

CHEM.422 Spring 2009 (2008-3)

C422.Spring.09-2

Relationship to other courses:

The pre-requisite is CHEM.420. Chemistry Seniors would normally also register for Inorganic Lab (CHEM.425) this quarter. CHEM422 is co- (or pre-)required for CHEM.425, though the reverse does not apply.

Planned Course Content.

Optical Spectra, Continued:

Products of representations, symmetry-based selection rule; application to CT; state symmetries and Tanabe-Sugano diagrams.

Background to some experimental methods.

- Introduction to inorganic electrochemistry: potentiometric measurements, (cyclic) voltammetry.
- Application of group theory: IR & Raman spectra for molecular vibrations.

Organometallic and other low oxidation-state compounds:

The synergic bonding model; electron-counting rules for constitutions & structures of binary metal carbonyls; nitrosyl complexes.

Complexes with alkenes, alkynes, dienes; allyls, $16e^-$ complexes.

Metallocenes, arenes, fluxionality.

Phosphine complexes, cone angle; electronic & steric factors.

Metal alkyls, metatheses; Oxidative addition.

Kinetics of substitution at T.M. centres:

Lability & inertness. Mechanism: associative, dissociative, interchange; Experimental aspects.

CFAE and other ligand effects. Solvolysis, anation. Square-planar associative, *trans*-effect

Special topic:

Combinatorial Chemistry. Elementary parallel and combinatorial approaches to inorganic synthesis; screen and array concepts.

Biological examples.

HSAB concept. Evolution of metals in biosphere. Protein structure.

Porphyrins as synthetic & natural macrocycles. Oxygen transport: hemocyanin & myoglobin; other small molecule binding by Mb, Hb.

Text Sources:

- 1) Shriver & Atkins: : *Inorganic Chemistry*. 4th Edn., Freeman 2005, or Housecroft & Sharpe: *Inorganic Chemistry*. The text has related web-based illustrative materials at: www.whfreeman.com/ichem
- 2) A. Vincent: *Molecular Symmetry & Group Theory*. 2nd Edn., Wiley, 2000.
- 3) Lecture notes will be available.
- 4) On Reserve in Hagerty Library: (i) C. Elschenbroich & A. Salzer's *Organometallics - a Concise Introduction* ; (ii) K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, New York : Wiley, 1986.

Objectives: Be able to assign transitions or transition types in electronic spectra of metal complexes. Determine potentials from voltammograms, predict the directions of redox reactions from E (E° , E_f , $E_{1/2}$) data. Appreciate the general and specific mechanistic properties of metal complexes with respect to ligand substitution reactions; understand how the various types of experimental results relate to the different mechanistic conclusions; be able to predict whether given metal centres are inert or labile. Use the $18\bar{e}$ rule to correlate with molecular stability/reactivity; appreciate the possibilities for, modes for, and consequences of binding of unsaturated acyclic hydrocarbon centres to transition metals; know about binding modes for, and how to correlate structure and composition with \bar{e} -counting rule formulations for cyclopentadienyl and other π -arene and NO complexes, including a metallocene MO scheme. Be able: to correlate steric effects for ligands in relationship to their cone angle values; to devise synthetical pathways for organometallic species; to predict the products of oxidative addition reactions. Be aware of contemporary multiple parallel synthetic methods, the need for screening and deconvolution, and the advantages of arrays. Appreciate various essential or undesirable rôles of metals in biological chemistry; know modes by which structural differentiation amongst metal-containing active sites is effected and how it steers metalloprotein function.

Other stuff: Work on the problem sets when I provide them ! Attempt to solve the homework problems as soon as we have covered the material in class. If you do not do the homework, you will find it hard to pass the exams, and virtually impossible to get a good grade. Your grade is based on the (usually three) exams: two midterms (15%, 25%) plus a final exam (60%). If you are not registered in the course, no midterms or quizzes will be graded or returned. Note that I subtract points on exams for incorrect spelling of chemical terms, particularly: valence (not that I'm so keen on this term anyhow), pyramid/pyramidal, fluorine, fluorescence, *etc.*

The 10-Minute Rule: If I'm more than ten minutes late, consider the class cancelled. If you are going to be more than ten minutes late for a class, please don't enter without prior arrangement. My grade ranges are: D= 43-45; D+=46-49; C-=50-53; C=54-56; C+=57-59; B-=60-64; B= 65-69; B+=70-75; A-=76-83; A=84-91; A+=92-100.

Much communication about exams, problem sets, *etc.*, will be by email, but don't let this comment discourage you from coming to see me. My students are important to me !

Make-Up Exams ?

You don't need an excuse to take the make-up exam if you miss a midterm or final. But you must then attend the make-up at the designated time and place or take a zero on it - no excuses. The required final exam will likely be on Tuesday June 9th. The make-ups will be held shortly thereafter - likely on the 11th. Tentative midterm dates are April 28th & May 19th. Graduating Seniors might wish to review the university policies on Final Examinations and Senior Privilege: (<http://www.drexel.edu/provost/policies/examinations.asp>)

Prof. Addison: 12-418; 215-895-2646; AddisonA@drexel.edu.