1. Review the Jacobi identities from homework #1; we’ll be using them! Remember, the Jacobians are determinants of derivatives, so the properties of determinants in the math notes can be used for proofs. Prove the following additional property: \( \frac{\partial (x,y,z,w)}{\partial (u,v,w,z)} = 1 / [\partial (u,v,w,z) / \partial (x,y,z,w)] \). This is the correct way to transform variables and then calculate the “inverse” derivatives. IF YOU USE properties of determinants in your proof, at least illustrate the truth of that/those properties with an example 2x2 matrix (you can put in numbers for matrix elements to illustrate, but not ‘trivial’ ones like the identity matrix, please!)

2. A gas expands quasi-statically in a molecular beam, so \( dq = TdS = 0 \) and \( n = \) const. Using Jacobi determinants and Maxwell relations, transform the appropriate derivative of temperature with respect to pressure to show that \( dT = \alpha VT/(nC_p) \) dP. Compute the coefficient for a monatomic ideal gas, and integrate the result to obtain \( T/T_0 \) as a function of \( P/P_0 \).

3. We’ll do phase transitions in lecture instead of heat engines. However, look at the summary sheet and the chapter on thermodynamic processes, and think about the idea of how much energy can be extracted as \( SdT \) (heat flow), and how much energy can be extracted from all the other terms (-\( PdV + \mu dN + \cdots = \) work flow). Using the reversible work theorem on the summary sheet, prove that the best possible efficiency \( E \) of a refrigerator is given by the relation

\[
\frac{dq}{d\varphi} = E = \frac{T_\omega}{T_\omega - T_\alpha}.
\]

[Hint: see chapter on thermo processes for answer!]

The hatches through \( dq \) and \( d\varphi \) are reminders used in many books that these are energy flows, not differentials of state functions. The efficiency \( E \) is defined as the ratio of the heat pumped from cooler refrigerator (the system ‘sys’) to hotter room (the heat sink ‘hs’), divided by the work required to do so. Note that the efficiency goes to 0 if you try to cool things to 0K, and it approaches \( \infty \) only if your refrigerator is no cooler than your room!

4. In class, we showed that \( 0 < C_\gamma < C_v \), but we made use of the canonical partition function from statistical mechanics to prove the first part. Now prove \( C_\gamma > 0 \) using thermodynamic relations only. Start by proving that \( \frac{\partial^2 U}{\partial S^2} = \frac{\partial T}{\partial S} \gamma > 0 \). Then use that to prove in one simple step that \( C_\gamma > 0 \) because \( T > 0 \). [Tip: feel free to consult the stat mech lecture notes, chapter 7, but make sure you explain every step in your own solution.]

5. Instead of Legendre transforming \( U = U(S,V,n) \) to \( U = A(T,V,n) \), start with \( S(U,V,n) \), and go through an analogous derivation to derive \( S[U] = f(T,V,n) \) and its differential \( dS[U] \)? Legendre transforms of the entropy are important in statistical mechanics and are called Massieu functions. \( S[U] = f(T,V,n) \) is the entropy analog of the Helmholtz free energy \( A(T,V,n) \).

6. A binary mixture (e.g. benzene and cyclohexane) has a free energy given by

\[
G(T,P,n_1,n_2) = n_1 f_1(T,P) + n_2 f_2(T,P) + n_1RT \ln \chi_1 + n_2RT \ln \chi_2 + wnR \chi_1 \chi_2.
\]

Show that above the temperature \( T_c = w/2 \), phase separation no longer occurs because the stability criterion \( d^2 G \) has only one minimum as a function of \( \chi \), whereas below that critical temperature, there are two local minima. (Hint: \( \chi = 1 - \chi_1 \), so there is only one independent variable to consider.)
Consider two substances (e.g. A=methanol and B=water) whose vapor and liquid are in equilibrium (a distillation).

a. According to Gibb’s rule, how many degrees of freedom \( f \) does the coexistence region have? Is it a line, like the \( P(T) \) for one substance and two phases?

b. The coexistence region at pressure \( P=1 \) atm is shown in gray as a function of \( T \) and mole fraction of A.

For example, if you start at ‘start’ and heat up, you have all liquid at first, then liquid and vapor coexist over a temperature range in the gray zone, then only vapor exists if you raise \( T \) even higher. For our case, the upper and lower bounding curves are \( T = T_B - (T_B - T_A)\chi_A^2 \) and \( T = T_B - (T_B - T_A)\chi_A(2 - \chi_A) \), where \( T_B \) is the boiling point of B, \( T_A \) is the boiling point of A, and \( T_B > T_A \).

Show that in a distillation of 50:50 liquid A and B by mole fraction, the composition of the vapor initially is \( \chi_A = (3/4)^{1/2} \). Is the vapor enriched or depleted in A compared to the liquid?

c. If the pressure were raised to 2 atmospheres, how would the coexistence region shift? Sketch both the ‘old’ 1 atm and the ‘new’ 2 atm coexistence regions on the same \( T,\chi_A \) diagram.