CHEM 1420: Physical Chemistry 2 – Thermodynamics, Statistical Mechanics, and Kinetics

Spring 2018 · Term 2184
Lecture: TTh 9:30 – 10:45 · 228 Eberly Hall
Recitation: T 4:00 – 4:50 pm · 307 Eberly
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Office hours: T 11-11:50 (tentative) or by appointment

Last updated 7 January 2019.

Goals of the course

This course, CHEM 1420 "Thermodynamics, Statistical Mechanics, and Kinetics", will extend and elaborate the molecular view developed in CHEM 1410. **Quantum mechanics** is set of tools to calculate and interpret the energy level structure of molecular systems. But few experiments outside of spectroscopy measure these quantum mechanical properties. PChem 1 leaves unanswered the question, "How do molecular properties appear in the macroscopic world?"

Our task is to develop tools to answer this question. **Thermodynamics** is a set of empirical rules derived from many experiments. These rules, along with some sophisticated mathematical machinery, can predict the direction of a spontaneous change; can predict the energy output of unknown chemical reactions from known ones; can predict the maximum efficiency of a heat engine – any heat engine, regardless of how it works!; and can predict equilibria. **Statistical mechanics** provides a molecular scale understanding of the thermodynamic results. Using mathematical tools from statistics, one can use atomic and molecular properties (*e.g.* interaction potentials) to calculate thermodynamic quantities. The partition function is the essential quantity which makes that connection. **Kinetics** addresses *how fast* reactions happen and why. For all its power, thermodynamics only gives the infinite time limit for equilibrium. The concepts of transition states, activation energies, free energy surfaces, and rate laws, let a chemist know how to understand and optimize the rates of chemical changes.

Overarching goals of the class are to improve your ability

- to build simple models of complex systems,
- to *quantitatively analyze* the models ("do math"),
- to *interpret* your results ("figure out what it means").

Putting the three together allows you to understand macroscopic (*i.e.* observable) behavior based on molecular properties: What is heat capacity? Why does a protein folding/unfolding curve look like *that*? Why is a rubber-band stretchy? Where do phase transitions come from? How do molecular collisions lead to fluctuations, diffusion, friction, viscosity, and dissipation?

You will learn how to develop and analyze simple models of very complex systems (often based on lattices or energy level diagrams); to calculate statistical properties like the multiplicity or the partition function of these models; to calculate the probability of finding a system in a certain state using the appropriate statistics; to analyze particle and energy flow from a statistical perspective; to analyze simple engines or machines with a known equation of state or energy level diagram to calculate quantities such as reversible work, heat flow, and efficiency; to determine if a function is a state function or a path function; to determine if thermodynamic functions are intensive or extensive; to analyze simple engines; to use the mathematical techniques of thermodynamics (Legendre transformations, Maxwell relations, the cyclic rule, partial derivatives of state functions) to derive unknown thermodynamic properties from known ones; to maximize functions (*e.g.* entropy) of a system using Lagrange's method of undetermined multipliers when there are constraints; to determine if a given process will occur spontaneously given some thermodynamic information; to calculate thermodynamic quantities from quantum mechanical Hamiltonians; to relate fluctuations in a quantity (*e.g.* energy) and susceptibilities (*e.g.* heat capacity). to estimate the rate of a chemical reaction given some information about its free energy landscape; to interpret rates as a function of concentration for different kinetic schemes; to derive an effective rate constant from a kinetic scheme.

Structure of class and assignments

We will devote our class time to an active investigation and derivation of the *key* concepts that underlie the physics and chemistry.

Most of the assignments for the course will be classic "homework". The homework assignments will be distributed at least a week before they are due. The purpose of these assignments is to give you practice applying the quantitative techniques to simple problems to build your "chemical intuition" and prepare you for the types of questions which will be on the midterms and final exam. Teamwork is great. Science rarely happens alone these days. Solving the assignments will be much easier if you work together.

Assignments will be collected via an online tool called Gradescope. You automatically have access with your pitt credentials. There is no need to make your own account, and this service costs you nothing.

Exams will contribute the bulk of your grade. There will be 2 midterms and a comprehensive final exam.

Please note, the exercises will be graded on a 0 – 1 – 2 basis:

- **0** The exercises show no significant progress towards solving the problems.
- **1** The exercises show some progress towards solving the problems. The solutions were either not complete or contained major mistakes.
- **2** The exercises show substantial progress towards the correct solutions, though there may be errors in detail.

Grading

The points in the course will be broken down as

- Exercises (25 %)

- Midterm 1 (25 %)
- Midterm 2 (25 %)
- Final exam (25 %)

Required text

- Dill and Bromberg, "Molecular driving forces" Second edition, (Garland Science) 2010.

Optional texts (on reserve)

- D. A. McQuarrie "Mathematics for Physical Chemistry: Opening doors"
- J. R. Barrante "Applied Mathematics for Physical Chemistry"

Feedback

Three times during the semester there will be feedback sessions outside of class for six students to give feedback on how the course is progressing. The sessions are purely voluntary, but participation will be rewarded with 1 homework point. The sign-ups will be first-come first-served through Courseweb.

Important days

Fr 8 February: Midterm 1 take home (tentative)

11 – 15 March Spring Recess

There will be no class this week.

Fri 29 March: Midterm 2 take home (tentative)

22–27 April Final comprehensive exam (take home)
The window for the take home will include Wed 24 April 4:00 – 5:50 PM.

Disability

If you have a disability for which you are or may be requesting an accommodation, please contact both me and Disability Resources and Services, 140 William Pitt Union, 412-648-7890 as early as possible in the term.

Disability Resources and Services reviews documentation related to a student's disability, provides verification of the disability, and recommends reasonable accommodations for specific courses.

Integrity

All students are expected to adhere to the standards of academic honesty. Any student engaged in cheating, plagiarism, or other acts of academic dishonesty would be subject to disciplinary action. Any student suspected of violating this obligation for any reason during the semester will be required to participate in the procedural process, initiated at the instructor level, as outlined in the University School of Arts and Sciences Academic Integrity guidelines at `http://www.as.pitt.edu/faculty/policy/integrity.html`.

Classroom recording

To ensure the free and open discussion of ideas, students may not record classroom lectures, discussion, or activities without the advance written permission of the instructor. Any such recording can be used solely for the student's own private use.

Religious observances

Please let me know as early as possible of any conflicts between class activities and religious observances so we can make appropriate arrangements.