# Physical Chemistry–Fall 2016

**Text**: T. W. Shattuck, *Physical Chemistry*, Colby College, 2016.

**Alternate texts:** I. M. Klotz, R. M. Rosenberg, *Chemical Thermodynamics: Basic Theory and Methods*, Benjamin/Cummings, Menlo Park, CA, 1986.

J. S. Winn, *Physical Chemistry*, Harper Collins, New York, NY, 1995.

K. A. Dill, S. Bromberg, *Molecular Driving Forces: Statistical Thermodynamics in Chemistry and Biology,* Garland Science, New York, NY, 2003. Chapts. 1-7.

D. A. McQuarrie, J. D. Simon, *Physical Chemistry: A Molecular Approach*, University Science Books, 1997.

P. W. Atkins, J. de Paula, *Physical Chemistry, 7th Ed.*, Freeman, New York, NY, 2002.

| Week | Chapter | Topic | Test | Lab |
|---|---|---|---|---|
| 1-9/7 | 1 | Chemical Reactivity, Concentrations | | |
| 2-9/12 | 2,3 | Partial Pressure, Kinetics | | Linear Fitting |
| 3-9/19 | 4,5.1 | Mechanisms, Photochemistry | | Methyl-Red |
| 4-9/26 | 6,7 | Applications of Kinetics, Heat and Work | | * Kinetics |
| 5-10/3 | 8,9 | First Law, Thermochemistry | | * Kinetics |
| 6-10/10 | 10,12 | Entropy | 10/14 Friday PM | * Thermochem |
| 7-10/17 | 12,13 | Entropy Applications | Semester Break | Break |
| 8-10/24 | 14,15 | Constraints, Spontaneity, Gibbs Energy | | * Thermochem |
| 9-10/31 | 16 | Foundations of Thermodynamics | | +Mechanics |
| 10-11/7 | 17 | Phase Transitions | | +CAMD |
| 11-11/14 | 18-19 | Solutions-ideal | 11/18 Friday PM | *Solutions |
| 12-11/21 | 19 | Solutions-real | Thanksgiving | +Dynamics$ |
| 13-11/28 | 20 | Chemical Equilibrium | | $K_{sp}$-$AgBrO_3$# |
| 14-12/5 | 21 | Electrochemistry | | Clean Up^ |

* Choose experiment from lab list + Molecular modeling computer calculations

$ A Tuesday morning session will be available.

# You must prepare your samples before 8:00 on the morning of your lab day.

^ Clean up, mandatory

## Point Distribution

| | |
|---|---|
| Hour Tests | 200 |
| Final | 200 |
| Homework | 100 |
| Laboratory | 300 |
| | 800 |

The schedule and point distribution given above is a close approximation, but we will deviate from this schedule as the semester progresses. Two of your lab reports will be written, two will be presented orally in my office, and for three you will just turn in the calculations and questions. If you have tests or papers coming up at the same time a lab is due, make sure to do your report early. Written lab reports are due on the Wednesday (for Monday lab) or Thursday (for Tuesday lab) of the next week after you complete your lab. Oral lab reports begin on the Monday of the week following the lab. Weekly homework is due on Friday, PM. No work will be accepted after the final.

## Graded Assignment Policy

Collaboration with your classmates is encouraged, because you can learn a lot from listening to each other and from explaining ideas to each other. However, whenever a grade is given for the work, it must represent the accomplishments of the individual, unless explicitly specified as a group project by the instructor. For some of the lab reports you will turn in your assignment with your partner. But otherwise,

lab reports, homework to hand in, and tests are to be your own work. Students might make the mistake of assuming that while cheating on tests is dishonorable, collaboration on lab reports or homework to hand in is OK. Please note that lab reports and homework are just as important with regards to academic dishonesty as tests. Science advances through the honest and careful reporting of laboratory work. In working with a partner in the lab, your collaboration **ends with the taking of data,** unless otherwise specifically stated.

On individual work for a grade, any assistance that you give or receive from another student must be limited to correcting errors in the data as recorded in the laboratory. It is wrong to show your work to another student as a means of helping. Recording another person's answer is also plagiarism, whether it is given verbally or in writing. Sharing spreadsheets or parts of spreadsheets is also not allowable. You must maintain access privileges on your server folders to ensure that other students do not have access. You may, however, honestly consult the instructor as a way of checking if you are on the right track.

On the other hand, working in a group on suggested problems that are not to be turned in for a grade is an excellent idea. The suggested homework provides ample opportunity to share ideas and provide help to others. Regular meetings of such help groups are a useful way to keep up with course work.

As in all your academic work, any ideas or information that you obtain from the literature must be properly cited. Citing literature sources is necessary even if you do not give a direct quote. Formal lab reports should use ACS format for references. References to text tables, the CRC, or Lange's Handbook can be given in-line, including the edition. For example:

The literature value for the enthalpy of formation is –134.23 kJ/mol (CRC 48$^{th}$ Ed.)

These guidelines are consistent with the Chemistry Department's and College's policy on academic honesty. If you have any problems on any assignment, you are strongly encouraged to come in to my office for help.

## Resources

The **Answers** for the textbook problems are on reserve in the Science Library. Previous tests are on the course Web page. Check the course Tracker often for up-to-date information and problem assignments. The back of the chapter homework assignments are also listed on-line on the Homework page.

## Process Skills and Learning Goals

The focus of any chemistry course is the in-depth understanding of chemical reactivity through the use of structure-function relationships. Thermodynamics, chemical kinetics, quantum mechanics, and statistical mechanics provide a coherent, unified, and powerful set of ideas and a point of view that enables chemists to be effective at solving important challenges in human health, energy technology, environmental stewardship, and improving the general quality of life. These theoretical ideas also satisfy the liberal arts desire to understand the world around us as completely as possible. We also wish to show the interrelationships among the sub-disciplines of chemistry, among the sciences, and between the sciences and the goals of society. To highlight these interrelationships, the course draws examples from diverse areas including biochemistry, energy technology, biogeoenvironmental chemistry, drug design, and aspects of ecology. Gaining facility with abstraction is the primary goal of the course. Building mathematical models, working through the implications of those models, and assessing the validity and inherent errors in the ability of the models to predict and explain physical phenomena is the central core of the curriculum. Students should also be able to express their scientific ideas orally. The first semester includes two oral lab reports to help improve student's communication skills.

## Physical Chemistry Laboratory

The purpose of the laboratory component of the course is several-fold. The lab reinforces the material you have learned in class and gives you a chance to apply your knowledge. You will learn some important experimental techniques that are necessary for you to become an effective chemist. The lab will allow you to delve more deeply in some topics and perhaps to cover others that we will not have time to touch upon during class. The lab will require you to learn how to deal with complexity, both in

experimentation and data analysis, which is an important component of any scientist's expertise. Two of the lab reports first semester are to be given orally. Oral reports are aids to you in learning how to express your scientific ideas verbally, something you will need to do the rest of your life.

The most important component of completing a laboratory successfully is your pre-lab preparation. You will make fewer mistakes if you have read and understood the lab write-up. You will need to figure out how to make up the necessary solutions for the lab before coming to the lab; there isn't enough time for these calculations during the lab. A half-hour of time spent before the lab will save hours on Monday or Tuesday afternoon. Short quizzes at the start of some of the labs will help you to remember to prepare. You may use your lab notebook for these quizzes, but not the lab write-up. You must change lab partners each week.

Laboratory reports are due one and a half weeks after completion of the experiment (on Wednesday for the Monday lab or Thursday for the Tuesday lab). Late lab reports will not be accepted more than two weeks late. All lab reports are due before the final. Oral reports will be scheduled during the week following the corresponding labs. Two of your lab reports will be written, two oral, and for three you will just hand in the calculations and answers to questions. For the two written or two oral labs, you may, if you like, turn in your calculations on Friday to be checked for problems. In this way, calculation errors can be corrected before you turn in your written or oral labs! You turn in your trial calculations on the special report sheets kept in the "Quick Check Calculation Sheets" section of the lab Web page, no later than the Friday of the week you complete the lab. The instructor will be more than happy to offer suggestions to help you with any problems that come up in writing up your labs, calculations included.

You will be required to complete 7 laboratories, which includes the initial pKa of methyl red lab. Chemistry is an experimental science, the key to which is the ability to verify our theories of the processes in the physical world. Have fun probing nature.

## Lab Reports

The goal of this course is to help build your independence. The calculations in physical chemistry can become complex. So, at first you may need to develop the mathematical skills to be successful with complex calculations. To ease your way, the first few lab reports will be done collaboratively with your lab partner. Please follow the following schedule. When collaborative work is done, turn in just one copy under both partner's names. When you aren't collaborating on calculations, you will work independently after you finish your measurements.

For the written labs, follow the guidelines given below. For your oral reports have all the tables, graphs, and calculations in your lab notebook. Your discussion and error analysis will be given orally, but you can make notes in your lab book. For the oral labs, please also fill out a report sheet, from the "Quick Check Calculation Sheets" section on lab Web page. Lab reports need not be typed.

*Written report guidelines:*

*Introduction:* In the introduction state the purpose of the experiment and the means that you used to achieve that purpose. The introduction should be just one to three sentences. You should not discuss the experimental procedure, nor the calculations that are necessary. For example, "a kinetics study determined the rate constant of the reaction at several temperatures and the corresponding activation energy."

*Theory:* For the Theory section, just reference the write-up, but include any requested derivations.

*Procedure:* Reference the lab write-up and briefly mention any changes in procedure from the lab write-up using past tense.

*Results for all Reports, Oral and Written:* For the Results section, provide the data in a tabular format, including **all information necessary to repeat your calculations**. Columns in your tables should have easily understood headings and include units. Your tables should be in the format used in journal articles. Use standard exponential notation ($2.3 \times 10^{-3}$ and not 2.3E-3) Your table should not appear to be fragments of a spreadsheet. Attach all your graphs. Graphs should fill at least a third of a page and include clearly labeled axes including units. (Figure captions, axes labels, and units, etc. can be hand written.) Include uncertainties for all derived values (see the error analysis handout for instructions for representing

uncertainties). For example, slopes and intercepts from curve fitting should always be given with uncertainties. Remember to use significant figure rules in presenting the final results if standard deviations are not determined.

*Discussion for Reports, Oral and Written:* Give the uncertainty of all the final results. If curve fitting was used (near the calculation of the final values), report standard deviations as propagated from the curve fit parameter uncertainties. If curve fitting is not used, report the final results indicating the appropriate number of significant figures. When using significant figures to represent the uncertainty, report two extra digits, but then underline the insignificant digits: for an example of three significant figures $1.2345 \times 10^{-4}$. Comment on the magnitude of the uncertainty of the final results: identify the predominate experimental error. Compare your final results to literature values, if available from the first listed reference of the lab write-up, the textbook appendices, Lange's Handbook, or the CRC. (You do not need to do a literature search for literature values; if results are not available in the previously mentioned sources, then you don't need to worry.) Make sure to give a citation for the literature values or any other information that you obtain from literature sources. Finally discuss the chemical significance of the results. In other words, state why these results are useful and important. For example, state how this experiment and technique fit into the larger world of chemistry. Discuss why someone might need to do a study of this type. Are the results for this system unusual or do they fall within the normal range for other systems? Answer any specific questions in the Calculations and Discussion section of the lab write-up.

*Calculations Only Reports:* For three of the labs you will hand in your calculations and the answers to any specific questions from the lab write-up. A discussion section is not otherwise required. Provide the data in a tabular format, including **all information necessary to repeat your calculations**. Attach all your graphs. Include uncertainties for all derived values (see the error analysis handout for instructions for representing uncertainties). For example, slopes and intercepts from curve fitting should always be given with uncertainties. Remember to use significant figure rules in presenting the final results (keep a couple of extra significant figures for intermediate results to avoid round-off error and help in checking the accuracy of your calculations, i.e. $2.3452$ kJ $mol^{-1}$).

*Computational Labs:* There are no lab reports for the computational labs. For the computational labs you just hand in the answers to the questions in the exercise write-up. You answer these questions independently. In other words, the computational labs are just like homework. The computational labs are the least means squares curve fitting assignment and the exercises done in the Schupf lab from the "Molecular Mechanics Tutorial" and the "Computer Aided Molecular Design Tutorial."

**Lab Report Schedule (non-computational labs)**

| Lab | Report format | Collaboration |
|---|---|---|
| 1 pKa Methyl-Red | written- full form | collaborate |
| 2 Kinetics | calculations and answers to questions* | collaborate |
| 3 Kinetics | calculations and answers to questions* | collaborate |
| 4 Thermochem | oral | collaborate on calculations |
| 5 Thermochem | oral | independent |
| 6 Equilibrium | written- short-form | independent |
| 7 Solubility of $AgBrO_3$ | calculations and answers to questions | independent |

* This lab is graded *all or nothing*: your calculations must be correct for credit and only full credit will be given. You may submit your calculations as many times as necessary (up to two weeks late). Calculations must be turned in directly in person with both partners present. The instructor will check your calculations while you wait. This procedure will guarantee fast turn-around times for grading and provide timely answers to questions when information is missing from the report.

## RULES OF THE ROAD

### PREPARATION

1. Read carefully and understand the lab write-up before coming to lab.
2. If you don't understand something--ask. Labs are a lot of fun, if you are prepared.
3. Look up all of the substances in the experiment in the **Merck Index** (or other suitable source) to determine if there are any health or safety hazards.
4. If you are doing a synthesis, look up the reagents in Fieser & Fieser, "Reagents for Organic Synthesis", to determine if there are any hazards, purification instructions or other tips.
5. Plan your solution preparation scheme before coming to lab.
6. Write everything down in your lab book.

### IN THE LAB -GENERAL

1. Wear eye protection (goggles or glasses with side shields).
2. Note the location of safety equipment, fire alarms, and exits.
3. Be conscious of what others are doing around you.
4. Clean up chemical spills immediately, especially in and around balances.
5. Check with the instructor for disposal information on all chemicals and solutions. Unless stated otherwise collect all waste in labeled waste containers. Keep aqueous and nonaqueous waste separate.
6. Never bring any library books, journals, reference books, etc. into the lab. Many people need to use these materials, they must be kept in good condition. Keep track of important information in your lab book instead.
7. Never heat volumetric glassware on a hot plate. Don't store solutions in volumetric flasks. If you get a solution into a pipet aid--wash it out immediately.
8. Check with the instructor for the proper procedure for washing spectrophotometer cuvettes and cells. Never wipe cell windows with paper towels.
9. Work with concentrated acids or bases in the hoods only.
10. Make up solutions in the P/Q lab, not in the Instrument lab.
11. Weigh out chemicals by difference or into small beakers. Don't use paper for weighing.
12. Never place a pipet directly into a solvent or solution bottle. Pour just what you need into a small beaker and pipet from the beaker.
13. Never return reagents to the bottle.
14. Record everything in your lab notebook.
15. You will often work in pairs. Both members of the pair must be present throughout the course of the experiment. If a person leaves early, they must complete the experiment on their own.

## CHEMICAL GRADES

Chemicals, especially solvents, come in many different purities or grades. Make sure to use the least expensive grade best suited to your experiment.

1. Technical grade solvents or chemicals are usually not pure enough for PChem or Quant experiments. Generally use reagent grade for this purpose.
2. Don't use "Primary Standard" or ultra high ("Ultrex") purity reagents unless specifically indicated in the write-up.
3. Don't use "Spectro" quality or "HPLC" grade solvents unless specifically indicated.
4. Never place a pipet directly into a solvent bottle.
5. Never return reagents to the bottle.
6. Always filter HPLC solvents, buffers, and samples using 0.2 micron filters.

7. Laboratory water comes in different grades, too. Think about the grade of water that you need to use. Distilled, deionized and high purity (grade 1 "reagent grade") water are available. Laboratory water is expensive--use it sparingly. In rinsing glassware, several rinses with small volumes of water are much more efficient than one rinse with a large amount of water.

All of the pointers above may seem bewildering at first, but they rapidly become automatic. Mastering good laboratory techniques will make you more confident, which means that lab will be a lot more fun and you will be able to exercise your creativity to a greater degree.

**Physical Chemistry Laboratory Experiments**

| Title | Instrument | Interest |
|---|---|---|
| **I. Thermochemistry** | | |
| 1. Enthalpy of Formation of Camphor (Isoperibol version) | Bomb Calorimeter | Biology |
| 2. Glycine Proton Transfer Enthalpies | Solution Calorimeter | Biochem |
| 3. Thermometric Titration of Cyclodextrin-Tronac version | Tronac Calorimeter | Biochem |
| 4. Thermometric Titration of Cyclodextrin-Microcal version | Microcal ITC | Biochem |
| 5. DSC: First and Second Order Transitions in Polmers | PE DSC-4* | Polymer |
| 6. DSC;First and Second Order Transitions in PETE | PE 8000 | |
| 7. DSC of Bilayer Membrane Phase Transitions | Microcal DSC | Biochem |
| **II. Equilibrium** | | |
| 8. Guest-Host Complexation of Cyclodextrin | Ocean Optics Diode* | Biochem |
| 9. Determination Of Enthalpy Of Enolization By NMR[1] | Varian VNMR NMR* | Organic |
| 10. Deuterium Exchange in Keto-Enol Tautomerization | Varian GC/Mass Spec* | Organic |
| 11. Equilibrium Constant of a Hydrogen Bonded Complex[1] | Varian VNMR NMR* | Organic |
| 12. The Solubility of $AgBrO_3$ | Spectro Arcos ICP | Analytical |
| **III. Phase Equilibria- Solutions** | | |
| 13. Vapor Pressure and Molecular Weight Pure Liquid | Vernier Pressor Sens. | Inorganic |
| 14. Liquid Vapor Equilibrium in a Binary System | Abbe' Refractometer | Organic |
| 15. Binary Solid-Liquid Equilibria | PE DSC 4* | Geology |
| 16. Purity Determinations by DSC | PE DSC 4* | Analytical |
| 17. log P and MR | LDC HPLC | General |
| 18. Henry's Law Constant and Free Energy of Solvation | Varian GC/Mass Spec* | Environ |
| 19. Partial Molar Volume | Mettler Density Meter | General |
| 20. Pressure Perturbation Calorimetry | Microcal DSC | Biochem |
| 21. Activities from Freezing Point Depression | Mettler Density Meter | General |
| **IV. Kinetics** | | |
| 22. Kinetics of Aquation of $Cl_2(en)_2Co(III)$ (Spec 20 version) | Spectronic 20 | Inorganic |
| 23. The Kinetics of the Saponification of Ethylacetate | Vernier Conductivity | Organic |
| 24. Kinetics of Ascorbic acid and Dichloroindophenol | Ocean Optics Diode* | Biochem |
| 25. Inversion of Sucrose | Rudolf Polarimeter | Biochem |
| 26. Laser Flash Photolysis | Luzchem LFP | Organic |
| 27. Hydration of Propionaldehyde by T-Jump Relaxation | Ocean Optics Diode* | Organic |
| 28. NMR Determination of the Rotational Barrier of N,N-dimethylacetamide[1] | Varian VNMR NMR* | Organic |
| 29. SPR Determination of Self-Assembly | Reichert SPR | Biochem |
| 30. Zeolite Molecular Sieves: Thermal Gravimetric Analysis | PE TGA 4000 | Inorganic |
| 31. Rate Constant for Fluorescence Quenching | Perkin Elmer 650-10S | Biochem |

* See the Instrument Instructions Section on the Laboratory Web page for instructions.

1. Schedule a training session on the NMR before your lab day if you haven't used the NMR before.