School of Physical and Chemical Sciences

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

General Course Information

CHEM434
Kinetics and Spectroscopy

0.125 EFTS	15 Points
First Semester	2022

Description

If you want to really understand chemistry, this is the course for you: it applies the fundamental physical and chemical principles developed in CHEM333 and CHEM343 for prediction, explanation and understanding of properties, structure and reactivity at a microscopic level.

The topics covered by this course are:

- Spectroscopy and quantum mechanics
- Advanced reaction kinetics

This course is presented in the first semester only. It counts 15 points towards a Bachelor of Science with Honours / Masters of Science / Postgraduate Diploma of Science degree and should be taken in conjunction with other 400-level courses as advised by the Director of Postgraduate Studies.

Timetable

Refer to the online course information system or MyTimetable.

Lectures: Two hours of lectures per week. Details to be confirmed on 'My Timetable' and the Web.
Tutorials: One hour every second week. Details to be confirmed on 'My Timetable' and the Web.

Students should note that in the Science Faculty that the average student is responsible for approximately 4.5 hours of additional study for each hour of lectures at 400-level.

Course Co-ordinator

A/Prof Greg Russell, School of Physical and Chemical Sciences
Room BT322, ext 95129, email: *greg.russell@canterbury.ac.nz*

Assessment

Assignments:	20% (comprising 10% from each of the 2 lecturers)
End-of-course Exam:	80%

Examination and Formal Tests

End of Semester Exam: Three hours, with questions from both lecturers.

Textbook

P W Atkins & J de Paula, *Atkins' Physical Chemistry* (recent edition). This text covers some of the material of this course, and should be used to supplement the lecture material prepared by each lecturer. The book also contains many helpful worked examples and tutorial problems.
Copies are available on short-term loan from the Engineering and Physical Sciences Library.

Each lecturer will in addition provide library references and information handouts as appropriate.

Prerequisites

There are no set prerequisites for the course but students are expected to have completed chemistry to the level found in CHEM333 and CHEM343.

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**.

Goals of the Course
The overarching goal of this course goes to the heart of chemistry and is as follows: that a student can have an understanding of the electronic structure and reactivity of any molecule. Specifically:

Students will become familiar with the concepts associated with electronic spectroscopy of transition metal systems, understand how quantum mechanical methods can be used to predict spectroscopic data, and learn to analyse the ultraviolet-visible spectra of simple transition metal complexes;

Students will become intimately familiar with all basic concepts of chemical kinetics, as employed throughout chemistry. They will learn that while there are millions of different chemical reactions, almost all of them reduce to one of four basic kinetic paradigms, and of these the so-called intermediate-complex model – involving the steady-state approximation – is the most profound. They will understand the most important theories for rates of chemical reactions, in particular transition-state theory, and be able to describe the variation of bimolecular and unimolecular rate coefficients with experimentally varied parameters.

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.
- 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 kinetics and spectroscopy.
- Know the concepts and phenomena of kinetics and spectroscopy.
- Communicate effectively in written English and chemical diagrams.

Transferable Skill Register
As a student in this course I will develop the following skills:

- Problem solving. This is a key skill that is transferable to most careers.
- Pattern spotting and logical analysis. A key feature of physical chemistry is the ability to understand similarities between processes and use this pattern recognition to address complex issues in a logical fashion.
- Critical analysis of data. This is a key skill that is transferable to most careers.
- Three-dimensional spatial awareness. The ability to think about molecules and chemical reactions in three dimensions is highly useful transferable skill.
- Graphical awareness. Graphs are the pictures of physical chemistry, as in "a picture paints a thousand words". It is important to understand how equations translate into graphical pictures, and what these pictures convey in terms of physical behaviour.
- Science communication. A particularly important skill is being able to communicate scientific principles.

Summary of the Course Content

The topics coved by this course are:

SPECTROSCOPY AND QUANTUM MECHANICS **(12 lectures)**
Transition metal complexes play an important role in nature as components of minerals and biochemical systems. They have also found a vast number of technological applications, as pigments and dyes, as catalysts, nano and structural materials and many more. Their utility stems from their geometric and electronic structure. The former can be probed by "unsporting" techniques, such as X-ray and electron diffraction, and (in some cases) NMR spectroscopy. But the latter requires more subtle "sporting" approaches including computational chemistry and optical spectroscopy. In these lectures it will be shown how ultraviolet and visible spectroscopy can be applied to the elucidation of the electronic states and structure of simple transition metal complexes. It will also be shown how modern electronic structure methods are rapidly becoming an integral part of mainstream chemistry research for predicting and confirming molecular structures and interpreting spectroscopic data (NMR, IR, UV-Vis).
Lecturer: A/Prof Sarah Masters, ext 94229, Room BT422, sarah.masters@canterbury.ac.nz

ADVANCED REACTION KINETICS **(12 lectures)**

Tables of thermodynamic data are comprehensive and are relatively easily used to say with certainty what will happen in chemical systems. But thermodynamics says nothing about how fast something will happen in chemistry. This is the domain of chemical kinetics, and really it is what chemistry is all about: the *timescale* on which chemical events happen. This course will equip students with an understanding of advanced chemical kinetics, with the following topics being covered:

- The language of kinetics: rate law, reaction order, rate coefficient, integrated rate law, pseudo-first-order kinetics, half-life, Arrhenius parameters.
- Experimental techniques for measuring rates, in particular spectroscopic methods.
- The steady-state approximation and the four most common paradigms for reaction mechanism: consecutive reactions, pre-equilibrium, parallel reactions and opposing reactions. In particular the potency and ubiquity of the pre-equilibrium (or intermediate-complex) model will be emphasized.
- Theories for bimolecular rate coefficients: collision theory, transition state theory, Smoluchowski theory for diffusion-controlled reactions.
- Detailed case studies: kinetics of enzyme-catalysed reactions, radical polymerization and (time permitting) emulsion polymerization.
- The effect on bimolecular rate coefficients of viscosity, pressure, solvent polarity, dielectric permittivity, ionic strength, reactant substituents and isotopic substitution (the so-called kinetic isotope effect).
- Gas-phase unimolecular reactions.

Lecturer: A/Prof Greg Russell, ext 95129, Room BT322, greg.russell@canterbury.ac.nz

Specific Learning Outcomes

Spectroscopy and Quantum Mechanics:

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

- Explain how an external crystal field perturbs and splits the states of an atomic ion.
- Demonstrate the nomenclature for and factors that determine the energies of a transition metal ion in octahedral, cubic and tetrahedral symmetries.
- Describe qualitatively how tetragonal and trigonal distortions perturb the electronic states of an (otherwise) octahedral system.
- Describe terms such as d-d transition, charge-transfer transition, spin-forbidden, Laporte forbidden, etc, as they apply to the spectroscopy of transition metal complexes.
- Analyse the ultraviolet-visible spectra of simple transition metal complexes.
- Demonstrate how quantum mechanics can be used to predict spectroscopic data.

Reaction Kinetics:

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

- Demonstrate a high degree of familiarity with the following basic concepts of kinetics, including the important results associated with each: rate law, reaction order, rate coefficient, integrated rate law, pseudo-first-order kinetics, half-life, determination of reaction order, variation of rate coefficient with temperature.
- Outline common experimental methods – in particular spectroscopy – for measuring rates, and explain their strengths and weaknesses.
- Justify the steady-state approximation and derive and use results for the four common reaction mechanisms of consecutive reactions, pre-equilibrium, parallel reactions and opposing reactions.
- Discuss, as detailed case studies, the kinetics of enzyme-catalysed reactions, radical polymerization and (time permitting) emulsion polymerization.
- Explain the following theories for bimolecular rate coefficients: collision theory, transition state theory, Smoluchowski theory for diffusion-controlled reactions.
- Explain how bimolecular rate coefficients are affected by viscosity, pressure, solvent polarity, dielectric permittivity, ionic strength, reactant substituents and isotopic substitution.
- Describe the variation of unimolecular rate coefficients with pressure.

GENERAL INFORMATION 2022

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.**

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.

Late Work: Acceptance of late work will be at the discretion of the course coordinator. Please contact the coordinator if your assessment is likely to be late.

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 Coordinator of 400-level studies, Dr Sarah Masters (Room 422, Beatrice Tinsley Building, phone 369 4229). 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*:** Dr Dan Foley is the coordinator of postgraduate chemistry courses. His 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 postgraduate studies should get in contact with Dan.

Dan Foley
Coordinator of Postgraduate Studies
School of Physical and Chemical Sciences
2022