University of Maryland CENTER FOR ENVIRONMENTAL SCIENCE	Modeling Chemical Equilibrium in Natural Waters 3 credits	MEES 698M Fall

Course Objectives / Overview

This course is designed to teach a broad range of environmental science students the foundations of chemical thermodynamics and kinetics as it applies to the composition of natural waters. The contents are focused on four processes that are major regulating forces in geochemical cycles: (i) pH control by the carbonate system; (ii) speciation of metals in solution; (iii) redox chemistry; and (iv) precipitation of pure metal salts and homogeneous or heterogeneous solid solutions. The main objective of the course is the development of quantitative skills.

Expected Learning Outcomes

1. An understanding of the relation between thermodynamic equilibrium constants and Gibbs free energy and their dependence on temperature, pressure, and ionic strength
2. The ability to characterize equilibria in aqueous systems by simultaneous solution of mass balance and mass-action equations, as well as a basic understanding of disequilibrium (kinetics)
3. The ability to calculate pH in both strongly and weakly buffered aqueous systems
4. The ability to calculate metal solution speciation in simple aqueous systems, as well as an understanding of its influence on metal solubility, mobility, and bioavailability
5. The ability to calculate the solubility and saturation state of inorganic salts (minerals) in aqueous systems, as well as an understanding of what processes may promote or inhibit their precipitation or dissolution
6. The ability to balance redox reactions and to characterize equilibria in hypothetical aqueous systems using the corresponding Nernst Equations, as well as an understanding of the practical limitations of interpreting redox potentials measured in natural systems

Items 1+2 are general learning outcomes. Items 3+4 and 5+6 are more specific learning outcomes that will be tested with targeted questions during the midterm and final exams, respectively.

Course Assessment / Grading

Weekly Homework Assignments (20%)
Midterm Exam (30%)
Final Exam (50%)

INSTRUCTOR DETAILS:

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(410) 326-7387

Faculty name 2
faculty email
faculty phone number

Faculty name 3
faculty email
faculty phone number

Faculty name 4
faculty email
faculty phone number

CLASS MEETING DETAILS:

Dates: M+W
Times: 8:30–9:50 AM
Originating Site: CBL
IVN bridge number: (*******)
Phone call in number: (***)
Room phone number:(*****)

COURSE TYPE:

Check all that apply

☐ Foundation
☐ Professional Development
☐ Issue Study Group
☐ Seminar
☒ Elective

Prerequisites
A basic understanding of equilibrium reactions and some familiarity with calculus and numerical analysis

Teaching Assistant
N/A

Tentative Weekly Course Schedule

Introduction – Thermodynamics and kinetics in environmental geochemistry:

Week 1 **B&A Ch. 1; S&M Ch. 1 and Sect. 2.1**
- Geochemical cycles and the importance of interfaces
- Application of thermodynamic vs. kinetic models – the concept of steady state
- Definition of concentration units

Week 2 **B&A Ch. 3 and 4; S&M Sect. 2.2–2.9**
- Principles of chemical thermodynamics
- Entropy, enthalpy, and Gibbs free energy
- Conditions for equilibrium
- Relation between Gibbs free energy and the equilibrium constant

Week 3 **B&A Ch. 3 and 5; S&M Sect. 2.10–2.17**
- Dependence of the equilibrium constant on temperature, pressure, and ionic strength – the van 't Hoff Equation, the Davies and the extended Debije-Hückel Equations, and the Pitzer-Mayorga Formalism
- Introduction to reaction kinetics

Part I. The dissolved inorganic carbon (DIC) system:

Week 4 **B&A Ch. 7; S&M Sect. 3.1–3.7**
- Acids, bases, and buffers

Week 5 **B&A Sect. 6.8; S&M Ch. 5**
- Dissolved gases – Henry's Law

Week 6 **B&A Ch. 8; S&M Sect. 4.1–4.5 and 4.7**
- DIC – P_{CO_2} – pH – alkalinity – $CaCO_3$ solubility
- The Phase Rule
- Evolution of Ca–HCO_3 waters under isothermal evaporation
- Weathering and soil acidification
- Buffering capacity of natural waters

Part II. Speciation of dissolved metals:

Week 7 **B&A Ch. 9; S&M Sect. 6.1–6.4**
- Principles of speciation
- Metal hydration and hydrolysis
- Solubility of metal hydroxides

Week 8 **Review and Midterm Take-Home Exam**
(two questions about everything covered so far)

Week 9 **B&A Ch. 9; S&M Ch. 6 excl. Sect. 6.6**
- Formation of ion pairs, complexes, and chelates
- Chemical classification of metals and ligands
- Strong ligands and organometallic compounds
- Metal buffers
- Kinetics of metal complexation

Part III. Precipitation of salts and solid solutions:

Week 10 **B&A Ch. 10; S&M Sect. 7.1–7.6**

- Control of the composition of natural waters by dissolution and precipitation
- Influence of metal hydrolysis and complexation
- Solubility of natural oxide, hydroxide, carbonate, sulfide, and phosphate minerals

Week 11 **B&A Ch. 15; S&M Sect. 7.8–7.9 and 13.6–13.7**
- Influence of particle size
- Homogeneous and heterogeneous solid solutions
- Processes that inhibit dissolution
- Nucleation and crystal growth

Part IV. Redox processes:

Week 12 **B&A Ch. 11 and 13; S&M Sect. 8.1–8.4**
- Rules for the assignment of oxidation states
- Balancing redox reactions
- Electrochemical cells, reference electrodes, and the electrochemical series
- The Nernst Equation
- Comparison with the theory of acid–base reactions
- Calculations with $p\varepsilon$ and E_H
- Stability field of water

Week 13 **B&A Ch. 11 and 12; S&M Sect. 8.5–8.8**
- Effect of complexation on $p\varepsilon$ – formal potentials
- Use of $p\varepsilon(W)$
- Ion-Selective Electrodes (ISEs)
- Difficulty of measuring $p\varepsilon$ in natural systems – mixed potentials
- Photosynthesis and the natural redox cycles of C, N, S, Fe, and Mn
- Bioregulation of natural water compositions – the Redfield concept
- The Froelich sequence of oxidation reactions

Week 14 **B&A Ch. 17; S&M Ch. 12**
- The role of light in natural redox cycles
- Theory of light absorption and photo-activation
- The Lambert-Beer Law
- Quantum yield
- Photoreactants and steady-state concentrations
- Photolysis of metal complexes
- Photochemical reactions in the atmosphere – ozone formation
- Heterogeneous photochemical reactions – reductive dissolution and semiconductor surfaces

Week 15 **Review and Final In-Class Exam**
(two questions, with emphasis on everything covered after the midterm exam).

Required textbooks, reading and/or software or computer needs

*** Textbook: Water Chemistry (P.L. Brezonik and W.A. Arnold) Oxford University Press**

Regular access to the book is essential for successful completion of this course. My original course was based on the classic—albeit now rather dated—Aquatic Chemistry (3rd ed., W. Stumm and J.J. Morgan, Wiley–Interscience), which I replaced in 2013 with the more contemporary text by Brezonik and Arnold (B&A), covering largely the same material yet with a more applied focus. It appears that the USM library system does not hold a copy of B&A, but a pdf version will be posted on Moodle; it is therefore not necessary to purchase the book. Stumm and Morgan (S&M) is also widely available in paper and electronic form and can be used as an alternative resource. The class schedule below lists the relevant chapters in both texts.

Course Communication

*** All supplementary course materials will be uploaded on Moodle**
*** Office hours (for MEES 626 only): Fridays 8:30–9:30 AM**

Resources

[Course website: www.moodle.com/xxxxx]

Campus Policies

The University of Maryland Center for Environmental Science has drafted and approved of various academic and research-related policies by which all students and faculty must abide.

Please visit http://www.umces.edu/consolidated-usm-and-umces-policies-and-procedures for a full list of campus-wide academic policies.

Course-Specific Policies and Expectations

[Separate from the campus-wide policies linked earlier, you may want to outline any additional course policies of which students need to be aware. Also include late work policy, etc.]