School of Physical and Chemical Sciences

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

General Course Information

CHEM 212 / BCHM 212
Chemical Reactivity

0.1250 EFTS 15 Points
First Semester 2021

Description

This course runs in semester one. It counts 15 points towards a Bachelor of Science degree. It is required to major in chemistry and biochemistry and preferably it is taken in conjunction with other 200-level chemistry and/or biochemistry courses.
The topics covered in this course are: foundational principles of organic and biochemical reaction chemistry; and bioinorganic chemistry and electrochemistry.

Timetable

Lectures & Workshops: Three hours of lectures/workshops per week. Details to be confirmed on 'My Timetable' and the web.

Tutorials: There will be problem-solving workshops held approximately fortnightly during the normal lecture slots. Additional tutorial sessions may be organised as necessary, especially for students needing further assistance.

Students should note that in the Science Faculty that the average student is responsible for approximately 3.2 hours of additional study for each hour of lecture/workshop contact time at the 200-level.

Course Co-ordinator

Professor Rudi Marquez, School of Physical and Chemical Sciences
Room BT403, ext 90162, Email: rudi.marquez@canterbury.ac.nz
Email me if you have any queries about the course.

Assessment

In order, with course component indicated:

- Test 40%
- Final Examination 60%

Examination and Formal Tests

Test: 2 hours, details to be advised.
Exam: 3 hours, details to be advised.

Textbooks

The general textbook for the course is:
A. Burrows, J. Holman, A. Parsons, G. Pilling and G. Price, *Chemistry*[3], Second Edition OUP, 2013.

Additional information may be taken from - Clayden, Greeves, Warren and Worthers, *Organic Chemistry*, Oxford University Press, 2012 (2nd edn.).

These textbooks will be available in the Engineering & Physical Sciences Library, where copies will be on reserve.

Prerequisites/Restrictions

P: CHEM112 R: BCHM205, CHEM232, ENCH241

Web-based resources: Various learning resources (lecture material, reference links, quizzes, discussion forums etc.) for this course are available via the University of Canterbury's *Learn* web site -- http://learn.canterbury.ac.nz/. This site will also be used regularly as a means of communication and information distribution for all of your Canterbury courses. You should familiarise yourself with *Learn* as soon as possible.

Goal of the Course
Develop an understanding of fundamental principles of structure and chemical reactivity relevant to organic and biological chemistry that builds on foundational principles from first year chemistry and provides a solid foundation for further study in chemistry and biochemistry.

Learning Outcomes (see also detailed Learning Objectives after Course Content, below)

- Develop the ability to apply scientific principles and concepts
- Develop problem-solving and numeracy skills in the context of organic and bioinorganic chemistry and electrochemistry
- Understand, evaluate, access and critically review new chemical information
- Demonstrate the ability to think independently about chemical concepts
- Develop a more in-depth knowledge of chemical reactivity in the areas of organic reactions, electrochemistry and bioinorganic chemistry
- Effectively access and use information relevant to chemistry and biochemistry
- Communicate effectively in written English

Summary of the Course Content

BLOCK 1: 12 Lectures/Problem sessions

Structures and properties of organic and biological molecules
Three-dimensional structure of organic and biological molecules and the importance of functional groups within molecules.

- Review of basic concepts of organic bonding: molecular orbital and valence bond representations. Three-dimensional structural issues: molecular representations; conformational analysis of simple acyclic and cyclic molecules; isomerism and stereoisomerism; chirality, enantiomers and diastereoisomers with examples taken from biomolecules.
- Common functional groups; nucleophiles and electrophiles; resonance and tautomerism; acidity and basicity of organic molecules.
- Biochemically relevant properties of biomolecules

Lecturer: Professor Rudi Marquez, Room BT403, ext 90162, *rudi.marquez@canterbury.ac.nz*

BLOCK 2: 6 Lectures/Problem sessions

Thermodynamics and Kinetics in action
Thermodynamic and Kinetic considerations are vitally important for all reactions in Organic Chemistry and Biochemistry. We will introduce these concepts and use them to predict the outcome of reactions.

- The application of enthalpy, entropy and Gibbs energy (ΔG) to organic transformations
- Kinetics and stereochemistry as tools to unravel reaction details
- Understanding Transition State structures in reactions – Catalysis, Solvent effects
- methods of monitoring the rates of organic reactions
- enzyme-catalysed reactions and Michaelis-Menten kinetics

Lecturer: Dr Dan Foley, BT323, ext 90479, *daniel.foley@canterbury.ac.nz*

BLOCK 3: 9 Lectures/Problem sessions

Introduction to Organic Reaction Mechanisms
Understanding mechanism is actually the key to grasping the whole of organic chemistry. This part of the course will consider in detail what can happen when a leaving group it attached to a carbon atom in an organic molecule.

The S_N2 reaction

- mechanism, reaction diagram, and stereochemical consequences
- effect of substrate structure on the rate of S_N2 reactions
- effect of the nature of nucleophile on the rate of S_N2 reactions
- basicity vs nucleophilicity; how to decide what is a good nucleophile and what is a good base
- effects of leaving group and solvent on S_N2 reactions

The S_N1 reaction

- mechanism, reaction diagram, and stereochemical consequences
- effect of substrate structure on the rate of S_N1 reactions
- effect of leaving group, solvent, and the nature of nucleophile on the rate of S_N1 reactions
- the S_Ni reaction
- a comparison of S_N1 vs S_N2: how to decide which happens

Elimination reactions

- The E2, E1 and E1cB mechanisms
- regiochemistry of elimination: Saytsev and Hofmann elimination
- stereochemistry of elimination: anti vs syn
- comparison of elimination vs substitution – how to decide which occurs: nature of base / nucleophile and effect of temperature.

Lecturer: Professor Antony Fairbanks Room BT324, ext 95217,
antony.fairbanks@canterbury.ac.nz

BLOCK 4: 9 Lectures/Problem sessions

Introductory chemistry of the carbonyl group

A thorough grasp of the chemistry of the carbonyl functional group is essential to an understanding of both organic chemistry and biochemistry; the carbonyl group is present in all of the important bio-macromolecules; e.g. amino acids in peptides / proteins, sugars in oligosaccharides, nucleosides in nucleic acids.

This part of the course will focus on examination of the basic reactivity and also the synthetic utility of carbonyl containing compounds. The chemistry of aldehydes, ketones, esters, amides and other carboxylic acid derivatives will be examined in detail.

The structure and reactivity of the of the C=O group

- mode of reactivity by nucleophilic addition
- structural factors affecting reactivity

Nucleophilic addition to aldehydes and ketones

- reversible addition - hemiacetal formation
- irreversible addition: reduction by metal hydrides, addition of organometallics

Nucleophilic substitution of aldehydes and ketones

- acetal formation and hydrolysis
- the formation of imines, oximes and hydrazones
- the formation of enamines
- reductive animation; the synthesis of amines
- amino acid synthesis

Nucleophilic substitution reactions of carboxylic acid derivatives

- explanations of relative reactivity / stability
- inter-conversions of carboxylic acid derivatives
- ester hydrolysis *via* several different mechanisms
- the stability of amides; their hydrolysis under forcing conditions
- the reactions of carboxylic acid derivatives with reducing agents and organometallics.

Lecturer: Professor Antony Fairbanks Room BT324, ext 95217,
antony.fairbanks@canterbury.ac.nz

LEARNING OBJECTIVES

BLOCK 1:
At the end of this lecture block you should be able to:

- Draw organic molecules in three dimensions using the appropriate representation.
- Understand the concept of hybridisation and bonding in organic molecules.
- Describe the effect of rotations about carbon-carbon single bonds and assess the relative stabilities of different conformers. Draw the different conformations of cyclohexane and its derivatives.
- Describe the different types of isomerism that are possible for organic molecules.
- Understand the importance of electron delocalisation, resonance, acidity and basicity in organic molecules and their reactions.
- Describe the important functional groups commonly found in organic and biological molecules.
- Understand how the physical properties of biological molecules underpin their role in biochemistry.

BLOCK 2:
At the end of this lecture block you should be able to:

- Demonstrate a working understanding of the following issues associated with organic reactions by data analysis and problem-solving:
- Mechanism analysing synthetic transformations – relationship of starting material to product; bonds broken and formed
- classification of organic reactions – substitution and elimination/addition
- identification of nucleophiles, electrophiles and leaving groups in organic reactions
- the role of electronic and steric factors in affecting organic reactivity
- curly arrows as a means of keeping track of electron-flow in organic reactions
- the relationship of enthalpy changes and bond dissociation energies
- the role of entropy in controlling the direction of spontaneous reactions
- use of Gibbs energy for understanding the thermodynamics of reversible organic reactions
- use of kinetic data to determine mechanisms
- rate laws for simple organic and enzyme-catalysed transformations
- structure-function relationships - relative reactivity of related chemicals
- solvent effects on reaction rates
- effect of steric and electronic factors on reactivity
- reaction energy diagrams and activation energies
- carbocations and carbanions as reactive intermediates in organic reactions
- Hammond's postulate

BLOCK 3:
At the end of this lecture block you should be able to:

- Appreciate why an understanding of reaction mechanisms is important.
- Be able to represent the bond breaking and bond making processes occurring during nucleophilic substitution and elimination reactions using curly arrows.
- Understand the similarities and differences between bases and nucleophiles; understand what makes a good nucleophile and what makes a good base.
- Understand what makes a good leaving group.
- Understand the S_N2 mechanism for nucleophilic substitution, including the reaction diagram and be able to rationalize the stereochemical consequence; inversion.
- Understand how the rate of an S_N2 reaction depends on the substrate structure, the identity of nucleophile, the solvent, and the leaving group.
- Understand the S_N1 mechanism for nucleophilic substitution including reaction diagram and be able to rationalize the stereochemical consequence; racemisation.
- Understand how the rate of an S_N1 reaction depends on the substrate structure, the identity of nucleophile, the solvent, and the leaving group.
- Appreciate the possibility of an S_Ni reaction.
- Understand that S_N1 and S_N2 reactions are competing processes, and be able to decide which is most likely to happen in a particular case.
- Understand that elimination reactions produce alkenes by removal of a proton and loss of a leaving group.
- Understand the various possible mechanisms for elimination - E1, E2, $E1_{CB}$ reactions - including being able to draw reaction diagrams for each.

- Understand the stereo- and regiochemical consequences of the different elimination mechanisms; anti vs syn elimination; Satytzeff vs Hoffman elimination.
- Understand that elimination and substitution reactions are competing processes, and be able to decide which is most likely to happen in a particular case.

BLOCK 4:
At the end of this lecture block you should be able to:

- understand the structure of the carbonyl group, why it is reactive, and its principal mode of reactivity.
- understand that structural factors can modulate reactivity of the carbonyl group; e.g. resonance effects.
- understand, and be able to draw mechanisms for reversible nucleophilic addition to aldehydes and ketones; e.g cyanohydrin formation, hydration and hemiacetal formation.
- understand, and be able to draw mechanisms for irreversible nucleophilic addition to aldehydes and ketones e.g. reduction by metal hydrides, the addition of simple organometallic reagents.
- understand, and be able to draw mechanisms for reversible nucleophilic substitution of aldehydes and ketones; e.g. acetal, imine, oxime, hydrazone and enamine formation.
- be able to explain the pH / rate dependence of reactions of aldehydes and ketones with nitrogen nucleophiles.
- understand, and be able to draw mechanisms for the uses of imines in synthesis: e.g. reductive amination.
- understand and be able to explain the relative reactivity of carboxylic acid derivatives towards nucleophiles.
- understand, and be able to draw mechanisms for nucleophilic substitution reactions of carboxylic acid derivatives by the formation of tetrahedral intermediates, and appreciate the importance of leaving group ability.
- understand how carboxylic acid derivatives can be inter-converted.
- understand, and be able to draw mechanisms for ester hydrolysis by the $B_{AC}2$, $A_{AC}2$, $A_{AL}1$, and $A_{AC}1$ mechanisms.
- understand and be able to draw mechanisms for amide hydrolysis.
- understand and be able to rationalize the reactions of carboxylic acid derivatives with reducing agents
- understand and be able to rationalize the reactions of carboxylic acid derivatives organometallic reagents.

GENERAL INFORMATION 2021

Chemistry Department Policy on 'Dishonest Practice'
The University has strict guidelines regarding 'dishonest practice' and 'breach of instructions' in relation to the completion and submission of examinable material. In cases where dishonest practice is involved in tests or other work submitted for credit a department may choose to not mark such work ('Academic Integrity and Breach of Instruction Regulations').

The Department of Chemistry upholds this policy. It considers plagiarism, collusion, copying, and ghost writing to be unacceptable and dishonest practices:

- ***Plagiarism*** is the presentation of any material (text, data or figures, on any medium including computer files) from any other source without clear and adequate acknowledgement of the source.
- ***Collusion*** is the presentation of work performed in whole, or in part, in conjunction with another person or persons, but submitted as if it has been completed by the named author alone. This interpretation is not intended to discourage students from having discussions about how to approach an assigned task and incorporating general ideas that come from those discussions into their own individual submissions, but acknowledgement is necessary.
- ***Copying*** is the use of material (in any medium, including computer files) produced by another person or persons with or without their knowledge and approval. **This includes copying of the lab reports (raw data may be shared within the group if permitted or required by the experiment) - data analysis and interpretation of obtained results MUST be performed individually.**
- ***Ghost writing*** is the use of other person(s) (with, or without payment) to prepare all or part of an item of work submitted for assessment.

Additional Information

Special consideration of assessment**:** If you feel that illness, injury, bereavement or any other critical extenuating circumstance beyond your control has prevented you from completing an item of assessment or affected your performance in that assessment, you may apply for special consideration. Special consideration is not available for items worth less than 10% of the course. Applications for special consideration should be made **within five days** of the due date for the work or examination. In the case of illness or injury, medical consultation should normally have taken place shortly before, or within 24 hours after, the due date for the required work or the date of the test or examination. For details on special consideration, or to make an application, refer to the Examinations Office website http://www.canterbury.ac.nz/exams/. ***You have the right to appeal any decision.***

Extensions of deadlines: Where an extension may be granted for an assessment item, this will be decided by application to the course co-ordinator.

Late withdrawal from the course: If you are prevented by extenuating circumstances from completing the course after the final date for withdrawing from the course, you may apply for special consideration for late discontinuation. For details on special consideration, or to make an application, refer to the Examinations Office website http://www.canterbury.ac.nz/exams/. Applications must be submitted ***within five days*** of the end of the main examination period for the semester.

Missing of tests**:** In rare cases a student will not be able to sit a test. In such cases, the student should consult with the course co-ordinator to arrange alternative procedures. **This must be done well in advance of the set date for the test.**

Past tests and exams: these can be found on our website using the link below:
www.chem.canterbury.ac.nz/for/undergraduate.shtml

Submission of reports and assignments**: Reports (including lab reports) and assignments should be handed in on time.** Extensions will be granted only in exceptional circumstances (such as illness or bereavement). If an extension is required, as early as possible you should request it from the lecturer concerned.
Note: If you do not submit an assignment for assessment, you will be allotted zero marks, which will affect your final result. You should ensure that you pick up marked assignments and keep them until the end of the course as evidence that the work was completed and marked in the case that either is disputed. To guard against accidental loss, it would be prudent to keep photocopies or electronic copies of anything submitted.

Marks and Grades: The following numbers should be considered as a guide to the expected grades under normal circumstances. The School reserves the right to adjust mark/grade conversions, if necessary.

Please note that for all invigilated assessments (tests and exams) worth 33% and above, failure to obtain a mark of at least 40% will result in a final grade no higher than an R at 100 and 200 level, and a C- at 300 level.

Grade:	**A+**	**A**	**A−**	**B+**	**B**	**B−**	**C+**	**C**	**C-**	**D**	**E**
Minimum mark %:	**90**	**85**	**80**	**75**	**70**	**65**	**60**	**55**	**50**	**40**	**0**

Reconsideration of Grades: Students should, in the first instance, speak to the course co-ordinator about their marks. If they cannot reach an agreeable solution, or have questions about their grade in a course, students should then speak to the Director of Undergraduate Studies, Professor Alison Downard (Room 426, Beatrice Tinsley Building, phone 3694228). Students can appeal any decision made on their final grade. You can apply at the Registry for reconsideration of the final grade within four weeks of the date of publication of final results. Be aware that there are time limits for each step of the appeals process.

Students with Disabilities: Students with disabilities should speak with someone at Equity and Disability Service, phone: 369 3334 (or ext. 93334), email: eds@canterbury.ac.nz).

Academic Advice**:** Professor Alison Downard is the coordinator of undergraduate chemistry courses. Her interest is in the academic performance and well-being of all such students. Anyone experiencing problems with their chemistry courses or requiring guidance about their B.Sc. in Chemistry should get in contact with Alison.

Staff-Class Rep Liaison**:** Professor Alison Downard is in charge of liaison with students in chemistry courses. Your class will appoint a student representative to the liaison committee at the start of the semester. Please feel free to talk to the Academic Liaison or the student rep about any problems or concerns that you might have.

Computer equipment**:** The University provides several student computer facilities. There is a suite of PCs in Ernest Rutherford which students are welcome to use OUTSIDE THE TIMES WHEN THESE COMPUTERS ARE NEEDED FOR CLASSES. Commonly used programs such as Word and Excel have been loaded onto these PCs.

Alison Downard
Director of Undergraduate Studies
School of Physical and Chemical Sciences
February 2021