Discussion 9

Name and section: ______________________________

$$\begin{aligned} U(S,V,N) &= TS - pV + \mu N \\ S(U,V,N) &= \frac{U}{T} + \frac{p}{T}V - \frac{\mu}{T}N \\ F(V,T) &= U - TS \\ G(p,T) &= U + pV - TS \\ H(S,p) &= U + pV \end{aligned}$$

1. Differential forms of energies

   In the past we have worked with the expression $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$ (for a single component system).

   (a) Write an expression for $\mathrm{d}F$.

   (b) Write an expression for $\mathrm{d}G$.

   (c) Write an expression for $\mathrm{d}H$.

2. A thermodynamic cycle for mutations in protein folding

   Suppose you can measure the stability of a protein, $\Delta G_{\mathrm{s}} = G_{\mathrm{folded}} - G_{\mathrm{unfolded}}$ (the free energy difference between folded and unfolded states) and $\Delta G_{\mathrm{f,m}} = G_{\mathrm{folded,type\ a}} - G_{\mathrm{folded,type\ b}}$ (the free energy difference between two types of a protein in their folded states). A mutant of a protein has a single amino acid replacement. Design a thermodynamic cycle that will help you find the free energy difference $\Delta G_{\mathrm{u,m}} = G_{\mathrm{unfolded,mutant}} - G_{\mathrm{unfolded,wild-type}}$, the effect of the mutation on the unfolded state.

3. Free energy of an ideal gas

   (a) For an ideal gas, calculate $F(V)$, the free energy versus volume at constant temperature. Hint: start from the differential form of $F(T, V, N)$.

   (b) Compute $G(V)$. Note that V is not a natural variable of $G = G(T, P, N)$.

4. Heat capacity of an ideal gas

   (a) The energy of an ideal gas does not depend on volume: $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Use this fact to prove that the constant-volume heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ for an ideal gas is independent of volume.

   (b) Show that the constant-pressure heat capacity $C_p = \left(\frac{\partial H}{\partial T}\right)_P$ for an ideal gas is also independent of volume.