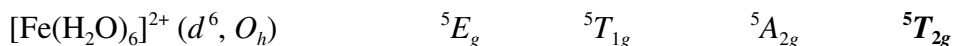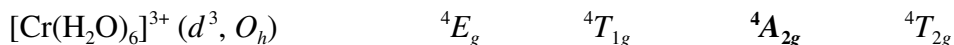Name_____Key_____

**Chem 370 - Spring, 2018**
Hour Exam III - Part 1
May 7, 2018

1. (32 points; 4 points each) Fill in the blanks. In some cases, answer choices are shown in **bold italics**.

a. From your recall of the appropriate Orgel diagram, indicate the number of bands expected in the visible spectra of the following complexes. (Disregard any possible bands resulting from Jahn-Teller effects or spin-forbidden transitions.)

$[Cr(H_2O)_6]^{3+}$ (d^3, O_h) ___3_____ $[Fe(H_2O)_6]^{2+}$ (d^6, O_h) ____1____
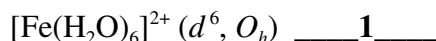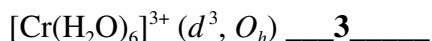
b. Circle the ground state term for each of the following complexes:

$[Cr(H_2O)_6]^{3+}$ (d^3, O_h) ^4E_g $^4T_{1g}$ $^4A_{2g}$ $^4T_{2g}$

$[Fe(H_2O)_6]^{2+}$ (d^6, O_h) ^5E_g $^5T_{1g}$ $^5A_{2g}$ $^5T_{2g}$

c. Indicate whether the following complexes in their ground states show **strong**, **weak**, or **no** Jahn-Teller distortion.

$[Cr(H_2O)_6]^{3+}$ (d^3, O_h) **none** $[Fe(H_2O)_6]^{2+}$ (d^6, O_h) **weak**
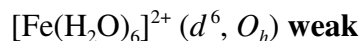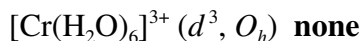
d. $[Ni(NH_3)_6]^{2+}$ (d^8, O_h) shows visible absorption bands at 10,750 cm^{-1}, 17,500 cm^{-1}, and 28,200 cm^{-1}. What is the value (cm^{-1}) of Δ_o for this complex, and what is the state-to-state notation (e.g., $^2E_g \rightarrow$ $^2T_{2g}$) for the transition that corresponds to Δ_o?

$\Delta_o =$ **10,750 cm^{-1}**   transition $^3A_{2g} \rightarrow {}^3T_{2g}$
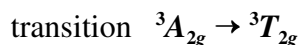
e. The visible spectrum of $[Fe(H_2O)_6]^{2+}$ (d^6, O_h) shows a broad absorption band with two distinct peaks at about 10,000 cm^{-1}. Give the state-to-state assignment for this band and suggest a reason why it is spit into two peaks.

For a d^6 high-spin O_h complex, a single transition, $^5T_{2g} \rightarrow {}^5E_g$ is expected (right side of the first Orgel diagram, or left side of the Tanbe-Sugano diagram). But the excited state is subject to strong Jahn-Teller distortion, creating in essence two distinct states to which transitions may occur. The triply degenerate ground state is not strongly split, so only two broad bands are visible.

f. In the reaction, $[Pt(NH_3)Br_3]^- + NH_3 \rightarrow [Pt(NH_3)_2Br_2]$, which isomer, **cis** or **trans**, will be favored for the product?

Answer: _____*cis*_____

Name_____

g. Consider the redox reaction,

$$[Cr(H_2O)_6]^{2+} + [Co(NH_3)_5Br]^{2+} + 5\ H_3O^+ \rightarrow [Cr(H_2O)_5Br] + [Co(H_2O)_6]^{2+} + 5\ NH_4^+$$
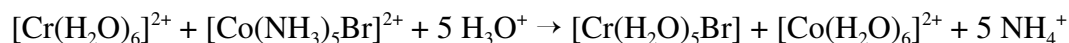
which occurs slowly in acidic aqueous medium. Is this redox reaction likely to be an ***inner-sphere*** or an ***outer-sphere*** mechanism? Explain briefly.

The slow rate and the complete change in coordination about both metal ions suggest an inner-sphere mechanism in which Br⁻ acts as the bridging ligands.

h. For the hydrolysis reactions,

$$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + X^-$$
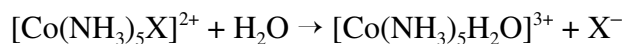
where X^- is a halide, the rates of reaction are found to increase in the order $F^- < Cl^- < Br^- < I^-$. Does this suggest a mechanism that is more *associative* (S_{N^2}, A, I_a) or *dissociative* (S_{N^1}, D, I_d)?

Because the rates depend on the identity of the leaving ligand, dissociation appears to be more important than association with the attacking ligand in determining the rate. This argues in favor of a dissociative mechanism (S_{N^1}, D, I_d, or some variant of these).

Name_____

2. (12 points) Consider the Tanabe-Sugano diagram for d^7 octahedral complexes shown below.
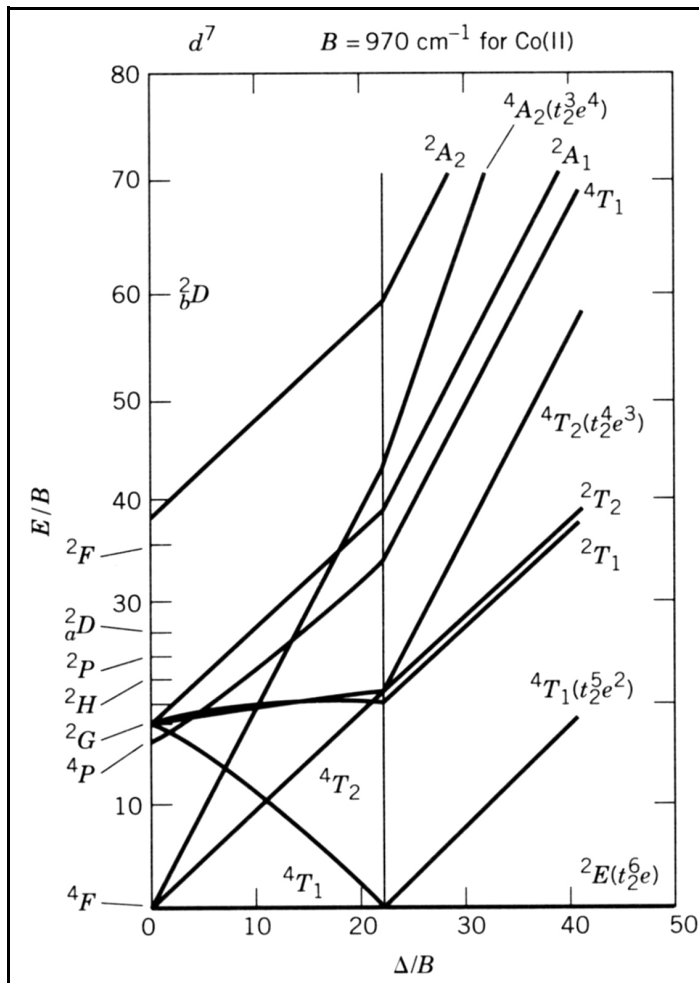
List the same-spin state-to-state transitions that are expected for both d^7 high-spin and d^7 low-spin ML_6 complexes, using the usual state-to-state notation (i.e., ground state → excited state).

d^7 high-spin	d^7 low-spin
$^4T_{1g}\,(F) \rightarrow {}^4T_{2g}$	$^2E_g \rightarrow {}^2T_{1g}$
$^4T_{1g}\,(F) \rightarrow {}^4T_{1g}\,(P)$	$^2E_g \rightarrow {}^2T_{2g}$
$^4T_{1g}\,(F) \rightarrow {}^4A_{2g}$	$^2E_g \rightarrow {}^2A_{1g}$
	$^2E_g \rightarrow {}^2A_{2g}$

What factors might lead to fewer observed bands in the visible spectrum from the number of possible transitions you have identified for each case?

For d^7 high-spin, ν_3, usually the $^4T_{1g}\,(F) \rightarrow {}^4T_{1g}(F)$ transition, often falls in the u.v., where it is obscured by the CT band. For d^7 low-spin, the first two transitions to $^2T_{1g}$ and $^2T_{2g}$ may be incompletely resolved (nearly degenerate), giving only one band. The highest energy transitions to $^2A_{1g}$ and $^2A_{2g}$ would fall in the u.v. and not be observed in most cases.