Chemistry 2740 Spring 2018 Test 3 solutions

1. (a)

$$\begin{aligned}
&\mathrm{Cu_{(s)}} \longrightarrow \mathrm{Cu^{2+}_{(aq)}} + 2\,\mathrm{e^-} \\
&2 \times \left(\mathrm{HNO_{3(l)}} + \mathrm{H^+_{(aq)}} + \mathrm{e^-} \longrightarrow \mathrm{NO_{2(g)}} + \mathrm{H_2O_{(l)}}\right) \\
\hline
&\mathrm{Cu_{(s)}} + 2\,\mathrm{HNO_{3(l)}} + 2\,\mathrm{H^+_{(aq)}} \longrightarrow \mathrm{Cu^{2+}_{(aq)}} + 2\,\mathrm{NO_{2(g)}} + 2\,\mathrm{H_2O_{(l)}}
\end{aligned}$$

   (b) There are two different ways to solve this problem.

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

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

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

$$\begin{aligned}
\therefore E^\circ &= -\frac{-144.6 \times 10^3\,\mathrm{J\,mol^{-1}}}{2(96\,485.342\,\mathrm{C\,mol^{-1}})} \\
&= 0.7495\,\mathrm{V}. \\
E^\circ &= E^\circ_{\mathrm{HNO_3/NO_2}} - E^\circ_{\mathrm{Cu^{2+}/Cu}}. \\
\therefore E^\circ_{\mathrm{HNO_3/NO_2}} &= E^\circ + E^\circ_{\mathrm{Cu^{2+}/Cu}} \\
&= 0.7495 + 0.3419\,\mathrm{V} = 1.0914\,\mathrm{V}.
\end{aligned}$$

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

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

      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,

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

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

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

The two answers differ slightly (by less than 2 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)

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

(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

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

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

second-order integrated rate law is

$$\begin{aligned}
\frac{1}{x} &= \frac{1}{x_0} + 2kt \\
\therefore t &= \frac{1}{2k}\left(\frac{1}{x} - \frac{1}{x_0}\right) \\
&= \frac{1}{2(5.5 \times 10^9\,\mathrm{L\,mol^{-1}s^{-1}})}\left(\frac{1}{1.8 \times 10^{-8}\,\mathrm{mol\,L^{-1}}} - \frac{1}{1.8 \times 10^{-6}\,\mathrm{mol\,L^{-1}}}\right) \\
&= 0.005\,\mathrm{s}.
\end{aligned}$$

(d)

$$\frac{d[\mathrm{OH^\bullet}]}{dt} = k_3[\mathrm{H^\bullet}][\mathrm{H_2O}]$$

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

$$\begin{aligned}
\frac{d[\mathrm{H^\bullet}]}{dt} &= k_1[\mathrm{e^-_{(aq)}}][\mathrm{H_2O}] + k_2[\mathrm{e^-_{(aq)}}][\mathrm{H^+}] - k_3[\mathrm{H^\bullet}][\mathrm{H_2O}] \approx 0. \\
\therefore [\mathrm{H^\bullet}] &\approx \frac{k_1[\mathrm{e^-_{(aq)}}][\mathrm{H_2O}] + k_2[\mathrm{e^-_{(aq)}}][\mathrm{H^+}]}{k_3[\mathrm{H_2O}]}. \\
\therefore \frac{d[\mathrm{OH^\bullet}]}{dt} &\approx [\mathrm{e^-_{(aq)}}]\left(k_1[\mathrm{H_2O}] + k_2[\mathrm{H^+}]\right).
\end{aligned}$$

The second-order $\mathrm{H^\bullet} + \mathrm{H^\bullet}$ 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 $\mathrm{H^+}$ concentration. Moreover, having $\mathrm{H^+}$ as a reactant in reaction 2 means that this reaction will remove $\mathrm{H^+}$ from solution. These two reactions (and a number of others not shown on this test) will therefore change the concentrations of the $\mathrm{H^+}$ and $\mathrm{OH^-}$ 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.