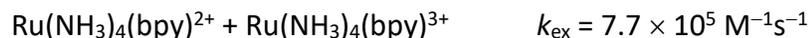
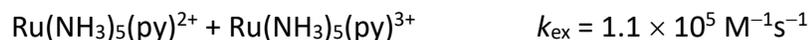


## Problem Set 8

Ch 153a – Winter 2026

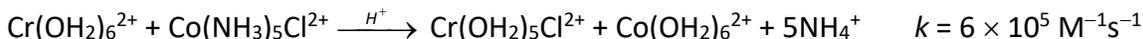
Due: 6 March 2026

1. (10 points) Brown and Sutin (*J. Am. Chem. Soc.* **1979**, *101*, 883-892) found that the rates of electron exchange between  $\text{Ru}^{3+}$  and  $\text{Ru}^{2+}$  complexes exhibit the following trend (py = pyridine; bpy = 2,2'-bipyridine):



How do Brown and Sutin rationalize the relative rates of electron exchange in these Ru complexes? Do you agree with their explanation? Why or why not?

2. (10 points) Explain the following reaction products and relative rates of reduction by the  $\text{Cr}(\text{OH}_2)_6^{2+}$  ion in aqueous solution:



3. (10 points) The reaction between  $\text{Ru}(\text{bpy})_3^+$  and  $\text{Ru}(\text{bpy})_3^{3+}$  produces light with a spectrum that closely matches that of MLCT-excited  $\text{Ru}(\text{bpy})_3^{2+}$  ( $^*\text{Ru}(\text{bpy})_3^{2+}$ ).

The relevant reduction potentials for  $\text{Ru}(\text{bpy})_3^{2+}$  are:

$$E^\circ(\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}) = 1.25 \text{ V vs. NHE}$$

$$E^\circ(\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^+) = -1.25 \text{ V vs. NHE}$$

The energy difference between the minimum of the ground-state potential energy surface and that of  $^*\text{Ru}(\text{bpy})_3^{2+}$  is approximately 2.0 eV.

Explain why the  $\text{Ru}(\text{bpy})_3^+ + \text{Ru}(\text{bpy})_3^{3+}$  reaction is chemiluminescent.

4. (10 points) Rate and driving force data for electron-transfer reactions of  $\text{Co}(\text{OH}_2)_6^{3+}$  and  $\text{Co}(\text{NH}_3)_6^{3+}$  are given in the following two tables.

- (a) Use the data in the tables and the Marcus cross-relation to estimate values for the self-exchange rate constants of  $\text{Co}(\text{OH}_2)_6^{3+}$  and  $\text{Co}(\text{NH}_3)_6^{3+}$ .
- (b) Compare these two self-exchange rate constants to values reported in the literature. Discuss the quality of the agreement between measured self-exchange rate constants and those calculated using the cross-relation. Offer possible explanations for any discrepancies that you find.

Co(OH <sub>2</sub> ) <sub>6</sub> <sup>3+</sup> Reactions			
Reductant	$k_{22}$ , M <sup>-1</sup> s <sup>-1</sup>	$k_{12}$ , M <sup>-1</sup> s <sup>-1</sup>	$-\Delta G^\circ$ , kJ mol <sup>-1</sup>
Co(Me <sub>2</sub> [14]4,7-dieneN <sub>4</sub> -6-one)(OH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup>	$4.40 \times 10^{-3}$	$3.84 \times 10^2$	128
Co(Me <sub>2</sub> pyo[14]trieneN <sub>4</sub> )(OH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup>	$9.3 \times 10^{-2}$	$3.46 \times 10^2$	131
Co(Me <sub>4</sub> [14]tetraeneN <sub>4</sub> )(OH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup>	$5.0 \times 10^{-2}$	$2.20 \times 10^2$	131
Co(Me <sub>6</sub> [14]4,11-dieneN <sub>4</sub> )(OH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup>	$4.50 \times 10^{-5}$	$1.0 \times 10^1$	131
Co([14]aneN <sub>4</sub> )(OH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup>	$8.00 \times 10^{-4}$	$6.65 \times 10^2$	145
Co([15]aneN <sub>4</sub> )(OH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup>	$6.00 \times 10^{-3}$	$2.70 \times 10^2$	124
Co(sep) <sup>2+</sup>	5	$5.77 \times 10^2$	156
Ru(NH <sub>3</sub> ) <sub>4</sub> (phen) <sup>2+</sup>	$3.25 \times 10^6$	$4.00 \times 10^4$	136
Ni([14]aneN <sub>4</sub> )(OH <sub>2</sub> ) <sub>2</sub> <sup>2+</sup>	$1.20 \times 10^3$	$8.6 \times 10^1$	89.4
Ni(Me <sub>6</sub> [14]4,11-dieneN <sub>4</sub> ) <sup>2+</sup>	6	$1.20 \times 10^2$	54
Fe(5-NO <sub>2</sub> -phen) <sub>3</sub> <sup>2+</sup>	$2.00 \times 10^9$	$1.49 \times 10^3$	59.3
Fe(5-Cl-phen) <sub>3</sub> <sup>2+</sup>	$2.00 \times 10^9$	$5.00 \times 10^3$	71.8
Fe(phen) <sub>3</sub> <sup>2+</sup>	$2.00 \times 10^9$	$1.40 \times 10^4$	77.6
Fe(5-CH <sub>3</sub> -phen) <sub>3</sub> <sup>2+</sup>	$2.00 \times 10^9$	$1.50 \times 10^4$	80.3
Fe(OH <sub>2</sub> ) <sub>6</sub> <sup>2+</sup>	4	$5.00 \times 10^1$	113.3
V(OH <sub>2</sub> ) <sub>6</sub> <sup>2+</sup>	$3.00 \times 10^{13}$	$9.00 \times 10^5$	207.2
Cr(OH <sub>2</sub> ) <sub>6</sub> <sup>2+</sup>	$1.00 \times 10^{15}$	$1.30 \times 10^4$	225
U <sup>3+</sup>	$5.00 \times 10^{11}$	$1.10 \times 10^6$	245.8

Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> reactions on following page.

Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup> Reactions			
Reductant	$k_{22}, \text{M}^{-1}\text{s}^{-1}$	$k_{12}, \text{M}^{-1}\text{s}^{-1}$	$-\Delta G^\circ, \text{kJ mol}^{-1}$
Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	$4.00 \times 10^3$	$2.4 \times 10^{-2}$	3.8
V(OH <sub>2</sub> ) <sub>6</sub> <sup>2+</sup>	$3.00 \times 10^{-3}$	$1.00 \times 10^{-2}$	31.4
Cr(bpy) <sub>3</sub> <sup>2+</sup>	$2.00 \times 10^9$	$3.10 \times 10^2$	34.7
Cr(phen) <sub>3</sub> <sup>2+</sup>	$2.00 \times 10^9$	$3.10 \times 10^2$	36.6
Cr(OH <sub>2</sub> ) <sub>6</sub> <sup>2+</sup>	$1.00 \times 10^{-5}$	$1.00 \times 10^{-3}$	49.2
U <sup>3+</sup>	$5.00 \times 10^{-1}$	1.30	69.9