Chem 529 – Advanced Solution Chemistry
Fall, 2014
3 credit hours

LECTURES: Mon., Weds., Fri. 1:10 PM, Fulmer 225
LOCATION: Fulmer Hall, room 225
INSTRUCTOR: Prof. Kenneth Nash (Alt. Joseph Lapka)
Office: Fulmer 639 **Phone:** 335-2654 **Email:** knash@wsu.edu

PREREQUISITES: Basic math skills, understanding of physical chemistry

COURSE STRUCTURE AND FOCUS: This is a three credit hour graduate level Chemistry course. The level of presentations will be such that upper division undergraduates should be able to handle the work. In this course, explorations of the fundamental nature of solvent-solvent and solvent-solute interactions in solution emphasizing water as a medium for reaction will be discussed. A significant focus will be placed on correlating the molecular-level details of the interactions of solutes with the solvent and with other solutes and the thermodynamic/kinetic features of these interactions. We will also consider biphasic systems involving immiscible liquid phases and ion exchange materials. Starting from comparatively simple systems (which are not as simple as they seem) of binary 1:1 electrolytes, the focus will shift to characterizing the interactions between polyvalent metal cations and complexing/chelating agents and the interactions of each with solvent molecules. These concepts will be discussed within the general framework of the physical chemistry (thermodynamics and kinetics) of solutions and reactions occurring in such condensed media. Attention will be given to experimental techniques for determining chemical equilibrium constants including some exercise of data analysis methods. We will also examine databases of thermodynamic data, use that data for prediction of equilibrium speciation and explore the evaluation of data from the literature. Some time will be invested in discussion of processes occurring at interfaces and a section will be devoted to separations techniques like solvent extraction and ion exchange.

There is no single textbook that covers in the desired level of detail all of the material of interest, hence reading material will be provided either directly or through the use of library resources. Heavy emphasis will be placed on “classics” from the historic literature, excerpts of which will be distributed electronically as needed. Many of these books are out of print, but some can be found in online “bookstores” like Amazon. The primary source materials are identified below.

Bibliography (all are recommended for different purposes – excerpts from these materials (constituting required reading material) will be distributed as needed for reference/background):

George H. Nancollas, *Interactions in Electrolyte Solutions*, Elsevier, 1966

Herbert Harned and Benton Owen, *The Physical Chemistry of Electrolytic Solutions*, Rheinhold Publishing, 1958

R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworth Scientific Publications, 1955

J. Burgess, *Metal Ions in Solution,* Ellis Horwood Ltd. 1978

F. J. C. Rossotti and H. Rossotti, *The Determination of Stability Constants,* McGraw-Hill, 1961

C. S. G. Phillips, R. J. P. Williams, *Inorganic Chemistry, Volume I and II*, Oxford University Press, 1965

A. E. Martell, R. M. Smith, *Determination and Use of Stability Constants,* VCH, 1988 et seq.

K. A. Connors, *Chemical Kinetics: The Study of Reaction Rates in Solution*, VCH, 1990

C. Baes, R. Messmer, *The Hydrolysis of Cations,* Krieger Publishing Co., 1976

F. Helfferich, *Ion Exchange*, Dover, 1995 (previously by McGraw-Hill, 1962)

R. G. Bates, *Determination of pH*, *Theory and Practice,* Wiley 1964 (earlier under a different title)

J. Rydberg, M. Cox, C. Musikas, G. R. Choppin, *Solvent Extraction Principles and Practice, Second Edition,* Marcel Dekker, 2004

GRADING: There will be an in-class mid-term exam and final examination, quite probably of a take-home nature (each exam represents 40% of semester grade). In addition, there will be a literature reading/research exercise on water structure (including a brief written report and discussion period in which all will participate during weeks 1-4 – 10% of semester grade). Later in the semester, there will be a computer-based exercise in data acquisition from the NIST Stability Constant database and speciation prediction using HYSS 2009 (10% of semester grade). Cooperation and collaboration on reading and any homework assignments is encouraged, but you are cautioned to learn the material, as this support group will not assist with examinations (nor can they help you during Preliminary Exams later, except during preparation). Class participation is important, as the preferred means of learning is dialog rather than the spewing of facts (and opinions) by the instructor. Class participation will also be given consideration in establishing semester grade.

There will be at least a couple of occasions when Dr. Nash will be absent. Dr. Joseph (Joey) Lapka will lead the class on those occasions.

Students with Disabilities:
Reasonable accommodations are available for students with a documented disability. If you have a disability and need accommodations to fully participate in this class, please either visit or call the Access Center (Washington Building 217; 509-335-3417) to schedule an appointment with an Access Advisor. All accommodations MUST be approved through the Access Center. For more information contact a Disability Specialist on your home campus:

Pullman or WSU Online: 509-335-3417
http://accesscenter.wsu.edu, Access.Center@wsu.edu

Spokane: http://spokane.wsu.edu/students/current/studentaffairs/disability/
Tri-Cities: http://www.tricity.wsu.edu/disability/
Vancouver: 360-546-9138 http://studentaffairs.vancouver.wsu.edu/student-resource-center/disability-services

Academic integrity statement:
Serious chemistry graduate students wouldn't contemplate cheating, as the principal harm would be self-inflicted wounds. The course will be structured such that cheating is virtually impossible – or (officially), *As an institution of higher education, Washington State University is committed to principles of truth and academic honesty. All members of the University community share the responsibility for maintaining and supporting these principles. When a student enrolls in Washington State University, the student assumes an obligation to pursue academic endeavors in a manner consistent with the standards of academic integrity adopted by the University. To maintain the academic integrity of the community, the University cannot tolerate acts of academic dishonesty including any forms of cheating, plagiarism, or fabrication. Washington State University reserves the right and the power to discipline or to exclude students who engage in academic dishonesty.*

Safety and emergency notification:
Pullman: "Washington State University is committed to enhancing the safety of the students, faculty, staff, and visitors. It is highly recommended that you review the Campus Safety Plan (http://safetyplan.wsu.edu/) and visit the Office of Emergency Management web site (http://oem.wsu.edu/) for a comprehensive listing of university policies, procedures, statistics, and information related to campus safety, emergency management, and the health and welfare of the campus community."

Student Learning Outcomes: This graduate-level chemistry course is designed to inform and educate graduate chemistry and material science students in the chemistry of reactions occurring in condensed liquid media emphasizing aqueous systems, organic media of relevance to liquid-liquid extraction reactions, and mixed biphasic systems (which constitute the most complex solution chemistry systems). It is expected that successful participants will have gained insights into the field that are far above that of the general population. As prospective chemistry Ph.D. candidates, the overarching student learning outcome is for the students to begin to develop a more sophisticated approach to solving complex problems (which is what most Ph.D. scientists are expected to do) through the reading of descriptions of prior knowledge on the subject, in class discussions of these concepts, and through opportunities to critically evaluate and use information from the chemical literature. Progress will be evaluated in the two exams, written exercises, and class discussions.

The course features approximately 85% faculty lectures/15% student-centered discussions. Student performance will be judged based on their performance on mid-term and final examinations (40% each), 20% on planned exercises with adjustments made for active participation in class activities. Aside from the above mentioned exercises, no "homework" will be assigned aside from a considerable quantity of reading materials transmitted to the students electronically by the instructor.

Approximate Schedule

Week 1 (Aug 25) – Introductions/water as a solvent/ions in solution

Spectroscopy assignment (Weds)

Week 2 (Sep 1) – **LABOR DAY (no class)**/ions in solution/ionic models

Week 3 (Sep 8) – *KN away on official travel (return 9/17)* Solvent Properties (Marcus)/Ionic Strength/activity **(Lapka)**

Week 4 (Sep 15) – Experimental methods for activity determination/conductivity theory **(Lapka Monday)**

Spectroscopy writeup/discussion (Weds)

Week 5 (Sep 22) – Conductivity/mobility/transport #s/ion pairs/Bjerrum

Week 6 (Sep 29) – Electrochemistry/s-l interface/glass electrodes/ISE

Week 7 (Oct 6) – titrations → pK_a → log K/ NIST database/Martell data analysis

Week 8 (Oct 13) – **Mid-term Exam (Monday)/** stability constant methods/Hydration and Hydrolysis of metal ions

Week 9 (Oct 20) – water/solvent exchange dynamics/demo NIST/HYSS/discuss thermodynamics transition metal complexes

NIST/HYSS speciation assignment (Weds)

Week 10 (Oct 27) – *KN away on official travel, return 10/31*

Lanthanide/actinide complexation thermodynamics/correlations ΔH, ΔS/Solvent Extraction basic concepts **(Lapka)**

Week 11 (Nov 3) – Solvent extraction thermodynamics/phase transfer kinetics (liquid-liquid interfaces)/hydrometallurgy strategic metals

NIST/HYSS Speciation Due (Weds)

Week 12 (Nov 10) – Separations in the nuclear fuel cycle/Ion Exch/EC/plant scale vs analytical separations

Week 13 (Nov 17) – *KN away on official travel 11/19-21*. Conventional TALSPEAK solution chemistry/Advanced TALSEPAK SC/mixed extractant systems **(Lapka Wed Fri)**

Week 14 (Nov 24) – THANKSGIVING Break

Week 15 (Dec 1) – Kinetics and mechanisms of interactions in solutions/theories and experiments

Week 16 (Dec 8) – Loose ends etc./topics of opportunity/review

Week 17 (Dec 15) - ***Final exam as scheduled or as we can work it in***