

Solutions to Problem Set 5

- 1) The $\text{Fe}(\text{CN})_6^{3-/4-}$ potential is 0.68 volts, and the corresponding electron exchange rate is $7.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. The $\text{W}(\text{CN})_8^{3-/4-}$ potential is 0.54 volts, and the corresponding exchange rate is $7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Use Marcus Theory (setting the frequency factor $f=1$) to calculate a value of the rate constant for the oxidation of $\text{W}(\text{CN})_8^{4-}$ by $\text{Fe}(\text{CN})_6^{3-}$. Compare your result with the observed value of $4.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Is an outer sphere mechanism reasonable?



$$E^0 = 0.68 - 0.54 = 0.14 \text{ V}$$

Given the Nernst equation: $\Delta G_{12}^0 = -RT \ln K_{12} = -n F E^0$,

we can write $\log K_{12} = E^0/0.059 = 2.373$, and $K_{12} = 236.0$

From Marcus Theory, the cross reaction rate constant k_{12} is $k_{12} = [k_1 k_2 K_{12} f]^{1/2}$

Setting $f = 1$ gives

$$k_{12} = [(7.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1})(7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}) \times 236]^{1/2}$$

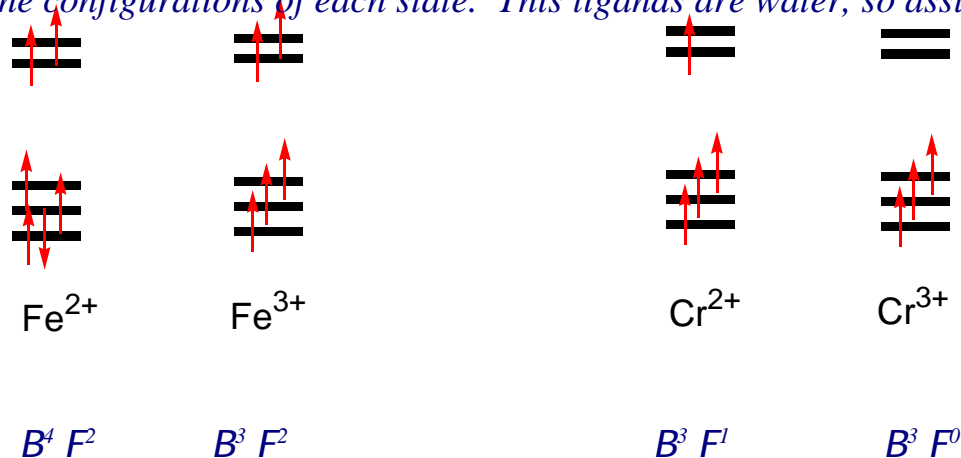
$$= 1.11 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

- 2) The following data (at 25°C) have been reported in the literature for the electron exchange reactions between aqueous Fe^{2+} and Fe^{3+} and between aqueous Cr^{2+} and Cr^{3+} .

Couple	EE, volts	k_{ex} ($\text{M}^{-1} \text{ sec}^{-1}$)
$\text{Fe}^{3+}/\text{Fe}^{2+}$	+0.771	4
$\text{Cr}^{3+}/\text{Cr}^{2+}$	-0.41	2×10^{-5}

- (i) Why is Fe^{3+} a better oxidant than Cr^{3+} ?

Check out the configurations of each state. This ligands are water, so assume high spin :



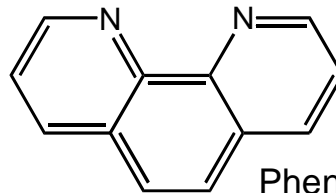
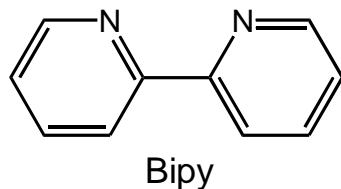
From a thermodynamic perspective $Fe(III)$ gains $4Dq$ upon reduction, while $Cr(III)$ loses $6 Dq$. That accounts for the difference in cell potentials.

- (ii) Given that an outer sphere electron transfer mechanism applies, why is exchange for the iron couple so much faster?

Again, if one expects the configurational changes, $Fe(III)/Fe(II)$ is a net **B** to **B** transfer, which should make for a fast outer sphere reaction (a small reorganizational energy). The $Cr(III)/Cr(II)$ reaction is **NET F** to **F**, and thus should be a real clunker outer sphere process.

- (iii) What ligand (instead of water) would you use to increase the rate of either reaction? Explain your reasoning.

Remember, the other key to a fast outer sphere is the presence of large, flat **B**-aromatic ligands like bipyridyl (bipy) or phenanthroline (phen) that can lead to near adiabatic electron transfer (an open window at the transition state).



- (iv) Assuming that the electron transfer is outer sphere, estimate the forward rate constant for the cross reaction (in water at 25°C):



Given the Nernst equation: $\Delta G_{12}^0 = -RT \ln K_{12} = -n F E^0$,

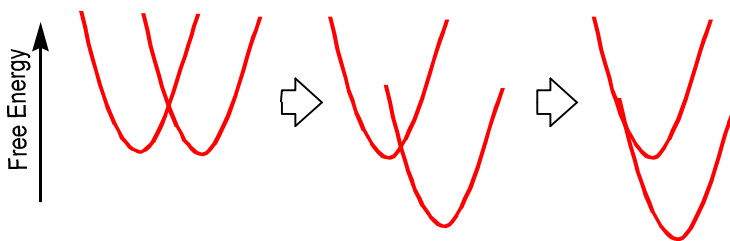
we can write $\log K_{12} = E^0/0.059 = 20$, and $K_{12} = 9.4 \times 10^{19}$

From Marcus Theory, the cross reaction rate constant k_{12} is $k_{12} = [k_1 k_2 K_{12} f]^{1/2}$

$$\begin{aligned} \text{Setting } f = 1 \text{ gives } \quad k_{12} &= [(4 \text{ M}^{-1} \text{ s}^{-1})(2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}) \times (9.4 \times 10^{20})]^{1/2} \\ &= 8 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} \end{aligned}$$

(v) Why are some extremely exergonic (large -ve ΔG) outer sphere redox reactions rather slow?

Remember the so-called Marcus inverted region, where the cross-over point for the reactant and product energy parabolas starts to rise up again with an increasing difference in their free energy, i.e.,



3) Show that for a redox reaction of the type:



where B is present in excess (i.e., not changing during the course of the reaction), the rate will be of the form:

$$\text{Rate} = \frac{k_1 [A^+]_0 [B]}{1 + k_2 [B]}$$

where $[A^+]_0 = [A^+] + [\text{intermediate}]$

As far as the maths is concerned, you've probably seen this stuff in kinetics courses. If B is in excess, its concentration will not be appreciably diminished by being tied up in the intermediate. Thus,

$$\text{Let } [A^+]_0 = [A^+] + [\text{Intermediate}]$$

$$[\text{Intermediate}] = K [A^+][B]$$

$$\text{Rate} = k_1 [\text{Intermediate}] = k_1 K [A^+][B]$$

work up (as with the SN_1CB and Id mechanisms), gives

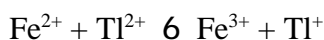
$$\text{Rate} = \frac{k_1 K}{1 + K[B]} [A^+]_0 [B]$$

- 4) Many redox reactions involve multiple electron transfers (these are called non-complementary reactions). For example, in the initial step of the stoichiometric reaction

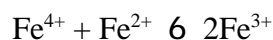


either Fe(IV) or Tl(II) species must be made. Neither of these represents a stable oxidation state. Consider the two possible two-step mechanisms shown below.

Mechanism I



Mechanism II



The observed rate law is of the form: $\text{Rate} = (a [\text{Fe}^{2+}]^2 [\text{Tl}^{3+}]) / ([\text{Fe}^{2+}] + b [\text{Fe}^{3+}])$

Assume a steady state approximation (for the concentration of Fe(IV) or Tl(II)) and determine which pathway is correct? (Note: this goes beyond class material, but have a go anyway.)

I'll just go through mechanism I here (it is the correct one). Mechanism II leads to rate law that is inconsistent with the experimental data.

Assuming a steady state for the concentration of $[\text{Tl}^{2+}]$

$$\frac{d[\text{Tl}^{2+}]}{dt} = k_1 [\text{Fe}^{2+}][\text{Tl}^{3+}] - k_{-1} [\text{Fe}^{3+}][\text{Tl}^{2+}] - k_2 [\text{Fe}^{2+}][\text{Tl}^{2+}] = 0$$

And hence the rate of formation of Fe(III) becomes:

$$\frac{d[Tl^+]}{dt} = k_2[Fe^{2+}][Tl^{2+}]_{ss} = \frac{k_1 k_2 [Fe^{2+}]^2 [Tl^{3+}]}{k_{-1}[Fe^{3+}] + k_2[Fe^{2+}]}$$

$$[Tl^{2+}]_{ss} = \frac{k_1 [Fe^{2+}][Tl^{3+}]}{k_{-1}[Fe^{3+}] + k_2[Fe^{2+}]}$$

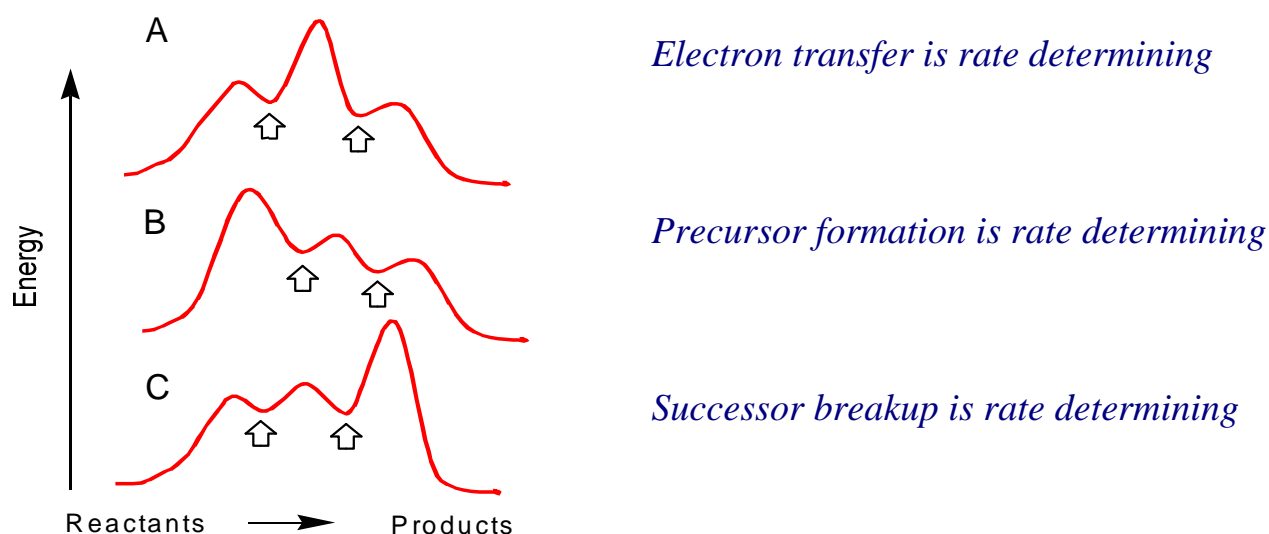
Note that according to this mechanism the addition of Fe[III] slows the reaction. In the mechanism, the addition of Tl[I] slows things down. Experimentally the former is observed.

- 6) A generalized mechanism for inner sphere electron transfer reactions involves three steps. Describe the nature of these steps and draw "potential energy versus reaction coordinate" profiles corresponding to the three possible rate-determining steps.

Select an example the of each possible type of inner sphere process from the following table of data. Explain your reasoning.

Reaction	$k^{-1}, M^{-1} s^{-1}$
(i) $V^{2+}(aq) + NCS^- \quad \delta$	28
(ii) $Cr^{2+}(aq) + [Co(NH_3)_5Cl]^{2+} \quad \delta$	6×10^5
(iii) $V^{2+}(aq) + [Ru(NH_3)_5py]^{3+} \quad \delta$	2×10^4
(iv) $Cr^{2+}(aq) + [Co(NH_3)_6]^{3+} \quad \delta$	2×10^{-7}
(v) $V^{2+}(aq) + [Co(NH_3)_5C_2O_4]^+ \quad \delta$	45
(vi) $Cr^{2+}(aq) + [Ru(NH_3)_5OC(O)CH_3]^{2+} \quad \delta$	10^{-2}
(vii) $Fe(CN)_6^{4-} + [Ru(phen)_3]^{3+} \quad \delta$	$> 10^8$

If you can answer this question, then your have inner and outer sphere reactions licked. Not all of these reactions are inner sphere. But for the record the three inner sphere profiles we discussed are:



Let's just walk through the reactions (there are some grey areas).

First, number (i) is not a redox reaction at all. It is a substitution reaction of V(II), which is $(t2g)^3$, i.e., inert. The rate is not fast, but note that it is about the same as the redox reaction (v), in which an inner sphere reaction is possible (there is an oxalate bridge on the oxidant). The near equivalence of the two rates suggests a similar rate determining step, which must be the shedding of a water molecule from the primary coordination sphere of vanadium (to make a "socket" for the bridge). So reaction (v) is a class B inner sphere.

Moving to reaction (iii), which also involves V(II), the oxidant is now Ru(III), which is $(t2g)^5$. Note that now we have a perfect electronic set-up for an outer sphere reaction (net B to B). It's hard to see this going by an inner sphere. It is tough to make the precursor, tough to effect transfer (the ligand pyridine cannot bridge), and the successor complex won't break up (the "tape on the fingers" problem). At best this is a class C inner sphere.

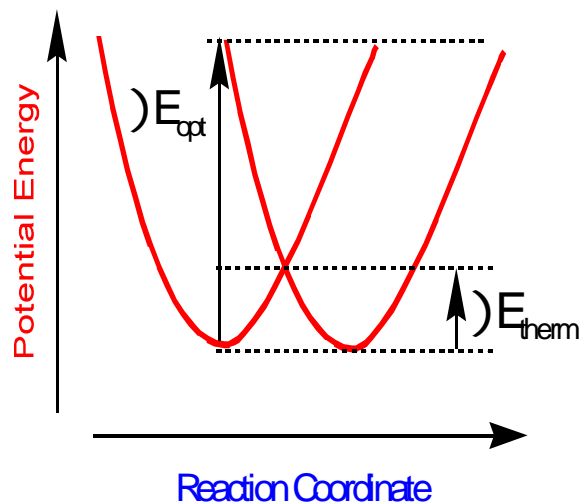
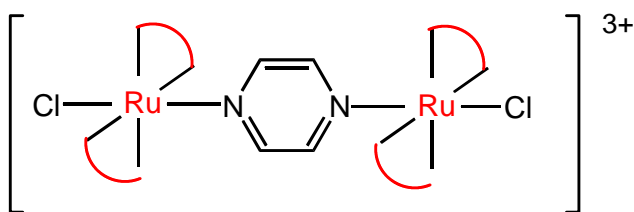
Now let's turn to reactions (ii) and (iv) together. They look similar, but have very different rates. These are bad outer sphere reactions, as both are net F to F transfers. From an inner perspective they seem better, as both there is a labile/inert pair on both sides of the equation. The trouble for (iv) is that it has no ligands on Co(III) capable of bridging to Cr(II) - there is a socket, but no plug. So the reaction is probably just a slow outer sphere, or at best a bad class B inner sphere.

Reaction (ii) is a beautiful class A inner sphere, as everything is now in place, including a bridging halide. The rate is limited simply by the overlap capability of the bridging ligand.

Finally we come to reaction 7, which is a not inner sphere at all. It is net B to B, therefore

a small reorganizational energy, everything involved is inert, and there are large flat aromatic ligands on one of the metals. All this supports a very efficient outer sphere mechanism, and the rate suggests it is so.

- 7) The complex $[(\text{bipy})_2\text{ClRu-pyrazine-Ru}(\text{bipy})_2\text{Cl}]^{5+}$ displays an intervalence charge transfer band at 7690 cm^{-1} (this is way off in the near IR region). Estimate the energy barrier to thermal electron transfer. If E_{th} can be loosely equated to ΔG^\ddagger for thermal electron transfer, estimate the rate constant. The thermal rate constant has been reported to be near 10^{10} s^{-1} .



Going back to the parabolas discussed in class:

$$E_{\text{th}} = 1/4 E_{\text{opt}}$$

$$= 1/4 (7.69 \times 10^3 \text{ cm}^{-1}) = 1.92 \times 10^3 \text{ cm}^{-1}$$

For a mole of complex ions

$$\Delta G^\ddagger = N E_{\text{th}} = 6.02 \times 10^{23} \text{ mol}^{-1} (1.92 \times 10^3 \text{ cm}^{-1})(6.63 \times 10^{-34} \text{ J sec}) (3.00 \times 10^{10} \text{ cm sec}^{-1})$$

$$= 2.30 \times 10^4 \text{ J mol}^{-1}$$

From activated complex theory, the thermal rate constant k is given by:

$$k = \frac{k_B T}{h} \exp \frac{-\Delta G^\ddagger}{RT}$$

Plugging in the appropriate values for temperature, the Boltzmann and gas constants gives

$$k = \frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{6.63 \times 10^{-34} \text{ J sec}} \exp \frac{(2.30 \times 10^4 \text{ J mol}^{-1})}{(8.33 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K})}$$

hence $k = 6.24 \times 10^{12} \text{ sec}^{-1} \exp(-9.20) = 6.24 \times 10^{12} \text{ sec}^{-1} (1.01 \times 10^{-4}) \text{ sec}^{-1}$

and $k = 6.3 \times 10^8 \text{ sec}^{-1}$, i.e., within an order of magnitude of the experimentally determined rate.