Chemistry 2740 Spring 2020 Test 2 Solutions

1. (a) The standard temperature is 25 °C, so we use the value of K at that temperature.

$$\begin{aligned}\Delta_r G^\circ &= -RT\ln K\\ &= -(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})\ln(5.80\times10^{-10})\\ &= 52.72\,\mathrm{kJ/mol}.\end{aligned}$$

   (b) A plot of $\ln K$ vs T^{-1} will have a slope of $-\Delta_r H^\circ/R$. My graph is shown in Fig. 1. The slope of the line is $-1586\,\mathrm{K}$. Therefore,

$$\begin{aligned}\Delta_r H^\circ &= -R(\text{slope})\\ &= -(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(-1586\,\mathrm{K})\\ &= 13.19\,\mathrm{kJ/mol}.\end{aligned}$$

   (c)

$$K = \frac{(a_{\mathrm{B(OH)_4^-}})(a_{\mathrm{H^+}})}{(a_{\mathrm{B(OH)_3}})(a_{\mathrm{H_2O}})} \tag{1}$$

Since $[\mathrm{B(OH)_3}] \gg K$, very little of the boric acid will react. Accordingly, we can assume that $a_{\mathrm{B(OH)_3}} \approx 0.013$. Since $Ka_{\mathrm{B(OH)_3}} \gg K_w$, water autoionization is negligible. It follows that $\mathrm{H^+}$ and $\mathrm{B(OH)_4^-}$ will be present at equal concentrations. Equation (1) can be written

$$K = \frac{\left(\gamma_\pm[\mathrm{B(OH)_4^-}]\right)\left(\gamma_\pm[\mathrm{H^+}]\right)}{(a_{\mathrm{B(OH)_3}})(a_{\mathrm{H_2O}})}$$

With equal concentrations of $\mathrm{H^+}$ and $\mathrm{B(OH)_4^-}$, the activities of these two ions are therefore the same. Thus we have

$$\begin{aligned}7.89\times10^{-10} &= \frac{(a_{\mathrm{H^+}})^2}{(0.013)(1)}.\\ \therefore a_{\mathrm{H^+}} &= \sqrt{(0.013)(7.89\times10^{-10})}\\ &= 3.2\times10^{-6}.\\ \therefore \mathrm{pH} &= -\log_{10} a_{\mathrm{H^+}}\\ &= -\log_{10}(3.2\times10^{-6}) = 5.49.\end{aligned}$$

2. (a)

$$\begin{array}{rcl}\mathrm{Zn_{(s)}} & \rightarrow & \mathrm{Zn^{2+}_{(aq)}} + 2e^-\\ \mathrm{2NO^-_{3(aq)}} + \mathrm{4H^+_{(aq)}} + 2e^- & \rightarrow & \mathrm{2NO_{2(g)}} + \mathrm{2H_2O_{(l)}}\\ \hline \mathrm{Zn_{(s)}} + \mathrm{2NO^-_{3(aq)}} + \mathrm{4H^+_{(aq)}} & \rightarrow & \mathrm{Zn^{2+}_{(aq)}} + \mathrm{2NO_{2(g)}} + \mathrm{2H_2O_{(l)}}\end{array}$$

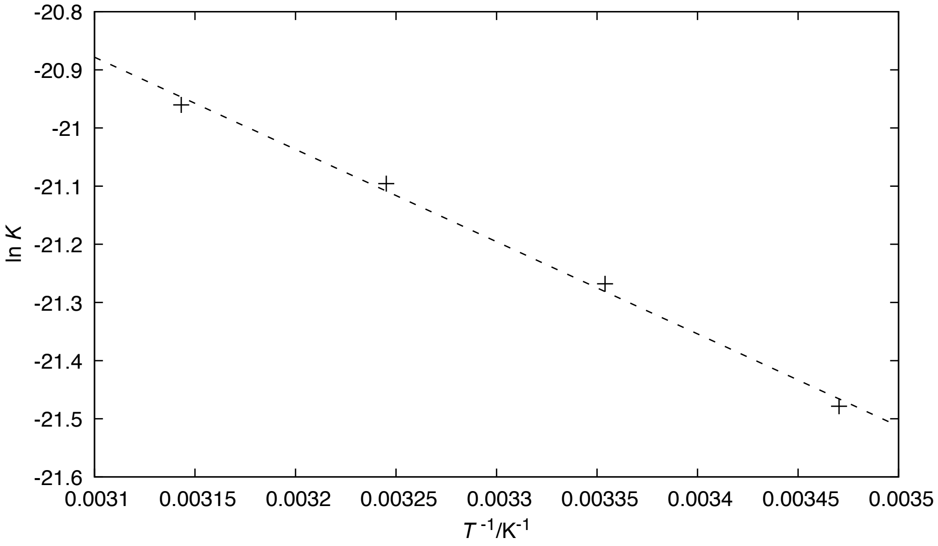

Figure 1: Graph of $\ln K$ vs T^{-1} for the reaction of boric acid with water.

(b)

$$\begin{aligned}\Delta_r G^\circ &= \Delta_f G^\circ(\mathrm{Zn}^{2+}) + 2\Delta_f G^\circ(\mathrm{NO}_2) + 2\Delta_f G^\circ(\mathrm{H_2O}) - 2\Delta_f G^\circ(\mathrm{NO}_3^-) \\ &= -111.62 + 2(51.32) + 2(-237.140) - 2(-108.74)\,\mathrm{kJ/mol} \\ &= -265.78\,\mathrm{kJ/mol}.\end{aligned}$$

From the balancing exercise above, $\nu_e = 2$. Therefore,

$$\begin{aligned}E^\circ &= -\frac{\Delta_r G^\circ}{\nu_e F} \\ &= \frac{265.78 \times 10^3\,\mathrm{J/mol}}{2(96\,485.342\,\mathrm{C/mol})} \\ &= 1.3773\,\mathrm{V}.\end{aligned}$$

We need the activity coefficient of the zinc ion. The ionic strength of the solution at the anode is dominated by the sulfuric acid. Since sulfuric acid is a strong acid, in solution it exists as H^+ and $\mathrm{HSO_4^-}$.

$$\begin{aligned}I_c &= \frac{1}{2}\left[(+1)^2[\mathrm{H}^+] + (-1)^2[\mathrm{HSO_4^-}]\right] \\ &= \frac{1}{2}\left[(+1)^2(0.0032) + (-1)^2(0.0032\,\mathrm{mol/L})\right] \\ &= 0.0032\,\mathrm{mol/L}. \\ \therefore \ln\gamma_{\mathrm{Zn}^{2+}} &= -Az_i^2(\varepsilon T)^{-3/2}\sqrt{I_c} \\ &= -(1.107\times10^{-10})(+2)^2\left[(6.939\times10^{-10}\,\mathrm{C^2J^{-1}m^{-1}})(298.15\,\mathrm{K})\right]^{-3/2} \\ &\qquad \times \sqrt{0.0032\,\mathrm{mol/L}}\end{aligned}$$

$$
\begin{aligned}
&= -0.27. \\
\therefore \gamma_{\mathrm{Zn}^{2+}} &= e^{-0.27} = 0.77. \\
E &= E^\circ - \frac{RT}{\nu_e F} \ln\left(\frac{(a_{\mathrm{Zn}^{2+}})(a_{\mathrm{NO}_2})^2}{(a_{\mathrm{NO}_3^-})^2(a_{\mathrm{H}^+})^4}\right) \\
&= 1.3773\,\mathrm{V} - \frac{(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})}{2(96\,485.342\,\mathrm{C/mol})} \\
&\qquad\qquad \times \ln\left(\frac{[(0.77)(1.0\times10^{-5})](0.24)^2}{[(0.968)(3.539)]^2[(0.968)(3.539)]^4}\right) \\
&= 1.660\,\mathrm{V}.
\end{aligned}
$$

There is a problem with this solution, which only occurred to me when I was marking the tests: If you do a quick estimate of the pH assuming that only the first proton of sulfuric acid is dissociated, you find that the pH (~ 2.5) is very close to the pK_a of the second proton (2.0). This means that there will be significant dissociation of the second proton. (I'll be honest: I just didn't think of this when I was designing the question.) To really do a good job of this problem, we would have to take that into account. And you would have the problem that you need to do a detailed Debye-Hückel calculation to figure out how much of the HSO_4^- is dissociated. Not super-hard, but time consuming. You could, alternatively, assume that the sulfuric acid is fully dissociated to H^+ and SO_4^-, which turns out to be closer to the truth than assuming that only the first proton is dissociated. If you do that, the calculation runs as follows:

$$
\begin{aligned}
I_c &= \frac{1}{2}\left[(+1)^2[\mathrm{H}^+] + (-2)^2[\mathrm{SO}_4^{2-}]\right] \\
&= \frac{1}{2}\left[(+1)^2(0.0064) + (-2)^2(0.0032\,\mathrm{mol/L})\right] \\
&= 0.0096\,\mathrm{mol/L}. \\
\therefore \ln\gamma_{\mathrm{Zn}^{2+}} &= -Az_i^2(\varepsilon T)^{-3/2}\sqrt{I_c} \\
&= -(1.107\times10^{-10})(+2)^2\left[(6.939\times10^{-10}\,\mathrm{C^2J^{-1}m^{-1}})(298.15\,\mathrm{K})\right]^{-3/2} \\
&\qquad \times \sqrt{0.0096\,\mathrm{mol/L}} \\
&= -0.46. \\
\therefore \gamma_{\mathrm{Zn}^{2+}} &= e^{-0.46} = 0.63. \\
E &= E^\circ - \frac{RT}{\nu_e F} \ln\left(\frac{(a_{\mathrm{Zn}^{2+}})(a_{\mathrm{NO}_2})^2}{(a_{\mathrm{NO}_3^-})^2(a_{\mathrm{H}^+})^4}\right) \\
&= 1.3773\,\mathrm{V} - \frac{(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})}{2(96\,485.342\,\mathrm{C/mol})} \\
&\qquad\qquad \times \ln\left(\frac{[(0.63)(1.0\times10^{-5})](0.24)^2}{[(0.968)(3.539)]^2[(0.968)(3.539)]^4}\right) \\
&= 1.663\,\mathrm{V}.
\end{aligned}
$$

The correct value is somewhere between these two numbers, but really, the difference is pretty small.