RSC Accreditation of Degree Programmes

RSC | Advancing the Chemical Sciences

www.rsc.org/accredit

ABOUT THE RSC

Since 1841, the Royal Society of Chemistry (RSC) has been the leading learned society and professional body for chemical scientists. It is committed to ensuring that an enthusiastic, innovative and thriving scientific community is in place to face future scientific challenges.

The RSC has a global membership of over 47,000 and is actively involved in the spheres of education, qualifications and professional practice. It runs conferences and meetings for chemical scientists, industrialists and policy makers, both in the UK and around the world. It is an internationally renowned publisher of scientific journals and books. In all of its work, the RSC is impartial, objective and recognised as an authoritative voice in chemistry and for chemical scientists.

The RSC has had a respected system of degree accreditation for many years. It currently accredits around 200 degree programmes. Within its vision to be foremost in the world for promoting and developing the chemical sciences, the RSC is expanding its accreditation activities to involve universities worldwide.

ABOUT THIS DOCUMENT

Through accreditation, the RSC promotes good practices in the university education of chemical scientists and ensures that future practising scientists are knowledgeable and competent.

These guidelines describe what the RSC requires of a degree programme that is to be accredited. A set of key requirements are outlined that set the threshold standards. RSC accreditation is designed to provide a flexible framework which permits innovation and the wider development of contemporary education. The RSC process for accreditation is explained and guidance is given on the information that universities need to submit.

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FOREWORD

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Chemistry is a broad scientific discipline. It underpins much of contemporary science, plays a vital role in developing modern technology, and influences all human activity.

Immediate challenges in the environment, healthcare, energy and materials are being addressed through the work of professional chemists. Discoveries and inventions beyond current scientific boundaries will be increasingly interdisciplinary and international with chemists at the hub of research activity. The RSC has identified where the chemical sciences can provide technological and sustainable solutions and is promoting action and awareness through its Chemistry Roadmap.[1] The technologies that the chemical sciences bring about will improve the quality of daily life, underpin prosperity and will increase our readiness to face the challenges of the future.

The RSC's vision is to be the global leader in promoting and developing the chemical sciences for the benefit of society. The supply chain of competent professional chemical scientists is key.

Within this, the chemical science profession requires people who:

- comprehend key chemical concepts
- possess wide ranging practical skills
- have an enhanced set of professional skills
- have a comprehensive understanding of a substantial area of the subject
- can adapt and apply methodology to solve chemistry-based problems
- work independently and be self critical

Accreditation is an effective method of identifying programmes which contribute effectively to professionalism in the chemical sciences. The process provides peer judgements on the quality of university education. It characterises programmes that suitably prepare students to work as successful professionals and advances the chemical science profession through the development of a well-educated workforce.

Programmes which are accredited by the RSC have been subject to rigorous evaluation of their curriculum and resources. They offer employers a measure of confidence in the competence of recruits, provide universities with a means of marketing their value, and assure students on the quality of their education.

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1 'Chemistry for Tomorrow's World' www.rsc.org/roadmap

PART ONE: WHAT IS RSC ACCREDITATION?

Why seek accreditation?

Accreditation of degree programmes by professional and statutory bodies is a mark of assurance that standards set by a profession are met. The advantages of achieving professional accreditation are increasingly recognised around the world. Accredited programmes offer potential marketing advantages for universities* and address the needs of employers and students.

RSC accreditation is a peer review process founded on the judgement of professional chemists. It applies to individual degree programmes and not to a department or university overall. It provides a structured mechanism to assess, evaluate, and enhance the quality of degree programmes and demonstrates a commitment to continuous improvement. This ultimately provides a credible, independently verifiable method to differentiate valuable accredited programmes from those which fall short of accepted professional standards.

Benefits of Accreditation

In the global market, undergraduate students are increasingly mobile; universities continue to seek the most talented, while employers are keen to engage the best scientists through international employment markets.

Accreditation is a rigorous evaluation process that commands respect both in the UK and internationally. It helps students, their parents and advisers choose quality degree programmes. It also confers market advantage to graduates from accredited programmes when they are seeking employment and when they go on to seek professional qualifications.

The benefits of RSC Accreditation are defined by six core values:

Global Outlook

- International Mark of 'good practice' and a quality assurance benchmark providing wide ranging comparability among high performing universities.
- Enhancing networking and collaboration opportunities for an international community of high performing universities.
- Mobility of students and academics through exchange programmes between accredited partners. (e.g. comparative educational standards)

Professionalism

- Association with an established professional body, maintaining professional standards for chemists and chemical science worldwide
- Peer recognition of high standards of intellectual challenge and effective development of students.
- Encouraging the next generation of career chemists to begin on the path to a programme of continuing professional development.

Informed View

- A thorough outcome based accreditation, underpinned by a robust, modern and flexible process.
- Advancement of educational standards and practice, guided by experienced and knowledgeable academics and industrialists.
- An understanding of global education system to permit transparency in international benchmarking and quality assurance mechanisms.
- Increased engagement with RSC activities
  - Conferences, events and specialist lectures
  - Interaction with an expanding portfolio of leading journals within the RSC's renowned publishing business.

Inspirational Approach

- Promoting incorporation of the latest trends to produce inspirational degree programmes in chemical science.
- Supporting the development of chemical content and delivery of chemistry-based programmes through an international network of external consultants and consultancy organisations.

Influence

- High profile process offering enhanced competitiveness for students in crowded global job markets.
- Promoting chemistry-based specifications and programme delivery to produce chemical scientists who can address future challenges.

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* 'University' in this document refers to any degree awarding body e.g. institute, college etc.

Innovation

- Close engagement with industry, working to support employer efforts to raise key workforce skills.
- Encompasses the professional skills base of the future in the areas such as:
  - Business and Customer Awareness
  - Entrepreneurship and Enterprise
  - Professional Ethics

Pathways to accreditation

University level education is traditionally founded on three levels of achievement; bachelor, master and doctoral. Increasingly in Europe these are referred to as 1st, 2nd and 3rd cycle respectively. RSC accreditation links to these cycles. 1st cycle degrees provide aspiring chemists with the fundamental knowledge of chemistry and skills for employment or further study. 2nd cycle degrees provide a depth of chemical knowledge with an ability to apply it to unfamiliar problems at the forefront of the chemical sciences. Completion of a 2nd cycle degree is viewed as full academic preparation for professional practice in chemistry-associated industries and for the award of Chartered status. 3rd cycle degrees extend the forefront of a discipline, usually through original research, and lead to a doctoral degree.

The RSC accredits at two levels: bachelor accreditation (1st cycle) and master accreditation (2nd cycle). Regardless of these cycles, the RSC maintains an international perspective on education and recognises that different countries may have alternative structures. By focussing on outcomes, RSC accreditation operates effectively within a variety of structures, modes of delivery and duration. Assessment can be applied to any chemistry-based programme and a judgement based on output standards is made against the accreditation levels.

How accreditation functions

RSC accreditation operates as a single, global, summative assessment process for all degree programmes based on the discipline of chemistry. It is a peer-review process managed by the RSC's Committee for Accreditation and Validation (CAV). It is responsible for assessing applications, applying the published criteria and making judgements. RSC Council appoints committee members from the RSC's membership. It ensures that reviewers have contemporary experience of university-level education and an understanding of the demands of employers within an international perspective. The RSC also employs professionally qualified staff whose role is to provide help and advice to universities and to manage the accreditation process. Collectively CAV members and RSC staff ensure the high quality of RSC accreditation.

Accreditation normally lasts for a period of 5 years after which universities are invited to submit their programmes for re-accreditation. Continued accreditation throughout the 5 year period is dependent on universities informing the RSC of any subsequent changes in their structure or content. For major changes a formal review of a programme's accreditation status is carried out.

Notably, accreditation functions beyond a single mark of quality. It provides wider engagement with the RSC through its extensive range of activities for promoting and developing science and ultimately progresses a common purpose of advancing the chemical sciences.

Reference Points

The RSC does not set its standards in isolation. It utilises internationally recognised guidelines and frameworks and exploits its global networks in order to define a robust accreditation process with a relevant set of academic values. In developing accreditation criteria, the RSC has made use of several internationally recognised external reference points both generic and subject specific.

In setting the required standards for RSC accredited degree programmes, the RSC subscribes to UNESCO and the Organisation for Economic Cooperation and Development's (OECD) joint *Guidelines for Quality Provision in Cross-Border Higher Education*.[2] The RSC is committed to enhancing global platforms for exchanging information and good practice, disseminating knowledge, increasing understanding of international developments and improving the competence and expertise of professional chemical scientists.

There are two key reference documents which influence the standards of these accreditation criteria. The first is *The Framework for Qualifications of the European Higher Education Area*.[3] It is an integral part of Europe's *Bologna process*[4] and is designed to overarch national qualification frameworks. Focussed on output standards not input measures, it describes each of the academic cycles in terms of outcomes. Bologna signatories have committed to elaborate their national qualification frameworks to the overarching framework. The principles of the *Bologna process* are extending into other continents and as such the framework's relevance to international university education is increasing.

The second key reference document is the *Chemistry Benchmark Statement*, which was published in revised form by the UK's Quality Assurance Agency for Higher Education (QAA) in 2007.[5] The QAA's benchmarking group was supported by the RSC and had representation not only from university departments in England, Scotland and Wales but also from the chemistry-based industries. The statement draws upon the definitions of bachelor's and master's degrees in the overarching European framework and contextualises them for chemistry programmes.

Uniquely among the QAA's set of published benchmarks, the *Chemistry Benchmark Statement* has been developed to be comprehensive, covering bachelor's and all types of master's degree programmes. It is a distinctive document within a wider geographical context and represents the most contemporary statement on chemical education standards. As such, the *Chemistry Benchmark Statement* is a valuable point of reference for the accreditation of degree programmes.

Universities seeking RSC accreditation should as a first step ensure that the specifications and output standards of their programmes can articulate clearly to published qualification frameworks and the *Chemistry Benchmark Statement*.

Bachelor Accreditation

A chemistry-based bachelor's qualification is a significant first step for many aspiring chemical scientists. Those who complete such degrees may pursue a career path in practical science or seek positions within the wider graduate employment market. Alternatively, and in many countries more commonly, chemistry-based bachelor's qualifications provide access to master's programmes in specialised areas of chemical science.

Bachelor's accredited programmes are expected to provide students with:

- a broad and balanced appreciation of key chemical concepts,
- a range of practical skills so that they can understand and assess risks and work safely in the laboratory,
- the ability to apply standard methodology to the solution of problems in chemistry,
- the knowledge and skills base from which they can proceed to graduate employment or to further study.

In terms of professional qualification, bachelor accreditation provides access to qualified membership of the RSC and forms a basis for satisfying the academic requirements for the RSC's award of Chartered Chemist (CChem) through further study or continuing professional development.

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2 http://www.oecd.org/dataoecd/27/51/35779480.pdf

3 www.bologna-bergen2005.no/Docs/00-Main_doc/050218_QF_EHEA.pdf

[4] www.ehea.info/

[5] http://www.qaa.ac.uk/Publications/InformationAndGuidance/Pages/Subject-benchmark-statement-Chemistry.aspx

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Master Accreditation

It has become accepted that those who aspire to practice in their chosen career at the full professional level should possess a master's level qualification (or attained a comparable level of achievement through other means). Employers of scientists and engineers increasingly recognise the high value that master's graduates provide in achieving their business objectives. This in turn is reflected by professional, statutory and regulatory bodies setting the academic requirements for professional registration and Chartered designations at the master's level.

Chemical science-based master's degrees are directed towards the forefront of chemical knowledge and provide the opportunity to study a more specialist range of topics in greater depth. Those who complete master's degrees in chemical science typically pursue a career path as a professional chemist and secure employment in chemistry-associated industries. They go on to make a significant personal contribution to chemical science practice and develop a high level of chemistry-related professional competencies. Many master's graduates will also progress on to doctoral programmes and pursue careers focussed on chemical research.

Master's accredited programmes are expected to provide students with:

- an in-depth understanding of specialised areas of chemical science,
- the ability to plan and carry out experiments independently and assess the significance of outcomes,
- the ability to adapt and apply methodology to the solution of unfamiliar types of problems,
- a critical awareness of advances at the forefront of the chemical science discipline,
- effective preparation for professional employment or doctoral studies in the chemical sciences.

In terms of professional qualification, master accreditation provides access to qualified membership of the RSC and fully satisfies the academic requirements for the RSC's award of Chartered Chemist (CChem).

There are generally two types of master's degree programmes, which are termed *discrete master's programme* and *integrated master's programme* in these guidelines.

a) Discrete master's programmes
These are programmes that normally follow on from the award of a bachelor/1st cycle qualification. This is the study pattern that is undertaken in most parts of the world. The chemical science qualification conferred is usually either titled *MSc* (Master of Science) or simply referred to as *Master's degree*. In the UK there are also several *MRes* (Master of Research) qualifications in the chemical sciences.

b) Integrated master's programmes
These are extended programmes that take students from university entry to master's level and so combine learning outcomes at bachelor's and master's levels. They are essentially unique to the United Kingdom, involving 4 or 5 years of full time study, and are currently the most common route to master's level for its chemistry students. The qualification conferred is usually titled *MChem* (Master in Chemistry) or *MSci* (Master in Science). Universities select students on these programmes so that only the more able are permitted to study them. Normally no intermediate award of a bachelor's qualification occurs.

Accreditation Values

In general terms, RSC accredited degree programmes provide:

- knowledge of chemical science that builds upon secondary education (i.e. study prior to university) and incorporates a critical understanding of theories and principles;
- essential skills for applying chemical knowledge and solving complex scientific problems with a strong emphasis on laboratory skills in synthesis and analysis;
- competence in dealing with challenging activities or projects while taking on responsibility for decision making in variable contexts.

More specifically, RSC accredited degree programmes stimulate students in the subject of chemistry and allow them to develop an appreciation of its application in different contexts. For this reason, standards are not expressed in terms of a detailed specification of required content since the RSC has no wish to inhibit well thought out curriculum development designed to meet evolving needs and regional demand. However, RSC accredited degree programmes must satisfy a range of criteria based on knowledge and understanding, intellectual abilities, and both practical and generic skills.

PART TWO: OUTPUT STANDARDS FOR RSC ACCREDITED PROGRAMMES

The criteria for accreditation are broken down into a number of key requirements. To gain accreditation, universities must demonstrate that they provide students with all the relevant key requirements for the programme type listed.

Key Requirements (KR) for Accreditation			bachelor	integrated master	discrete master
Breadth (Knowledge)	*KR1:*	Evidence of study of the three main branches of chemistry is provided at some point during university study.	✓	✓	
	KR2:	Programme outcomes should include a breadth of understanding of chemistry with the ability to solve problems at the threshold level of competence as exemplified in Appendix A.	✓	✓	
	KR3:	Breadth of understanding of chemistry through prior learning must be assured through admissions processes.			✓
Depth (Knowledge)	*KR4:*	Programmes should build on knowledge base to allow students to appreciate developments, in some areas, at the forefront of the discipline.	✓		
	KR5:	Programmes should ensure a depth of knowledge in specialist areas of chemical science demonstrated by an ability to solve problems at the level exemplified in Appendix B.		✓	✓
Practical Skills	*KR6:*	Students must develop a range of practical skills.	✓	✓	✓
Project Work	*KR7:*	Programmes must incorporate some independent investigative methodology.	✓		
	KR8:	Programmes must provide research training to enable students to complete a substantial project, the outcome of which is potentially publishable.		✓	✓

Key Requirements (KR) for Accreditation		bachelor	integrated master	discrete master
Placement	*KR9:* Any external placements must be subject to assessment against explicit and demanding criteria with universities retaining control and supervision of its students.	✓	✓	✓
Professional Skills	*KR10:* Programmes must develop a broad range of transferable key skills.	✓	✓	
	KR11: Programmes must develop the professional skills for those intending to practice chemical science as a profession.		✓	✓
Assessment	*KR12:* Assessment should be varied, appropriate and rigorous, and require students to apply their knowledge and solve problems.	✓	✓	✓
Title	*KR13:* The title of a programme should be indicative of content and address the assumptions an employer will make on the graduates' abilities based on the title.	✓	✓	✓
Quality Assurance	*KR14:* Universities must have robust quality assurance mechanisms in place for all aspects of its programmes.	✓	✓	✓
	KR15: Resources devoted to a programme should provide students with a suitably supportive environment so enabling them to be successful in achieving the stated learning outcomes.	✓	✓	✓

GUIDANCE NOTES ON KEY REQUIREMENTS

Further guidance on each key requirement is provided below.

Breadth (Knowledge)

KR1: Evidence of study of the three main branches of the chemistry is provided at some point during university study	Applicable to: i) Bachelor ii) Integrated master

- The chemical sciences represent a broad field of study so it is essential that those studying an accredited programme demonstrate knowledge of underlying chemical concepts.
- These studies should lead on from secondary/high school science education and are likely to feature at an introductory stage of the degree programme.
- Students must develop an ability to evaluate and interpret key chemical principles.

KR2: Programme outcomes should include a breadth of understanding of chemistry with the ability to solve problems at the threshold level of competence as exemplified in Appendix A.	Applicable to: i) Bachelor ii) Integrated master

- Students completing an accredited programme must be able to demonstrate a systematic understanding of fundamental physicochemical principles and an ability to apply that knowledge to the solution of theoretical and practical problems.
- Students must also be enabled to gain knowledge of a range of inorganic and organic materials and be able to realise their understanding in the synthesis of such materials and the analysis of their properties.
- The required threshold level is exemplified by the standard of problem questions in Appendix A.
- For bachelor's programmes, the threshold for breadth of study must be achieved within a programme's learning outcomes.
- For integrated master's programmes, the threshold for breadth of study should be achieved at an intermediate stage of the programme. Typically for full time programmes in the United Kingdom, this would be by the end of Year 3 in Scotland or year 2 in England, Wales and Northern Ireland.
- Programmes that are developed to provide a wide ranging and extensive knowledge of chemistry, for example those titled simply "*chemistry*", would normally be expected to offer the required level of breadth across the chemistry discipline.
- Programmes with more specialist objectives, e.g. those titled "*medicinal chemistry*", can provide reduced coverage in the least relevant areas. This must be compensated for by an increased coverage in more relevant areas of chemical science.
- Problems in Appendix A are intended to be indicative of the standard which the RSC expects students to attain and are in no way intended to define curriculum content.

KR3: Breadth of understanding of chemistry through prior learning must be assured through admissions processes.	Applicable to: Discrete master only

- There is an expectation that those embarking on discrete master's programmes have already developed a level of subject knowledge, abilities and skills in chemistry that enables them to pursue studies in chemical science at the master's level and successfully achieve the prescribed learning outcomes.
- Typically those applying for discrete master's programmes will have a 1st cycle qualification in chemistry or one which contained greater part chemistry. Through scrutiny of diploma supplements, interviews and/or any other means the university chooses, it must be established before admission that any prior qualification(s) has caused the student to develop subject knowledge and understanding at bachelor's level together with the appropriate abilities and skills described in the *Chemistry Benchmark Statement*.
- Admission processes can also be applied to those with a first cycle qualification in a related interdisciplinary area and/or those with suitable experiential learning. In admitting such students, universities may wish to prescribe a programme of supplementary studies in order to strengthen areas of weakness.
- The accreditation process will seek to ensure that university admissions processes are robust and applied effectively.

Depth (Knowledge)

KR4: Programmes should build on the knowledge base to allow students to appreciate developments at the forefront of some areas of chemical sciences.	Applicable to: Bachelor only

- Programmes must provide significant enhancement beyond the required level for breadth of study (defined by *KR1* and *KR2*).
- Students should gain a detailed knowledge and critical understanding in one or more chemical science specialisms some of which are informed by or at the forefront of the subject.
- Specialisation should provide students with the knowledge base from which they can proceed to graduate employment or to further studies in the chemical sciences.

KR5: Programmes should ensure a depth of knowledge in specialist areas of chemical science demonstrated by an ability to solve problems at the level exemplified in Appendix B.	Applicable to: All master programmes

- Depth of study cross references to master's level in the *Chemistry Benchmark Statement* (ref - *Advanced studies, Problem-solving*) and is exemplified by the provision of a number of problems of an advanced nature in Appendix B. These are suitable for inclusion in unseen examinations, open-book examinations, and examinations where questions are issued in advance.
- Material at the level of appendix B problems would normally be included in the latter stages of a full time integrated master's programme.
- Material at the level of appendix B problems would be a fundamental feature of a discrete master's programme.
- There is an expectation that problems presented to students in assessments are unfamiliar, in that they have not been previously coached to tackle problems of a particular type.
- The range of problems that students will be expected to be able to solve will usually be narrower than in the case of those presented in Appendix A. This allows institutions freedom to continue to develop specialist chemical science programmes. In all cases intellectual rigour demonstrated by depth of study will be necessary.
- Problems contained in Appendix B are intended to be indicative of the standard which the RSC expects students to attain and are in no way intended to define curriculum content.

Practical Skills

KR6: Students must develop a range of practical skills.	Applicable to: All programmes

- Practical work, while supporting theoretical aspects should be stimulating and challenging in its own right and provide the essential *Chemistry-related practical skills* described in the *Chemistry Benchmark Statement*.
- The practical component should be laboratory based and designed so that students are exposed to a variety of synthetic and measurement techniques.
- Practical work must be rigorously and appropriately assessed and contribute towards the final mark of the degree programme.
- For bachelor's programmes students should typically complete at least 300 timetabled hours (exclusive of project work).
- For integrated master's programmes, students should typically complete at least 400 timetabled hours (exclusive of the substantial project).
- Computational work, case studies and short investigative tasks can contribute to the total timetabled hours.
- The RSC will consider a lower value for programmes which incorporate a period of study in industry or for part time modes of study. In such cases a condition may be imposed on the accreditation status of the programme and applicants may be required to provide evidence of developing appropriate practical skills within a workplace context.
- For discrete master's programmes, students must have prior learning of appropriate practical skills at bachelor's level and programmes should seek to develop these further, for example, through project work.

Project Work

KR7: **Programmes must incorporate some independent investigative methodology**	Applicable to: **Bachelor only**

- These are open ended activities which require students to manage their own learning.
- Activities should require students to apply information that they have learned earlier in the programme in order to consolidate and extend their knowledge and understanding of chemistry.
- One or more activities can be incorporated and could include:
  - research project
  - literature investigation
  - collaborative project work
  - external placement
- These activities would typically account for 25% of student workload in the final year.

KR8: **Programmes must provide research training to enable students to complete a substantial project, the outcome of which is potentially publishable.**	Applicable to: **All master programmes**

- Project work is an important element in the education of a professional chemist since it facilitates the development of essential high-level career skills.
- Programmes should provide suitable research training to enable students to successfully complete a substantial research project.
- The project, which can include those in computational and theoretical chemistry or in chemical pedagogy, would normally be completed in the final stage of a programme.
- It must be of an investigative nature and contain a substantial amount of advanced chemistry, drawing on the chemical and related literature.
- Projects should require some originality and be of a quality that is potentially publishable, i.e. work that has not been reported previously in the literature.
- The project should be an individual project, although team projects can be considered, and may be undertaken either in an academic institution or in industry.
- Assessment criteria for projects should be transparent and clearly explained to students before the project work commences.
- Project work must be assessed rigorously and contribute significantly to the final classification or grade.
- For integrated master's programmes, the substantial project should normally account for not less than one half of student workload in the final year.
- For discrete master's programmes, the substantial project should normally account for not less than one third of the entire programme.

External Placements

KR9:	**External placements must be subject to assessment against explicit and demanding criteria with universities retaining control and supervision of its students**	Applicable to: **All relevant programmes**

- Many chemical science programmes incorporate a placement either in industry or at university in a different country. For purposes of accreditation, placements need to be carefully selected on the basis of an agreed programme of work acceptable to both the home university and the external partner.
- Placements should be subject to assessment against explicit and demanding criteria and make an appropriate contribution to the final degree classification or grade.
- Industrial placements will usually involve both a major work-related assignment and elements of guided study when incorporated in integrated master's programmes.
- The guided study component would normally be broadly based in chemistry with content and level of learning outcomes comparable with respective studies at the university.
- Typically for a placement lasting one academic year, guided study would form around one quarter of learning activity/credit. Industrial partners should be made aware of the need for guided study and allow students to be released from work to complete their studies.
- Universities are encouraged to make best use of technology to ensure that students are provided with quality distance learning materials and can readily access support from the university.
- Placements at a university in a different country can follow a similar format to placements in industry although alternatively and possibly more commonly, students will study courses provided by the partner university. Such courses must be of a comparable level of outcome to those at the home university.
- Students returning to their home university after a placement must be suitably prepared to continue their chemical science studies at the appropriate level.
- The RSC recognises that some universities offer placement opportunities that extend the length of study normally associated with a degree programme. While these may be credit rated, they tend not to contribute to the final classification or grade of the degree awarded. Such programmes allow students to focus more on the placement experience and do not necessarily lend themselves towards a guided study component.

Professional Skills

KR10: **Programmes must develop a broad range of transferable key skills.**	Applicable to: **i) Bachelor** **ii) Integrated master**

- Transferable skills development is an essential feature of all degree programmes.
- Requisite transferable skills cross reference to generic skills outlined in the *Chemistry Benchmark Statement* at bachelor's level. These incorporate written and oral communication, data handling, numerical and mathematics skills, time management and an ability to interact with other people.
- Programmes should promote a sense of proper scientific conduct and ethical responsibility.
- Collectively students' generic skills should provide a basis to undertake further training of a professional nature.
- Students' competence in the exercise of transferable skills must be assessed and appropriately rewarded.

KR11: **Programmes must develop the professional skills for those intending to practice chemical science as a profession**	Applicable to: **All master programmes**

- Professional skills development is an essential feature of all master's programmes and relates directly to employability as a professional chemist.
- Requisite professional skills cross reference to generic skills outlined in the *Chemistry Benchmark Statement* at master's level. These incorporate independent learning ability, self direction and originality, and the ability to exercise initiative and personal responsibility.
- Programmes should provide the independent learning ability for continuing professional development and progression to Chartered Chemist through subsequent work practice.
- Students' competence in the exercise of professional skills should be assessed.

Assessment

KR12: **Assessment should be varied, appropriate and rigorous, and require students to apply their knowledge and solve problems**	Applicable to: **All programmes**

- Universities are encouraged to use of a wide range of assessment techniques matched to particular aspects of the programme which have been carefully designed and applied to ensure validity and reliability as discriminators.
- Programmes should seek to ensure students are encouraged to:
  - complete various forms of in-course assessment with particular, but not exclusive, evaluation of practical competence;
  - apply their understanding of earlier fundamental principles at advanced stages of the programme;
  - complete assessments in a diverse range of topics;
  - demonstrate their problem solving abilities;
  - critically analyse information, construct synopses, and devise solutions;
  - deal with topics expansively using reason and argument.
- A significant proportion of marks should be assigned on the basis of formal examinations conducted under controlled conditions. Such examinations can be open or closed book.
- Progression to subsequent stages of a programme should only be possible when a minimum competence has been demonstrated in pre-requisite areas.
- Universities must demonstrate that assessment of project work is rigorous and conducted against clear criteria.
- For master's programmes, assessment of the project work is central to determining whether or not a programme has provided the subject knowledge, abilities and skills associated with master's level learning outcomes and hence the basis for professional practice in the chemical sciences.
- The final grading of an award should be substantially weighted to student performance in the final stages of their programme, but should not rely exclusively on it.

Programme Title

KR13: The title of a programme should be indicative of content and address the assumptions an employer will make on the graduates' abilities based on the title.	Applicable to: All programmes

- When selecting programmes, students will often equate their career aspirations to the title. Similarly an employer of chemists will have preconceptions about graduates from a programme based on title. The title of a programme should be indicative of the content and it should follow that the subject knowledge, abilities and skills provided to successful students are directly relevant to the title.
- The RSC's general expectations are:
  - Programmes titled simply "*chemistry*" provide a balanced programme across the discipline. The substantial project can be any chemistry topic.
  - Programmes with titles such as "*chemistry with medicinal chemistry*" or "*chemistry with analytical chemistry*" imply a balanced programme with a specialism in a particular area of chemical science.
    - Bachelor's programmes should provide study in the specialism in the final year of study (see *KR4*)
    - Master's programmes must contain taught material from the implied specialism at master's level and require students to conduct their substantial project in an area of chemical science related to specialism (see *KR5* and *KR8*).
  - Programmes which combine studies in chemistry with that in another discipline such as "*chemistry with French*" and "*chemistry with mathematics*" denote a major/minor split.
    - Generally the minor subject would typically account for at least a quarter of the programme.
    - For master's programmes, chemistry studies should be taken to master's level and form the substantial project.

Quality Assurance

KR14: Universities must have robust quality assurance mechanisms in place for all aspects of its programmes	Applicable to: All programmes

- A clear quality assurance framework should be in place and actively applied to ensure that outcome standards are appropriate, consistent and fair.
- QA processes must at least assure that:
  - programmes are adequately supported by learning resources,
  - agreed specifications are followed,
  - assessments are set at the appropriate standard,
  - assessment processes are impartial and robust,
  - successful students achieve the stated learning outcomes and are graded accordingly,
  - students can progress fairly and effectively,
  - content and assessments are regularly reviewed.

KR15: Resources devoted to a programme should provide students with a suitably supportive environment so enabling them to be successful in achieving the stated learning outcomes.	Applicable to: All programmes

- RSC accredited degree programmes must be delivered by an appropriate level of fully-qualified, full and/or part-time staff (academic, administrative and technical) who are knowledgeable and suitably skilled in the areas they are teaching and able to set assessments to an appropriate standard.
- Universities are expected to provide evidence that students on an accredited programme are adequately supported by appropriate learning resources and support such as computing and communication facilities (access to software, internet and email) and suitable library provision, including appropriate accessibility to key textbooks, major online chemical databases and the primary chemical literature, such as the range of peer-reviewed journals published by the RSC.
- Lecture theatres and classrooms should have demonstration facilities, projection capabilities and internet access. Laboratories should adhere to strict safety guidelines and should house appropriate instrumentation for teaching and research, which should be up to date, high quality and properly maintained.
- Ultimately, adequate support is judged by whether or not the resources devoted to a programme provide students with a suitably supportive environment so enabling them to be successful in achieving the stated learning outcomes.

PART THREE:- HOW TO ACHIEVE RSC ACCREDITATION

The Accreditation Process

The process is summarised below.

CONSULT	University enters into discussions with RSC.
APPLY	Documentation is prepared and submitted to RSC.
REVIEW	Documentation is peer reviewed by the Committee for Accreditation and Validation (CAV).
VISIT	Campus visit to discuss the application and to check resources.
JUDGEMENT	Application is considered at a meeting of CAV and a decision agreed.
ACCREDIT	University markets its RSC accreditation status and RSC promotes the university's accredited degrees.
ENGAGE	As an accredited partner, university and RSC work together to advance the chemical sciences.

Consultation

The first phase to achieving accreditation is to discuss the degree programmes with the RSC's professionally qualified staff. They can provide informed advice on a programme's potential for accreditation. They can also assist with identifying and collating information for an accreditation submission.

Application

Universities must provide comprehensive information on their degree programmes and so allow a judgement to be formed on the programmes' quality. The preparation of a submission can be the rate-determining step. As such the university needs to devote time and effort into completing the self-assessment form and organising supplementary information. RSC staff can help with this process and provide guidance on how to prepare an accreditation submission.

Review

Once all the information is collected, an application is submitted. The documentation is distributed to members of the accreditation committee for detailed consideration against the key requirements. Each prepares a set of preliminary comments, which are circulated to other committee members. Any issues and matters for clarification are identified for discussion at the campus visit.

Campus Visit

The campus visit is a key feature of the accreditation process and is designed to constructively assist the committee is forming its judgement. It provides a valuable opportunity to discuss the features of the programmes with university staff and with students and to check out the infrastructure and resources devoted to delivery.

In carrying out the campus visit, claims made in the submission documentation can be substantiated. Any issues or matters for clarification can be resolved and if there any omissions in the documentation, they can be discussed in person. Ultimately having a campus visit allows the accreditation committee to expedite its decision making processes.

Campus visits last one to two working days and are normally conducted by a team of trained assessors (2-3 committee members who are Chartered Chemists) and a member of the RSC's professionally qualified staff.

The scale of the visit is dependent upon the committee's preliminary review comments. Once these are to hand the RSC will propose an agenda to the university. The agenda will outline activities and expectations for the visit and identify any further information required on the day.

There is an expectation that senior staff of the department will be available to meet the assessors at some point. A meeting with some current students to discuss their learning experiences is also an essential feature of the visit.

A typical one-day itinerary is shown below. It must be noted that this is presented simply as an example and that the scale and duration of a visit will vary.

Example of a campus visit agenda

09.30	Arrival and Initial Meeting with Head of Department
10.00	Private Meeting of Visiting Team and Review of Additional Materials This meeting enables the RSC's visiting team to review the preliminary comments (i.e. identifying the specific areas for clarification or discussion) and to agree its primary objectives for the visit. Any material that has been requested prior to the campus visit should be made available to the team.
10.30	Tour of Facilities The tour allows the visiting team to determine whether the learning resources available to support the programme are appropriate. The tour must include teaching laboratories and may include the library, IT facilities and any other specialist teaching areas or learning resources.
11.30	Meeting with Management, including Programme Director, Departmental Head This meeting allows the team to discuss the programme in terms of how the programme fits within the wider departmental and institutional strategy and about the department or university's vision for chemistry.
12.30	Lunch Meeting with Students This meeting allows the team to listen to the views of students and to gauge their experience of studying at the university. Ideally the meeting would include around 8-10 students from various year groups. If more than this number wish to attend, they are welcome to do so.
13.30	Meeting with Programme Team (i.e. Head of Department, Head of Teaching, Heads of Sections or Programme Leaders) This meeting focuses on the specific areas for clarification or discussion. It involves a wide ranging discussion on particular aspects of the programmes and is likely to drill down to more specific detail.
15.00	Private Meeting of Visiting Team This meeting enables the visiting team to review the day, to ensure that its objectives have been satisfied, and to prepare some provisional feedback.
15.30	Feedback Meeting – Outline of Next Steps Some informal feedback is given on the accreditation visit. However no decision can be given on accreditation at this stage. The remaining stages of the process, together with a timescale for an accreditation outcome, are outlined.
16.00	Finish

It is the RSC's intention to keep the campus visit relatively informal so that any aspects of the programme can be discussed openly. The RSC does not publish campus visit reports. Instead notes for the visit are used to inform the accreditation committee.

Judgement

After the campus visit has taken place, the submission is formally considered at the next available meeting of the Committee for Accreditation and Validation.

The final decision of the committee is based on its review of the submitted documentation and the campus visit report. If the committee are fully assured that all the key requirements are satisfied, accreditation is approved.

Subsequent to the meeting the university will receive a letter of approval together with a feedback document. The feedback document will contain up to four general components.

1. Evident strengths
   The RSC values good practices in teaching and learning and is keen to ensure that those involved in such activities receive appropriate acknowledgment of their commitment to the students' learning experiences. If appropriate the RSC will seek to promote and disseminate good practices through its networks and published materials.

2. Requirements
   In some instances, a condition for accreditation will be specified. It would normally involve a minor change to the programme and be something that the university can attend to with minimal effort. However, the university is required to implement the condition to receive or maintain the programme's accreditation. A timescale is normally stipulated for completion of the condition.

3. Recommendations
   These are continuous enhancement features which the university should attend to during the accreditation period. They may involve more significant change and require the university to review its specifications, procedures and practices. There is an expectation that, when programmes are submitted for re-accreditation after 5 years, the committee's recommendations will have been addressed.

4. Suggestions
   Committee members will often identify features that might be enhanced through alternative approaches. These are communicated to universities as constructive suggestions. It is hoped that they will stimulate initiatives for programme development. The university is not obliged to act upon suggestions to retain accreditation.

Confirmation

Universities with accredited degree programmes receive an embossed certificate denoting accreditation, which they should display prominently to their students and other stakeholders. Universities are encouraged to publicise their achievement within internal publications, websites, marketing material and local media. The RSC can offer assistance with media communications on request.

Universities are permitted to use the RSC logo as an accompaniment to its course marketing information, such as websites and advertising material. The RSC logo is an internationally recognised mark of a high quality organisation. It features prominently on the RSC's range of high impact academic journals and is linked prominently to a variety of successful activities in the promotion and advancement of the chemical sciences. In using the logo, the RSC's conditions of use must be observed at all times.[6]

The RSC publishes a list of accredited degree programmes on its website which allows students to identify where quality chemical education exists with minimal effort. The list includes web links to university websites so assisting potential students to make direct contact with admissions tutors.

The monthly membership magazine *RSC News* is regularly used to inform the chemical science community of accreditation successes. In particular original submissions or those received from emerging markets are featured.

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[6] http://www.rsc.org/styleguide/logo-introducing.html

Engagement with RSC

RSC accreditation should be viewed as a part of a wider engagement with an organisation which is committed to the promotion and advancement of the chemical sciences.

The RSC is keen to engage with those studying chemistry whether on accredited degree programmes or as research postgraduates. It actively promotes RSC membership to students at discounted subscription rates. Students will be made aware of the professionalism of being associated with the RSC, of how to develop into a fully competent professional chemical scientist and achieving Chartered Chemist (CChem) status.

In addition to the wide range of membership benefits, the RSC has developed a network of student chemical societies and aims to encourage communication and enhance interactions for aspiring chemical scientists. For example, the RSC advises and supports student chemical societies in staging events for students at their university.

Academic staff are encouraged to join the RSC. Through their contribution to the profession, many leading faculty members will be eligible to become Fellows (FRSC) which is the RSC's senior membership category. Others can join as Members (MRSC) and may wish to qualify as Chartered Chemists. Irrespective of membership category, a wide range of membership benefits are available.

Association with the RSC provides access to specialist networks and an ability to influence policy in education, science and professional practice. In education, the RSC is constantly working to promote good practice in teaching and stimulate the interest of young people in studying chemical science. In science, the RSC is forward thinking through its Roadmap and is committed to shaping the future direction of the chemical sciences. In professional practice, the RSC sets and provides guidance on standards of professional conduct and ensures that practising chemical scientists maintain a contemporary interest in their chosen profession.

The RSC is one of the world's leading scientific publishers. It offers an exceptional range of peer-reviewed journals, magazines, books, databases and publishing services to the chemical science community. Universities with accredited programmes will already have some association with RSC Publishing. Enhancement of this relationship is a goal and it is anticipated that faculty members will consider publishing their best work in the high impact RSC journals.

Ultimately it is hoped that universities can appreciate the wealth of opportunity the RSC offers and take an active part in the RSC chemical science community.

APPENDICES

Appendix A - Threshold questions

A1 Hydrogen sulfide, H_2S, and sulfur dioxide, SO_2, are toxic components of natural gas which must be removed before gas is supplied to a customer. One possible reaction is:

$$2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$$

(a) Using the data below, calculate the standard Gibbs free energy change for the reaction at 25 ˚C and 500 ˚C and comment on the values you obtain in terms of the feasibility of the reaction.

(b) Calculate the equilibrium constant, K_p, at both temperatures.

(c) Mixing H_2S and SO_2 does not in fact result in the above reaction. Comment.

(d) Predict the effect of (i) increasing the temperature and (ii) increasing the gas pressure on both the value of K_p and the extent of reaction of H_2S.

(e) How might the reaction conditions be changed to make it more acceptable in industrial terms?

	$H_2S(g)$	$SO_2(g)$	$H_2O(l)$	S(s)
$\Delta_f H^o_{298}$ / kJ mol^{-1}	−22.2	−296.6	−285.8	0
S^o_{298} / J K^{-1} mol^{-1}	205.6	247.9	70.1	31.9
Cp / J K^{-1} mol^{-1}	34.23	39.87	75.29	22.64

A2 (a) Write expressions for K_3, K_6, and β_3 for the stepwise replacement of water from $[Cu(H_2O)_6]^{2+}$ by NH_3.

(b) Stability constants K_n are given in the Table.

		Log K_n					
Metal Ion	**Ligand**	**n:1**	**2**	**3**	**4**	**5**	**6**
Sn^{2+}	Cl^-	1.51	0.73	−0.21	−0.55		
Pd^{2+}	Cl^-	6.1	4.6	2.4	2.6	−2.1	
Ni^{2+}	NH_3	2.67	2.12	1.61	1.07	0.63	−0.09
Cu^{2+}	NH_3	3.99	3.34	2.73	1.97	−1.1	
Cu^{2+}	en	10.6	9.1	−1.0			

en = $NH_2CH_2CH_2NH_2$

(i) Calculate the values of log β_4 and log β_5 for the Pd^{2+}/Cl^- system.

(ii) What are likely to be the predominant species in solution in the Pd^{2+}/Cl^- and the Sn^{2+}/Cl^- systems?

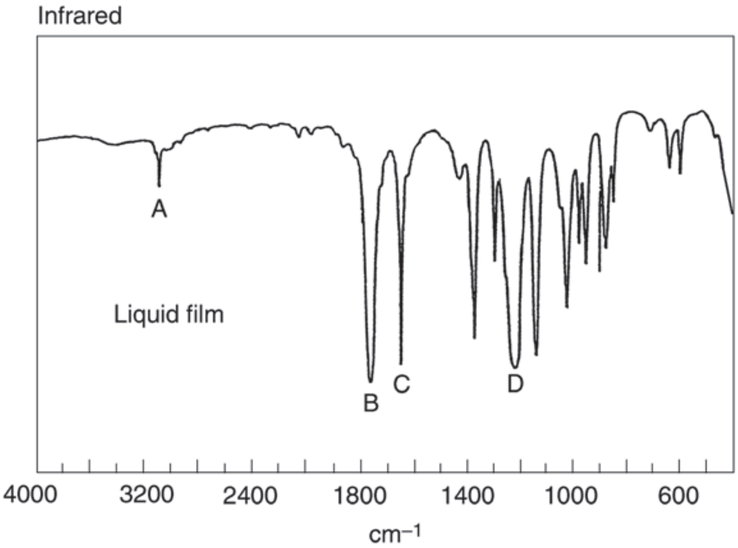
(iii) Account for the variations in log K_n values for both the Ni^{2+}/NH_3 and Cu^{2+}/NH_3 systems.

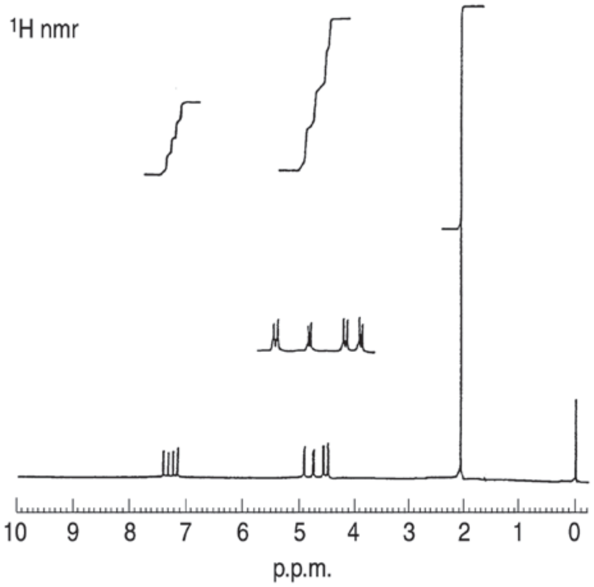
(iv) What is meant by the terms *chelate effect* and *macrocyclic effect*?

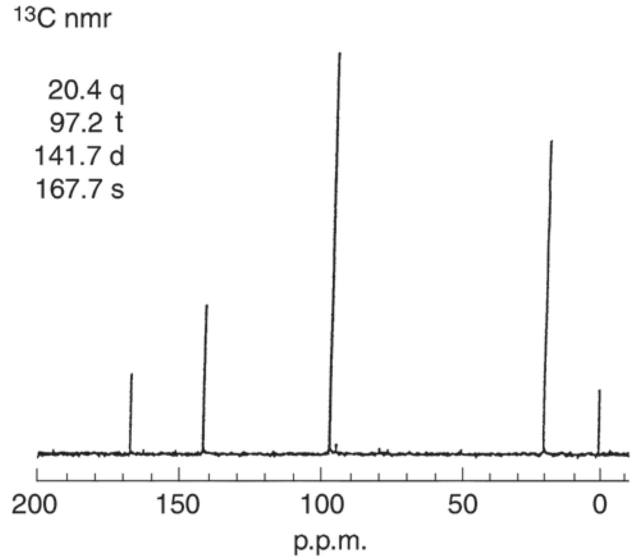
(v) Explain why log K_1 for Cu^{2+}/en is larger than log β_2 for Cu^{2+}/NH_3.

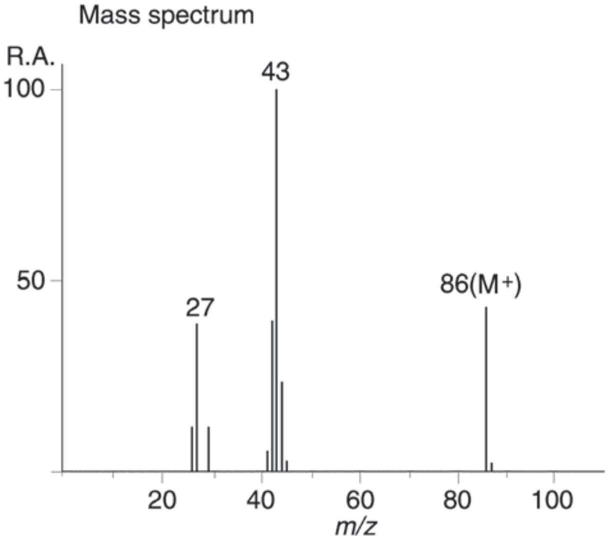
(vi) Explain why log K_3 for Cu^{2+}/en is so small.

A3 An aliphatic compound of empirical formula C_2H_3O has the IR, ^1H, ^{13}C NMR and mass spectra shown below. Deduce the molecular structure and suggest structures for the fragmentation peaks at 43 and 27 mass units. Assign all the ^1H and ^{13}C NMR signals and the IR bands labelled **A, B, C** and **D**. Finally sketch the ^{13}C NMR DEPT(135) spectrum.









A4 (a) A group 16 element chloride, **A**, reacts with ammonia to give a bright orange, cyclic product **B**. When **B** is heated with silver wool *in vacuo* ring contraction occurs to give **C** which, on sublimation, gives a lustrous golden polymer **D** that conducts electricity. Elemental analysis shows that **B, C** and **D** each contain 30.4% by mass of nitrogen. Identify, and draw the structures of **A, B, C** and **D**. Give equations to show each of the transformations. Why does **D** conduct electricity?

(b) Use the following reactions to show how xenon fluorides can react as fluoride donors or as fluoride acceptors. Identify **A** to **C** and describe their structures.

(i) $2XeF_2 + SbF_5 \rightarrow$ **A**

(ii) $XeF_6 + AsF_5 \rightarrow$ **B**

(iii) $XeF_6 + 2(NOF) \rightarrow$ **C**

(c) Write balanced equations for the following reactions and describe the structures of any xenon compounds in the products.

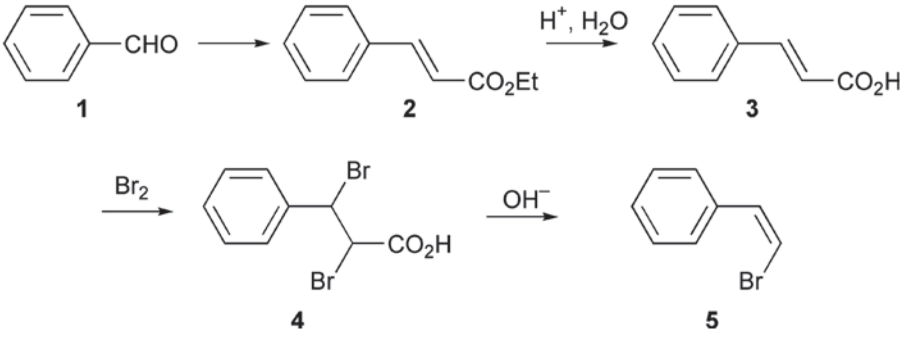
(i) $XeF_6 + 3H_2O \rightarrow$ 2 products

(ii) $XeF_4 + 2H_2O \rightarrow$ 4 products.

Alkaline solutions of the xenon-containing product which is common to both reactions are not stable and immediately begin to disproportionate slowly.

Write equations summarising this alkaline hydrolysis, describe the structure of the solid which is ultimately produced, and comment on its properties.

A5 The following reaction sequence was used to prepare the (Z)-alkene **5**.



(a) Suggest a reagent or reagents to effect the transformation from **1** to **2**, and account for the stereochemistry of **2**.

(b) Give mechanisms for the reactions **2** to **3**, and **3** to **4**.

(c) Only one diastereoisomer of **4** could be isolated. Draw its structure.

(d) Give a mechanism for the last step. Why is the less stable (Z)-isomer formed?

A6 (a) How can the adsorption of gases onto solids lead to a lowering of reaction activation energies and hence heterogeneous catalysis?

(b) The experimental adsorption data for hydrogen on a sample of copper at 298 K are given below.

P / Torr	0.19	0.97	1.90	4.05	7.50
V / cm^3	0.042	0.163	0.251	0.343	0.411

Show that these data fit the Langmuir model, with H_2 molecularly adsorbed. Calculate the value of K for the adsorption equilibrium and the adsorption volume of hydrogen (at atmospheric pressure) corresponding to monolayer coverage.

(c) Data for the adsorption of krypton on graphite at 100 K do not fit the Langmuir model. Explain why and mention which model you would use to determine the surface area.

(d) The following data were obtained from a decomposition of carbon monoxide on platinum at 773 K.

reaction half life / s	6.9	7.0	6.8	7.5	16.1	31.9	65.0
initial pressure / kPa	1	2	4	8	16	32	64

Comment on the data in terms of the Langmuir model. Find the true rate constant and the Langmuir constant for the decomposition reaction.

A7 (a) Calculate the first 5 terms of the electrostatic potential energy, E, of a cation in a two-dimensional square array, A^+B^-, where the closest interionic distance is d. How are such calculations incorporated into the equation for the lattice energy of an ionic solid?

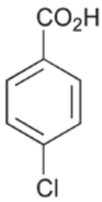
(b) Use the data given below to show that, although BaF_3 has a favourable enthalpy of formation, the most stable fluoride of barium is BaF_2.

			ΔH / kJ
Ba(s)	→	Ba(g)	180
Ba(g)	→	$Ba^+(g) + e^-$	503
$Ba^+(g)$	→	$Ba^{2+}(g) + e^-$	965
$Ba^{2+}(g)$	→	$Ba^{3+}(g) + e^-$	3454
$F_2(g)$	→	2F(g)	159
$F^-(g)$	→	$F(g) + e^-$	330

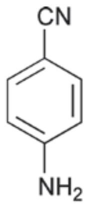
$r(Ba^{3+}) = 126$ pm; $r(Ba^{2+}) = 136$ pm; $r(F^-) = 133$ pm.

Kapustinskii constant = 107 100 (with radii in *pm*)

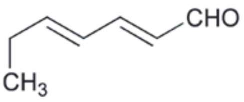
A8 (a) The IR and ^{1}H NMR spectroscopic data of five organic compounds **A** - **E** (below), each of which contains seven carbon atoms, are provided below.



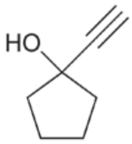
A



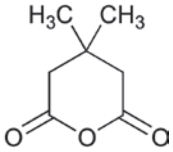
B



C



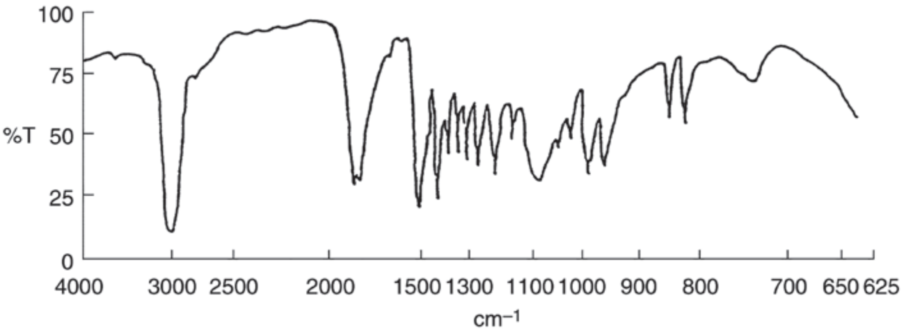
D



E

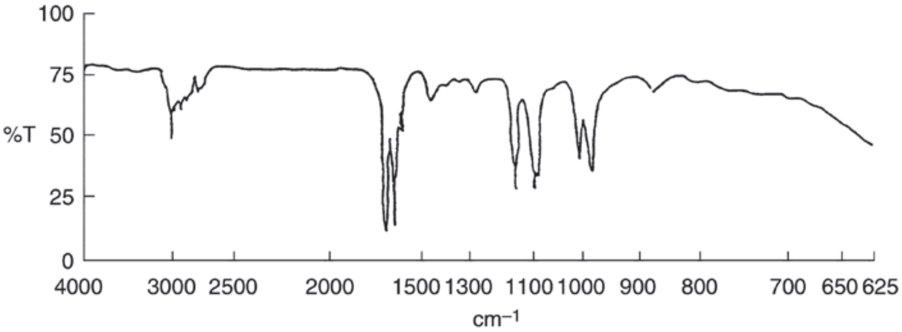
Indicate which structure gives rise to each set of spectroscopic data and assign the spectroscopic data for each compound.

(i)



ν_{max} 3170–2860, 1820, 1775 cm^{-1}.
^{1}H NMR δ 2.61 (4H, s), 1.16 (6H, s).

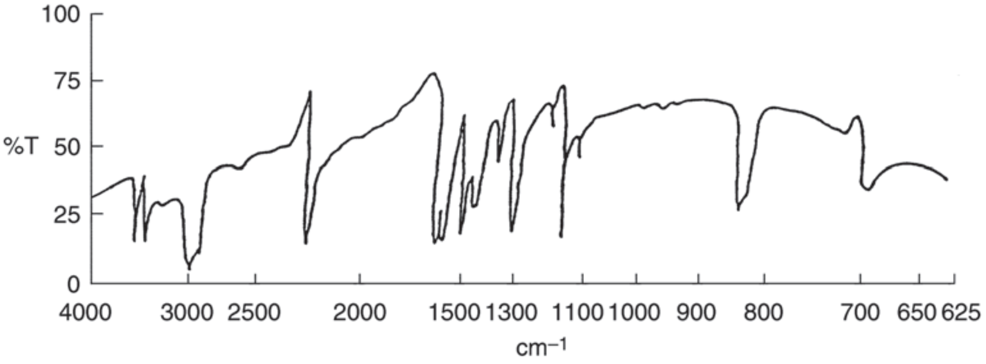
(ii)



ν_{max} 3100–2630, 1680, 1645, 1595 cm^{-1}.
^{1}H NMR δ 9.53 (1H, d, *J* = 7.4 Hz), 7.10 (1H, dd, *J* = 15.0 and 10.5 Hz), 6.40–6.24 (2H, m), 6.08 (1H, dd, *J* = 15.0 and 7.4 Hz), 2.26 (2H, qd, *J* = 7.5 and 5.5 Hz), 1.09 (3H, t, *J* = 7.5 Hz).

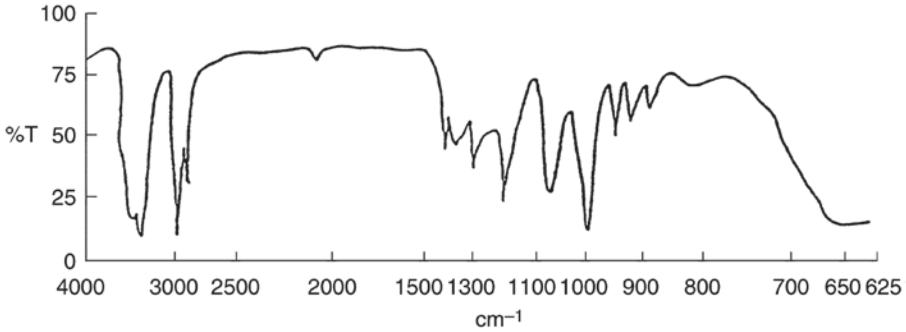
A8 **(Continued)**

(iii)



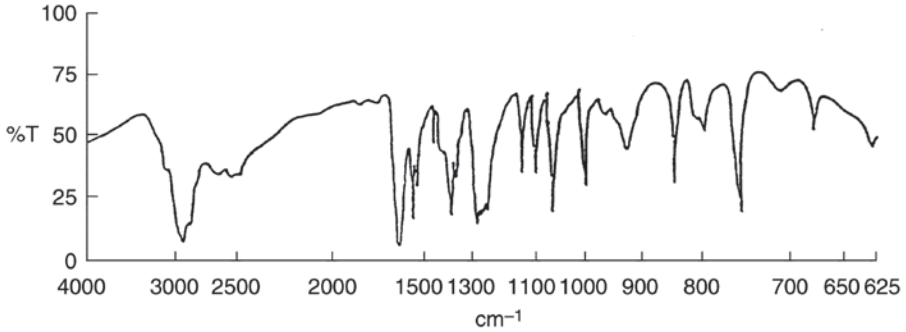
ν_{max} 3450, 3380, 3020-2860, 2220, 1610 cm^{-1}.
^{1}H NMR δ 7.38 (2H, d, *J* = 9.0 Hz), 6.63 (2H, d, *J* = 9.0 Hz), 4.31 (2H, broad s)

(iv)



ν_{max} 3500–3010, 3300, 3010–2790, 2100 cm^{-1}.
^{1}H NMR δ 2.50 (1H, s), 2.38 (1H, broad s), 2.00-1.88 (4H, m), 1.88-1.67 (4H, m).

(v)



ν_{max} 3350–2260, 1680 cm^{-1}.
^{1}H NMR δ 7.96 (2H, d, *J* = 8.9 Hz), 7.45 (2H, d, *J* = 8.9 Hz).

A8 **(Continued)**

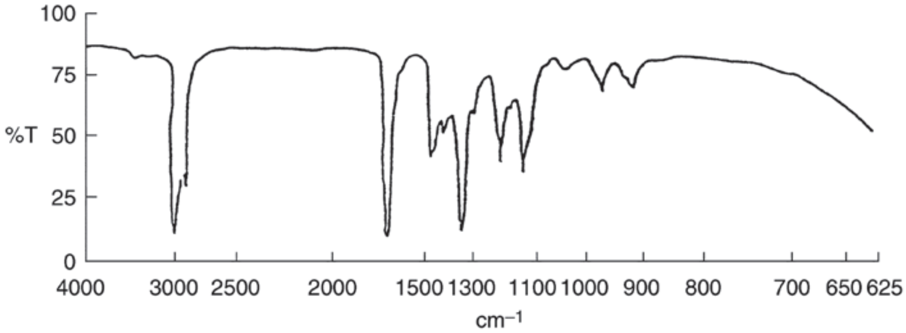
(b) (i) For each compound **A** - **E**, indicate how many signals you would expect to observe in its ^{13}C NMR spectrum

(ii) Predict the values of *m/z* and the relative sizes of the two highest mass peaks in the mass spectrum of compound A

(c) Another compound containing seven carbon atoms has the spectroscopic data shown below.

(i) What is the structure of this compound?

(ii) Assign its spectroscopic data.



ν_{max} 3010–2800, 1725 cm^{-1}.
m/z M^+ 114.
^1H NMR δ 2.33 (2H, s), 2.12 (3H, s), 1.01 (9H, s).
^{13}C NMR δ 208.4, 56.0, 32.3, 30.9, 29.8 (3C).

A9 Devise suitable analytical procedures to investigate each of the following situations (Your account should include the physical basis of the method, consider appropriate detection limits and interferences, indicate the advantages of your chosen method over other possible methods and also the steps necessary to ensure appropriate sampling and statistical significance of the results)

(a) A spillage of metal ion solutions into sea water.
(b) A mixture of tablets of analgesic drugs including aspirin, paracetamol and morphine.
(c) The concentration of lead in roadside vegetation.
(d) A mixture of organic dyes in aqueous solution.
(e) The concentration of hydrogen sulfide in natural gas.
(f) Trace levels of chlorinated hydrocarbons in river water.
(g) The composition of a mixture of several chiral sugars.
(h) The level of potassium cyanide in an aqueous industrial effluent.
(i) The concentrations of additives in a plastic food packaging polymer.

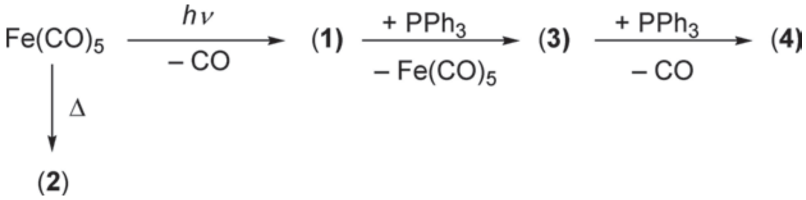
A10 (a) For the following molecules or ions, draw the structures, count the total number of valence electrons associated with the metal and work out the metal formal oxidation state and d-electron count:

$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ $[W(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(CO)_2]$

$[RhCl(PPh_3)_3]$ $[RhCl_2(PPh_3)_3Me]$

(b) Irradiation of $[Fe(CO)_5]$ with UV light produces a gold-yellow solid (**1**) which gives rise to infrared absorptions indicating terminal and bridging carbonyl ligands in a 2:1 ratio. Direct heating of $[Fe(CO)_5]$ yields a green-black solid (**2**) with empirical formula FeC_4O_4. Reaction of (**1**) with triphenylphosphine (PPh_3) at room temperature gives a compound (**3**) along with one equivalent of $[Fe(CO)_5]$. Heating (**3**) with excess PPh_3 in cyclohexanol yields a compound (**4**) with composition $C_{39}H_{30}FeO_3P_2$ which gives rise to one resonance in its ^{31}P NMR spectrum.

Identify the compounds (**1**) to (**4**) and draw their structures. Indicate the possible isomers which exist for (**4**) and, using the data provided, indicate which geometry is most likely to be adopted and explain your reasoning.



(c) The reaction of 2-butyne with $PdCl_2$ in hot ethanol as solvent gives a crystalline dimeric complex **A**. The metal atoms in the complex obey the *18-electron rule* and its mass spectrum shows a molecular ion at 570 amu and additional fragment ions at 285 and 108 amu (but not 54 amu). The ^1H NMR spectrum of **A** shows only one signal: a singlet at 1.9 ppm, while its ^{13}C NMR spectrum has two signals at 26 and 130 ppm. Treatment of **A** With PPh_3 gives a new complex **B** which also obeys the 18-electron rule. Complex **B** shows a molecular ion at 547 amu in its mass spectrum and its ^1H and ^{13}C NMR spectra are similar to those of **A**, although with additional signals for PPh_3.

(i) Give the structures of the complexes **A** and **B** and account for their formation.

(ii) Show how both complexes obey the 18-electron rule.

(iii) Account for the spectroscopic evidence given for complexes **A** and **B**.

(iv) Discuss the nature of the organic ligand present in these complexes and suggest why it is unstable as a free molecule but stable when coordinated to a metal.

A11 (a) The experimental data given below were obtained for the temperature dependence of the rate constant, *k*, for the reaction:

$$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$$

(b) (i) From the units of *k*, what is the order of this reaction?

(ii) Determine graphically the activation energy and pre-exponential (or frequency) factor for this reaction.

Temperature / K	430	450	470	490	510	530
1000*k* / dm^3 mol^{-1} s^{-1}	3.82	13.6	43.3	125.7	335.6	831.9

(c) The ozone cycle comprises a series of photochemically-induced reactions which maintain the protective ozone layer in the upper atmosphere. Two key reactions in the cycle are:

$$O + O_2 \xrightarrow{k_1} O_3 \qquad \text{.....(1)}$$

$$O + O_3 \xrightarrow{k_2} 2O_2 \qquad \text{.....(2)}$$

(i) If the Arrhenius parameters for reaction (2) are $A = 3.16 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $E_a = 23.9$ kJ mol^{-1}, calculate the rate constant for the reaction at a temperature of 240 K, typical for the upper atmosphere.

(ii) Derive an expression for the steady state concentration of O_3 using reactions (1) and (2).

(d) Nitric oxide (NO) in the atmosphere can react with ozone by the reaction

$$NO + O_3 \xrightarrow{k_3} NO_2 + O_2 \qquad \text{.....(3)}$$

By incorporating this reaction into the scheme, derive a new expression for the steady state concentration of ozone.

(e) If $[O] = 8.30 \times 10^{-12}$ mol dm^{-3}, $[NO] = 1.66 \times 10^{-13}$ mol dm^{-3} and $k_3 = 2.31 \times 10^6$ dm^3 mol^{-1} s^{-1}, calculate the ratio of ozone concentration in the presence and absence of nitric oxide. Comment on the practical significance of your calculated ratio.

A12 (a) Using a value for the Rydberg constant, R_H, of 1.09737×10^5 cm^{-1},

(i) calculate the wavelengths of the first three transitions in the absorption spectrum of a hydrogen atom in the 3s state;

(ii) determine the ionisation energy of the hydrogen atom in the 4s state, expressing your answer in kJ mol^{-1}.

(b) (i) Derive an expression for the energy levels of a particle of mass *m* in a one-dimensional box of length *a*.

(ii) A particle confined to a one-dimensional box of length 5.0×10^{-9} m has an energy of 1.0×10^{-20} J for n = 2. Calculate the mass of the particle.

(iii) Explain what happens to the energy levels for a one-dimensional box when,

- the size of the box is doubled,
- the mass of the particle is doubled,
- one side of the box is removed to infinity.

(c) An electron, mass m_e, is confined to a one-dimensional well of length a = 1 nm. The potential energy is zero within the well and infinity elsewhere. Deduce the following information about the electron in this well.

(i) The wavelengths associated with the lowest five energy levels of the electron.

(ii) The wavelength of the light emitted when the electron moves from the third to the second energy level.

(iii) The number of energy levels available to the electron between 8 and 20 eV.

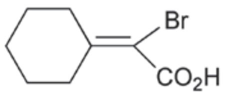
(d) What are the degeneracies and energies, in units of $h^2/8m_ea^2$, of the first five energy levels when the electron is confined instead to a three-dimensional well (box) with equal sides of length *a*?

A13 Indicate clearly those of the molecules **A** to **E** below that are:

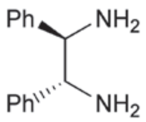
(a) chiral and contain a C_2 axis of rotation;

(b) achiral and contain a C_2 axis of rotation;

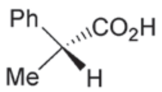
(c) chiral and lack a C_2 axis of rotation.



A



B



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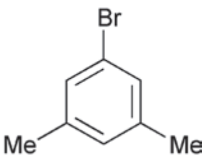
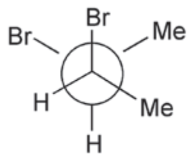
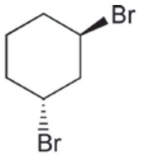


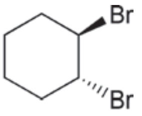
D



A14 (a) Draw both chair conformers for each of the dibromides **H** and **I**.



H



I

(b) (i) Using the data outlined below calculate the strain energy of the conformers of **H**.

(ii) Also calculate the additional strain energy of the conformers of **I** relative to cyclohexane.

Interaction	**Energy Cost / kJ mol^{-1}**
1,3-Diaxial H----Br	1
Gauche Br----Br	3

(c) In addition, use these data to calculate the percentage of the more stable conformer for both the dibromides **H** and **I** at 25 ˚C (298 K).

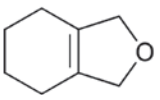
(d) Experimental evidence indicates that the diaxial conformer of **I** is more stable than the diequatorial conformer. Comment on this in the light of your answer to part (b) (ii).

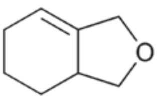
A15 Cobalt(II) chloride hexahydrate was dissolved in water and 1,2–diaminoethane added. The solution was oxidised with H_2O_2 and a green complex (**A**) isolated after heating with hydrochloric acid. The green complex was shown to contain 1,2–diaminoethane and analysis also established that it contained 20.6% Co and 37.3% Cl. The green complex was diamagnetic and had two d–d bands at 19 300 cm^{-1} and 26 000 cm^{-1}. In addition a single Co–Cl stretching frequency was observed in the IR at 370 cm^{-1}. The complex had a molar conductivity of 110 S cm^2 mol^{-1} at 25 °C in water, and the conductivity was observed to increase with time finally reaching a value of 370 S cm^2 mol^{-1} after several hours. Heating the green complex with hydrochloric acid gave a violet complex (**B**), which also contained 20.6% Co and 37.3% Cl. The violet complex had two d–d bands at 19300 and 26000 cm^{-1}, however, the extinction coefficients were roughly twice those observed for the green complex.

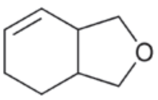
Reaction of the violet complex with 1,2–diaminoethane gave an orange complex (**C**), % Co = 17.1; % Cl = 30.8; % N = 24.3; which had two d–d bands at 21 000 cm^{-1} and 28 000 cm^{-1}. When **C** (346 mg) was dissolved in water and passed through a cation exchange column in the hydrogen form, it released acid which required 60 cm^3 of aqueous sodium hydroxide (0.05 mol dm^{-3}) for neutralisation.

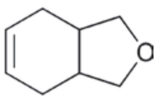
Suggest structures for the three complexes **A**, **B** and **C**, account for the experimental data provided and discuss the d–d spectra.

A16 (a) State, with explanation, which of the following molecules are chiral:

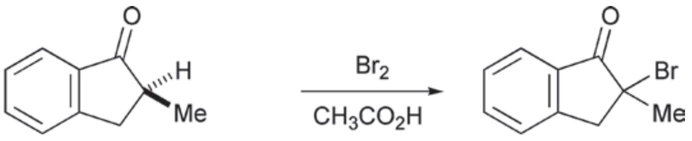


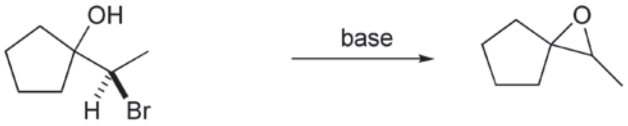


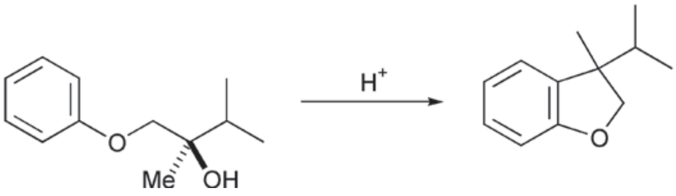




(b) Deduce, with mechanistic explanations, the stereochemistry of the products of the following reactions. All the starting materials are single enantiomers.







A17 (a) Sketch and fully label the phase diagram for pure ammonia, NH_3, from the following data:

triple point	195.4 K; 6.12 kPa
critical point	405.9 K; 11.35 MPa
normal boiling point	239.8 K
normal melting point	195.5 K

(b) What would be observed if:

(i) a sample of gaseous NH_3 was cooled from 500 K to 150 K at a constant pressure of 50 kPa

(ii) a sealed tube half-full of liquid NH_3 was heated from 200 K to 500 K.

(c) The vapour pressures (in bar) of liquid and solid benzene are given at low temperatures (in Kelvin) by the expressions

$\ln p = -4110/T + 11.70$ (liquid)

$\ln p = -5320/T + 16.04$ (solid)

(i) Calculate the pressure and temperature at the triple point of benzene and the enthalpy change of fusion of the solid.

(ii) Close to its triple point, the molar volume of benzene increases on melting by approximately 10^{-5} m^3. Assuming that the slope of the solid-liquid coexistence line is constant, estimate the temperature at which benzene melts under a pressure of 1 kbar

A18 (a) For each of the following radionuclides, predict the decay mode, write a balanced equation for the nuclear transformation which occurs, and suggest a suitable detector.

(i) ^{95}Nb

(ii) ^{16}N

(iii) ^{230}U

(b) Soil from south west Scotland is analysed by gamma ray spectroscopy. In May 2000, the activity of ^{137}Cs in the soil is found to be 2.74 Bq g^{-1}. Calculate

(i) the ^{137}Cs activity in the soil in May 1986, immediately following the Chernobyl nuclear accident,

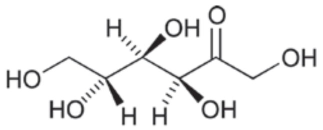
(ii) the count rate which would be obtained if a 10 g sample of the soil was counted on a detector of 29% efficiency in May 1986.

DATA: Half life ^{137}Cs = 30.2 years

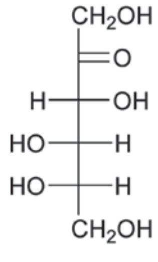
(c) A contaminated soil sample is being analysed for Ni and Co by UV-visible spectroscopy. The Ni and Co from 10 g of the soil sample are extracted, filtered and made up to 100 cm^3 of solution. The ions were then complexed with 1,10-phenanthroline and the absorbencies of the solution measured to be 0.96 at 550 nm and 0.75 at 650 nm. Calculate the amount of Ni and Co in the soil sample in ppm given the molar absorptivities of the complexes in the table below.

	ε (550 nm) /dm³ mol⁻¹ cm⁻¹	**ε (650 nm) /dm³ mol⁻¹ cm⁻¹**
Ni complex	20 533	7400
Co complex	9867	27 346

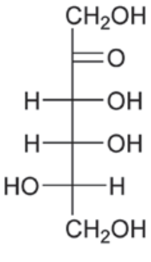
A19 (a) Which of the Fisher projections, **A** to **D** below, correctly represents the keto-sugar D-fructose?



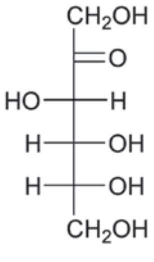
D-fructose



A



B



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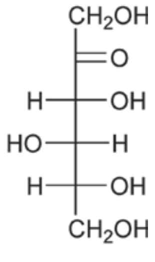


D

(b) Treatment of D-fructose with $NaBH_4$ in methanol, and subsequent acidification, results in the formation of two products, **E** and **F**. What are their structures?
(You may use any representation you see fit).

(c) Exposure of the aldohexose D-mannose to $NaBH_4$ in methanol also affords compound **E**, whereas exposure of either of the aldohexoses D-glucose or L-glucose to the same conditions affords **F**. Explain. What are the structures of D-mannose, D-glucose and L-glucose? Assign the structures **E** and **F** exactly.

(d) Treatment of **E** with acetone and an acid catalyst results in the formation of a new compound, $C_{12}H_{22}O_6$, which reacts with $NaIO_4$ to form two molecules of **G**, $C_6H_{10}O_3$. Give the structure of **G** and name the simple sugar of which it is a protected form.

A20 (a) (i) Write down the selection rules for rotational excitation arising from the absorption of electromagnetic radiation and identify the region of the electromagnetic spectrum in which you would expect such absorption to occur.

(ii) The first two lines in the rotational absorption spectrum of carbon monoxide lie at 3.84 cm^{-1} and 7.68 cm^{-1} respectively. Show that these results are in agreement with the predictions of the rigid rotor model and calculate the value of *B*, expressing the result in frequency units.

(b) For each of the following molecules,

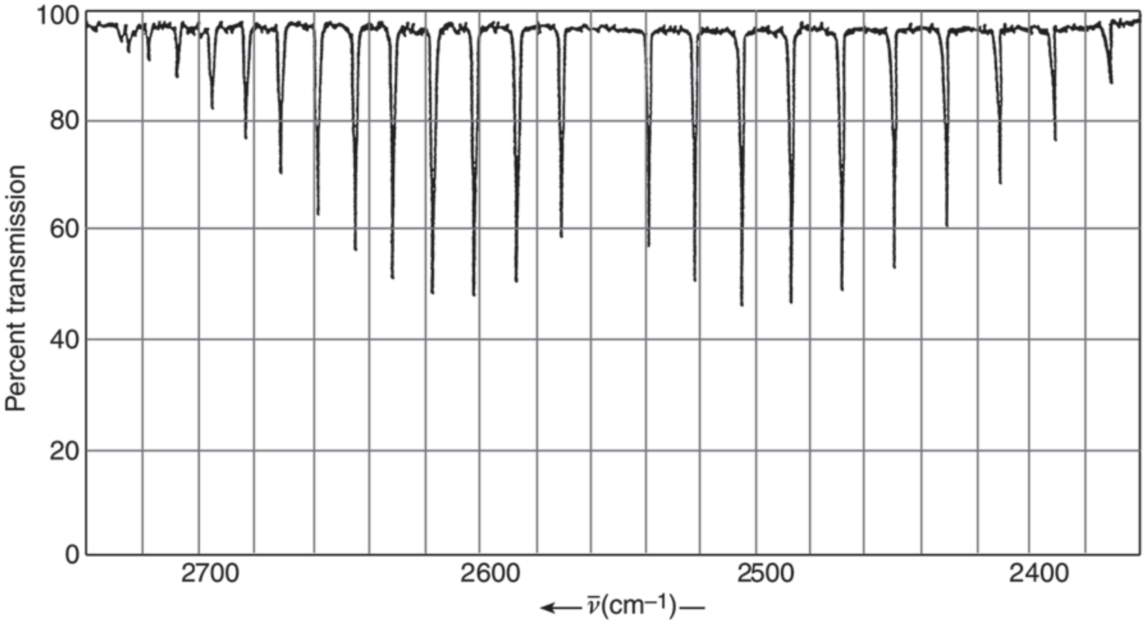
$$CS_2 \; SO_2 \; H_2 \; HD$$

(i) give the number of vibrational modes,

(ii) sketch the form of each vibration,

(iii) state, with your reasoning, whether or not each vibration is infra-red active.

(c) The medium resolution gas phase infrared spectrum of hydrogen bromide is shown below.



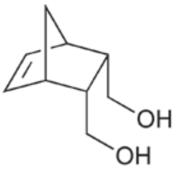
Assuming the molar mass of bromine to be 80 g mol^{-1}:

(i) make a rough estimate (within 5%) of the force constant of HBr;

(ii) make a rough estimate (within 5%) of the rotational constant of HBr;

(iii) explain, by means of an energy diagram, the origin of the spectrum.

A21 (a) Propose syntheses of the following molecules from the indicated starting materials. Any commonly-available additional organic or inorganic reagents may be used. Show clearly your retrosynthetic analysis, and indicate any reasoning behind your choice of reagents and/or conditions.



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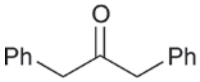

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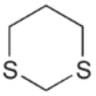

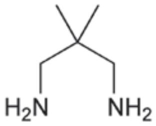

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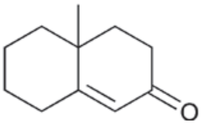

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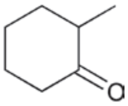
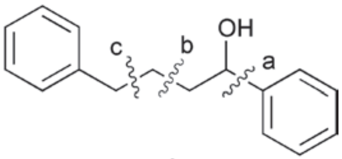


(b) Suggest three possible syntheses of target molecule (**1**), one based on a key disconnection at position **a**, one on a disconnection at position **b** and the third on a disconnection at position **c**. In each case show clearly the retrosynthetic analysis. Give reagents and mechanism for each synthesis.



1

A22 (a) Write Lewis structures for the following:

(i) 3 resonance forms of O_2NNH^-

(ii) 3 isomeric forms of HNSO

(iii) 2 resonance forms of HN_3.

(b) For a diatomic molecule X_2 show how suitable combinations of p–orbitals can lead to the formation of (a) σ–bonding, (b) σ^* anti-bonding, (c) π-bonding and (d) π^* anti-bonding molecular orbitals. Assign the (+) and (–) symmetry notation and state whether the resulting molecular orbitals are gerade or ungerade.

Construct a molecular orbital energy level diagram for dinitrogen (N_2) and label clearly all the resulting molecular orbitals.

Using this diagram evaluate the most likely values for the data missing in the table below and then rationalise the collective trends for the series.

Diatomic Species	**Bond distance/pm**	**Bond dissociation energy/kJ mol^{-1}**
N_2	110	945
N_2^-		765
N_2^+	112	

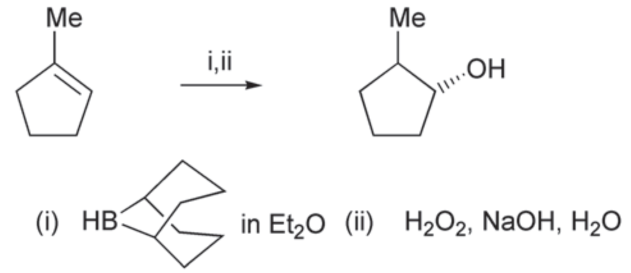
Predict the magnetic behaviour (paramagnetic or diamagnetic) for each species.

(c) The diboron molecule, B_2, is paramagnetic with a magnetic moment corresponding to two unpaired electrons per B_2 molecule. How can this be explained by Molecular Orbital Theory?

A23 Explain the regioselectivity, or stereoselectivity, or both, in the following additions to carbon carbon double bonds:

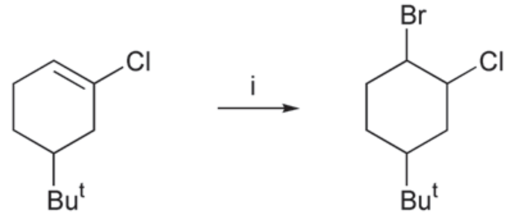
(a) $H_2C{=}CHBr$ + HBr(in Et_2O) $\longrightarrow$ $H_3C{-}CHBr_2$

(b)



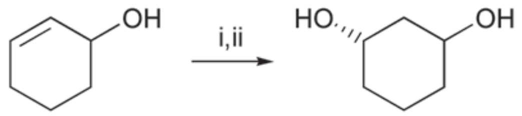
(i) HB in Et_2O (ii) H_2O_2, NaOH, H_2O

(c)



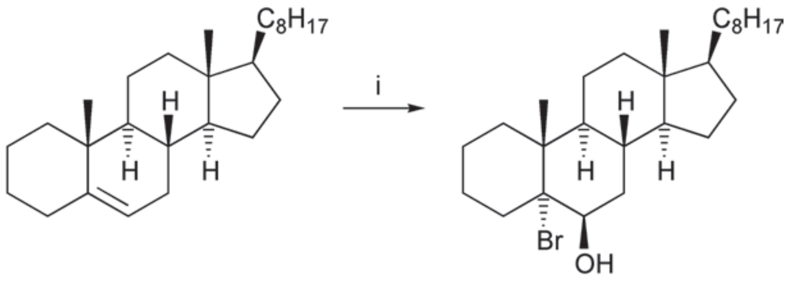
(i) HBr in pentane with ultraviolet irradiation

(d)



(i) $Hg(OAc)_2$ in H_2O (ii) $NaBH_4$ in H_2O

(f)



(i) $CH_3CONHBr$, H_2SO_4 in H_2O-1,4-dioxane

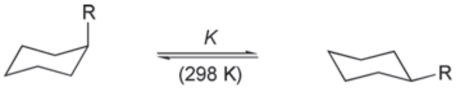
A24 (a) The energy required to remove an electron from the 2s orbital of an excited H atom is 330 kJ mol^{-1}. Calculate the ionisation energy of Li^{2+} [*i.e.* of Li^{2+}(1s^1) → Li^{3+} (1s^0)].

(b) Use Slater's rules to calculate the effective nuclear charge for a valence electron in the Be and B atoms. Comment on the observation that the first ionisation energy of Be (900 kJ mol^{-1}) is greater than that of B (800 kJ mol^{-1}).

(c) The enthalpies of formation of gaseous XeF_2, XeF_4 and XeF_6 are –110, –216 and –294 kJ mol^{-1}, respectively and the bond energy in F_2 is 159 kJ mol^{-1}. Calculate the average bond energy in each of these three compounds and comment on the values obtained in relation to their fluorinating ability. Use the value for XeF_2 to obtain a value for the electronegativity of xenon, assuming the electronegativity of fluorine to be 4.0.

A25 Explain as fully as possible the following sets of observations:

(a)



R =	Me	i-Pr	Bu^t
K =	19	42	~3000

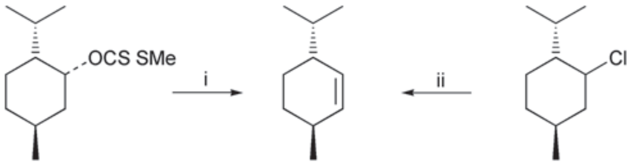
(b)

$$\mathrm{MeCHBrCHBrMe} \xrightarrow{i} \mathrm{MeCH{=}CHMe}$$

(i) KI/Me$_2$CO/60°C

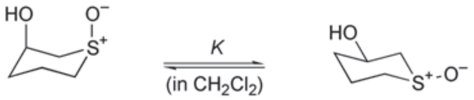
Reactant	Composition of but-2-ene	
R,S	4% *Z*	96% *E*
R,R/S,S	91% *Z*	9% *E*

(c)



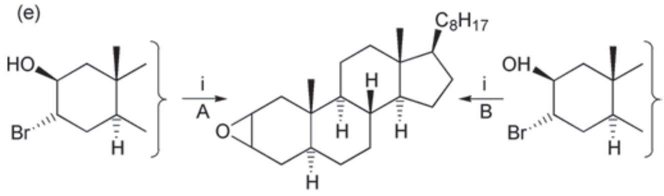
(i) 200 °C (ii) NaOEt/EtOH/60 °C

(d)



Concentration/mol dm^{-3}	K
2.8	5.4
2.3 x 10^{-3}	0.11

(e)



(i) NaOH in H$_2$O/1,4-dioxane
Relative rates of reaction: **A** : **B** = 9000 : 1

A26 (a) The efficiency of a certain strain of algae in producing oxygen via photosynthesis was measured by irradiating for 10 minutes with a 10 W lamp operating at a wavelength of 450 nm. The volume of oxygen evolved (measured at STP) was 7.58 cm^3 and 50% of the incident light was absorbed. Assuming that each molecule of O_2 produced requires the absorption of four photons, calculate the quantum yield for the production of oxygen.

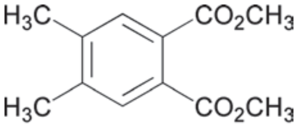
(b) Comment on the result from (a) in terms of a possible mechanism for the reaction.

(c) The intensity of fluorescence (I_f), observed from a solution containing a fluorescent substance (D), was progressively reduced by the addition of a quencher (Q). The results, measured in a spectrofluorimeter, were as follows:

[Q] / mol dm^{-3}	**I_f (relative)**
0.000	100.0
0.001	81.0
0.002	69.0
0.003	61.0
0.004	52.3
0.005	47.4
0.006	42.5

If the rate constant for the fluorescence decay is 10^8 s^{-1}, and internal conversion and intersystem crossing are insignificant, calculate the rate constant for the energy transfer process.

A27 A compound **A** (C_3H_6O) was treated with magnesium amalgam followed by dilute hydrochloric acid to give **B** ($C_6H_{14}O_2$). Reaction between **B** and concentrated sulfuric acid gave **C** ($C_6H_{12}O$). Base-catalysed hydrogen-deuterium exchange on **C** gave $C_6H_9D_3O$. Vapour-phase dehydration of **B** gave **D** (C_6H_{10}). Reaction between **D** and H_3CO_2C-C≡C-CO_2CH_3 gave **E** ($C_{12}H_{16}O_4$) which could be dehydrogenated by heating with Pt/C to give **F**.



F

Using the following spectroscopic information deduce the structures of the compounds **A** - **E**.

Give the mechanism for the transformation of **B** into **C**.

Spectroscopic data:

	IR ν / cm^{-1}	**^{1}H NMR δ**	**^{13}C NMR / ppm**
A	1720	2.29 (s)	206.3 (s) 30.7 (q)
B	3350	1.25 (s, 12 H) 2.25 (s, 2H, disappears on treatment with D_2O)	
C	1720	1.25 (s, 9H) 2.27 (s, 3H)	206.3 (s) 69.0 (s) 31.4 (q) 30.7 (q)

A28 Describe a suitable chromatographic method to carry out FOUR of the following determinations. In each case give your reasons for the choice of mobile phase, stationary phase and detector and any sample treatment required.

(a) Methyl heptanoate in a fruit flavour

(b) Trace amounts of fluorobenzene in a mixture of solvents

(c) 1,2-Dihydroxybenzene in a wood preservative solution

(d) Ethylene glycol (1,2-dihydroxyethane) in a sample of wine

(e) Carbon monoxide in a car exhaust fumes

(f) Riboflavin in fruit juice

A29 (a) (i) Sketch the π-MO diagram for ethylene (i.e. constructed from the two p-orbitals perpendicular to the molecular plane), labelling them with their *g/u* symmetry. What would be the consequences for the molecule of exciting an electron from the lower orbital to the upper one?

(ii) Show how the form of the π-MOs of *trans*-butadiene can be derived by combining two sets of ethylene π-MOs. Give the *g* or *u* classification of each butadiene orbital and show the position of the nodal planes.

(iii) Show, in the form of a correlation diagram of orbital energy versus chain length, *n*, how the stack of π-MOs evolves in the sequence of *even* number polyenes. Indicate how the HOMO-LUMO energy gap changes with *n*. In the case of butadiene ($n = 4$), explain how the bond orders between each pair of adjacent C atoms change on promoting an electron from the HOMO in the ground state to the LUMO. Is this transition allowed?

(b) The valence bond wavefunction for H_2 has the form

$$\Psi = s_a(1)s_b(2) \pm s_b(1)s_a(2)$$

where s_a and s_b are orbitals centred on the two H atoms. The corresponding energy expression is

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S^2}$$

with $\alpha = 2\varepsilon_{1s} + J + 1/R$

$\beta = (2\varepsilon_{1s} + 1/R)S^2 + K,$

where $J = j - 2j'$

$K = k - 2Sk'.$

(i) Give the meaning and physical significance of the terms that occur in the expressions for α and β.

(ii) Is β negative or positive at the equilibrium bond distance in H_2. Why?

(iii) Which is the lower energy solution (a) + sign or (b) – sign?
The solution with the + sign corresponds to a singlet wavefunction and solution with the – sign is a triplet. What is the meaning of this statement?

(iv) The MO wavefunction for H_2 contains ionic terms. Show how this arises by giving the MO wavefunction in valence bond configurations.

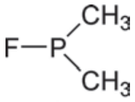
(v) The MO method cannot correctly predict the dissociation products for homolytic dissociation. Discuss this statement.

A30 (a) For compound, **1**, use labelled line diagrams to predict the appearance of:

(i) the ^{1}H NMR spectrum

(ii) the ^{31}P {^{1}H} NMR spectrum

(iii) the ^{19}F NMR spectrum



(1)

You may ignore all interactions with the ^{13}C nucleus.

^{1}J (P-F) = 1500 Hz; ^{2}J (P-H) = 15 Hz; ^{3}J (F-H) = 2 Hz

(b) The ^{31}P–{^{1}H} NMR spectrum of $[RhH(CO)(PPh_3)_3]$ consists of a doublet. (Note that ^{103}Rh has $I = ½$ and is 100% abundant.)

(i) Deduce the structure of the five-coordinate complex.

(ii) Sketch the signal that you would expect to see for the hydrido ligand in the ^{1}H NMR spectrum of the complex.

(iii) In what chemical shift region would you expect to find the signal due to the hydrido ligand in the ^{1}H NMR spectrum of the complex?

(c) Treatment of $[Fe(\eta^5\text{–}C_5H_5)_2]$ with acetyl chloride in the presence of anhydrous aluminium chloride affords compound A. The ^{1}H NMR spectrum of A consists of two complex multiplets at $\delta = 4.68$ and $\delta = 4.40$ (4 H each) and a singlet at $\delta = 2.12$ (6 H). There is a prominent peak at 1658 cm^{-1} in the infrared spectrum of A. Explain the spectroscopic data and suggest a structure for A. Note that the ^{1}H NMR spectrum of $[Fe(\eta^5\text{–}C_5H_5)_2]$ consists of a singlet at $\delta = 4.04$.

A31 (a) $H = A + B/\mu + C\mu$ is the general form of the van Deemter equation describing band broadening in packed column chromatography. Explain the terms and describe how A, B and C influence the separation efficiency of a column.

Sketch and label a typical van Deemter plot for a packed gas chromatography column and show and explain how the plot would change;

(i) if a smaller particle size were used,

(ii) if a packed column were replaced by an open tubular capillary column.

(b) Two components were injected onto a 20 metre long gas capillary column. Their retention times t_1 and t_2 are the retention times of components 1 and 2 respectively and W_B is the peak width of the second component. Calculate the efficiency of the column with respect to the second component in terms of the number of plates N and the plate height H.

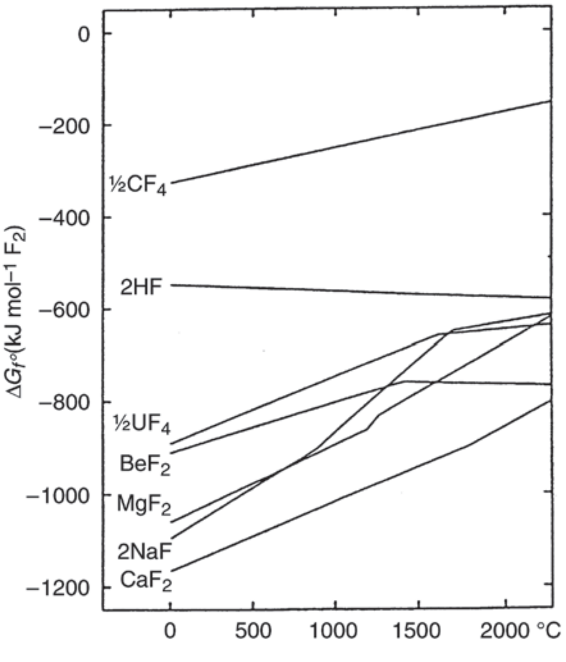
A32 (a) From the following thermodynamic data, with the assumption that the heat capacities of the components are negligible, calculate the temperature above which carbon could be used to reduce TiO_2 to titanium metal at standard pressure.

	$\Delta_f H^o$ / kJ mol^{-1}	S^o / J K^{-1} mol^{-1}
$C_{(graphite)}$	0	5.74
$CO_{(g)}$	−110.53	197.67
$Ti_{(s)}$	0	30.63
$TiO_{2(s)}$	−944.7	50.33

(b) The Gibbs free energies of formation of some fluorides (per mol of F_2 consumed) are plotted against temperature in the Ellingham diagram below.

(i) Comment on the feasibility of using carbon as a reductant to produce metals from their fluorides.

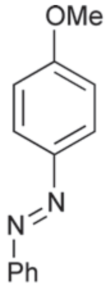
(ii) How could uranium be produced from uranium tetrafluoride?



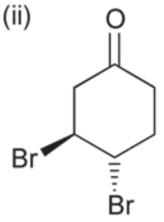
Ellingham diagram for the formation of several fluorides

A33 (a) Show how you would prepare the following using a monosubstituted benzene as one of the starting materials.

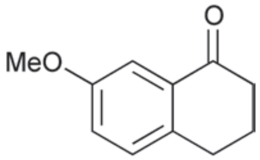
(i)



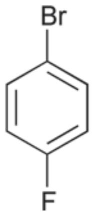
(ii)



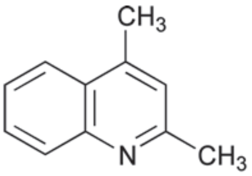
(iii)



(iv)



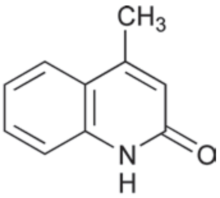
(b) Describe synthetic routes to compounds **A** and **B** from aniline and other suitable building blocks and discuss the mechanisms of the reactions.



from $PhNH_2$

A

[$Ph = C_6H_5$]



from $PhNH_2$

B

A34 Answer *all* parts (a) to (g), using the standard electrode potentials for aqueous acid solutions (E°, in volts) given below.

$$ClO_4^- \xrightarrow{+1.19} ClO_3^- \xrightarrow{+1.47} Cl_2 \xrightarrow{+1.36} Cl^-$$

(a) Give the oxidation state of Cl in each of these species.

(b) Write balanced half-cell reactions, with explicit inclusion of electrons, for the reduction of ClO_4^- to ClO_3^- and for the reduction of ClO_3^- to Cl_2.

(c) Calculate the value of E° for the ClO_4^-/Cl_2 couple.

(d) State whether the ClO_3^- ion is expected to disproportionate in aqueous solution at pH 0 (standard conditions) to give ClO_4^- and Cl_2, and show your reasoning.

(e) Write a balanced equation for the disproportionation reaction in part (d).

(f) Comment on the expected pH dependence of this disproportionation reaction.

(g) Which of the Cl species are, in principle, capable of oxidising water to oxygen under standard concentration conditions?

[$E^\circ = +1.23$ V for O_2/H_2O].

A35 For the following species:

NO_2^+ ; ICl_3 ; BBr_3 ; XeF_5^+ ; $SOCl_2$; IF_4^+

(a) Use the VSEPR method to predict the shapes, including any distortions from ideal geometries

(b) Assign each to the appropriate point group, listing and illustrating the diagnostic symmetry elements.

A36 The rate law for the reaction of benzenediazonium salts with weakly basic nucleophiles (H_2O, Br^-, Cl^- etc)

$$(PhN_2)^+X^- + Y^- \rightarrow PhY + N_2 + X^-$$

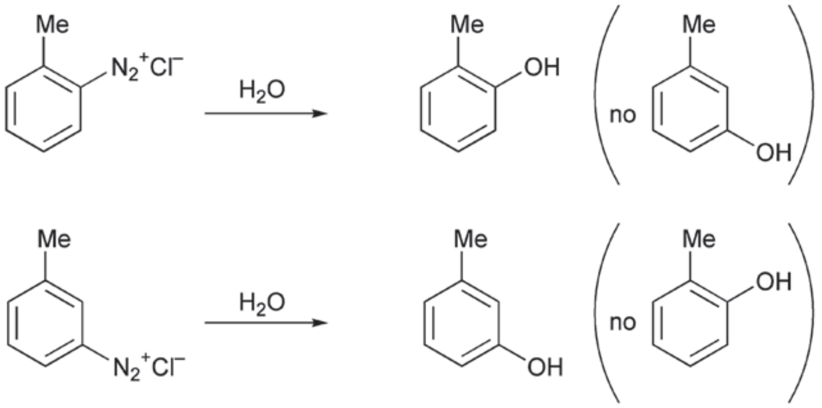
is of the form

$$\text{Rate} = k\,[(PhN_2)^+\,X^-]$$

(a) Suggest two possible mechanisms for the reaction that are consistent with the above rate law.

(b) Show how the following additional data can be interpreted in favour of just one of your possible mechanisms.

(i)



(ii) The entropy of activation for the reaction was large and positive

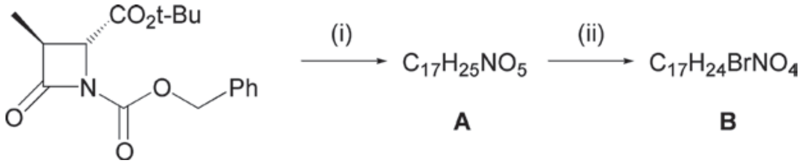
(iii) $k_{H_2O}/k_{D_2O} = 0.98$

(iv) A Hammett plot indicates that the rate of reaction of substituted arenediazonium salts is accelerated by substituents in the *meta* and *para*-positions that have a negative σ value.

Appendix B - Depth questions

B1 Assign the spectral data where possible, suggest intermediates and propose mechanisms for the following processes.

(a)



(i) $NaBH_4$, MeOH

(ii) Ph_3P, CBr_4

Selected spectral data for A:

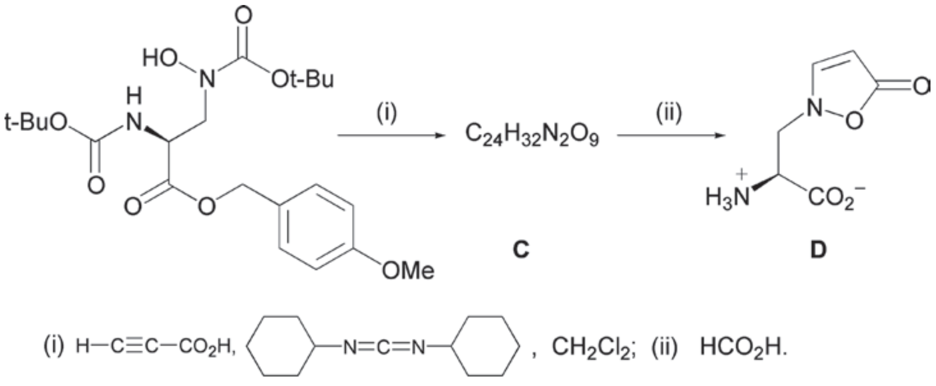
IR data, ν_{max}
3374 cm^{-1} (broad)
1710–1730 cm^{-1} (broad, strong)

Selected spectral data for B:

IR data, ν_{max}
1710–1730 cm^{-1}(broad, strong)

NMR data, δ_H ($CDCl_3$):
1.09 (3H, d, *J* = 7 Hz)
1.49 (9H, s)
2.34–2.37 (1H, m)
3.31 (1H, dd, *J* = 10, 8 Hz)
3.49 (1H, dd, *J* = 10, 5.5 Hz)
4.41 (1H, dd, *J* = 8, 5 Hz)
5.13 (2H, s)
5.52 (1H, d, *J* = 8 Hz, exch. D_2O)
7.33–7.41 (5H, m).

(b)



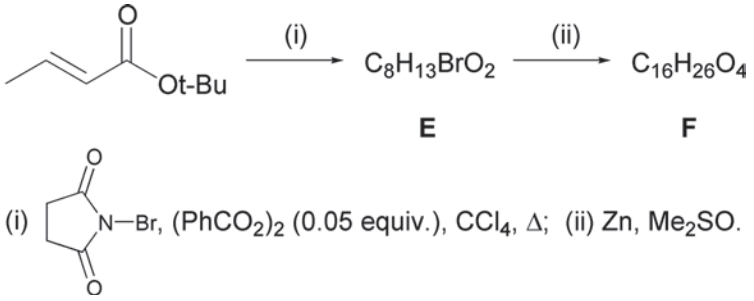
B1 (Continued)

Selected spectral data for D:

IR data, ν_{max}:
1700 cm^{-1} (strong), 1600 cm^{-1} (strong)
NMR data, δH (D_2O):
3.98 (1H, t, $J = 5$ Hz)
4.19 (2H, d, $J = 5$ Hz)
5.15 (1H, d, $J = 3.5$ Hz)
8.11 (1H, d, $J = 3.5$ Hz)

NMR data, δ_C (D_2O):
55.0 (two directly bonded hydrogens)
55.8 (one directly bonded hydrogen)
90.3 (one directly bonded hydrogen)
157.1 (one directly bonded hydrogen)
177.2 (no directly bonded hydrogens)

(c)



Selected spectral data for F:

IR data, ν_{max}:
1720 cm^{-1} (strong),
1650 cm^{-1} (strong)

NMR data, δ_H ($CDCl_3$):
1.33 (9H, s)
1.35 (9H, s)
2.26 (1H, ddt, $J = 13.5, 1, 7$ Hz)
2.46 (1H, ddt, $J = 13.5, 1, 7$ Hz)
2.94 (1H, apparent q, $J = 7$ Hz)
5.00 (1H, dd, $J = 5, 1$ Hz)
5.01 (1H, dd, $J = 10, 1$ Hz)
5.60 (1H, dt, $J = 16, 1$ Hz)
5.62 (1H, ddd, $J = 15, 10, 7$ Hz)
6.60 (1H, dt, $J = 16, 7$ Hz).

B2 (a) What is meant by the statement that a certain reaction in solution is *diffusion controlled*? What factors may contribute towards departure from the simple diffusion-control description?

(b) The rate constant, k, of a diffusion-controlled reaction between neutral species A and B can be written as

$k = 4\pi d(D_A + D_B)$

where d is the collision diameter and D_A, D_B are the diffusion coefficients of the two species. Show that with some further approximations this expression can be used to relate k to the viscosity, η, of the solvent.

(c) The data given below refer to the reaction

$2CH_3 \rightarrow C_2H_6$

in water. Use a graphical method to assess the claim that this is a diffusion-controlled reaction.

T/ °C	k / 10^9 dm^3 mol^{-1} s^{-1}	η / 10^{-3} kg m^{-1} s^{-1}
10	2.11	1.31
20	2.80	1.00
30	3.64	0.80
40	4.67	0.65

B3 (a) The *reaction cross section*, S_r, can be expressed by the equation

$$S_r = \int_0^\infty 2\pi b P_r(b)db$$

where *b* is the impact parameter and $P_r(b)$ is the probability of reaction for that impact parameter. How is S_r related to the *collision cross section,* S_c? Discuss briefly reasons why S_r might be (i) smaller, (ii) larger than S_c.

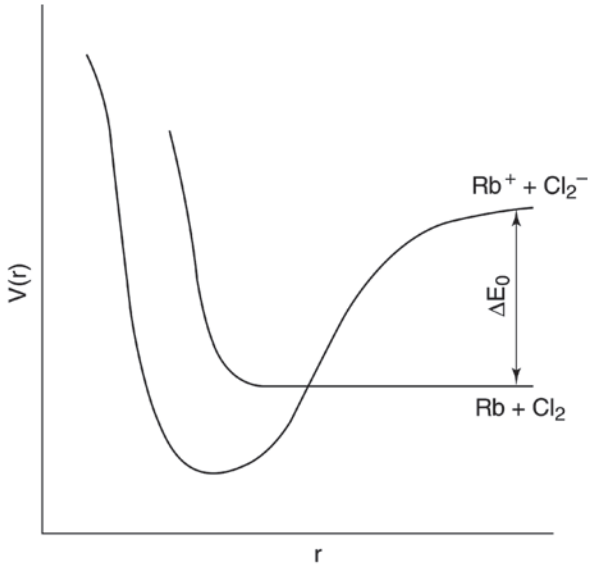
(b) The reaction

$Rb + Cl_2 \rightarrow RbCl + Cl$

proceeds extremely rapidly. Use the potential energy diagram below to suggest a possible mechanism for the reaction that would explain the kinetics of the process. Estimate the reaction cross section by assuming that the potential curve leading to $Rb + Cl_2$ is independent of *r* (*V(r)* = 0) at large r, and that the curve leading to $Rb^+ + Cl_2^-$ is dominated by electrostatic attraction for *r* beyond the potential minimum. Comment on your result.

$$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r} \quad = \quad \frac{-1.44}{r} \quad \text{for } V(r) \text{ in } eV \text{ and } r \text{ in } nm$$

The ionisation potential of Rb is 4.2 eV and the electron affinity of Cl_2 is 2.4 eV.



B4 Interpret the following observations and accompanying data.

On refluxing with sodium cyclopentadienide (NaC_5H_5) in tetrahydrofuran (*thf*), molybdenum hexacarbonyl yields an orange, air-sensitive solution of a compound **A**, with evolution of three molar equivalents of a gas.

Treatment of **A** in *thf* with methyl bromide leads to precipitation of **B**, a white solid which proves soluble in water, and a compound **C** can be isolated from the *thf* solution. The latter is soluble in hydrocarbon solvents, and its ^1H NMR spectrum shows two singlet resonances at $\delta = 5.1$ and 0.4 ppm, with relative intensities 5:3. Reaction of **A** in *thf* with allyl bromide produces again a precipitate of **B**, together with a compound **D** which can be extracted as a yellow-brown oil having the empirical formula $MoC_{11}H_{10}O_3$.

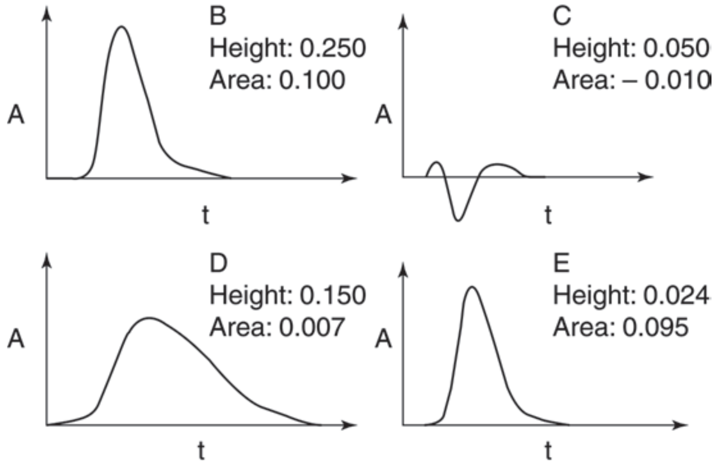
On photolysis or careful heating, **D** is converted to **E**, though the yield is improved by treating **D** with Me_3NO. The ^1H NMR of **E** shows a singlet ($\delta = 5.1$ ppm), a triplet (1:2:1) of triplets (1:2:1) ($\delta = 2.5$ ppm) and two doublets ($\delta = 1.5$ and 0.9 ppm) with the intensity ratio 5:1:2:2. The IR absorption spectrum of **E** shows two intense bands at 1835 and 1920 cm^{-1}; detailed spectroscopic studies at low temperature indicate that it is a mixture of two isomers.

Treatment of **A** with Fe(III) in ethanoic acid under carbon monoxide yields a red compound **F**, the mass spectrum of which shows a parent ion structure, centred about $m/z = 490$, with an isotope distribution pattern indicative of two molybdenum atoms per molecule. Photolysis of **F** in hexane with an argon purge leads to **G**, with a mass spectrum having the parent ion feature around $m/z = 434$ and displaying an isotope pattern very similar to that of **F**. The precursor **F** may be recovered by treating **G** with CO. Furthermore, **G** reacts with trimethylphosphine to form **H**, the ^1H NMR of which shows two singlets at $\delta = 4.5$ and 0.9 ppm, with relative intensities 5:9.

X-ray diffraction studies of **F** and **G** reveal Mo-Mo bond lengths of 323.5 pm and 244.8 pm, respectively.

[The metallic radius of molybdenum is 139 pm.]

B5 The following signals were obtained for selenium by electrothermal atomic absorption spectrometry (ETAAS).



Details

B 20 ng ml^{-1} Se standard solution

C 20 ng ml^{-1} Se in diluted urine; D_2 background correction used

D 20 ng ml^{-1} Se in diluted urine; Zeeman-effect background correction used

E 20 ng ml^{-1} Se in diluted urine; Zeeman-effect background correction used platform atomization and a chemical modifier used

Answer the following:

(a) Compare signals B and C. Explain why the signals for Se are so different

(b) Compare signals C and D. Comment on why the Zeeman-effect background correct system has made a difference to the signal obtained.

(c) Compare signals B and D.

(i) Calculate the extent of chemical interference caused by the urine matrix for both the height and area signals.

(ii) Comment on the most likely causes of the interference observed and on any differences between the two modes of measurement (height and area).

(d) Compare signals B, D and E.

(i) Explain why the use of a platform and modifier has apparently reduced the extent of chemical interference.

(ii) Give an example of a possible modifier and explain its mode of action. Comment on any limitations in the use of the modifier you select.

(e) Describe how analysis of a time resolved peak (e.g. B) in ETAAS can be used to obtain an idea of the main mechanism of atom formation.

B6 Treatment of a tetrahydrofuran solution of $[(C_5H_5)Fe(CO)_2Cl]$ with propene, in the presence of $AlCl_3$, gave compound (**A**).

Characterisation data for (**A**):

Microanalysis: C, 30.95; H, 2.85; Cl, 36.55%
IR(ν(CO), cm^{-1}) 2070, 2035
^1H NMR (ppm, $CDCl_3$) 5.62 (s, intensity 5H),
5.20 (ddq, intensity 1H, $^3J_{HH}$ =14.0 Hz, 8.0 Hz, 6.0 Hz),
3.98 (d, intensity 1H, $^3J_{HH}$ = 8.0 Hz).
3.53 (d, intensity 1H, $^3J_{HH}$ = 14.0 Hz),
1.88 (d, intensity 3H, $^3J_{HH}$ = 6.0 Hz).

When compound (**A**) was reacted with one equivalent of $LiCH(CO_2Me)_2$ two products, (**B**) and (**C**), were isolated.

Characterisation data for (**B**):

Microanalysis: C, 51.45; H, 5.14; Cl, 0.00%
IR(ν(CO), cm^{-1}) 2005, 1955
^1H NMR (ppm, $CDCl_3$) 4.77 (s, intensity 5H),
3.62 (s, intensity 6H),
3.50 (dd, intensity 1H, $^3J_{HH}$ = 13.0 Hz, 3.0 Hz),
2.60 (ddd,intensity 1H, $^3J_{HH}$ = 4.0 Hz, 3.0 Hz, $^2J_{HH}$ = 3.0 Hz),
2.10 (ddd, intensity 1H, $^3J_{HH}$ = 14.0 Hz, 13.0 Hz, $^2J_{HH}$ = 3.0 Hz),
1.6 (ddq, intensity 1H, $^3J_{HH}$ = 14.0 Hz, 6.5 Hz, 4.0 Hz),
1.25 (d, intensity 3H, $^3J_{HH}$ = 6.5 Hz).

Characterisation data for (**C**):

Microanalysis: C, 51.45; H, 5.14; Cl, 0.00 %
IR(ν (CO), cm^{-1}) 2003, 1954
^1H NMR (ppm, $CDCl_3$) 4.82 (s, intensity 5H),
3.65 (s, intensity 6H),
3.40 (d, intensity 1H, $^3J_{HH}$ = 14.0 Hz),
2.80 (dddq, intensity 1H, $^3J_{HH}$ = 14.0 Hz, 13.0 Hz, 7.0 Hz, 4.0 Hz),
2.40 (dd, intensity 1H, $^3J_{HH}$ = 13.0 Hz, $^2J_{HH}$ = 3.0 Hz),
2.10 (dd, intensity 1H, $^3J_{HH}$ = 4.0 Hz, $^2J_{HH}$ = 3.0 Hz),
0.95 (d, intensity 3H, $^3J_{HH}$ = 7.0 Hz).

Using the data provided answer *all* parts (i)–(v)

(i) Write a balanced equation for the formation of (**A**). Draw a structure for compound (**A**) and propose a mechanism for its formation.

(ii) What is the oxidation state of iron in compound (**A**) and the overall electron count? Assign the spectroscopic data for compound **(A)** to confirm your answer to part (i).

(iii) Using the Davies-Green-Mingos rules for nucleophilic attack at a coordinated polyene propose structures for products (**B**) and (**C**).

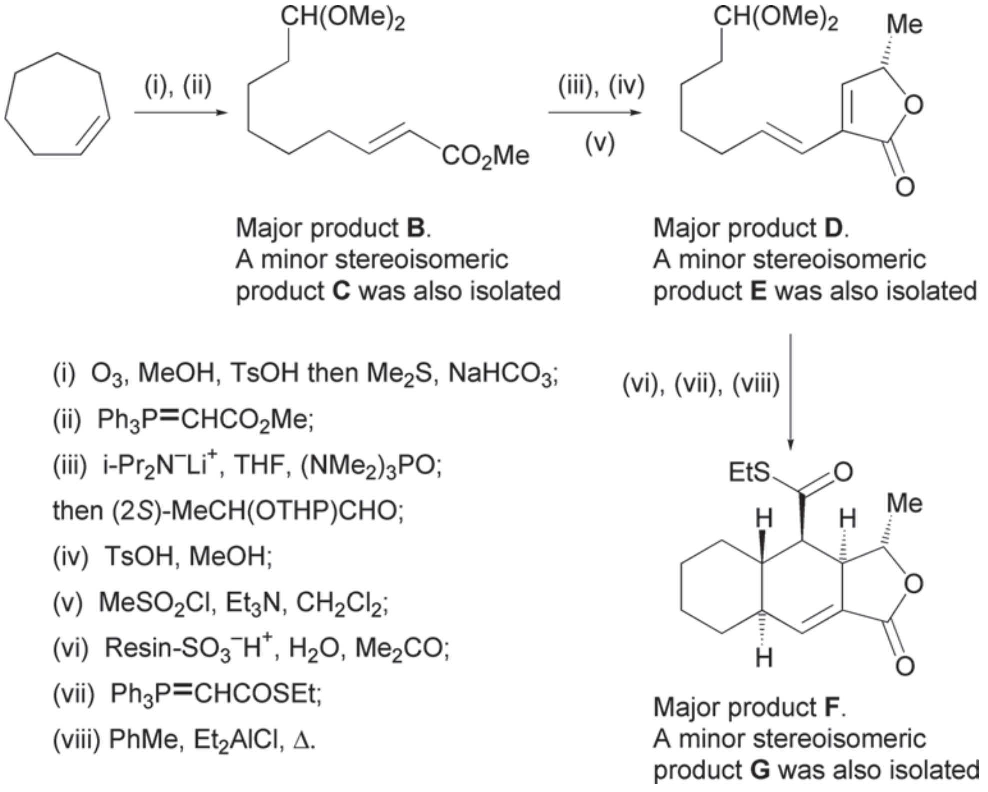
(iv) Support your answer to (iii) by assigning the spectroscopic data provided (chemical shifts and coupling constants).

(v) Why are the IR stretching frequencies for (**B**) and (**C**) different from (**A**)?

Show all working and calculations in your answer to gain full marks.

(open book question)

B7 The following scheme illustrates steps from an asymmetric synthesis of the alkaloid himbacine **A**. Answer all questions.

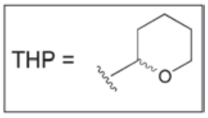


Major product **B**.
A minor stereoisomeric product **C** was also isolated

Major product **D**.
A minor stereoisomeric product **E** was also isolated

(i) O_3, MeOH, TsOH then Me_2S, $NaHCO_3$;
(ii) $Ph_3P{=}CHCO_2Me$;
(iii) $i\text{-}Pr_2N^{-}Li^{+}$, THF, $(NMe_2)_3PO$;
then (2*S*)-MeCH(OTHP)CHO;
(iv) TsOH, MeOH;
(v) $MeSO_2Cl$, Et_3N, CH_2Cl_2;
(vi) Resin-$SO_3^{-}H^{+}$, H_2O, Me_2CO;
(vii) $Ph_3P{=}CHCOSEt$;
(viii) PhMe, Et_2AlCl, Δ.

Major product **F**.
A minor stereoisomeric product **G** was also isolated



Question B7 continued

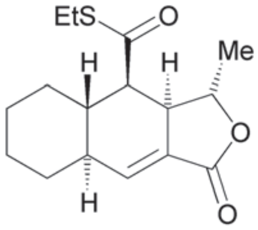
(a) Suggest mechanisms for steps (i) and (ii). Rationalise the stereochemical outcome of step (ii) and predict the structure of the minor product **C** formed.

(b) Starting from **B** suggest mechanisms for steps (iii), (iv) and (v) and predict the structure of the minor product **E** formed.

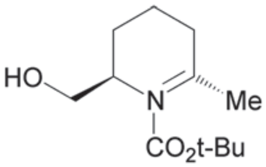
(c) Suggest a method to convert **E** into **D**.

(d) Starting from **D** identify products formed in steps (vi) and (vii).

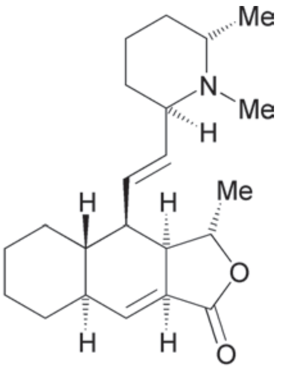
(e) Rationalise the stereochemical outcome of step (viii) and predict the structure of the minor product **G** formed.



F



H



A, himbacine

(f) Propose a synthesis of himbacine **A** from **F** and **H**. Briefly explain the reasons for your choice of reagents and indicate possible problems. Note that **F** and **H** may be modified before coupling.

B8 (a) Describe briefly the different types of colloidal phase. Derive an expression for the surface area to volume ratio of a colloidal dispersion of spherical particles. Hence calculate this ratio for particles with a radius, *a*, of 5 nm at a volume fraction, ϕ, of 0.1.

(b) Derive the critical polymer adsorption energy per segment for a cubic lattice. Plot the data below which represent a polymer layer adsorbed on a colloidal particle. Using the data, calculate the average layer thickness and the adsorbed amount of polymer, assuming that the polymer density is 1000 kg m^{-3}. From the calculations and the graph discuss to what kind of adsorbed polymer system(s) the data could refer.

ϕ (z)	0.62	0.60	0.56	0.46	0.3	0.0
z / Å	100	200	300	400	500	600

(c) The diffusion rate of an aqueous dispersion of a *monodisperse* colloid through a sintered glass disc was measured at 25°C. On one side of the glass membrane (area 1 cm^2, thickness 1.50×10^{-5} m) was 15 cm^3 of a 1.000×10^{-3} mol dm^{-3} solution of the colloid. On the other side there was 10 cm^3 of a solution with an initial colloidal concentration of 1.000×10^{-5} mol dm^{-3}. After 3000 seconds, the colloidal concentration of the second solution had increased to 1.360×10^{-5} mol dm^{-3}.

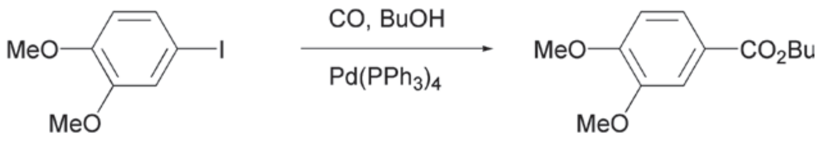
(i) From these data and Fick's law, calculate the diffusion coefficient, *D*, of the colloid.

(ii) Use the *Stokes-Einstein equation*, which relates *D* to particle size, to determine the radius of the colloidal particles.

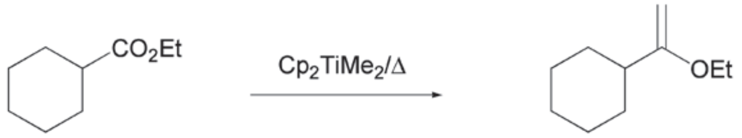
(iii) Scanning electron microscope measurements of colloidal size for this system produce a particle size measurement which is significantly different from the value obtained by these diffusional measurements. Compare and contrast the information obtained by the two measurements and hence suggest reasons for the discrepancy.

B9 Propose mechanisms for the following reactions

i)

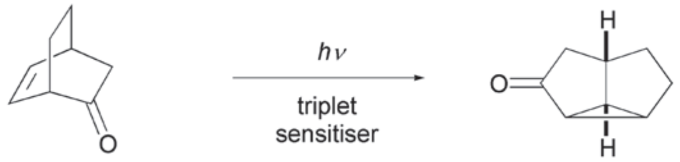


ii)

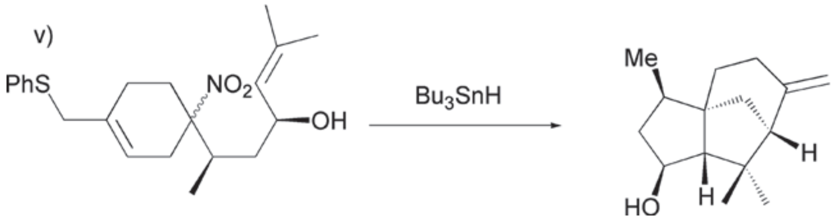


iii)

iv)

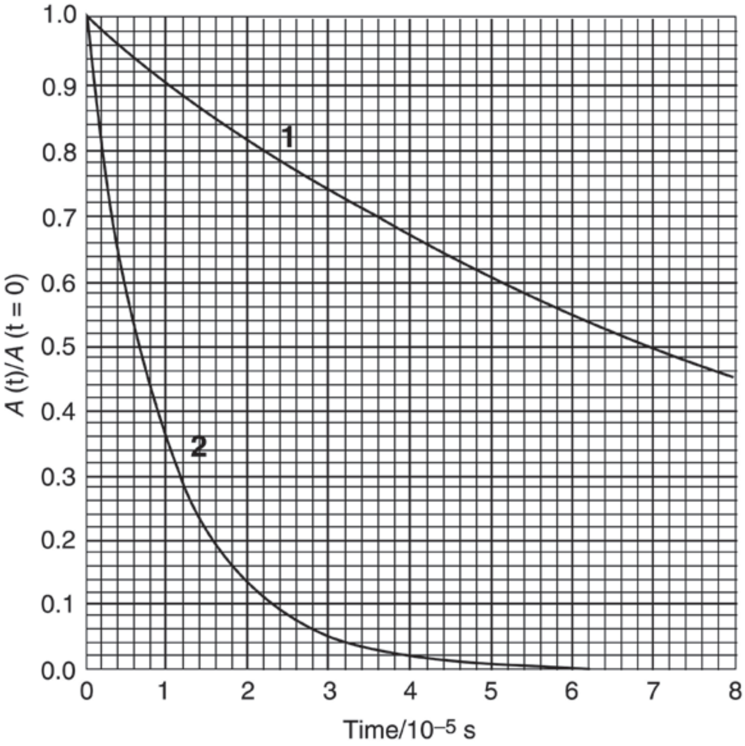


v)



B10 (a) A sample of a polycyclic aromatic hydrocarbon is dissolved in *n*-hexane and, after removal of dissolved oxygen, is frozen in liquid nitrogen to form a glass. The fluorescence and phosphorescence decay lifetimes are measured and found to be 1.5×10^{-8} s and 8 s respectively. The rate constant for intersystem crossing from S_1 to T_1 is $2 \times 10^{7}\ s^{-1}$. Calculate the ratio of the triplet and singlet concentrations under steady state illumination in the singlet absorption band of the aromatic compound. Outline briefly the processes that you consider in your calculations. What would happen to the triplet:singlet ratio if the glass was melted?

(b) The triplet state of diphenylketone is quenched by small concentrations of naphthalene. The figure below shows transient triplet-triplet absorption decay curves for diphenylketone in *n*-hexane. Curve 1 was obtained in the absence of naphthalene, whereas curve 2 was recorded in the presence of 1×10^{-5} mol dm^{-3} naphthalene. Analyse the decay curves to obtain information about the kinetics of the quenching process. Comment on the result of your calculations and suggest further experiments that could be used to test your conclusions.



Triplet-triplet absorbance decay curves. 1) no added naphthalene, 2) 10^{-5} mol dm^{-3} naphthalene. (The curves have been normalised by dividing the absorbance at time t by the absorbance at t = 0.)

B11 Answer the following questions by reference to the paper, "A Novel [2,3] Intramolecular Rearrangement of N-Benzyl-***0***-allylhydroxylamines", S.G. Davies, S. Jones, M.A. Sanz, F.C. Teixeira and J.F. Fox, ***Chem.Commun***., **1998**, 2235-6, a copy of which is provided,

(a) Explain the term ***intramolecular sigmatropic rearrangement*** and what is meant by the notation ***[2,3] and [3,3] processes*** (paragraph 1).

(b) Why must the tetrahydrofuran solvent used for the rearrangements be dry (paragraph 4)? How would it have been dried?

(c) What changes in the ^{1}H NMR spectrum would you expect to signify the ***essentially quantitative conversion*** of **3a** into **4a** (paragraph 4)?

(d) Why do you think the rearrangement of **3c** to **4c** is harder to achieve than the other rearrangements (paragraph 4)

(e) Explain why the rearrangement of the crotylhydroxylamine **3b** rules out the possibility of 1,2-anionic shift (paragraph 5).

(f) Explain the logic behind the test used to distinguish between inter- and intra-molecular rearrangements and hence explain why Scheme 3, as drawn, is misleading (paragraph 5).

(g) What is implied by the term ***envelope transition*** state (paragraph 6)?

(h) Redraw structure **8** to show more accurately all bonds being made or broken and redistribution of charge(s) in the transition state.

(i) Explain how the pK_a values quoted for EtOH and $EtNH_2$ relate to the driving force proposed for the reaction (paragraph 6) and also to the use of different bases (t-BuOK and n-BuLi) in the two deprotonation steps between oxime reactants **1** and hydroxylamine products **4**.

B12 (a) Plot a Hammett correlation and determine the value of the reaction constant for epoxidation of substituted *trans*-stilbenes ($X\text{-}C_6H_4CH{=}CHPh$) with *meta*-chloroperbenzoic acid, for which rate constants at 30ºC (k_2 / $dm^3\ mol^{-1}\ s^{-1}$) are as follows.

X =	**4-OMe**	**4-Me**	**3-Me**	**H**	**4-Cl**	**3-Cl**	**3-NO$_2$**	**4-NO$_2$**
k_2	31.4	14.9	7.46	6.64	4.28	2.76	1.14	0.98
σ	–0.27	–0.14	–0.06	0.0	0.24	0.37	0.71	0.78
σ^+	–0.78	–0.30			0.11			
σ^-								1.23

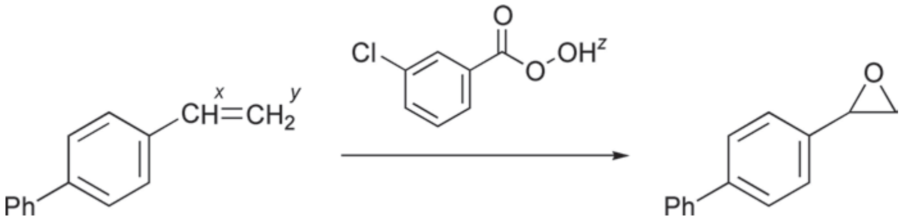
(b) Discuss the mechanism and the nature of the rate-determining transition state for epoxidation of alkenes by peracids in the light of the following observations together with your result from part (a).

(i) Reactions of *trans*-PhCH=CHPh with substituted perbenzoic acids $X\text{-}C_6H_4CO_3H$ correlate with Hammett's σ with $\rho = +1.4$.

(ii) Rates of epoxidation in non-protic, non-basic solvents increase with increasing solvent polarity. In basic solvents the reactions are slow and depend little upon solvent polarity.

(iii) The reaction below exhibits the following deuterium kinetic isotope effects:

$k_H/k_D\,\boldsymbol{x} = 0.99$ $k_H/k_{D_2}\,y = 0.82$ $k_H/k_D\,\boldsymbol{z} = 1.17$



(iv) Epoxidations are stereospecifically *syn.*

B13 (a) Photoexcitation of molecular oxygen to its two lowest ionised states is summarised below.

$O_2(^3\Sigma_g) \rightarrow$ $O_2^+(^2\Pi_g)$ Ionisation energy = 12.1 eV.

$O_2(^3\Sigma_g) \rightarrow$ $O_2^+(^4\Pi_g)$ Ionisation energy = 16.2 eV.

Comment on the expected overall relative intensities for these two transitions.

(b) Account for the relative magnitudes of the vibrational wavenumbers for the molecular species tabled below.

Molecule	**Equilibrium bond length /nm**	**Vibrational wavenumber /cm^{-1}**
$O_2(^3\Sigma_g)$	0.121	1580
$O_2^+(^2\Pi_g)$	0.112	1850
$O_2^+(^4\Pi_g)$		1200

(c) Estimate the equilibrium bond length for the excited $O_2^+(^4\Pi_g)$ molecular ion.

(d) Methyl bromide, CH_3Br, a prolate symmetric top, has rotational constants

$A = 5.082$ and $B = 0.319$ cm^{-1}, respectively.

(i) Assuming that the CH_3Br has been cooled in a supersonic jet to a temperature of 15 K, show that only rotational levels in the $K = 0$, 1 and 2 stacks have significant populations.

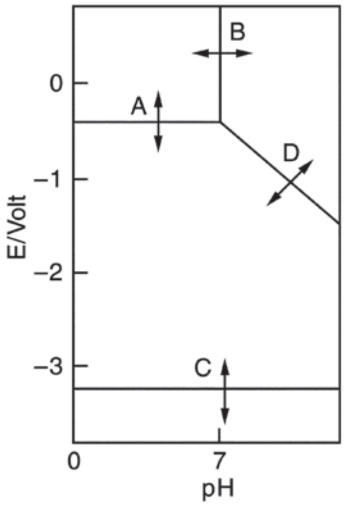
(ii) Sketch the expected appearance of a jet-cooled perpendicular rovibrational band of methyl bromide, taking care to label the *K* sub-bands.

(e) It is common to assume that rotational constants are unchanged by a vibrational transition. However, this is only an approximation.

(i) Derive formulae for the *P*- and *R*-branch rovibrational transitions in a parallel band of a linear molecule assuming that the rotational constants in the upper and lower vibrational levels differ slightly. (use B' and B'' to label the upper and lower state rotational constants, respectively).

(ii) Show that the *R*-branch reaches a turning point (a so-called bandhead) at some value of J'' if $B'' > B'$, whereas the *P*-branch has a turning point if $B'' < B'$.

B14 (a) Shown below is the Pourbaix (standard potential *vs*. pH) diagram for a lanthanide element Ln.



(i) Write equations for the half-cell reactions occurring at each of the points **A**, **B**, **C**, and **D** in the diagram.

(ii) Identify the element Ln, making clear your reasons.

(iii) What might be found were the diagram extended to higher pH?

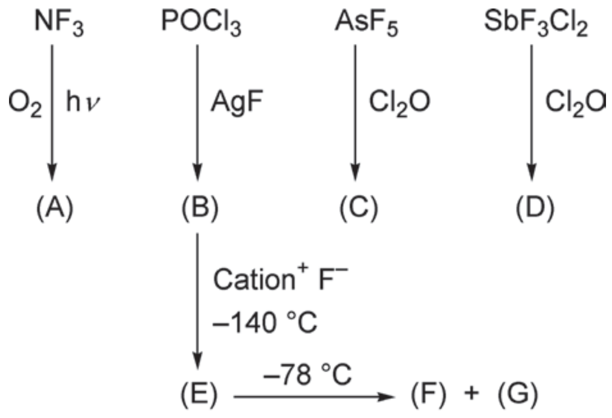
(b) What may be inferred from the standard potentials of the aqueous Ag(I)/Ag couple measured in the presence of unit activity of (i) perchlorate ions, + 0.80 V, (ii) chloride ions, + 0.22 V, and (iii) cyanide ions, - 0.02 V?

(c) In acidic aqueous solutions a radioactive element **X** is believed to have the following standard reduction potentials (in V).

$$\mathrm{X(VII)} \xrightarrow{>+1.6} \mathrm{X(V)} \xrightarrow{+1.5} \mathrm{X(I)} \xrightarrow{+1.0} \mathrm{X(0)} \xrightarrow{+.0.3} \mathrm{X(-I)}$$

What can you deduce about the element **X** and its behaviour in acid solution?

B15 In the following scheme, some chemistry of elements from Group 15 is described.



(A), (B), (C) and (D) all have the same formula $[MO_xF_y]$ (where x and y are constant for M = N, P, As, Sb). However, (A) and (B), which are isostructural, are volatile gases whilst (C) and (D), which are also isostructural, are involatile solids.

The IR spectrum of (A) shows three stretching vibrations at 1691, 883 and 743 cm^{-1}.

The ^{31}P NMR spectrum of (B) is a 1:3:3:1 quartet and the ^{19}F NMR spectrum of (B) is a 1:1 doublet. The couplings in the two spectra are identical.

(a) Deduce the empirical formulae of (A), (B), (C) and (D) and deduce the molecular structures of (A) and (B) accounting for all the spectroscopic data.

(b) Suggest reasonable structures for (C) and (D) and account for the difference in chemistry between the heavier and lighter elements of Group 15.

(E) is the first product from the reaction of (B) with a good source of fluoride ions. It is a 1:1 electrolyte which is stable in solution below –140˚C; at higher temperatures it decomposes into (F) and (G) which are formed in equimolar amounts and are both 1:1 electrolytes in solution.

The ^{31}P NMR spectrum of (E) contains one signal, a 1:2:1 triplet of 1:2:1 triplets. The ^{19}F NMR spectrum of (E) contains 2 signals in a 1:1 ratio. Both signals are 1:1 doublets of narrower 1:2:1 triplets. The ^{31}P NMR spectrum of (F) is a 1:2:1 triplet which is mutually coupled to a 1:1 doublet in the ^{19}F NMR spectrum of (F). The ^{31}P NMR spectrum of (G) is a 1:6:15:20:15:6:1 septet which is mutually coupled to a 1:1 doublet in the ^{19}F NMR spectrum of (G).

(c) Deduce the molecular formulae and draw the structures of (E), (F) and (G), accounting for all the NMR data.

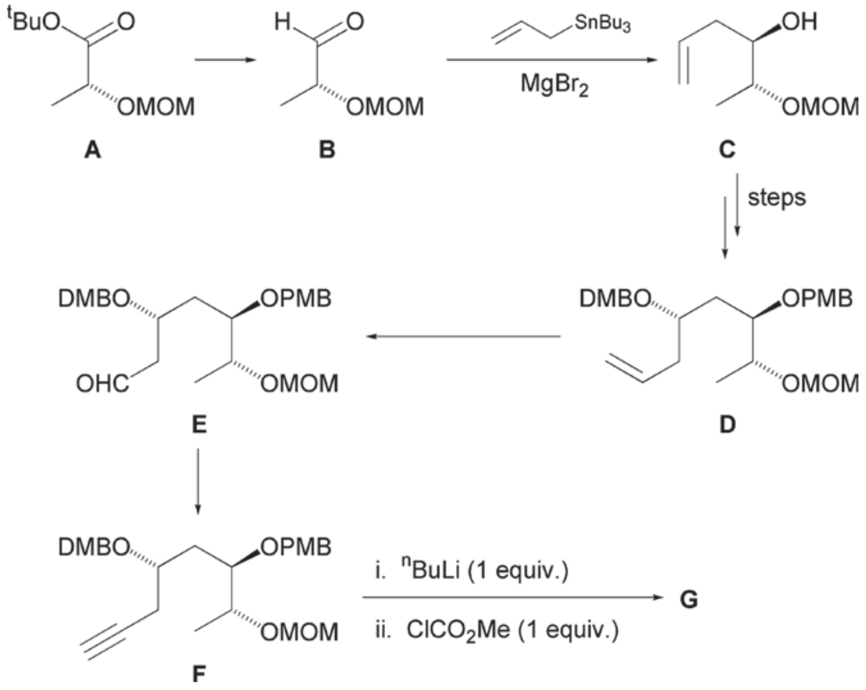
(d) Suggest reasons why (A), (C) and (D) do not react with fluoride ion in solution.
[NMR Data: ^{19}F, I = ½, 100%; ^{31}P, I = ½, 100%; ^{16}O, I = 0, 100%]

B16 (a) The synthesis of a fragment of the natural product, bryostatin, is shown below. (Note that MOM, PMB and DMB are simply alcohol protecting groups).

(i) Suggest reagent(s) for the conversions A → B, D → E and E → F.

(ii) What is the structure of G and how is it formed?

(iii) Explain the stereoselectivity observed in the conversion of B → C.

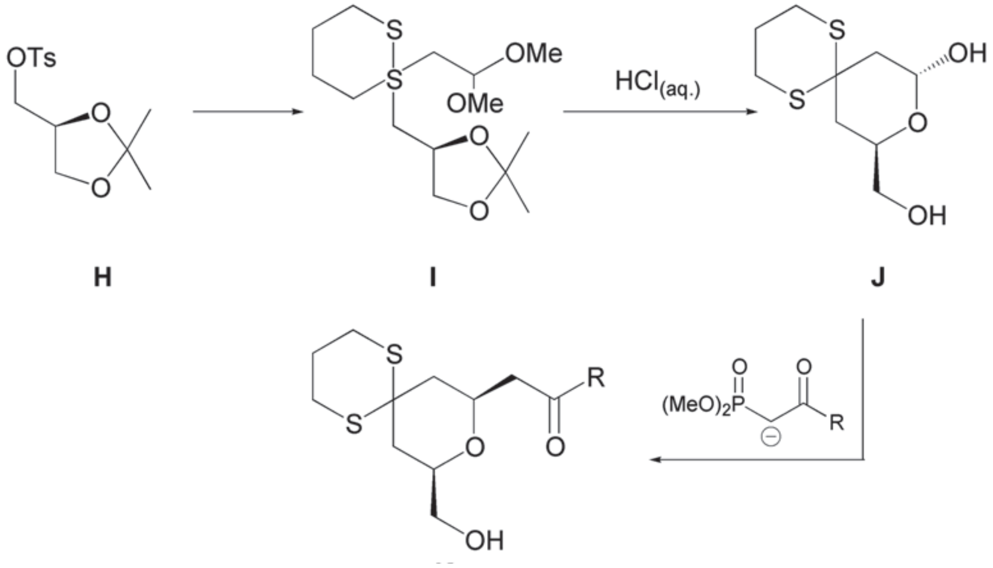


(b) The synthesis of a second bryostatin fragment is given below.

(i) Suggest reagent(s) for the conversion H → I

(ii) Suggest a synthesis of H as a single enantiomer from an achiral starting material.

(iii) Provide a mechanism for the formation of K.



B17 (a) The separation of ethanol and propanol by gas chromatography gave the following results.

Run	Retention Time			Peak Width	
	Unretained compound/min	Ethanol/s	Propanol/s	Ethanol/s	Propanol/s
1	1.01	131	173	19	26
2	1.00	129	165	16	23
3	1.03	133	177	21	28

From the above information, calculate:

(i) the number of theoretical plates for each compound,

(ii) the capacity factor for each compound, and

(iii) the resolution between ethanol and propanol

(b) After a disruption to the carrier gas supply, the mean retention times for ethanol and propanol were 196 and 249 seconds respectively. For a series of 3 injections, the relative standard deviation (RSD) was less than 5%. Comment on this result.

(c) Explain with reasons, the method of sample introduction you would employ for the following gas chromatographic analyses:

(i) ethanol in blood

(ii) benzene in petrol

(iii) a polymer

B18 First order rate constants at 10°C for the oxidation of the [Mo^V_2 ethylenediaminetetracetato] complex [Mo_2O_4(edta)]$^{2-}$ present in an excess concentration with [Fe^{III}(bipy)$_3$]$^{3+}$:

$$Mo^V{}_2 + Fe^{III} \xrightarrow{k_1} Mo^VMo^{VI} + Fe^{II}$$

have been determined by monitoring the formation of [Fe^{II}(bipy)$_3$]$^{2+}$. There is no dependence of rate constants on [H^+] in the range 0.02 - 0.40 mol dm$^{-3.}$ The ionic strength, ***I***, was 1.0 mol dm^{-3} ($LiClO_4$).

(a) From the data listed, determine $\boldsymbol{k_1}$ by a graphical method for the rate law:

$$\frac{d[Fe^{II}]}{dt} = k_{obs}[Fe^{III}] = 2k_1[Mo_2^V][Fe^{III}]$$

10^6 [Fe^{III}] / mol dm^{-3}	**10^5 [Mo^V_2] / mol dm^{-3}**	**10^3 k_{obs} / s^{-1}**
5.0	1.3	10.8
5.0	1.5	14.0
5.0	2.5	19.0
5.0	3.1	24.0
5.0	3.8	31.4
10.0	5.1	36.4

(b) Further runs were carried out with a large excess of [Fe^{II}(bypy)$_3$]$^{2+}$ over [Fe^{III}(bipy)$_3$]^3, when the following rate constants were obtained.

10^5 [Mo^V_2] / mol dm^{-3}	**10^5 [Fe^{II}(bipy)$_3$$^{2+}$] / mol dm^{-3}**	**10^3 k_{obs} / s^{-1}**
5.1	1.5	31.6
2.5	2.5	14.0
3.1	3.8	15.0
1.5	5.0	6.4
1.5	6.0	6.0

Show by graphical method that the following rate law applies and determine k_1 and k_{-1}/k_2.

$$\frac{d[\mathrm{Fe^{II}}]}{dt} = k_{obs}[\mathrm{Fe^{III}}] = \frac{2k_1k_2[\mathrm{Mo_2^V}][\mathrm{Fe^{III}}]}{k_{-1}[\mathrm{Fe^{II}}]+k_2}$$

(c) The above rate law is consistent with a mechanism:

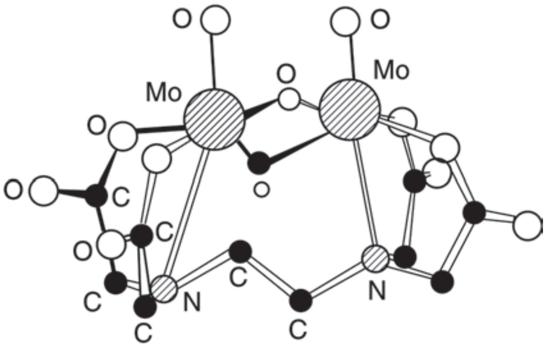
$$\mathrm{Mo^V{}_2 + Fe^{III}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mo^VMo^{VI} + Fe^{II}}$$

$$\mathrm{Mo^VMo^{VI}} \xrightarrow{k_2} \mathrm{Mo^V + Mo^{VI}}$$

$$\mathrm{Mo^V + Fe^{III}} \xrightarrow{\text{fast}} \mathrm{Mo^{VI} + Fe^{II}}$$

Using the stationary-state approximation for $\mathrm{Mo^VMo^{VI}}$ derive a rate law of this form.

(d) The structure of the $\mathrm{Mo^V{}_2}$ reactant is as shown.



(i) What influence will the edta have on the mechanism?

(ii) What might happen with $[\mathrm{Mo_2O_4(H_2O)_6}]^{2+}$ as the $\mathrm{Mo^V{}_2}$ reactant.

(ii) What structure will $\mathrm{Mo^{VI}}$ have in such acidic solutions?

(open book question)

B19 (a) A 1.0 mol dm^{-3} solution of a nylon salt, $H_3N^+(CH_2)_8COO^-$, was polymerised in an inert solvent using a 0.001 mol dm^{-3} solution of a catalyst. The concentration, C, of the salt was followed as a function of polymerisation time, t, with the results shown below.

t / hr	0	1	2	5	10	15	20
C / mol dm^{-3}	1.0	0.22	0.14	0.07	0.0035	0.0026	0.0019

(i) Derive an expression for C as a function of the polymerisation time and hence calculate the rate constant for the polymerisation reaction and the average molecular weight of the polymer recovered after a reaction time of 20 hr.

(ii) Assuming that the reaction kinetics are unaffected, calculate the molecular weight that would be achieved after 20 hr if the nylon salt had been contaminated with 2 mol% of a monocarboxylic acid, $CH_3(CH_2)_7COOH$.

(b) Polymerisation of a 1 mol dm^{-3} solution of acrylonitrile was initiated by 0.001 mol dm^{-3} AIBN and the concentration of acrylonitrile [M] was measured as a function of time.

t / hr	0	1	2	3	4	5
[M] / mol dm^{-3}	1.000	0.959	0.919	0.881	0.845	0.810

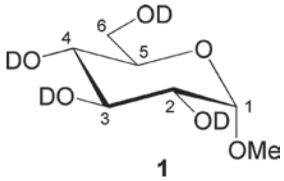
(i) Calculate the rate constant for the polymerisation and comment on any assumptions you make in the calculation.

(ii) The resulting molecular weight was too high for a particular application. Suggest two ways in which this parameter be controlled during the reaction and show the quantitative effect of the methods.

(c) Two samples of polystyrene were prepared by different methods. Analysis by light scattering showed the molecular weight of both to be 100 000. The ideal osmotic pressures of solutions of the polymers with concentration 1.0 g dm^{-3} were 25.5 Pa and 49.1 Pa at 298 K. Calculate the polydispersities of the polymer and suggest, with reasons, the methods used for their preparation.

(e) Polymerisation of two samples of MMA was separately initiated with benzoyl peroxide or with butyl lithium in an inert solvent. The polymerisations yielded polymers with the same number average molecular weights. **Sketch** the gel permeation chromatograms you would expect for the two samples, accounting for any differences. Comment on any differences you might expect in the ^1H NMR spectra and in the glass transition temperatures of the two polymers.

B20 Several NMR experiments (^{1}H, ^{13}C, COSY, HETCOR) were performed upon methyl-α-D-glucopyranoside (1) and are presented with this question. These experiments were performed using deuterium oxide (D_2O) as solvent, hence the hydroxyl protons are not observed in the ^{1}H NMR spectrum. Fully interpret the spectroscopic data and use this information to assign the ^{1}H and ^{13}C NMR spectra of compound 1. The numbering system indicated below should be used in your answer.



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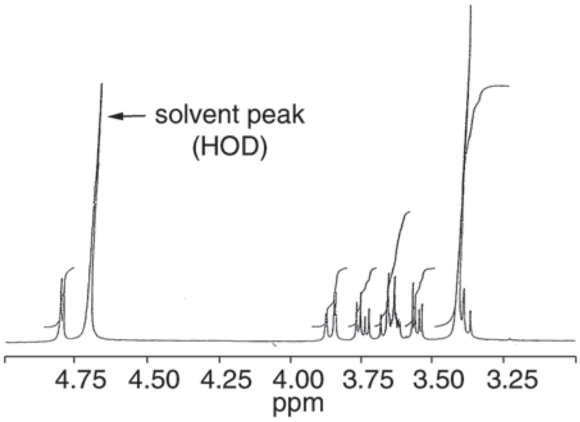
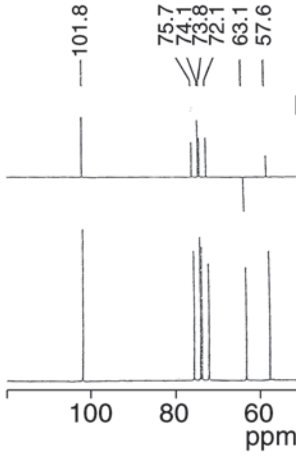
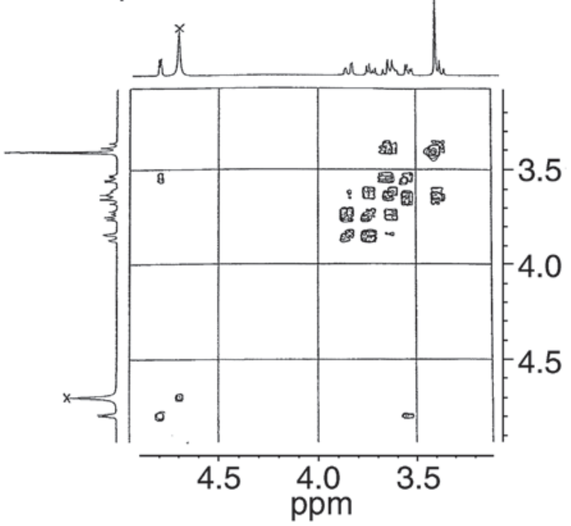
^{1}H NMR spectrum (D_2O)



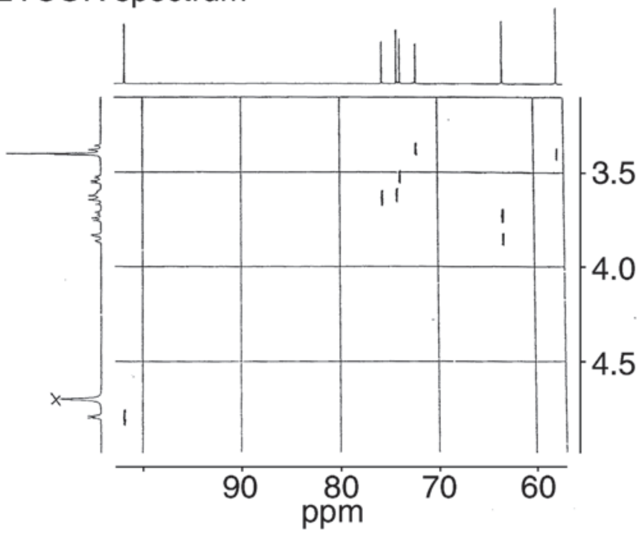


^{13}C NMR spectrum
DEPT 135 plotted above

COSY spectrum



HETCOR spectrum



B21 The ionic conductivity of two samples of KCl, labelled **A** and **B**, was measured as a function of temperature under a large applied voltage, with the following results:

Sample A		**Sample B**	
Temperature/K	**Conductivity/ S cm^{-1}**	**Temperature/K**	**Conductivity/ S cm^{-1}**
1049	1.848×10^{-4}	1049	1.842×10^{-4}
996	5.996×10^{-5}	996	6.010×10^{-5}
952	1.880×10^{-5}	952	1.906×10^{-5}
915	7.233×10^{-6}	915	7.181×10^{-6}
878	2.192×10^{-6}	903	4.803×10^{-6}
846	8.151×10^{-7}	843	2.268×10^{-6}
828	4.263×10^{-7}	782	1.146×10^{-6}
802	2.555×10^{-7}	733	5.056×10^{-7}
787	1.817×10^{-7}	693	2.387×10–^{7}
769	1.431×10^{-7}		
749	9.833×10^{-8}		

One sample had been carefully purified by repeated recrystallisation, while the other had been doped with a small amount of $SrCl_2$. Use the measurements and an appropriate graphical method to answer the following questions.

(a) Which sample (**A** or **B**) is the doped material?

(b) What are the approximate temperatures at which the ionic conductivity of each of the materials changes from extrinsic to intrinsic behaviour, and what is the mechanism of conduction in each case in each of these regimes?

(c) Use the data to calculate both the energy of formation and the activation energy for migration of the charge carriers in KCl.

(d) The ionic conductivity of KCl is too low for it to be useful as a solid electrolyte for most applications. Discuss the factors that favour fast-ion conductivity, with references to materials that display this phenomenon.

B22 (a) What is the electronic contribution to the molecular partition function and internal energy of $^{35}Cl_{(g)}$ at 25 °C and 2707 °C, given that the ground state and first excited state are four-fold and two-fold degenerate respectively and they are separated by 878 cm^{-1}.

(b) Calculate the translational contribution to the molar entropy of $^{35}Cl_{(g)}$ at 25 °C and 1 bar.

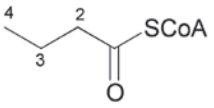
(c) Evaluate the molar entropy change at 25 °C for

$$^{35}Cl_{(g)} + e^{-}_{(g)} \rightarrow {}^{35}Cl^{-}_{(g)}$$

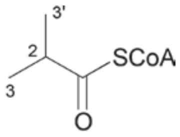
given that the ground state degeneracies of e^- and Cl^- are 2 and 1 respectively.

(d) The vibrational partition function of the Cl_2 molecule increases from $f_{vib} = 1.07$ at 300 K to $f_{vib} = 1.57$ at 800 K. What physical significance can be attached to these numbers?

B23 (a) Give a mechanism for the interconversion of butyryl CoA, **1**, and isobutyryl CoA, **2**, catalysed by the B_{12}-dependent enzyme isobutyryl CoA mutase.



1



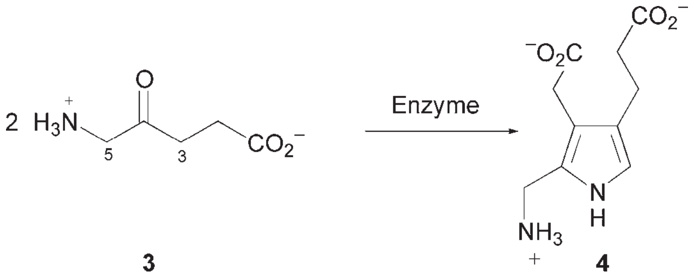
2

Explain the following isotopic labelling results:

(i) If [3,3-$^2H_2$,2-^{13}C]butyryl CoA, **1**, is incubated with the enzyme then the **2** produced is almost entirely [2,3-$^2H_2$,3-^{13}C]isobutyryl CoA.

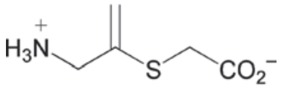
(ii) If [3,3-$^2H_2$,2-^{13}C]butyryl CoA, **1**, is mixed with an excess of unlabelled **1** and incubated with the enzyme then most of the molecules of product **2** which have ^{13}C at C-3 do not have a deuterium atom attached to C-3.

(b) Give a possible mechanism for the enzymic conversion of **3** to **4** which is consistent with the observations given below, explaining what each of the observations tells us about the mechanism and why



3 **4**

The enzyme is irreversibly inhibited by $NaBH_4$ in the presence of **3** but not in its absence. Thioester **5** irreversibly inhibits the enzyme at a rate which is proportional to the square of its concentration.

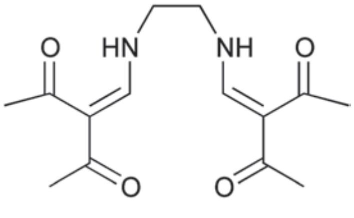


5

The k_{cat} value for the reaction is 3.5 times slower when **3** is deuteriated at C-3 but unchanged if **3** is deuteriated at C-5. The K_M value is unchanged in either case. The **3** recovered after 50% reaction has not lost any deuterium.

B24 (a) In order to maximise the yield of macrocyclic ligands chemists often rely on **template reactions**. Explain, with appropriate examples, what is meant by a template reaction.

(b) Reaction, in a 1:1 mole ratio, of $[Ni(CH_3CO_2)_2].4H_2O$ with the tetradentate ligand **1** in warm methanol (55 °C) results in the precipitation of an orange crystalline material (**A**), and the production of CH_3CO_2H (2 moles) and H_2O (4 moles). Compound (**A**) has a molecular mass of 337.03 g mol^{-1}, and analyses for C, 49.99; H, 5.40; N, 8.33; O, 19.04; Ni, 17.24%. It displays two intense bands in the IR spectrum (nujol mull) at 1650 cm^{-1} and 1590 cm^{-1}.



1

Refluxing (**A**) with excess 1,2-diaminoethane for 1 hour, followed by cooling and addition of water, results in the precipitation of a red crystalline material (**B**). Compound (**B**) has a molecular mass of 361.11 g mol^{-1}, and analyses for C, 53.22; H, 6.14; N, 15.52; O, 8.86; Ni, 16.25%. The ^1H NMR ($CDCl_3$) of (**B**) displays four resonances at δ 7.5 (2*H*), 3.2 (8*H*), 2.42 (6*H*) and 2.26 (6*H*). It also displays a broad intense band in the IR spectrum (nujol mull) at 1600 cm^{-1}.

(i) Identify and draw the structures of the products (**A**) and (**B**).

(ii) Assign the resonances in the ^1H NMR of (**B**) as far as you are able.

B25 Chromium(II) chloride crystallizes in an orthorhombic unit cell with a = 6.64, b = 5.98, c = 3.48 Å, which contains two molecules. The two Cr atoms occupy the special positions (0,0,0), (½, ½, ½) of space group Pnnm, and one of the four symmetry related Cl atoms is at (x = 0.36, y = 0.28, z = 0).

(a) Calculate the density of $CrCl_2$.

(b) Give the site symmetry of the Cr atoms, and of the Cl atoms.

(c) Draw a projection of one complete unit cell as seen down the c axis direction.

(d) Show that the Cr atom is surrounded by two Cl atoms at 2.92 Å and four at 2.37 Å.
Describe the Cr atom coordinate geometry. Give a possible explanation for this geometry.

(e) The unit cell derived from the neutron diffraction pattern of $CrCl_2$ is four times larger than the X-ray determined cell. Give a qualitative explanation for this observation.

B26 Attempt to assign the ^{13}C-NMR signals to the structure presented. Those carbons that were enriched with ^{13}C following a feeding experiment with 2-^{13}C-acetate are marked with an asterisk (*). On the basis of this information, propose a plausible biogenesis for the natural product.

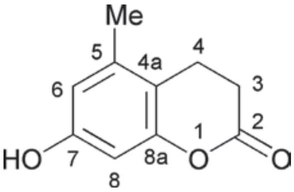


Table - proton-coupled natural abundance spectrum

δ-value	Multiplicity	
25.2	q	(*)
41.6	t	
44.2	t	(*)
110.9	s	
114.5	s	(*)
122.3	d	(*)
131.4	d	(*)
140.5	s	
149.2	s	
175.1	s	

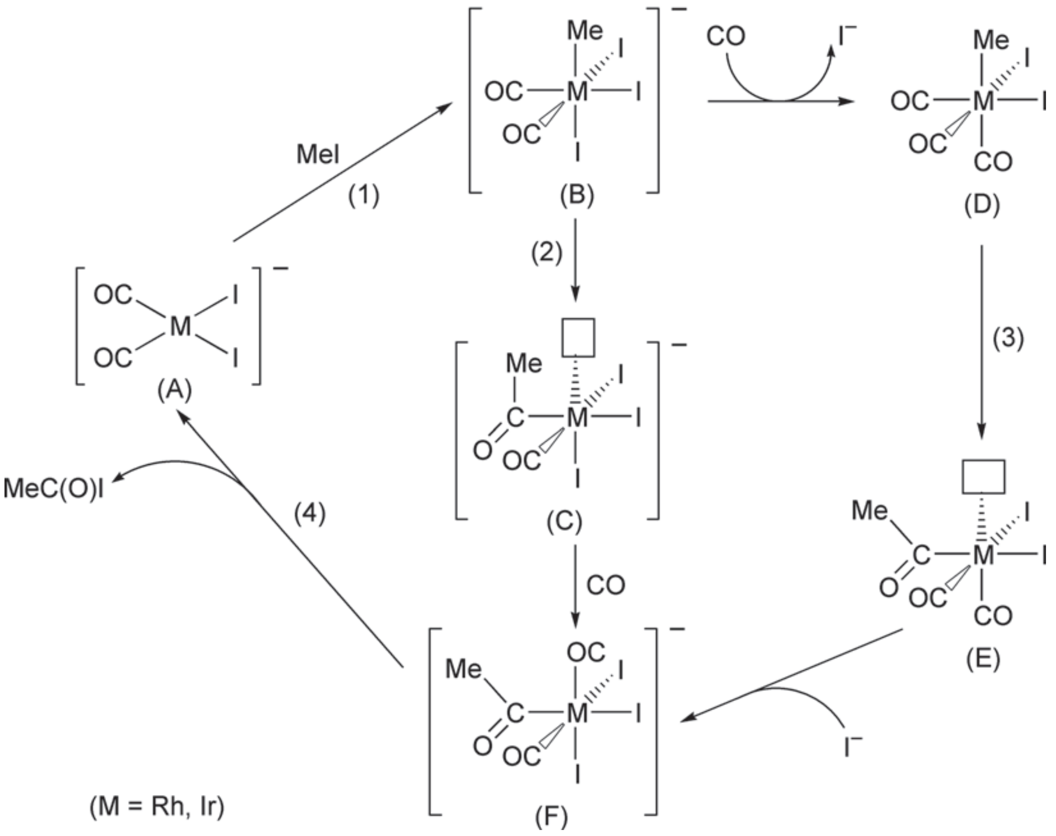
B27 (a) The complex [RhCl(PPh$_3$)$_3$] will catalyse the hydroformylation of alkenes:

$RCH = CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO$

Write a mechanistic cycle for this reaction, giving the oxidation state of the Rh for each intermediate species.

(b) Explain in detail why the hydroformylation of an equilibrium mixture of but-1-ene and but-2-ene affords $CH_3CH_2CH_2CH_2CHO$ as the major product.

(c) Parts of the catalytic cycles involved in the carbonylation of methanol with a rhodium or iridium catalyst are shown below.



(i) Classify the key reaction steps (1) to (4).

(ii) Using the data given below, identify which cycle A → B → C→ F → A or A → B → D → E → F → A is correct for each metal, identify the rate determining step in each case and hence deduce which species is most likely to have the highest concentration in each case. Explain all reasoning.

For Rh rate= k[Rh][MeI]

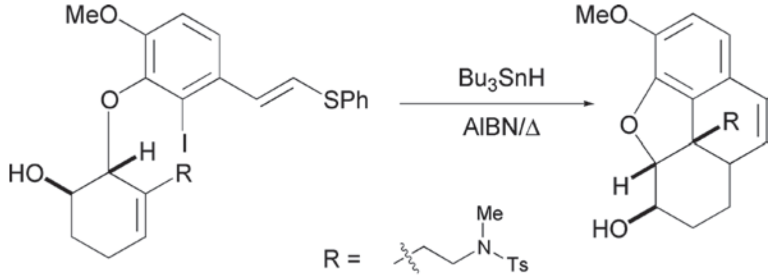
For Ir rate = k[Ir][CO] independent of MeI above a threshold level

(A) → (B) is 120 times faster for Ir,

(D) → (E) is 10^5 times slower than (B) → (C).

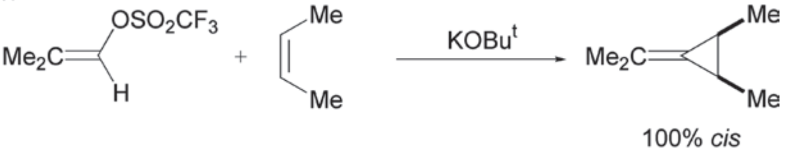
(iii) How are acetic acid and methyl iodide generated in the carbonylation process?

B28 (a) In a synthesis of the painkiller codeine, free-radical chemistry has been used to assemble part of the multiple ring system. The key step shown below, involves three consecutive radical processes which occur after initial radical generation. Identify these processes, explaining the transformation mechanistically.

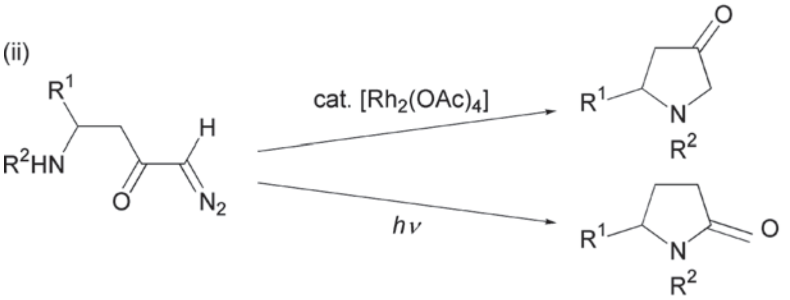


(b) Rationalise the following transformations, giving as much mechanistic detail as possible:

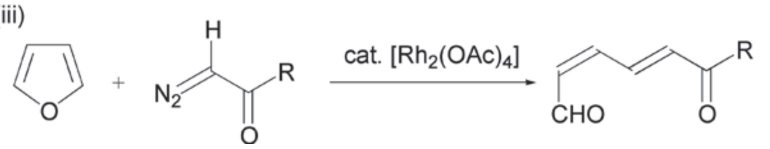
(i)



(ii)



(iii)



B29 (a) $[PtH_4]^{2-}$ is used as a model for the theoretical study of electronic structure and bonding in column-stacked mixed valence square planar platinum complexes. Given the D_{4h} character table, derive symmetry-adapted linear combinations of the four H atom 1*s* orbitals and give their symmetry species (irreducible representations). Give the symmetry species of all the Pt valence orbitals (5*d*, 6*s*, and 6*p*). Hence construct a qualitative molecular orbital energy level diagram for $[PtH_4]^{2-}$, taking the H 1*s* orbitals to be of lower energy than the orbitals of Pt. Indicate clearly which Pt orbitals remain non-bonding, and which molecular orbitals contain electrons.

Now consider the approach of two axial (***z*** axis) ligands with only σ-bonding capability. Construct symmetry-adapted linear combinations of these two orbitals and show which orbitals on Pt can interact with them.

(b) A new volatile molecular compound of low thermal stability is believed to be PF_2H_3. Its infrared and Raman spectra show bands assigned to stretching vibrations at the following wavenumbers (in cm^{-1}):

Infrared	***Raman***
2488 *w*	2488 *m*, dp
722 *vs*	2419 *s*, p
	578 *s*, p

s = strong; ***vs*** = very strong; ***m*** = medium; ***w*** = weak;

p = polarised ($\rho < ¾$); dp = depolarised ($\rho = ¾$).

Consider whether these results are consistent with the formulation of the compound as PF_2H_3 and, if so, what they tell you about the likely structure of the compound.

B30 (a) Three different kinds of Fe/S cluster are used in nature. Draw a clear diagram of each cluster, indicate which oxidation states are used for electron transfer, and explain how redox information would be obtained experimentally.

(b) First-order rate constants, k_{obs}, for oxidation of ***Clostridium pasteurianum*** ferredoxin with a range of inorganic oxidants (298 K; pH 8.0; [ferredoxin] = 10^{-6} mol dm^{-3}) are tabulated below.

$10^4[Co(C_2O_4)_3{}^{3-}]$/ mol dm^{-1}	2.0	4.0	7.0	10.0	20.0
k_{obs}/s^{-1}	1.0	2.0	3.2	4.8	9.5

$10^4[Co(edta)^-]$/ mol dm^{-1}	5.0	8.0	12.1	16.1	20.1
k_{obs}/s^{-1}	5.6	9.1	13.0	16.5	23.8

$10^4[Co(acac)_3]$/ mol dm^{-1}	0.8	1.7	3.4	5.4	7.8
k_{obs}/s^{-1}	3.0	5.5	10.4	16.9	23.8

$10^4[Pt(NH_3)_6]^{4+}$/ mol dm^{-1}	0.8	1.5	2.9	3.2	5.8
k_{obs}/s^{-1}	8.8	14.5	22.0	23.8	29.4

(i) Plot the data in a suitable graphical form and propose a mechanism for the reaction.

(ii) What does the graph suggest about the nature of the electron transfer site for the inorganic complexes? Give an expression for k_{obs} and use this to account qualitatively for the different behaviour of each complex.

(iii) For the complex ion $[Pt(NH_3)_6]^{4+}$, show how linearisation of the data can be used to gain additional mechanistic information. Hence calculate the magnitude of the association constant and the rate constant for the electron transfer (giving units).

[edta = ethylenediaminetetraacetate; acac = acetylacetonate]

B31 (a) The bulk scale benzoylation of glycol ($HOCH_2CH_2OH$) is monitored by ^1H NMR spectroscopy. After the first stage of the reaction the product mixture contains some unchanged diol, the monobenzoate and the dibenzoate, and the ^1H spectrum shows bands for the methylene groups $-CH_2OH$ and $-CH_2OBz$ in the ratio 0.54:1.00. A second stage of the reaction is carried out at a lower temperature such that the monobenzoate will not react further. After this second stage the diol is totally consumed and the ^1H spectrum shows that the ratio of the methylene groups is now 0.33:1.00. Determine the molar percentage composition of the mixture after the first stage.

(b) Describe the rules which determine the number and relative intensity of lines in an NMR multiplet when coupling is present to spins with I = ½ and I = 1. Illustrate your answer with reference to the species F_3CCD_3.

B32 (a) Identify the isomers which would be possible for the cluster of molecular fomula $K[H_2RhOs_3(CO)_{12}]$.

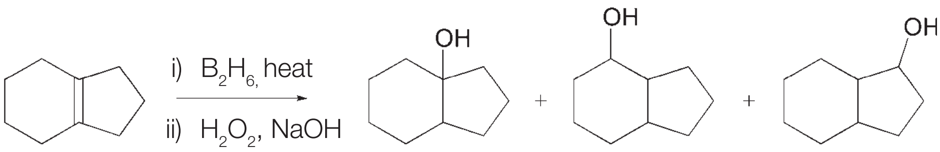
The ^1H NMR spectrum of a solution of $K[H_2RhOs_3(CO)_{12}]$ shows two doublets of relative intensity 1:10 with a coupling constant of 20 Hz for the doublet of intensity 1 and 10 Hz for the doublet of intensity 10. The relative intensity of the lines was found to vary with the temperature. There was a number of bands in the IR spectrum in the region of 1900 cm^{-1} and weak bands in the region of 1500 cm^{-1}. On deuteration the bands at 1900 cm^{-1} were unaffected whilst the bands at 1500 cm^{-1} were replaced by absorption at 1100 cm^{-1}. The IR spectrum also showed a variation in the relative intensity of the bands at 1900 and 1500 cm^{-1} with temperature. On thermolysis, two new complexes were isolated, $HRhOs_4(CO)_{15}$ and $HRhOs_4C(CO)_{14}$.

Suggest possible structures for the above species.

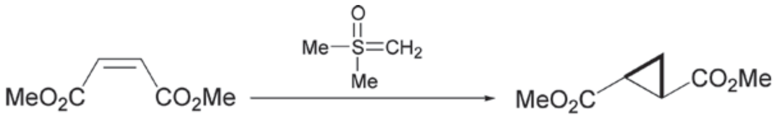
[Rh, I = ½,100%]

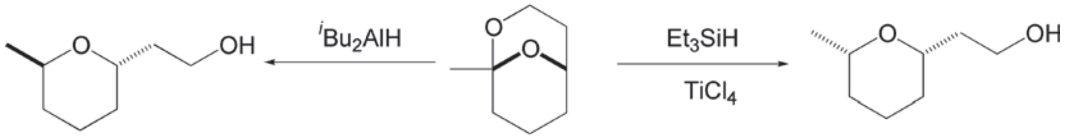
(b) Pentanuclear clusters are found in a wide variety of structural types. Give examples of these and show how Wade Mingos rules and the extended 18e-rule can be used in structure rationalisation. Include in your answer the following pentanuclear compounds; Pb_5^{2-}, Bi_5^{3+}, Tl_5^{7-}, $Fe_3(CO)_9(Se)_2$, and $C_2B_3H_5$.

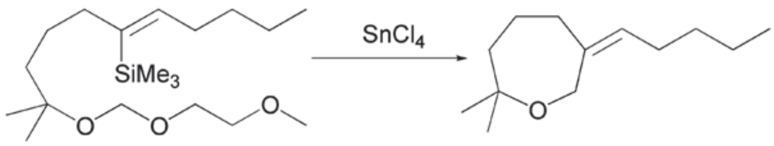
B33 (a) Account mechanistically for the formation of the following mixture of isomeric alcohols, and predict the likely stereochemistries.



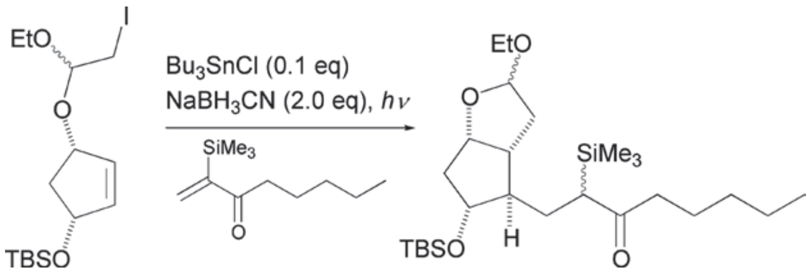
(b) Account mechanistically for the products formed in each of these reactions and explain any selectivity.



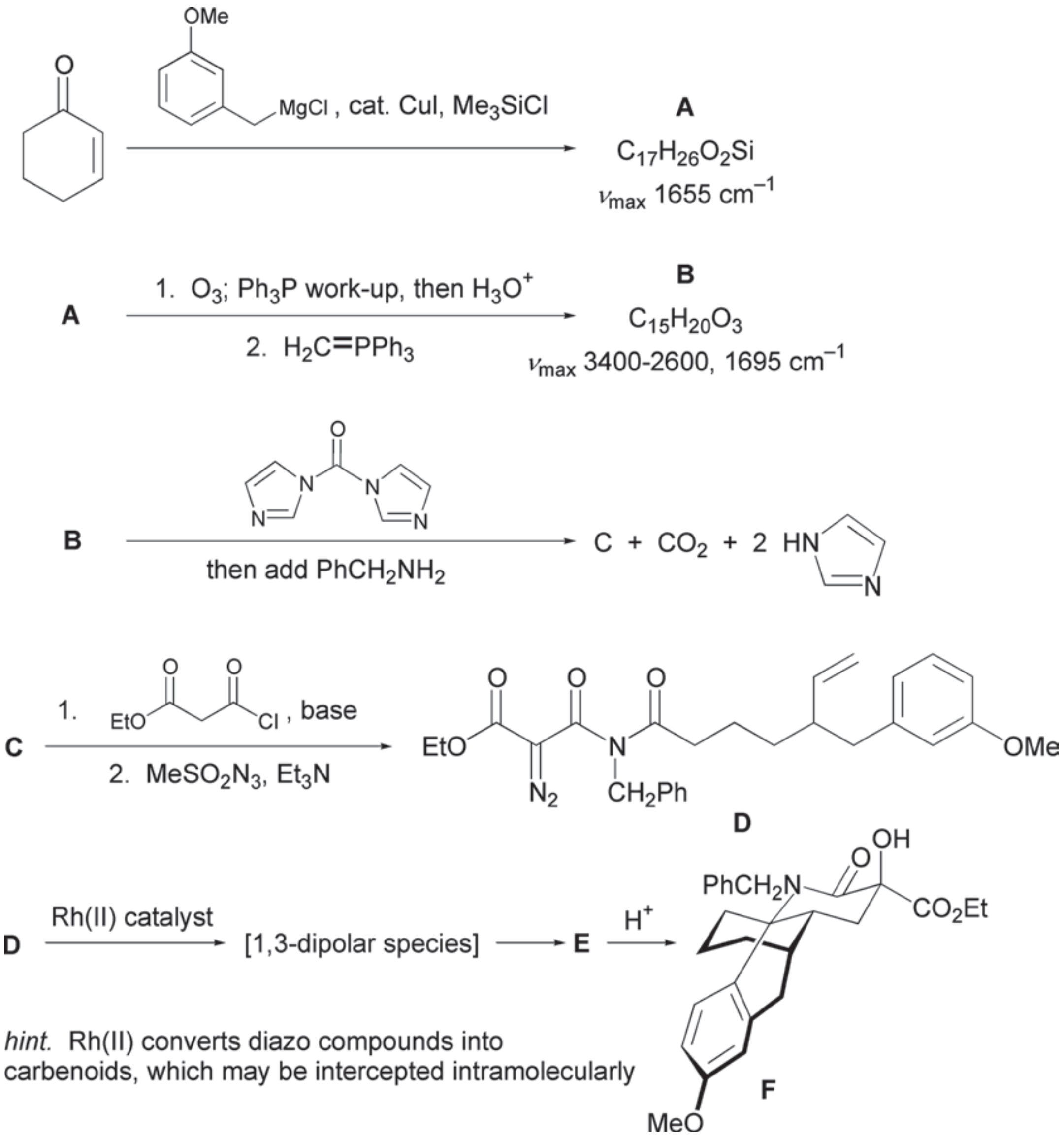




(c) Account for the following reaction, explaining the selectivity. Why was this procedure preferred to the simple use of a stoichiometric amount of Bu$_3$SnH?



B34 Suggest structures for the lettered compounds **A**, **B**, **C** and **E** in the synthetic sequence below, which was developed as part of a programme directed towards the synthesis of the alkaloid lycopodine. Assign the infrared data given for **A** and **B**. Give a mechanism for the conversion of **B** into **C**, the formation of **E** from **D**, and of the cyclisation reaction which occurs to give **F** when **E** is treated with acid.



hint. Rh(II) converts diazo compounds into carbenoids, which may be intercepted intramolecularly

B35 An electrochemical cell is set up in which the reduction process

$$\mathrm{Ox} + ne^- \rightleftharpoons \mathrm{Red}$$

occurs at the cathode when a suitable potential is applied. The current flowing as the cathode is made increasingly negative depends on the rate of potential change, and has the form in dicated in Figure 1.

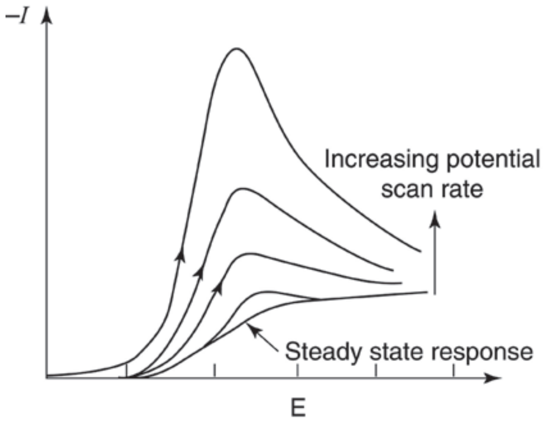


Figure 1

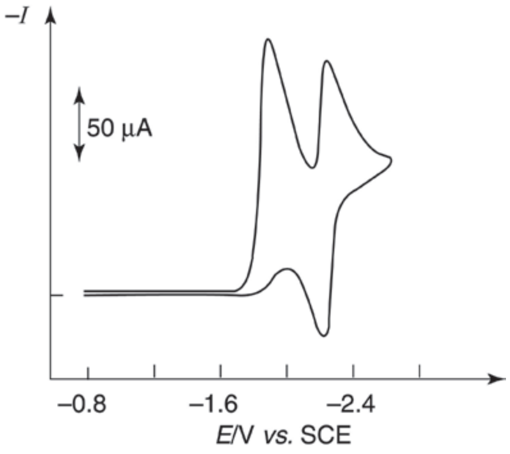


Figure 2

(a) Explain the appearance of the curves in Figure 1, labelling any key values on the potential axis. What might the current response look like when the potential sweep is reversed? Discuss the types of information that can be obtained from measurements of the currents produced by cyclic forward and reverse potential sweeps.

(b) The reduction of 4-chlorobenzonitrile is postulated to occur ***via*** the mechanism

$\mathrm{ClC_6H_4CN} + e^- \qquad [\mathrm{ClC_6H_4CN}]^{-\bullet}$

$[\mathrm{ClC_6H_4CN}]^{-\bullet} + e^- + \mathrm{H}^+ \rightarrow \mathrm{C_6H_5CN} + \mathrm{Cl}^-$

$\mathrm{C_6H_5CN} + e^- \qquad [\mathrm{C_6H_5CN}]^{-\bullet}$

The second step is assumed to be irreversible. A cyclic voltammogram for a solution of 4-chlorobenzonitrile in dimethylformamide is shown in Figure 2. Show that this voltammogram is consistent with the proposed mechanism. Predict the appearance of the cyclic voltammogram for unsubstituted benzonitrile.

B36 The molecular ion group (m/z = 138, 139, 140) in the 70 eV electron bombardment mass spectrum of an organic compound showed the following relative intensities:

M+.	(m/z = 138)	84.30%
M+. + 1	(m/z = 139)	6.17%
M+. + 2	(m/z = 140)	0.52%

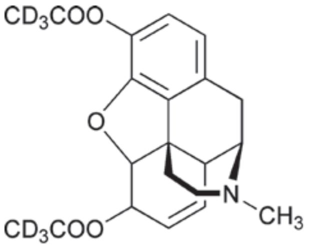
The relative abundance of the ^{15}N and ^{18}O isotopes are 0.36% and 0.20% respectively. Calculate the empirical formula of the molecular ion.

The major fragment ions in the spectrum occurred at m/z = 122, 92, 76, 75, 74 and 52. Identify the molecular formula of the compound as completely as possible.

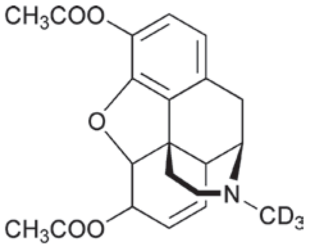
B37 You have been requested to develop a method for the quantitative determination of diamorphine in a sample of heroin, using gas chromatography–mass spectrometry (GC-MS), with a deuterated internal standard.

(a) Explain the desirable characteristics of a suitable internal standard for such an analysis.

(b) Deuterated internal standards are not available and you are requested to synthesise your own standard.



d$_6$-Diamorphine
1

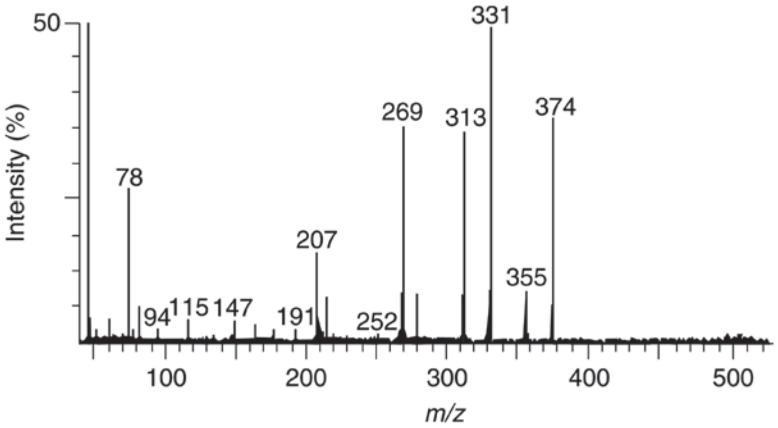


d$_3$-Diamorphine
2

(i) Evaluate why d$_6$-diamorphine (**1**) is a more suitable internal standard than d$_3$-diamorphine (**2**).

(ii) Explain how you would synthesise and purify d$_6$-diamorphine from the commonly available opiate morphine.

(c) The electron impact mass spectrum of d$_6$-diamorphine, after GC-MS analysis, is shown below



Interpret this mass spectrum as far as you are able.

(d) Explain how you would use the d$_6$-diamorphine to quantify diamorphine in a heroin sample.

CONTACT US

Informal discussions are welcomed on any aspect of accreditation. Guidance and support in preparing an application is available from professionally qualified RSC staff.

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