Week 2: Due Monday October 10, 2011

Chemistry 223A
Homework Assignment # 2
Reading: Callen Chapter 3

Here we derive some basic formal relationships between the thermodynamic variables, and apply them to simple model systems.

1. **Callen 3.3-3**

A system obeys the equtions

$$P = -\frac{NU}{NV - 2AVU} \tag{1}$$

and

$$T = 2C\,\frac{U^{1/2}\,V^{1/2}}{N - 2AU}\,e^{AU/N} \tag{2}$$

Find the fundamental equation.

Hint: To integrate, let

$$s = Du^n v^m e^{-Au} \tag{3}$$

where D, n, and m are constants to be determined.

2. **Callen 3.4-3 & 3.4-4**

Two moles of a monoatomic ideal gas are at a temperature of 0°C and a volume of 45 liters. The gas is expanded adiabatically ($đQ = 0$) and quasi-statically until its temperature falls to −50°C. What are its initial and final pressures and its final volume?

By carrying out the integral $\int P\,dV$, compute the work done *by* the gas. Also compute the initial and final energies, and corroborate that the difference in these energies is the work done.

3. **Callen 3.4-5**

In a particular engine, a gas is compressed in the initial stroke of the piston. Measurements of the instantaneous temperature, carried out during the compression, reveal that the temperature increases according to

$$T = (\frac{V}{V_o})^{\eta} T_o \tag{4}$$

where T_o and V_o are the initial temperature and volume, and η is the a constant. The gas is compressed to the volume V_1 (where $V_1 < V_o$). Assume the gas to be monatomic ideal, and assume the process to be quasi-static.

- a)Calculate the work W done on the gas.
- b)Calculate the change in energy ΔU of the gas.
- c)Calculate the heat transfer Q to the gas (through the cylinder walls) by using the results of (a) and (b).
- d)Calculate the heat transfer directly by integrating $đQ = TdS$.
- e)From the result of (c) and (d), for what value of η is $Q = 0$? Show that for the value of η the locus traversed coincides with an adiabat (as calculated in Problem 3.4-2)

4. **Callen, 3.4-12**

Show that μ_j, the electrochemical potential of the jth component in a multicomponent simple ideal gas, satisfies

$$\mu_j = RT \ln(\frac{N_j v_o}{V}) + f(T) \tag{5}$$

and find the explicit form for $f(T)$.

Show that μ_j can be expressed in terms of the "partial pressure" (Problem 3.4-11) and the temperature, T.

5. **Callen 3.5-3**

Repeat Problem 3.4-3 for CO_2, rather than for a monoatomic ideal gas. Assume CO_2 can be represented by an ideal van der Waals fluid with constants given in Table 3.1.
At what approximate pressure would the term $(-a/v^2)$ in the van der Waals equations of state make a 10% correction to the pressure at room temperature?

6. **Callen 3.6-1**
The universe is considered by cosmologists to be an expanding electromagnetic cavity containing radiation that now is at a temperature of 2.7 K. What will be the temperature of the radiation when the volume of the universe is twice its present value? Assume the expansion to be isentropic (this being a nonobvious prediction of cosmological model calculations).

7. **Callen 3.7-2**
A rubber band is stretched by an amount dL, at constant T. Calculate the heat transfer $đQ$ to the rubber band. Also calculate the work done. How are these related and why?

8. **Callen 3.9-6**
A simple fundamental equation that exhibits some of the qualitative properties of typical crystalline solids is

$$u = A\, e^{b(v-v_0)^2} s^{4/3} e^{s/3R} \tag{6}$$

where A, b, and v_0 are positive constants.

- a)Show that the system satisfies the Nernst theorem.
- b)Show that c_v is proportional to T^3 at low temperature. This is commonly observed (and was explained by P. Debye by a statistical mechanical analysis which will be developed in Chapter 16).
- c)Show that $c_v \to 3k_B$ at high temperatures. This is the "equipartition value", which is observed and which will be demonstrated by statistical mechanics analysis in Chapter 16.
- d)Show that for zero pressure the coefficient of thermal expansion vanishes in this model – a result that is incorrect. *Hint*: Calculate the value of v at $P = 0$.