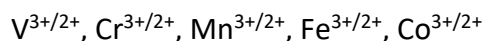


Problem Set 8

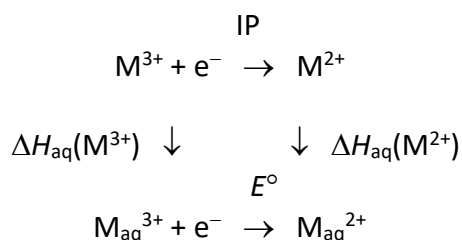
Ch 153a – Winter 2022

Due: 25 February, 2022

- 1) Consider the following series of redox couples in aqueous solution:



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:



- Find the standard reduction potentials (E°) for each pair, citing the reference used.
 - Find the ionization potential for each M^{2+} ion, citing the reference used.
 - Find the enthalpies of hydration for each M^{2+} and M^{3+} ion, citing the reference used.
 - Plot IP, E° , $\Delta H_{\text{aq}}(\text{M}^{3+})$, and $\Delta H_{\text{aq}}(\text{M}^{2+})$ vs. the atomic number of each metal. Explain the trends in terms of the electronic structures of the ions.
- 2) The reaction between $\text{Ru}(\text{bpy})_3^+$ 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.

- 3) 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. 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}):

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$

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

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

- 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 $\text{Co}(\text{NH}_3)_6^{3+}$.
- 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	$k_{22}, \text{M}^{-1}\text{s}^{-1}$	$k_{12}, \text{M}^{-1}\text{s}^{-1}$	$-\Delta G^\circ, \text{kJ mol}^{-1}$
Co(Me ₂ [14]4,7-dieneN ₄ -6-one)(OH ₂) ₂ ²⁺	4.40×10^{-3}	3.84×10^2	128
Co(Me ₂ pyo[14]trieneN ₄)(OH ₂) ₂ ²⁺	9.3×10^{-2}	3.46×10^2	131
Co(Me ₄ [14]tetraeneN ₄)(OH ₂) ₂ ²⁺	5.0×10^{-2}	2.20×10^2	131
Co(Me ₆ [14]4,11-dieneN ₄)(OH ₂) ₂ ²⁺	4.50×10^{-5}	1.0×10^1	131
Co([14]aneN ₄)(OH ₂) ₂ ²⁺	8.00×10^{-4}	6.65×10^2	145
Co([15]aneN 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]aneN ₄)(OH ₂) ₂ ²⁺	1.20×10^3	8.6×10^1	89.4
Ni(Me ₆ [14]4,11-dieneN ₄) ²⁺	6	1.20×10^2	54
Fe(5-NO ₂ -phen) ₃ ²⁺	2.00×10^9	1.49×10^3	59.3
Fe(5-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-CH ₃ -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 MnO₄^{-/2-} reduction potential, the pK_a of Mn(OH)O₃⁻, the dissociation enthalpy of H₂, and the solvation enthalpy of H[•] to estimate the H–O bond dissociation enthalpy of Mn(OH)O₃⁻.

Using an analogous thermodynamic cycle, along with the bond-dissociation enthalpies and pK_a 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 ^{•/–}	14	119.2
CH ₃ O ^{•/–}	16	104.4
t-C ₄ H ₉ OO ^{•/–}	4.5	89.4
I ^{•/–}	–10	71.4
Br ^{•/–}	–8.5	86.5
Cl ^{•/–}	–7	102
F ^{•/–}	3.45	134