Chem 531: Problem Set #4

Due in class: Tues, Oct. 10th

(1) Show that $\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$ and $\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$ (note: these should be brief)

(2) (a) Given that $S = f(T,P)$, derive an expression for dS in terms of T and P that is valid for any fluid (i.e., in terms of quantities like C_p, α, and κ).

(b) The coefficient of thermal expansion α of Fe(s) at 25ºC is 355 x 10^{-7} K^{-1}. What is the change in molar entropy of iron when the pressure is raised from 1 to 1000 bar at a constant temperature of 25ºC? (The density of iron at 25ºC is 7.86 g cm^{-3}.)

(3) In the thermodynamics of elastic materials, $dA = -SdT + fdL$, where f is the force exerted and L is the stretching displacement. Derive the appropriate Maxwell relation and then use this to obtain an expression for ΔS for isothermal stretching.

(4) Steam is compressed reversibly to liquid water at the boiling point (100ºC) and 1 atm. The heat of vaporization of water at 100ºC and 1.01325 bar is 2258 J g^{-1}. Calculate w per mole and q per mole and each of the thermodynamic quantities $\Delta\bar{H}$, $\Delta\bar{U}$, $\Delta\bar{G}$, $\Delta\bar{A}$, and $\Delta\bar{S}$. You can assume that the volume of the liquid is negligible compared to that of the gas.

(5) When a liquid is compressed its Gibbs energy is increased. The increase in molar Gibbs energy can be calculated using $\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$. What is the change in molar Gibbs energy for liquid water (ρ = 1.0 g cm^{-3}) when it is compressed from 1 to 1000 bar (assuming $\bar{V}$ is constant)?

(6) Starting with the fundamental equation for U, derive the relation $\left(\frac{\partial U}{\partial P}\right)_T = V(\kappa P - \alpha T)$