

(2)

b **i** Ionic bonding (1)

ii



$$\begin{array}{c} NH_3^+ \\ | \\ H-C-CO_2^- \\ | \\ H \end{array}$$

(1)

c Solution of sample; spotted onto chromatography paper; samples of glycine and alanine spotted on alongside; developed using a suitable solvent; dried, sprayed with ninhydrin and heated; R_f values compared.

any four good points (4)

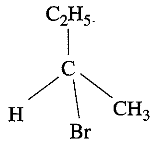
Total 8 marks

14.9

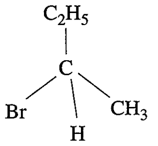
a $-\!\!\!\!+CH(C_2H_5)CH_2-CH(C_2H_5)CH_2-CH(C_2H_5)CH_2+\!\!\!\!-_n$ (2)

b **i** HBr

ii B is chiral



and



(2)

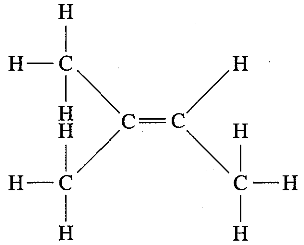
iii By their ability to rotate the plane of plane-polarized light in opposite directions (2)

c Both molecules are involved in the rate determining step/S_N2. (2)

Total 8 marks

14.10

a

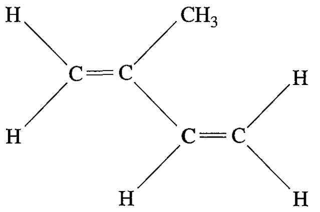


(1)

b Electrophilic addition. (2)

c **i** Removal of hydrogen in presence of a catalyst. (2)

ii



d **i** More tyres needed (because more cars). (1)

ii Natural rubber unavailable. (1)

iii Any two from:

Natural rubber is a renewable resource; increasing cost of oil; running out of oil (2)

Total 9 marks

14.11

a **i** Free radical substitution. (2)

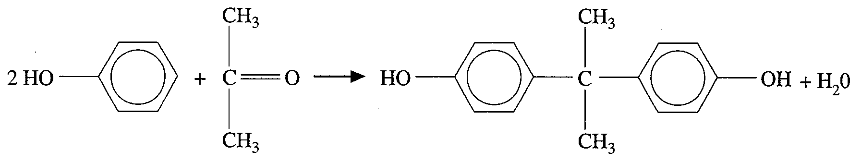
ii To form chlorine atoms/free radicals. (1)

iii 1,2-dichloropropane $CH_2Cl — CHCl — CH_3$. (2)

iv Double (π) bond acts as a source of electrons (or equivalent statement). (1)

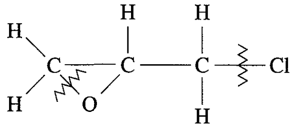
v A small molecule, HCl, is removed. (1)

b



(2)

c **i**



(2)

ii A long chain molecule is formed by elimination of a small molecule/HCl from the two monomers. (1)

d **i** A cross-linked structure. (1)

ii Structure is a rigid network/three dimensional structure of covalent bonds. (1)

Total 14 marks

14.12

Mark by impression

Difference between addition and condensation polymerization. (4)

Differences between thermosetting polymers, elastomers and thermoplastic polymers. (6–9)

Investigation of the physical properties of a polymer. (5–2)

The answer should include examples with formulae.

Total 15 marks

TOPIC 15

The transition elements

Introduction

A transition element is defined as one which contains an incomplete d-shell in at least one *compound*. It is not synonymous with a d-block element. The distinction between these two terms is made clear at the start of this Topic in the *Students' book*. The effect of the 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. Only the first row of transition elements are considered in this Topic, that is, the elements titanium to copper inclusive.

To introduce this Topic, the following points should be covered:

- The definition of a *transition element*, and how it differs from a *d-block element*
- 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 15.3.
- All form many complex ions. These are discussed in section 15.4.
- All have coloured ions, that is, their ions absorb light in the visible part of the spectrum.
- All exhibit catalytic activity. This is discussed in section 15.5.

Content

	Timing	*Students' book*
15.1	1 hour	Pages 437–438
15.2	1 hour	Pages 438–441
15.3	6 hours	Pages 442–448
15.4	5 hours	Pages 448–454
15.5	3 hours	Pages 454–456
15.6	3 hours	Pages 456–460
15.7	1 hour	Pages 460–463
15.8	Homework	Pages 463–466
Total about 4 weeks		

15.1 Metallic bonds. Ions in a sea of mobile electrons.

15.2 Crystal structures of metals. The HCP, FCC and BCC structures in metals.

15.3 Variable oxidation number. Experimental study of redox reactions of iron and of vanadium; analysis of 'iron tablets'; *investigation of the redox reactions of a transition metal*

15.4 Complex ion formation. Stability constants; experimental study of copper(II) complexes; preparation of compounds containing complex ions; entropy considerations; *investigation of the formula of a complex.*

15.5 Transition elements as catalysts. Homogeneous catalysis; kinetic study of the reaction between manganate(VII) and ethanedioic acid; autocatalysis; homogeneous catalysts and standard electrode potentials.

15.6 A study of the chlorides of iron. Reaction of iron with chlorine or hydrogen chloride gas; properties of the chlorides of iron; free energy change of the reaction.

15.7 The special properties of the transition elements. Similarity of physical properties; variable oxidation number; ability to form complex ions; colour; catalytic activity, energy changes.

15.8 Study Task. Micronutrients.

Objectives

1. To draw attention to some of the special characteristics of the transition elements.
2. To carry out experiments on various transition elements to study these special properties.
3. To provide opportunities to use standard electrode potentials to predict the direction taken by reactions.
4. To provide illustrations of the application of thermodynamics to chemical systems.

15.1 Metallic bonds

Timing About 1 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 delocalization.

Any discussion of energy bands is beyond the scope of this chemistry course but some classes could have the importance of energy levels brought to their attention. The fact that electrons in isolated atoms are arranged in energy levels has already been discussed in Topic 3. 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.

15.2 Crystal structures of metals

Timing About 1 hour.

Suggested treatment

The procedure described in the *Students' book* involves rather more preparation and the use of more polystyrene spheres than the procedures described in other Nuffield publications. But in this course we are concerned with the basic packing patterns, ABAB... and ABCABC..., rather than counting nearest neighbours and determining co-ordination numbers. If teachers wish to use triangular trays we recommend the use of 6 × 6 × 6 trays so that the relationship of the FCC structure to hexagonal arrays can be clearly demonstrated.

Other procedures can be used such as the use of slides or an OHP, or demonstrating the structures with fully pre-assembled models. But for most students real understanding only develops through being personally involved in the building of model structures.

Experiment 15.2 Models of metallic structures

Each group of student will need:
4 rafts of sixteen close-packed polystyrene spheres, 25 mm diameter
1 FCC model built of 25 mm diameter polystyrene spheres
1 bag of 24 separate polystyrene spheres
1 rectangular tray into which a raft of sixteen spheres will fit
or
1 bag of 56 separate polystyrene spheres
1 triangular tray into which a 6 × 6 × 6 array of spheres will fit

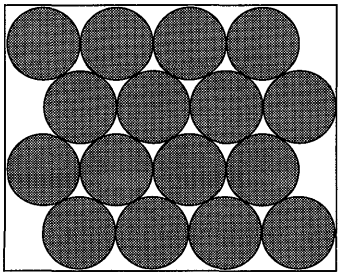


Figure 15.1 A raft of sixteen close-packed spheres.

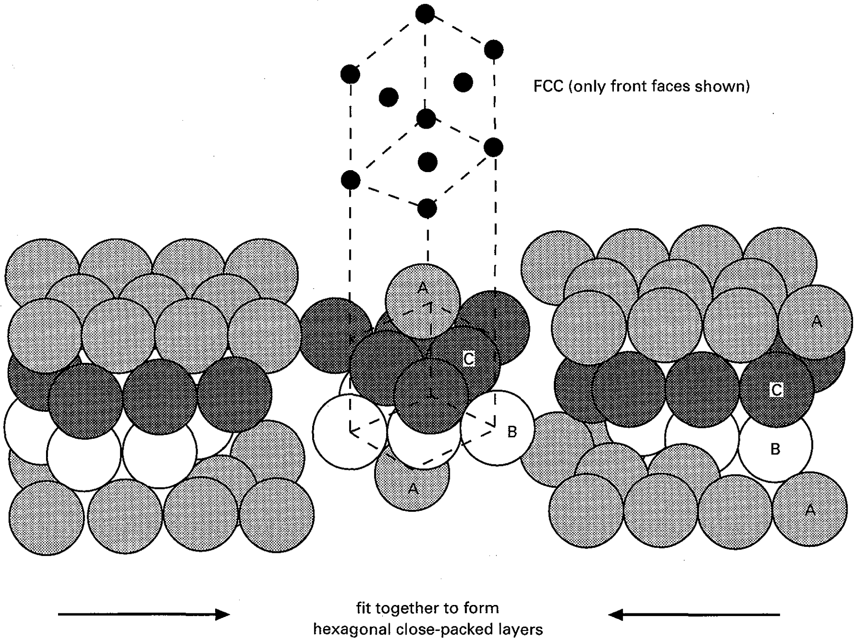


Figure 15.2 Face-centred cubic model.

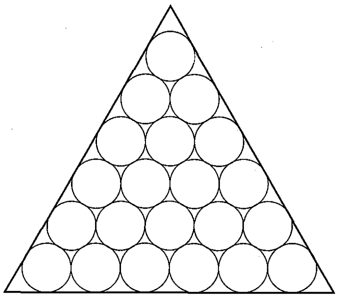


Figure 15.3 Alternative 6 × 6 × 6 tray for use in the close packing of spheres, approximately 17 cm each side.

Procedure

Full details of the students' experiment are given in the *Students' book.*

Unless a student group is going to be allowed to glue together their own spheres (at least the first time the rafts are used) there is some preliminary preparation needed.

Polystyrene spheres can be glued together using a rapid setting PVA glue of the type used in wood-working. To build rafts of sixteen spheres, spheres can be glued in rows of four first, sandwiched between strips of wood to keep the rows straight. When the glue has set, four rows can then be glued together in one operation to make a complete raft.

To build a FCC model glue spheres in rows of three and two. Then glue the rows together, plus an extra sphere, to make two 3 × 3 × 3 arrays for each model. Next glue the two 3 × 3 × 3 arrays together and finally add single spheres at centre top and centre bottom.

Trays should be built to match the actual spheres being used as the quoted 25 mm diameter can vary.

15.3 Variable oxidation number

Timing About 6 hours.

Suggested treatment

In the first experiment students investigate the reactions of Fe^{2+} and Fe^{3+} compounds. The *Students' book* gives the standard electrode potentials needed to predict the outcome of the reactions, and full details of the experiment.

Figure 15.6 in the *Students' book* is a development of the 'anticlockwise' chart introduced in Topic 13. Teachers should emphasise the unusual axes (negative to the right, and upwards).

Experiment 15.3a The redox reactions of iron

Each group of students will need:
Eye protection
Test-tube rack
8 test-tubes
Dropping pipette
Access to:
Zinc powder FLAMMABLE
0.1 M iron(II) sulphate in dilute sulphuric acid, about 40 cm^3 IRRITANT
0.1 M iron(III) chloride in dilute hydrochloric acid, about 40 cm^3 IRRITANT
0.1 M bromine solution, 10 cm^3 CORROSIVE
0.1 M potassium manganate(VII), 10 cm^3
0.1 M chlorine solution, 10 cm^3 TOXIC
0.1 M sodium chloride, 10 cm^3
Sulphur dioxide solution, 10 cm^3 TOXIC
Silver nitrate solution, 10 cm^3 (0.05 M or less is suitable)
0.1 M potassium iodide, 10 cm^3

⚠ Hazards

Silver nitrate solid is severely irritant to the eyes.
Sulphur dioxide may be harmful to those who suffer from respiratory complaints.

Procedure

Full details of the procedure are given in the *Students' book.* The outcome of the experiments is as follows:

a Iron(II) is oxidized 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 oxidized by potassium manganate(VII); the purple colour disappears.
g Iron(III) oxidizes iodide ions to iodine; 'iodine colour' is produced.
h Iron(II) is oxidized to iron(III) by chlorine water; the NaOH test gives the red-brown colour of iron(III) hydroxide.

In experiment 15.3b students analyse 'iron tablets' and calculate the percentage of iron in the tablets.

Experiment 15.3b Analysis of 'iron tablets'

Each group of students, will need:
Eye protection
Access to balance, to weigh to 0.001 g
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) (standardized)

Hazards

Potassium manganate(VII) solid is an oxidizing agent and is harmful.

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.

Some results obtained by a class of sixth-form students (using only one tablet instead of the two recommended) are as follows; average titres refer to the volume of 0.005 M potassium manganate(VII) solution used:

Mass of tablet /g	Average titre /cm^3	Mass of $FeSO_4$ /mg	%Fe
0.595	4.96	188	11.8
0.642	5.00	190	10.9
0.580	4.95	187	11.8
0.597	4.65	177	10.9
0.493	4.60	174	13.0

ANSWERS TO THE QUESTIONS

The answers to the questions at the end of the experiment are as follows:

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 (see experiment 15.2a);
- 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 (see the Study Task 'Micronutrients' at the end of this Topic in the *Students' book*).

Experiment 15.3c The redox reactions of vanadium

Each group of students, will need:

Eye protection
Test-tube rack
8 test-tubes

Access to:

0.1 M ammonium vanadate(V) in dilute sulphuric acid, 20 cm^3 IRRITANT
Zinc powder 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

Hazards

The bromine produced by oxidation of potassium bromide is toxic by inhalation.

Procedure

Full details are given in the *Students' book.* The outcome of the experiment is as follows:

Part 1

VO^{2+} can be obtained using potassium iodide solution followed by sodium thiosulphate, or by using tin and decanting the solution when the reaction has reached the appropriate stage.

V^{3+} can be obtained using granulated tin.

V^{2+} can be obtained using powdered zinc, but the reaction is quite slow.

Part 2

VO^{2+} and V^{2+}: the green colour of V^{3+} should be seen.

VO_2^{+} and V^{3+}: the blue colour of VO^{2+} should be seen but excess of either reagent will make the solution appear green.

VO^{2+} and Fe^{3+}: no reaction is expected.

VO^{2+} and Br^{-}: no reaction is expected.

V^{2+} and Cu^{2+}: a red precipitate of copper should be formed.

V^{3+} and Fe^{3+}: a blue solution containing VO^{2+} should be produced but excess of either reactant will make the solution appear green.

For further information about vanadium compounds see the article by Malate, M.A., 'Experiments with vanadium salts', *Education in Chemistry*, **21**, pages 18–19, 1984.

For additional ideas see the articles below.

Reed, N.V., 'The aqueous chemistry of iron(III) ions with sulphur oxoanions', *School Science Review*, **67**, *241*, pages 768–70, 1986.

Hunt, C., Hunt, W.G. and Waffling, R.E.L., 'Investigating the synthesis of copper iodide', *School Science Review*, **68**, *242*, pages 86–7, 1986.

Masson, A.J., 'Some thoughts on the silver(I)–thiosulphate complex', *School Science Review*, **69**, *246*, pages 86–7, 1987.

Worley, R., 'Redox reactions of iron revisited', *School Science Review*, **73**, *262*, pages 102–103, 1991.

Investigation 15.3d An investigation of the redox reactions of a transition element

There is plenty of scope in this investigation for students to make a thorough collection of data and to use data in the interpretation of their results. The first edition of this course included a study of manganese but it is not reproduced here as it concentrated on the effect of pH on electrode potentials.

Teachers could defer this investigation if they wished in order to include complex ions in the scope of the investigation.

15.4 Complex ion formation

Timing About 5 hours.

Suggested treatment

Teachers are likely to find it an advantage to explain the procedures in advance before students start this experiment. There is an introduction in the *Students' book.*

It is most important that students think about the questions at the end of each section of practical work and answer them before going on to the next section. Without this, the practical work will have little or no meaning.

Experiment 15.4a Some copper(II) complexes

Each group of students, will need:
Eye protection
Test-tube rack
8 test-tubes
Dropping pipette
0.5 M copper(II) sulphate, 10 cm^3 HARMFUL
Concentrated hydrochloric acid, 5 cm^3 CORROSIVE
8 M ammonia solution, 15 cm3 CORROSIVE
0.2 M edta, 10 cm^3
0.1 M sodium 2-hydroxybenzoate (sodium salicylate), 20 cm^3
0.1 M 1,2-dihydroxybenzene (catechol) in 0.5 m sodium hydroxide, 10 cm^3 IRRITANT

Hazards

Open stock bottles of ammonia with care.

Care should be taken when preparing 1,2-dihydroxybenzene (catechol) as the solid is an 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. NH_3. $Cu(NH_3)_4^{2+} > CuCl_4^{2-} > Cu(H_2O)_4^{2+}$. The more stable complexes have the higher stability constants.
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.

At the end of this experiment the *Students' book* gives the formulae of the various ligands, and classifies them as monodentate, bidentate, or hexadentate. The next experiment describes one possible preparation, but there is much scope for variation here.

Teachers should note that the complex with 1,2-dihydroxybenzene is with the anion, not the molecule.

Experiment 15.4b Stabilizing an unusual oxidation number: chromium(II) ethanoate, $Cr_2(CH_3CO_2)_4(H_2O)_2$

Each group of students will need:
Eye protection and gloves
Ground glass joint flask, 50 cm^3 and apparatus as in figure15.4
Measuring cylinder, 10 cm^3
Beaker
2 boiling tubes in rack
Access to:
Rough balance
Concentrated hydrochloric acid, 14 cm^3 CORROSIVE
Zinc granulated, 3 g FLAMMABLE
Sodium dichromate(VI), 1 g IRRITANT
Sodium ethanoate, saturated solution, 10 cm^3 HARMFUL

Hazards

Wear gloves when using sodium dichromate(VI)

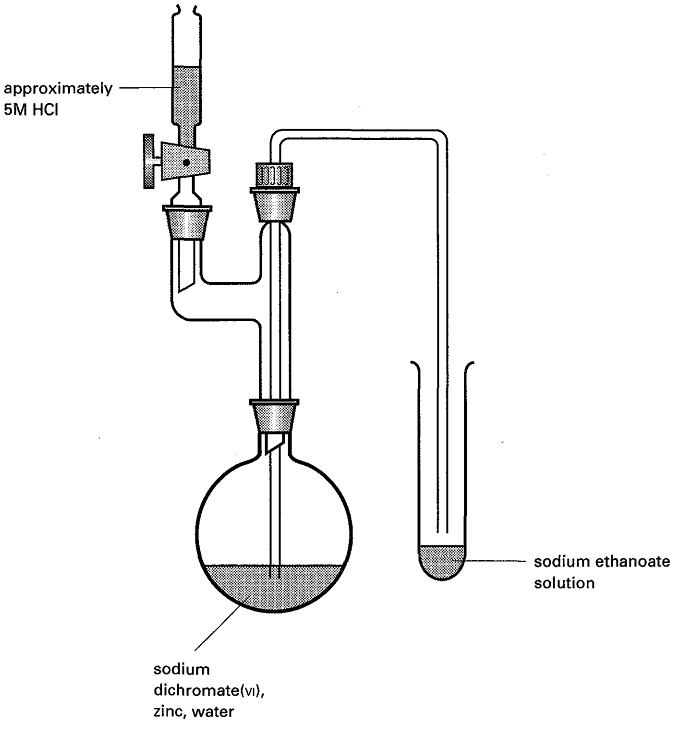


Figure 15.4 Apparatus for experiment 15.4b.

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 15.5.

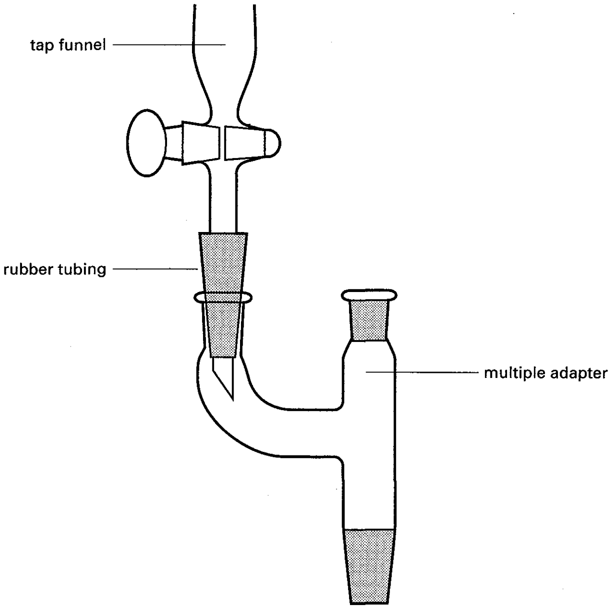


Figure 15.5 Rubber tubing in place of a glass joint fitting.

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

ANSWERS TO THE QUESTIONS

1 The relevant electrode potentials are:

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

$$Cr^{3+}(aq),\ Cr^{2+}(aq)\,|\,Pt \quad E^{\ominus} = -0.41\ V$$

$$[\,Cr_2O_7^{2-}(aq) + 14H^+(aq)],\ [2Cr^{3+}(aq) + 7H_2O(l)]\,|\,Pt \quad E^{\ominus} = +1.33\ V$$

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.

Investigation 15.4c The formula of a complex

It is possible to judge fairly reliably by eye the point at which the maximum colour due to a complex is reached, but a colorimeter can be used to estimate the maximum and puts the investigation on a quantitive basis. Some notes on the use of the colorimeter are given in Topic 18.3.

Three possible complexes to investigate are:
0.1 M nickel sulphate with 0.1 M edta
0.005 M iron(III) chloride in hydrochloric acid with 0.005 M potassium thiocyanate
0.1 M copper(II) sulphate with 0.1 M phenylamine

If any of these complexes are investigated, risk assessments are needed.

For teachers who wish to carry out an experiment rather than an investigation the following instructions are reprinted from the first edition and may be photocopied for use in the laboratory.

Alternative Experiment 15.4c

The formula of a complex

The stoichiometry of a complex can be found by a simple application of the method of **continuous variation**, as long as only one species is formed. Solutions are made up containing nickel(II) and edta in molar proportions 0:10, 1:9, 2:8, 3:7, etc. If the complex is Ni(edta)^{2-} then the highest concentration of complex would be in the 5:5 mixture and the others would be more dilute. Hence if the concentration of complex can be determined in each mixture, the stoichiometry of the complex ion can be found.

Many complex ions, including the Ni^{II}–edta ion, are coloured, and the concentration of a coloured substance can be found by using a colorimeter (described in section 18.3). The absolute concentration of the complex is not required, only a measurement which is proportional to the concentration. Thus a meter reading, *m*, can be measured for each mixture and then a graph of *m*, on the *y* axis, against the molar proportions drawn.

In eleven tubes which fit the colorimeter make up mixtures:

1 0 cm^3 0.050 M Ni^{II} solution + 10 cm^3 0.050 M edta solution
2 1 cm^3 + 9 cm^3
3 2 cm^3 + 8 cm^3
4 3 cm^3 + 7 cm^3
5 4 cm^3 + 6 cm^3
6 5 cm^3 + 5 cm^3
7 6 cm^3 + 4 cm^3
8 7 cm^3 + 3 cm^3
9 8 cm^3 + 2 cm^3
10 9 cm^3 + 1 cm^3
11 10 cm^3 + 0 cm^3

Choose the most suitable filter and then find the meter reading, *m*, for each mixture, adjusting the colorimeter to give $m_0 = 1$ with a tube of water in place before each measurement.

Plot a graph of meter reading *m* against the molar proportions of edta and Ni^{II} and hence find the stoichiometry of the complex.

Alternative Experiment 15.4c

Teachers guide

Each group of students will need:
Eye protection
2 burettes
2 racks of similar tubes that fit the colorimeter
Access to:
0.050 M nickel sulphate HARMFUL
0.050 M edta
Colorimeter

Procedure

This experiment may need some explanation as students will not have used continuous variation before. Some notes on the use of the colorimeter are given in section 18.3.

It may help the students to decide on the correct empirical formula if a second experiment is devised in which 1 cm^3 portions of solution **A** are treated with 0.5, 1.0, 1.5 cm^3, etc., portions of solution **B**, and a judgement is again made of the mixture which gives the maximum colour of the complex.

If the complex is $Ni(edta)^{2-}$ the graph will have the form shown in figure 15.6.

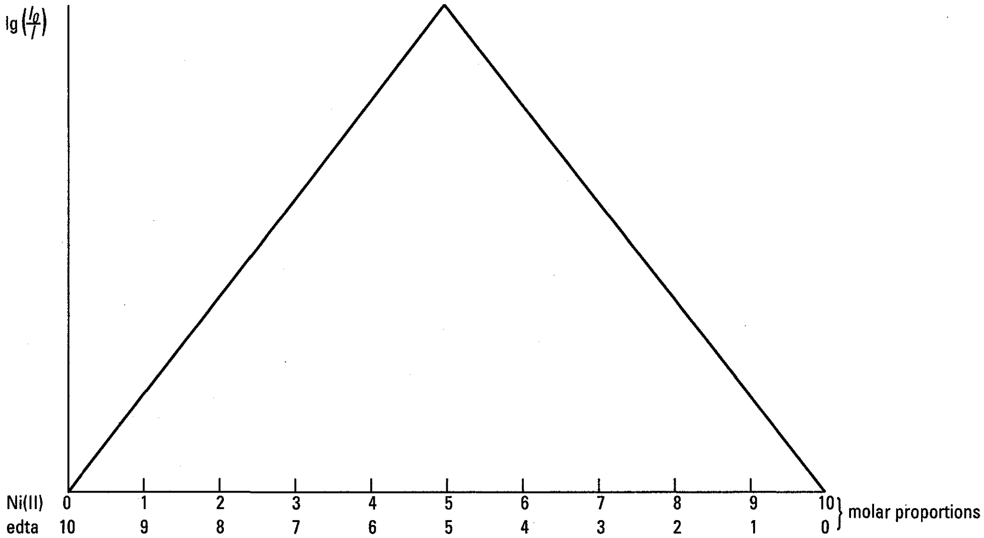


Figure 15.6 Result of Ni^{II}–edta experiment.

15.5 Transition elements as catalysts

Timing About 3 hours.

Suggested treatment

This section starts with a kinetic study providing a useful opportunity to revise aspects of Topic 8. Here we are concerned with homogeneous catalysis but there is a Study Task which asks students to review their work on all aspects of catalysis.

This would be suitable for homework.

Experiment 15.5 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.

Two methods are available; the second method uses a colorimeter and is described in this book in Topic 18.3.

Each group of students will need:
Eye protection
Flat-bottom 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
0.2 M ethanedioic acid (oxalic acid), 100 cm^3 HARMFUL
0.02 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 of 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 15.7.

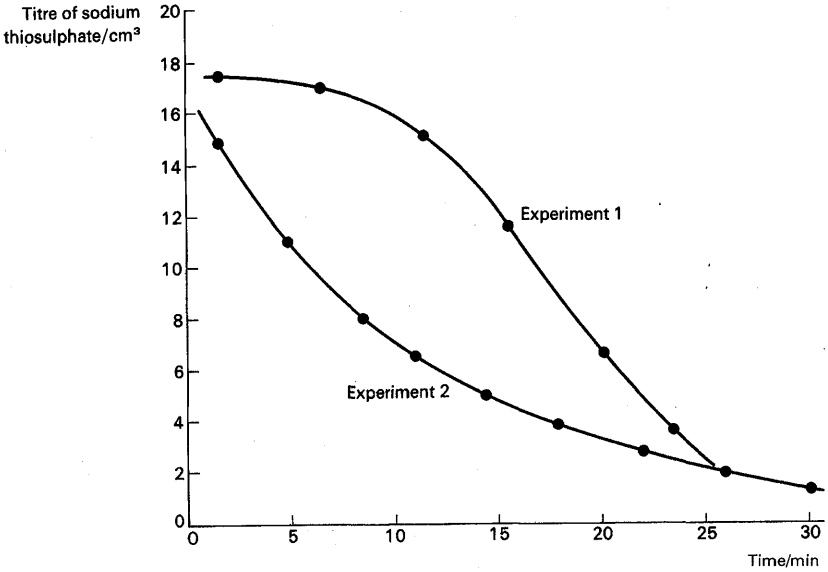


Figure 15.7 Results of kinetic study of Mn^{VII}–ethanedioic acid reaction.

ANSWERS TO THE QUESTIONS

1 A measure of the concentration of the manganate(VII) ion is given by the titre of 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 15.7.

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.

15.6 A study of the chlorides of iron

Timing About 3 hours.

Suggested treatment

This study of the chlorides of iron provides an opportunity, provided suitable facilities are available, for students to attempt an experiment that is quite demanding in manipulative skills and attention to safety. Students need only attempt one of these preparations and the class should be divided so that the results of both reactions can be discussed.

The reaction between iron and chlorine is vigorous and will give a good yield but the use of chlorine will require care; the reaction with hydrogen chloride is easier to manage but gives small yields which usually have to be scraped off the unreacted iron wire.

Experiment 15.6a Preparation of the chlorides of iron

This study is intended to provoke the question 'why does the reaction of hydrogen chloride with iron produce iron(II) and not iron(III) chloride?'. An answer is provided at the end of the section by the calculation of the Gibbs free energy change of the reaction.

Each group of students will need:
Eye protection
Gas generation apparatus and combustion apparatus (see figure 15.8) with ground glass joint flask, 50 cm^3, and 2 combustion tubes, Nuffield type small filter funnel and beaker to match

Access to:
Iron wire
Concentrated hydrochloric acid CORROSIVE
Concentrated sulphuric acid CORROSIVE
Calcium chlorate(I) (calcium hypochlorite), 65% available chlorine, granular IRRITANT
Calcium chloride, anhydrous granular IRRITANT
2 M sodium hydroxide CORROSIVE
Emery paper
Ceramic fibre
Pumice stone
Measuring cylinder, 10 cm^3
Dropping pipette
Petri dish and lid

Hazards

The products:
Iron(III) chloride and iron(II) chloride are irritant.
Chlorine gas is toxic and can cause severe lung damage.
Hydrogen chloride gas is corrosive and toxic and is extremely irritating

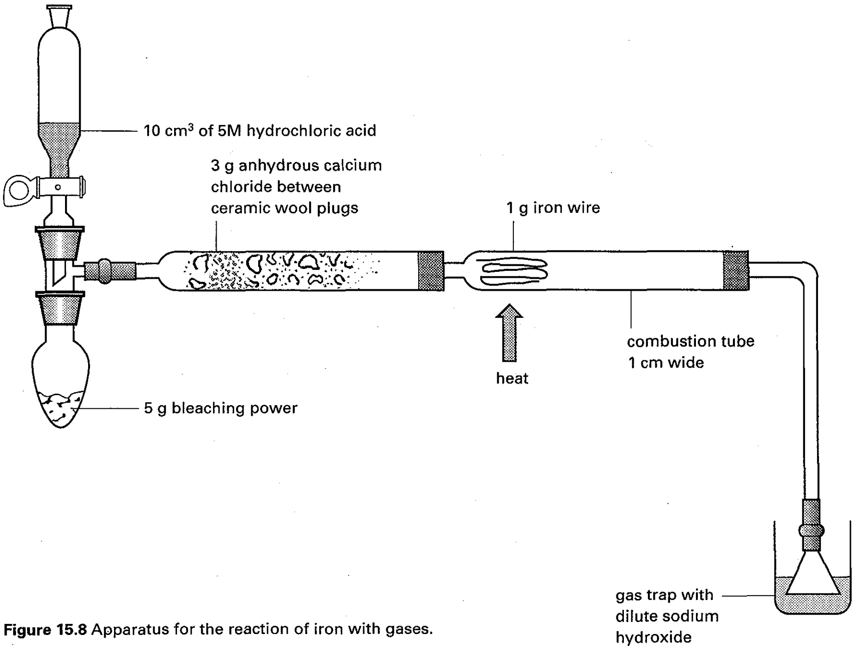


Figure 15.8 Apparatus for the reaction of iron with gases.

Procedure

Full details are given in the *Students' book.* The gas traps will retain all excess gas very efficiently, but dismantling the apparatus should be done in a fume cupboard if possible. Otherwise the operation of dismantling and moving the apparatus must be done speedily to minimize the escape of gases.

One answer to the Question is that the iron wire might be heated electrically.

Experiment 15.6b The properties of the chlorides of iron

Each group of students will need:
Eye protection
Test-tubes and rack
Watch glass
Access to:
Hydrocarbon solvent (petroleum spirit 120–160 °C) FLAMMABLE
0.1 M silver nitrate
2 M sodium hydroxide CORROSIVE
0.1 M potassium thiocyanate
If no products are available from experiment 15.6a:
Iron(III) chloride IRRITANT
Iron(II) chloride IRRITANT

Procedure

Full details are given in the *Students' book.* The products should behave as pure samples. Iron(III) chloride is very deliquescent so this experiment should follow on very quickly from its preparation.

ANSWERS TO THE STUDY TASK

1 They have the properties of salts: crystalline, soluble in water, solutions have the expected ionic reactions.
2 The solubility of iron(III) chloride in hydrocarbon solvent suggests that it is covalent, and the sublimation of iron(II) chloride suggests that it is also covalent; but the evidence available does not really lead to a firm conclusion.
3 Calculation of the Gibbs free energy change of the reactions gives the results:

$$Fe(s) + 2HCl(g) \rightarrow FeCl_2(s) + H_2(g) \qquad \Delta G^{\ominus} = -112 \text{ kJ mol}^{-1}$$

$$FeCl_2(s) + HCl(g) \rightarrow FeCl_3(s) + \tfrac{1}{2}H_2(g) \qquad \Delta G^{\ominus} = +63.4 \text{ kJ mol}^{-1}$$

15.7 The special properties of the transition elements

Timing About 1 hour.

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 d-block elements in which these elements have as many different oxidation numbers as possible.

It will also be useful to have an energy level display board (see Topic 3, figure 3.3) and 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 ionization energies was broken after calcium, and that the ten 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 15.9.

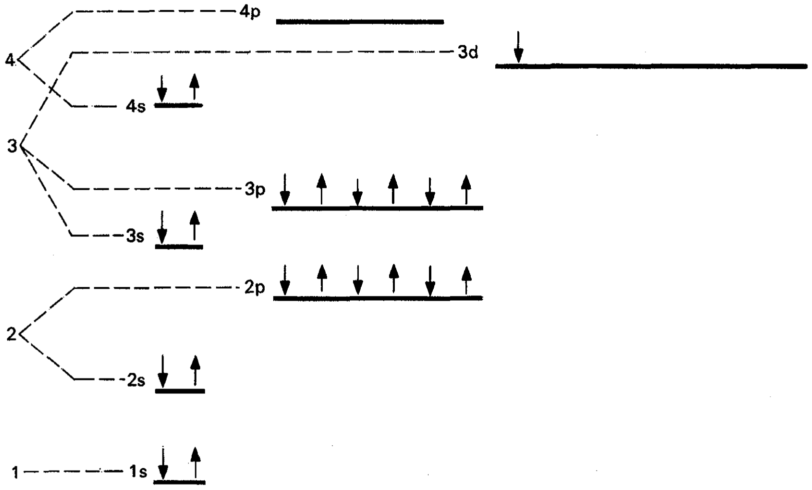


Figure 15.9 Electronic structure of scandium.

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 realize 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. The change of energy level with atomic number is shown in figure 15.10.

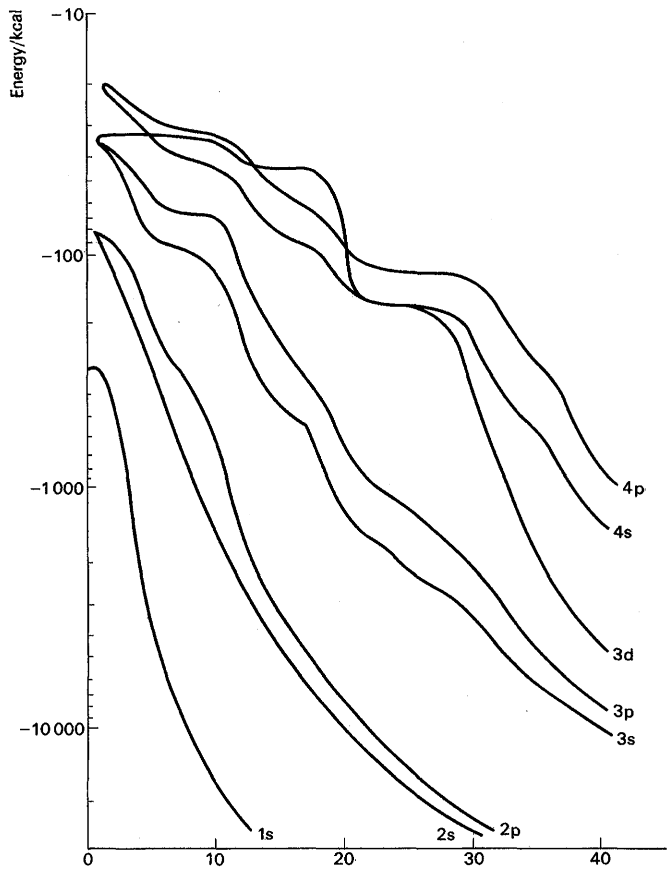


Figure 15.10 Change of energy level with atomic number (1 kcal = 4.2 kJ).

15.8 Study Task: Micronutrients

Timing Homework assignment.

In this Study Task students are asked to fill in a table and this could be set for homework. For more information see Frausto de Silva, J.J.R. and Williams, R.J.P. *The biological chemistry of the elements*, Oxford University Press, 1991.

Element	Why is it needed in plants?	What is the deficiency disease in animals?
Fe	to make chlorophyll	anaemia
Mn	enzymes, to reduce nitrate to amino acid	sterility and skeleton deformity
Zn	production of carbohydrates and fats	not stated, stored in the liver
Cu	promotes growth	anaemia and bone disorders
Mo	reduction of nitrates to amino acids	restricted growth
Co	not essential	‘pining’, pernicious anaemia

Answers to Questions in the *Students’ book*

A suggested mark allocation is given in brackets after each answer.

Review questions

15.1

a (I) and (IV) (2)

b According to the standard electrode potentials the manganate(VI) ions change into black manganese(IV) oxide and purple manganate (VI) ions.
The reaction is called disproportionation. (3)

c It should disproportionate into manganese(II) ions (colourless) and manganese(IV) oxide (black solid). (2)

d **i** Zn^{2+}, as there is no higher oxidation number of Zn.
Co^{2+}, as the electrode potential for oxidation to Co^{3+} is too highly positive. (2)

ii Chromium(II) ions in solution are very readily oxidized by the air to chromium(III) ions. (2)

iii Green (V^{3+}) to purple (excess of MnO_4^-). (2)

Total 13 marks

15.2

a The relevant electrode potentials are:
$Zn^{2+}(aq) \mid Zn(s)$ $E^{\ominus} = -0.76$ V
$Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt$ $E^{\ominus} = +0.77$ V
Application of the anticlockwise rule shows that Zn(s) should reduce $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$. (3)

b The use of sulphuric acid minimizes hydrolysis of the iron(II) ions. (1)

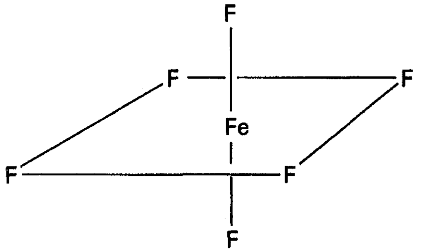
c The percentage of iron by mass is 23.2% (to 3 SF). (5)

Total 9 marks

15.3

a $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ (2)

b The shape should be octahedral.



(2)

c The oxidation number of iron in FeF_6^{4-} is +2. (1)

d The relevant electrode potentials are:
$I_2(aq), 2I^-(aq) \mid Pt$ $E^{\ominus} = +0.54$ V
$Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt$ $E^{\ominus} = +0.77$ V
Application of the anticlockwise rule shows that $Fe^{3+}(aq)$. should oxidize $I^-(aq)$ to $I_2(aq)$ and be reduced to $Fe^{2+}(aq)$. (3)

Total 8 marks

15.4

a It would turn from pink to green. (2)

b It would turn from green to pink since the hydrochloric acid reacts with the ammonia to give ammonium ions which are not ligands. (3)

c There would probably not be much change of colour despite the likelihood of edta replacing the water molecules as ligands, because both complexes are pink. (3)

d The entropy change for the reaction in which edta replaces water molecules is positive because six water molecules are being replaced by one molecule of edta. (2)

Total 10 marks

15.5

a –147.5 kJ mol^{-1} (2)

b Yes. (1)

c Solid silver chloride dissolves in aqueous ammonia. (2)

Total 5 marks

Examination questions

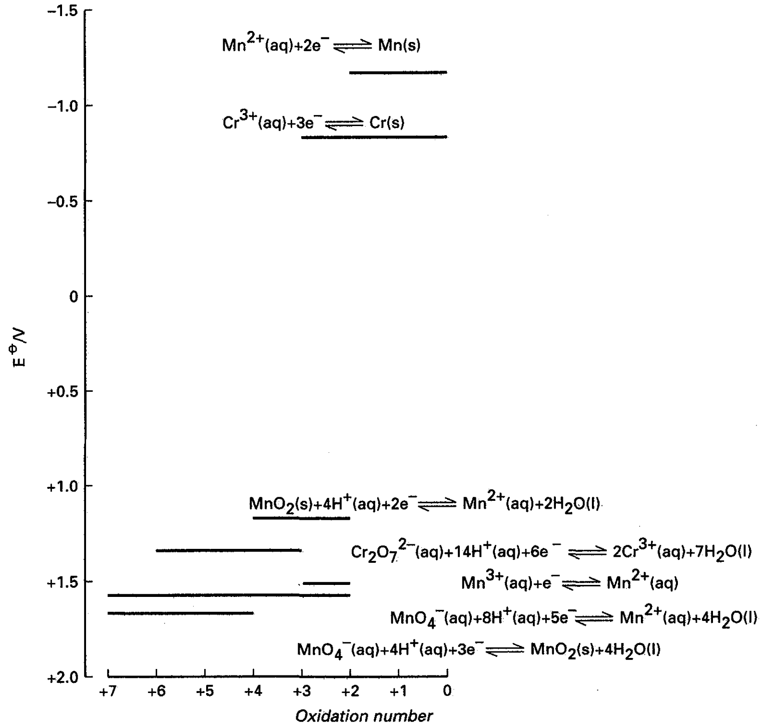
15.6

Mark by impression

a An acceptable oxidation chart for manganese would be:

+7	MnO_4^-	
+6	MnO_4^{2-}	
+5		
+4	MnO_2	
+3	Mn^{3+}	Mn_2O_3
+2	Mn^{2+}	MnO
+1		
0	Mn	

A diagram of $E^\ominus$ against oxidation number:



Data for reactions in alkaline solution are not appropriate e.g. Mn^{VI}/Mn^{IV} + 0.59 V, and Cr^{VI}/Cr^{III} – 0.13 V (6)

b From the diagram, the $Cr_2O_7^{2-}$(aq) ions can only be reduced to Cr^{3+}(aq) ions. Although further reduction to Cr(s) by Mn(s) is possible, in the presence of excess $Cr_2O_7^{2-}$(aq) this will not happen. Mn will be oxidized to Mn^{2+}(aq). The latter can then be oxidized further by $Cr_2O_7^{2-}$(aq) to MnO_2(s), but not to Mn^{3+}(aq).
Observable colour changes for this sequence would be:

- orange solution turning to green.
- brown/black precipitate appearing.

The relevant half-reactions are:

$$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s) \qquad E^{\ominus} = -1.19\ V$$

$$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l) \qquad E^{\ominus} = +1.23\ V$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\ominus} = +1.33\ V$$

The overall equations are:

$$Cr_2O_7^{2-}(aq) + 3Mn(s) + 14H^+(aq) \rightleftharpoons 2Cr^{3+}(aq) + 3Mn^{2+}(aq) + 7H_2O(l)$$

$$Cr_2O_7^{2-}(aq) + 3Mn^{2+}(aq) + 14H^+(aq) \rightleftharpoons 2Cr^{3+}(aq) + 3MnO_2(s) + 7H_2O(l)$$

(7)

c Both oxidizing agents can be used for the oxidation, but while the colour change for MnO_4^-(aq) to Mn^{2+}(aq) can be used as a clear end-point indicator, that for $Cr_2O_7^{2-}$(aq) to Cr^{3+}(aq) cannot. (2)

Total 15 marks

15.7

a **i** $Fe(s)\,|\,Fe^{2+}(aq)\,\vdots\vdots\,[O_2(g) + 2H_2O(l)], 4OH^-(aq)\,|\,Pt$ (2)
(or the other way round)
ii +0.84 V (or –0.84 V)

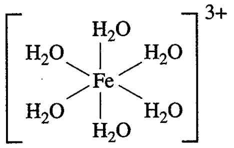
value (1)
sign and units (1)

iii $2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$
all species and state symbols correct (1)
balancing (i.e. 2Fe and $2Fe^{2+}$ or $2Fe(OH)_2(s)$) (1)

iv Any two from: temp not 298 K; pressure of O_2 not 1 atm; NaCl present; non-standard concentration. (2)

b **i** Contains dissolved CO_2 (1)
$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$
or $CO_2 + H_2O \rightarrow 2H^+ + CO_3^{2-}$ (1)
or $CO_2 + H_2O \rightarrow H_2CO_3$
ii pH = 5 so $[H^+(aq)] = 10^{-5}$ mol dm^{-3}
$\therefore [OH^-(aq)] = 10^{-9}$ (1)

c **i**



octahedral shape (1)

ii $Fe(H_2O)_6^{3+} \rightleftharpoons H^+ + Fe(H_2O)_5(OH)^{2+}$ [or $(OH^-)^{3+}$] (2)

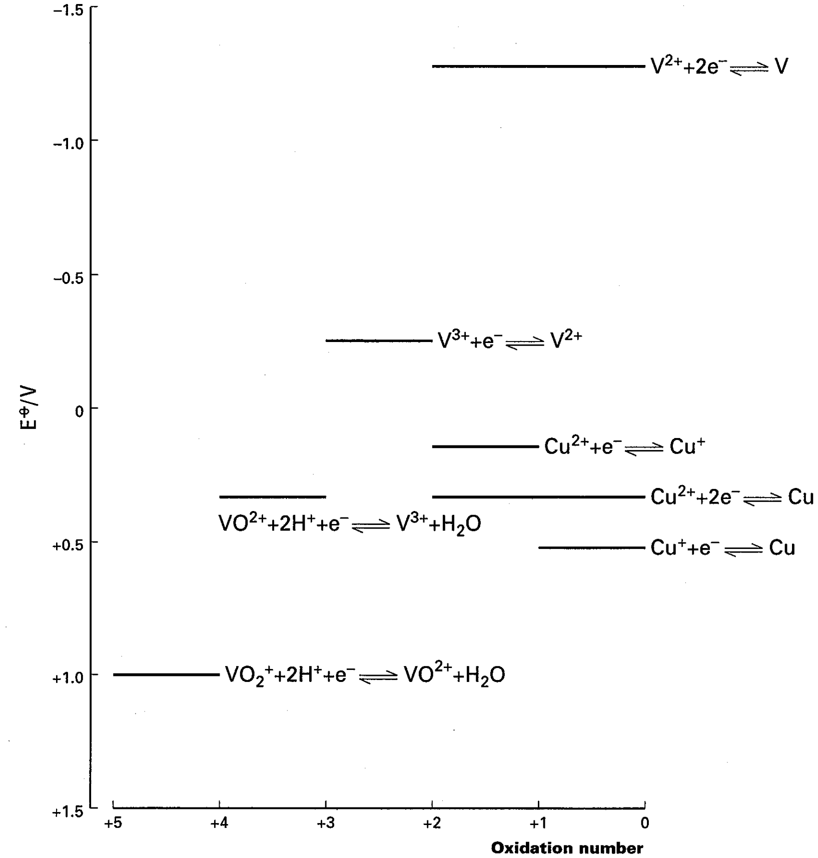
Total 14 marks

15.8

Mark by impression

Data from table 6.1 in the *Book of data*

$Cu^{2+}(aq), Cu^{+}(aq) \mid Pt$	$E^{\ominus} = +0.15$ V
$Cu^{2+}(aq) \mid Cu(s)$	$E^{\ominus} = +0.34$ V
$Cu^{+}(aq) \mid Cu(s)$	$E^{\ominus} = +0.52$ V
$V^{2+}(aq) \mid V(s)$	$E^{\ominus} = -1.18$ V
$V^{3+}(aq), V^{2+}(aq) \mid Pt$	$E^{\ominus} = -0.26$ V
$[VO^{2+}(aq) + 2H^{+}(aq)], [V^{3+}(aq) + H_2O(l)] \mid Pt$	$E^{\ominus} = +0.34$ V
$[VO_2^{+}(aq) + 2H^{+}(aq)], [V^{2+}(aq) + H_2O(l)] \mid Pt$	$E^{\ominus} = +1.00$ V



$V + Cu^{2+} \rightarrow Cu + V^{2+}$	$E^{\ominus} = 1.52$ V
$2V^{2+} + Cu^{2+} \rightarrow Cu + 2V^{3+}$	$E^{\ominus} = 0.60$ V
$2V^{3+} + 2H_2O + Cu^{2+} \rightleftharpoons Cu + 2VO^{2+} + 4H^{+}$	$E^{\ominus} = 0$ V

Colour changes from blue to blue/violet to blue/green to blue with red-brown precipitate forming.

No predictions about rate possible; can predict that first two reactions go to completion and third to equilibrium mixture.

Total 15 marks

15.9

Mark by impression

The data:

$V^{2+}(aq) + 2e^{-} \rightleftharpoons V(s)$	$E^{\ominus} = -1.18$ V
$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(s)$	$E^{\ominus} = -0.26$ V
$Sn^{2+}(aq) + 2e^{-} \rightleftharpoons Sn(s)$	$E^{\ominus} = -0.14$ V

$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$ $E^\ominus = +0.15$ V
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$ $E^\ominus = +0.34$ V
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{2+}(aq) + H_2O(l)$ $E^\ominus = +1.00$ V

VO_2^+(V) yellow, VO^{2+}(IV) blue, V^{3+}(III) green, V^{2+}(II) mauve, Sn^{2+}, Sn^{4+} colourless.

Tin should convert VO_2^+ to VO^{2+}, mixture turns from yellow to blue.

$Sn(s) + 2\,VO_2^+(aq) + 4H^+(aq) \rightarrow Sn^{2+}(aq) + 2VO^{2+}(aq) + 2H_2O(l)$
$E^\ominus = +\ 1.14$ V

Then tin should convert VO^{2+} to V^{3+}, mixture turns from blue to green.

$Sn(s) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow V^{3+}(aq) + 2H_2O(l) + Sn^{2+}(aq)$
$E^\ominus = +\ 0.48$ V

Both reactions may be kinetically hindered.

Tin should not be able to convert V^{3+} to V^{2+} under standard conditions ($E^\ominus$ is only – 0.12 V) but reaction may occur in non-standard conditions. (9)

The second reaction described above has E_{cell} nearest to 0.5 V

$Sn(s)\,|\,Sn^{2+}(aq)\,\vdots\vdots\,[VO^{2+}(aq) + 2H^+(aq)], [V^{3+}(aq) + H_2O(l)]\,|\,Pt$

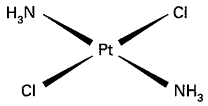
Diagram should show:

- Tin electrode dipping into 1.0 M Sn^{2+}(aq) solution.
- Platinum electrode dipping into equimolar mixture of V^{IV} and V^{III}, and a salt bridge. (6)

Total 15 marks

15.10

a **i** Dative covalent. (1)
ii Lone pair of electrons on the nitrogen 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 by displacing both chlorine atoms from *cis*-diplatin, but this is not possible with the other isomer where the chlorine atoms are not close enough together. (2)

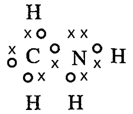
Total 9 marks

15.11

a Complex formation, coloured compounds. (2)
b Water, monodentate. (2)
c Tetrahedral and square planar. (2)
d Tetra-amminecopper(II). (1)
e Solution changes from blue through green to yellow.
as $CuCl_4^{2-}$ forms
more stable complex than with water
pale blue precipitate forms
of $Cu(OH)_2$
and royal blue solution
of $Cu(NH_3)_4^{2+}$
the most stable complex any six (6)

Total 13 marks

15.12

a **i**  (2)

ii H — C — H 109.5°, H — N — H 105.8° (105–100°). (2)

b Higher boiling point is due to hydrogen bonding between molecules. (2)

c **i** Two. (1)

ii Standard solutions of 1,2-diaminoethane and copper(II) sulphate can be mixed in definite proportions by volume and the colour intensity measured in a colorimeter; or titrated measuring the change in pH or e.m.f. (4)

Total 11 marks

15.13

Mark by impression

In 1.53 g of green crystals

$$\textbf{I}\ \text{mass Co} = 1.53 \times \frac{16.25}{100} = 0.25\ \text{g}$$

$$\textbf{II}\ \text{mass C} = 2.81 \times \frac{12}{44} = 0.77\ \text{g}$$

$$\text{mass H} = 0.81 \times \frac{2}{18} = 0.09\ \text{g}$$

$$\text{mass O} = 1.53 - (0.25 + 0.77 + 0.09) = 0.42\ \text{g}$$

so molar composition

Co	4.24	1
C	64.2	15.1
H	90	21.2
O	26.3	6.2

a Formula is $CoC_{15}H_{21}O_6$ or $Co(C_5H_7O_2)_3$

b $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

$$\text{moles of electrons} = \frac{24.4}{1000} \times 0.05 \times 2 = 2.44 \times 10^{-3}$$

$$\text{moles of cobalt} = 0.88 \times \frac{16.25}{100} \times \frac{1}{59} = 2.42 \times 10^{-3}$$

2 electrons per cobalt atom, so oxidation number of Co = + 3
Octahedral shape with Co — O bonds

Total 15 marks

15.14

Mark by impression

Information from the *Book of data*:
Oxidation numbers in compounds:

Scandium	+3
Titanium	+2, +3, +4
Vanadium	+2, +3, +4, +5
Chromium	0, +3, +6
Manganese	+2, +3, +4, +7
Iron	0, +2, +3

Electronic configurations:

Sc	$3d^1 4s^2$
Ti	$3d^2 4s^2$
V	$3d^3 4s^2$
Cr	$3d^5 4s^1$
Mn	$3d^5 4s^2$
Fe	$3d^6 4s^2$

Oxide	$\Delta G_f^{\ominus}$ /kJ mol^{-1}
Sc_2O_3	–1819.4
Ti_2O_3	–1434.3
V_2O_3	–1139.3
Cr_2O_3	–1058.1
Mn_2O_3	–881
Fe_2O_3	–742.2

All oxides stable with respect to elements.

Should suggest strongest bonds in scandium oxide

Students may comment on:

- possible change from ionic bonds to some covalency.
- lower ionization energies of scandium compared to iron or lattice energies.
- stability of oxidation states related to shells being empty or half-filled with complete set of data. (9)

For a complete set of data, greatest stability with respect to element for Sc. Reasons could include relative ionization energies, lattice energies and ionic/covalent character. (6)

Total 15 marks

TOPIC 16

Organic synthesis

Introduction

This 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.

Content

	Timing	*Students' book*
16.1	4 hours	Pages 474–484
16.2	4 hours	Pages 484–486
16.3	2 hours	Pages 486–492
Total about 2 weeks		

16.1 Devising a synthesis. Behaviour of nitriles; Study Task on synthetic routes; Study Task on mapping synthetic routes; Study Task on planning synthetic routes.
16.2 A two-step synthesis. Formation, and then nitration, of the ester methyl benzoate.
16.3 The identification of organic compounds. Combustion analysis of organic compounds; calculation of empirical formulae; identification of organic compounds from mass spectra, infra-red spectra and chemical tests.

Objectives

1 To map synthetic routes between functional groups and use the maps to solve significant synthetic problems.
2 To introduce students to the behaviour of the nitrile functional group.
3 To carry out a two-step synthesis and develop experimental skills.
4 To develop an understanding of how organic molecular formulae are determined by calculation from combustion data, analysis of mass spectra and infra-red spectra, and chemical tests.

16.1 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.

The first section on carbon-carbon bond-forming reactions introduces the reactions of nitriles because of their value in increasing by one the number of carbon atoms in a molecular chain. Students are then introduced to the idea of **intermediate** and **target molecules**. The strategy of **working backwards** is emphasized as the procedure to use when constructing synthetic routes.

Study Task: Some synthetic routes

Students are presented with three problems and they are led through them in simple steps.
Using the strategy of working backwards, the overall answers are:

1 $CH_3CH_2CH_2CO_2H \xleftarrow{\text{oxidation}} CH_3CH_2CH_2CH_2OH \xleftarrow{\text{substitution}} CH_3CH_2CH_2CH_2Br$

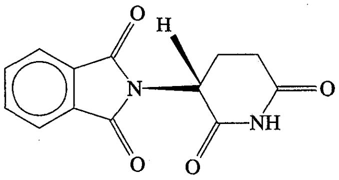
2 $CH_3CH_2CH_2CO_2H \xleftarrow{\text{hydrolysis}} CH_3CH_2CH_2CN \xleftarrow{\text{substitution}} CH_2CH_2CH_2Br \xleftarrow{\text{substitution}} CH_3CH_2CH_2OH$

3 $CH_3CH_2CHBrCH_2Br \xleftarrow{\text{addition}} CH_3CH_2CH = CH_2 \xleftarrow{\text{dehydration}} CH_3CH_2CH_2CH_2OH$

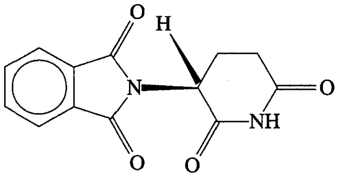
Study Task: Mapping synthetic routes

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. They are repeated here for teachers to photocopy if they wish.

Students are not expected to learn how to synthesize different isomers. The ability to synthesize different isomers is mentioned in connection with the drug thalidomide and students are asked to identify the chiral centre in figure 16.5 in the *Students' book.* The isomers are shown in figure 16.1. 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).



R(+) is safe and effective
against sickness in pregnancy



S(–) is a mutagen and
causes birth defects

Figure 16.1 The isomers of thalidomide. R(+) is safe and effective against morning sickness, S(-) is a mutagen and causes birth defects.

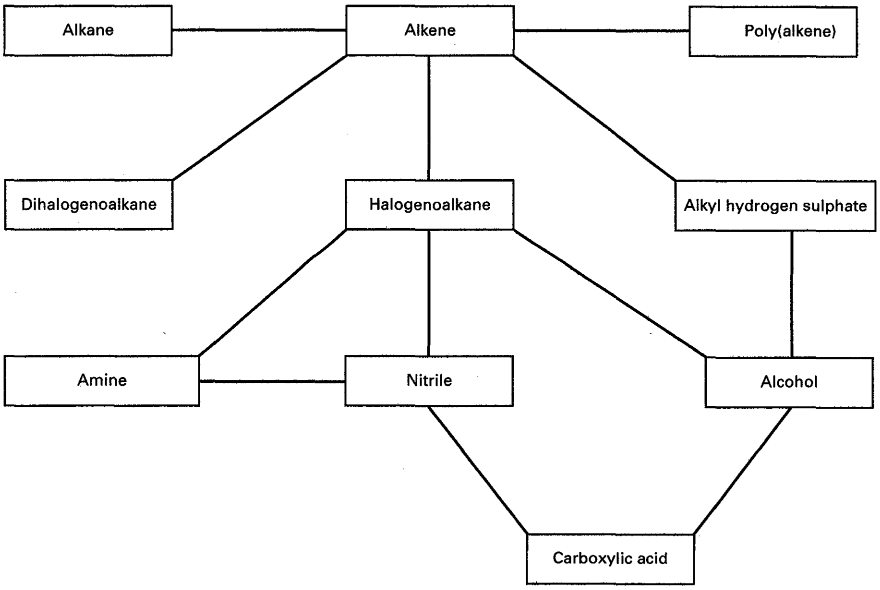


Figure 16.2

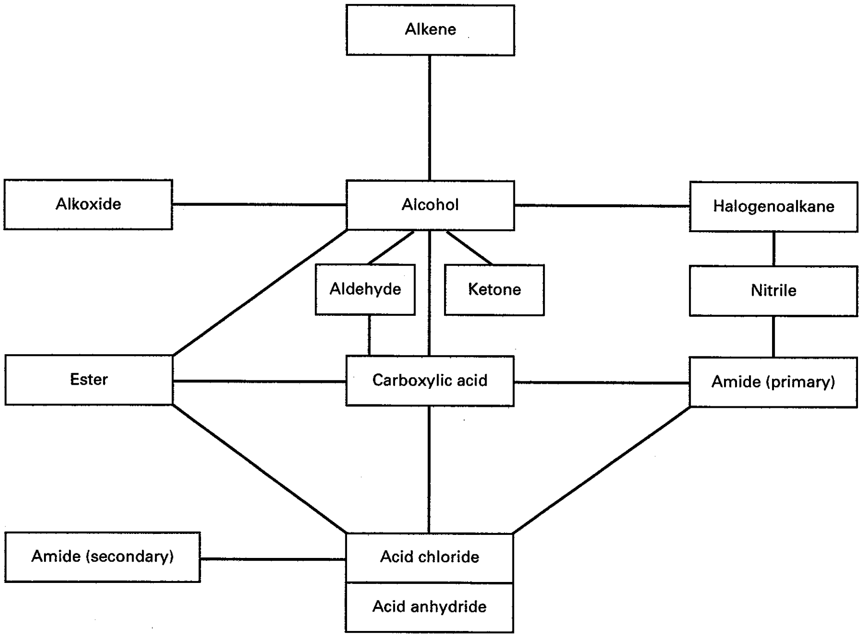


Figure 16.3

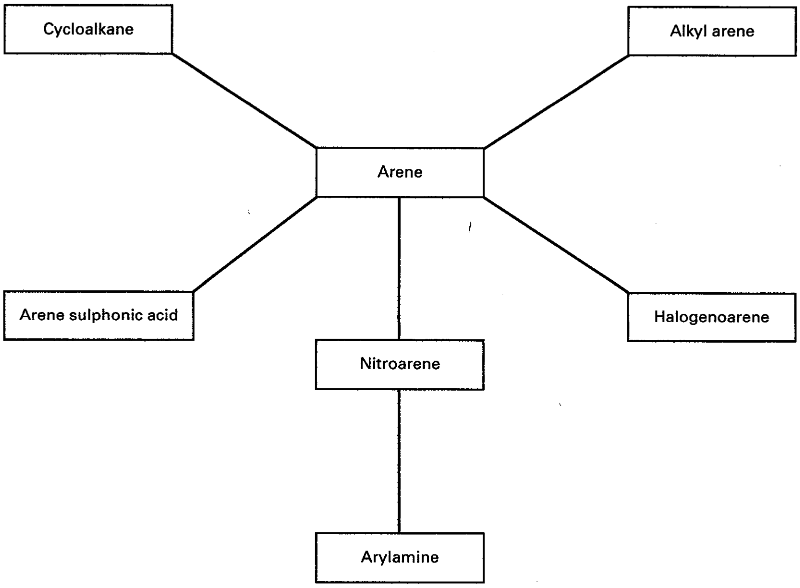


Figure 16.4

Study Task: Planning synthetic routes

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 Study Task 2.

They should be able to produce the following answers to the problems:

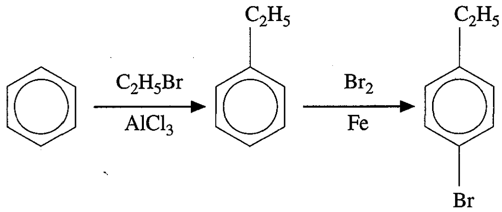
1 **a** $CH_3CH_2OH \xrightarrow{Al_2O_3} CH_2 = CH_2 \xrightarrow{H_2/Ni} CH_3CH_3$

b $CH_3CH_2OH \xrightarrow{Na_2Cr_2O_7/acid} CH_3CO_2H \xrightarrow{ethanol/acid} CH_3CO_2CH_2CH_3$

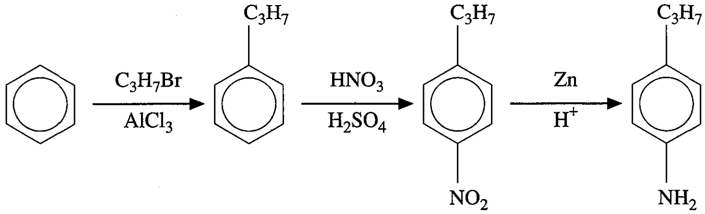
c $CH_3CH_2OH \xrightarrow{Na_2Cr_2O_7/acid} CH_3CO_2H \xrightarrow{NH_3/\,heat} CH_3CONH_2$

d $CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br \xrightarrow{NH_3} CH_3CH_2NH_2$

2 **a**



b

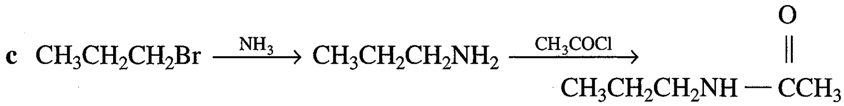


COMMENT

In this question students are told to assume that substitution occurs with the 4-position.

3 **a** $CH_3CHBrCO_2H \xrightarrow{KOH} CH_3CHOHCO_2H \xrightarrow{Na_2Cr_2O_7/acid} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CO_2H$

b $CH_3CHOHCO_2H \xrightarrow{HBr} CH_3CHBrCO_2H \xrightarrow{NH_3} CH_3CHNH_2CO_2H$



c $CH_3CH_2CH_2Br \xrightarrow{NH_3} CH_3CH_2CH_2NH_2 \xrightarrow{CH_3COCl} CH_3CH_2CH_2NH-\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

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.

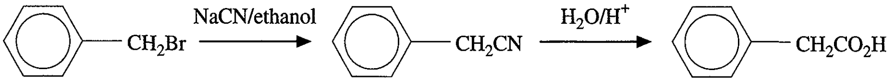
a $CH_3CH_2CH = C(CH_3)CH_2CH_2CH_3 \xrightarrow{HBr}$

$CH_3CH_2CHBrCH(CH_3)CH_2CH_2CH_3 \xrightarrow{KOH(aq)}$

$CH_3CH_2CH(OH)CH(CH_3)CH_2CH_2CH_3$

b $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{Na_2Cr_2O_7/acid} CH_3CH_2CH_2CH_2CO_2H$

c



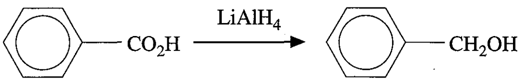
d i $CH_3CO_2H + HOCH_2CH_2CH(CH_3)CH_3$

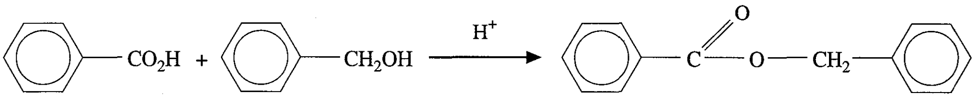
ethanoic acid 3-methylbutan-1-ol

d ii $CH_3CH_2CH_2CO_2H + CH_3(CH_2)_5CH_2OH$

butanoic acid heptan-1-ol

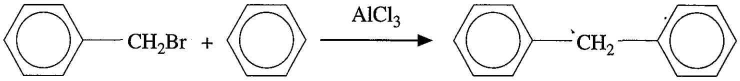
d iii



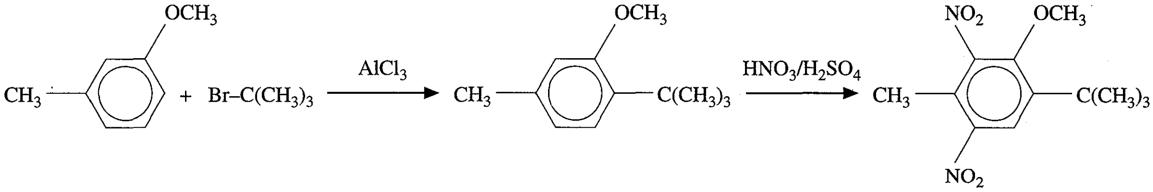


5 This set of questions deals with compounds that are used in perfumes.

a

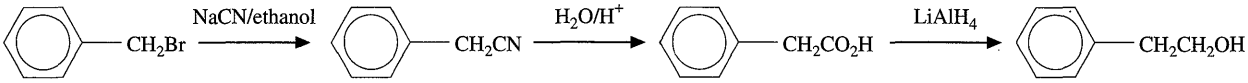


b

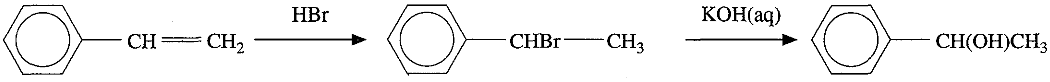


Nitration followed by alkylation is equally acceptable. Students are not expected to be familiar with the position of subsitution on the benzene ring or oxidation problems.

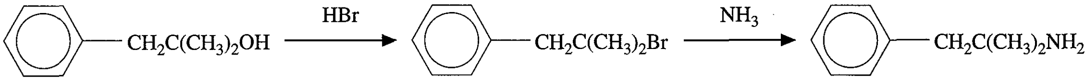
c



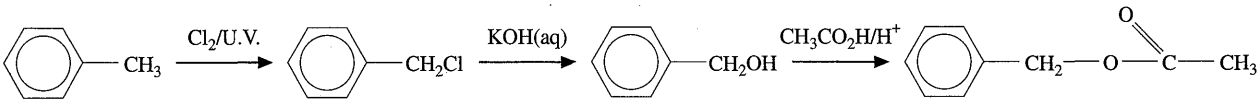
d



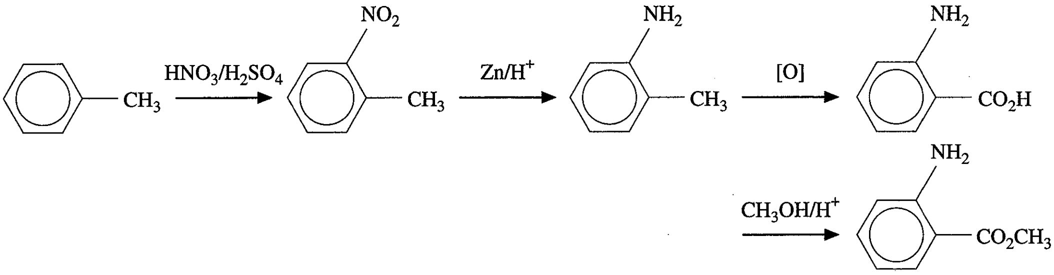
e



f i



f ii



16.2 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 16.2 The synthesis of methyl 3-nitrobenzoate in two steps

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

Procedure

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

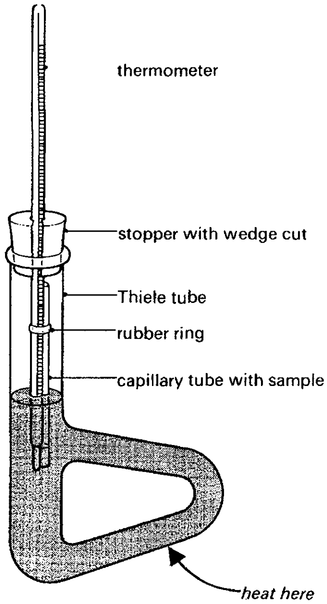


Figure 16.5 The Thiele melting point apparatus.

Step 2 The nitration of methyl benzoate

Each group of students will need:
Eye protection
4 conical flasks, 100 cm^3
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
Ultra-violet 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 OXIDIZING
Concentrated sulphuric acid, 12 cm^3 CORROSIVE

⚠ Hazards

The ultra-violet lamp should be arranged so that students cannot look directly at the light source.

Ethoxyethane (ether) is extremely flammable and can ignite at 160 °C.

Procedure

Full instructions for this preparation are given in the *Students' book.*

The melting point apparatus illustrated in figure 16.5 and in the *Students' book* is the Thiele type filled with dibutyl benzene-1,2-dicarboxylate (dibutyl phthalate). Other forms of melting point apparatus are, of course, also acceptable.

Ether is dangerously flammable; there should be no naked flames anywhere in the laboratory when it is being used.

If an ultra-violet lamp is used it should be correctly shielded, and students must be warned not to look directly at the source of the light.

The infra-red absorption spectrum of methyl 3-nitrobenzoate is given in figure 16.6.

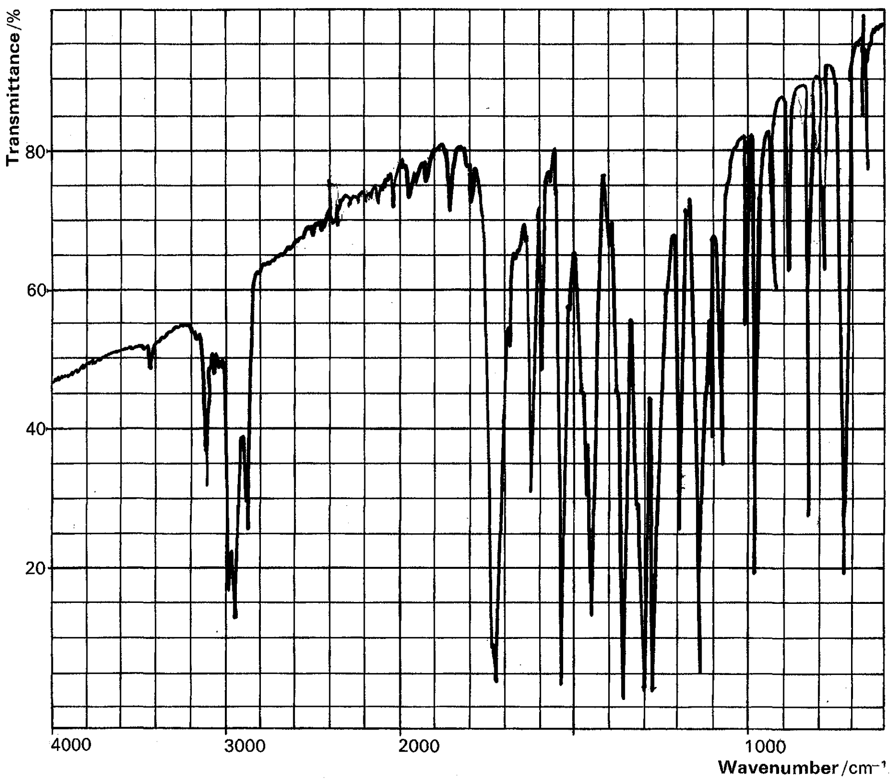


Figure 16.6 The infra-red spectrum of methyl 3-nitrobenzoate.

16.3 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 this to 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 and infra-red spectra together with chemical tests as an approach to the full determination of structural formulae, and hence the identity of the compound in question.

Experiment 16.3 The identification of organic compounds

Each group of students will need:

Eye protection

Combustion spoon

Test-tubes and rack
Access to:
Bromine water CORROSIVE
1 M sodium carbonate solution
0.1 M sodium dichromate(VI) solution IRRITANT
1 M sulphuric acid IRRITANT
Unknown A (benzoic acid)
Unknown B (propan-2-ol) HIGHLY FLAMMABLE
Unknown C (*N*-phenylethanamide, acetanilide) HIGHLY FLAMMABLE, HARMFUL
Melting point apparatus
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 infra-red spectrum – see figure 16.11 in the *Students' book.*
4 d 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 infra-red spectrum – see figure 16.12 in *Students' book.*
5 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 infra-red spectrum – see figure 16.13 in the *Students' book.*
5 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

Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

16.1

i Homolytically and **ii** heterolytically.
i Free radicals, **ii** nucleophiles, and **iii** electrophiles.
i Substitution, **ii** addition, and **iii** elimination.

1 mark each (8)
Suitable examples (8)
Total 16 marks

16.2

a Free radical substitution. (2)
b Electrophilic addition. (2)
c Electrophilic substitution. (2)
d Oxidation. (1)
e Nucleophilic addition. (2)
f Elimination. (1)
g Nucleophilic substitution (addition–elimination). (2)

Total 12 marks

16.3

a React with HBr (from KBr + concentrated H_2SO_4). Nucleophilic substitution. (2)
b React with hot, concentrated alcoholic solution of KOH. Elimination. (2)
c Reflux with an alcoholic solution of NaCN. Nucleophilic substitution. (2)
d React with CH_3OH and concentrated H_2SO_4 catalyst. Esterification (nucleophilic substitution). (2)
e React with $LiAlH_4$. Reduction. (2)

Total 10 marks

16.4

a 2-methylbutan-1-ol. (1)

b **i** $CH_3—CH_2—CH(CH_3)—CH_2I$ (1)

ii KI and phosphoric(v) acid. (1)

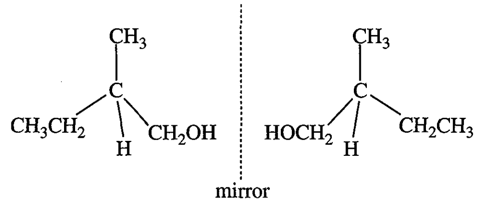
iii $CH_3—CH_2—CH(CH_3)—CH_2NH_2$
or $CH_3—CH_2—CH(CH_3)—CH_2NH_3^+I^-$ (1)

iv $(CH_3—CH_2—CH(CH_3)—CH_2)_2NH$
or $(CH_3—CH_2—CH(CH_3)—CH_2)_3N$
or $(CH_3—CH_2—CH(CH_3)—CH_2)_4N^+I^-$ (2)

c **i** Oxidize with $Na_2Cr_2O_7/H_2SO_4$ (2)

ii $LiAlH_4$ (1)

d **i**



(2)

ii The carbon atom attached to the $—CH_2OH$ group is chiral. (1)

Total 12 marks

16.5

a B Pass vapour over hot Al_2O_3 or treat liquid with phosphoric(v) acid.

C $Na_2Cr_2O_7/H_2SO_4$.

F Na.

I CH_3CO_2H and concentrated H_2SO_4 catalyst; CH_3COCl or $(CH_3CO)_2O$. (4)

b A Esterification. (Nucleophilic substitution, in fact, addition–elimination.)

B Elimination.

C Oxidation.

I Esterification. (4)

c Formation of F. (1)

d Aqueous sodium hydroxide. (1)

e $CH_3—CH(OH)—CO_2^-NH_4^+$
Heat slowly to dehydrate. (2)

f G is formed by esterification between two molecules of 2-hydroxypropanoic acid. (1)

g Negative test with Benedict's reagent. (1)

h **i** $CH_3CHBrCO_2H$ or $CH_2BrCH_2CO_2H$ (2)

ii $CH_2=CHCO_2H + H\overset{\curvearrowright}{—}Br \rightarrow CH_3C^+HCO_2H + Br^-$
$\rightarrow CH_3CHBrCO_2H$ (2)

Total 18 marks

16.6

A	Butan-1-ol	$CH_3-CH_2-CH_2-CH_2OH$	(2)
B	Butanal	$CH_3-CH_2-CH_2-CHO$	(2)
C	But-1-ene	$CH_3-CH_2-CH=CH_2$	(2)
D	2-iodobutane	$CH_3-CH_2-CHI-CH_3$	(2)
E	Butanone	$CH_3-CH_2-CO-CH_3$	(2)
			Total 10 marks

16.7

A	CH_3CO_2H	(2)
B	$CH_3CO_2C_2H_5$	(2)
C	CH_3CONH_2	(2)
D	CH_3CN	(2)
E	$CH_3CH_2NH_2$	(2)
		Total 10 marks

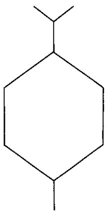
Examination questions

16.8

a	**i** Acidified $Na_2Cr_2O_7$. Oxidation.	(2)
	ii CH_3COCl. Esterification.	(2)
b	Any two suitable reactions.	(4)
c	By recrystallizing from a suitable solvent (hot water).	(1)
d	The direct route: only CO_2 is consumed.	(2)
e	Disprin is fully ionized.	(1)
f	Plastics.	(1)
		Total 13 marks

16.9

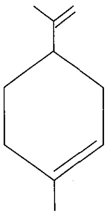
a 2 moles. (1)

b  (1)

c By adding 2 moles of HCl. (1)

d By refluxing with aqueous NaOH. (1)

e **i** Tertiary alcohol groups would not be oxidized without destruction of the molecule. (2)

ii  (but other dienes are possible) (2)

Total 8 marks

16.10

a Infra-red spectroscopy and any suitable chemical reaction. (2)

b A reducing agent such as $NaBH_4$. (2)

c By vapour phase reduction with H_2/Ni. (2)

d One OH group has phenolic reactions and the other has the reactions of an alcohol. A good list of reactions is expected. (6)

e Radioactive labelling of one of the carbon atoms in ethanoic acid, followed by biosynthesis and destructive analysis of the steroid. (2)

Total 14 marks

16.11

a i (1)

C	H	O
= 70.5/12	= 5.9/1	= 23.6/16
= 5.9	= 5.9	= 1.48
= 4	= 4	= 1

so empirical formula is C_4H_4O. (1)

ii C_4H_4O has molar mass of 68 g mol^{-1} and parent ion peak is mass 136 (1)

so molecular formula is $C_8H_8O_2$. (1)

b

136	$C_8H_8O_2^+$
105	$C_7H_5O^+$
91	$C_7H_7^+$
77	$C_6H_5^+$

(one less mark if all positive charges missing) (4)

c A Phenylethanoic acid or a methylbenzoic acid.

B Methylbenzoate

Reasonable isomer for **A**. (1)

Benzene rings. (1)

Ester side chain. (1)

d pH test; hydrolysis by acid or alkali; reaction with acyl chloride; etc. (2)

Total 13 marks

16.12

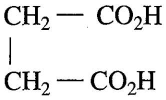
Brief account of infra-red spectra. (3)

Compound **B**

C	H	O
= 40.7/12	= 5.1/1	= 54.2/16
= 3.39	= 5.1	= 3.39
= 2	= 3	= 2

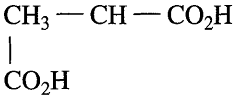
Molar mass = 118 g mol^{-1} so $C_4H_6O_4$

Acidic so $C_2H_4(CO_2H)_2$



$$\begin{array}{l} CH_2-CO_2H \\ | \\ CH_2-CO_2H \end{array}$$

or



$$\begin{array}{l} CH_3-CH-CO_2H \\ | \\ CO_2H \end{array}$$

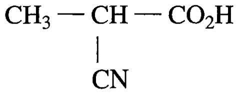
Compound **A**

Acidic so $C_3H_4N(CO_2H)$

Functional group hydrolysed by acid to carboxylic group

so $C_2H_4(CN)(CO_2H)$

Optically active so



$$\begin{array}{l} CH_3-CH-CO_2H \\ \quad\quad\;\; | \\ \quad\quad\; CN \end{array}$$

(9)

Infra-red spectrum of **A**

Bond	Wavenumber
C — H stretch	2900 cm^{-1}
C — H bend	1400 cm^{-1}
C = O stretch	1700 cm^{-1}
O — H stretch	3300–2500 cm^{-1}
C ≡ N stretch	2250 cm^{-1}

(3)

Total 15 marks

16.13

Mark by impression

C	H
= 85.7/12	= 14.3/1
= 7.1	= 14.3
= 1	= 2

Molar mass = 70 g mol^{-1}

Hence molecular formula **X** is C_5H_{10}

Infra-red peaks indicate this is an alkene, so possible isomers of **X**:

$CH_3-CH_2-CH_2-CH=CH_2$

$CH_3-CH_2-CH=CH-CH_3$

$CH_3-CH_2-C(CH_3)=CH_2$

$CH_3-CH=C(CH_3)-CH_3$

$CH_3-CH(CH_3)-CH=CH_2$

(plus *cis*- and *trans*- isomers) (6)

Y could be a variety of cycloalkanes.
Chemical properties might include:

- Addition (at least 3 examples)
- Oxidation
- Polymerization
- Combustion.

All with reaction conditions. (8)
Differences in physical properties are expected but not normally chemical differences. (1)

Total 15 marks

16.14

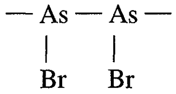
Mark by impression

A good answer should suggest at least five properties and describe them in considerable detail or describe at least eight properties in lesser detail, without making any serious chemical errors.

- Solubility in water: salt plus possibility of hydrogen bonds so 'likely' to be soluble; acid solution formed.
- Likely to be less soluble in acid conditions (although ionic $—NH_3^+Cl^-$) than in alkali when it would form phenoxide ions.
- Infra-red spectrum

C — H stretching vibration arene		3030
C — H bending vibration	1 H atom	880
	2 H atoms	830
N — H stretching vibration		3500–3300
O — H stretching vibration		3750–3200
C ═ C stretching vibration arene		1600 1580 1500 1450

- Halogens
  i Substitution in benzene rings
  ii Addition to As ═ As
  e.g.



$—\underset{Br}{\underset{|}{As}}—\underset{Br}{\underset{|}{As}}—$

- Combustion: smoky flame, products are CO_2, H_2O, N_2, As_2O_3, HCl.
- In alkaline solution, free amine groups so possibility of complex ions with Cu^{2+}.
- Other possibilities are: HNO_2 should form two diazo groups $—N_2^+Cl^-$ (Topic 17); colour due to delocalization of electrons; mass spectrometer trace; reaction with $FeCl_3$; reaction with Na; reaction with Na_2CO_3; reaction with ethanoic anhydride → ester; reaction with nitric acid.

Total 15 marks

16.15

Mark by impression

First compound:

$$\frac{17.2}{1000} \times 0.10 \text{ moles of alkali}$$

$$\text{so molar mass} = \frac{0.21 \times 1000}{17.2 \times 0.10} = 122.09 \text{ g mol}^{-1}$$

The functional group CO_2H has mass 45 which leaves 77 for the carbon chain, most likely to be C_6H_5, because of smoky flame, so the first compound is benzoic acid. (5)

Second compound:

C	H	O	N
= 32/12	= 6.7/1	= 42.7/16	= 18.7/14
= 2.67	= 6.7	= 2.67	= 1.33
= 2	= 5	= 2	= 1

so empirical formula is $C_2H_5O_2N$

Ninhydrin reaction suggests amino acid, but without chiral centre so $CH_2(NH_2)CO_2H$ (5)

and original amide is:

$C_6H_5 — CONH — CH_2 — CO_2H$ (3)

Preparation of amides by 2 methods. (2)

Total 15 marks

TOPIC 17

Nitrogen compounds

Introduction

This is the last Topic that students are intended to study as a whole as the final Topic on *Instrumental Methods* is expected to be used as support material at appropriate stages of the course. And just as the first Topic on iron included a poem by Roger McGough there is a poem on 'Nitrogen'.

In this Topic students are extending their knowledge of inorganic chemistry but the main emphasis is intended to be the application of theoretical ideas from previous Topics to some unfamiliar reactions of nitrogen compounds.

Content

	Timing	*Students' book*
17.1	2 hour	Pages 508–510
17.2	4 hours	Pages 510–512
17.3	5 hours	Pages 512–518
17.4	4 hours	Pages 518–522
17.5	Homework	Pages 522–525
Total about 3 weeks		

17.1 Structure and energetics in nitrogen compounds. Electronic structure of some nitrogen compounds, stability of some nitrogen compounds.
17.2 The properties of nitric acid. Nitric acid as an acid; nitric acid as an oxidizing agent; *investigation of nitrous acid.*
17.3 The properties of ammonia. The equilibrium reaction of ammonia with water; pH of ammonium compounds in solution; quantitative determination of ammonia by back-titration; entropy changes in the Haber process.
17.4 Azo-dyes. Diazotization and coupling reactions to form dyes; the dyeing of different fabrics.
17.5 Study Task. Dyestuffs – the origins of the modern organic chemical industry; *some suggestions for long-term investigations.*

Objectives

1. To carry out experimental studies on nitrogen compounds.
2. To interpret the reactions of nitrogen compounds using theoretical ideas from previous topics, especially redox and acid-base reactions.
3. To develop an understanding of the diazotization reaction and the behaviour of dyes.

17.1 Structure and energetics in nitrogen compounds

Timing About 2 hours.

Suggested treatment

Students can be introduced to the chemistry of nitrogen by reading on their own about those compounds of nitrogen which they have already met – ammonia, nitrogen dioxide, nitrites, and nitrates amongst others. The oxidation numbers of nitrogen in these compounds should be calculated and then the students should draw an oxidation number table. This can be added to during the Topic and will be useful for the experiments.

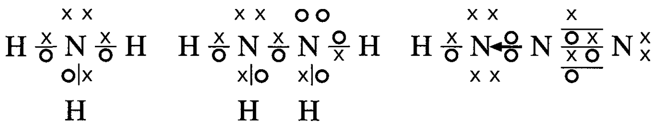
The reason for five electrons being available for bonding should be discussed, and also the fact that nitrogen normally achieves an octet of electrons in compounds (and in molecular nitrogen). It is useful to point out that the promotions of electrons which are discussed do not actually occur before a nitrogen reaction, just as the various stages in a Born–Haber cycle do not occur in turn. But such ideas are the basis of a useful model. During this discussion ideas concerning electronic structure and ionization energies, and covalent and dative covalent bonds should be revised.

The structure of the nitrogen molecule and its stability should be discussed. This can lead to a consideration of the special methods required to 'fix' atmospheric nitrogen in a form in which it can be assimilated by plants.

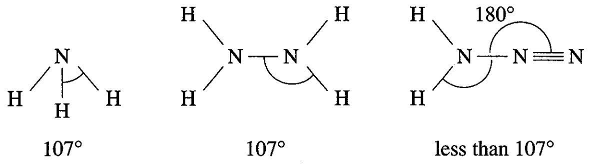
ANSWERS TO THE QUESTIONS

In the Questions students are intended to interpret some nitrogen chemistry by applying their understanding of dot-and-cross diagrams, bond angles, entropy and Gibbs free energy.

1 Dot-and-cross diagrams.



2 Displayed formulae with estimated bond angles.



3 Free energy change.

$3N_2H_4 \rightarrow 4NH_3 + N_2$

$\Delta G^{\ominus}_{\text{reaction}} = (-16.5 \times 4) - (149.2 \times 3)$

$= -514\ \text{kJ mol}^{-1}$ (to 3 SF)

Reaction is likely to 'go' at 298 K.

4a Bond energy data from table 4.6

$\text{N} = \text{N}\ 945.4\ \text{kJ mol}^{-1}$

$\text{N} — \text{N}\ 158$

$\text{H} — \text{N}\ 391$

$\text{H} — \text{H}\ 435.9$

$\Delta H_f^{\ominus}[\text{HN}_3(\text{l})] = \{1\tfrac{1}{2}E(\text{N} = \text{N}) + \tfrac{1}{2}E(\text{H} — \text{H})\} - \{E(\text{N} — \text{H}) + E(\text{N} — \text{N}) + E(\text{N} = \text{N})\}$

$= 1636.0 - 1494.4$

$= +142\ \text{kJ mol}^{-1}$

b $H_2(g) + 3N_2(g) \rightarrow 2HN_3(l)$
Entropy change in the system is likely to be negative.

c Entropy changes in both the surroundings (ΔH is +ve) and system (change from 4 molecules of gas to 2 molecules of liquid) are negative so the formation of hydrazoic acid from its elements is unlikely to be feasible.

5a

Entity	$\Delta G_f^\ominus$/kJ mol^{-1}
$NO(g)$	+86.6
$NO_2(g)$	+51.3
$N_2O_4(g)$	+97.8

$2NO + O_2 \rightarrow 2NO_2$ $\qquad \Delta G^\ominus_{reaction} = (51.3 \times 2) - (86.6 \times 2) = -70.6$ kJ mol^{-1}

$2NO_2 \rightarrow N_2O_4$ $\qquad \Delta G^\ominus_{reaction} = 97.8 - (51.3 \times 2) = -4.8$ kJ mol^{-1}

b The formation of nitrogen dioxide and its dimer are favoured but the low value for the dimer (less than −10) shows that it will predominate in an equilibrium.

17.2 The properties of nitric acid

Timing About 4 hours.

Suggested treatment

Experiment 17.2a Study of nitric acid as an acid

Each group of students will need:
Eye protection
5 test-tubes and rack
Dropping pipettes
Access to:
2 M nitric acid, **dilute** IRRITANT
Indicator solutions that are familiar to the students, but avoid ethanolic solutions in case students use concentrated acid in error
2 M sodium hydroxide CORROSIVE
2 M ammonia
1 M sodium carbonate
Oxides of metals that are familiar to the students (MgO, ZnO, CuO)
Carbonates that are familiar to the students (marble chips, $MgCO_3$, $ZnCO_3$, $CuCO_3$)
Metals in small pieces (Mg, Zn, Fe, Cu)

Hazards

The oxides of nitrogen which are produced are toxic by inhalation, and there is a danger of delayed effects.

Procedure

Students are asked to devise their own experiments to study the properties of nitric acid as an acid. Nothing more is necessary than the mixing of small quantities of pairs of reactants in test-tubes and the systematic recording of the results in a suitable table. Only the reactions with metals are likely to involve more than acid–base reactions: iron may become 'passive' and stop reacting, copper will produce oxides of nitrogen (CARE: toxic) rather than hydrogen.

Experiment 17.2b Study of nitric acid as an oxidizing agent

Each group of students will need:
Eye protection
5 test-tubes and rack
Dropping pipettes
Access to:
Copper turnings
Nitric acid, concentrated CORROSIVE
and to solutions of
0.1 M sodium sulphite (freshly prepared, to serve as sulphur dioxide solution) TOXIC
plus test reagent such as:
starch solution
0.1 M barium chloride HARMFUL
2 M sodium hydroxide CORROSIVE
0.1 M potassium iodide
0.1 M iron(II) sulphate

Hazards

A number of the products are harmful or toxic: oxides of nitrogen, sulphur dioxide and iodine.

Procedure

The students should predict that all four reducing agents can be oxidized by nitric acid producing copper ions, sulphate ions, iodine and iron(III) ions. Theoretically the nitrate ions could be reduced to ammonia.

In testing their predictions by simple test-tube experiments students should be expected to confirm the products by a suitable test. The failure to produce ammonia will be evident by the evolution of brown fumes of oxides of nitrogen (CARE: TOXIC) but in the next section students will discover that the reduction can be achieved in alkaline conditions.

Investigation 17.2c Study of nitrous acid

A good investigation would start by collecting information from the *Book of data* and drawing a redox potential chart for appropriate substances.

Nitrous acid and nitrites will act as both reducing and oxidizing agents and a well drawn redox potential chart should make this clear.

Reduction: potassium manganate(VII), sodium dichromate(VI), bromine water and hydrogen peroxide.

Oxidation: potassium iodide, iron(II) salts, and sulphur dioxide.

Two unusual reactions which students are unlikely to discover themselves are:

$$NH_3OH^+ Cl^- + NaNO_2 \rightarrow N_2O + 2H_2O + NaCl$$

and $NH_4Cl + NaNO_2 \rightarrow N_2 + 2H_2O + NaCl$
although the second reaction is included in experiment 10.1.

Hazards

Students must carry out and have approved their own risk assessment; sodium nitrite is oxidizing and toxic.

17.3 The properties of ammonia

Timing About 5 hours.

Suggested treatment

In this section students have an opportunity to revise their understanding of acid–base equilibria and apply their understanding to the chemistry of ammonia.

ANSWERS TO THE QUESTIONS

1 K_b will be unfamiliar to students but they should be able to apply their understanding of K_a to perform the calculation.
From the *Book of data:*
$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$ $K_b = 1.8 \times 10^{-5}$ mol dm^{-3}
Assuming $[NH_3]_{eq} = 0.1$ M
$[NH_4^+] = (1.8 \times 10^{-5} \times \frac{1}{10})^{\frac{1}{2}}$
$= 1.3 \times 10^{-3}$ mol dm^{-3} (to 2 SF)

2 $1.8 \times 10^{-5} = (\frac{1}{10} \times [OH^-])/\frac{1}{10}$
therefore $[OH^-] = 1.8 \times 10^{-5}$ mol dm^{-3}

3 From the *Book of data:*

Ion	K_a/mol dm^{-3}
phenylammonium	2.0×10^{-5}
ammonium	5.6×10^{-10}
ethane-1,2-diammonium	(about 10^{-10})
butylammonium	(about 10^{-11})

Alkyl groups stabilize the ion, producing stronger bases than ammonia; the benzene ring has the opposite effect and phenylamine is a weaker base than ammonia.

Experiment 17.3a Reactions of ammonia solution

Each group of students will need:
Eye protection
Test-tubes and rack
Dropping pipettes
Access to:
pH meter or Full-range Indicator

Apparatus for catalytic oxidation of ammonia (see figure 17.1)
Magnesium ribbon
and to solutions of
0.1 M sodium hydroxide
0.1 M ammonia
0.1 M ammonia/0.1 M ammonium chloride mixture
0.1 M butylamine HIGHLY FLAMMABLE and IRRITANT
0.1 M copper(II) sulphate
0.1 M zinc sulphate
8 M ammonia solution IRRITANT

Hazards

Ammonia gas is toxic by inhalation.

Procedure

1 The solution of bases should be fresh and prepared with some care so that the measurement of pH values gives reasonable results. Some typical values are:

Solution	**pH**
0.1 M NaOH	12.8
0.1 M NH_3	10.6
0.1 M NH_3/0.1 M NH_4Cl	9.1
0.1 M $CH_3(CH_2)_3NH_2$	11.6

2 The buffer action of NH_3/NH_4Cl should be tested by adding drops of very dilute acid and alkali and measuring the pH of the mixture.

3 Students should be able to suggest that the production of hydrogen from ammonium chloride solution and magnesium could be due to a greater hydrogen ion concentration than in water and therefore a faster rate of reaction.

4 Sodium hydroxide gives precipitates with Cu^{2+}(aq) and Zn^{2+}(aq) and, when sufficient sodium hydroxide solution is added, zinc hydroxide dissolves to give anions. Ammonia solution gives precipitates of hydroxides which dissolve in more ammonia solution to give complex cations.

5 The highly exothermic nature of the catalytic oxidation process can be demonstrated using the apparatus in figure 17.1, in a fume cupboard.

The ammonia solution should be no more concentrated than 8 M and oxygen should not be used in place of air.

Heavy gauge copper wire is heated to red heat and inserted in the conical flask. It will continue to glow spontaneously. Note that 24 gauge copper wire will melt and deep blue $Cu(NH_3)_4^{2+}$ ions form in the ammonia solution.

Brown fumes of nitrogen dioxide and white fumes of ammonium nitrate may be seen.

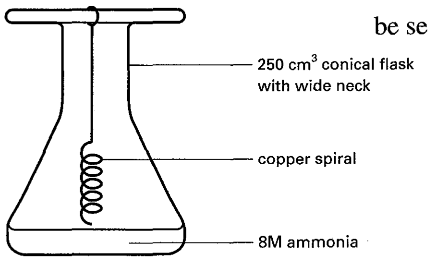


Figure 17.1 The catalytic oxidation of ammonia.

Experiment 17.3b To estimate the percentage of nitrogen in a fertilizer

Each group of students will need:
Eye protection
Apparatus as in figure 17.2
10 cm^3 and 25 cm^3 pipettes and safety filler
100 cm^3 volumetric flask
Titration apparatus

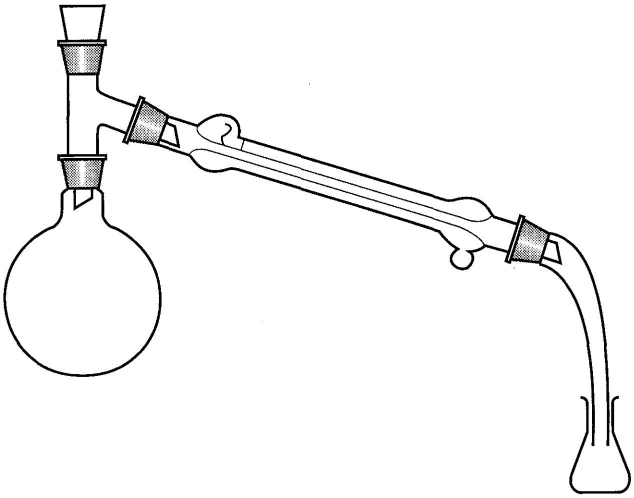


Figure 17.2 Apparatus for distillation.

Access to:
Nitrogen-based fertilizer, 0.2 g
Devarda's alloy, 0.5 g
0.100 M hydrochloric acid
1 M sodium hydroxide, 20 cm^3 IRRITANT
Red litmus paper
0.100 M sodium hydroxide
Phenolphthalein indicator solution

Hazards

Ammonia gas is toxic by inhalation.

Procedure

Full details are given in the *Students' book.* The redox potentials at pH 14 are:

$$3e^- + 2H_2O(l) + AlO_2^-(aq) \rightleftharpoons Al(s) + 4OH^-(aq) \qquad E = -2.87\ V$$

$$8e^- + 6H_2O(l) + NO_3^-(aq) \rightleftharpoons NH_3 + 9OH^-(aq) \qquad E = -2.35\ V$$

and in the non-standard conditions nitrate ions are reduced to ammonia by aluminium.

The formula for the aluminate ion is more correctly $H_2AlO_3^-(aq)$ but the simpler formula AlO_2^- is used in the *Students' book.* So the equation balances as:

$8Al(s) + 3NO_3^-(aq) + 5OH^-(aq) + 2H_2O(l) \longrightarrow 3NH_3(aq) + 8AlO_2^-(aq)$

The section concludes with an analysis of the Haber process in terms of the entropy changes as the reaction progresses and the pressure and temperature are varied. Students are not expected to recall this analysis but they should be able to follow the argument and apply the principles, from Topics 10 and 11, to similar systems when provided with information.

17.4 Azo dyes

Timing 4 hours plus homework

Suggested treatment

Experiment 17.4a The diazotization and coupling reactions

Each group of students will need:
Eye protection and gloves
3 beakers, 100 cm^3
3 beakers, 250 cm^3
Test-tubes and rack
Thermometer, 0–100 °C
Butylamine, 0.5 cm^3 HIGHLY FLAMMABLE, IRRITANT
2 M hydrochloric acid, 30 cm^3
Naphthalen-2-ol (2-naphthol), 3 g HARMFUL
2 M sodium hydroxide, 20 cm^3 CORROSIVE
Sodium nitrite, 1.5 g TOXIC
Ethyl 4-aminobenzoate (benzocaine), 0.5 g
Ice

Hazards

Dyes should be treated as both HARMFUL and IRRITANT and gloves worn when handling the solids and solutions. The selection of alternative amines must be risk assessed (see Association for Science Education *Topics in Safety*, 1988).

Procedure

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

In reactions with nitrous acid, ammonia produces nitrogen gas, alkylamines produce nitrogen and a mixture of alcohol, alkene, and nitroalkane, but arylamines produce relatively stable diazonium salts.

In the 'blank' diazotization reaction mixture, a pale yellow crystalline solid will separate on adding the naphthalen-2-ol solution, due to nitrosation of naphthalen-2-ol. The same product may be observed in the butylamine reaction mixture if an excess of sodium nitrite is present. Acidification quickly turns this into a black tar, but this should only be demonstrated in a 'throw-away' container.

The electrophile, NO^+, is considered to be the attacking group in conditions of high acidity and in a sequence of steps the ion $R - N^+ \equiv N$ is formed. Unless this ion is stabilized in some way a nitrogen molecule will be formed:

$$R-NH_2 \xrightarrow{NO^+} R-N^+\equiv N \rightarrow R^+ + N_2$$

The new ion R^+ will then take part in a variety of further reactions. In the case of arenes stabilization of $R-N^+\equiv N$ occurs by interaction involving delocalization with the benzene ring. The diazonium salts that are formed are useful reactive intermediates.

Experiment 17.4b The dyeing of different fabrics

Each group of students will need:
Eye protection and gloves
Dyebath (400 cm^3 beaker)
Tongs
Dyes mixture (Direct Red 23, Disperse Yellow 7, Acid Blue 40, 2:1:2 by weight), 0.05 g
25 cm^2 fabrics, e.g. cotton, nylon, cellulose ethanoate (acetate), polyester

Hazards

Dyes should be treated as both HARMFUL and IRRITANT and gloves worn when handling the solids and solutions.

Procedure

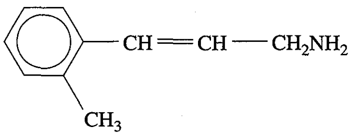
Full details are given in the *Students' book.* The mixture of three dyes, Direct Red 23, Disperse Yellow 7, and Acid Blue 40, has been selected to dye mainly one fabric in preference to other fabrics. Cotton is dyed red by Direct Red 23, polyester and cellulose ethanoate are dyed yellow by Disperse Yellow 7, nylon and wool are dyed green by a mixture of Acid Blue 40 and Disperse Yellow 7.

The experiment demonstrates how a knowledge of the structure of dyes and fabrics enables the chemist to dye successfully the wide variety of fabrics that are manufactured today.

17.5 Study Task: Dyestuffs – the origins of the modern chemical industry

This Study Task describes Perkin's innovative discovery of mauve but how the industrial initiative moved to Germany. There is also an elementary account of the origin of colour in dyes. For more information see Travis, T. 'Perkin and mauve', *Education in Chemistry*, **25,** pages 81–4, 1988.
Possible answers to the questions posed are:

1 Five structural formulae:



etc.

2 Molecular formula of mauve is $C_{26}H_{22}N_4Cl$.

3 Suggestions should include: arene ring structure
covalency of carbon, hydrogen and nitrogen
ionic bonding
single and double covalent bonds

In Topic 7 students are told that the benzene ring structure was not proposed until 1865.

Investigations

The investigations listed at the end of the topic could be used to stimulate library searches and planning rather than practical work as the time required would be extensive.

1 The Field Studies Council have published a booklet *Nitrate: Environment and Health.* Nitrate test strips are available from laboratory supply companies; one test strip uses the diazotization reaction and coupling to form a violet coloured dye.

2 A method of studying the effect of nitrate concentration on the growth of radishes is described in Hewitson, J. and Price, R. 'Plant mineral nutrition in the classroom: the radish, *Raphanus sativus L.* is a good plant for such studies, *School Science Review.* **76**, 274, September 1994. Further information is available from Science and Plants for Schools (SAPS), Homerton College, Cambridge CB2 2PH.
Telephone: 0223 411141, extension 233.

Individual radish seeds are grown in film canisters filled with a 1:1 mixture of silver sand and Perlite, fed through a hole in the bottom of the can. P and K at 5 mM is applied and N varied from 0.5–16 mM. Maximum growth after 14 days appears to be around 8 mM of N.

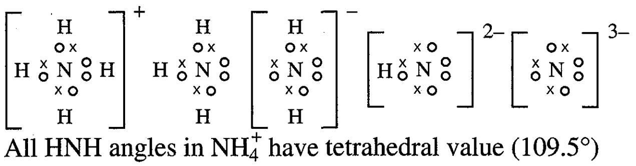
Answers to Questions in the *Students' book*

A suggested mark allocation is given in brackets after each answer.

Review questions

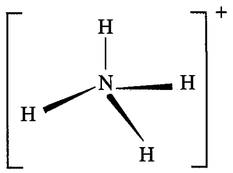
17.1

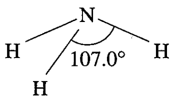
a



(2)

b All HNH angles in NH_4^+ have tetrahedral value (109.5°)



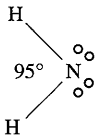


(2)

The HNH bond angles in NH_3 are smaller than those in NH_4^+ (107.0° against 109.5°).

The explanation is that lone pair/bond pair repulsion is more effective than bond pair/bond pair. The lone pair of electrons in NH_3 'pushes NH bonds away'.

c Any answer between 90° and 109.5° for HNH angle would be reasonable. (2)



d CH_5^+ not expected
The reason is that in CH_4 all the valency electrons are used in single bonds with H, and no lone pair is available, as it is in NH_3, for further bonding. (2)

Total 8 marks

17.2

a Low temperature (5–15 °C), excess acid, and $NaNO_2$ (2)
b **i** The energetic instability is because of the tendency to form the very stable molecule N_2 (2)
ii Diazonium salts are stabilized by delocalization with the benzene ring. (2)
c **i** The phenate ion has been formed under alkaline conditions. (1)
ii Electrophile. (1)
iii Substitution of H by the electrophile. (1)
d **i** Nitrogen is more electronegative than carbon and carries a full positive charge. The electrons of the azo group are delocalized with the benzene ring and electrons are withdrawn from it on account of the positive charge on the nitrogen atom. (2)
ii The H atom is normally substituted. N_2^+ is expected when diazonium salts react because of the stability of N_2 as a leaving group. (2)
iii There is nucleophilic attack by H_2O or OH^- at the C atom carrying the azo group. (2)
iv Iodobenzene by nucleophilic substitution. (1)

Total 16 marks

Examination questions

17.3

a Nitrous acid can disproportionate to NO and NO_3^- (1)
b Iodine and NO(g) (2)
c Bromide ions and nitrate ions. (2)
d Oxidizing agent in **b.** (1)
Reducing agent in **c.** (1)
e **i** Iodine and NO(g). (2)
ii Purple colour in the organic layer. (1)

Total 10 marks

17.4

a From the *Book of data*:
$E(N—N) = +158\ kJ\ mol^{-1}$
$E(N—H) = +391\ kJ\ mol^{-1}$
$E(N \equiv N) = +945\ kJ\ mol^{-1}$
$E(H—H) = +436\ kJ\ mol^{-1}$ (1)

Energy cycle:

$$\begin{tikzcd}
N_2(g) \arrow[d, "\Delta H_1"'] & + & 2H_2(g) \arrow[d, "\Delta H_2"'] \arrow[r, "\Delta H^{\ominus}_{f}"] & N_2H_4(l) \\
2N(g) & + & 4H(g) \arrow[ur, "\Delta H_3"'] &
\end{tikzcd}$$

(3)

$\Delta H_f^{\ominus} = \Delta H_1 + \Delta H_2 + \Delta H_3$

$= 945 + 2 \times 436 + [-158 - 4 \times 391]$

$= +95 \text{ kJ mol}^{-1}$ (2)

b *Mark by impression*

The *Book of data* gives information on two relevant physical properties:

- melting/boiling points
- very soluble in water.

Both of these are in line with what may be predicted from a comparison with ammonia, and should be linked to the structure of hydrazine and its ability to form hydrogen bonds.

Predictions of chemical properties could include:

- alkaline nature of solution
- salt formation with acids
- reaction with, e.g. alkyl halides to form alkylhydrazines
- reaction with oxygen
- complex ion formation

but other valid predictions are possible. (9)

Total 15 marks

17.5

a Milky suspension becomes clear (or less cloudy). (1)

b **i** The solution turns from orange (not yellow) to green. (1)

ii +6 (1)

iii Sulphuric acid or sulphate ion. (1)

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

formulae (1)
balancing (1)

c **i** Moles $S_2O_3^{2-} = \frac{11.6}{1000} \times 0.01$

$= 1.16 \times 10^{-4}$ (1)

ii Moles of I_2 which reacted with thiosulphate

$= \frac{1}{2} \times 1.16 \times 10^{-4} = 5.8 \times 10^{-5}$ (1)

iii Moles of I_2 left $= 5.8 \times 10^{-5} \times \frac{1000}{20} = 2.9 \times 10^{-3}$

Moles of I_2 at start $= 1 \times 0.005 = 5 \times 10^{-3}$

Therefore, moles of I_2 which reacted with sulphur dioxide

$= (5 \times 10^{-3}) - (2.9 \times 10^{-3}) = 2.1 \times 10^{-3}$ (1)

iv Therefore, moles of SO_2 in 10 g of charcoal

$= 2.1 \times 10^{-3}$ (1)

v Gas molecules interacting with surface atoms or molecules of a solid (1)

d **i** 1 mol $CaSO_4{\cdot}2H_2O = 40 + 32 + 64 + 36 = 172$ g

Moles per year $= (55\,000 \times 1000 \times 1000)/172 = 3.2 \times 10^8$ mol (1)

ii From equation $1SO_2 \rightarrow 1CaSO_4$

Therefore, moles of $SO_2 = 3.2 \times 10^8$

and volume of $SO_2 = 3.2 \times 10^8 \times 24$ dm^3

$= 7.68 \times 10^9 = 7.7 \times 10^9$ dm^3 (1)

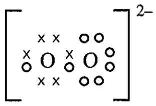
e Allow plaster products, soil conditioner, cement additive, school chalk, garden gnomes etc. (1)

Total 14 marks

17.6

a Lithium oxide or Li_2O (1)

ii



octets of electrons (1)

more detail (1)

iii Contains an unpaired electron or 7 electrons in outer shell (1)

b **i** Oxygen (1)

–1 to 0 and –1 to –2 (1)

ii Releases oxygen (1)

so risk of fire (1)

c **i** $2Li_2O_2 + 2CO_2 \rightarrow 2Li_2CO_3 + O_2$ or ÷ 2 (1)

ii Less mass for same effect (not less dense) (1)

iii Any three from:

Length of voyage; Number of people in space capsule

Volume of capsule; Activity of crew (amount of CO_2 produced/ O_2 needed); or any other suitable answer (3)

Total 13 marks

17.7

a **i** Ethanoyl chloride CH_3COCl

or ethanoic anhydride $(CH_3CO)_2O$ (2)

ii Sodium nitrite/hydrochloric acid or sulphuric acid or nitrous acid (1)

< 15 °C or ice bath (1)

iii Diazonium or diazo (1)

iv Structural formula of 4-methylphenol, or ionic form. (1)

b Any two from:

Need to bond to fabric; Must not change colour in air/light or on washing; Non-irritant to skin (context explained); Water soluble (context explained)

or other suitable answer (2)

Total 8 marks

17.8

Mark by impression

i Clear calculations of the quantities required

Iodobenzene 20 g = 20/204 moles ≈ 0.1 moles

Phenylamine 100/75 × 0.1 moles ≈ 0.14 × 93 g ≈ 13 g

Density =1.02 g cm–3 therefore 13 g ≈ 13 cm^3

Sodium nitrite 100/75 × 0.1 moles ≈ 0.14 × 69 g ≈ 10 g

Hydrochloric acid 2 × 100/75 × 0.1 moles ≈ 0.3 moles

= 50 cm^3 of 6 M etc.

Potassium iodide 100/75 × 0.1 moles ≈ 0.14 × 166 = 24 g

Solubility is 148 g in 100 cm3

Therefore ≈ 20 cm^3 of water required. (7)

ii Suitable description of apparatus required.

Good answers will probably include clear diagrams.

In the first stage reactants need to be mixed and kept cool.

In the second stage mixture needs to be refluxed. (5)

iii Separation and purification techniques:
T_m 242 K, T_b 461 K, density 1.83 g cm^{-3}
Good answers will suggest separating funnel, wash, dry and distillation. (3)

Total 15 marks

17.9

Mark by impression

Answers should include:

- interactions with water – pH values, salt formation
- reactions as a ligand
- reactions with electrophiles, for example halogenoalkanes and acyl chlorides
- reactions with nitrous acid.

Significant differences requiring some explanation are likely to include the less basic nature of arylamines, and the reaction of arylamines with nitrous acid.

When correct formulae and equations throughout (10)

Important industrial applications include:
formation of nylon by reaction of the amine group with a carboxylic acid (or acyl chloride) using appropriate monomers.
formation of azo-dyes from diazonium compounds using a coupling reaction. (5)

Total 15 marks

17.10

Mark by impression

Answers should match the question, covering the range, variety and detail required.
The different definitions can be justified by their appropriateness and ease of application to particular reactions.

About 3 marks for each example.
Total 15 marks

17.11

Mark by impression

Answers should use data as well as describing the reactions involved, Le Châtelier as well as equilibrium constants, free energy changes and activation energy is appropriate.
The investigation of alternative catalysts could be discussed.
Suggestions for the separation of ammonia could include liquefaction, absorption in water or even acid.

About 6 marks maximum for each problem.
Total 15 marks

17.12

Mark by impression

Answers should cover the points required for a standard risk assessment and should be related to substantial A-level experiments.
Hazards should be described precisely in 4 experiments involving 4 different substances requiring a variety of protective measures.

About 4 marks maximum for each experiment.
Total 15 marks

TOPIC 18

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. In particular information about instrumental methods that students may wish to use during investigations is collected here rather than described in the sections where the use of the various techniques is first met.

Content

Timing
No time 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 18.5 and 18.7 will require 1 hour.

18.1 Using a pH meter. The glass electrode; the reference electrode; calibration by the use of buffer solutions (see 3.5, 11.3–11.6, 12.1).
18.2 Using a conductivity meter. Comparison with pH meter for titrations (see 3.4).
18.3 Using a colorimeter. Selection of a filter; calibration (see 8.2, 15.4).
18.4 Using an electrical compensation calorimeter. Calculation of results (see 4.1, 6.2).
18.5 The mass spectrometer. How the spectrometer works; calculation of molar masses from mass spectra; interpretation of mass spectra of organic compounds (see Topics 7, 12, and 14.4, 16.3).
18.6 X-ray diffraction. Electron density maps (see 3.4, 6.1, 7.7, 15.1).
18.7 Infra-red spectrometry. How the spectrophotometer works; interpretation of infra-red spectra (see Topics 7, 12 and 16 and the *Book of data*, table 3.3).
18.8 Nuclear magnetic resonance spectroscopy. How NMR works (see the *Book of data*, table 3.4); the discovery of fullerenes.

Objectives

1 To provide information about the use of instruments, such as the pH meter, that students are likely to meet during their practical work.
2 To provide information about instruments such as the mass spectrometer which produces data that students will be expected to interpret.

18.1 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 laboratory demonstrations.

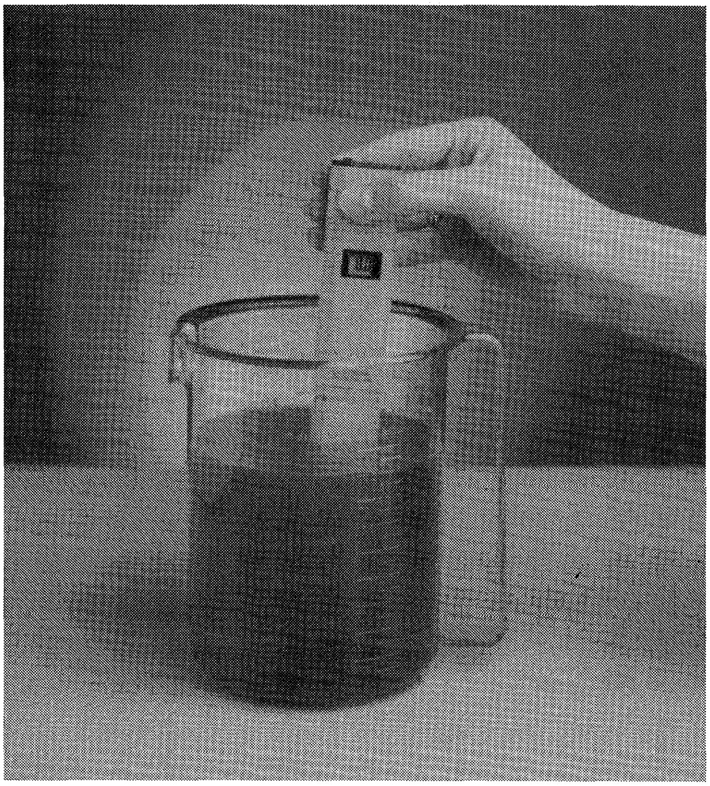


Figure 18.1 A 'dipstick' pH meter.

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 buffer solution rather than 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.

18.2 Using a conductivity meter

Measurement of the electrical conductivity of a solution is a useful alternative to pH measurement especially in acid-base titrations and in the study of rates of reaction. Students planning investigations could be encouraged to consider using a conductivity meter: the technique produces quantitative measurements which can be processed by information technology and the data require thoughtful evaluation of their accuracy and limitations. Experiment 3.4 uses a conductivity meter.

For more information see Betts, J. 'Acid–base titrations: an integrated physical chemistry experiment', *Education in Chemistry*, **19**, pages 51–3, 1982.

18.3 Using a colorimeter

A colorimeter can often be shared by several students because readings can be taken so quickly. This is particularly so in the study of rates of reaction; for example experiment 8.2b. *The kinetics of the reaction between iodine and propanone in acid solution* and experiment 15.5 *A kinetic study of the reaction between manganate(VII) ions and ethanedioic acid* can both be modified so that the reactions can be studied in a few minutes. Investigation 15.4d,*The formula of a complex* can be carried out successfully by estimating the relative colour intensities by eye but a better planned investigation would use a colorimeter. A procedure is described in this book in Topic 15.4.

Instructions for experiments 8.2b and 15.5 are given below and may be photocopied for use in the laboratory.

Alternative experiment 8.2b

The kinetics of the reaction between iodine and propanone in acid solution

You are going to investigate the reaction between iodine and propanone, the equation for which is:

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

Procedure

Put a few cm^3 of propanone in a test-tube and add a few drops of 0.05 M iodine solution. Observe what happens; then add about 5 cm^3 dilute hydrochloric acid and observe what happens.

You will know from earlier work that changes of concentration may affect the rate of reactions. We shall now investigate how the concentrations of propanone, of iodine, and of hydrogen ions affect the rate of this reaction. In order to do this we will determine the initial rate of the reaction starting with different concentrations of propanone, iodine, and hydrogen ions. A convenient method of determining the rate of this reaction is to measure the rate of disappearance of iodine using a colorimeter.

Use one of the mixtures set out in the table in such a way that the class covers the full range and the results can be compared. The volumes have been calculated so that in **a**, **b**, and **c** the concentrations of iodine and of hydrogen ions remain constant and that of propanone changes; in **a**, **d**, and **e** the concentrations of propanone and of hydrogen ions remain constant and that of iodine changes; and in **a**, **f**, and **g** the concentrations of propanone and iodine remain constant and that of hydrogen ions changes.

1 Put the iodine solution, acid, and water into a test-tube that fits the colorimeter, using a burette to deliver the correct quantity of each liquid.

2 Put the propanone solution into another test-tube, again measuring from a burette.

3 Add the propanone solution to the other solution, *stopper the test-tube*, mix the contents by rapid shaking, and start the clock.

4 Adjust the meter of the colorimeter to maximum with a tube of water in place at about 15 seconds before each minute.

5 Put the test-tube of the reaction mixture into the colorimeter and note the meter reading at each minute. Continue taking readings for up to 6 minutes.

6 Finally, find the meter reading at time zero by making up a mixture containing water instead of propanone solution and placing this in the colorimeter. Note the meter reading which is obtained.

	Volume of 2 M propanone /cm^3	**Volume of 0.01 M iodine (I_2) /cm^3**	**Volume of 2 M HCl /cm^3**	**Volume of water /cm^3**	**Total volume /cm^3**	**[propanone] /mol dm^{-3}**	**[I_2] /mol dm^{-3}**	**[H^+] /mol dm^{-3}**
a	2	2	2	4	10	0.4	0.002	0.4
b	4	2	2	2	10	0.8	0.002	0.4
c	6	2	2	0	10	1.2	0.002	0.4
d	2	4	2	2	10	0.4	0.004	0.4
e	2	1	2	5	10	0.4	0.001	0.4
f	2	2	4	2	10	0.4	0.002	0.8
g	2	2	6	0	10	0.4	0.002	1.2

Alternative experiment 8.2b continued

From the colorimeter readings determine the molarity of the solution with respect to iodine at various times, and then plot a graph with these molarities on the vertical axis against time (in seconds) on the horizontal axis.

The *rate of decrease of concentration* of iodine (which is positive) is equal to the *rate of change of concentration* of iodine (which is negative) multiplied by –1, and therefore the initial rate of the reaction can be found from the initial slope of the graph.

To measure the gradient, draw a tangent to the curve at time = 0, and determine the gradient of this tangent. Many of the graphs will approximate to straight lines, and it may not therefore be necessary to draw tangents to obtain the initial rate.

Compare the various rates for the different initial concentrations and so find out if and how the concentrations of the three substances affect the rate of the reaction. In order to compare the rates, we must have some idea of the errors involved. If two rates are:

a 1.3 ± 0.3 mol dm^{-3} s^{-1}, and
b 0.8 ± 0.2 mol dm^{-3} s^{-1}

then although inspection of 1.3 and 0.8 mol dm^{-3} s^{-1} might suggest that the reaction in **a** was nearly twice as fast as that in **b**, the errors indicate that **a** can be as low as 1.0 mol dm^{-3} s^{-1} and **b** as high as 1.0 mol dm^{-3} s^{-1}, so the rate in the two experiments may be the same. Comparison with other students' results will enable you to gain some idea of the errors, and, indeed, an average of several experimental results will give better figures with which to decide whether the rate is being affected.

Questions

Using the experimental results of the whole class, try to answer these questions:

1 Is the rate of the reaction affected by the concentration of propanone?
2 How is it affected?
3 Can you express this mathematically?
Plot a graph of rate against concentration of propanone.
4 Can you obtain a value for the constant in the mathematical expression in question **3** from this graph?
5 What are the units of this constant?
6 Is the rate of the reaction affected by the concentration of iodine?
7 Is it affected by the hydrogen ion concentration?
8 Can you express this mathematically?
9 Bearing questions **3** and **8** in mind, can you suggest an equation that describes how the rate of this reaction depends on the concentrations of reactants?
10 What are the units of the constant in your expression?

You will be discussing your answers to these questions in class, and arriving at a mathematical expression connecting the rate of the reaction at any instant with the concentration of the reactants present at that time.

Alternative experiment 8.2b

Teachers' guide

Each group of students will need:
1 stop-watch
Test-tubes and rack
Access to:
Colorimeter, with cuvettes
Access to communal burettes containing:
0.01 M iodine solution (2.54 g iodine and 8 g potassium iodide made up to 1 dm^3 with water) HARMFUL
2 M propanone (142 cm^3 propanone made up to 1 dm^3 with water) FLAMMABLE
2 M hydrochloric acid
Water

Procedure

These concentrations are for a specific colorimeter. Thus the iodine concentration may require modification for the colorimeter used. The propanone and/or acid concentrations may be modified so that the reaction proceeds more quickly or slowly if desired. It is worth reminding students that iodopropanone may make their eyes water, although, in these concentrations, it is unlikely to prove hazardous.

Students carry out an experiment showing that when iodine and propanone solutions are mixed, little happens; but on addition of hydrochloric acid, the solution loses its colour. As iodine is known not to react with hydrochloric acid, it must have reacted with the propanone, and the acid must have affected the rate of this reaction in some way.

How the concentrations of propanone, iodine, and hydrogen ions affect the rate of the reaction is then investigated. The initial rate is found for varying concentrations of propanone, iodine, and hydrogen ions. It is important to note that only the *initial rate* is required in this experiment; the form of the rest of the curve is not important here. Students will probably find, with the limited number of points that they plot, that the curve is a straight line. The different mixtures, details of which are given in the *Students' book*, should be investigated by different pairs of students so that the class investigates them all and each one is investigated at least twice so that some idea of the errors involved can be obtained.

It will be found that within experimental error the rate is proportional to the concentration of propanone:

$$\text{rate} = k\,[\text{propanone}]$$

and the numerical value of the rate constant can be determined.

The rate is in terms of decrease in concentration of iodine in unit time and therefore in the above equation the units on the left hand side are

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

and those on the right hand side are

$$\text{mol dm}^{-3} \times (\text{units of } k)$$

Thus the units of k must be s^{-1}.

It will also be found that the rate is not affected by the iodine concentration, and that it is proportional to the hydrogen ion concentration

$$\text{rate} = k_1[\text{H}^+]$$

An overall expression for the rate is therefore:

$$\text{rate} = k_2[\text{propanone}][\text{H}^+]$$

The units on the left hand side are

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

and those on the right hand side are

$$\text{mol dm}^{-3} \times \text{mol dm}^{-3} \times (\text{ units of } k_2)$$

Thus the units of k_2 must be $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$.

Alternative experiment 15.5

A kinetic study of the reaction between manganate(VII) ions and ethanedioic acid

SAFETY Ethanedioic acid (oxalic acid) is POISONOUS.

Using a burette, put 10 cm^3 of a solution which is 0.1 M in ethanedioic ions and 1.2 M in sulphuric acid into a test-tube.

Put 0.2 cm^3 of a 0.02 M solution of manganate(VII) ions into a test–tube that fits the colorimeter.

Adjust the meter of the colorimeter to maximum with a tube of water in place.

Add the ethanedioic solution to the manganate(VII) solution, shake the mixture, and start the clock.

Put the tube of reaction mixture into the colorimeter and take readings every 20 seconds. As the reaction proceeds you may want to take readings more frequently, but as the experiment is completed in four to five minutes, it is easy to repeat it.

Questions

1. How does the rate of the reaction change with time?
2. Can you suggest a reason for the changes in the rate that you observe?
3. Can you suggest any experimental work that you could do to see if your suggestion is correct?

Alternative experiment15.5

Teachers' guide

Each group of students will need:
1 stop-watch
1 test-tube
1 colorimeter with tubes (or cuvettes) to fit
Access to communal burettes containing:
Solution which is 0.1 M with respect to ethanedioic acid and 1.2 M with respect to sulphuric acid HARMFUL, IRRITANT
0.02 M potassium manganate(VII)
0.02 M manganese(II) solution
Carbon dioxide generator

The concentration of manganate(VII) may need adjustment for the particular colorimeter used. The ethanedioic acid concentration may require modification depending on the manganate(VII) concentration chosen, so that the experiment takes about four or five minutes.

Procedure

Having adjusted the meter to maximum with a tube of water in place, students mix the ethanedioic acid and manganate(VII) solutions and take readings with this solution in place. The reaction takes about four minutes, at the end of which time the manganate(VII) will have been consumed. Students are instructed to start by taking readings every thirty seconds but after two minutes, when the rate of the reaction increases, they will need to take readings more frequently, possibly at ten second intervals.

If they do not obtain all the readings they require, the experiment can easily be repeated as it only takes three or four minutes. The colorimeter readings are then converted to molarities and a graph of concentration against time drawn. This will be of the form shown in figure 18.2.

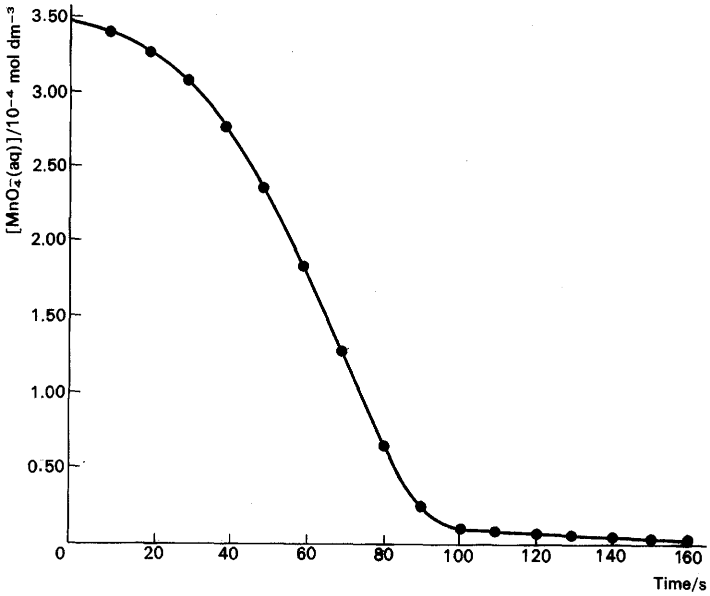


Figure 18.2 Graph of concentration against time.

Teachers may think it useful for students to take gradients from this graph, and to plot the rates obtained in this way against time. We might expect the rate to depend on the concentrations of manganate(VII), ethanedioic acid, and hydrogen ions but these are decreasing with time, and the rate of the reaction must depend upon the concentration of something which is *increasing* in concentration with time, that is, something which is produced in the reaction. Students will probably need help before they suggest that catalysis by something produced in the reaction is occurring.

Looking at the stoicheiometric equation,

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

there are two obvious candidates, $Mn^{2+}(aq)$ and $HCO_3^-(aq)$ from dissolved carbon dioxide. Other possibilities are intermediates that may be produced in the reaction such as manganese in other oxidation states. Students can investigate these possibilities by repeating the experiment, adding 1, 2, 4, or 6 drops (approximately 0.02, 0.04, 0.08, or 0.12 cm^3) of 0.2 M manganese(II) solution or by saturating the ethanedioic acid solution with carbon dioxide before the experiment.

They will find that the addition of manganese(II) moves the $[MnO_4^-]$ against time graph to the left, that is, moving towards a more 'normal' graph. If enough manganese(II) is added the increase in rate will not occur at all. This indicates that manganese(II) is catalysing the reaction.

Whichever method is used, students should finally be introduced to the term 'autocatalysis', which is used to describe this type of reaction.

18.4 Using an electrical compensation calorimeter

The electrical compensation calorimeter has the advantage of greater accuracy than the use of a thermometer to measure changes in temperature associated with enthalpy changes. The method measures the number of joules directly, without calculation or assumption about the value of specific heat capacity. However, it has the disadvantage of greater expense, and so is offered as an alternative. Details of the apparatus are given in the *Students' book.* The method is suitable for experiment 4.1 *Measuring some energy changes* plus the investigations 4.2 *Determining an enthalpy change that cannot be measured directly* and 9.5b *An investigation of an enthalpy change of hydration.* The joulemeter can also be used as an alternative method in experiment 6.2 *To find the enthalpy changes of combustion of some alcohols.*

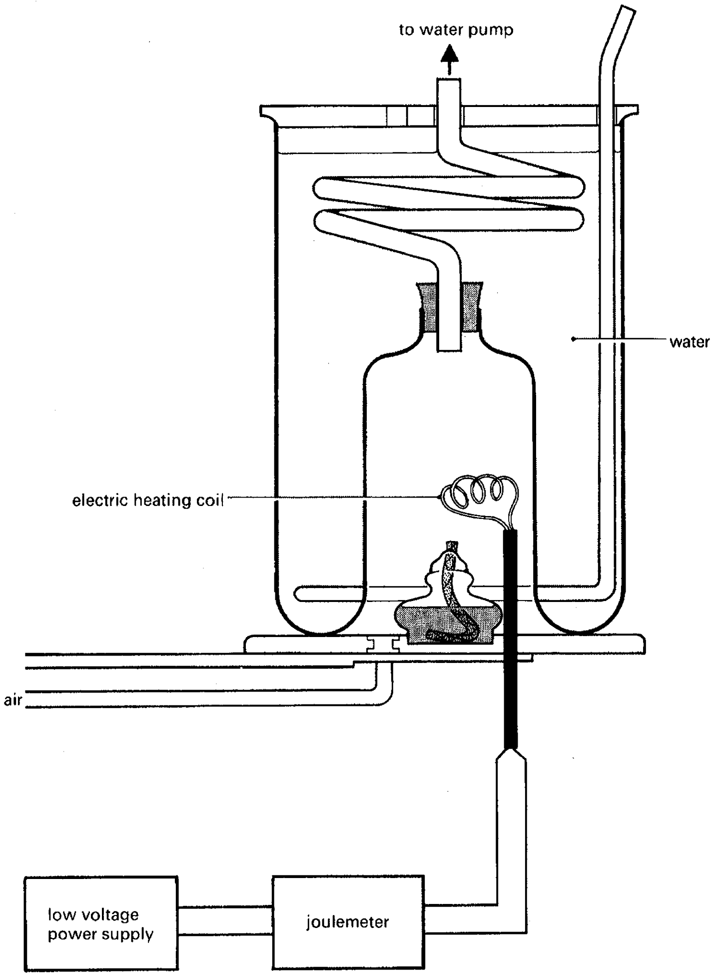


Figure 18.3 Using a joulemeter for experiment 6.2.

The important aspect of this experimental method is, of course, the use of the electrical heater, rather than the vacuum flask; indeed, thermal insulation that is very nearly as effective can be obtained at lower cost, using a plastic container surrounded by a block of expanded polystyrene foam.

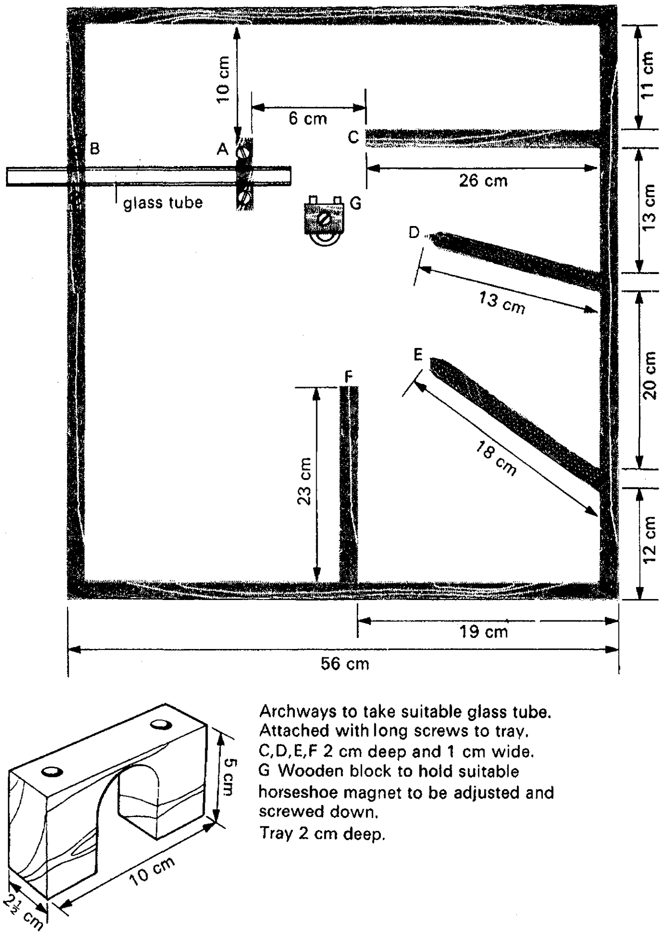
A possible source of error lies in the fact that the heater may continue to transfer energy to the solution in the calorimeter even after it has been switched off, and thus the number of joules that is recorded is too high.

18.5 The mass spectrometer

The *Students' book* shows a simplified diagram 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.

Several different models which demonstrate the principle of the mass spectrometer can be constructed. One of them is described here.

The model consists of a tray in which there are three compartments, as shown in figure 18.4. Ball bearings of different masses are rolled down a glass tube into the tray and are then deflected by a magnet. Adjustment of the slope of the glass tube and of the position of the magnet enable the ball bearings to be deflected into the three compartments according to their masses.



Archways to take suitable glass tube. Attached with long screws to tray.
C,D,E,F 2 cm deep and 1 cm wide.
G Wooden block to hold suitable horseshoe magnet to be adjusted and screwed down.
Tray 2 cm deep.

A and B

Figure 18.4 Model to show the principle of the mass spectrometer.

Materials required:

1 Eclipse horseshoe magnet – width across limbs 44 mm, thickness 10 mm
Ball bearings diameters 11 mm, 6 mm, and 4 mm
Wood for tray, or transparent base for use on an OHP.
Glass tube about 30 cm long, internal diameter greater than 11 mm
The dimensions of the tray are not critical. Nominal dimensions are given in figure 18.4.

There is also a **Study Task**.

1 Students are asked to work out the molar masses of naturally occurring lithium and iron. These elements have been selected to link the task to Topic 1.

Table 2.2 in the *Book of data* gives the exact mass of nuclides in atomic mass units and percentage abundances (in brackets).

Lithium 6.0151 (7.42), 7.0160 (92.58)
Iron 53.9396 (5.82), 55.9349 (91.66), 56.9354 (2.19), 57.9333 (0.33)
giving molar masses Li = 0.4463 + 6.4954 = 6.94 (to 3 SF)

Fe = 3.1393 + 51.2699 + 1.2469 + 0.1912 = 55.8 (to 3 SF)

The conversion factor from atomic mass units to molar mass units is × 1.

2 The comparison of the molar masses of I, Te, Ar and K relative to their positions in the Periodic Table needs data from Table 2.1 in the *Book of data.* This table uses mass numbers, rather than the exact mass of the nuclides used in Table 2.2. Consequently the answers obtained Te 127.73; 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 co-incidentally their molar masses. $^{130}_{52}Te$ and $^{40}_{18}Ar$ atoms are responsible for the breakdown of the molar mass pattern.

The second Study Task asks 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 phenylethanone, phenylethanal and methylbenzaldehyde.

The molecule breaks up giving fragments:

Molar mass/g mol^{-1}	**Fragment**
105	$C_6H_5CO^+$
15	CH_3^+
77	$C_6H_5^+$
28	CO^+

Students are then asked to look at the infra-red spectrum of **V** in the next Study Task (section 18.7).

18.6 X-ray diffraction

X-ray diffraction is 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 (figures 3.17, 6.1, 6.2, 6.3, 7.30 and 15.4 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 before any Nobel prizes were awarded for the elucidation of the structure of DNA.

18.7 Infra-red spectrometry

It is suggested that students shake gently a ball-and-spring model of the molecule of methane when holding it by one hydrogen atom. They should be able to spot both stretching and bending modes of vibration.

Students should be aware that the absorption 'peaks' are actually troughs in the spectra and that the positions are referred to by their *wavenumber*, the reciprocal of the wavelength.

The Study Task asks 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
1700–1680	Ketone, aryl, alkyl
1600, 1580, 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.

18.8 Nuclear magnetic resonance spectroscopy

This important method is described briefly but it is not referred to elsewhere in the *Students' book.*

The text concludes with an account of the discovery of fullerenes, named after the American architect Buckminster Fuller who is famous for his geodesic structures. For those who want to make a model of C_{60}, sometimes called 'buckey ball' or 'soccerene' an enlarged photocopy can be made of the template.

Fullerene laboratory kits are available from some laboratory supply companies.

For more information and a template for making a C_{60} model see Wolf, A.A. 'Modelling molecular footballs', *Education in Chemistry*, **30**, pages 76-7, 1993.

The Bucky*box* introduces A and GNVQ Advanced students to Buckminsterfullerene; for more information please contact
Dynamic Enterprises Ltd, Unit 2, Old Farmhouse, Hanwell, Banbury, Oxfordshire
OX17 1HN.

Reference sources and bibliography

The books which are listed here are intended as a general guide to some sources of further information which teachers may from time to time find it helpful to consult. The works listed here are arranged under a series of headings, beginning with general sources of information for the course as a whole, and continuing with individual subject headings arranged alphabetically. The list is not claimed to be exhaustive; it is merely a collection of some sources which have been found to be helpful.

General

Asimov, I. *Asimov's biographical dictionary of chemistry.* Pan Books, 1975.
Faraday, M. *Faraday's chemical history of a candle.* Chicago Review, 1988.
McGee, H. *On food and cooking: the science and lore of the kitchen.* Harper Collins, 1991.
Sharp, D.W.A. *The Penguin dictionary of chemistry.* Penguin Books, 2nd edn, 1990.
Sutton, C. *Words, science and learning.* Open University Press, 1992.

Applications of chemistry

Selinger, B. *Chemistry in the marketplace.* Harcourt Brace Jovanovich, 4th edn, 1989.

Chemical nomenclature and units

Association for Science Education. *Chemical nomenclature, symbols, and terminology.* 3rd edn, 1985.

Computing

This book was produced using an Apple Macintosh® computer with Microsoft Word 4.0 and Pagemaker 5. Some of the chemical formulae were produced using MathType 3 and the suggestions for spreadsheets were developed using Claris Works 2.0.

Data books

Revised Nuffield Advanced Science. *Book of data.* Longman, 1984.
Lide, D.R. (ed) *Handbook of chemistry and physics.* Special student edition, CRC Press.

History of chemistry

Knight, D.M. (ed) *Classical scientific papers: chemistry (second series).* Bell & Hyman, 1970.
Lavoisier, A-L. *Elements of chemistry.* Dover, 1965.
Roberts, R.M. *Serendipity: accidental discoveries in science.* John Wiley, 1989.

Inorganic chemistry

Cotton, F.A., Wilkinson, G. and Gaus, P.L. *Basic inorganic chemistry.* John Wiley, 2nd edn, 1987.
Dasent, W.E. *Inorganic energetics.* Cambridge University Press, 2nd edn, 1982.
Puddlephatt, R.J. and Monaghan, P.K. *The periodic table of the elements.* Oxford University Press, 2nd edn, 1986.

Journals

School Science Review, published quarterly by the Association for Science Education.
Education in Chemistry, published bi-monthly by the Royal Society of Chemistry.
Journal of Chemical Education, published monthly by the Division of Chemical Education of the American Chemical Society.

Learned societies and organizations

The Association for Science Education, College Lane, Hatfield, Hertfordshire AL10 9AA. The ASE is the largest organization in the country for science teachers at secondary and primary level. Several publications of the ASE are referred to in this book, especially the journal *School Science Review (SSR).*
CLEAPSS (School Science Service), Brunel University, Uxbridge UB8 3PH. CLEAPSS is an organization funded by most local authorities and many independent and GM schools to advise them in school science equipment, materials, procedures and safety. Further details and information about subscriptions can be obtained from CLEAPSS.
The Royal Society of Chemistry, Burlington House, London W1V 0BN. The Royal Society of Chemistry operates an 'affiliation scheme' for schools, under which participating chemistry departments obtain *Education in Chemistry (Educ. Chem.),* and other periodicals and information at favourable rates. For details of this scheme, apply to the Education Officer.

Models

The molecular models in the illustrations are Molymod^{R} models supplied by Spiring Enterprises Ltd.

Organic chemistry

Fieser, L.F. *Organic experiments.* Heath, 7th edn, 1991.
Fraústo da Silva, J.R.R. and Williams, R.J.P. *The biological chemistry of the elements.* Oxford University Press, 1991.

Mann, F.G. and Saunders, B.C. *Practical organic chemistry.* Longman, 4th edn, 1979.
Streitwieser, A., Heathcock, C.H. and Kosower, E.M. *Introduction to organic chemistry.* Macmillan, 4th edn, 1992.
Sykes, P. *A guidebook to mechanism in organic chemistry.* Longman, 6th edn, 1986.

Physical chemistry

Atkins, P.W. *Physical chemistry.* Oxford University Press, 4th edn, 1990.
Bent, H.A. *The second law.* Oxford University Press, New York, 1965.
Smith, D.W. *Inorganic substances: a prelude to the study of descriptive inorganic chemistry.* Cambridge University Press, 1990.
Wells, A.F. *Structural inorganic chemistry.* Oxford University Press, 5th edn, 1984.

Safety

Association for Science Education. *Safeguards in the school laboratory.* 8th edn, 1981.
Association for Science Education. *Topics in safety.* 2nd edn, 1988.
Crellin, J.R. 'School fume cupboards', *Educ. Chem.*, 1984(6), 21.
Luxon, S.G. (ed) *Hazards in the chemical laboratory.* Royal Society of Chemistry, 5th edn, 1992.
CLEAPSS *Hazcards.* 2nd edn, 1994.
CLEAPSS *Laboratory handbook.* Updated, 1992.
Everett, K. and Jenkins, E.W. *A safety handbook for science teachers.* John Murray, 4th edn, 1991.
HSC. *COSHH: Guidance for schools,* HMSO, 1989.
HSC. *Chemicals (Hazard information and packaging) Regulations (CHIP). Approved guide. Approved supply list.* HSE Books, 1993.

SATIS 16–19

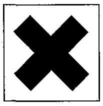
Hunt, A. (ed) *SATIS 16-19, Units 1–100.* ASE, 1990–92

The science and technology in society (SATIS) project was set by the Association for Science Education to produce a bank of resources for use with science students. The units listed opposite are particularly appropriate to this Nuffield chemistry course.

SATIS unit	Chemical context	Student activities	Topic
12 Trouble with CFCs	Properties of halogenoalkanes Formation and reactions of free radicals	Interpreting tables of data	7
14 William Perkin – founder of the synthetic dyestuffs industry	Nitration of arenes Properties of aryl amines	Explore the role of an innovative scientist and business man	17
15 A problem of dyeing	Intermolecular forces (van der Waals, polar, ionic and hydrogen bonds) Effect of molecular structure on solubility	Work co-operatively to solve a problem	17
17 Aspirin	Properties of organic acids, esters and phenolic –OH	Discussing alternative explanations	12
40 Steel (with related video)	Redox reactions Energy changes in reactions	Interpreting industrial data	1
41 Accident or arson?	Gas–liquid chromatography	Group work weighing evidence and assessing its reliability	18
42 Chlorine bleach	Halogen chemistry	Plan and carry out an investigation using a redox titration	5
43 Liquid crystals	Chirality	Interpret technical information	14
65 Catalytic converters	Redox reactions. Catalysis	Group work to master a technical case and present it clearly	8
66 Swimming pool chemistry	Aqueous chemistry of chlorine and iodine	Plan and carry out a quantitative investigation	5
67 The perfume industry	Solvent extraction and steam distillation	Carry out a survey	16
68 Perfume chemicals	IR spectroscopy and NMR	Explore the link between molecular shape and odour	16
89 Handedness	Chirality	Use of molecular models to solve problems Communicate chemical ideas to a lay audience	14
90 Do we need zinc?	Characteristics of d-block elements	Assess evidence related to a controversial theory	15
91 Helping asthmatics	Bromination, esterification, Friedel-Crafts, reduction	Match IR spectra to structures	16

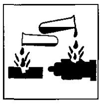
Appendix

Hazardous laboratory chemicals



HARMFUL
or IRRITANT

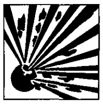
HIGHLY
FLAMMABLE



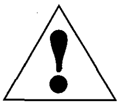
CORROSIVE

OXIDIZING

TOXIC



EXPLOSIVE



DANGER

EYE PROTECTION
MUST BE WORN

Laboratory safety is about **avoiding exposure to risk** as well as protecting ourselves and our students from the results of mishaps. All the experiments in this course have been checked for safety but when students are going to do an investigation of their own you will need to check the risk assessments they are told to make before starting any practical work. 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. 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 and this *Teachers' guide* includes a list of guidelines which you can photocopy and enlarge if you wish to hang a copy in the students' laboratory.

Risk assessments should normally be made on a standard form and an example is shown. It may be adapted to suit particular situations and photocopied for use on this course.

The steps in making an assessment are:

1 **Write down the procedures** that will be used (chemicals, quantities, techniques).

2 Use reference sources to **identify any hazardous chemicals** that will be used or made. The appropriate warning symbol 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. Use a standard reference source such as the 'Hazcards' supplied by CLEAPSS to subscribers to their services.

4 **Decide what protective measures to take** so that you can carry out the procedure in safety. The protective measures you need to take will depend on your laboratory as well as the procedure.

5 Find out how to dispose of any hazardous residues from your practical work.

The most common mishaps in the laboratory involve splashes from liquids and burns from hot apparatus.

- In the event of getting a chemical in an eye, or on skin, **flood the area with large quantities of water.** Keep the water running for at least 10 minutes. 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 im**mersing the area in cool water** for at least 10 minutes.

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 being used or made	Control measures and precautions
Any non-chemical hazards and precautions to be taken			Signed:
Disposal of residues			Date:

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 likely 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 for the use of your own students the list of hazardous substances included in this section. But teachers should remember that this list is incomplete as it only aims to cover chemicals needed in the standard experiments.

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.

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.

Limit value The limits of exposure to chemicals are described in occupational exposure standards (OES). These are expressed as long-term and short-term exposure limits (LTEL and STEL) which are time-weighted averages. The values quoted are usually the short-term occupational exposure limits. There is no evidence, at present, of injury to health when adults are exposed to the concentrations quoted for 10 minutes on a daily basis. The degree of care needed in handling different compounds can be assessed from the limit values.

Hazardous substances used in the experiments

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	**Flammable** Dust is irritant to respiratory system and eyes. Avoid contact with water. Limit value 10 mg m^{-3}.
Aluminium chloride (anhydrous)	**Corrosive** Causes burns; highly irritant to all tissues. Limit value 2 mg m^{-3}.
Ammonia gas	**Toxic, Corrosive, Flammable** Do not breathe, toxic by inhalation; irritates respiratory system and eyes. Limit value 24 mg m^{-3}.
Ammonia solution	**Corrosive** Solution causes burns and is irritant to all tissues; the 35% solution (0.880) develops pressure in its bottle in warm weather and the 25% solution (0.90) is safer to handle. **Corrosive** when > 21 M. **Irritant** when 21–6 M.
Ammonium chloride	**Harmful, Irritant** Irritant to skin and eyes; harmful by skin absorption. Limit value 20 mg m^{-3}.
Ammonium nitrate	Can cause fire or explosion with combustible materials; irritant to all tissue.
Aniline	see Phenylamine
Anisole	see Methoxybenzene
Barium compounds	**Harmful** > 0.05 M is harmful; soluble salts are very toxic if swallowed; can be irritant to skin and eyes. Limit value 0.5 mg m^{-3}.
Benzene	**Toxic, Highly flammable** May cause cancer. Toxic by contact with skin, by inhalation and if swallowed. *All educational use is illegal.* Limit value 16 mg m^{-3}.
Benzene-1,2-dicarboxylic anhydride (phthalic anhydride)	**Irritant** Dust is irritating to skin, eyes and respiratory system. Limit value 24 mg m^{-3}.

Benzene-1,2-diol (catechol)	Irritant to the eyes causing burns; irritant to the skin and poisonous by skin absorption. Limit value 20 mg m^{-3}.
Benzene-1,3-diol (resorcinol)	**Harmful** Harmful if swallowed. Irritant to eyes and skin; absorption by the skin may cause itching and dermatitis; in severe cases can cause convulsions and death. Limit value 90 mg m^{-3}.
Benzoyl chloride	**Corrosive** Causes burns; very irritating to all tissues.
Benzyl alcohol	**Harmful** Harmful by skin contact and inhalation; seek medical attention if eye contact occurs.
Boric acid	Irritant to eyes and respiratory system; harmful if swallowed. Limit value 20 mg m^{-3}.
Bromine	**Very toxic, Corrosive** Very toxic by inhalation; causes severe burns; seek medical attention if exposed. Limit value 2 mg m^{-3}.
Butanoic acid	**Corrosive** Causes burns; irritates or burns the skin and especially the eyes.
Butan-1-ol	**Flammable, Harmful** Harmful by inhalation; irritating to eyes and skin; readily absorbed through the skin. Limit value 150 mg m^{-3}.
Butan-2-ol	**Flammable, Harmful** Irritant to eyes and skin; can be absorbed through the skin; causes narcotic action and depression. Limit value 450 mg m^{-3}.
Butan-2-one	**Highly flammable, Irritant** Vapour can cause dizziness and nausea, can cause severe damage to the eyes. Limit value 885 mg m^{-3}.
tertiary Butyl alcohol	see 2-Methylpropan-2-ol
Butylamine	**Highly flammable, Irritant** Irritant to skin, eyes, and respiratory system; assumed to be poisonous if taken by mouth. Limit value 15 mg m^{-3}.
Calcium chlorate(I) (calcium hypochlorite)	**Corrosive, Oxidizing** Causes burns; dust irritates all tissues; contact with acid liberates toxic chlorine; may cause fire.
Calcium chloride	**Irritant** Irritating to the eyes.

Chlorine	**Toxic** Toxic by inhalation; irritant to all tissues and causes severe lung damage. Limit value 3 mg m^{-3}.
1-Chlorobutane	**Highly flammable**
Chloroethanoic acid	**Toxic, Corrosive** 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.
Copper compounds	**Harmful, Irritant** Dust and solution irritate the eyes; toxic if swallowed, may cause violent vomiting, pain and collapse. Limit value 2 mg m^{-3}.
Copper(I) oxide	**Harmful** Harmful if swallowed.
Cyclohexane	see Hexanes
Cyclohexanol	**Harmful, Irritant** Harmful by inhalation and if swallowed; irritant to skin and respiratory system; absorption by the skin may lead to tremors. Limit value 200 mg m^{-3}.
Cyclohexanone	**Flammable, Harmful** Harmful by inhalation; irritant to skin, eyes and respiratory system. Limit value 400 mg m^{-3}.
Cyclohexene	**Highly flammable** Irritant to respiratory system. Limit value 1015 mg m^{-3}.
Decanedioyl dichloride (sebacoyl dichloride)	Irritant to tissue; harmful by inhalation or skin absorption.
Dibutyl phthalate	Irritant to skin, eyes and respiratory system; can cause nausea and dizziness. Limit value 10 mg m^{-3}.
Dichloroethanoic acid	**Corrosive** Causes severe burns.
di(Dodecanoyl) peroxide (lauroyl peroxide)	Irritant and may burn the eyes and skin.
Ethanamide (acetamide)	**Harmful** Possible risk of irreversible effects. Irritant to the skin, eyes and respiratory system; harmful by skin absorption; experimental carcinogen.
Ethanedioic acid (oxalic acid)	**Harmful** Harmful if swallowed and in contact with skin; irritant to eyes and respiratory system; if swallowed causes severe pain and collapse. Limit value 2 mg m^{-3}.

Ethane-1,2-diol (ethylene glycol)	**Harmful** Dangerous if swallowed. Limit value 125 mg m^{-3}.
Ethanoic acid (acetic acid)	**Corrosive, Flammable** Causes severe burns; extremely irritant to all tissues. > 4 M is **Corrosive** 4-1.7 M is **Irritant** Limit value 37 mg m^{-3}.
Ethanoic anhydride (acetic anhydride)	**Corrosive, Flammable** Causes burns; severely irritant to all tissues. Limit value 20 mg m^{-3}.
Ethanol	**Highly flammable** Harmful if swallowed, intoxicant. Limit value 1900 mg m^{-3}.
Ethanoyl chloride	**Highly flammable, Corrosive** Causes burns; severely irritant to all tissues. Violent reaction with water.
Ethoxyethane (diethyl ether, ether)	**Extremely flammable** May form explosive peroxides; inhalation of vapour may cause dizziness and, in high concentrations, unconsciousness; repeated inhalation is habit forming. Limit value 1500 mg m^{-3}.
Ethyl ethanoate (ethyl acetate)	**Highly flammable** Irritant to eyes and respiratory system. Limit value 1400 mg m^{-3}.
Formaldehyde	see Methanal
Hexanes	**Highly flammable** Vapours irritate the respiratory system and may have a narcotic effect; serious damage by prolonged exposure. Limit value 3600 mg m^{-3} (n-hexane 70 mg m^{-3}).
Hexane-1,6-diamine (diaminohexane)	**Flammable, Harmful** Strongly irritant and corrosive to all tissues; harmful by skin absorption. Limit value 25 mg m^{-3}.
Hexanol	**Harmful** Harmful if swallowed.
Hexanedioic acid	**Irritant** Irritant to eyes; Harmful if swallowed.
Hydrochloric acid	**Corrosive** Causes burns, irritating to respiratory system. > 7 M is **Corrosive** 7–2.7 M is **Irritant** Limit value 7 mg m^{-3}.
Hydrogen	**Extremely flammable**

Hydrogen chloride gas	**Corrosive** Causes severe burns, irritating and extremely destructive to respiratory system. Limit value 7 mg m^{-3}.
Hydrogen peroxide	**Corrosive, Oxidizing** 100 vol (30%) is **Corrosive** 100–40 vol (12%) is **Irritant** 20–60% causes burns. Limit value 3 mg m^{-3}.
2-Hydroxybenzoic acid (salicylic acid)	Irritant to all tissues.
Iodine	**Harmful** Harmful by inhalation and in contact with the skin; vapours irritate the respiratory system and eyes; solid burns the skin. Limit value 1 mg m^{-3}.
Iron(III) chloride	Anhydrous salt can cause painful burns to moist skin and eyes.
Lauroyl peroxide	see di(Dodecanoyl) peroxide.
Lead (powder)	Irritant when inhaled. Limit value 0.15 mg m^{-3}.
Lead compounds	**Harmful** Harmful by inhalation and swallowing; danger of cumulative effect. Limit value 0.15 mg m^{-3}.
Lead ethanoate	**Harmful** Possible risk of irreversible effects, may cause birth defects.
Magnesium powder	**Highly flammable** Fine dust is irritant to eyes and respiratory system; avoid contact with water.
Manganese(IV) oxide (manganese dioxide)	**Harmful** Inhalation of dust may lead to increased respiratory infections. Limit value 5 mg m^{-3}.
Methanal (formaldehyde)	**Toxic, Corrosive** Toxic by inhalation, in contact with the skin and if swallowed; the concentrated solutions cause burns and are especially hazardous; severely irritant to the eyes and respiratory system; possible risk of irreversible effects. Limit value 2.5 mg m^{-3}.
Methanoic acid	**Corrosive** Causes severe burns.
Methanol	**Toxic, Highly flammable** Toxic by inhalation, may cause headache, nausea, dizziness and stupor; very dangerous to the eyes with the effects sometimes delayed many hours. Limit value 260 mg m^{-3}.

Methoxybenzene (anisole)	May be irritant or harmful if absorbed into the body.
Methylbenzene (toluene)	**Highly flammable, Harmful** Inhalation can cause dizziness, nausea and mental confusion; irritant to the eyes; poisonous by skin absorption; explosive mixture with air. Limit value 560 mg m^{-3}.
Methyl 2-methylpropenoate (methyl methacrylate)	**Highly flammable, Irritant** Irritates the eyes, respiratory system and skin; inhalation may cause narcosis leading to death; may cause sensitization by inhalation or contact; possible risk of irreversible effects. Limit value 510 mg m^{-3}.
2-Methylpropan-2-ol	**Highly flammable, Harmful** Harmful by inhalation.
Naphthalen-2-ol	**Harmful, Irritant** Irritant to all tissues.
Nickel salts	**Harmful, Irritant** May cause sensitization by skin contact; possible risk of irreversible effects; irritant to the eyes. Limit value 0.1 mg m^{-3}.
Nitric acid	**Corrosive, Oxidizing** 20–70% causes severe burns. 70% may cause fire. Vapour and liquid are severely irritant and corrosive to all tissues. > 3 M is **Corrosive** 3-0.8 M is **Irritant** Limit value 5 mg m^{-3}.
Nitrogen dioxide	**Very toxic, Irritant** Very toxic by inhalation and skin contact; danger due to delay in effect; may cause weakness, coldness, headache and nausea; in severe cases can cause convulsions.
Nitrophenols	**Harmful** Harmful by skin contact, inhalation and if swallowed; danger of cumulative effects.
Oxalic acid and oxalates	see ethanedioic acid.
Pentanols (amyl alcohol)	**Flammable, Harmful** Harmful and irritating by inhalation and skin contact; damaging to liver and kidneys.
Petroleum spirit (80 °C and above)	**Flammable** Inhalation of high concentrations of the vapour can cause intoxication, headache, nausea and coma, particular the lower boiling fractions.

Phenol	**Toxic, Corrosive** Toxic by skin contact and if swallowed; causes burns; vapour irritates respiratory system and eyes; rapid absorption through the skin causes dizziness, difficult breathing and collapse. *Avoid using this compound whenever possible.* Limit value 38 mg m^{-3}.
Phenylamine (aniline)	**Toxic** Toxic by skin absorption and inhalation; causes headache, drowsiness and, in severe cases, convulsions; dangerous to the eyes. Danger of serious damage by prolonged exposure. *Avoid using this compound whenever possible.* Limit value 10 mg m^{-3}.
Phosphoric(V) acid	**Corrosive** Causes burns to eyes and skin. > 4 M is **Corrosive** 4–1.7 M is **Irritant** Limit value 1 mg m^{-3}.
Phosphorus, red	**Highly flammable, Toxic** Explosive when mixed with oxidizing substances; relatively harmless when free of white allotrope.
Phosphorus pentachloride	**Corrosive** Causes burns; irritant to respiratory system. Limit value 1 mg m^{-3}.
Phosphorus pentoxide	**Corrosive** Causes severe burns.
Phthalic anhydride	see Benzene-1,2-dicarboxylic acid.
Potassium bromate(V)	**Toxic, Oxidizing** May cause cancer, explosive with combustible materials; toxic if swallowed.
Potassium chlorate(V)	**Oxidizing, Harmful** Explosive with combustible materials; harmful by inhalation and if swallowed; dust and strong solutions may irritate the eyes and skin.
Potassium hexacyanoferrate(III) (ferricyanide)	Irritating to skin and eyes, harmful if swallowed although toxicity is low because cyanide is bound.
Potassium hexacyanoferrate (II) (ferrocyanide)	Irritating to skin and eyes, harmful if swallowed although toxicity is low because cyanide is bound.
Potassium hydroxide (caustic potash)	**Corrosive** Causes severe burns; solid and solution are strongly irritant and burn the skin and eyes. > 0.9 M is **Corrosive** 0.9–0.2 M is **Irritant** Limit value 2 mg m^{-3}.
Potassium iodate(V)	Irritant to all tissues.

Potassium manganate(VII) (permanganate)	**Harmful, Oxidizing** May cause fire with combustible materials; extremely destructive to all tissues; can be absorbed through the skin; harmful if swallowed.
Potassium nitrate	Can be explosive when mixed with oxidizing substances; irritating to all tissue; toxic if swallowed.
Potassium peroxodisulphate (persulphate)	Irritant to skin and eyes; harmful if swallowed.
Propanal (propionaldehyde)	**Highly flammable, Irritant** Irritates the respiratory system, eyes and the skin.
Propanoic acid	**Corrosive** Causes burns.
Propan-1-ol	**Highly flammable** Irritates the eyes and respiratory systems; narcotic at high concentrations. Limit value 625 mg m^{-3}.
Propan-2-ol	**Highly flammable** Liquid can cause severe damage to the eyes; vapour may cause dizziness, nausea and coma. Limit value 1225 mg m^{-3}.
Propanone (acetone)	**Highly flammable** Inhalation of the vapour may cause dizziness and coma; liquid may cause severe damage to the eyes. Limit value 3560 mg m^{-3}.
Propenamide (acrylamide)	**Toxic, may cause cancer** Toxic by inhalation and contact with the skin ; irritates the eyes and skin; affects the central nervous system. May cause heritable genetic damage. Limit value 0.3 mg m^{-3}.
Pyridine	**Highly flammable, Harmful** Harmful by skin contact and inhalation; vapour irritates the respiratory system and eyes and can cause headache and nausea; liquid irritates the skin and may cause dermatitis. Limit value 15 mg m^{-3}.
Salicylic acid	see 2-Hydroxybenzoic acid
Sebacoyl dichloride	see Decanedioyl dichloride
Silver nitrate	**Corrosive** Causes burns; solid and solution severely irritate the eyes. Limit value 0.01 mg m^{-3}.
Sodium	**Corrosive, Flammable** Violent reaction with water; moisture on the skin can cause thermal and caustic burns, fumes from burning sodium are highly irritant to all tissues.

Sodium borate (*di*-sodium tetraborate, borax)	**Irritant** Irritant to skin, eyes and respiratory system; toxic by skin absorption. Limit value 5 mg m^{-3}.
Sodium carbonate	**Irritant** Irritating to the eyes.
Sodium chlorate (I) (hypochlorite)	**Corrosive, Harmful** 10% available chlorine is **Corrosive**, causes burns; 5–10% available chlorine is **Irritant**, painful to skin and eyes.
Sodium chromate(VI)	see Sodium dichromate(VI)
Sodium dichromate(VI)	**Irritant** Irritant to all tissues; may cause sensitization by skin contact; absorption can cause stomach pains, vomiting and diarrhoea; can cause skin ulcers; after skin contact by solid or solution wash off immediately. Limit value 0.05 mg m^{-3}.
Sodium ethanedioate (sodium oxalate)	**Harmful** Harmful in contact with skin and if swallowed; irritant to eyes and respiratory system; if swallowed causes severe pain and collapse. Limit value 2 mg m^{-3}.
Sodium hydrogensulphite	Extremely destructive to tissue; individuals with pre-existing respiratory conditions may experience hypersensitivity. Limit value 5 mg m^{-3}.
Sodium hydroxide (caustic soda)	**Corrosive** Causes severe burns; dilute solution is irritant to skin and eyes. > 1.2 M is **Corrosive** 1.2-0.2 M is **Irritant** Limit value 2 mg m^{-3}.
Sodium nitrite	**Toxic, Oxidizing** Toxic if swallowed; irritant to skin , eyes and respiratory system. May cause fire with combustible material.
Sodium phosphate(V)	Irritant to tissue.
Sodium vanadate	Causes vomiting and excessive salivation if swallowed.
Sulphamic acid	**Irritant** Irritating to the skin and eyes.
Sulphur dioxide	**Toxic, Irritant** Toxic by inhalation; irritates the respiratory system and eyes. Limit value 5 mg m^{-3}.
Sulphuric acid	**Corrosive, Irritant** 1.5 M or more can cause severe burns. 1.5–0.5 M is irritant. Limit value 1 mg m^{-3}.
Toluene	see Methylbenzene

Trichloroethanoic acid	**Corrosive** Causes severe burns; inhalation of vapour is extremely destructive. Limit value 5 mg m^{-3}.
Urea	Irritant to tissue.
Zinc powder	**Flammable** Avoid contact with water; may cause skin and eye irritation.

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.

Good Laboratory Practice

- **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. 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 and cardigans hang freely, where they could be a fire hazard. We strongly recommended the wearing of laboratory coats.
- **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.
- **If you are asthmatic you should not smell gases** without a report from other students because gases such as chlorine are harmful. 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.
- Study carefully the best techniques for safely heating chemicals. Boiling tubes are safer than test-tubes (because of their greater volume), but should be less than one-fifth full. **Use a water bath to heat flammable liquids, NEVER use a naked flame.**
- **A heat burn from apparatus**, scalding liquids or steam is treated by ***immersing the area in cool water*** for at least 10 minutes.
- **In the event of getting a chemical in your eye**, or on your skin, ***flood the area with large quantities of water.*** Keep the water running for at least 10 minutes. 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.
- **You must always clear up chemical spillages straight away.** Whilst a few spills may need chemical neutralization or similar treatment, most minor spills can be dealt with by a damp cloth.
- **Report all accidents at once.**

NUFFIELD ADVANCED SCIENCE

CHEMISTRY

TEACHERS GUIDE

This edition of the Teachers' Guide has been produced to fully support the teaching of the Nuffield Advanced Chemistry course using the Third Edition of the Students' Book and the Revised Book of Data.

The chapters in this book are designed to be used directly with their equivalent topic in the Students' Book. Each chapter opens with a brief summary of the topic, an outline of its objectives and an introduction to the basic principles required at the start of the topic.

Teaching notes for each section follow with a summary at the end. These notes include details of experiments, apparatus, safety instructions and answers to the questions set within the Students' Book.

Appendices containing bibliographic information and detailed information on hazards in the laboratory are included at the end of the book.

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