Week 1: Due Monday October 3, 2011

Chemistry 223A
Homework assignment # 1
Reading: Callen Chapters 1 and 2

Here we briefly review the fundamentals of thermodynamics as discussed in the first two chapters of Callen. There are seven problems in all. Each is worth ten points.

1. **Callen 1.8-5**
The energy of a particular system, of one mole, is given by

$$U = AP^2V \tag{1}$$

where A is a positive constant with dimensions of inverse pressure. Find the equation of adiabats in the PV plane.

2. **Callen 1.8-7**
Two moles of a particular single-component system are found to have a dependence of internal energy U on pressure and volume given by

$$U = APV^2 \qquad \text{(for } N = 2\text{).} \tag{2}$$

Note that doubling the system doubles the volume, energy, and mole number, but leaves the pressure unaltered. Write the complete dependence of U on P,V, and N for <u>arbitrary mole number</u>.

3. **Callen 2.2-4 and 2.2-5**
(a) Find the three equations of state for a system with the fundamental equation

$$u = \left(\frac{\theta}{R}\right)s^2 - \left(\frac{R\theta}{v_0^2}\right)v^2 \tag{3}$$

and show that, for this system, $\mu = -u$.

(b) Express the chemical potential μ as a function of temperature T and pressure P for this system.

4. **Adiabats – one more time. From Callen, 2.2-9**
We have seen for a single component idea gas has adiabats of the form:

$$pV^k = \text{const}, \tag{4}$$

where k is some positive, dimensionless constant.
Using this result show that

$$U = \frac{1}{k-1} pV + Nh\left(pV^k/N^k\right), \tag{5}$$

where $h(x)$ is an unknown function. You would have to be given more information about this particular material to determine h.

Hint: Convince yourself that pV^k is a function of only S (entropy) and N (number of particles). From the equation of state Eq. 4 you can then determine the fundamental relation Eq. 5 up to the unknown function as shown above.

5. **Callen 2.6-4**
Two systems with equations of state

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}} \tag{6}$$

$$\frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}} \tag{7}$$

are separated by a diathermal wall. There respective mole numbers are $N^{(1)} = 2$ and $N^{(2)} = 3$. The initial temperatures are $T^{(1)} = 250\text{K}$ and $T^{(2)} = 350\text{K}$. What are the values of the internal energies $U^{(1,2)}$ after equilibrium has been established? What is the equilibrium temperature?

6. **Callen 2.8-2**
A two-component gaseous system has a fundamental equation of the form

$$S = AU^{1/3}V^{1/3}N^{1/3} + \frac{BN_1N_2}{N}, \tag{8}$$

where $N = N_1 + N_2$ and where A, B are positive constants. A closed cylinder of total volume $2V_0$ is separated into two equal sub volumes by a rigid diathermal partition permeable only to the first component [i.e. molecules of type (1)]. One mole of the first component, at a temperature T_ℓ is introduced in the left-hand sub volume, and a mixture of 1/2 mole of each component, at temperature T_r is introduced into the right sub volume. Find the equilibrium temperature T and the mole numbers in each volume when the system has come to equilibrium, assuming that $T_r = 2T_\ell = 400\text{K}$ and that $37B^2 = 100A^3V_0$. Neglect the heat capacity of the walls of the container.

7. **Preparation for Chapter three – A Generalized Euler Theorem:** In this problem you will examine a purely mathematical issue that will be important to us in the next chapter. Given that a function f has the property:

$$f(\lambda^{p_1} x_1, \ldots, \lambda^{p_n} x_n) = \lambda^m f(x_1, \ldots, x_n) \tag{9}$$

show that

$$\sum_{j=1}^{n} p_j x_j \frac{\partial f}{\partial x_j} = m f(x_1, \ldots, x_n). \tag{10}$$