HW 5
CHEM 362
Answer Key

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?

A transition element is one that possesses a partially filled d or f orbital shell when involved in its chemistry. While the group 11 elements (Cu, Ag, Au) are considered elements because the common oxidation states shown by this set contain partially filled d-shells, the group 12 elements (Zn, Cd, Hg) are not transition metals because their reactions don't involve incomplete (less than d^{10}) d-shells. Of the 111 elements listed on the periodic table, 62 (36+26) are considered transition metals.

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

Transition elements are typically hard, strong, metals that conduct both heat and electricity very well. The compounds they form are often (but not strictly) highly colored and may exhibit paramagnetism.

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

The term high spin refers to a d-orbital splitting arrangement in which the maximum numbers of electrons are spin paired. That is, all the non-degenerate orbitals are filled according to maximum spin multiplicity (i.e. maximum number of unpaired electrons). In an octahedral field, where the d-orbitals are split into two sets (e_g and t_{2g}), a high spin d^5 configuration would result in all orbitals containing 1 unpaired electron (see below).

The term low spin refers to a d-orbital splitting arrangement in which the maximum number of electrons are spin paired. The degenerate orbitals are filled completely before filling orbitals of higher energy. In an octahedral crystal field a low spin d^5 configuration would have all 5 electrons in a t_{2g} level and only one electron would be spin unpaired (see below).
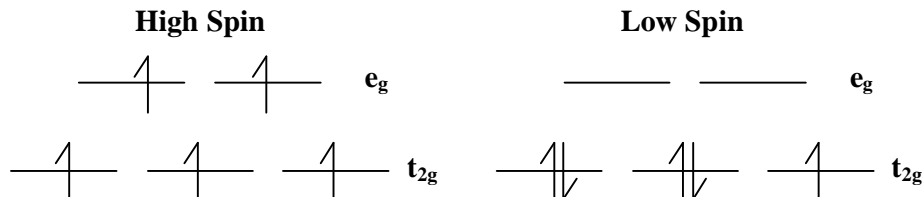
4.   Predict the magnetic properties and the LFSE for the following:
      When appropriate, explain why you chose a L.S. versus a H.S. electronic configuration.

Please note: I'm not drawing out the orbital splitting diagram for every problem, but that is where I'm getting the electronic configuration and the number of unpaired electrons. For reference compare problem 4a to the low spin d^5 diagram given in the answer for problem 3 (above).

a. $[Fe(CN)_6]^{3-}$
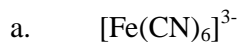
Fe^{III}, d^5. Cyanide is a strong field ligand so the complex will be low spin.
$t_{2g}^5 e_g^0 \rightarrow 5(-2/5\ \Delta_o) + 2P_E = -2\Delta_o + 2P_E$
1 unpaired electron → paramagnetic.

b. $[Co(H_2O)_6]^{3+}$

Co^{III}, d^6. Water is generally considered a weak field ligand (although it's in the center of the spectrochemical series.), so a high spin complex is expected. However, Co^{III} is generally low spin (without very weak field ligands). Since the lecture did not cover this either high spin or low spin answers will be accepted.
High Spin: $t_{2g}^4 e_g^2 \rightarrow 4(-2/5\ \Delta_o) + 2(3/5\ \Delta_o) + P_E = -2/5\ \Delta_o + P_E$
4 unpaired electrons → paramagnetic
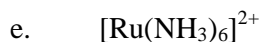Low Spin: $t_{2g}^6 e_g^0 \rightarrow 6(-2/5\ \Delta_o) + 3P_E = -12/5\ \Delta_o + 3P_E$
0 unpaired electrons → diamagnetic

c. $[Fe(H_2O)_6]^{3+}$
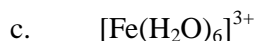
Fe^{III}, d^5. Water is a weak field ligand so a high spin complex is expected.
$t_{2g}^3 e_g^2 \rightarrow 3(-2/5\ \Delta_o) + 2(3/5\ \Delta_o) = 0$
**5 unpaired electrons → paramagnetic**

d. $[CoF_6]^{3-}$

Co^{III}, d^6. Fluoride is a weak field ligand, so a high spin complex is expected.
$t_{2g}^4 e_g^2 \rightarrow 4(-2/5\ \Delta_o) + 2(3/5\ \Delta_o) + P_E = -2/5\ \Delta_o + P_E$
**4 unpaired electrons → paramagnetic**

e. $[Ru(NH_3)_6]^{2+}$

Ru^{II}, d^6. Ruthenium is a second row transition metal, so a low spin complex is expected (second row, and lower, transition metals are always low spin).
$t_{2g}^6 e_g^0 \rightarrow 6(-2/5\ \Delta_o) + 3P_E = -12/5\ \Delta_o + 3P_E$
0 unpaired electrons → diamagnetic

f. $[Mn(H_2O)_6]^{2+}$

Mn^{II}, d^5. Same as in 4c (above).

g. $[CoCl_4]^{2-}$
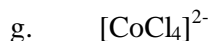
Co^{II}, d^7. This is a tetrahedral molecule in is thus always high spin. (Chloride is also a weak field ligand, but the tetrahedral versus octahedral molecule is more important).
$e^4 t_2^3 \rightarrow 4(-3/5\ \Delta_t) + 3(2/5\ \Delta_t) + 2P_E = -6/5\ \Delta_t + 2P_E.$

h. $[Cr(H_2O)_6]^{2+}$
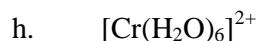
Cr^{II}, d^4. Water is generally considered a weak field ligand, so a high spin complex is expected.
**$t_{2g}{}^3 e_g{}^1 \rightarrow 3(-2/5\ \Delta_o) + 1(3/5\ \Delta_o) = -3/5\ \Delta_o$**

5. Why are tetrahedral complexes usually not low spin?

   Tetrahedral complexes are not usually low spin because the energy difference between the e and t_2 levels in the d-orbital splitting diagram is less than the energy cost of spin pairing the electrons (i.e. $\Delta_t < P_E$). In fact $\Delta_t = 4/9\ \Delta_o$ for the same metal and ligands. The higher energy cost of spin pairing electrons means it is more favorable for a tetrahedral molecule to be high 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.

   The drawing below shows the π^* orbital on the CO and the favorable overlap with one of the t_{2g} orbitals from the metal (d_{xy} is an arbitrary choice, d_{xz} or d_{yz} behave in the same way).
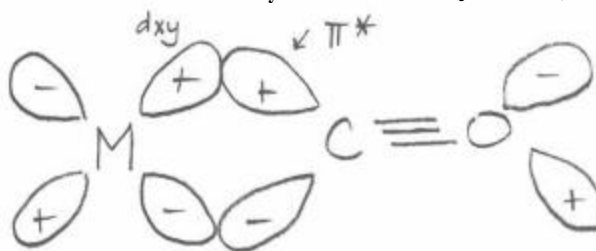
7. Prepare a diagram that shows how the d-orbital splitting pattern changes as an octahedral complex is altered via a tetragonal distortion that is first weak and then reaches the extreme case where a square, four coordinate complex is obtained.


Removal of z ligands

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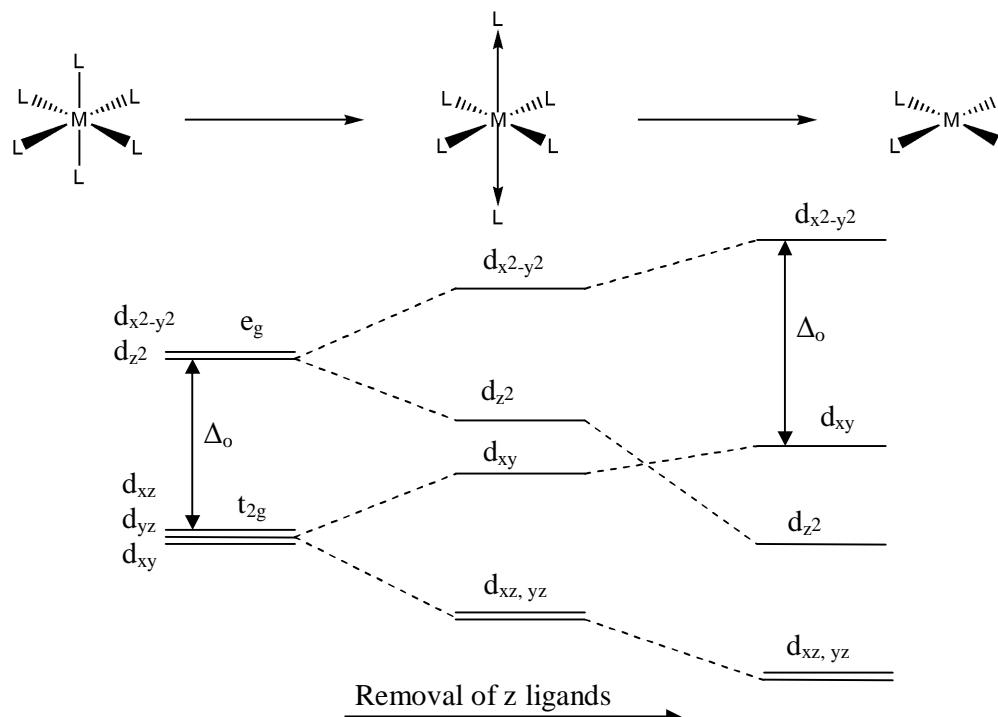
8. How does Δ_o (10Dq) change on going from one octahedral metal complex to another with the same ligand set, but with the following changes:

    a. M^{3+} instead of M^{2+}

        When changing from a divalent to a trivalent oxidation state on the metal, Δ_o increases.

    b. A second row transition element instead of a first row transition element.

        Second and third row transition elements show comparatively larger Δ_o values than their first row counterparts.

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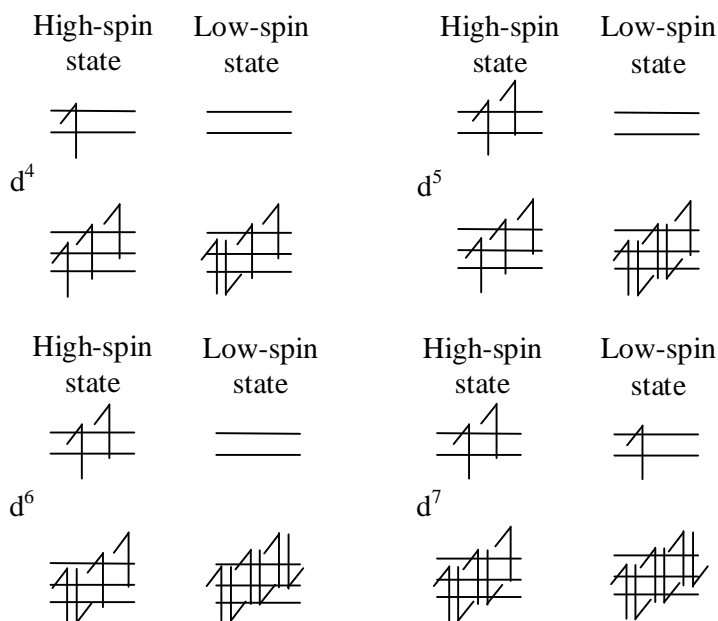
10. Why are the d-d transitions weak? Why are the absorptions observed at all if they are Laporte (orbitally) forbidden?

    THIS PROBLEM WAS NOT COVERED AND IS NOT ON THE TEST

    d-d transitions are so weak because they are orbitally (Laporte) forbidden. This rises from a selection rule which indicates that transitions between orbitals containing a "g" designation are forbidden (both the t_{2g} and e_g sets have this symmetry label).
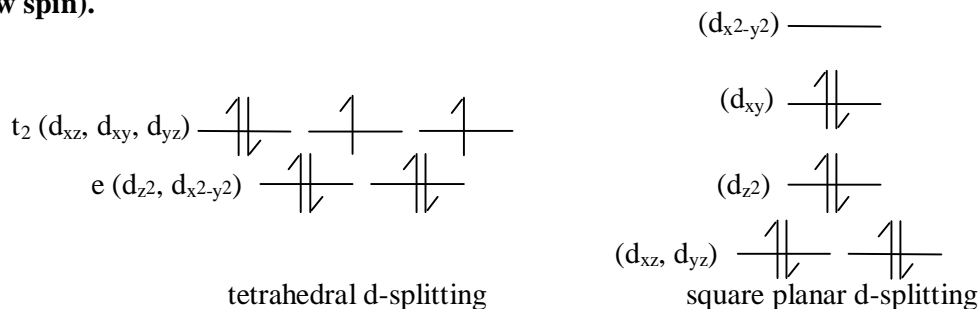
11. What is the spectrochemical series and what limitations must be remembered when using it?

The spectrochemical series is an empirically derived series of ligands which are ordered based on their effect on the Δ_o d-orbial splitting for metal complexes.

This series is a tool based on generalizations, so within the series it is sometimes difficult to compare ligand sets for two different metals. In such circumstances, differences may be observed for two ligands which flip their order in the series presented in the text (i.e. it's a general trend, not absolute!).

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.

Both complexes are 4-coordinate and so they can either be tetrahedral or square planar. Both compounds are Ni^{II}, d^8, so we can prepare the following two diagrams: (remember, tetrahedral systems are always high spin and square planar are always low spin).

(d_{x2-y2}) ⎯⎯⎯

$t_2 (d_{xz}, d_{xy}, d_{yz})$ ⎯⎯ ⎯ ⎯

$e (d_{z2}, d_{x2-y2})$ ⎯⎯ ⎯⎯

tetrahedral d-splitting

(d_{xy}) ⎯⎯

(d_{z2}) ⎯⎯

(d_{xz}, d_{yz}) ⎯⎯ ⎯⎯

square planar d-splitting

Since the tetrachloronickelate(II) is paramagnetic, it must adopt the tetrahedral geometry because it is the only way it could have unpaired electrons.

Since the tetracyanonickelate(II) is diamagnetic, it must adopt the square planar geometry because it is the only way it could have no unpaired electrons.

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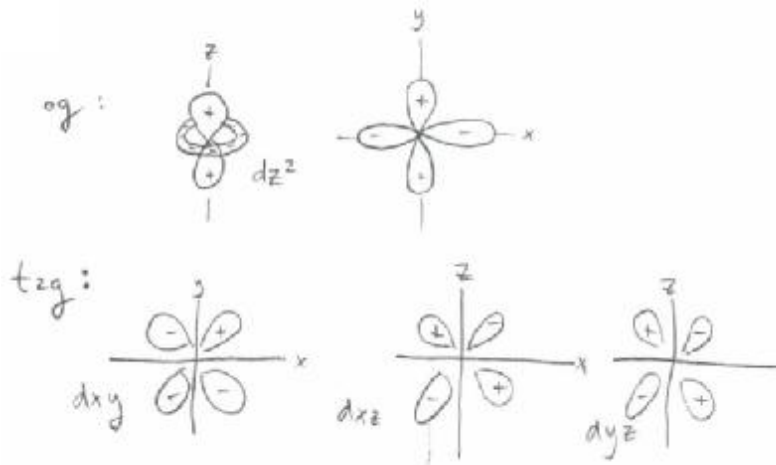
15.   What is the Jahn-Teller Effect? How does one go about detecting it?

THIS PROBLEM WAS NOT COVERED AND IS NOT ON THE TEST

The Jahn-Teller effect says that degeneracy of a given configuration must be broken by geometric distortion of the molecule to result in non-degenerate configurations. A classic example is a Ti^{3+} molecule which had is d^1 in an 'octahedral' ligand set. The single electron would reside in the t_{2g} level, but since this would result in degeneracy, the geometry of this molecule changed with a non-degenerate configuration for the single electron (tetragonal compression).

The detection of the Jahn-Teller effect can be made in several ways. The X-ray structure of the molecule will show different bond distances for ligands that are Jahn-Teller distorted. Further, since the degeneracy of the ground state is broke these complexes, additional absorption bands are observed in the electronic spectroscopy of this molecule (there are more levels for the excited electron to go to).

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.

THIS PROBLEM WAS NOT COVERED AND IS NOT ON THE TEST

If an electron is excited from the t_{2g} to the e_g level in $[Mn(H_2O)_6]^{2+}$ (high spin d^5), that electron must change it's spin to enter an orbital on the e_g level (which already contains one electron). So transitions in this molecule are both spin and orbitally forbidden. This compound should be very lightly colored (if at all) because absorption of energy in the visible range is insufficient to carry out forbidden transitions. Only vibronic coupling to remove the oribitally forbidden nature will provide transitions in the visible range.