CHEMISTRY 331
CHEMICAL METHODS OF ANALYSIS
Fall 2004, MWF 8:00 – 9:15

Lecture: Tom Shattuck
Office Hours:
Office: Keyes 208A (x3315)
Lab: Martin Lemaire Keyes 208B
Office: Keyes 208B

Supplemental Texts (These are helpful, but not required; they're available in the Sci. Lib.)
1. Stephen Brewer, "Solving Problems in Analytical Chemistry"
2. Douglas A. Skoog and Donald West, "Fundamentals of Analytical Chemistry"

Grading

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
<th>Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homework</td>
<td>10%</td>
<td>100</td>
</tr>
<tr>
<td>Quizzes</td>
<td>5%</td>
<td>40</td>
</tr>
<tr>
<td>Class Exams</td>
<td>20%</td>
<td>200</td>
</tr>
<tr>
<td>Final Exam</td>
<td>20%</td>
<td>200</td>
</tr>
<tr>
<td>Pre-labs</td>
<td>10%</td>
<td>60</td>
</tr>
<tr>
<td>Lab</td>
<td>40%</td>
<td>400</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100%</strong></td>
<td><strong>1000</strong></td>
</tr>
</tbody>
</table>

Lecture Topics and Exam Schedule

1-9/9: Introduction, Review  
Read chapter 0-2
2-9/14: Chemical Equilibria and Solubility  
Read chapter 6

1st Quiz – September 16 / Electrolytes (15 min)
3-9/21: Volumetric Analysis  
Read chapter 7
4-9/27: Experimental Error, Statistics  
Read chapters 3-4
5-10/5: Calibration Methods  
Read chapters 4-5

1st Exam -- October 7 / Equilibria, Error Analysis, Statistics
6-10/12: Activity and Systematic Equilibrium Calculations  
Read chapters 8 & 9
7-10/21: [Break] Acid-Base Equilibria  
Read chapter 10 & 11
8-10/26: Titrations and Distribution Functions  
Read chapters 12

2nd Quiz – October 28 / Charge and Mole balance (15 min)
9-11/2: Complex Formation  
Read chapter 13
10-11/9: Fundamentals of Electrochemistry  
Read chapter 14

2nd Exam -- November 11 / Real Acids, Bases, Complexation
11-11/16: Potentiometry and Redox Methods  
Read chapters 15 & 16
12-11/22: Electrogravimetric and Coulometric Analysis  
Read chapter 17-2-3
13-11/30: Voltammetry  
Read chapter 17-4-6
14-12/7: Spectrophotometric Analysis  
Read chapter 18, 19

Final Exam
Homework

The Homework is a very important component of the course. The homework will be problems assigned from the text or handouts. Homework from the text will be assigned at the end of most lectures. Some of these will be designated to hand in. Copies of the answers to the homework will be placed on reserve in the Science Library four days after the assignment is made.

Late homework will be accepted and graded up to the time that the answers to the assignment are available. For Excel based exercises you should hand in a hard copy of the results and also place the program/spreadsheet used to solve the problem into your folder on the chemistry file server. **You should have your own backup copy of your homework disk!!!** You will be allowed to use some of your computer programs to solve problems during hour exams.

Prelab assignments

Prelab exercises are an important component of the laboratory. The prelabs familiarize you with the current week's experiment making you more efficient in the laboratory and often improving your results. Prelab assignments are due at 10:00 on Wednesday before the Wednesday lab. You cannot start the lab until you have correctly completed the prelab assignment.

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 two 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, perhaps even more important. Science advances through the honest and careful reporting of laboratory work. Dishonesty in the lab impedes scientific progress and cannot be allowed. In working with a partner in the lab, your collaboration **ends with the taking of data**, unless otherwise specifically stated. Let's make it clear what is appropriate for individual lab reports and homework to hand in for this course.

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 also maintain access privileges on your Chemserver folders to ensure that other students do not have access to your work. 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. In other words, 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 should 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 Harris tables, the CRC, or Lange’s Handbook can be simply given in-line, including the edition. For example:

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

These guidelines are consistent with the College's policy on academic honesty as discussed in the College Student Handbook and the Catalog. If you have any problems on any assignment, you are strongly encouraged to come in to my office for help.
CHEMICAL METHODS OF ANALYSIS
LABORATORY SCHEDULE

Week 2. Calibration and Titration System assembly.
You will assemble an automated titration system, which you will use throughout the course of
the semester. You will evaluate the accuracy and precision of the titration system in addition to
a number of other quantitative measurement techniques. We will also discuss the relative
advantages and disadvantages of gravimetric and volumetric methods of solution preparation.
Prelab reading. Harris, pp. 26-41
Prelab assignment: Excel spreadsheet to calculate air buoyancy corrections.

Week 3 & 4. Alkalinity and Dissolved Oxygen, DO, Determination
We will travel to Great Pond to use the "remote sampling platform." We will sample as a
function of depth for pH, DO, conductivity, ORP, chlorophyll, and hardness using a YSI multi-
sensor sonde. At the Outing Club cabin we will do titrations for alkalinity and DO. For the
alkalinity titration a graphical procedure known as a Gran Plot will be used to determine the
equivalence points of the titration. For the DO measurements we will use the Winkler titration,
a classical redox titration used to determine dissolved oxygen concentration in water samples.
The Winkler and sensor-based results will be compared to verify the proper calibration and
function of the sensor. The hardness samples will be frozen for later analysis using a
complexometric titration.
Prelab reading: Handouts on Alkalinity and Winkler Methods;
http://www.colby.edu/chemistry/CH331/YSI%20Sonde.pdf, pp 33-34,177-181;
Prelab assignment: A complete list of everything (and we mean everything) you will need to do
you titrations at the Outing Club cabin.

Week 5. Determination of the pKa of a Weak Acid using Potentiometric, Conductimetric,
and Thermometric Titrations.
You will standardize an NaOH solution and use the standard to titrate a weak acid. You will
use a pH-meter, a conductivity probe, and a sensitive thermistor bridge to follow the course of
the titration. A Gran Plot will be used to determine the equivalence point of the pH titration.
You will also calculate the pKa and concentration of the weak acid.
Prelab reading. Harris, pp. 227-239.
Prelab assignment. Example Gran Plot on supplied data.

Week 6. Ion Exchange Equilibria
Solid phase extraction, SPE, cartridges will be used to determine the Na\(^+\) and Cu\(^{2+}\) ion content
of an unknown. The Na\(^{+}\) ion concentration will be measured by a pH titration of H\(^+\) ions
displaced from the cartridge. The Cu\(^{2+}\) ions will be preconcentrated on the column, eluted with
NaCl and determined by an ion specific electrode.
Prelab assignment. Detailed solution preparation scheme.
**Week 7. A Simple Photometer**
You will assemble a photometer from laboratory fiber optic components and record data for the construction of a spectrum and calibration curve as well as determine the concentration of an unknown.

*Prelab reading.* Handout.
*Prelab assignment.* Detailed solution preparation scheme.

**Week 8. pH Stat Complexometric Titration for Hardness.**
You will determine the amount of calcium and magnesium in a Great Pond water sample by complexing the Ca$^{2+}$ and Mg$^{2+}$ with EDTA. The titration will be monitored using a pH electrode.

*Prelab reading.* Harris pp. 261-277. Handout on pH stat titrations and EDTA titrations.
*Prelab assignment.* List of all the simultaneous reactions involved in the titration with the expected direction of the shift in equilibrium for each stage of the titration.

**Week 9. Spectrophotometric Titration of Metal Ions.**
In this experiment you will use a large volume cell in an LED based spectrometer to titrate a solution mixture of Ca$^{2+}$ and Cu$^{2+}$ with your standard EDTA solution.

*Prelab reading.* Harris pp. 261-277. Handout on spectrophotometric titrations.
*Prelab assignment.* TBA

**Week 10. Fe(II) Determination by FIA.**
A semi-automated method known as Flow Injection Analysis (FIA) will be used in conjunction with a visible spectrophotometer to determine the Fe(II) content of a natural water sample. Weather permitting, each student will collect a water sample from a different lake and we will compare the results at the end of the experiment.

*Prelab reading.* Harris 442-443. Handout on flow injection analysis.
*Prelab assignment.* Detailed solution preparation scheme.

**Week 11. Titrations with Dual Polarized Electrodes**
The titration of Fe$^{2+}$ with Ce$^{4+}$ will be followed using dual polarized electrodes in both potentiometric and amperometric modes.

*Prelab assignment.* The predominant, balanced, half-cell reactions for the different stages of the potentiometric titration.

**Week 12. Salicylate Ion Selective Electrode.**
You will make your own Salicylate ion selective electrode and use the electrode to determine the salicylate concentration of an aloe vera suspension. We will also have a demonstration of other ion-selective electrodes and discuss the operating principles of each.

*Prelab reading.* Harris 320-321, 330-337. Handout on ion selective electrodes.
*Prelab assignment.* Web assignment on aloe vera and detailed solution preparation scheme.

**Week 13. Cyclic Voltammetry**
We will use cyclic voltammetry to determine a metal-ligand binding constant. Since we have only one CV, pairs of students will sign up for times throughout the week.

*Prelab reading.* Harris 386-397. Handout on Cyclic Voltammetry.
*Prelab assignment.* Detailed solution preparation scheme.