Problem Set 6
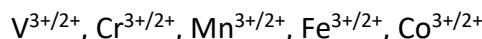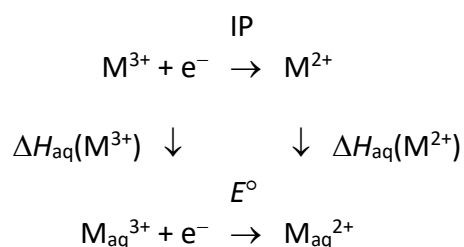**Ch 153a – Winter 2025**
Due: 21 February 2025
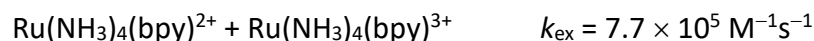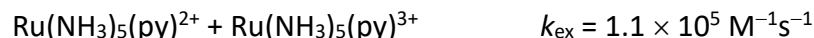
1. (10 points) Consider the following series of redox couples in aqueous solution:

$$V^{3+/2+}, Cr^{3+/2+}, Mn^{3+/2+}, Fe^{3+/2+}, Co^{3+/2+}$$

The reduction potentials for these couples ($E°$) can be defined in terms of the ionization potentials for the gaseous ions (IP) and the heats of hydration for the ions (ΔH_{aq}), as suggested by the following Born-Haber cycle:
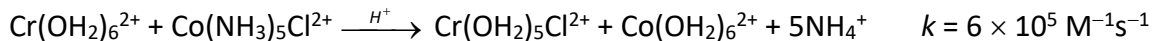
$$IP$$
$$M^{3+} + e^- \rightarrow M^{2+}$$

$$\Delta H_{aq}(M^{3+}) \downarrow \qquad \downarrow \Delta H_{aq}(M^{2+})$$
$$E°$$
$$M_{aq}^{3+} + e^- \rightarrow M_{aq}^{2+}$$

   a. Find the standard reduction potentials ($E°$) for each pair, citing the reference used.
   b. Find the ionization potential for each M^{2+} ion, citing the reference used.
   c. Find the enthalpies of hydration for each M^{2+} and M^{3+} ion, citing the reference used.
   d. Plot IP, $E°$, $\Delta H_{aq}(M^{3+})$, and $\Delta H_{aq}(M^{2+})$ vs. the atomic number of each metal. Explain the trends in terms of the electronic structures of the ions.

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

   $Ru(NH_3)_6^{2+} + Ru(NH_3)_6^{3+}$ $\qquad\qquad$ $k_{ex} = 4.3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$

   $Ru(NH_3)_5(py)^{2+} + Ru(NH_3)_5(py)^{3+}$ $\qquad$ $k_{ex} = 1.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$

   $Ru(NH_3)_4(bpy)^{2+} + Ru(NH_3)_4(bpy)^{3+}$ $\qquad$ $k_{ex} = 7.7 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$

   $Ru(NH_3)_2(bpy)_2^{2+} + Ru(NH_3)_2(bpy)_2^{3+}$ $\qquad$ $k_{ex} = 8.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$

   $Ru(bpy)_3^{2+} + Ru(bpy)_3^{3+}$ $\qquad\qquad$ $k_{ex} = 4.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$

   Do you agree with the explanation given by Brown and Sutin for the relative rates of electron exchange in these Ru complexes? Why or why not?

3. (10 points) Explain the following reaction products and relative rates of reduction by the $Cr(OH_2)_6^{2+}$ ion in aqueous solution:

$$Cr(OH_2)_6^{2+} + Co(NH_3)_6^{3+} \xrightarrow{H^+} Cr(OH_2)_6^{3+} + Co(OH_2)_6^{2+} + 6NH_4^+ \qquad k = 1 \times 10^{-3}\ M^{-1}s^{-1}$$

$$Cr(OH_2)_6^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{H^+} Cr(OH_2)_5Cl^{2+} + Co(OH_2)_6^{2+} + 5NH_4^+ \qquad k = 6 \times 10^{5}\ M^{-1}s^{-1}$$

4. (10 points) The reaction between $Ru(bpy)_3^+$ and $Ru(bpy)_3^{3+}$ produces light with a spectrum that closely matches that of MLCT-excited $Ru(bpy)_3^{2+}$ ($*Ru(bpy)_3^{2+}$).

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

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

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

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

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