Chemistry 2740 Spring 2021 Test 2 Solutions

1. We're going to use the Nernst equation:

$$E = E^\circ - \frac{RT}{\nu_e F}\ln Q.$$

The biggest problem is that E° is related to $\Delta_r G^\circ$ by

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

and $\Delta_r G^\circ$ depends on T:

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ.$$

This means that we will need $\Delta_r H^\circ$ (generally easily calculated from thermodynamic tables) and $\Delta_r S^\circ$ (either calculated directly from entropy tables or indirectly from standard free energy and enthalpy tables). Then we can calculate $\Delta_r G^\circ$ at the appropriate temperature, and from there E°.

2. (a) The reaction is

$$\mathrm{Pb(N_3)_{2(\mathit{s})}} \longrightarrow \mathrm{Pb^{2+}_{(aq)}} + 2\,\mathrm{N^-_{3(aq)}}.$$

For this reaction

$$\begin{aligned} K_{\rm sp} &= (a_{\mathrm{Pb^{2+}}})(a_{\mathrm{N_3^-}})^2 \\ &= \gamma_\pm^3[\mathrm{Pb^{2+}}][\mathrm{N_3^-}]^2/(c^\circ)^3. \end{aligned}$$

If we call the solubility s, then $[\mathrm{Pb^{2+}}] = s$ and $[\mathrm{N_3^-}] = 2s$. Thus,

$$K_{\rm sp} = \gamma_\pm^3 s(2s)^2 = 4\gamma_\pm^3 s^3.$$

To calculate $\gamma_\pm$, we need I_c:

$$\begin{aligned} I_c &= \frac{1}{2}\left\{(+2)^2[\mathrm{Pb^{2+}}] + (-1)^2[\mathrm{N_3^-}]\right\} \\ &= \frac{1}{2}(4s + 2s) = 3s. \\ \therefore \ln\gamma_\pm &= Az_+z_-(\varepsilon T)^{-3/2}\sqrt{I_c} \\ &= -2A(\varepsilon T)^{-3/2}\sqrt{3s}. \end{aligned}$$

We are now all set to do the calculations. At 25 °C, we have (remembering to convert the temperature to Kelvin, and leaving out the units for convenience)

$$\begin{aligned} \ln\gamma_\pm &= -2(1.107\times10^{-10})\left[(6.939\times10^{-10})(298.15\,\mathrm{K})\right]^{-3/2}\sqrt{3(7.5\times10^{-4})} \\ &= -0.11. \\ \therefore \gamma_\pm &= e^{-0.11} = 0.89. \\ \therefore K_{\rm sp} &= 4(0.90)^3(7.5\times10^{-4})^3 \\ &= 1.2\times10^{-9}. \end{aligned}$$

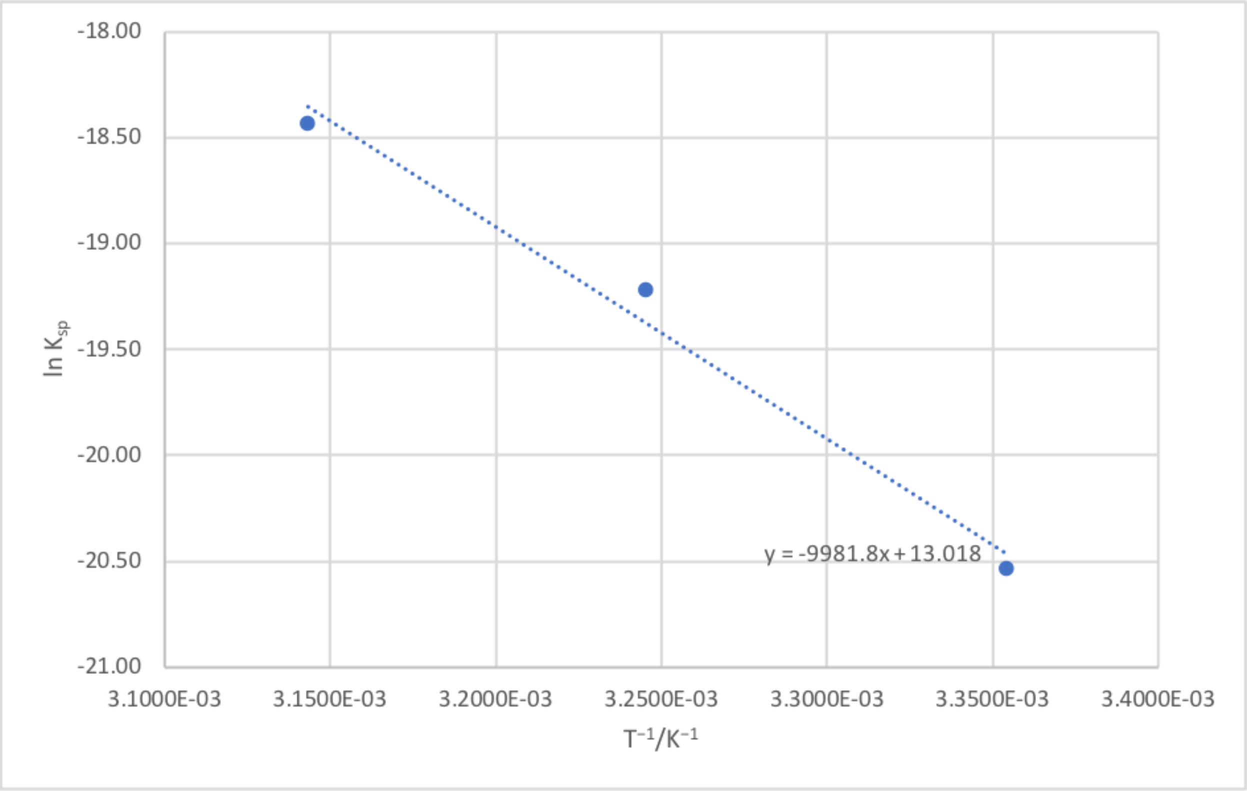

Figure 1: Graph of $\ln K_{\text{sp}}$ vs T^{-1}.

Repeating these calculations at the other two temperatures, we get the following table of values:

T/K	298.15	308.15	318.15
K_{sp}	1.2×10^{-9}	4.5×10^{-9}	9.9×10^{-9}

(b) We can get the enthalpy change from a graph of $\ln K_{\text{sp}}$ vs T^{-1}. My graph is shown in figure 1. The slope of the graph is $-9982\,\text{K}$.

$$\begin{aligned} \text{slope} &= -\Delta_r H^\circ/R \\ \therefore \Delta_r H^\circ &= -R(\text{slope}) \\ &= -(8.314\,472\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(-9982\,\text{K}) \\ &= 83.0\,\text{kJ}\,\text{mol}^{-1}. \end{aligned}$$

(c)

$$\begin{aligned} \Delta_r H^\circ &= \Delta_f H^\circ(\text{Pb}^{2+}) + 2\Delta_f H^\circ(\text{N}_3^-) - \Delta_f H^\circ(\text{Pb(N}_3)_2) \\ \therefore \Delta_f H^\circ(\text{Pb(N}_3)_2) &= \Delta_f H^\circ(\text{Pb}^{2+}) + 2\Delta_f H^\circ(\text{N}_3^-) - \Delta_r H^\circ \\ &= 0.92 + 2(274.2) - 83.0\,\text{kJ}\,\text{mol}^{-1} = 466.3\,\text{kJ}\,\text{mol}^{-1}. \end{aligned}$$

(d) The standard free energy change is the free energy of reaction at 25 °C. We can calculate this from the equilibrium constant at 25 °C. There are two options for doing this. The first is to take the equilibrium constant we calculated at this temperature at face value:

$$\begin{aligned}\Delta_r G^\circ &= -RT\ln K_{\text{sp}}\\ &= -(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})\ln(1.2\times10^{-9})\\ &= 50.9\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

Arguably though, since there is some amount of experimental error in any given measurement, we should estimate $\ln K_{\text{sp}}$ using our regression line, which combines all of our measurements and therefore averages out errors across our data set. My line of best fit has the equation

$$\begin{aligned}\ln K_{\text{sp}} &= -9981.8\frac{1}{T}+13.018\\ \therefore \ln K_{\text{sp}}(298.15\,\mathrm{K}) &= -9981.8\frac{1}{298.15\,\mathrm{K}}+13.018=-20.46.\\ \therefore \Delta_r G^\circ &= -RT\ln K_{\text{sp}}\\ &= -(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})(-20.46)\\ &= 50.7\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

Admittedly, not a huge difference from the "direct" calculation, but probably a better way to proceed. I'm therefore going to use the value from the regression in the calculations that follow. I gave full credit either way.

(e)

$$\begin{aligned}\Delta_r G^\circ &= \Delta_f G^\circ(\mathrm{Pb^{2+}})+2\Delta_f G^\circ(\mathrm{N_3^-})-\Delta_f G^\circ(\mathrm{Pb(N_3)_2})\\ \therefore \Delta_f G^\circ(\mathrm{Pb(N_3)_2}) &= \Delta_f G^\circ(\mathrm{Pb^{2+}})+2\Delta_f G^\circ(\mathrm{N_3^-})-\Delta_r G^\circ\\ &= -24.24+2(348.4)-50.7\,\mathrm{kJ\,mol^{-1}}=621.8\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

(f)

$$\begin{aligned}\Delta_r S^\circ &= \frac{\Delta_r H^\circ-\Delta_r G^\circ}{T}\\ &= \frac{83.0-50.7\,\mathrm{kJ\,mol^{-1}}}{298.15\,\mathrm{K}}\\ &= 108\,\mathrm{J\,K^{-1}mol^{-1}}.\\ \Delta_r S^\circ &= S^\circ(\mathrm{Pb^{2+}})+2S^\circ(\mathrm{N_3^-})-S^\circ(\mathrm{Pb(N_3)_2})\\ \therefore S^\circ(\mathrm{Pb(N_3)_2}) &= S^\circ(\mathrm{Pb^{2+}})+2S^\circ(\mathrm{N_3^-})-\Delta_r S^\circ\\ &= 21+2(96.76)-108\,\mathrm{J\,K^{-1}mol^{-1}}=106\,\mathrm{J\,K^{-1}mol^{-1}}.\end{aligned}$$