SYLLABUS
CHEMISTRY 402/502
Spring, 2019

Advanced Inorganic Chemistry

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Office Hours:
Monday 1:30-3:00 pm
Thursday 9:00-10:30 am
(and by appointment)

Course Description: This course is intended for chemistry majors and graduate students. It is designed to help prepare the student for graduate school or employment in the physical sciences. The course is intended to expand the student's knowledge base in inorganic chemistry by providing new ways of understanding molecular orbitals, bonding, and reactivity. The mathematics of symmetry is applied to chemical issues, such as bonding, spectroscopy and crystallography. Organometallic and solid state chemistry are introduced and a number of physical and analytical instrumental techniques are discussed.

Texts: G. L. Miessler, P. J. Fischer, and D. A. Tarr, Inorganic Chemistry, 5th ed.; Prentice Hall: Upper Saddle River, NJ, 2014.

L. E. Smart and E. A. Moore, Solid State Chemistry, 4th ed. CRC Press, Boca Raton, FL, 2012.

Supplementary Texts on Reserve in ISC 1022:

F. A. Cotton, Chemical Applications of Group Theory, 3rd ed.; Wiley: New York, 1990.
A. F. Hill, Organotransition Metal Chemistry; Wiley-Interscience: New York, 2002.
E. A. V. Ebsworth, D. W. H. Rankin, and S. Cradock, Structural Methods in Inorganic Chemistry, 2nd ed.; CRC Press: Boca Raton, FL, 1991.

Lectures: Monday, Wednesday, Friday, 9:30–10:50 am, Integrated Science Center 2018.

Examinations: (20, 20, 15%) February 25/26*, March 28*/29, April 18/19*. (*No lecture)

Each exam is given in a self-scheduled two hour block. On the starred date there will be no lecture, so this time can be used as part of the exam time. The lowest of the three exam grades for each student will be counted as 15%, while the other two exam grades will count 20% each.

Final Examination: (30%) Take-home final to be completed during a 48-hour block by May 3.

Problem Sets: (15%) These are very important to your success in the course for two reasons: (a) They count as 15% of the grade and (b) They will prepare you for the sort of material that will appear on the exams. Late submission of problem sets will not be permitted. Collaboration is allowed on the problem sets, but it is important develop independent skills for use in the exams.

Master's Requirement X-ray Crystallography Practicum: (Chem 502: required, Chem 402: extra credit – replaces one problem set with full credit)

The student is expected to grow crystals, solve a crystal structure (with the instructor's help). Master's students must write a report on the details and novelty of the structure with information from the Cambridge Crystallographic Database. The compound(s) chosen can be inorganic or organic and can originate from the student's own research or be an off-the-shelf solid.

Course Outline: Chapter reading assignments in Miessler, Fischer, & Tarr (MFT) and Smart & Moore (SM) indicated in parenthesis.

I. Introduction to the Study of the Transition Metals (MFT 6, 9, and handouts)

- A. The Basics
    1. Why the transition metals?
    2. Oxidation states and natural occurrence
    3. Electron counts
- B. Ligands
    1. Lewis acids and bases and coordinate covalent bonding
    2. L and X type ligands
    3. Polydentate ligands and the chelate effect
    4. Hard and soft acids and bases
    5. Non- and weakly-coordinating anions
- C. Coordination geometry and isomerism
    1. Geometric isomerism
    2. Optical isomerism
    3. Structural isomerism

II. Group Theory (MFT 4, SM 1, and handouts)

- A. Introduction
- B. Basic definitions and theorems regarding mathematical groups
- C. Assignment of symmetry
    1. Symmetry elements
    2. Symmetry operations
    3. Point groups
- D. Some elementary applications of symmetry
    1. Chirality
    2. Dipole moment
    3. Chemical equivalence
- E. Matrix representations of groups
    1. Transformation matrices
    2. Character tables
    3. Reducible and irreducible representations
    4. Reduction of representations
- F. A further application of group theory – vibrational spectroscopy
    1. Vibrational modes of H_2O
    2. Vibrational modes of $(CO_3)^{2-}$
    3. Vibrational modes of $[Mo(CO)_4(P(OPh)_3)_2]$ isomers and $[Cr(CO)_6]$

III. Symmetry-based Molecular Orbital Theory (MFT 5, 10)

- A. Introduction to LCAO-MO
- B. Second row diatomic molecules
    1. Homonuclear diatomics, N_2
    2. Heteronuclear diatomics, CO

- C. Molecules of type: AB_n
    1. $(CO_3)^{2-}$
    2. $[FeF_6]^{3-}$
- D. Crystal field theory
    1. Crystal field theory
    2. Contributions to Δ_o from the metal
    3. Contributions to Δ_o from the ligands
    4. Spectrochemical series
    5. Other coordination geometries and crystal field stabilization energy
    6. Jahn-Teller effect

IV. Organometallic Chemistry - (MFT 13, 14)

- A. Introduction - The eighteen electron rule
- B. A survey of organometallic ligands and their complexes
    1. π-Acid ligands
        - a. carbonyl
        - b. phosphine and phosphite
        - c. nitrosyl
        - d. cyanide and isocyanide
        - e. dinitrogen and dioxygen
        - f. dihydrogen
        - g. alkylidene and alkylidyne
    2. π-Olefin ligands
        - a. ethylene and acetylene
        - b. butadiene and benzene
        - c. allyl and cyclopentadienyl
    3. σ-Donor ligands
        - a. alkyl
        - b. hydride
        - c. halide
        - d. bridging donors and agostics
- C. Reactions of organometallic complexes
    1. Ligand dissociation and substitution
    2. Oxidative addition and reductive elimination
    3. Migratory insertion and deinsertion
    4. Hydride elimination and abstraction
    5. Nucleophilic and electrophilic attack at coordinated ligands
- D. Homogeneous catalytic cycles
    1. Acetic acid syntheses
    2. Hydroformylation
    3. Hydrogenation
    4. Olefin metathesis and cyclooligomerization
    5. Ziegler-Natta polymerization

V. Physical Methods in Inorganic Chemistry (SM 1, 2 and handouts)
- A. NMR spectrometry
  - 1. Nuclei for inorganic NMR
  - 2. NMR analysis of non-rigid compounds
    - a. fluxionality *vs.* tautomerism
    - b. NMR line-broadening
    - c. ring whizzing
    - d. polyene rotation
    - e. ligand exchange
  - 3. Solid state NMR
- B. X-ray techniques
  - 1. Generation and diffraction of X-rays
  - 2. The unit cell and Miller indices
  - 3. Space group symmetry
    - a. crystal systems and Bravais lattices
    - b. new symmetry operations: the glide plane and screw axis
    - c. space groups and systematic absences
  - 4. Diffraction techniques: powder vs. single crystal
  - 5. X-ray fluorescence and X-ray photoelectron spectroscopies
- C. Electrochemical techniques
  - 1. Cyclic voltammetry
  - 2. Spectroelectrochemistry
  - 3. Electron paramagnetic resonance spectrometry

VI. The Solid State (SM 3, 4, 5, 6)
- A. Kinds of solids
  - 1. States, phases and phase diagrams
  - 2. Crystalline and amorphous compounds
  - 3. Unary, binary, ternary materials
- B. Solid synthesis techniques
  - 1. Solid heating of solids
  - 2. Hydrothermal synthesis
  - 3. Chemical transfer agents
  - 4. Chemical vapor deposition
  - 5. Epitaxy
- C. Band theory and conductivity
  - 1. Metals
  - 2. Semiconductors
- D. Ionic lattices and applications
  - 1. Ionic lattices
  - 2. Defect structures
- E. Porous Materials
  - 1. Zeolites
  - 2. Clays
  - 3. Metal-organic frameworks