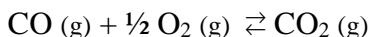


Handin Homework 10: Foundations of Thermodynamics

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]



T (K)	298.2	400.0	500.0	750.0	1000.0
$\Delta_r G^\circ$ (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: $\text{M (s)} \rightleftharpoons \text{M (aq)}$
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 $n_t = n_s + n_{\text{aq}}$. 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:

$$dG = -S dT + V dP + \mu_s dn_s + \mu_{\text{aq}} dn_{\text{aq}}$$

[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 $n_t = n_s + n_{\text{aq}}$ then $dn_t = dn_s + dn_{\text{aq}}$]

(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 $dn_{\text{aq}} > 0$ or $dn_{\text{aq}} < 0$, at constant temperature, pressure, and chemical potential of the pure solid. Assume that M has a lower chemical potential in the aqueous phase: $\mu_{\text{aq}} < \mu_s$.

(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: $\text{CO (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} = \text{CO}_2 \text{ (g)}$. Why is using an “=” symbol a useful representation of the equilibrium state of a chemical reaction? Be explicit about the underlying thermodynamic relationship.