CHEMISTRY 531
CHARACTERISTICS OF INORGANIC COMPOUNDS
STUDY GUIDE TO THE THIRD EXAMINATION

The third examination will be of the same format as the first two. It will be held during the alternatives period at a time agreeable to the class. The outlines must be turned in by their due dates! The exam will cover chapter 19 through chapter 28 and materials chemistry as outlined.

Ch 19 - Coordination Compounds:

1) Stereochemistry of coordination numbers 2-10. Types of isomerism. Crystal field theory. Molecular orbital diagram of $O_h$ complex. Complementary Colors of absorption and observation. Free ion terms, splitting of free ion term in cubic fields. The "hole" formalism and state inversions on $O_h$ to $T_d$. Crystal field stabilization energies (CFSE) of "d" electron configurations. Relative value of $\Delta_o$ vs $\Delta_e$. The effect on color of complexes of an octahedral to tetrahedral transformation, effect on absorption intensity. Magnetism of complexes, spin only moment, spin orbit coupling (SOC), effect of SOC on magnetic moment, occurrence of SOC. The spectrochemical series, pi donor ligands, pi acceptor ligands, their effect on, molecular orbital diagrams explaining this effect. The effect of tetragonal distortions on octahedral ligand fields and orbital energies, Jahn-Teller distortions and where they occur. A familiarity with Tanabe Sugano Diagrams, there use in interpreting UV-VIS spectra.

2) Be able to describe/illustrate the sigma and pi bonding of a transition metal atom(s) to a) an alkyl ligand, b) an alkylidene (carbene) ligand, c) an alkylidyne (carbyne, cf nitrido). Consider the (de)stabilizing effect of alpha substituent groups or heteroatoms on the strength of the metal-carbon bonding. Consider the influence of beta-hydrogen atoms on the stability of each of the above. Consider whether the ligand is acting as an electron donor or acceptor in each sigma and pi bonding interaction.

3) Be able to describe/illustrate the sigma and pi bonding of a transition metal atom(s) to a) an $\eta^2$ olefin (alkene) ligand, b) a two-electron donor acetylene ligand, c) a four-electron acetylene donor ligand, d) an $\mu^2\eta^2$ acetylene ligand, e) an allyl ligand and f) $\eta^4$cyclopentadienyl ligand. In parts a) and b) consider the effect on the Dewar-Duncanson bonding model of extensive ligand $\pi$-acceptor/metal donor character. Describe an alternative bonding model which reflects this extreme state of affairs. Be sure to consider orbital overlaps, types of bonds, bond orders, bond angles, hybridization, relative bond lengths and how substituents will affect sigma and pi bonding. Be able to describe and use the "hapto" system and illustrate how a given ligand may have variable hapticities and how this is independent of the electron contribution.

4) Consider the various ways carbon monoxide may bond to transition metals. Be able to describe the bonding, molecular orbital diagram, illustrate the molecular orbital shapes in a terminal CO, illustrate orbital overlaps for a bridging CO. Be able to describe the bonding of NO its similarities and differences to CO. Ditto N$_2$. 
Use the following subjects to construct outlines for the final chapters.

Ch 20/21/22 - Sc, Y, La, Ac; Ti, Zr, Hf; V, Nb, Ta:

Ch 23/24/25 - Cr, Mo, W; Mn, Tc, Re; Fe, Ru, Os:
- Jahn-Teller distortions in $\text{CrF}_6^{4-}$. Metal-metal bonding in $[\text{M}_2\text{Cl}_6]^{3-}$ clusters of Cr, Mo, W. Bonding in $[\text{M}_6\text{Cl}_8]^{4+}$ clusters of Cr, Mo, W. Metal-metal bonding (bond order and bond length) in $[\text{Mo}_2\text{Cl}_6]^{4+}$, $[\text{Mo}_2\text{OAc}_4]$, $[\text{Re}_2\text{Cl}_8]^{2-}$, $[\text{Tc}_2\text{Cl}_8]^{2-}$, $[\text{Tc}_2\text{Cl}_8]^{3-}$. Be able to draw orbital overlaps showing how a quadruple bond is made. Be able to describe the metalloccyclobutane mechanism of the "olefin metathesis" reaction in which propylene is catalytically converted into ethylene and butylene. Show the active catalyst and describe the active site. Describe the structure of the simplest binary carbynls of each metal and the following anions: $\text{Fe(CO)}_4^{2-}$, $\text{Mn(CO)}_5^-$, $\text{Fe}_2\text{(CO)}_8^{2-}$. Describe the manipulations required to construct the molecular orbital diagram of the "osmyl" group (p 1261), the $[\text{Cl}_3\text{Ru-O-RuCl}_3]^{4+}$ (p 1264) and obtain the proper bond orders. Structures and bonding in Re$_3$Cl$_9$ clusters. Structures and EAN in clusters: $[\text{Fe}_4\text{(CO)}_{13}]^{2-}$, $[\text{Os}_6\text{(CO)}_{18}]^2$. Properties and magnetism in bis cyclopentadienyl metal derivatives.

Ch 26/27/28 - Co, Rh, Ir; Ni, Pd, Pt, Cu, Ag, Au:
- The effect of ligand field on the Co(II)/Co(III) couple. The effect of changing the Cl$^-$ concentration in an aqueous solution of Co$^{2+}$ (color changes blue to pink). Mechanism of the hydrogenation of olefins by Wilkinson's catalyst, $\text{RhCl(PPh}_3)_3$. The mechanism of hydroformylation of propylene with Wilkinson's $\text{Rh(CO)H(PPh}_3)_3$. Describe the structure of the simplest binary carbynls of Co and Ni; the differences in structure of $[\text{M}_4\text{(CO)}_{12}]$, $\text{M} = \text{Co, Rh and Ir}$. The Reppe synthesis. Structure and EAN in Clusters: $\text{Ir}_4\text{(CO)}_{12}$, $\text{Rh}_6\text{(CO)}_{12}$, $[\text{Ni}_5\text{(CO)}_{12}]^{2-}$, $[\text{Ni}_6\text{(CO)}_{12}]^{2-}$, $[\text{Pt}_3\text{(CO)}_6]^{2-}$ ($n = 2,3$), $[\text{CuXL}]_4$ ($L = \text{PR}_3, \text{AsR}_3, X = \text{hal.}$), $[\text{Cu}_4\text{(SPh)}_{6}]^{2-}$, $\text{CuOCl}_6(\text{OPPh}_3)_4$. Properties and magnetism in bis cyclopentadienyl metal derivatives.

Review $B_6\text{H}_6$ closo-hydridoborane anion BONDING from Ch 7 (Boron). Review Wade's rules as they apply to closo-clusters of $\text{M}_3-12$.

Materials Chemistry:
The Solid State taken from “Inorganic Chemistry”, by Catherine E. Housecroft & Alan G. Sharpe. Consider the following: close packing of spheres; alloys/intermetallic cmpds; crystal defects & F-centers; band structure of insulators, metals, semiconductors (intrinsic/extrinsic); conduction in ionic solids (electron & ion); basics of CVD methods.