

ChemE 240, Homework 2

Assigned: January 25, 2007

Due: February 1, 2007

Topics: First and Second Laws, reversibility, Legendre transforms, Gibbs-Duhem equation, equations of state for an ideal gas, thermal/mechanical/mass/electric... equilibrium,

1) Closely follow the comments in Chandler pages 8, 9, and 10, and then answer the following questions *in your own words*. The purpose here is to have you closely read a conceptually important section of the text.

a) Why is there no entropy change for an adiabatic and reversible process? What happens to the energy that is transferred during an adiabatic and reversible process if it doesn't go toward changing the entropy?

b) If we can define a quasi-static process as one in which the system is always close to an equilibrium configuration, is every quasi-static process also reversible? Is every reversible process quasi-static? If the answer to either of these is no, give an example.

c) Compare the form of the first law with the form of the second law.

$$dE = \delta Q + \mathbf{f} \cdot d\mathbf{X} \quad \text{First Law}$$

$$dE = TdS + \mathbf{f} \cdot d\mathbf{X} \quad \text{Second Law}$$

A quick comparison seems to suggest that $\delta Q = TdS$. Is this always the case?

2) Let's consider another rubber band question. If the equation of state for a rubber band is given by $E = \theta S^2 L / n^2$ where θ is a constant and L is the length of the rubber band, determine the chemical potential, $\mu(T, L/n)$. Also, show this equation of state satisfies the Gibbs-Duhem equation.

3) Construct Legendre transforms of the entropy that are natural functions of $(1/T, V, N)$ and of $(1/T, P/T, N)$. Are these similar to any thermodynamic potentials we've already seen?

4) For what values of the constant c (if any) does a gas described by the following equation obey the ideal gas law? Note: $N = nN_A$, which means $Nk = nR$.

$$E = an \left(\frac{n}{V} \right)^c \exp \left(\frac{cS}{Nk} \right)$$

5) Let's say you have two capacitors with charge $q^{(1)}$ and $q^{(2)}$ that are in electrical equilibrium with each other (see figure below). The voltages across the plates are $V^{(1)}$ and $V^{(2)}$ respectively. The capacitors are adiabatically insulated from the surroundings. Use energy minimization to determine the relationship between $V^{(1)}$ and $V^{(2)}$ at equilibrium. Can you also use entropy maximization to show the relationship between $V^{(1)}$ and $V^{(2)}$ at equilibrium? Do so if possible.

