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*]

$$CO\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightleftarrows CO_2\ (g)$$

T (K)	298.2	400.0	500.0	750.0	1000.0
$\Delta_r G°$ (kJ mol^{-1})	-257.26	-247.50	-239.61	-216.52	-195.64

2. Consider the solubility of a pure substance, M, in aqueous solution: M (s) $\rightleftarrows$ 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 μ_s, which is constant. The chemical potential of dissolved M is μ_{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 ΔG a good spontaneity criterion (i.e. when what is held constant)?

(b). The chemical potential of the pure solid, μ_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 ΔR 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 μ_s and μ_{aq}.

3. Some texts use an "=" symbol when writing reactions at equilibrium. For example: $CO\ (g) + \tfrac{1}{2}\ O_2\ (g) = CO_2\ (g)$. Why is using an "=" symbol a useful representation of the equilibrium state of a chemical reaction? Be explicit about the underlying thermodynamic relationship.