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

The examination will be similar in format to the first exam. You will have a choice of questions. Chapter outlines must be turned in to JLA by their due dates. They will be returned to you immediately prior to the exam (make copies to study by!). The exam will cover chapter 8 through chapter 18.

1) Consider graphite intercalation compounds, the idealized stoichiometries of Stage 1-4 potassium intercalates. Suggest reasons for the uniform staging of intercalates from an energy standpoint, the long-range order of the cations (and by analogy anions). The intercalates of the halogens other than fluorine are analogous but differ, how so. Why does fluorine behave differently.

2) Consider the geometry of fullerenes, what generalizations can be made about those individuals which are most readily prepared and hence more stable. Consider the electron density distributions in C₆₀, in La@C₆₀. Consider the composition and electronic properties of the alkali fullerides. Into what reaction category do the unsaturated rings of C₆₀ fall? What are some example reactions. What is the structural relationship of one structural model of the Ti₈C₁₂ metallocarbohedranes to the fullerenes. What other structural models can be used to describe them.

3) Give a basic description of the early transition metal interstitial carbides. Why is this description not applicable to the carbides of TM’s beyond group 6. Use the delocalized bonding model of metallic bonding to explain the remarkable changes in metallic properties which occur on incorporation of carbon into the early TMs.

4) Consider the environment of a carbido-carbon atom at the center of a closo-octahedral cluster of metal atoms. What molecular orbital bonding scheme might you derive for the CM₆ unit in the vicinity of the carbon atom. What similarities/differences do you notice between molecular orbitals derived for a closo-octahedral cluster of metal atoms with and without the carbon atom (a O₄ character table might be helpful).

5) Consider the effect on the chemical properties of organic functional groups when they are bonded to alkyl/aryl (R) groups versus the corresponding perfluoroalkyl (Rₗ) groups. Consider the ligating ability of CO₂ and CS₂.
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6) What are the basic structural units of silicates? How may they be structurally related to the various types of silicones? Describe the Rochow synthesis and how the products are used in silicone synthesis. What property gives the silicates and silicones great stability. What property causes the higher silanes to decompose?

7) Be able to compare/contrast the properties and behavior of carbonic vs silicic acid and CO₂ vs SiO₂; C-X vs Si-X vs Ge-X vs Sn-X vs Pb-X bond strengths where X = themselves, C, Si, H, F, Cl, Br, I, O, N; basicity between amines and silyl amines, relative stabilities or ethers, silicones, "germaneones". Compare/contrast structures, properties and reactivities of Fluorides and chlorides of C, Si, Ge, Sn, Pb; the trends in metallic behavior, electronegativities of Group 14 elements.

8) Compare the ligating ability of NF₃, PF₃ and AsF₃ with transition metals. The bonding/structure, aggregation and F⁻ acceptor ability of PF₅, AsF₅, SbF₅ and BiF₅. The gaseous and solid phase bonding of PF₅, PCl₅ and PBr₅. Compare and/or contrast a) the structure and bonding in nitrogen and phosphorous oxides, oxoacids and oxoanions; b) the stability of covalent and ionic azides; c) The ligating ability and bonding of amines, phosphines and arsines to transition metals; d) The ligating ability, modes of bonding of NO₂⁻ and NO to transition metals.

9) Be able to describe and compare the structures and bonding in cyclophosphazenes having six and eight membered rings. Describe a phosphorous alkylidene phosphorane (Ylid). Account for the unusual strength and stability of the P=O group.

10) The following clusters have been characterized: Bi₃⁺ (D₃h), Ge₄²⁻ (Tₐ), P₄ (Tₐ), Sn₅²⁻ (tbp), Bi₅³⁺ (tbp), Bi₈²⁺ (sq. antiprism), Sn₉⁴⁻ (capped sq. antiprism). Be able to use Wades rules to determine the number of electron pairs needed to satisfy each structural type, determine the electrons available for bonding in each cluster, determine electron deficiency, sufficiency or excess and possible reflections in chemical behavior. Determine for each cluster the orbitals and electron utilization in cluster and non cluster binding. Be able to draw the structures and indicate pictorially the kinds of orbital overlaps that can occur.
Ch 14 - Oxygen:

Be able to describe/explain a) the electronic states and the molecular orbital diagram of O_2; b) the orbital overlaps, bonding and energy level diagram for O_2 bonded to a transition metal in Dewar Duncanson mode; c) other modes of O_2 to transition metal bonding. d) Bonding in O_2F_2 and O_2H_2; ozone. e) Reactions of "singlet oxygen" and explanation of similarities of TM and dye sensitized oxidations.

Ch 15/16 - Sulfur; Selenium, Tellurium and Polonium:

Bonding in and similarities between S_4^{2+} and S_2N_2; S_8^{2+} and S_4N_4; Modes of bonding of S and S_2 to transition metals. Reactions which make S-S bonds; structures of sulfanes. Sulfur fluorides, chlorides: synthesis, structures and reactions. Structures/names of oxoacids/oxoanions of sulfur. Acid strengths/structures of oxoacids and hydrides -group trends. S, Se & Te cations. Structure/bonding in [Te_6]^{4+} cluster application of Wade's rules.

Ch 17/18 - Halogens/Noble Gases: