CHAPTER 11
SOLUTIONS TO SELECTED PROBLEMS

8. Ni^{2+} is a d^8 system. It looks like the lowest transition is not curved, therefore Δ_O should be the energy of the lowest transition, which is about 8700 cm^{-1}.

(the splitting is because of a Jahn-Teller distortion in the excited state, but that isn't particularly important)

9. (a) Cr^{3+} is d^3. From the T-S diagram the lowest energy state is not curved, therefore the lowest energy transition is Δ_O = 17 400 cm^{-1}.

(b) Ti^{3+} is d^1, therefore Δ_O is 18 400 cm^{-1}. Again, splitting is due to the J-T effect in the excited state.

(c) Ni^{2+} is d^8. By the same rationale as #8, Δ_O is 11 200 cm^{-1}.

(d) V^{3+} is d^2. The ground state is curved, so the lowest energy transition is not Δ_O, but instead the difference between the ${}^3A_{2g} \leftarrow {}^3T_{1g}$ and the ${}^3T_{2g} \leftarrow {}^3T_{1g}$ is Δ_O. Because the energy of the third peak is not known, we can't actually solve this question with the information given, because we can't be sure which peaks are the correct ones. We could follow the example in the book (pp. 402-405), but this is beyond the scope of the course.

(e) Another *d*2 ion, which we don't know how to solve (unless we follow the procedure in the book)

14. I has the highest-energy orbitals ($5p > 4p > 3p$), so is closest in energy to the metal orbitals. Therefore, it is the lowest energy CT-band. 4*p* is further, and 3*p* is further still, so the order is I < Br < Cl.

15. CN^- is a strong field (low spin) ligand. In $Fe(CN)_6^{3-}$, Fe is 3+, and filling in the octahedral *d*-splitting diagram gives a vacancy in both the t_{2g} and the e_g orbitals. CT can occur into either orbital (into the e_g higher in *E* because it is the higher-energy orbital). With $Fe(CN)_6^{4-}$, Fe is 2+ and therefore the t_{2g} set is full of 6 Fe electrons, so only the higher-energy e_g can accept CT electrons.

18. (a) Remember that $\mu = (N(N+2)^{½}\mu_B$, solving for N gives the # of unpaired electrons.
low temperature ($0.65\mu_B$) gives N = 0.19; high temperature ($5.2\mu_B$) gives N = 4.3.
(b) As temperature is raised, more and more electrons will want to be in the excited states. Eventually, a flip from low spin (d^6, 0 unpaired electrons) to high spin (4 unpaired electrons) takes place.

22. $Ni(NO_2)_2$ (*aq*) is actually mostly $Ni(H_2O)_6^{2+}$. H_2O is a low-field ligand, so the absorption is in the red (to make the solution appear green). NH_3 is a higher-field ligand, so the absorption moves into the orange (and the solution appears blue). Finally, en is an even stronger ligand and the absorption moves into the yellow (and sol'n appears purple). This is expected from the spectrochemical series.

FOR QUESTIONS 16 AND 19, SEE PART II OF THIS CHAPTER'S SOLUTIONS