HW 5
CHEM 362

Available: March 17, 2008 Due: March 24, 2008

1. What is the practical definition of a transition element? What fraction of the approximately 111 elements are of this type?

2. What are some of the important characteristics of transition elements?

3. What do the terms low-spin (L.S.) and high-spin (H.S.) mean?

4. Predict the magnetic properties and the LFSE for the following:
When appropriate, explain why you chose a L.S. versus a H.S. electronic configuration.
   a. $[Fe(CN)_6]^{3-}$
   b. $[Co(H_2O)_6]^{3+}$
   c. $[Fe(H_2O)_6]^{3+}$
   d. $[CoF_6]^{3-}$
   e. $[Ru(NH_3)_6]^{2+}$
   f. $[Mn(H_2O)_6]^{2+}$
   g. $[CoCl_4]^{2-}$
   h. $[Cr(H_2O)_6]^{2+}$

5. Why are tetrahedral complexes usually not low spin?

6. Prepare a drawing that shows the π-bond system in CO that is responsible for it being a very strong ligand (it is at the high end of the spectrochemical series). Clearly show the donor orbital of the metal and the acceptor orbital of the CO ligand.

7. Prepare a diagram that shows how the d-orbital splitting pattern changes as an octahedral complex is altered via a tetragonal distortion that is first weak and then reaches the extreme case where a square, four coordinate complex is obtained.

8. How does Δ_o (10Dq) change on going from one octahedral metal complex to another with the same ligand set, but with the following changes:
   a. M^{3+} instead of M^{2+}
   b. A second row transition element instead of a first row transition element.

9. By using orbital diagrams for the five d orbitals, show which d^n (n = 0-10) configurations are capable of having both low-spin and high-spin configurations in an octahedral geometry.

10. Why are the d-d transitions weak? Why are the absorptions observed at all if they are Laporte (orbitally) forbidden?

11. What is the spectrochemical series and what limitations must be remembered when using it?

12. The complex $[NiCl_4]^{2-}$ is paramagnetic with two unpaired electrons whereas the compound $[Ni(CN)_4]^{2-}$ is diamagnetic. Deduce the geometries of the two compounds and explain the observations in terms of ligand field theory.

14. Make drawings of the d orbitals and state which of them fall into the category of e_g and which fall into the category of t_{2g} orbitals in an octahedral ligand field.

15. What is the Jahn-Teller Effect? How does one go about detecting it?

16. Consider a high-spin Mn^{2+} complex such as $[Mn(H_2O)_6]^{2+}$. Sketch the d orbitals and put the electrons in them. If one excites an electron from the t_{2g} to the e_g set, what will have to happen? What ramification does this have on the spectrum of the Mn^{2+} complex.