CHEM.523 Spring 2006 (2005-3)

Relationship to other courses:

The pre-requisite is CHEM.522.

Planned Course Content.

Background to some experimental methods.

• Optical spectra; application of group theory - sums & products of representations: spin & symmetry selection rules (simple doublet states); CT transitions.
• Application of group theory: Raman spectra for molecular vibrations.
• Introduction to inorganic electrochemistry: potentiometric measurements, (cyclic) voltammetry.

Special topic:

• Valence & hypervalence.

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

Organometallic and other low oxidation-state compounds:

The Eighteen-Electron Rule; Simple carbonyls; synergic bonding model; MO's for complexes with π-bonding. Constitutions & structures of binary metal carbonyls.

Complexes with alkenes, alkynes, dienes; allyls, 16ē complexes.
Metallocenes, arenes, fluxionality.
Phosphine complexes, cone angle; electronic & steric factors.
Nitrosyl complexes; Metal alkyls, metatheses; Oxidative addition.

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) Housecroft & Sharpe: *Inorganic Chemistry*. 2nd Edn., Prentice-Hall 2005. The text has related web-based illustrative materials at:
http://wps.pearsoned.co.uk/ema_uk_he_housecroft_inorgchem_2
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 decide whether electronic and vibrational transitions are allowed or forbidden in simple cases. Distinguish amongst various types of electronic transitions in 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. Be able to correlate symmetry-based MO schemes for molecules with models for synergic (σ, π) bonding in complexes of unsaturated ligands; 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.

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.

Much communication about exams, problem sets, *etc*., will be by Email.

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. Tentative midterm dates are April 27th & June 1st. The final exam will be on Monday June 12th or Thurs. June 15th. The make-ups will be held shortly thereafter - on the 13th (or 19th, if the final is on the 15th).

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