Problem Set 3

6.10
To solve this problem we use the van’t Hoff equation,

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

The process is \( \text{CO}_2(\text{s}) \rightleftharpoons \text{CO}_2(\text{g}) \), with equilibrium constant \( K_p = \left( \frac{P_{\text{CO}_2}}{P^0} \right) \)
Since \( K_p \) is proportional to \( P_{\text{CO}_2} \)

\[ \ln \left( \frac{K_2}{K_1} \right) = \ln \left( \frac{P_{\text{CO}_2,2}}{P_{\text{CO}_2,1}} \right) = \left( \frac{\Delta_f H^\circ}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]
\[ \ln \left( \frac{1486 \text{ torr}}{672.2 \text{ torr}} \right) = \left( \frac{\Delta_f H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \left( \frac{1}{193.2 \text{ K}} - \frac{1}{203.2 \text{ K}} \right) \]
\[ \Delta_f H^\circ = 2.59 \times 10^4 \text{ J mol}^{-1} \]

6.15
For the reaction \( \text{cis-2-butene(g)} \rightleftharpoons \text{trans-2-butene(g)} \)

\[ \Delta_f G^\circ = \Delta_f G^\circ \left[ \text{trans-2-butene} \right] - \Delta_f G^\circ \left[ \text{cis-2-butene} \right] \]
\[ = 64.10 \text{ kJ mol}^{-1} - 67.15 \text{ kJ mol}^{-1} \]
\[ = -3.05 \text{ kJ mol}^{-1} \]

Since \( K_p = \left( \frac{P_{\text{trans-2-butene}}}{P_{\text{cis-2-butene}}} \right) \)
the equilibrium constant gives the ratio of the equilibrium pressures of the isomers. This ratio can be determined using \( \Delta_f G^\circ \).

\[ \ln K_p = -\Delta_f G^\circ / RT = (-3.05 \times 10^3 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = 1.231 \]
\[ K_p = \left( \frac{P_{\text{trans-2-butene}}}{P_{\text{cis-2-butene}}} \right) = 3.42 \]
The dissociation constant can be obtained by plotting $Y/[L]$ vs $Y$. The slope is $-1/K_d$. $L$ and $Y$ are obtained from the following relations:

$$[L] = [Ca^{2+}]_{\text{total}} - [Ca^{2+}]_{\text{bound}}$$

$$Y = [Ca^{2+}]_{\text{bound}} / 96 \, \mu M$$

According to the data given, the values of $[L]$, $Y$, and $Y/[L]$ are

<table>
<thead>
<tr>
<th>$[L]$ ($\mu M$)</th>
<th>28.2</th>
<th>68.8</th>
<th>116.6</th>
<th>169.2</th>
<th>396.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y$</td>
<td>0.3250</td>
<td>0.5333</td>
<td>0.6604</td>
<td>0.7375</td>
<td>0.8688</td>
</tr>
<tr>
<td>$Y/[L]$</td>
<td>11.28</td>
<td>7.751</td>
<td>5.664</td>
<td>4.359</td>
<td>2.191</td>
</tr>
</tbody>
</table>

The units for $Y/[L]$ are $M^{-1}$ and the results tabulated above were multiplied by $10^{-3}$. The slope of the plot shown below is $-16.72 \times 10^{-3}$. Therefore, $K_d = 1/(16.72 \times 10^{-3}) = 59.8$

Notice, though, that this result has units of $\mu M$. We want $K_d$ to be dimensionless, so better to convert to $M$ (since standard concentrations are 1 M). Then we multiply by $10^6 M/1 \, \mu M$, so that

$$K_d = 5.98 \times 10^{-5}$$

Since there is only one binding site, we would not need to solve the problem graphically (except that the problem asks us to). For one set of values for $[L]$, $[P]$, and $[PL]$, we find a very similar answer by solving directly for $K_d = \frac{([L]/1M)([P]/1M)}{[LP]/1M}$. 
\[ \Delta_i G = \Delta_i G^\circ + RT \ln Q = \Delta_i G^\circ + RT \ln \frac{\text{[glucose-6-phosphate]}}{\text{[glucose][HPO}_4^{2-}]} \]

\[ = 13.4 \times 10^3 \text{ J mol}^{-1} + \]
\[ (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(310 \text{ K}) \ln((1.6 \times 10^{-4})/(4.5 \times 10^{-2})(2.7 \times 10^{-3})) \]

\[ = 14.1 \text{ kJ mol}^{-1} > 0 \]

The reaction is therefore not spontaneous.

\[ 6.32 \]

\[ \Delta_i G^\circ \text{ is calculated from the standard molar Gibbs energy of formation of reactants and products} \]
\[ \Delta_i G^\circ = \Delta_i G^\circ (\text{glycylglycine}) + \Delta_i G^\circ (\text{H}_2\text{O}) - 2\Delta_i G^\circ (\text{glycine}) \]
\[ = (-493.1 \text{ kJ mol}^{-1}) + (-237.2 \text{ kJ mol}^{-1}) - 2(-379.9 \text{ kJ mol}^{-1}) \]

\[ = 29.5 \text{ kJ mol}^{-1} > 0 \]

Furthermore,

\[ \ln K' = -\frac{\Delta_i G^\circ}{RT} = -(29.5 \times 10^3 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = -11.91 \]

\[ K' = 6.72 \times 10^{-6} \]

We can assume that \( K' \) is similar at 310 K. The large, positive \( \Delta_i G^\circ \) and very small \( K' \) tell us that this synthesis is not spontaneous. In the cell, ATP is present to aid in this reaction.