Handin Homework 10: Foundations of Thermodynamics

1. The reaction Gibbs energy is given in the table below as a function of temperature for the following reaction. Calculate the reaction enthalpy and entropy. Include a printout of any plots that you use. (You need not calculate uncertainties, but do estimate the proper number of significant figures in the results.) [Try Chapter 16 Problem 8, first]

\[
\text{CO (g) + } \frac{1}{2} \text{O}_2 (g) \rightleftharpoons \text{CO}_2 (g)
\]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>298.2</th>
<th>400.0</th>
<th>500.0</th>
<th>750.0</th>
<th>1000.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta G^\circ) (kJ mol(^{-1}))</td>
<td>-257.26</td>
<td>-247.50</td>
<td>-239.61</td>
<td>-216.52</td>
<td>-195.64</td>
</tr>
</tbody>
</table>

2. Consider the solubility of a pure substance, M, in aqueous solution: \(M (s) \rightleftharpoons M (aq)\)

Let the number of moles of pure solid be \(n_s\) and the number of moles of M dissolved in solution be \(n_{aq}\). The total number of moles of M is \(n_t = n_s + n_{aq}\). The chemical potential of the pure solid is \(\mu_s\), which is constant. The chemical potential of dissolved M is \(\mu_{aq}\). The chemical potential of dissolved M is an increasing function of concentration. The total change in Gibbs energy for dissolving \(dn_s\) moles of pure solid to give \(dn_{aq}\) moles of dissolved M is:

\[
dG = -S\,dT + V\,dP + \mu_s\,dn_s + \mu_{aq}\,dn_{aq}
\]

[Try Chapter 16 Problem 31, first]

(a). Under what conditions is \(\Delta G\) a good spontaneity criterion (i.e. when what is held constant)?

(b). The chemical potential of the pure solid, \(\mu_s\), is constant. Define a new state function:

\(R \equiv G - n_t\,\mu_s\). What are the independent variables for \(R\)?

[Hint: given \(n_t = n_s + n_{aq}\) then \(dn_t = dn_s + dn_{aq}\)]

(c). Under what conditions is \(\Delta R\) a good spontaneity criterion (i.e. when what is held constant)?

(d). Find the direction for spontaneous change, either \(dn_{aq} > 0\) or \(dn_{aq} < 0\), at constant temperature, pressure, and chemical potential of the pure solid. Assume that M has a lower chemical potential in the aqueous phase: \(\mu_{aq} < \mu_s\).

(e). Find the relationship at equilibrium between the chemical potentials of the pure solid and dissolved M, that is between \(\mu_s\) and \(\mu_{aq}\).

3. Some texts use an “=” symbol when writing reactions at equilibrium. For example: \(\text{CO (g) + } \frac{1}{2} \text{O}_2 (g) = \text{CO}_2 (g)\). Why is using an “=” symbol a useful representation of the equilibrium state of a chemical reaction? Be explicit about the underlying thermodynamic relationship.