

Week 1 & 2: Due Friday October 12, 2007

## Chemistry 223A Homework assignment # 1

Reading:

Chandler Chapter 1

*Supplemental* Reif Chapters 1 and 2.

Here are somewhat rapidly reviewing basic thermodynamics. As noted by Chandler, reading the first few chapters of Callen's text is an excellent idea for a concise and logically presented refresher.

There are eight problems in all. All are worth ten points.

### 1. A Generalized Euler Theorem:

*From Chandler, Chapter One*

We have noted that various thermodynamic functions obey a simple Euler relation. Here we consider a generalization of that theorem: Given that a function  $f$  has the property:

$$f(\lambda^{p_1} x_1, \dots, \lambda^{p_n} x_n) = \lambda^m f(x_1, \dots, x_n) \quad (1)$$

show that

$$\sum_{j=1}^n p_j x_j \frac{\partial f}{\partial x_j} = m f(x_1, \dots, x_n). \quad (2)$$

### 2. Conservation of Energy and Adiabats:

For a particular gas, the energy  $E$  is given by

$$E = \frac{5}{2} PV + E_0, \quad (3)$$

where  $E_0$  is a constant.

a) The system is initially in a state,  $p_1, V_1$  as shown by the point  $A$  in Figure 1. The system is taken quasi-statically through the cycle  $A \rightarrow B \rightarrow C \rightarrow A$ . Calculate the work done on the gas and the heat flow into it for each stage in the process.

b) Find the equation of the adiabat:  $p = p(V)$  for this gas that passes through the point marked  $A$  in the above figure.

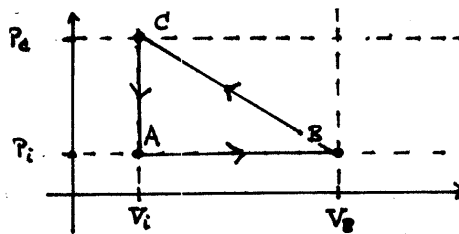


Figure 1:  $pV$  diagram of the gas. The path taken in the  $pV$  diagram is marked above.

### 3. Energy, heat, and work:

Based on Callen 3.4-5

In the quasi-static compression of a monatomic ideal gas we find that

$$T = T_0 \left( \frac{V}{V_0} \right)^\eta, \quad (4)$$

where  $T_0, V_0$  are the initial temperature and volume of the gas respectively. The gas is compressed to a final volume of  $V_f$ .

- Find the work done **on** the gas.
- Calculate the change in energy of the gas,  $\Delta E$ .
- Calculate the heat transfer by integrating:

$$\delta Q = T dS. \quad (5)$$

d) Check your answer to part c by using parts a and b. **Hint:** Think about conservation of energy.

- Find the value of  $\eta$  if the gas were compressed adiabatically.

### 4. Adiabats – one more time:

From Callen, 2.2-9

We have seen for a single component ideal gas has adiabats of the form:

$$pV^k = \text{const}, \quad (6)$$

where  $k$  is some positive, dimensionless constant.

Using this result show that

$$E = \frac{1}{k-1} pV + Nh \left( pV^k / N^k \right), \quad (7)$$

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. 6 you can then determine the fundamental relation Eq. 7 up to the unknown function as shown above.

## 5. A Photon Gas and the Expansion of the Universe

*From Callen, 3.6-1*

A gas of photons obeys the Stefan-Boltzmann law:

$$E = bVT^4, \quad (8)$$

where  $b = 7.56 \times 10^{-16} \frac{\text{J}}{\text{m}^3\text{K}^4}$  is a constant. It also obeys an equation of state

$$p = \frac{E}{3V}. \quad (9)$$

We will understand why this is later in the class, but for now let's try to see how a gas of photons cools as it adiabatically expands. Please note that  $N$  – the particle number is not a conserved variable in this problem.

a) The photon gas is at temperature  $T_0$  at volume  $V_0$ . Using these constants and the above equations, find the dependence of the temperature of the gas on its volume assuming that it expands adiabatically. Thus, you should find a function of the form:  $T = T(V)$ . This is a simple model for the cooling of the cosmic background radiation during the continuing expansion of the universe.

b) Find the work done **by** the gas when its volume is adiabatically doubled from  $V_0$  to  $2V_0$ .

c) Find the work done **by** the when its volume is doubled at *constant temperature*.

d) How much heat flowed into the gas in part c?

## 6. The Relationship Between Equations of State and the Fundamental Relation:

*From Callen, 3.3-1*

This problem helps you think about the formal structure of the thermodynamics of a one-component fluid. We know that there are three equations of state and one fundamental relation, which we typically write either as  $E = E(S, V, N)$  or  $S = S(E, V, N)$ . We found that knowing two equations of state is sufficient to know all about the thermodynamics of the system (why?). Let's try that out in an example.

A fluid obeys some fundamental relation:  $E = E(S, V, N)$ . You know that this fluid obeys a *thermal equation of state*:

$$T = \frac{3As^2}{v}, \quad (10)$$

where  $A$  is a constant and  $v = V/N$ ,  $s = S/N$  are molar quantities. It also is known to obey a *mechanical equation of state*:

$$p = \frac{As^3}{v^2}. \quad (11)$$

a) Find the chemical potential  $\mu$  as a function of  $s$  and  $v$ . Then find the fundamental relation. **Hint:** The Euler Relation will help here.

b) Do this problem another way: Find the fundamental relation of this system by directly integrating the differential molar form of the energy equation, i.e.  $d(E/N) = \dots$ .

**Not to be graded:** Do you end up with an unknown constant? Is so why and what, if anything does it mean?

### 7. Two Level Systems, Lasers, and Negative Temperature

Consider a system of  $N$  strangium atoms in a lattice. Each of these atoms can exist in one of two electronic states having energies  $\varepsilon_1, \varepsilon_2$ . To be definite, we where will take  $\varepsilon_1 < \varepsilon_2$ .

You will soon learn how to compute the Helmholtz Free Energy of this system. For the moment, assume that this free energy can be written as

$$F = -Nk_B T \left( e^{-\varepsilon_1/k_B T} + e^{-\varepsilon_2/k_B T} \right). \quad (12)$$

Please note that there is no volume  $V$  defined in this problem.

a) Find the energy  $E$  of the system as a function of temperature. Be sure to note the values of the energy in the limits  $T \rightarrow 0$  and  $T \rightarrow \infty$ . **Explain why these makes sense.**

b) Find the fundamental relation of this system in the **entropy** representation. In other words you should be able to find a result of the form:  $S = S(E, N)$ . Recall, there is no  $V$  defined in this problem.

c) Using your result from part b, make a sketch of  $S$  vs.  $E$  for this system at fixed  $N$ .

d) Consider the case in which the above system has energy

$$E > \frac{N}{2} (\varepsilon_1 + \varepsilon_2). \quad (13)$$

What is the *sign* of the temperature in this system?

e) Imagine that the strangium crystal with internal energy satisfying Eq. 13 is now allowed to exchange energy with an ideal gas at temperature  $T$ . Which way does the heat flow? Explain in terms of the maximum entropy principal. Is the crystal hotter than the gas?

**Not to be graded:** Can you see what property of strangium caused this odd set of results?

### 8. Rubber Bands: Chandler 1.13