

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

21/22

**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 come 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 mobilities.
- Kohlrausch's 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  $E^0$ ,  $\Delta G$  and  $K$ . Nernst equation. Sign convention.
- Experimental measurement of standard electrode potentials.
- Reference electrodes.
- Determination of  $\Delta S$  and  $\Delta H$  from  $E^0$ . 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
  - The connection between micro (quantum mechanics) and macro (thermodynamics) [L1]
  - The concept of ensemble and ensemble average [L1]
  - The concept of phase space [L2]
  - The concept of partition function [L2]
  - The NVE ensemble [L2]
  - [Key Skills 1] Liouville theorem and molecular dynamics – the ergodic principle [K1]
- The canonical ensemble
  - The canonical partition function [L3]
  - Thermodynamic quantities from the NVT partition function [L3]
  - Molecular partition functions [L4]
  - Fermi-Dirac, Bose-Einstein, and Boltzmann statistics [L4]
  - [Pen&paper Workshop 1] [PPW1]
- Toward chemical equilibrium: the diatomic ideal gas
  - The equilibrium constant of chemical reactions in terms of molecular partition functions [L5]
  - [Key Skills 2] The electronic partition function [K2]
  - The translational partition function - the thermal De Broglie wavelength [L6]
  - The vibrational partition function - choosing the zero of energy [L7]
  - The rotational partition function [L8]
  - Symmetry considerations and ortho-/para- hydrogen [L9]
  - [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
  - The Statistical Mechanics of liquids: hard spheres and Lennard-Jones liquids [L10]
  - The radial distribution function [L11]
  - [Computational Workshop 1] Coordination numbers [CW1]
  - Ions in aqueous solutions [L12]
  - Debye-Hückel theory [L13]
  - [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

[Reading lists can be found in Talis](#)

## 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%)
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 D2

Assessment component	Weighting	Study time	Eligible for self-certification
Computational project	20%	8 hours	Yes (extension)
Computational project via Jupyter Notebooks (Statistical Mechanics)			

	<b>Weighting</b>	<b>Study time</b>	<b>Eligible for self-certification</b>
--	------------------	-------------------	--

Reassessment component is the same

**Assessment component**

Online Examination on-line examination ~Platforms - AEP	80%	20 hours	No
---	-----	----------	----

Reassessment component is the same

## 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:

- CH3F7-15 Energy
- CH3G3-30 Advanced Chemistry (Organic, Inorganic and Physical) Industrial Placement
- CH416-15 Energy
- CH3F4-15 Molecular Structure and Dynamics
- CH3F3-30 Advanced Chemistry (Organic, Inorganic and Physical)
- CH3F1-15 Advanced Physical Chemistry and Laboratory

## 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 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)