Chemistry 2740 Spring 2018 Test 3 solutions

1. (a)

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2\,e^-$$

$$2 \times \left(HNO_{3(l)} + H^+_{(aq)} + e^- \longrightarrow NO_{2(g)} + H_2O_{(l)} \right)$$

$$\overline{Cu_{(s)} + 2\,HNO_{3(l)} + 2\,H^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2\,NO_{2(g)} + 2\,H_2O_{(l)}}$$
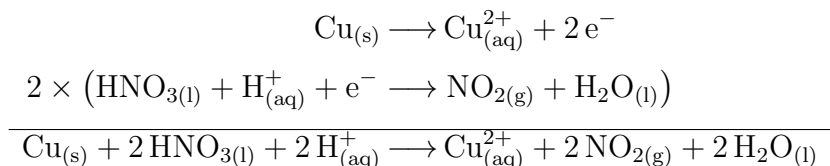
(b) There are two different ways to solve this problem.

   i. The first method uses the overall reaction and the reduction potential of Cu^{2+}:

$$\begin{aligned}
\Delta_r G^\circ_m &= \Delta_f G^\circ(Cu^{2+}) + 2\Delta_f G^\circ(NO_2) + 2\Delta_f G^\circ(H_2O) \\
&\quad - \left[\Delta_f G^\circ(Cu) + 2\Delta_f G^\circ(HNO_3) + 2\Delta_f G^\circ(H^+) \right] \\
&= 65.6 + 2(51.32) + 2(-237.140) - [0 + 2(-80.7) + 2(0)]\ kJ\,mol^{-1} \\
&= -144.6\ kJ\,mol^{-1}
\end{aligned}$$

$$E^\circ = -\frac{\Delta_r G^\circ_m}{\nu_e F}$$

   From the balancing procedure, we have $\nu_e = 2$.

$$\begin{aligned}
\therefore E^\circ &= -\frac{-144.6 \times 10^3\ J\,mol^{-1}}{2(96\,485.342\ C\,mol^{-1})} \\
&= 0.7495\ V. \\
E^\circ &= E^\circ_{HNO3/NO2} - E^\circ_{Cu^{2+}/Cu}. \\
\therefore E^\circ_{HNO3/NO2} &= E^\circ + E^\circ_{Cu^{2+}/Cu} \\
&= 0.7495 + 0.3419\ V = 1.0914\ V.
\end{aligned}$$

   ii. The second method uses just the nitric acid half-reaction:

$$HNO_{3(l)} + H^+_{(aq)} + e^- \longrightarrow NO_{2(g)} + H_2O_{(l)}$$
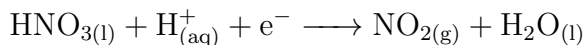
   Because the electron won't appear in any overall reaction, it doesn't "count" in terms of free energy. To put it another way, the electron in a half-reaction is not a solvated electron. It's an electron that will be transferred directly to another substance during a redox reaction. For this half-reaction,

$$\begin{aligned}
\Delta_r G^\circ_m &= \Delta_f G^\circ(NO_2) + \Delta_f G^\circ(H_2O) - \left[\Delta_f G^\circ(HNO_3) + \Delta_f G^\circ(H^+) \right] \\
&= 51.32 + (-237.140) - [-80.7 + 0]\ kJ\,mol^{-1} \\
&= -105.1\ kJ\,mol^{-1}
\end{aligned}$$

$$E^\circ = -\frac{\Delta_r G^\circ_m}{\nu_e F}$$

Here, we get $\nu_e = 1$ from the half-reaction.

$$\therefore E^\circ = -\frac{-105.1 \times 10^3 \, \text{J} \, \text{mol}^{-1}}{1(96\,485.342 \, \text{C} \, \text{mol}^{-1})}$$
$$= 1.089 \, \text{V}.$$

The two answers differ slightly (by less than $2 \, \text{mV}$) because data from different sources was used, and these data are not always entirely consistent. In particular, the free energy data are not entirely consistent with the source I used for the standard reduction potential of the copper(II) ion. But again, the difference is in the last significant figure of the second calculation, which is somewhat uncertain.

2. (a)

$$\frac{d[\text{e}^-_{(\text{aq})}]}{dt} = -2k[\text{e}^-_{(\text{aq})}]^2$$
$$= -2(5.5 \times 10^9 \, \text{L} \, \text{mol}^{-1}\text{s}^{-1})(1.8 \times 10^{-6} \, \text{mol} \, \text{L}^{-1})^2$$
$$= -3.6 \times 10^{-2} \, \text{mol} \, \text{L}^{-1}\text{s}^{-1}$$

(b) The half-life formula is derived for a reactant that obeys a rate law

$$\frac{dx}{dt} = -kx^2,$$

but here we actually have

$$\frac{dx}{dt} = -2kx^2,$$

where x is the concentration of solvated electrons, so we have to replace k by $2k$ in the half-life formula. Thus,

$$t_{1/2} = \frac{2^{n-1} - 1}{2kx_0^{n-1}(n-1)}$$

For this reaction, $n = 2$, so we have

$$t_{1/2} = \frac{2-1}{2kx_0^1(1)} = \frac{1}{2kx_0}$$
$$= \frac{1}{2(5.5 \times 10^9 \, \text{L} \, \text{mol}^{-1}\text{s}^{-1})(1.8 \times 10^{-6} \, \text{mol} \, \text{L}^{-1})}$$
$$= 5.1 \times 10^{-5} \, \text{s} \equiv 51 \, \mu\text{s}.$$

(c) We have $x_0 = 1.8 \times 10^{-6} \, \text{mol} \, \text{L}^{-1}$ and $x = 0.01x_0 = 1.8 \times 10^{-8} \, \text{mol} \, \text{L}^{-1}$. The

second-order integrated rate law is

$$\frac{1}{x} = \frac{1}{x_0} + 2kt$$

$$\therefore t = \frac{1}{2k}\left(\frac{1}{x} - \frac{1}{x_0}\right)$$

$$= \frac{1}{2(5.5 \times 10^9 \,\text{L}\,\text{mol}^{-1}\text{s}^{-1})}\left(\frac{1}{1.8 \times 10^{-8}\,\text{mol}\,\text{L}^{-1}} - \frac{1}{1.8 \times 10^{-6}\,\text{mol}\,\text{L}^{-1}}\right)$$

$$= 0.005 \,\text{s}.$$

(d)

$$\frac{d[\text{OH}^\bullet]}{dt} = k_3[\text{H}^\bullet][\text{H}_2\text{O}]$$

The intermediate to eliminate from this rate equation is $\text{H}^\bullet$. We can apply the steady-state approximation:

$$\frac{d[\text{H}^\bullet]}{dt} = k_1[\text{e}^-_{(\text{aq})}][\text{H}_2\text{O}] + k_2[\text{e}^-_{(\text{aq})}][\text{H}^+] - k_3[\text{H}^\bullet][\text{H}_2\text{O}] \approx 0.$$

$$\therefore [\text{H}^\bullet] \approx \frac{k_1[\text{e}^-_{(\text{aq})}][\text{H}_2\text{O}] + k_2[\text{e}^-_{(\text{aq})}][\text{H}^+]}{k_3[\text{H}_2\text{O}]}.$$

$$\therefore \frac{d[\text{OH}^\bullet]}{dt} \approx [\text{e}^-_{(\text{aq})}]\left(k_1[\text{H}_2\text{O}] + k_2[\text{H}^+]\right).$$

The second-order $\text{H}^\bullet + \text{H}^\bullet$ reaction would make the steady-state condition a quadratic. This can be solved by hand, but it's a lot more work.

(e) Reaction 1 produces hydroxide ions which, among other things, will reduce the hydrogen ion concentration. Reaction 2 has hydrogen ions as a reactant. This makes the rate of reaction 2 depending on the H^+ concentration. Moreover, having H^+ as a reactant in reaction 2 means that this reaction will remove H^+ from solution. These two reactions (and a number of others not shown on this test) will therefore change the concentrations of the H^+ and OH^- ions, altering the rates of any reactions in which these two species appear as reactants. Keeping these concentrations constant by using a pH buffer eliminates one source of variability in these experiments.