

Problem Set 9

Ch 153a – Winter 2022

Due: 9 March, 2022

- 1) The $\text{Co}(\text{NH}_3)_6^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$ electron self-exchange reaction involves a large spin-state change, owing to the fact that the $\text{Co}(\text{NH}_3)_6^{2+}$ ground state is high-spin (${}^4\text{T}_{1g}$) and the $\text{Co}(\text{NH}_3)_6^{3+}$ ground state is low-spin (${}^1\text{A}_{1g}$). It has been suggested that a spin-state change in $\text{Co}(\text{NH}_3)_6^{2+}$, producing a ${}^2\text{E}_g$ state, or in $\text{Co}(\text{NH}_3)_6^{3+}$, producing either a ${}^3\text{T}_{1g}$ or ${}^5\text{T}_{2g}$ state, precedes the electron transfer. Use the spectroscopic data and ligand field parameters given below to estimate the relative Boltzmann populations of the ${}^2\text{E}_g$ state in $\text{Co}(\text{NH}_3)_6^{2+}$, and of the ${}^3\text{T}_{1g}$ and ${}^5\text{T}_{2g}$ states in $\text{Co}(\text{NH}_3)_6^{3+}$. Does population of any of these excited states prior to electron transfer seem likely? Explain your reasoning.

$$\text{Co}(\text{NH}_3)_6^{2+}: \Delta_o = 10,100 \text{ cm}^{-1}; B = 900 \text{ cm}^{-1}; C = 3,600 \text{ cm}^{-1}$$

$$\text{Co}(\text{NH}_3)_6^{3+}: \Delta_o = 24,000 \text{ cm}^{-1}; B = 619 \text{ cm}^{-1}; C = 3,656 \text{ cm}^{-1}$$

Energies of d^6 states:

${}^1\text{A}_{1g}$	0
${}^3\text{T}_{1g}$	$\Delta_o - 3C$
${}^3\text{T}_{2g}$	$\Delta_o + 8B - 3C$
${}^1\text{T}_{1g}$	$\Delta_o - C$
${}^1\text{T}_{2g}$	$\Delta_o + 16B - C$
${}^5\text{T}_{2g}$	$2\Delta_o - 5B - 8C$

Energies of d^7 states:

${}^4\text{T}_{1g}({}^4\text{F}, {}^4\text{P})$	$\begin{vmatrix} \Delta_o + 9B - \epsilon & 6B \\ 6B & -\epsilon \end{vmatrix}$
${}^4\text{T}_{2g}$	$\Delta_o - 3B - E[{}^4\text{T}_{1g}({}^4\text{F})]$
${}^4\text{A}_{2g}$	$2\Delta_o - 3B - E[{}^4\text{T}_{1g}({}^4\text{F})]$
${}^2\text{E}_g$	$-\Delta_o + 4B + 4C - E[{}^4\text{T}_{1g}({}^4\text{F})]$

Huang-Rhys Parameters and vibrational frequencies for $\text{Co}(\text{NH}_3)_6^{3+}$ relative to the ${}^1\text{A}_{1g}$ ground state:

$${}^3\text{T}_{1g}, {}^3\text{T}_{2g}, {}^1\text{T}_{1g}, {}^1\text{T}_{2g}, S = 2.4, \hbar\omega = 480 \text{ cm}^{-1}$$

$${}^5\text{T}_{2g}, S = 9.6, \hbar\omega = 435 \text{ cm}^{-1}$$

Huang-Rhys Parameters and vibrational frequencies for $\text{Co}(\text{NH}_3)_6^{2+}$ relative to the ${}^4\text{T}_{1g}({}^4\text{F})$ ground state:

$${}^4\text{T}_{1g}({}^4\text{P}), {}^4\text{T}_{2g}, S = 2.4, \hbar\omega = 300 \text{ cm}^{-1}$$

$${}^4\text{A}_{2g}, S = 9.6, \hbar\omega = 250 \text{ cm}^{-1}$$

$${}^2\text{E}_g, S = 2.4, \hbar\omega = 400 \text{ cm}^{-1}$$

- 2) The Ti(III) oxidation state is rare in terrestrial minerals due to the comparatively highly oxidizing environment on Earth. Trivalent titanium does occur in extraterrestrial materials; one example is a titanium pyroxene found in the Allende meteorite. The empirical formula for this mineral is $\text{Ca}_{1.01}\text{Mg}_{0.38}(\text{Ti}^{3+})_{0.34}(\text{Ti}^{4+})_{0.14}\text{Al}_{0.87}\text{Si}_{1.26}\text{O}_6$. The crystal structure reveals that this mineral contains chains of edge-shared distorted octahedra with $\text{Ti}^{3+/4+}$ ions at the center. The Ti-Ti distance is 3.15 Å. The polarized single-crystal absorption spectra of the Ti^{3+} - Ti^{4+} pyroxene from the Allende meteorite at different pressures are shown below (α and β refer to two different polarization directions).

Propose assignments for the absorption bands at 14,000, 16,000, and 20,000 cm^{-1} (1 bar). On the basis of your assignments, offer explanations for the pressure dependent behavior of the three bands.

