Quiz 12

Answer the questions in the spaces provided. If you run out of room for an answer, continue on the back of the page.

Question:	1	2	3	Total
Points:	10	15	0	25
Score:				

Name: _____

1. Consider a system in which we can control the temperature T, number N, and surface area a. For this system, we can define a generalized free energy $J(T, N, a)$ as

$$\mathrm{d}J = -S\,\mathrm{d}T + \mu\,\mathrm{d}N + \gamma\,\mathrm{d}a \tag{1}$$

where $\mu = \left(\frac{\partial J}{\partial N}\right)_{S,a}$ and $\gamma = \left(\frac{\partial J}{\partial a}\right)_{S,N}$.

(a) (5 points) At constant temperature, define a Maxwell relation between a derivative of the chemical potential μ and the surface tension γ.

Solution:

$$\left(\frac{\partial \mu}{\partial a}\right)_N = \left(\frac{\partial \gamma}{\partial N}\right)_a$$

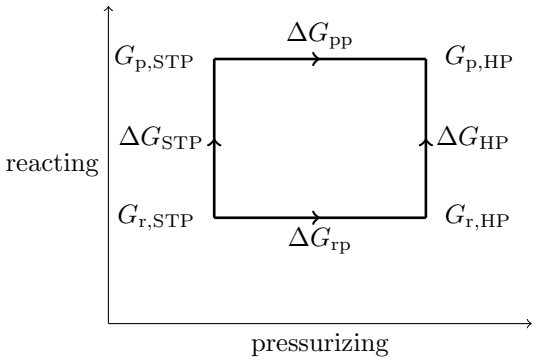
(b) (5 points) If instead we moved to an ensemble where we could control the surface tension γ, using a Legendre transform how could a different generalized free energy $K(T, N, \gamma)$ be defined in terms of J?

Solution:

$$K = J - \gamma a$$

2. For some chemical reaction, at STP (1 bar and 0 °C) ΔG_{STP} tells us that the products are slightly favored ($\Delta G_{\mathrm{STP}} < 0$). Your advisor hypothesizes that the reaction will be more favorable at higher pressure ($\Delta G_{\mathrm{HP}} < \Delta G_{\mathrm{STP}}$). However, she would like you to calculate ΔG_{HP} using literature values for Gibbs free energy changes for pressurizing the reactants ΔG_{rp} and pressurizing the products ΔG_{pp} before buying you a shiny, new pressure reactor.

(a) (10 points) Label the four ΔG values on the following diagram. Be sure to indicate the directionality of the values (ΔG = final − initial).



(b) (5 points) What is an expression for ΔG_{HP}?

Solution:

$$\Delta G_{\mathrm{HP}} = -\Delta G_{\mathrm{rp}} + \Delta G_{\mathrm{STP}} + \Delta G_{\mathrm{pp}}$$

3. For fun if you have time: Under what condition will the high-pressure reaction be more favored than the STP reaction? If the higher pressure reaction is more favorable, does that suggest anything about the enthalpic (ΔH) versus the entropic (ΔS) contributions to ΔG?

Solution:

$$\Delta G_{\mathrm{rp}} > \Delta G_{\mathrm{pp}} \tag{2}$$

Unfortunately, there is no simple way to deconvolve those contributions for this case. If this were high temperature versus low temperature, then it would be fairly simple to look at ΔH compared to ΔS.