CH273-15 Properties of Solutions and Foundations of Electrochemistry and Statistical Mechanics

23/24

Department
Chemistry
Level
Undergraduate Level 2
Module leader
Julie Macpherson
Credit value
15
Module duration
10 weeks
Assessment
20% coursework, 80% exam
Study location
University of Warwick main campus, Coventry

Description

Introductory description

N/A

Module web page

Module aims

This module brings together two disciplines, statistical mechanics and electrochemistry, which in many cases offer two complementary perspectives on the very the same subject. Perhaps the most notable example is given by the physical chemistry of ionic species in aqueous solutions, a key concept of practical relevance for the experimental electrochemist - which in fact builds upon the theoretical foundations of the statistical mechanics of liquids.

In the attempt to make a connection between these two fields of study, the module will be split between three members of staff: Dr. Gabriele C. Sosso (Statistical Mechanics) and Profs. Julie Macpherson and Patrick Unwin (Solution Properties / Electrochemistry). Here follows a short

summary of the principal aims for the two sections of the module, namely, Statistical Mechanics and Solutions Properties/Electrochemistry.

Part 1: Solution Properties / Electrochemistry
Electrolyte Solutions and electrochemistry play an important role not only in physical chemistry, but in many areas of science in general: from biology (e.g. nerve signalling, vision) through chemistry (e.g. synthesis and analysis) to materials science (e.g. design of novel materials, such as nanowires and nanoparticles) and physics (e.g. electronics).

Students will be provided with an introduction to the fundamentals of solution properties and electrochemistry and their roles in many of the areas highlighted above.

Part 2: Statistical Mechanics
The foundations of Statistical Mechanics aims to establish a connection between quantum mechanics and thermodynamics - that is, between the microscopic world (a single water molecule) and the macroscopic world (a bucket of tap water). This module seeks to harness the theoretical tools of Statistical Mechanics to:

1. Unravel why things in chemistry are the way they are - for instance, where does the value of the molar specific heat of a diatomic gas comes from.
2. Perform molecular simulations, from basic concepts to practical applications.
3. Understanding chemical equilibrium from a molecular perspective.
4. Provide a theoretical and computational framework to understand and investigate the properties of liquids and ionic solutions.

From Solution Properties to Statistical Mechanics
The following concepts introduced in part 1 will be developed further within the last part of the Statistical Mechanics section, namely:

- The Statistical Mechanics of liquids
- The pair correlation function
- Ions in aqueous solutions
- Debye-Hückel theory

Outline syllabus

This is an indicative module outline only to give an indication of the sort of topics that may be covered. Actual sessions held may differ.

The module will be taught in two distinct sections. Here follows an illustrative syllabus for each section of the module.
Part 1: Properties of Solution and Electrochemistry

1. Electrolyte Solutions
   -Structure of water.
   -Ion solutes in water
   -Hydration spheres. Structure making and breaking effects. Thermochemistry of ion solvation.
   -Single ion hydration enthalpies and entropies. Partial molar quantities. Revision of ideal solutions.

-Activity coefficients and non-ideality. Molarity and ionic strength.
-Debye-Huckel theory and its application to solubilities and rates of reaction in solution (transition state theory).

2. Electrical Conductivity and Ion Transport in Solution.
   -Conductivity and molar conductivity. Experimental measurement. Molar conductivity at infinite dilution. Determination of strong and weak electrolyte
   -Conductivity versus concentration effect for weak and strong electrolytes.
   -Relaxation and electrophoretic effects.
   -Determination of dissociation constants for a weak acid (electrolyte).
   -Ion mobilites.
   -Kohlrauschs law of independent migration.
   -Influence of ion size on mobility. Stokes Law.
   -Grotthus mechanism of ion transport.

3. Electrode Surface and Electrified Interfaces
   Characterisation of electrode structures using microscopy, brief introduction to optical, electron and scanning tunnelling microscopy.
   -Relationship between surface charge, surface potential, electrical fields and the electrical double layer.
   -Helmholtz, Gouy Chapman, Stern models.
   -Practical applications of the electrical double layer.

4. Electrochemical Cells
   -Thermodynamics of electrochemical cells. Relation between EO, deltaG and K. Nernst equation. Sign convention.
   -Experimental measurement of standard electrode potentials.
   -Reference electrodes.
   -Determination of deltaS and deltaH from EO. Worked examples.
   -Fuel Cell and battery introduction.

5. Biological Electrochemistry
   -Membrane transport. Diffusion, convection, migration, osmosis. Transdermal drug delivery.
   -Membrane potentials.
   -Electrical signals in biological systems.
   -Microelectrochemical techniques for measuring membrane transport processes. Brain electrochemistry.
   -Artificial membrane potentials: the pH electrode

6. Dynamic Electrochemistry
   -Experimental arrangement for dynamic electrochemical measurements.
   -Role of mass transport versus electron transport in controlling the current signal.
   -Diffusion-controlled current-voltage processes.
   -Randles Sevcik equation.

There will be 2-3 problem set classes run in small groups so the students are given opportunities to practice answering questions on this part of the course

Part 2: Statistical Mechanics

- The basic concepts of Statistical Mechanics
  - o The connection between micro (quantum mechanics) and macro (thermodynamics) [L1]
  - o The concept of ensemble and ensemble average [L1]
  - o The concept of phase space [L2]
  - o The concept of partition function [L2]
  - o The NVE ensemble [L2]
  - o [Key Skills 1] Liouville theorem and molecular dynamics – the ergodic principle [K1]
- The canonical ensemble
  - o The canonical partition function [L3]
  - o Thermodynamic quantities from the NVT partition function [L3]
  - o Molecular partition functions [L4]
  - o Fermi-Dirac, Bose-Einstein, and Boltzmann statistics [L4]
  - o [Pen&paper Workshop 1] [PPW1]
- Toward chemical equilibrium: the diatomic ideal gas
  - o The equilibrium constant of chemical reactions in terms of molecular partition functions [L5]
  - o [Key Skills 2] The electronic partition function [K2]
  - o The translational partition function - the thermal De Broglie wavelength [L6]
  - o The vibrational partition function - choosing the zero of energy [L7]
  - o The rotational partition function [L8]
  - o Symmetry considerations and ortho-/para- hydrogen [L9]
  - o [Pen&paper Workshop 2] Equilibrium constants of chemical reaction in gas phase: di-/a-ssociation of alkali metal vapours [PPW2]
- The statistical mechanics of liquids
  - o The Statistical Mechanics of liquids: hard spheres and Lennard-Jones liquids [L10]
  - o The radial distribution function [L11]
  - o [Computational Workshop 1] Coordination numbers [CW1]
  - o Ions in aqueous solutions [L12]
  - o Debye-Hückel theory [L13]
  - o [Computational Workshop 2] Molecular simulations [CW2]

Learning outcomes

By the end of the module, students should be able to:

- Describe how Statistical Mechanics enables to make a connection between Quantum Mechanics (microscopic world) and Thermodynamics (macroscopic world)
- Remember the concepts of ensemble, phase space and partition function.
- Understand the significance of the ergodic principle
- Explain why Statistical Mechanics can be considered as the cornerstone of molecular simulations.
- Elaborate on the conceptual and formal differences between the microcanonical and the canonical ensemble
- Compute the translational, vibrational, rotational and electronic contribution to molecular partition functions.
- Take into account symmetry considerations (due to the bosonic/fermionic nature of subatomic particles) when computing rotational partition functions
- Extract thermodynamic quantities such as entropy and free energy from molecular partition

functions
- Calculate equilibrium constants for simple chemical reactions
- Discuss the structural properties of liquids and ionic solutions
- Compute the pair correlation function of a simple liquid from molecular dynamics trajectories
- Understand the molecular origins of the properties of ionic solutions and of Debye-Hückel theory
- Analyse the structure of water around selected cations - as obtained via molecular simulations
- Make a connection between the statistical mechanics of liquids and the foundations of Electrochemistry
- Write computer scripts in Python to e.g. analyse the results of molecular simulations.

Indicative reading list

Part 1: Electrochemistry
The Chemistry primer 'Electrode Potentials' by R. G. Compton and G. H. W. Saunders, Oxford University Press 1996, covers most of the material in this course. Atkins ' Physical Chemistry' also provides a good introduction to ions in solution and electrochemical cells.

Part 2: Statistical Mechanics
None of these books is essential, in that the whole of the course content will be covered within the lectures. However, these books will definitely make the students' life easier, as they all contain a number of solved problems. They also present many of the topics of this module in great detail. Whoever is curious/keen on the topic of molecular simulations should definitely indulge in the Tuckerman (Statistical Mechanics: Theory and Molecular Simulation), while an excellent addition to anyone's library would be the Chandler (Introduction to Modern Statistical Mechanics).

- Statistical Mechanics: Theory and Molecular Simulation - Mark Tuckerman 2010
- Highly Recommended - This excellent book offers a very clear overview of Statistical Mechanics. The key concepts of ensemble, phase space, and partition function are especially well covered. The following chapters will thus be of particular interest: 2. Theoretical Foundations of Classical Statistical Mechanics 3. The Microcanonical Ensemble and Introduction to Molecular Dynamics 4. The Canonical Ensemble. Incidentally, it is arguably one of the best, most useful textbooks ever written for those who are interested in molecular simulations.
- Statistical Mechanics - Donald A. McQuarrie 2000
- Highly Recommended - This classic textbook provides a comprehensive, rigorous introduction to Statistical Mechanics. It is very concise and goes well beyond the course. The following chapters will be of particular relevance: 4. Boltzmann statistics, Fermi-Dirac statistics, and Bose-Einstein statistics 5. Ideal monoatomic gas 6. Ideal diatomic gas 9. Chemical equilibrium 13. Distribution functions in classical monoatomic liquids.
- Introduction to Modern Statistical Mechanics - David Chandler 1987
- Recommended - This is a rather old, amazingly concise book which nonetheless manages to cover most of the essential principles and applications of Statistical Mechanics. It also contains a good number of problems, and on top of everything is quite cheap. A very good addition to anyone's library.
- Statistical Mechanics: A Concise Introduction for Chemists - B Widom 2002

- Recommended - This book contains a number of useful, chemistry-oriented examples. It also covers a good portion of the course (particularly with reference to Chapter 5), but fails to provide a rigorous presentation of the basic principles of Statistical Mechanics. Highly recommended in terms of applications and case studies.
- Statistical Mechanics: An Advanced Course with Problems and Solutions - Ryogo Kubo, H. Ichimura, T. Usui, N. Hashitsume 1988
- Further Reading - Here be dragons!

Research element

e.g. essay, dissertation, individual or group research, research skills activity, etc.

Subject specific skills

Numeracy
Problem solving
Critical thinking
Written communication
Oral communication
Organisation and time management
Independence and initiative
Information literacy and research skills
Digital skills and literacy

Transferable skills

Numeracy
Problem solving
Critical thinking
Written communication
Oral communication
Organisation and time management
Independence and initiative
Information literacy and research skills
Digital skills and literacy

Study

Study time

Type	Required
Lectures	30 sessions of 1 hour (20%)
Practical classes	6 sessions of 2 hours (8%)
Total	150 hours

Type	Required
Other activity	7 hours (5%)
Private study	73 hours (49%)
Assessment	28 hours (19%)
Total	150 hours

Private study description

N/A

Other activity description

x 2 Revision sessions
x5 Problem set classes - small group workshops

Costs

No further costs have been identified for this module.

Assessment

You do not need to pass all assessment components to pass the module.

Assessment group D4

	Weighting	Study time
Computational project Computational project via Jupyter Notebooks (Statistical Mechanics)	20%	8 hours
In-person Examination	80%	20 hours

- Answerbook Green (8 page)
- Students may use a calculator
- Graph paper
- Periodic Tables

Feedback on assessment

Feedback comments and grade on assessed work (computational projects and Moodle quizzes) provided on Moodle. Individual feedback with respect to the computational project (Part 2: Statistical Mechanics) will also be provided, addressing the assessment criteria of (i.) scientific soundness, (ii.) originality and (iii.) technical skills.

Cohort level examination feedback provided via Moodle following the Exam Board.

Past exam papers for CH273

Availability

Pre-requisites

To take this module, you must have passed:

- All of
  - CH162-30 Introduction to Physical Chemistry

Post-requisite modules

If you pass this module, you can take:

- CH3G3-30 Advanced Chemistry (Organic, Inorganic and Physical) Industrial Placement
- CH3F7-15 Energy
- CH3F1-15 Advanced Physical Chemistry and Laboratory
- CH3F3-30 Advanced Chemistry (Organic, Inorganic and Physical)
- CH3F4-15 Molecular Structure and Dynamics

Courses

This module is Core for:

- UCHA-4 Undergraduate Chemistry (with Intercalated Year) Variants
  - Year 2 of F101 Chemistry (with Intercalated Year)
  - Year 2 of F122 Chemistry with Medicinal Chemistry (with Intercalated Year)
- UCHA-3 Undergraduate Chemistry 3 Year Variants
  - Year 2 of F100 Chemistry
  - Year 2 of F100 Chemistry
  - Year 2 of F121 Chemistry with Medicinal Chemistry
- UCHA-F110 Undergraduate Master of Chemistry (with Industrial Placement)
  - Year 2 of F100 Chemistry
  - Year 2 of F110 MChem Chemistry (with Industrial Placement)
  - Year 2 of F112 MChem Chemistry with Medicinal Chemistry with Industrial Placement
- Year 2 of UCHA-F107 Undergraduate Master of Chemistry (with Intercalated Year)
- UCHA-F109 Undergraduate Master of Chemistry (with International Placement)
  - Year 2 of F109 MChem Chemistry (with International Placement)
  - Year 2 of F111 MChem Chemistry with Medicinal Chemistry (with International Placement)
- UCHA-4M Undergraduate Master of Chemistry Variants
  - Year 2 of F100 Chemistry

    - Year 2 of F105 Chemistry
    - Year 2 of F110 MChem Chemistry (with Industrial Placement)
    - Year 2 of F109 MChem Chemistry (with International Placement)
    - Year 2 of F125 MChem Chemistry with Medicinal Chemistry
- Year 2 of UCHA-F127 Undergraduate Master of Chemistry with Medicinal Chemistry(with Intercalated Year)