Chemistry 2740 Spring 2022 Test 2 Solutions

1. (a)

$$\begin{array}{rcl} \mathrm{Al_{(s)}} + 4\mathrm{H_2O_{(l)}} & \rightarrow & \mathrm{Al(OH)^-_{4(aq)}} + 4\,\mathrm{H^+_{(aq)}} + 3\mathrm{e^-} \\ \mathrm{MnO^-_{4(aq)}} + 4\,\mathrm{H^+_{(aq)}} + 3\mathrm{e^-} & \rightarrow & \mathrm{MnO_{2(s)}} + 2\mathrm{H_2O_{(l)}} \\ \hline \mathrm{Al_{(s)}} + 2\mathrm{H_2O_{(l)}} + \mathrm{MnO^-_{4(aq)}} & \rightarrow & \mathrm{Al(OH)^-_{4(aq)}} + \mathrm{MnO_{2(s)}} \end{array}$$

   (b) From the balancing process, we have $\nu_e = 3$.

$$\begin{aligned} \Delta_r G^\circ &= \Delta_f G^\circ(\mathrm{Al(OH)_4^-}) + \Delta_f G^\circ(\mathrm{MnO_2}) - \left[2\Delta_f G^\circ(\mathrm{H_2O}) + \Delta_f G^\circ(\mathrm{MnO_4^-})\right] \\ &= -1301 + (-465.2) - [2(-237.140) + (-425.1)]\ \mathrm{kJ\,mol^{-1}} \\ &= -867\,\mathrm{kJ\,mol^{-1}} \\ E^\circ &= \frac{-\Delta_r G^\circ}{\nu_e F} \\ &= \frac{867 \times 10^3\,\mathrm{J\,mol^{-1}}}{3(96\,485.342\,\mathrm{C\,mol^{-1}}} \\ &= 2.99\,\mathrm{V} \end{aligned}$$

2. This is an application of the formula

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

   The reaction is

$$\mathrm{SrF_{2(s)}} \rightleftharpoons \mathrm{Sr^{2+}_{(aq)}} + 2\mathrm{F^-_{(aq)}}$$

$$\begin{aligned} \Delta_r H^\circ &= \Delta_f H^\circ(\mathrm{Sr^{2+}}) + 2\Delta_f H^\circ(\mathrm{F^-}) - \Delta_f H^\circ(\mathrm{SrF_2}) \\ &= -545.51 + 2(-335.35) - (-1217.13)\,\mathrm{kJ\,mol^{-1}} \\ &= 0.92\,\mathrm{kJ\,mol^{-1}} \end{aligned}$$

   For this problem, we have

$$\begin{array}{ll} K_1 = 2.6 \times 10^{-9} & \text{at } T_1 = 298.15\,\mathrm{K} \\ K_2 \text{ is the unknown} & \text{at } T_2 = 373.15\,\mathrm{K} \end{array}$$

$$\begin{aligned} \ln\left(\frac{K_2}{2.6 \times 10^{-9}}\right) &= \frac{920\,\mathrm{J\,mol}}{8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}}\left(\frac{1}{298.15\,\mathrm{K}} - \frac{1}{373.15\,\mathrm{K}}\right) \\ &= 0.075 \\ \therefore \frac{K_2}{2.6 \times 10^{-9}} &= e^{0.075} = 1.08 \\ \therefore K_2 &= 1.08(2.6 \times 10^{-9}) = 2.8 \times 10^{-9} \end{aligned}$$

3. The hint says to start by solving the equilibrium problem. The relevant equilibrium is

$$\mathrm{ClCH_2COOH_{(aq)}} \rightleftharpoons \mathrm{ClCH_2COO^-_{(aq)}} + \mathrm{H^+_{(aq)}}$$

For simplicity of notation, I will write AH for the acid, and A^- for the conjugate base. The corresponding K_a expression is

$$K_a = \frac{(a_{\mathrm{A}^-})(a_{\mathrm{H}^+})}{a_{\mathrm{AH}}}$$

The activity coefficient of acid is approximately 1, so $a_{\mathrm{AH}} \approx [\mathrm{AH}]/c^\circ$. For the ions however, we have to take the activity coefficients into account. Thus, $a_{\mathrm{A}^-} = \gamma_\pm[\mathrm{A}^-]/c^\circ$ and $a_{\mathrm{H}^+} = \gamma_\pm[\mathrm{H}^+]/c^\circ$. Note that I'm using $\gamma_\pm$ to save a bit of algebra (although with both ions having the same charge, there isn't a real saving in this case). The concentrations of the acid, base and H^+ are related, as can be determined using an ICE table:

	[AH]	$[\mathrm{A}^-]$	$[\mathrm{H}^+]$
I	5.28×10^{-3}	0	0
C	$-x$	x	x
E	$5.28 \times 10^{-3} - x$	x	x

The K_a expression thus reads

$$K_a = \frac{\gamma_\pm^2 x^2}{5.28 \times 10^{-3} - x}$$

To calculate $\gamma_\pm$, we need the ionic strength at equilibrium:

$$\begin{aligned} I_c &= \frac{1}{2}\left\{(+1)^2[\mathrm{H}^+] + (-1)^2[\mathrm{A}^-]\right\} \\ &= \frac{1}{2}\{x + x\} = x \end{aligned}$$

Thus we have

$$\begin{aligned} \ln\gamma_\pm &= Az_+z_-\,(\epsilon T)^{-3/2}\sqrt{I_c} \\ &= (1.107 \times 10^{-10}) * (1)(-1) * \left[(78.37)(8.854\,188 \times 10^{-12})(298.15)\right]^{-3/2}\sqrt{x} \\ &= -1.176\sqrt{x} \\ \therefore \gamma_\pm &= e^{-1.176\sqrt{x}} \end{aligned}$$

The final equation we have to solve is therefore

$$K_a = 1.4 \times 10^{-3} = \frac{\left(e^{-1.176\sqrt{x}}\right)^2 x^2}{5.28 \times 10^{-3} - x} = \frac{e^{-2.353\sqrt{x}} x^2}{5.28 \times 10^{-3} - x}$$

You can solve this equation using any convenient tool. I used my TI-89 calculator with an initial guess for x of 10^{-3}. The solver gave a solution of

$$x = 2.2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$$

We don't just want the concentration. We want the pH:

$$\begin{aligned}
\mathrm{pH} &= -\log_{10} a_{\mathrm{H}^+} \\
a_{\mathrm{H}^+} &= \gamma_{\pm}[\mathrm{H}^+]/c^{\circ} \\
&= e^{-1.176\sqrt{x}}x/c^{\circ} \\
&= 2.1 \times 10^{-3} \\
\therefore \mathrm{pH} &= -\log_{10}(2.1 \times 10^{-3}) = 2.68.
\end{aligned}$$