Imperial College
London

Department of Chemistry

Third Year Syllabus

2004 - 2005

Contents

Inorganic III

Organic III

Physical III

Department of Chemistry – Imperial College

INTRODUCTION TO THIRD YEAR CHEMISTRY

Aims

The third year of the degree in Chemistry aims to provide consolidation of fundamental material already learnt and, for the first time, allows the student to take his/her own direction in chemistry. This is brought about by options in the third year and the choice to specialise in particular areas that interests the student the most. This year aims to provide a platform to initiate their research based final year.

The course goals are achieved by the students studying, at a more advanced level, elements of organic, physical, inorganic and analytical chemistry. At this level student will be competent at all basic laboratory skills and will be able to complement and develop these with more advanced techniques available in the third year. At the end of this year students will have a more advanced level of understanding, of both theoretical and practical of their chosen, specialised areas. A general, broad background of chemistry obtained from their compulsory courses complements this knowledge.

Summary of Content

In the first term both courses study a core 66 hours of compulsory lectures and in the following term an additional 56 hours from a choice of 120 hours. Throughout the lectures, workshops, problem classes, and larger group tutorials are used to complement and underpin these courses. Students can also specialise in two laboratory courses out of three (physical, inorganic, organic) giving them a total of ca. 160 hours lab work. In addition there are a wide variety of ancillary subjects (e.g. medicinal chemistry, language courses, humanities, management, mathematics, conservation science, chemical engineering) that serve to complement their main chemistry course. Students also carry out a scientific literature report. The students present a poster/oral session on their technical literature report. The third year is evaluated by two three-hour exams on the compulsory course (January) and the optional course (June). This is also complemented by an oral exam (30 mins) that is given to each student.

The compulsory lectures share substantial overlap reflecting the multidisciplinary approach taken in this year, therefore many course are closely related and complementary. The organic courses cover advanced elements of non-aromatic heterocylics biological chemistry, organometallic and radical chemistry. Inorganic chemistry covers advanced organometallics, inorganic mechanisms, symmetry, spectroscopy and advanced main group chemistry. Physical chemistry covers quantum chemistry, molecular reaction dynamics and surface solid state chemistry.

Optional course cover a wide range of topics. These typically are advanced stereochemistry, molecular modelling, polymers, mass spectrometry, reactive intermediates and carbohydrate chemistry. Inorganic chemistry covers macrocyclic, solid state chemistry, electronic, lanthanide and actinide Chemistry, Inorganic medicinal chemistry. Physical chemistry covers nature at the nanoscale, molecular electronics colloids complex fluids, bioanalytical, separation technique sensing and detection.

Inorganic III

Inorganic Synthesis Laboratory

Britovsek, George

200 hours (run in conjunction with the 3rd year organic synthesis course)

Objectives

- To give practice in multistep and more demanding syntheses
- Exposure to new techniques such as the manipulation of gases and the use of Schlenk line techniques.
- To give further experience with instrumental techniques.
- To demonstrate some of the aspects of transition metal and main group chemistry described in the lecture course.

Experiments

The inorganic component of the 3rd year synthesis laboratory comprises seven compulsory experiments one taking two weeks and the others one week. An appreciation of the safety aspects of each experiment is required before it is carried out. The experiments are:

1. Vacuum line techniques, the generation and manipulation of SiF4
2. NMR and Mass Spectrometry of tropyllium complexes of molybdenum
3. Nickel and iron catalysts for the polymerisation of ethene
4. Dioxygen Determination, preparation of a cobalt salen complex
5. Boranes and metallaboranes, preparation and characterisation of an Ru borane complex
6. Metals in Organic Synthesis, oxoruthenium complexes as oxidation catalysts
7. Fluxional ferrocenophanes, their synthesis and characterisation

Inorganic Mechanisms and Catalysis

Britovsek, George

6 hours + 1 problem class

Aims

- To present an overview of the fundamental reactions that can occur at a transition metal centre and how these reactions collectively make up a catalytic cycle.
- To give an overview of industrially important applications of homogeneous catalysis.

Structure

The course builds on inorganic mechanisms introduced in the 2nd year courses Transition Metal Chemistry and Introduction to Organometallic Chemistry and puts these mechanisms in the context of catalytic cycles, with a focus on industrial applications of homogeneous catalysis. The course is related to the courses Advanced Organometallic Chemistry (3.I3) and Organometallic Complexes in Organic Synthesis (3.O3), which run parallel, and forms the basis of some more specialist courses in catalysis: Palladium Reagents in Organic Synthesis (3.I5) and Catalytic Asymmetric Synthesis (4.O11)

Lecture 1 + 2: Introduction to the fundamentals of homogeneous catalysis and the mechanisms in inorganic and organometallic chemistry
Lecture 3: Hydroformylation
Lecture 4: Oligomerisation/Polymerisation
Lecture 5: Carbonylation
Lecture 6: Asymmetric Catalysis
Problem class

Objectives

By the end of the lecture course, the student should

- have an understanding of the different types of reactions that can occur at a transition metal centre;
- have an understanding of how these individual reactions make up a catalytic cycle;
- have an overview of the type of reactions that can be catalysed by transition metal complexes and
- have an appreciation of the importance of catalysis in biological and industrial processes.

Building upon

This material from this course builds upon Transition Metal Chemistry and Organometallic Chemistry (2nd year).

Looking forward to

The material from this course will be the basis for lectures on Palladium Reagents in Organic Synthesis (3rd year) and Catalytic Asymmetric Synthesis (4th year).

Advanced Main Group Chemistry

Lickiss, Paul

6 hours

Aims

- To introduce more advanced topics than covered in the 2nd year Main Group course or extend them to more recent developments.
- To gain an understanding of the classic problem of the reluctance of many main group elements to participate in multiple bonding and how this problem may be overcome.
- To introduce hypervalent group 17 compounds, interhalogens and their structure.
- To introduce the chemistry of elements of group 18.
- To extend the electron counting rules used for boranes in the 2nd year to cover other p-block elements.

Structure

Lecture 1: Why is multiple bonding in compounds of the lower main group elements rare? Synthetic strategies to overcome the problems and the use of bulky ligands to stabilise multiply bonded species.
Lecture 2: Synthesis and structure of compounds containing multiple bonds to lower group 14 elements, emphasis on silenes and disilenes.
Lecture 3: Synthesis and structure of compounds containing multiple bonds to lower group 15 elements. Borazenes and phosphazenes.
Lecture 4: The controversy surrounding compounds reported to contain triple bonds to gallium. Introduction to group 17 elements.
Lecture 5: Group 17 elements. Cations and anions, Xn+ and Xn-. Interhalogens. Hypervalency, structure and bonding.
Lecture 6: Synthesis and structure of compounds of group 18 elements. Extension of electron counting to include the isoelectronic idea and the structure of main group clusters including Zintl anions.

Objectives

- An understanding of how, once apparently insurmountable synthetic problems, have been overcome by suitable choice of reagents, reaction conditions and substituents.
- An understanding of some of the current active and exciting areas of modern main group chemistry.
- An appreciation of the chemistry of groups 17 and 18 elements.
- A much extended use of electron counting rules in order to understand the structure of main group clusters.

Building upon

This material from this course builds upon Periodicity (1st year) and Main Group Chemistry (3rd year).

Advanced Organometallic Chemistry

Britovsek, George & Gibson, Vernon

8 hours

Aims

- To present an overview of the coordination of polyene ligands to transition metals, including their synthesis and applications.
- To give an MO description of the bonding in polyene metal complexes.
- To describe the synthesis, reactivity and applications of organometallic complexes with metal-carbon single and multiple bonds.
- To describe the interaction of C-H bonds with metal complexes.
- To describe C-H bond activation at transition metals.

Structure

Lecture 1 + 2: Polyene ligands
Lecture 3 + 4: Organometallic complexes with metal- carbon multiple bonds
Lecture 5 + 6: Organometallic complexes with metal-carbon single bonds
Lecture 7 + 8: Interaction of metal centres with C-H bonds, agostic interactions and C-H activation

Objectives

By the end of the lecture course, the student should be able to:

- Have an overview of the different types of polyene ligands and their bonding modes.
- Describe the bonding of polyene ligands to a transition metal in terms of a MO description.
- Understand the basic routes for the synthesis of organometallic complexes containing polyene ligands and complexes with metal-carbon single and multiple bonds and their reactivity and applications in catalysis.
- Understand C-H interactions with transition metals (agostic interactions) and how C-H activation can occur at a transition metal centre.

Building upon

This material from this course builds upon Transition Metal Chemistry and Organometallic Chemistry (2nd year).

Symmetry and Spectroscopy

Taylor, Alan

7 hours

Aims

To provide an introduction to group theory and enable students to use character tables to understand and predict the infrared, Raman and electronic spectroscopy of chemical compounds.

Structure

Lectures 1-2: Revision of point groups and their assignment. Introduction to groups and their properties and how to use a basis to build reducible representations.
Lectures 3-4: Character tables, Mulliken symbols, the reducible representation, reduction formula and irreducible representations. Determination of the vibrational representation.
Lectures 5-6 and ***problem class***: Using infrared and Raman spectroscopy to determine symmetry, Electronic selection rules and the direct product representation. Simple molecular orbital diagrams from symmetry adapted linear combination of atomic orbitals.

Objectives

- To demonstrate the power of symmetry in chemistry.
- To familiarise students with character tables and enable them to use them to predict infrared, Raman and electronic spectra of inorganic compounds.
- To provide an understanding of molecular orbital diagrams from the perspective of symmetry

Building upon

This material from this course builds upon Characterisation of Inorganic Compounds (1st year) and Spectroscopy (1st year) and Transition Metal Chemistry (2nd year).

Palladium Catalysis in Organic Synthesis

Hii, Mimi

8 hours

Aims

Role of palladium reagents in modern synthetic methodology.

Structure

Lecture 1-2: Revision of the basic coordination/organometallic chemistry of palladium complexes. Construction of a catalytic cycle. Basic terminology. Transmetalation reactions: Formation of C-C bonds: Negishi, Stille, Suzuki, Sonigashira cross-coupling reactions. Asymmetric examples. Dynamic kinetic resolution. Formation of C-X bonds: Aryl halide amination, etheration and cynation.
Lecture 3-4: Migratory insertion/□-hydride elimination: Heck arylation reactions. Cationic vs neutral catalytic cycles: Effect of substrate, ligand and additives on regioselectivity. Asymmetric Heck reaction – origins of stereoselectivity. Baldwin's rules.
Lectures 5-6: □1- and □3-allylpalladium complex. Palladium-catalysed allylic substitution reactions. Stereochemistry. Asymmetric allylic substitution reactions: origins of stereoselectivity.
Lecture 7: Hydridopalladium species. Addition of pronucleophiles to dienes. Anion-capture. Tandem, domino and cascade processes.
Lecture 8: Problems class.

Objectives

By the end of the course students should

- Appreciate the versatility of palladium catalysis;
- Able to identify key catalytic precursors and intermediates involved in palladium-catalysed processes and to construct basic catalytic cycles from a given set of substrates and precursors;
- Explain the origins of stereoselectivity in each of the processes.

Building upon

This material from this course builds upon Inorganic Mechanistics and Catalysis (3rd year).

Lanthanide and Actinide Chemistry

Hill, Michael

8 hours

Aims

To provide an understanding of the chemistry of the 4f and 5f elements and their increasingly technologically important compounds.

Structure

Lectures 1-3: The shapes of f-orbitals and the chemistry of the 4f- (lanthanide) elements in terms of their electronic structures and available oxidation states. The occurrence and isolation of the elements, atomic and ionic radii (lanthanide contraction), coordination chemistry and f-orbital participation in bonding.

Lectures 4-5: Inorganic lanthanide derivatives for use in organic oxidation and reduction and the increasing use of trivalent and low oxidation state organolanthanide derivatives in homogeneous catalysis.

Lectures 6-8: The actinide elements; their occurrence, formation and applications. Recent developments in organoactinide chemistry and the use of these compounds in small molecule activation.

Objectives

- To develop an appreciation of how occupancy of the 4f- and 5f-orbitals influences oxidation state, ionic radius and chemical reactivity.
- An appreciation of the unique chemical, magnetic and spectroscopic properties of the lanthanide and actinide elements.
- To illustrate and emphasise the unique chemistry emerging from recent research of inorganic and organometallic 4f- and 5f-derivatives.

Metals in Medicine

Davies, Rob

8 hours

Aims

To give a detailed overview, including many specific examples, of the use of inorganic pharmaceuticals in medicine for both therapeutic and diagnostic applications.

Structure

- Historical introduction to metals in medicine and key areas
- Chelation therapy: Bertrand diagram, metal poisoning, the chelate effect, ligands used in chelation therapy, biologic considerations
- Cis-platin: history, structure-reactivity relationships, aquation, biologic targets , DNA damage on adduct formation, DNA repair systems, biotransformation, side-effects, modes of resistance
- Why is trans platin inactive? Adducts formed and damage to DNA, repair systems
- 2nd generation Pt drugs: Carboplatin, oxaliplatin and nedaplatin modes of operation and side-effects
- 3rd generation Pt drugs: sterically hindered Pt complexes, Pt(IV) complexes, complexes with biologically active carrier ligands, water soluble complexes, multinuclear Pt complexes, trans-Pt complexes, other metal complexes
- 99mTc radiopharmaceuticals for diagnosis; principle of use, synthesis of pharmaceuticals, Tc-tagged drugs, Tc-essential drugs
- Re radiopharmaceuticals for therapy: drug targeting
- Radioimmunotherapy: antibodies, use of 131I and 90Y, pre-targeting techniques
- Boron neutron capture therapy: the BNC reaction, drug design and targeting using cellular building blocks, liposomes or other approaches

Objectives

By the end of the course the students should understand and be able to discuss:

- Chelation therapy including biological considerations for ligand choice
- Platinum anti-cancer drugs (structure-reactivity relationships, biological targets, mechanism of Pt-DNA binding and damage caused to DNA, characterization of Pt-DNA adducts, DNA repair systems, biotransformation of Pt drugs and side-effects, the inactivity of trans-platin, resistance to cis-platin, 2nd and 3rd generation Pt anti-cancer drugs)
- Radiopharmaceuticals in diagnosis (99mTc use and preparation, Tc tagged drugs, Tc essential drugs)
- Radiopharmaceuticals for therapy (Re compounds, radioimmunotherapy)
- Boron neutron capture therapy (principles, drug design)

Building upon

This material from this course builds upon Bioinorganic Chemistry (2nd year)

Chemistry of Macrocycles

Long, Nick

8 hours

Aims

To introduce many aspects of the chemistry of ring systems, examine the various types of cyclic ligand systems and show how the use of metals or 'guest' species can control the formation and reactivity of cyclic molecules containing domains suitable for metal binding.

Structure

Lectures 1 - 2: An introduction to macrocycles. History, nomenclature and general classes of compound. Why study macrocyclic ligands and their complexes? A discussion of metal - ligand interaction, bonding, conformational and behavioural changes on binding metals to ring systems.
Lectures 3 - 5: An in-depth study on macrocyclic and macrobicyclic compounds, focusing on crown- (O-containing), azacrown- (N-containing) and thiacrown- (S-containing) ethers. The synthesis (templates vs. condensation and high dilution), structures (free ligands, and metal-bound species) and complexes (selectivity, stability, thermodynamics and 'the macrocyclic effect') will be discussed.
Lectures 6 - 8: Applications of macrocycles (as synthetic reagents, in analysis, chiral recognition, in switches and sensors. Introduction and brief discussion on other cage or ring compounds e.g. cryptands, sepulchrates and calixarenes.

Objectives

By the end of the course, students should be able to identify the properties specific to macrocyclic systems and what differentiates them from 'open-chained' species. They should understand how complexation can change the structures and impart unusual and important behaviour and how this can be applied to everyday life.

Building upon

This material from this course builds upon Coordination Chemistry (1st year) and Transition Metal Chemistry (2nd year).

Looking forward to

The material from this course will be the basis for lectures on Designer Ligands (4th year).

Non-Aqueous Solvents

Welton, Tom

8 hours

Aims

This course investigates the properties of liquids that are relevant to their use as solvents for synthesis and spectroscopy. The course explores how solvents can affect solute species and s their reactivities. The course begins with the classification of liquids by physical properties, chemical properties and by empirical parameters.

Structure

- Introduction to solvents, solution formation (1 lecture)
- Classification of solvents, by physical properties and chemical properties. Solvent-solute interactions (1 lecture)
- Solvent effects on chemical equilibria (2 lectures)
- Solvent effects on chemical kinetics (2 lectures)
- Solvent effects on spectra (1 lecture)
- Empirical polarity scales (1 lecture)

Objectives

By the end of the course the students should:

- Be able to select an appropriate solvent for a reaction for which they know the mechanism.
- Be able to use the effect of changing solvent on the rate of a reaction to help to elucidate its mechanism.
- Be able to relate changes in physical properties (e.g. spectra) of solute species to changes in their reactivities.

Recommended reading

There are no books that are ideal for this course the best available is:
E. Buncel, R. Stairs and H. Wilson, “The role of the Solvent in Chemical reactions”, Oxford Chemistry Masters, ISBN0 19 851100 0. (From a very physical perspective).

Building upon

- Foundation Course, Thermodynamics and Equilibria, Chemical Kinetics.
- Physical Organic Chemistry.
- Organic Synthesis.
- Liquids and Liquid Interfaces.

Leading to

Ionic liquids (4th year)

Organic III

Organic Laboratory

Spivey, Alan

200 hours

Aims

To continue to develop the students' abilities in practical organic chemistry, including the use of advanced techniques. Further experience in the applications of computational techniques and database searching are also included.

Scope

Students perform all of the following experiments:

1. Advanced Compound Identification (spectra provided; students gain experience in spectroscopic interpretation and database searching)
2. The Synthesis of Arenetricarbonylchromium (0) Complexes (use of vacuum line, air-sensitive compounds)
3. The Penicillin-Cephalosporin Conversion (including flash chromatography)
4. Palladium Catalysed Cross Coupling Reactions (purification by sublimation)
5. Reductions with Lithium Aluminium Hydride (use of pyrophoric compounds; purification by distillation)
6. Ozonolysis of an Olefin (including purification by steam distillation)
7. Catalytic Asymmetric Dihydroxylation of Olefins (including recrystallisation and measurement of optical rotations)
8. Introduction to Computational Techniques for Organic Chemistry (molecular mechanics, semi-empirical and ab initio calculations used for the rationalisation and prediction of the properties of organic molecules; medicinal chemistry homology modelling).

Throughout the course, 270MHz NMR spectra are run on students' samples. The students are given the FIDs, which they must process themselves off-line, thus gaining experience in the use of NMR processing software. They are also required to research recent examples from the literature to be included in the reports for each experiment. All reports are submitted in RSC (Organic and Biomolecular Chemistry) format, with electronic submission compulsory for expt. 8 and optional for other experiments.

Objectives

At the end of the course, students should:

- Have further developed skills in the preparation and purification of organic compounds
- Be able to process NMR spectra electronically
- Be able to assign the NMR and IR spectra of the compounds they make
- Be able to apply computational techniques to rationalise and predict molecular properties
- Be capable of searching information from the literature by using online databases such as Web of Science and Beilstein Crossfire
- Be able to produce reports in RSC journal style
- Be able to manage their time in the laboratory effectively

Transition Metals in Organic Synthesis

Gibson, Sue

6 hours

Aims

To provide an introduction to the uses of transition metal complexes in stoichiometric and catalytic processes for organic synthesis, particularly for carbon-carbon bond formation.

Structure

- the chemical mechanisms of some of the most commonly observed reactions of transition metal – carbon bonds.
- a general survey of some commonly encountered transformations brought about by representative transition metals and their characteristic reactivities.
- representative examples of the use of the metals in the synthesis of complex organic molecules

Objectives

At the end of the course, the student will be expected to:

- recognise, when they are involved, the 'standard' mechanisms in descriptions of TM induced transformations;
- understand the characteristic reactivities of the TMs;
- analyse and rationalise the use of TMs in synthesis;
- use a mechanistic approach to the planned application of TMs to synthesis

Polymers: The essential guide

Steinke, Joachim

6 hours + 1 problem class

Aims

To provide the student with a guide to the fundamental aspects of polymer synthesis and fundamental polymer properties covering all basic polymerisation mechanisms and methodologies to access linear and branched polymer architectures.

Structure

Lecture 1. Introduction and Dendrimers: Course overview, terminology, properties that set polymers apart from small molecules, particularly their relevance to synthetic considerations. Molecular weight and molecular weight distribution, biopolymers and biosynthetic fundamentals juxtaposed to conventional polymer synthesis. Synthesis of dendrimers, convergent and divergent approach, hypercore and hypermonomer approaches, differences to hyperbranched polymers, synthesis of hyperbranched polymers. Discussion of differences of polymer properties related to branching and thus chain entanglement. Examples of uses of dendrimers.

Lecture 2. Properties and Polymerisation Mechanisms Part 1: Chain and step growth polymerisation incl. thermodynamic and kinetic considerations. Change of MW and MWD over time and vs conversion. Properties: crystalline, semi-crystalline and amorphous polymers, reptation, glass transition temperature, melting point, viscoelasticity, change of properties vs molecular weight, effect of polymer backbone structure (side-chain and tacticity) on Tg and Tm. Carothers' equation.

Lecture 3. Properties and Polymerisation Mechanisms Part 2: Part 1 continued.

Lecture 4: Polymer Characterisation and Living Polymerisation Part 1: Polymer characterisation with focus on GPC and MALDI-tof. Living free radical polymerisation, anionic, cationic, ROMP, GTP, ring-opening and ring-opening vinyl polymerisation.

Lecture 5: Living Polymerisation Part 2: Part 1 continued. Precursor chemistry, chain transfer and catalytic chain transfer to control MW and end-groups. Control of tacticity

Lecture 6: Linear Copolymers. Copolymerisation parameters, statistical, tapered and alternating copolymerisation. SOMO/HOMO, SOMO/LUMO interactions, synthesis of blockcopolymers. Branched Architectures. Synthesis of branched polymers via macromonomers, graft onto and graft from approaches. Summary of copolymer architectures. Synthesis of Merrifield resins, the idea of insoluble supports and their use in synthesis; polymer-analogous reactions. Outlook on advanced and smart polymer materials with examples from nanomaterials and devices, chemical biology and pharmaceutical.

Problem Class: To support lecture material.

Objectives

By the end of the course the students should be able to

- highlight the differences in structure and properties of small molecules and synthetic polymers and synthetic polymers and biopolymers.
- synthesise linear polymers and copolymers by chain and step growth polymerisation.
- synthesise linear polymers using living polymerisation technique and distinguish mechanistically between conventional and living polymerisation systems.
- synthesise branched polymers (graft from, graft onto, dendrimer, hyperbranched polymer, crosslinked network) and to select appropriate monomers and synthetic strategies.
- explain fundamental polymer properties and how polymer structure influences these properties with regards to molecular weight and backbone architecture.
- select the appropriate polymerisation method for a randomly chosen monomer or monomer system.
- select the appropriate strategy to control molecular weight and molecular weight distribution.

Building upon

All of 1st and 2nd year organic chemistry courses. Thermodynamic and kinetic topics from physical chemistry courses., 2.O1 Organic synthesis, 2.O2 Introduction to stereoelectronics, 2.O3 NMR spectroscopy, 2.O6 Alicyclic and non-aromatic heterocycles, 2.I2 Transition metal chemistry, 2.I5 Introduction to organometallic chemistry, 2.P4 Molecular thermodynamics.

In parallel to

3.I3 Advanced Organometallic Chemistry, 3.I9 Chemistry of Macrocycles, 3.O4 Reactive Intermediates 1 - Radicals

Looking forward to

Properties of Polymers, 4.I2 Supramolecular Chemistry of Nanomaterials, 4.I6 Inorganic and Organometallic Polymers, 4.I10 Green Chemistry, 4.A3 Advanced Polymers, 4.A10 Chemistry and Engineering of Polymers, 4.A9 Advanced NMR Spectroscopy, 4.O4 Combinatorial and Solid Phase Synthesis.

Introduction to Chemical Biology

Miller, Andy

7 hours

Aims

This course aims to give a complete overview of the structures of biological macromolecules/macromolecular assemblies (involving nucleic acids, proteins, carbohydrates and lipids). Special attention is given to the structural and physical characteristics of these macromolecules and how these characteristics determine not only three-dimensional structure but lead to biological function.

Structure

- Structures of nucleic acids from nucleotides to oligonucleotides, through to the polymeric structures of DNA and RNA (2 lectures)
- Structures of proteins (globular and fibrous) from amino acids to polypeptides, through to tertiary/quaternary structures (2 lectures)
- Structures of structural carbohydrates from pentose and hexose monomers to complex primary sequences through to tertiary structures (2 lectures)
- Structures of lipids and the phase behaviour of lipid assemblies (1 lecture)

Objectives

By the end of the course the students should be able to:

- Comprehend the structures of the main building blocks of biological macromolecules or macromolecular assemblies, understand how these building blocks are combined into macromolecule structures/assemblies, and how the properties of these building blocks and/or the properties of the biological macromolecules/assemblies themselves influence three-dimensional structure.
- Appreciate the role that three-dimensional structure plays in giving biological macromolecules/assemblies function.
- Possess adequate knowledge of biological macromolecule/assembly structures to be able to understand the course content of Year 4 courses O1 Molecular Recognition in Chemical Biology and O7 Chemistry of Enzymes, together with other Year 4 courses with a chemical biology/biological theme.

Introduction to Physical Organic Chemistry

Blackmond, Donna

5 hours

Aims

To provide an introduction to important physical aspects of organic chemistry as a complement to synthetic chemistry modules.

Structure

Lecture 1: Review of structure and bonding; review of acid-base chemistry.
Lecture 2: Kinetics and Thermodynamics; reactive intermediates and transition states.
Lecture 3: Developing the languages we use to describe chemical reactions: energy diagrams and reaction rate laws.
Lecture 4: Linear free energy relationships: Hammett plots; Hammond postulate.
Lecture 5: Reaction mechanisms: multi-step reactions; introduction to catalysis; introduction to experimental methods in mechanistic analysis

Objectives

- Appreciate the relationships between physicochemical properties and reactivity of molecules
- Have an appreciation of the main factors influencing the rates and outcomes of chemical reactions
- Be aware of the basic methods used for experimental mechanistic analysis
- Understand how free energy relationships can be used to analyze and predict reactivity.
- Understand experimental approaches to studying reaction mechanisms
- Apply all the above to unfamiliar examples.

Building upon

Foundation Chemistry and Organic Synthesis

Looking forward to

Year 4 “Reaction Kinetics” and “Advanced Problems”

Advanced Stereochemistry 3

Craig, Donald

6 hours

Aims

To provide a detailed account of the fundamentals of organic stereochemistry, and applications to advanced phenomena and problems in organic synthesis

Structure

Lecture 1/2: fundamentals of organic stereochemistry; axes, planes of symmetry; chirality; diastereomerism: Axial and planar chirality; enantiotopicity, diastereotopicity; CIP nomenclature
Lecture 3: Stereoelectronics: Stereoelectronic effects on conformations and reactivity; acetals, esters and amides; the anomeric effect
Lecture 4: Strategy-level reactions in-depth: The aldol reaction; Zimmerman–Traxler transition-states; diastereoeslective reactions of chiral auxiliary-bound substrates
Lecture 5: Strategy-level reactions in-depth: The Diels–Alder reaction; inter- and intramolecular reactions; steric effects on reactivity and selectivity
Lecture 6: Strategy-level reactions in-depth: The Claisen rearrangement; variants of the Claisen rearrangement; steric effects on reactivity and selectivity

Objectives

By the end of the course the students should be able to

- recognise symmetry in organic molecules
- predict/rationalise stereochemical outcomes in organic reactions
- understand origins of stabilising effects in ground states and transition states

Building upon

Year 2 “Organic Synthesis” and “Stereoelectronics”

Looking forward to

Year 4 “Catalytic Asymmetric Synthesis”, “Advanced Synthesis” and “Advanced Problems”.

Properties of Polymers

Law, Robert

8 hours

Aims

To reinforce and consolidate existing materials learnt in the previous year. To provide the students with the fundamentals of structure of polymeric materials (e.g. crystallinity, amorphousness), to understand how molecular structure can relate to physical properties (e.g. crystallinity affects shear properties), to understand how it is possible to use these ideas to design new materials (e.g. use of two or more polymers to make blends), to understand the issues and problems of this task (e.g. miscibility and immiscibility), to understand how it is possible to characterise these complex materials.

Structure

- Amorphous structure
- Glass transition
- Crystallinity
- Structure-property relationships
- Polymer alloys and blends
- Design of new materials
- Characterisation

Objectives

By the end of the course the students should be able to

- Understand basic structures of polymeric materials
- How these structures relate to macroscopic physical properties
- To design and characterise new materials using the ideas of structure-property relationships
- To characterise the final materials that have been designed

Reactive Intermediates: Radicals, Carbenes, Nitrenes, Photochemistry

Armstrong, Alan and Smith, Ed

8 hours

Aims

To provide an account of the synthesis and reactivity of radicals, carbenes and nitrenes, and an introduction to organic photochemistry.

Structure

Lectures 1 and 2: Types of reactive intermediate. Introduction to radical chemistry: advantages, reactivity; chain reaction processes. Functional group transformations involving radicals: dehalogenation, deoxygenation, deamination, decarboxylation, desulfurisation
Lecture 3: Radicals in Carbon-Carbon bond formation: Inter- and intramolecular processes; stereochemical aspects. Synthetic applications of radical chemistry: Examples of the application of radical chemistry to total synthesis.
Lecture 4: Carbenes and nitrenes. Rearrangements of carbenes and nitrenes: [1.2]-shifts of alkyl carbenes, acyl carbenes and acyl nitrenes, electrocyclic ring opening of cyclopropylidenes. General reactivity. Cyclopropanation of alkenes, aziridination of alkenes, multiplicity and stereochemistry
Lecture 5: Additions to arenes and heteroarenes, rearrangement of cycloadducts. Heteroatom-H insertions of carbenes, C-H insertions of carbenes and nitrenes. Regioselectivity.
Lecture 6: Ylide formation, rearrangements and cycloadditions. Introduction to organic photochemistry.
Lecture 7: Photochemical cycloadditions: alkene-enone, deMayo reaction; alkene-arene, 1,2-addition, 1,3-addition; alkene-carbonyl (Paterno-Buchi reaction)
Lecture 8: Photochemical hydrogen abstractions, □-cleavage followed by H-abstraction (Norrish Type-I); intramolecular H-abstraction followed by □-cleavage or cyclisation (Norrish Type-II); photoenolisation, o-nitrobenzyl deprotection.

Objectives

- At the end of the course, students should:
- Appreciate the properties and reactivity of the main classes of reactive intermediate
- Have an appreciation of the main factors influencing the rates and outcomes of free-radical reactions
- Be aware of the advantages and disadvantages of free radical chemistry compared to ionic reactions
- Be able to identify reagents and mechanisms for specific functional group transformations covered in the course
- Be able to recognise precursors to carbenes and nitrenes and know that decomposition pathways of those precursors may lead to singlet or triplet species.
- Predict the sites of reactivity of carbenes and nitrenes depending upon their multiplicity.
- Understand the basic theory of organic photochemistry.
- Predict the photochemical pathways for some common organic functional groups.
- Apply all the above to unfamiliar examples.

Building upon

Year 2 “Alicyclic and Non-Aromatic Heterocycles” and “Organic Synthesis”

Looking forward to

Year 4 “Advanced Synthesis”, “Advanced Problems” and “Advanced Heterocyclic Chemistry”

Carbohydrate Chemistry

Barrett, Tony

8 hours

Aims

To introduce the key concepts of carbohydrate chemistry and the chemistries thereof.

Structure

1. "Open Chain" Carbohydrate Chemistry . a) Nomenclature: pentose, hexose, etc. aldose, ketose b) Chemistry of the carbonyl group: oxidation; reduction; hydrazone and osazone formation; Kiliani homologation; Weerman degradation; structural correlation.
2. Cyclisation of Carbohydrates - Hemiacetal Formation a) Mutarotation of D-glucose; b) Glycosidation: under thermodynamic control, under kinetic control; the anomeric effect; stability of glycosides; c) Reactions of Carbohydrates: acetylation; etherification; acetal and ketal formation; sulfonate esters; keto sugars; unsaturated sugars; amino sugars; d) Use of Carbohydrates: fermentation; in antibiotics; chiral pool.

Objectives

At the end of this course the student should be able to:

- Identify correctly the various open and closed forms of carbohydrates;
- Predict the product of a reaction involving a carbohydrate with a given reagent;
- Select reagents for transformations of a given carbohydrate within the scope of this course;
- Explain the mechanistic rationale underpinning the above.

Physical III

Physical Laboratory

de Mello, John

120 hours

Aims

The 3rd year physical chemistry lab course introduces students to many of the key experimental skills required in modern state-of-the-art research. The course provides direct hands-on experience of important analytical techniques including: a broad range of optical spectroscopies, atomic resolution imaging, and real-time kinetic studies. Major areas of research include superconductivity, electrochemiluminescence, and charge transfer processes in dye-sensitised titanium dioxide. Experiments are deliberately open-ended, with students being encouraged to find improvements to proposed methodologies and to extend analyses beyond those explicitly set out in the lab scripts. Particular emphasis is placed on quantitative analysis and appropriate evaluation of associated errors.

Available Experiments

Group A – Single Experiments
A3. Visible absorption spectrum of a thermochromic compound
A4. Kinetic isotope effects

Group B - New techniques and Novel Materials
B1. Excited state complex formation in pyrene
B2. High temperature oxide superconductor
B3. The structure of molecular films of fatty acids.
B5. Computer simulation of a liquid using the Monte Carlo method
B6. Synthesis and phase behaviour of thermotropic liquid crystals.
B7. Franck-Condon factors
B8. Dye-sensitised solar cells
B9. Electrochemiluminescence
B10. Exploring Chemistry with Electronic Structure Methods

Group C - Classical Analytical and Physical Chemistry
C2. Electrode processes
C4. A kinetic study of fast reaction using the stopped flow method.
C5. Kinetics of copper dissolution
C6. Flash photolysis
C7. HPLC determination of Analgesics

Building upon

Year 2 Physical Chemistry Laboratory and lecture courses.

Looking forward to

4th year research project.

Sensing and detection

De Mello, Andrew

8 hours

Aims

This course intends to provide an overview of how optical spectroscopy can be used to analyse a variety of chemical and biological systems. The course will build upon ideas and theories introduced in Molecular Spectroscopy and Photochemistry given in Years 1 and 3. The course will primary focus on the use of luminescence as a probe of molecular species and molecular environments.

Summary

To begin with, the basic hardware of optical measurements will be discussed. This will centre on light sources (Lasers and flashlamps), wavelength selectors (monochromators and filters) and photon detectors (Photomultiplier tubes). Furthermore, advanced techniques for the generation of ultra-short light pulses will be described and mathematically understood (e.g. mode locking and q-switching).

The course will then develop the theories of unimolecular photophysics and demonstrate how luminescence can be used to identify and quantify molecular species, and provide information on microenvironments. These ideas will be supplemented with a description of how fluorescence lifetimes (on the nano and pico-second timescale) can be measured and interpreted. The phenomena of fluorescence quenching and fluorescence anisotropy will also be introduced and shown to be powerful probes of biochemical environments.

Finally, the ideas presented in the first six lectures will be brought together to show demonstrate: (1) the detection of single molecules in solution and (2) the construction and application of chemical- and bio-sensors. By the end of the course students will understand how the basic concepts of molecular photophysics can be used to provide high-sensitivity and selectivity information about chemical and biological systems, and the state-of-the-art instruments involved in these measurements.

Objectives

Students should:

- know all primary photophysical processes (radiative and non-radiative) which interconvert excited states with each other or with the ground state, and understand terms such quantum efficiency, excited state lifetime and quenching.
- know the generic requirements for laser action, the difference between 3- and 4-level laser systems, and methods for creating laser pulses (primarily cavity dumping, mode locking and Q-switching)
- learn how to build an optical detection system in terms of three fundamental components (light source, wavelength selector and photon detector) and how to build a system to measure fluorescence lifetimes on a nanosecond timescale.
- appreciate that variations in luminescence tell us significant things about molecular structure and environment. Furthermore students will be expected to use experimental data to calculate quantities such as concentration, number of emitting species and diffusion coefficients.
- understand the underlying mechanisms behind the operation of chemical- and bio-sensors and be able to describe the operation of at least one example of each.

Building upon

Year 1 spectroscopy and quantum mechanics lecture courses, Year 2 Photochemistry and Years 1 and 2 Physical Chemistry Laboratories.

Looking forward to

Miniaturised Analytical Chemistry.

The Chemistry of Solid Surfaces

Jones, Tim

8 hours

Aims

This course will provide a basic introduction to processes that occur at the interface between solid surfaces and molecules in the gas phase. Specifically the course will cover the following four basic areas:

Summary

The students will be expected to have a good knowledge of chemical thermodynamics, chemical kinetics and the properties of the solid state. The students will be introduced to the basic thermodynamic and kinetic aspects of gas adsorption and the use of adsorption isotherms. The structural and electronic properties of solid surfaces will be introduced and compared with bulk solid state properties. The concept of surface sensitivity will be introduced and a wide range of surface sensitive techniques will be explained that probe the structure of solids surfaces and adsorption behaviour. These include low energy electron diffraction, scanning tunnelling microscopy, x-ray photoelectron spectroscopy, Auger electron spectroscopy, reflection absorption infrared spectroscopy and high resolution electron energy loss spectroscopy. A wide range of adsorption systems will be used to demonstrate adsorption structure and surface reactivity.

Objectives

By the end of this course, the students should be able to

- understand the physical and chemical properties of solid surfaces and how they differ from bulk properties
- understand the thermodynamics and kinetics of gas phase adsorption at solid surfaces
- understand the structure of solids surfaces and the application of surface structure techniques
- understand the principles behind a wide variety of surface spectroscopic techniques and how these are applied to the characterisation of molecular adsorption and surface reactivity.

Building upon

2nd Year Electronic Properties of Solids and Thermodynamics lecture courses.

Looking forward to

Options courses including Molecular Electronics, Structure of Matter, Complex Solids.

Molecular Reaction Dynamics

Klug, David

8 hours

Aims

This course introduces time dependency into the handling of quantum chemistry, and develops classical reaction dynamics to include transition state theory.

Summary

- Classical 2-D potential energy surfaces.
- The effects of zero point energy.
- Transition states.
- Time dependent quantum mechanics and wavepackets
- Entropy and reactivity
- Transition state theory.
- Reactions out of equilibrium
- Electron transfer theory.

Objectives

At the end of this course, students should show familiarity with the principles of time dependency of wavefunctions and wavepackets. The students should be aware of the consequences of such time dependency and know how related phenomena can be measured.

The students should be able to derive transition state theory from first principles and determine the relative importance of enthalpies and entropies in the overall reactive behaviour of a system. Awareness of the assumptions behind transition state theory and its breakdown are required.

Understanding of the role of classical mechanics in determining the outcome of a collisional encounter in simple reactive systems. Reasons for breakdown of the classical picture should be understood.

A working knowledge of non-adiabatic electron transfer theory and the principles of distance and free energy dependence is expected, as well as the principles underlying the theory.

Building upon

2nd Year Theoretical Methods, Statistical Thermodynamics and Photochemistry lecture courses. 3rd year Quantum Chemistry course.

Looking forward to

Options courses including Mechanistic Photochemistry and Dynamics of Complex Systems.

Quantum Chemistry

De Mello, John

8 hours

Aims

The aims of this course is to give the student a thorough grounding in the application of Quantum Mechanics to Chemistry. An understanding of the importance of QM to explaining underlying molecular phenomena characterising chemical processes, particularly bonding, is a critical component of undergraduate chemistry .

The nomenclature and mathematical formalism of QM will be illustrated. The concepts of Molecular Orbital and Valence Bond Theory will be addressed with respect to the H2+ molecule and extension to H2 . The origin and application of the simplified Huckel theory to polyatomics will be investigated.

Summary

- Illustrating the use of quantum mechanics in chemistry.
- Development of mathematical formalism of QM
- Concept of Eigenvalue and Eigenfunction and operators
- Concept of Spin Orbitals
- Introduction of H2 and Molecular Orbitals
- The variational theorem
- Development of LCAO-MO theory through H2
- Introduction of Valence Bond theory
- Introduction of Hartree-Fock Theory
- Development of Huckel Theory
- Application of Huckel Theory

Objectives

To be able to:

- define and interpret the underlying principles of QM
- evaluate eigenvalues and eigenfunctions of simple systems
- derive expressions for the energies and wavefunctions of simple systems
- distinguish Molecular Orbital and Valence Bond theory as applied to simple chemical systems
- define, interpret and apply Huckel theory

Building upon

1st Year Quantum Mechanics. 2nd Year Theoretical Methods,

Looking forward to

Options courses including Mechanistic Photochemistry and Dynamics of Complex Systems, Molecular Electronics and Optical and electrical properties of Nanomaterials.

Colloids

Quirke, Nicholas

8 hours

Aims

This course is an introduction to the physical chemistry of colloids, dealing with morphology, thermodynamic properties , charged interfaces, kinetic properties and stability.

Summary

Topics to be covered will be chosen from classification, size and shape, formation, degradation processes, aggregation processes, nucleation and growth, monodisperse sols, uses, distributions of size and shape, the normal distribution, the log-normal distribution, continuous distribution functions, determination of size and shape, optical and electron microscopy, light scattering, centrifugation, electrical counting, determination of surface area, Van der Waals interactions between colloids: Hamaker theory, Retardation effects and the suspension medium, surface tension, surface Free Energy and the Gibbs adsorption equation, The behaviour of gas bubbles in liquids, and droplets in gas, The Young-Laplace equation, vapour pressure over a curved surface: The Kelvin Equation, The Thompson Equation, nucleation of droplets in a one component gas, solid particles in liquids or gases, how small particles differ from large particles, behaviour of liquids in capillaries, capillary pressure, capillary condensation, The double layer, models for the double layer, Limits of double layer models, double layer around a sphere, interaction between double layers, interaction between two spherical particles, response to a gravitational field, Brownian motion and diffusion, response to an Electric field, Kinetics of coagulation, methods of stabilising colloids, steric stabilisation, depletion Stabilisation, thermodynamic and microscopic origins of stabilisation.

Objectives

Students would be expected to leave this course with a good knowledge of the nature, uses and importance of colloids to everyday life, including contemporary concerns such as global warming and nano technology. Concepts which the students should be able to describe include how small particles differ from large particles, nucleation theory, capillarity, electric double layers, stability. They should be able to calculate for example scattered intensities from the Rayleigh Scattering equation, vapour pressures for drops and bubbles using the Kelvin equation, the Force between two particles due to capillary condensation, values of the Debye-Hückel parameter from ionic concentrations.

Building upon

Interfacial Thermodynamics, Electrochemical Dynamics

Structure of Matter

Seddon, John

8 hours

Aims

This course provides an introduction to the structural information that can be obtained from diffraction studies of matter. The emphasis is on soft condensed matter (colloids, polymers, liquid crystals) rather than single crystal analysis.

Summary

The course covers: the basis of X-ray and neutron scattering; the geometry of the scattering experiment; atomic scattering factors and nuclear scattering lengths; interference, and scattering by molecules and groups of molecules; Fourier transforms and convolution; lattices and reciprocal lattices; the effects of disorder; the phase problem of crystallography, and contrast variation techniques; electron density maps.

Objectives

By the end of the course the students should have gained a good understanding of the basis of diffraction experiments, the concept of reciprocal space, the unit cell and the lattice, and their reciprocal space counterparts, and methods for obtaining the phases of diffraction peaks. They should be familiar with the calculation of scattered amplitudes and intensities from model structures by Fourier transformation / summation.

Building upon

Structure and Function in Physical Chemistry. Theoretical Methods 2. Electronic Properties of Solids, The Chemistry of Solid Surfaces

Looking forward to

Supramolecular Chemistry of Nanomaterials, Nanostructured Semiconductor Materials, Chemistry and Engineering of Polymers, Complex Solids

Complex Fluids

Templer, Richard

8 hours

Aims

In the course students learn about the thermodynamics and energetics of amphiphilic self assembly in aqueous solution.

Summary

The course covers: the origins of the hydrophobic effect; thermodynamic models of amphiphile aggregation; concepts of molecular shape and their use in predicting micelle shape; aggregation into lyotropic liquid crystalline phases; modelling the liquid crystalline phase behaviour in terms of competition between curvature elastic energy and chain packing energy and using the concepts curvature elastic and chain packing costs to interpret lipid-protein interactions.

Objectives

The student will be able to:

- Describe the origins of the hydrophobic effect
- Define the thermodynamic conditions necessary for amphiphile aggregation
- Derive the closed association model for aggregation
- Derive the ‘opposing forces’ model for aggregation
- Calculate micellar shape from a knowledge of the ratio of molecular volume to the product of optimal headgroup area and amphiphile length
- Describe observed patterns in critical aggregation concentration as a function of amphiphile chemistry
- Describe the observed pattern in lyotropic mesomorphism in terms of the interfacial curvature
- Describe and sketch the structure of the observed phases
- Define and determine the mean and Gaussian curvature of simple geometrical interfaces
- Describe the Helfrich Hamiltonian for the curvature elasticity
- Describe the origin of packing frustration
- Describe how observed phase behaviour results from a competition between the two
- Use the Helfrich Hamiltonian to calculate stored elastic energy in various simple interfacial geometries
- Use the Helfrich Hamiltonian to calculate the release of stored curvature elastic energy during the binding of amphipathic alpha-helical protein to the membrane
- Use the stretching energy to calculate the free energy associated with deformations in membrane thickness by the presence of trans-membrane proteins

Building upon

Molecular Dynamics and Interfacial Thermodynamics Lecture Courses

Looking forward to

Colloids, Structure of Matter (year 3), Dynamics of Complex Systems and Complex Solids (year 4)

Molecular Electronics

De Mello, John

8 hours

Aims

This course deals with the fundamental properties of organic semiconductors and their use in electronic devices. It examines the importance of conjugation in determining optoelectronic properties, and explores how these properties may be exploited in electronic devices such as solar cells and light-emitting diodes (LEDs).

Summary

The course examines the unique processing advantages of molecular semiconductors, and compares and contrasts the properties of organic semiconductors with their inorganic counterparts (e.g. Si, GaAs). The course covers fundamental principles of solid-state organic devices, and places particular emphasis on the operating mechanisms of solar cells and LEDs. Supporting electronic notes and supplementary information are available on-line.

Objectives

By the end of the course, the students will have acquired a detailed quantitative knowledge of the design considerations behind modern state-of-the-art organic devices.

Building upon

1st Year Quantum Mechanics. 2nd Year Electronic Properties of Solids and Photochemistry. 3rd Year Quantum Chemistry.

Looking forward to

Optical and electrical properties of Nanomaterials.

Nature at the nanoscale: insights from molecular simulation

Quirke, Nick

8 hours

Aims

Nanotechnology is an exciting possibility that is rapidly becoming real. The scientific literature and the web are full of papers describing new developments in our ability to make and to manipulate nanoscale objects such as carbon nanotubes, quantum dots, etc. Many important industrial (e.g. separations, heterogeneous catalysis) and biological processes (e.g. transport across cell walls) take place at surfaces and are controlled on the nanoscale. Molecular simulation methods can provide a unique insight into the way molecules behave at the nanoscale. Indeed molecular modelling and simulation has a unique role in chemistry as an intermediary between theory and experiment and as an experimental tool in its own right. The software (numerical methods) provides a direct numerical link between intermolecular interactions and the properties of a) individual molecules (e.g. minimum energy conformations) and b) collections of molecules (thermodynamics, structure and dynamics of solids, liquids, and gases) both at the nanoscale and in bulk systems. Much of the excitement in modern chemistry is related to the behaviour of molecules at nanoscale interfaces, where properties can be quite different to those of bulk materials. This course provides an introduction to the basic principles involved in molecular simulation and its application to interfacial/nanoscale problems. In order to do so, some simple ideas from statistical mechanics will be reviewed and the standard simulation algorithms discussed.

Summary

- What is modelling: overview, examples and research/industrial applications.
- Potentials and potential energy surfaces: graphics, energy minimisation and complex molecules. Modelling at $T>0K$. The molecular simulation algorithms, Monte Carlo and molecular dynamics.
- Applications to problems in physisorption, wetting, and transport of molecules and electrons in nanoscale structures

Objectives

At the end of the course students should be able to

- Explain what a model is and how molecular modelling relates to other types of modelling
- Describe molecular dynamics and Monte Carlo methods
- Describe example applications to interface science, colloid chemistry, fluidics and transport phenomena

Building upon

1st Year Molecular Dynamics. 2nd Year Theoretical Methods Lecture Course and Laboratory,

Looking forward to

Modelling of Nanomaterials.