Fall, 2017 **Chem 529 – Advanced Solution Chemistry**

2 credit hours

LECTURES: Weds., Fri. 1:10-2:00 PM, Fulmer 432

INSTRUCTOR: Prof. Kenneth Nash

Office**:** Fulmer 639 **Phone:** 335-2654 **Email:** knash@wsu.edu

Office hours: usually available as needed

PREREQUISITES: Basic math skills, understanding of physical chemistry

Student Learning Outcome: Upon completion of this course, the student should have significantly improved understanding of solvent-solute interactions in aqueous/non-aqueous/biphasic interactions that define chemistry in condensed fluid media.

COURSE STRUCTURE AND FOCUS: This is a two credit hour, graduate level Chemistry course. As such, it is expected that students will be in attendance regularly, will inform the instructor of scheduled absences, and expend effort appropriate for success as a graduate student. In this course, explorations of the fundamental nature of solvent-solvent and solvent-solute interactions in condensed fluid media (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 explore in some detail 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. Some attention will be given to experimental techniques for determining chemical equilibrium constants, possibly 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 there will be significant amount of time 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 will be provided from the books identified below.

ALL FEATURES OF THE STRUCTURE AND SCHEDULING ARE SUBJECT TO ADJUSTMENT BASED ON MUTUAL AGREEMENT BETWEEN THE INSTRUCTOR AND STUDENTS.

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 (or take home) mid-term exam and final examination (not cumulative), quite possibly of a take-home nature (each exam represents 30% of semester grade). Starting in week 3, we will review/critique published papers from the literature (including a brief written report and discussion period in which all will participate) via student-led discussions. This exercise will be a weekly feature of the class from week 3 through week 15 – 20% 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 (20% of semester grade). Cooperation and collaboration on reading and any homework assignments is encouraged, but students 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 a couple of occasions when Dr. Nash will be absent due to travel obligations; during these periods, students will be assigned literature reading, reviewing, writing exercises.

Grading scale 100-90 (A), 90-80 (B), 80-70 (C), 70-60 (D), > 60 (F) (subject to normalization

Students with Disabilities:

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 [Pullman] or Disability Services at [name of campus] address on your campus] to schedule an appointment with an Access Advisor. All accommodations MUST be approved through the Access Center or Disability Services. 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

Academic integrity statement:

Academic integrity is the cornerstone of higher education. As such, all members of the university community share responsibility for maintaining and promoting the principles of integrity in all activities, including academic integrity and honest scholarship. Academic integrity will be strongly enforced in this course. Students who violate WSU's Academic Integrity Policy (identified in Washington Administrative Code (WAC) 504-26-010(3) and -404) will receive [*insert academic sanction (e.g., fail the course, fail the assignment, etc.*)], will not have the option to withdraw from the course pending an appeal, and will be reported to the Office of Student Conduct.

Cheating includes, but is not limited to, plagiarism and unauthorized collaboration as defined in the Standards of Conduct for Students, WAC 504-26-010(3). You need to read and understand all of the definitions of cheating: http://app.leg.wa.gov/WAC/default.aspx?cite=504-26-010. If you have any questions about what is and is not allowed in this course, you should ask course instructors before proceeding. If you wish to appeal a faculty member's decision relating to academic

Classroom Safety Statement

Classroom and campus safety are of paramount importance at Washington State University, and are the shared responsibility of the entire campus population. WSU urges students to follow the "***Alert, Assess, Act***," protocol for all types of emergencies and the *"Run, Hide, Fight"* response for an active shooter incident. Remain ***ALERT*** (through direct observation or emergency notification), ***ASSESS*** your specific situation, and ***ACT*** in the most appropriate way to assure your own safety (and the safety of others if you are able).

Please sign up for emergency alerts on your account at MyWSU. For more information on this subject, campus safety, and related topics, please view the *FBI's Run, Hide, Fight video* and visit the *WSU safety portal*.

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 80% faculty lectures/20% student-centered discussions. Student performance will be judged based on their performance on mid-term and final examinations (30% each), 40% on planned reading/writing/presenting 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 21) – Introductions/water as a solvent/ions in solution

Week 2 (Aug 28) –ions in solution/ionic models

Week 3 (Sep 4) – **LABOR DAY week** Solvent Properties (Marcus)/Ionic Strength/activity

Week 4 (Sep 11) – Experimental methods for activity determination/conductivity theory

Week 5 (Sep 18) – Conductivity/mobility/transport #s/ion pairs/Bjerrum

Week 6 (Sep 25) – Electrochemistry/s-l interface/glass electrodes/ISE

Week 7 (Oct 2) – titrations - pKa - log K/ NIST database/Martell data analysis

Week 8 (Oct 9) – **Mid-term Exam (Wednesday)/** stability constant methods/Hydration and Hydrolysis of metal ions

Week 9 (Oct 16) – water/solvent exchange dynamics/demo NIST/HYSS/discuss thermodynamics transition metal complexes

NIST/HYSS speciation assignment (Weds)

Week 10 (Oct 23) – Lanthanide/actinide complexation thermodynamics/correlations ΔH, ΔS/Solvent Extraction basic concepts

Week 11 (Oct 30) – Solvent extraction thermodynamics/phase transfer kinetics (liquid-liquid interfaces)/hydrometallurgy strategic metals

NIST/HYSS Speciation Due (Weds)

Week 12 (Nov 6) – ISEC – NO CLASS – READING WRITING ASSIGNMENT

Week 13 (Nov 13) –Conventional TALSPEAK solution chemistry/Advanced TALSPEAK SC/mixed extractant systems

Week 14 (Nov 20) – **THANKSGIVING Break**

Week 15 (Nov 27) – Kinetics and mechanisms of interactions in solutions/theories and experiments

Week 16 (Dec 4) – Loose ends etc./topics of opportunity/review

Week 17 (Dec 11) - ***Final exam as scheduled or as we can work it in***