Problem Set 8
Ch 153a – Winter 2022
Due: 25 February, 2022

1) 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:

$$\begin{tikzcd}
M^{3+} + e^- \arrow[r, "\mathrm{IP}"] \arrow[d, "\Delta H_{aq}(M^{3+})"'] & M^{2+} \arrow[d, "\Delta H_{aq}(M^{2+})"] \\
M_{aq}^{3+} + e^- \arrow[r, "E^\circ"] & M_{aq}^{2+}
\end{tikzcd}$$

   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) 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.

3) Rate and driving force data for electron-transfer reactions of $Co(OH_2)_6^{3+}$ and $Co(NH_3)_6^{3+}$ are given in the following two tables. Marcus developed a "cross-relation" that describes the rate constant for a cross reaction (k_{12}) in terms of the equilibrium constant for the reaction (K_{12}) and the electron self-exchange rate constants for each reactant (k_{11}, k_{22}):

$$k_{12}=\left(k_{11}k_{22}K_{12}f_{12}\right)^{½}$$

$$\ln\left(f_{12}\right)=\frac{\left(\ln\left(K_{12}\right)\right)^2}{4\ln\left(\frac{k_{11}k_{22}}{Z^2}\right)}$$

The collision frequency (Z) is assumed to be 10^{11} $M^{-1}s^{-1}$

a) Use the data in the tables and the Marcus cross-relation to estimate values for the self-exchange rate constants of $Co(OH_2)_6^{3+}$ and $Co(NH_3)_6^{3+}$.

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.

$Co(OH_2)_6^{3+}$ Reactions			
Reductant	k_{22}, $M^{-1}s^{-1}$	k_{12}, $M^{-1}s^{-1}$	$-\Delta G°$, kJ mol^{-1}
$Co(Me_2[14]4,7\text{-diene}N_4\text{-6-one})(OH_2)_2^{2+}$	4.40×10^{-3}	3.84×10^{2}	128
$Co(Me_2pyo[14]triene N_4)(OH_2)_2^{2+}$	9.3×10^{-2}	3.46×10^{2}	131
$Co(Me_4[14]tetraene N_4)(OH_2)_2^{2+}$	5.0×10^{-2}	2.20×10^{2}	131
$Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{2+}$	4.50×10^{-5}	1.0×10^{1}	131
$Co([14]ane N_4)(OH_2)_2^{2+}$	8.00×10^{-4}	6.65×10^{2}	145
$Co([15]ane N_4)(OH_2)_2^{2+}$	6.00×10^{-3}	2.70×10^{2}	124
$Co(sep)^{2+}$	5	5.77×10^{2}	156
$Ru(NH_3)_4(phen)^{2+}$	3.25×10^{6}	4.00×10^{4}	136
$Ni([14]ane N_4)(OH_2)_2^{2+}$	1.20×10^{3}	8.6×10^{1}	89.4
$Ni(Me_6[14]4,11\text{-diene}N_4)^{2+}$	6	1.20×10^{2}	54
$Fe(5\text{-}NO_2\text{-phen})_3^{2+}$	2.00×10^{9}	1.49×10^{3}	59.3
$Fe(5\text{-Cl-phen})_3^{2+}$	2.00×10^{9}	5.00×10^{3}	71.8
$Fe(phen)_3^{2+}$	2.00×10^{9}	1.40×10^{4}	77.6
$Fe(5\text{-}CH_3\text{-phen})_3^{2+}$	2.00×10^{9}	1.50×10^{4}	80.3
$Fe(OH_2)_6^{2+}$	4	5.00×10^{1}	113.3
$V(OH_2)_6^{2+}$	3.00×10^{-3}	9.00×10^{5}	207.2
$Cr(OH_2)_6^{2+}$	1.00×10^{-5}	1.30×10^{4}	225
U^{3+}	5.00×10^{-1}	1.10×10^{6}	245.8

$Co(NH_3)_6^{3+}$ Reactions			
Reductant	k_{22}, $M^{-1}s^{-1}$	k_{12}, $M^{-1}s^{-1}$	$-\Delta G^\circ$, kJ mol^{-1}
$Ru(NH_3)_6^{2+}$	4.00×10^3	2.4×10^{-2}	3.8
$V(OH_2)_6^{2+}$	3.00×10^{-3}	1.00×10^{-2}	31.4
$Cr(bpy)_3^{2+}$	2.00×10^9	3.10×10^2	34.7
$Cr(phen)_3^{2+}$	2.00×10^9	3.10×10^2	36.6
$Cr(OH_2)_6^{2+}$	1.00×10^{-5}	1.00×10^{-3}	49.2
U^{3+}	5.00×10^{-1}	1.30	69.9

4) Jim Mayer and coworkers examined the reactions of permanganate with a variety of H-atom donors (*Inorg. Chem.* **1997**, *36*, 2069-2078). They used a thermodynamic cycle based on the $MnO_4^{-/2-}$ reduction potential, the pKa of $Mn(OH)O_3^-$, the dissociation enthalpy of H_2, and the solvation enthalpy of $H^\bullet$ to estimate the H–O bond dissociation enthalpy of $Mn(OH)O_3^-$.

   Using an analogous thermodynamic cycle, along with the bond-dissociation enthalpies and pKa values given in the Table below, estimate the reduction potentials for the couples given in the Table. Try to find E° values for these redox couples in the literature. How do they compare? Suggest possible reasons for any significant discrepancies.

Couple	pK_a	BDE (kcal/mol)
$HO^{\bullet/-}$	14	119.2
$CH_3O^{\bullet/-}$	16	104.4
$t\text{-}C_4H_9OO^{\bullet/-}$	4.5	89.4
$I^{\bullet/-}$	−10	71.4
$Br^{\bullet/-}$	−8.5	86.5
$Cl^{\bullet/-}$	−7	102
$F^{\bullet/-}$	3.45	134