DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
CHEMISTRY 3411, SPRING 2015
AQUATIC CHEMISTRY

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Course Description: This is a course in *aquatic chemistry*. We will examine the chemical processes which dominate natural waters in oxic and anoxic environments in the earth system. We will discuss basic properties such as alkalinity and then move to advanced topics such as red-ox equilibria, chemical equilibria and solubility as a function of pH. In a small laboratory component, we will tackle a real problem dealing with the remediation of heavy-metals in drinking water. A common theme of this course will be to understand how the chemistry of the system can help to dictate water quality, as well as water treatment for drinking water.

It is assumed that you have a sound knowledge of general chemistry and a basic understanding of the concepts of equilibrium. Of most importance is a good handle on Equilibrium Systems (CHEM 2011), as Aquatic Chemistry is a direct extension of many of the concepts learned there.

Textbooks: There is one textbook listed for this course. There are required readings from this textbook, and I highly suggest obtaining a copy. This is a relatively basic textbook, and I will provide supplementation as/if needed.

- Manahan SE; *Water Chemistry,* 2011, CRC Press, ISBN: 978-1-4398-3068-0

I will also be drawing off of the following textbook, although it is not necessary to purchase:

- Stumm W and Morgan JL; Aquatic Chemistry: Chemical equilibria and rates in natural waters, 3rd Ed, 1996, John Wiley & Sons, ISBN: 978-0-471-51185-4

Other Resources: In addition to the textbook, lecture presentations, and handouts, you will have the opportunity (and requirement) to consult other resources. These will consist of websites (laboratories, trade associations, government sites, user groups, and list-servers), electronically available journals, and paper-based journals. Most journal articles published 1970-present are available in electronic format and may be printed and/or stored in journal publication format as *.pdf format. Two examples of where to look are as follows: A) the ACS journals (pubs.acs.org) are available from any DU-based URL; and B) many other journals are available free of charge from several databases available at the DU Library website (www.library.du.edu/). The most useful databases are A) www.sciencedirect.com, "Sciencedirect", a service with > 1000 full-text journals which the DU library subscribes to, and B) the Web of Science, which can be accessed directly from the Penrose Library webpage (search the Databases at http://library.du.edu/site/). All of the library databases are available without a personal account from any campus-based URL; however, you can access them from off-campus through the DU library's website with

proxy identification.

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Course Topics

I. Introduction / bulk properties (~ 1 week)

- *Hydrological cycle*
- *Importance and anomalies of water*
- *Bulk properties of water – alkalinity and acidity*
- *Charge balance*
- *Activity*

II. Acid-base chemistry (~ 2 weeks)

- *Carbonate Equilibria*
- *Multiple components*
- *pC – pH diagrams*

III. Red-ox equilibria (~ 2 weeks)

- *Importance of oxidative and reductive environments in aquatic waters*
- *Free energy and its relation to red-ox reactions*
- *The "power" of an electron: metal speciation and pE-pH diagrams (Pourbaix diagrams)*

IV. Water Treatment Processes (~ 1 week)

V. Student Presentations (see details at the end of the syllabus) (1 week)

Note that this class is not a prerequisite for any further classes. Therefore, this schedule is ***extremely*** flexible. If you want to go deeper into a topic currently under discussion or if there is a general consensus that we should skip something so we can get into other topics, then say so!

Evaluation Methods

Over the 10 week quarter, you will be evaluated by several criteria. Specifically, you will be expected to complete the following:

- 2 in-class exams – the 2nd will be during the Final Exam period and is cumulative.
- Sporadic homework (3-4)
- 1 laboratory report (in pairs) (see end of syllabus).
- 1 **individual** presentation 10-12 min (+3 min questions) presentation, including a written report, described in detail at the end of the syllabus.

In the event that you must miss an in-class exam, please let me know ASAP (in advance if possible) and a makeup will be scheduled. I am generally reasonable, but reserve the right to deny makeup exams for confabulated reasons, in which case your missed exam will be counted as a zero.

The breakdowns, immediately below, reflect the "default" grading distribution. As with everything in life, **this is negotiable.** If you believe that you would perform better with different weightings, then we can meet in-person to discuss this by **Monday, March 30**.

* Summary of evaluation:

Exams (2 x 20)	= 40 %
Homework	= 10 %
Individual Project	= 30 %
Laboratory Project	= 20 %

A	≥ 93 %	C	≥ 69 %
A-	≥ 90 %	C-	≥ 65 %
B+	≥ 87 %	D+	≥ 62 %
B	≥ 83 %	D	≥ 58 %
B-	≥ 80 %	D-	≥ 54 %
C+	≥ 74 %	F	≤ 54 %

I reserve the right to make downward adjustments to this scale (i.e. adjustments in the direction of leniency). In no event will the actual scale used be adjusted upward from that described above.

Important Dates:
March 23: Classes begin
March 29: Last day to drop for 100% refund and drop deleted from record
May 3: Last day to drop without approval
May 25: Memorial Day
May 28: Last day of class (Thursday)
June 2: Final Exam 12:00 – 1:50

Individual Project:

In the last week of this course, you will lead a 15 min (10-12 min presentation + 3-5 min discussion) presentation. Given the time-constraints, **it is important that you stick to these limits**. In addition, a **4-6 page** (title page and references excluded) report of your findings will be turned in on the date of your presentation. Technical details of the report are below:

- Double spaced
- 12 pt Times New Roman **or** 11 pt Arial
- 1" x 1" margins (this is NOT the default in MS Word).
- Need **at least** five references, only **two** of which can be from reputable web sites. The others must be primary research articles. In general, a ".gov" site is OK (EPA, USGS), in addition to international agencies such as UNEP and the WHO. Some ".com" sites may be OK, but talk to me if you have questions about the integrity of a specific site.

Please be prepared to lead the class for your presentation. Here are some tips for a successful discussion:

1. You are free to use slides, powerpoints, demonstrations, skits, or anything else which will help the class learn the material. Feel free to have an interactive portion, as well.
2. This is not a trivial task – I suggest that you start your research at the beginning of the quarter.
3. I am happy to meet with you as much as you'd like for consultation. However, you are **required** to meet with me at least **twice** during the quarter.

Relevant Dates for the Special Project:

- Tues, March 31: Turn in one piece of paper for your topic (see below). This paper should contain 1) your name and 2) your preferred topic + one back-up topic.
- Thurs, April 2: I will approve your choice or suggest an alternative (in class).
- Thurs, April 16: Deadline for Meeting #1: progress of research and obtaining references
- **Tues, May 5: Rough draft of paper due with bibliography**
- Tues, May 12: Deadline for Meeting #2: will discuss rough draft and upcoming presentation
- May 26 and 28 – Presentations

Ideas for topics (there are many others and original ideas are certainly encouraged!!)

- Water quality and treatment in underdeveloped countries
- Isotope dating and tracing of aquatic organisms
- Ocean acidification
- Iron ocean fertilization
- Acid-mine drainage
- Pharmaceuticals in drinking water
- Emerging pollutants: engineered metallic nanoparticles in drinking water
- Desalinization of seawater
- Mercury pollution and poisoning
- Fluoride removal

Project grade break-down (100 pts total):

Preparation (5 *pts*)

Meeting #1 (prior to end of April 16) (2.5 *pts*)
Meeting #2 (prior to end of May 12) (2.5 *pts*)

Two multiple choice questions (with answers) for Exam III (5 pts)

Presentation (45 pts)

Content (*25 pts*)

- Appropriate scope (5 *pts*)
- Relevant and correct chemistry/concepts (*5 pts*)
- Summary/Conclusions (*10 pts*)
- Answers to questions (5 *pts*)

Form and style (*20 pts*)

- Slide quality (uncluttered, clear) (*5 pts*)
- Clear explanations (5 pts)
- Verbal quality, eye-contact, body-language (*5 pts*)
- Timing (*5 pts*)

Written report (*45 pts*)

- Appropriate **introduction** of the problem/topic (10 pts)
- Appropriate **level of research** into the problem/topic (15 pts)
- Independent **conclusions** based on research (10 pts)
- Grammar/spelling (5 pts)
- References (5 pts)

Laboratory Project

Thallium in drinking water

Motivation:

Thallium (Tl) is a heavy metal which is more toxic to humans than mercury, cadmium, and lead (EPA). For drinking water, the EPA maximum contaminant level (MCL) is 2 μg Tl L^{-1}, or 2 ppb. The MCL goal (MCLG) is 0.5 ppb. A recent situation has been uncovered in a small village near Tuscany, Italy, where Tl concentrations were measured as high as **9,000 ppb** in ground and surface waters (ResearchGate). As a result, drinking water concentrations are on the order of 10-30 ppb Tl. This has obvious implications on the health and well-being of people drinking the water, but also leads to contaminated soils and, as a result, crops and livestock. This scenario has also been observed in China, and a primary research article is posted on Bb.

Objectives:

a) To determine reasonable removal mechanisms for Tl from water
b) Determine if the water treatment should take place at the source (9000 ppb) or after the standard water treatment (30 ppb)?

Overview of method:

The class will work in **groups of two** and each group will test a different sorbent for Tl removal at various concentrations. We will test the ability of ~ micron sized particles to act as a sorbent to remove Tl from the water. The particles to be tested are:

1. Two types of clays
2. Hematite (Fe_2O_3)
3. Activated carbon
4. Silica

The lab should require 4 full class periods. During the first two lab periods, we will vary the Tl concentration in **pure water** to determine where the greatest removal efficiency lies. The 2nd half of the lab, we will choose the best Tl concentration and test the effect of **ionic strength** by adding nitrates of both Ca and K. In the end, the class will pool their data and we will determine which sorbent most effectively removes Tl from solution at various concentrations and ionic strengths. Most of the lab work will occur in Dr. Majestic's research laboratory (SGM 143) and we will use inductively coupled plasma – mass spectrometry (ICP-MS) to measure the Tl concentrations. Because this is not an instrumental analysis course, you do not need any prior knowledge about the technique. However, you will learn your fair share after completion of this lab.

Details of method:

Due to the toxicity of Tl, Dr. M will prepare a diluted solution (1000 ppm) of Tl for use. Dr. M will also prepare calibration standards for the instrumental analysis. This method is divided into "Weeks" and will take 4 class/laboratory periods.

1. Preparing the experiment:
    a. Prepare 6 vials of 5 g L^{-1} sorbent (total volume will be 40 mL). To do this, prepare 50 or 100 mL of a 50 g L^{-1} stock suspension and pipet a 10x dilution 6 times from there.
    b. Add about 20 mL of high-purity water (this value does not have to exact, at this point).
    c. Label each vial as 30, 100, 300, 1000, 3000, and 10000 ppb and add the correct amount of 1000 ppm Tl stock solution to get to that concentration.
    d. Fill each vial to the 40 mL line with high-purity water
    e. Put on shaker or rotator and let sit until next lab period.

2. Analysis of samples

    a. Bring all of your samples to room 267 SGM (Dr. Margittai's research lab). We will be using the centrifuges to separate the sorbent from the rest of the solution (details provided that day).
    b. **Carefully** (do not mix/agitate) bring your samples back to 143 and pipet exactly 3 mL of the **supernatant** into a clean, labeled 15 mL analysis vial.
    c. Add 15 µL concentrated nitric acid (**ask for help** if you have never used a micropipette). This will bring the solutions to 2% HNO_3, which is necessary for analysis. You will have to take account for this small dilution in your data analysis.
    d. Dr. Majestic will give a brief overview of the technique and we will proceed with sample analysis by quadrupole ICP-MS.

This will complete the first half of the lab. You next step is to calculate the "removal efficiency" of your sorbent at each concentration. In other words, how much Tl was left in the supernatant of the total? If 1 ppb was left from your 100 ppb Tl solution, then you have a 99% removal. Make a graph of "removal efficiency" vs "Tl concentration." We will share this in class and decide the Tl concentration for Part II of this experiment.

Part II of this experiment is the same as Part I, except that we will vary **ionic strength** instead of Tl concentration. This approximates a more realistic system.

3. Preparing the experiment:

    a. Pipet in 4 mL of your stock 50 g sorbent L^{-1} solution into each of six 50 mL centrifuge vials
    b. Prepare a 2 M stock solution of KNO_3 and a 2 M stock solution of $Ca(NO_3)_2$ (this may be prepared for you)
    c. In your 6 vials, prepare 0.05 M, 0.10 M, and 0.5 M KNO_3 and 0.05 M, 0.10 M, and 0.5 M $Ca(NO_3)_2$ from the respective 2 M stock solutions.
    d. From the 1000 ppm stock Tl solution, add the agreed upon Tl to each vial (**Tl concentration will be the same in each vial**).
    e. Fill each vial to the 40 mL line with high-purity water
    f. Put on shaker or rotator and let sit until next lab period.

4. Analysis of samples

    a. This part of the experiment is identical to Week 2.

Again, the data will be pooled so that everyone has access to everyone's data. The reports are handed in in pairs. Here is what your report should focus on:

1. An introduction of the problem you are trying to solve / address
2. Overview (not the details) of methods used to address the issue
3. Observations – what did you learn? What sorbents worked best in pure water? What concentrations were the "sweet spot?" Did ionic strength have any effect? Was there any major difference between Ca and K? This is where you can present figures. At the minimum, you should have two figures "% removal vs Tl conc" from the first half and "% removal vs ionic strength" for the second half. More are fine…
4. Discussion: Why did different sorbents have different removals (if they did?)? % removal as a function of concentration – would it make more sense to remediate at the source or at the "tap?" Comment on the differences observed with ionic strength – what is the origin of these differences?

References:

http://www.researchgate.net/profile/Emilia_Bramanti/topics
http://water.epa.gov/drink/contaminants/basicinformation/thallium.cfm