Chapter 20 Thermodynamics
Homework Problems

1. Using the data from Appendix B, calculate $\Delta H^\circ$, $\Delta S^\circ$, and $\Delta G^\circ$ for the following reactions that produce acetic acid:
   
   a. $\text{CH}_4(g) + \text{CO}_2(g) \rightarrow \text{CH}_3\text{COOH}(l)$
   
   b. $\text{CH}_3\text{OH}(g) + \text{CO}(g) \rightarrow \text{CH}_3\text{COOH}(l)$

Which reaction would you choose as a commercial method for producing acetic acid at standard conditions?

What temperature conditions would you choose for the reaction? Assume $\Delta H^\circ$ and $\Delta S^\circ$ do not depend on temperature.

2. Is the following reaction for the dimerization of nitrogen dioxide (acid deposition pollutant) spontaneous or nonspontaneous at 298 K and standard conditions?

\[
2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)
\]

Use Appendix B:

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_2(g)$</td>
<td>34</td>
<td>240</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_4(g)$</td>
<td>10</td>
<td>304</td>
</tr>
</tbody>
</table>

What is the value of $\Delta G^0$ at 298 K?

Assume $\Delta H^\circ$ and $\Delta S^\circ$ do not depend on temperature. At what temperature is $\Delta G^0 = 0$?

Is $\Delta G^\circ$ negative above or below the calculated temperature?

What is the temperature range where the reaction is spontaneous?
3. According to the advertisement, “a diamond is forever”.
   a. Calculate $\Delta H^o$, $\Delta S^o$, and $\Delta G^o$ for the phase change, diamond $\rightarrow$ graphite, at 298 K.
   
   b. What are the conditions under which diamond jewelry is normally kept, and argue for or against the ad’s statement.
   
   c. What conditions would be required to produce synthetic diamonds from graphite?
   
   d. Assuming $\Delta H^o$ and $\Delta S^o$ do not change with temperature, can graphite be converted spontaneously to diamond at 1 atm?

4. The Haber process for the productions of ammonia from the elements nitrogen and hydrogen is a very important industrial process for nitrogen fixation.
   a. Write the balanced equation for the reaction.
   
   b. Assuming $\Delta H^o$ and $\Delta S^o$ do not change with temperature, find the temperature at which $K_p = 1.00$.
   
   c. Find $K_p$ at 400°C, a typical industrial temperature.
   
   d. Given the lower $K_p$ at higher temperature, why is this condition used industrially?
5. The equilibrium constant for the following reaction is measured at several temperatures.

\[
\text{CO}_2(g) \quad + \quad \text{H}_2\text{O}(g) \quad \rightleftharpoons \quad \text{CO}_2(g) \quad + \quad \text{H}_2(g)
\]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(K_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>(1.4 \times 10^3)</td>
</tr>
<tr>
<td>450</td>
<td>(3.6 \times 10^2)</td>
</tr>
<tr>
<td>489</td>
<td>(1.5 \times 10^2)</td>
</tr>
<tr>
<td>502</td>
<td>(1.2 \times 10^2)</td>
</tr>
<tr>
<td>522</td>
<td>(8.0 \times 10^1)</td>
</tr>
</tbody>
</table>

a. Design a spreadsheet and graph to help you determine \(\Delta H^\circ\) and \(\Delta S^\circ\) for the reaction.

b. Assuming \(\Delta H^\circ\) and \(\Delta S^\circ\) do not change much with temperature, over what temperature range is the reaction spontaneous if other conditions are standard-state.