Problem Set 1
Ch153a – Winter 2022
Due: 7 January 2022

1) When a solution of 0.024 M $CoSO_4$ in 0.48 M H_2SO_4 at a pressure of 25 MPa is heated to 625 K the intensity of the main visible absorption band increases and the maximum shifts to lower energy (Figure 1). The change in the absorption spectrum is attributed to the following transformation:

$$Co(OH_2)_6^{2+} \rightleftharpoons Co(OH_2)_4^{2+} + 2H_2O \qquad \Delta H^{\circ\prime} = +17 \text{ kJ mol}^{-1}$$

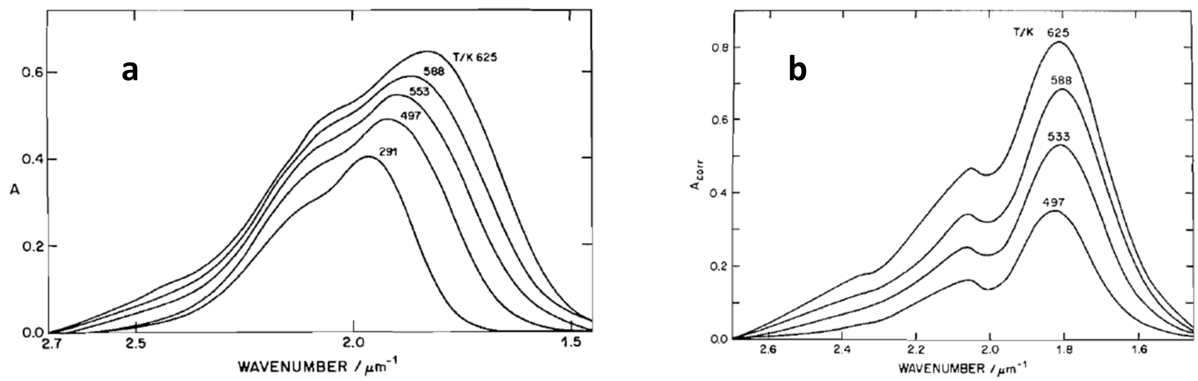

Figure 1. (a) Absorption spectra of 0.024 M $CoSO_4$ in 0.48 M H_2SO_4 at a pressure of 25 MPa at the indicated temperatures. (b) Difference spectra produced by subtracting the 291 K spectrum from the spectrum measured at the indicated temperature. All spectra corrected for solvent expansion.

In working on the following problems, consider just the *d*-orbital manifold and assume that $Co(OH_2)_6^{2+}$ has O_h symmetry and $Co(OH_2)_4^{2+}$ has T_d symmetry. Term symbols are used to describe electronic states of atoms and molecules. For atoms in the Russell-Saunders coupling limit, term symbols have the form: ^{2S+1}L, where S is the total spin angular momentum quantum number and L is a letter corresponding to the orbital angular momentum of the state (*i.e.*, S, L = 0; P, L = 1, D, L = 2, F, L = 3, …). For molecular electronic states, term symbols have the form: $^{2S+1}\Gamma$, where Γ is the upper-case letter of the irreducible representation that describes the symmetry properties of the spatial part of the electronic state wavefunction (*e.g.*, A_{1g}, E_g, T_{1g}, T_{2g}, …).

a) Give the term symbols and strong-field electronic configurations for all quartet (*i.e.*, S=3/2) states in $Co(OH_2)_6^{2+}$.

b) Give the term symbols and strong-field electronic configurations for all quartet (*i.e.*, S=3/2) states in $Co(OH_2)_4^{2+}$.

c) In the strong-field limit, compare the ligand field stabilization energies of the $Co(OH_2)_6^{2+}$ and $Co(OH_2)_4^{2+}$ ground states (assume that $\Delta_t = (4/9)\ \Delta_o$). Define the *d*-orbital energy splittings as follows: Δ_o in O_h and Δ_t in T_d.

2) The strong-field energy matrix for the quartet states of $Co(OH_2)_6^{2+}$ is given below:

	$\phi_1[(t_{2g})^5(e_g)^2]$	$\phi_2[(t_{2g})^4(e_g)^{3]}$	$\phi_3[(t_{2g})^4(e_g)^3]$	$\phi_4[(t_{2g})^3(e_g)^4]$
$\phi_1[(t_{2g})^5(e_g)^2]$	$21A-40B+14C-0.8\Delta_o$	6B	0	0
$\phi_2[(t_{2g})^4(e_g)^{3]}$	6B	$21A-31B+14C+0.2\Delta_o$	0	0
$\phi_3[(t_{2g})^4(e_g)^3]$	0	0	$21A-43B+14C+0.2\Delta_o$	0
$\phi_4[(t_{2g})^3(e_g)^4]$	0	0	0	$21A-43B+14C+1.2\Delta_o$

The parameters A, B, and C are the Racah electron-electron repulsion parameters.

Make a strong-field energy matrix for the quartet states of $Co(OH_2)_4^{2+}$.

3) In the weak-field limit, the ligand field is treated as a perturbation on the free-ion states. For the Co^{2+} ion, there are two quartet states: ^4F and ^4P.

a) Using the energy matrix for $Co(OH_2)_6^{2+}$ in the limit of $\Delta_o \to 0$, determine the energies of the ^4F and ^4P states in terms of A, B, and C.

b) Determine the energies of the quartet states of $Co(OH_2)_6^{2+}$ in the weak-field limit.

c) Determine the energies of the quartet states of $Co(OH_2)_4^{2+}$ in the weak-field limit.

d) Compare the ligand field stabilization energies of the ground states of $Co(OH_2)_6^{2+}$ and $Co(OH_2)_4^{2+}$ in the weak-field limit (assume that $\Delta_t = (4/9)\ \Delta_o$).

4) Does the weak-field or strong-field limit seem more appropriate for Co^{2+} aquo ions? Explain your answer.