Chemistry 2720 Fall 2002 Test 2 Solutions

1.

$$\begin{aligned}
\Delta\bar{S}_{298\to400} &= \bar{C}_P \ln\left(\frac{T_2}{T_1}\right) = (28.87\,\mathrm{J\,K^{-1}mol^{-1}})\ln\left(\frac{400\,\mathrm{K}}{298.15\,\mathrm{K}}\right) = 8.484\,\mathrm{J\,K^{-1}mol.} \\
\therefore \bar{S}^\circ_{400} &= \bar{S}^\circ_{298} + \Delta\bar{S}_{298\to400} = 191.609 + 8.484\,\mathrm{J\,K^{-1}mol} = 200.093\,\mathrm{J\,K^{-1}mol^{-1}}.
\end{aligned}$$

2. We want to know if the reaction

$$\mathrm{Pb^{2+}_{(aq)}} + \mathrm{SO^{2-}_{4(aq)}} \to \mathrm{PbSO_{4(s)}}$$

is spontaneous under the given conditions. For this reaction,

$$\begin{aligned}
\Delta\bar{G}^\circ &= \Delta\bar{G}^\circ_{f(\mathrm{PbSO_4})} - \left(\Delta\bar{G}^\circ_{f(\mathrm{Pb^{2+}})} + \Delta\bar{G}^\circ_{f(\mathrm{SO_4^{2-}})}\right) \\
&= -813.04 - (-24.24 + (-744.00))\ \mathrm{kJ/mol} = -44.80\,\mathrm{kJ/mol.}
\end{aligned}$$

When we mix the two solutions, the initial concentrations of the two reactants are reduced by dilution:

$$\begin{aligned}
[\mathrm{Pb^{2+}}] &= \frac{(20\,\mathrm{mL})(0.04\,\mathrm{mol/L})}{35\,\mathrm{mL}} = 0.0229\,\mathrm{mol/L.} \\
[\mathrm{SO_4^{2-}}] &= \frac{(15\,\mathrm{mL})(0.003\,\mathrm{mol/L})}{35\,\mathrm{mL}} = 1.29\times10^{-3}\,\mathrm{mol/L.}
\end{aligned}$$

We can now calculate the free-energy change:

$$\begin{aligned}
\Delta\bar{G} &= \Delta\bar{G}^\circ + RT\ln Q \\
&= \Delta\bar{G}^\circ + RT\ln\left(\frac{a_{\mathrm{PbSO_4}}}{(a_{\mathrm{Pb^{2+}}})(a_{\mathrm{SO_4^{2-}}})}\right) \\
&= -44.80\,\mathrm{kJ/mol} \\
&\quad + (8.314472\times10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})\ln\left(\frac{1}{(0.0229)(1.29\times10^{-3})}\right) \\
&= -18.93\,\mathrm{kJ/mol.}
\end{aligned}$$

Since $\Delta\bar{G}$ is negative, the reaction is spontaneous, so a precipitate will form.

3. The maximum possible electrical work is $-\Delta\bar{G}$.

$$\begin{aligned}
\Delta\bar{G}^\circ &= 2\Delta\bar{G}^\circ_{f(\mathrm{ZnO})} - \left(2\Delta\bar{G}^\circ_{f(\mathrm{Zn})} + \Delta\bar{G}^\circ_{f(\mathrm{O_2})}\right) \\
&= 2(-320.48\,\mathrm{kJ/mol}) = -640.96\,\mathrm{kJ/mol}. \\
\therefore \Delta\bar{G} &= \Delta\bar{G}^\circ + RT\ln Q \\
&= \Delta\bar{G}^\circ + RT\ln\left(\frac{a^2_{\mathrm{ZnO}}}{(a_{\mathrm{Zn}})^2(a_{\mathrm{O_2}})}\right) \\
&= -640.96\,\mathrm{kJ/mol} \\
&\quad + (8.314472\times10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})\ln\left(\frac{1}{0.2}\right) \\
&= -636.97\,\mathrm{kJ/mol}.
\end{aligned}$$

This is per two moles of zinc, so the free energy change is $-318.49\,\mathrm{kJ/mol}$ Zn. A battery stores 500 J, which corresponds to

$$\begin{aligned}
n_{\mathrm{Zn}} &= \frac{500\,\mathrm{J}}{318.49\times10^3\,\mathrm{J/mol}} = 1.57\times10^{-3}\,\mathrm{mol}. \\
\therefore m_{\mathrm{Zn}} &= (1.57\times10^{-3}\,\mathrm{mol})(65.38\,\mathrm{g/mol}) = 0.103\,\mathrm{g}.
\end{aligned}$$

4. The process which concerns us is

$$\mathrm{s} \rightleftharpoons \mathrm{g}.$$

Ice fog will form below the temperature at which the vapor is just in equilibrium with the solid. Since the vapor pressure of ice at 0°C is 6.025×10^{-3} bar, $K_{273} = P_{\mathrm{H_2O}}/P^\circ = 6.025\times10^{-3}$. At the threshold temperature, we will have $K_T = 0.004$. We can use the equation

$$\ln\left(\frac{K_{273}}{K_T}\right) = \frac{\Delta\bar{H}^\circ}{R}\left(\frac{1}{T} - \frac{1}{273.15\,\mathrm{K}}\right)$$

if we can find $\Delta\bar{H}^\circ$ for our process. Since enthalpy is a state function, the path doesn't matter, so imagine that we break the sublimation process shown above into two steps:

$$\mathrm{s} \xrightarrow{1} \mathrm{l} \xrightarrow{2} \mathrm{g}.$$

We know the enthalpy changes for the subprocesses 1 and 2:

$$\begin{aligned}
\Delta\bar{H}^\circ_1 &= \Delta\bar{H}^\circ_{\mathrm{fusion}} = 6.007\,\mathrm{kJ/mol}. \\
\Delta\bar{H}^\circ_2 &= \Delta\bar{H}^\circ_{\mathrm{vap}} = 44.91\,\mathrm{kJ/mol}. \\
\therefore \Delta\bar{H}^\circ &= 6.007\,\mathrm{kJ/mol} + 44.91\,\mathrm{kJ/mol} = 50.92\,\mathrm{kJ/mol}. \\
\therefore \frac{1}{T} &= \frac{8.314472\,\mathrm{J\,K^{-1}mol^{-1}}}{50.92\times10^3\,\mathrm{J/mol}}\ln\left(\frac{6.025\times10^{-3}}{0.004}\right) + \frac{1}{273.15\,\mathrm{K}} \\
&= 3.728\times10^{-3}\,\mathrm{K^{-1}}. \\
\therefore T &= 268.25\,\mathrm{K} \equiv -4.9^\circ\mathrm{C}.
\end{aligned}$$

5. (a) From K_1, we can calculate the concentration of H_2Xan which will be present in solution at equilibrium:

$$\begin{aligned} K_1 &= a_{H_2Xan(aq)} = 1.29 \times 10^{-4}. \\ \therefore [H_2Xan] &= 1.29 \times 10^{-4}\,\mathrm{mol/L}. \end{aligned}$$

The acid ionization determines the amount of $HXan^-$ at equilibrium:

$$\begin{aligned} K_2 &= \frac{(a_{HXan^-})(a_{H^+})}{a_{H_2Xan}}. \\ \therefore a_{HXan^-} &= K_2 \frac{a_{H_2Xan}}{a_{H^+}}. \\ a_{H^+} &= 10^{-pH} = 10^{-6.5} = 3.16 \times 10^{-7}. \\ \therefore a_{HXan^-} &= (2.95 \times 10^{-8}) \frac{1.29 \times 10^{-4}}{3.16 \times 10^{-7}} = 1.20 \times 10^{-5}. \\ \therefore \text{solubility} &= 1.29 \times 10^{-4} + 1.20 \times 10^{-5}\,\mathrm{mol/L} = 1.41 \times 10^{-4}\,\mathrm{mol/L}. \end{aligned}$$

(b)

$$\begin{aligned} \ln\left(\frac{K_{310}}{K_{298}}\right) &= \frac{\Delta\bar{H}^\circ}{R}\left(\frac{1}{298.15\,\mathrm{K}} - \frac{1}{310.15\,\mathrm{K}}\right). \\ \therefore \Delta\bar{H}^\circ &= \frac{R \ln\left(\frac{K_{310}}{K_{298}}\right)}{\frac{1}{298.15\,\mathrm{K}} - \frac{1}{310.15\,\mathrm{K}}} \\ &= \frac{(8.314472\,\mathrm{J\,K^{-1}mol^{-1}}) \ln\left(\frac{2.04\times10^{-4}}{1.29\times10^{-4}}\right)}{\frac{1}{298.15\,\mathrm{K}} - \frac{1}{310.15\,\mathrm{K}}} \\ &= 2.94 \times 10^4\,\mathrm{J/mol} \equiv 29.4\,\mathrm{kJ/mol}. \end{aligned}$$

The enthalpy change for reaction 1 is

$$\begin{aligned} \Delta\bar{H}^\circ &= \Delta\bar{H}^\circ_{f(aq)} - \Delta\bar{H}^\circ_{f(s)}. \\ \therefore \Delta\bar{H}^\circ_{f(aq)} &= \Delta\bar{H}^\circ + \Delta\bar{H}^\circ_{f(s)} \\ &= 29.4 + (-379.6)\,\mathrm{kJ/mol} = -350.2\,\mathrm{kJ/mol}. \end{aligned}$$

(c) The formation reaction for xanthine is

$$5C_{(s)} + 2H_{2(g)} + 2N_{2(g)} + O_{2(g)} \rightarrow C_5H_4N_4O_{2(s)}.$$

We already know the enthalpy of formation of xanthine. (It's given in question 5b.) All we need is the entropy of formation:

$$\begin{aligned}
\Delta\bar{S}^{\circ}_{f(\text{xanthine})} &= \bar{S}^{\circ}_{f(\text{xanthine})} - \left(5\bar{S}^{\circ}_{f(\text{C})} + 2\bar{S}^{\circ}_{f(\text{H}_2)} + 2\bar{S}^{\circ}_{f(\text{N}_2)} + \bar{S}^{\circ}_{f(\text{O}_2)}\right) \\
&= 161.1 - (5(5.74) + 2(130.680) + 2(191.609) + 205.152)\,\text{J}\,\text{K}^{-1}\text{mol}^{-1} \\
&= -717.33\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}. \\
\therefore \Delta\bar{G}^{\circ}_{f(\text{xanthine})} &= \Delta\bar{H}^{\circ}_{f(\text{xanthine})} - T\Delta\bar{S}^{\circ}_{f(\text{xanthine})} \\
&= -379.6\,\text{kJ/mol} - (298.15\,\text{K})(-717.33 \times 10^{-3}\,\text{kJ}\,\text{K}^{-1}\text{mol}^{-1} \\
&= -165.7\,\text{kJ/mol}.
\end{aligned}$$

(d) For reaction 1, we have

$$\begin{aligned}
\Delta\bar{G}^{\circ} &= -RT\ln K_1 \\
&= -(8.314472\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(298.15\,\text{K})\ln(1.29 \times 10^{-4}) \\
&= 22.2\,\text{kJ/mol}. \\
\text{However, } \Delta\bar{G}^{\circ} &= \Delta\bar{G}^{\circ}_{f(\text{aq})} - \Delta\bar{G}^{\circ}_{f(\text{s})}. \\
\therefore \Delta\bar{G}^{\circ}_{f(\text{aq})} &= \Delta\bar{G}^{\circ} + \Delta\bar{G}^{\circ}_{f(\text{s})} \\
&= 22.2 + (-165.7\,\text{kJ/mol}) = -143.5\,\text{kJ/mol}.
\end{aligned}$$