1. The fundamental equation for a two-component system is given by
\[ S = An + nR \ln \left( \frac{VU^{1/2}}{n^{5/2}} \right) - n_1R \ln(n_1 / n) - n_2R \ln(n_2 / n) \]
where \( n = n_1 + n_2 \), \( A \) is constant and \( R = 8.31 \, \text{J/mole/K} \) are constants. 

A closed 10 liter cylinder is divided into two chambers of equal volume by a RIGID diathermal membrane, permeable to component #1, but not to #2. In one chamber is placed a sample of the above system with initial \( n_1 = 0.5 \) moles, \( n_2 = 0.75 \) moles, \( T = 300 \, \text{K} \). In the second chamber is placed a sample with initial \( n_1 = 1 \) mole, \( n_2 = 0.5 \) moles, \( T = 250 \, \text{K} \). After equilibrium is established, what is the temperature of the composite system? (Hint: you can convert to the energy representation and use the energy minimum principle for equilibrium, if you wish.) What are the equilibrium concentrations \( n_1 \) and \( n_2 \) on each side?

2. Consider the reaction \( 2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \). At some temperature \( T \), the equilibrium constant is 5 liters/mole.
   a. A closed vessel of 10 liters is initially filled with 2 moles of \( \text{NO}_2 \). Draw a \( G(x) \) consistent with \( K_{eq} \) the volume and the reaction stoichiometry, where \( x \) is the number of moles of \( \text{N}_2\text{O}_4 \).
   b. Draw \( \Delta G(T) = \partial G / \partial x \big|_T \) on the same \( x \)-axis. Indicate the equilibrium point in both plots.

3. Consider a chemical reaction \( A \rightarrow B \) at constant \( P \). The temperature-independent heat capacity change at constant pressure is \( \Delta C_p \) (\( = C_{p,A} - C_{p,B} \)). The temperature of the reaction mix is slowly scanned, but the reaction is maintained near equilibrium at each \( T \), so \( \Sigma_i \mu_i \, dn_i = 0 \).
   a. Calculate \( \Delta H \) and \( \Delta S \) by integrating \( d\Delta H \) and \( d\Delta S \) from \( T_0 \) to \( T \). Your formulas should contain \( \Delta C_p, T_0 \) and integration constants \( \Delta H^{(0)} \) and \( \Delta S^{(0)} \) as parameters.
   b. Write \( \Delta G(T) \) in terms of the integration constants \( \Delta H^{(0)}, \Delta S^{(0)} \) and \( T_0 \). Take the derivative \( \partial \Delta G / \partial T \) to show that the derivative really equal \( -\Delta S(T) \).
   c. Make a plot of \( \Delta G(T) \) assuming \( \Delta H^{(0)} = -7000 \, \text{J/mole}, \Delta S^{(0)} = -20 \, \text{J/K}, \Delta C_p = -100 \, \text{J/K} \) and \( T_0 = 350 \, \text{K} \) (plot in the 200 to 400 K range). If B were a folded protein, and A an unfolded protein, what happens at about 230 K and 350 K? What happens below about 230 K is known as “cold denaturation” of the protein. Can you rationalize in terms of a microscopic argument that what happens at 230 K does not violate the second law of thermodynamics?

4. Let’s derive the canonical partition function \( z_{\text{trans}} \) for translational kinetic energy of a particle of mass \( m \) in a one-dimensional box of length \( L \) quantum-mechanically.
   a. The quantum energy of a particle in a box is \( \hbar^2 n^2 / (8mL^2) \), \( n = 1, 2, \ldots \). What is the microcanonical partition function at each allowed energy?
   b. Write down the canonical partition function as a sum.
   c. Integrals can be approximated by a sum over little “boxes” of width \( \Delta x \). Let’s do the opposite here, and approximate the sum by an integral: write the expression in (b) as an integral, replacing \( n \) by \( x \) and the interval \( \Delta n = 1 \) by the interval \( dx \).
d. As one more approximation (valid if $T$ is large enough so many states $n$ are populated, especially true if the box is large), change the lower integration limit to 0 and evaluate the integral. Why does this approximation fail as $T$ approaches 0?

e. Without doing any more work, what is the partition function for a three dimensional box of volume $V$? [Hint: the three momenta each correspond to an independent subsystem.] When you calculate $z = z_{\text{trans}} z_{\text{vib}} z_{\text{rot}}$ for a molecule “i”, this is the translational partition function you need

5. At temperatures above 200 °C, the dissociation of phosphorus pentachloride is approximately an ideal gas reaction $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$. 1.9 g of $\text{PCl}_5$ at 320 °C initially has $P = 0.31$ atm. After equilibrium has been reached, the volume is 2.4 liters. Use this information to compute the equilibrium constant for the reaction at 320 °C.

6. In class we showed that the vibrational canonical partition function is $z_{\text{vib}} = \left(1 - e^{-\hbar\omega/k_B T}\right)^{-1}$. A rigid rotating diatomic molecule has energy $E_{\text{rot}}(J) = BJ(J+1)$ and degeneracy $W = 2J+1$.

a. Write down its rotational partition function $q_{\text{rot}}$ as a sum.

b. Show that $q_{\text{rot}}(T) \approx k_B T / B$ by approximating the partition function sum by an integral over $dJ$, where $J$ is no a continuous variable and for large $J$, assume $W \approx 2J$ and $E_{\text{rot}}(J) \approx BJ^2$.

c. Why does the approximation fail when $T \to 0$? Why is the integral approximation usually justified for rotations at room temperature, but not for vibrations at room temperature?

d. Use the same method to calculate the partition function for a rotor with just one rotation axis, whose energy is $E_{\text{rot}} = BM^2$ and whose degeneracy is $W = 2$ (except for the $M=0$ state, where $W=1$ because if it doesn’t rotate, there’s no “left” and “right” rotation). Compare the 2-D and 1-D results and explain their relationship in terms of the partition functions for two noninteracting systems.

e. The ro-vibrational energy of a diatomic molecule has small corrections: $E = E_{\text{vib}} + E_{\text{rot}} + E_{\text{corr}}$. By applying quantum-mechanical perturbation theory to the diatomic molecule Hamiltonian, it can be shown that $E_{\text{corr}} / \hbar = -\omega x_e (n+1/2)^2 - D_e J(J+1)^2 - \alpha_e (n+1/2) J(J+1)$ to a first approximation. $\omega$ is the vibrational frequency. $x_e << 1$ is the vibrational anharmonicity constant, $D_e << B$ is the centrifugal distortion constant, and $\alpha_e << B$ gives the change in rotational constant as the molecule is stretched by vibration. Compute a high temperature correction $z_{\text{corr}}$ to the partition function such that $z \approx z_{\text{vib}} z_{\text{rot}} z_{\text{corr}}$. [Hint: you may assume that $E_{\text{corr}} / k_B T$ is so small that an exponential of it can be approximated by a first order Taylor expansion.]

7. For the chemical reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$, write down a formula for the equilibrium constant $K_{\text{eq}}(T)$, assuming ideal gas behavior and $z_{\text{vib}} \approx 1$. Your formula needs to include $z_{\text{trans}}$, $z_{\text{rot}}$, and the appropriate electronic energy difference in dissociation energies. (The latter is necessary because if you pick the ground state energy of HI to be zero, then the ground state energies of $\text{H}_2$ and $\text{I}_2$ cannot be arbitrarily referenced as zero any longer.) Note that your formula should depend only on the molecular masses, the three rotational constants, the dissociation energies $D$ of the three molecules, and temperature. (Note that $\text{H}_2$ and $\text{I}_2$ are homonuclear diatomic molecules: their rotational partition functions should each be divided by 2 compared to your result in problem 6 so as not to over-count rotational states.)