1. In class we showed that \( dS_V = dq_{V,n,.}/T = dU/T \) at constant volume.
   a. Now that you know that enthalpy is the Legendre transform \( H = U + PV \), show similarly that \( dS = dq_{P,n,.}/T = dH/T \) at constant pressure instead of constant volume.
   b. Since enthalpy is heat flow at constant pressure, write down a formula for the heat capacity \( C_P(T) \) at constant pressure in terms of an enthalpy derivative. Then write down a formula for \( dH \) in terms of \( C_P(T) \).
   c. In lecture, we derived the Clausius equation from the Gibbs-Duhem equation (lower case quantities are molar entropy and volume):
   \[
   \frac{dP}{dT} = \frac{s_g - s_l}{v_g - v_l}
   \]
   Vaporization from a liquid to its gaseous vapor occurs at constant temperature and pressure. Integrate the formula in a. at constant \( T \) to replace \( s_g-s_l \) by the constant \( \Delta h_{\text{vap}} \), the molar enthalpy of vaporization. Next make the approximation \( v_g-v_l \approx v_g \) because the gas volume is much greater than the liquid volume, and use the ideal gas law to express \( v_g \) in terms of \( P, R \) and \( T \). Write down the resulting Clausius-Clapeyron equation for \( dP/dT \).
   d. The vapor pressure of water at 0 °C is 4.58 torr (760 torr = 1 atm). Assuming that the heat of vaporization of water is 595 calories/gram (1 calorie = 4.18 Joules) and temperature-independent, use the Clausius-Clapeyron equation to estimate the boiling point of water. [Careful: cal/g ≠ cal/mole!]

2. Work out the problem of spins in a magnetic field \( B \) at the end of “Survey” chapter 3:
   a. The energy of the system ranges from 0 (all \( N \) spins down, or \( s_{zj} = -1/2 \)) to \( U = NB \) (all \( N \) spins up, or \( s_{zj} = +1/2 \)). With energy as a vertical axis, plot a couple of the lowest and highest energy levels of this system. What is the degeneracy \( W \) of the ground state, first excited state, highest state, and next-highest state?
   b. Explain briefly why the formula for \( W(U) \) given in the text is the correct general formula for this system. Calculate \( S = k_B \ln[W(U)] \).
   c. Now sketch what a plot of \( S(U) \) looks like from \( U = 0 \) to \( U = NB \). Is there a problem with monotonicity?
   d. Take the derivative \( \partial S/\partial U = 1/T(U) \) and solve for energy as a function of \( T \). Does the energy go to \( NB \) when \( T \) approaches \( \infty \)? What is the highest value of \( U \) that can be achieved by heating? Since we can never heat the system above \( T = \infty \), under equilibrium conditions it can never enter a regime where \( S \) does not monotonically increase with \( U \).
   e. What is \( U \) if the temperature were just slightly below 0 K? This state, called an “inverted population” cannot be reached in equilibrium in a closed system: negative temperatures correspond to inversion populations. Inversions can be prepared however in open systems, since the postulates of stat mech (and laws of thermo) do not hold for open systems.

3. For the problem of RNA folding in Survey Chapter 4, start with the formula for \( U \) and
a. show that the heat capacity at constant volume can be written as \( \rho U \rho F (\varepsilon / T)^2 / R \).

b. Pick \( \varepsilon = 10 \) kJ/mole and \( W_F = 1 \), and plot \( c_V \) in kJ/mole/K against \( T \) in Kelvin over an appropriate temperature range to show its features. Make the plot for \( W_U = 5 \) and \( W_U = 50 \).

4. Two identical closed systems “\( i \) = 1,2” have fundamental relation \( S_i = C(N_i V_i U_i)^{1/3} \), where \( C \) is a constant.
   a. Is this entropy properly extensive?
   b. What is the fundamental relation for the composite system in terms of \( N_i , V_i , U_i \), \( i = 1,2 \), with all constraints still in place? [Hint: entropy is an extensive quantity.]
   c. Given that the two systems are identical, what is the fundamental relation of the closed composite system in terms of \( N , V , U \) (\( N = N_1 + N_2 \), etc.) once the two systems are combined and all internal restraints are relaxed?
   d. Is the entropy in c. greater than, or equal to, the entropy in b.? Which should it be, based on common sense? This is called the “Gibbs paradox.” Comment on how it might be resolved if the systems truly are composed of identical particles.

5. Instead of Legendre transforming \( U = U(S,V,n) \) to \( A(T,V,n) \), start with \( S(U,V,n) \), and go through an analogous derivation to derive
   a. the Legendre transform of \( S \) with respect to \( U \), \( S_U(T,V,n) \).
   b. its differential \( dS_U \).

Legendre transforms of the entropy are important in statistical mechanics and are called Massieu functions. \( S_U(T,V,n) \) is the entropy analog of the Helmholtz free energy \( A(T,V,n) \). It is a fundamental relation that contains all thermodynamic information about the system.

6. 10 g of NaCl and 15 g of sugar (\( C_{12}H_{22}O_{11} \)) are dissolved in 50 grams of pure \( H_2O \). The volume of the resultant simple system is 55 cm\(^3\). What are the mole numbers of the three components? The mole fractions? The molar volume (i.e. the volume where the system contains a grand total of 1 mole of particles, treating NaCl as a unit)?

7. For a binary mixture, \( dG = -SdT + VdP + \sum \mu_i dn_i \) where the sum over \( i \) goes from 1 to 2. Show that at equilibrium (\( dG = 0 \)) and constant \( T \) and \( P \), \( d\mu_i = -(\chi_2/\chi_1) d\mu_2 \), where \( \chi_i \) are the mole fractions.

8. By integrating \( F = -PdV \), compute the work done in the slow isothermal compression from \( V_1 \) to \( V_2 \) of:
   (a) an ideal gas \( P = nRT / V \)
   (b) a van der Waals gas \( P = nRT / (V - nb) - a(n/V)^2 \)

Discuss the constants \( a \) and \( b \) in terms of the differences in 7(a) and 7(b) and their microscopic meaning (assume \( a > 0 , b > 0 \)).