Assignment 7
Physics/ECE 176

Made available: Tuesday, March 15, 2011
Due: by beginning of class, Tuesday, March 22, 2011.

Problem 1: Review question: the ultimate two-vessel ideal gas entropy change problem

A rigid vessel of volume V_A and pressure P_A contains an ideal gas of N_A identical A-type molecules, each with f_A degrees of freedom, and a second rigid vessel contains a different kind of ideal gas with volume V_B and pressure P_B that consists of N_B identical B-type molecules, each of which has f_B degrees of freedom. The two vessels are then connected by a tube of negligible volume and allowed to come to thermodynamic equilibrium. In terms of these data, calculate

1. the equilibrium temperature T_f;
2. the equilibrium pressure P_f;
3. the total work W_{total} done by the gases;
4. the heat Q that is transferred from vessel A to vessel B;
5. the total change in entropy ΔS_{total}. Hint: because entropy is a state function, you can choose any quasistatic sequence of processes that take you from the initial state to the final state and use those processes to calculate the change in entropy.
6. the total change in entropy ΔS_{total} assuming that the molecules are in fact atoms so that you can use the Sackur-Tetrode equation. Does your answer then agree with the previous answer, obtained without the Sackur-Tetrode equation?
7. the total change in entropy assuming that the molecules are in fact atoms and the A-atoms and B-atoms are all the same kind of atom.
8. the equilibrium chemical potential μ_f and the change in the chemical potential μ_A for system A, assuming that all the molecules are in fact atoms.

Problem 2: Review question: pressure balance by effusion

Consider a volume V containing an ideal gas that is divided into two chambers by a partition that is impermeable to heat and particles such that the temperature in chamber 1 is maintained at a constant value T_1 and the temperature in chamber 2 is maintained at a constant value T_2.

1. If a *large* hole is made in the partition and the system eventually becomes time-independent (although not in thermodynamic equilibrium), how is the final pressure P_1 in chamber 1 related to the final pressure P_2 in chamber 2?

2. If a *small* hole is made in the partition, so small that molecules can only pass through by effusion, and the system eventually becomes time-independent (although not in thermodynamic equilibrium), how is the final pressure P_1 in chamber 1 related to the final pressure P_2 in chamber 2?

Problem 3: Schroeder Problems

1. Problem 6.1 on page 224 of Schroeder. The Mathematica file

   `http://www.phy.duke.edu/~hsg/176/lectures/coupled-einstein-solids.nb`

   will be helpful here.

2. Problem 6.5 on page 225 of Schroeder. Here use Eq. (6.10), that the partition function Z for some small system with M energy states E_m that is in thermal equilibrium with a large thermal reservoir of energy T is given by the following sum:

$$Z = e^{-E_1/(kT)} + e^{-E_2/(kT)} + \ldots + e^{-E_M/(kT)}. \tag{1}$$

   The probability p_m of observing the small system to have energy E_m is then given by

$$p_m = \frac{e^{-E_m/(kT)}}{Z}, \tag{2}$$

   and it should be clear from the above that $\sum p_m = 1$, i.e. the small system is certain to be in one of the energy states E_m.

3. Problem 6.13 on page 228.

4. Problem 6.14 on page 228.

5. Problem 6.15 on page 231.

6. Problem 6.18 on page 231. Also explain how the formula $\sigma_E = kT\sqrt{C/k}$ implies that

$$C(T) \propto \frac{1}{T}, \tag{3}$$

   for large temperatures T if the energy levels E_i lie in a finite range $[E_{\min}, E_{\max}]$. This result explains why the heat capacity of a paramagnet decays to zero at large T for a paramagnet, since the magnetic dipoles in a paramagnet have just two energy levels, $E_i = \pm\mu B$.

   In case you have not seen (or don't remember) some elementary manipulations related to the standard deviation σ_E of some quantity E_s that varies from measurement to measurement (say the energy E_s of a small system in equilibrium with a large heat bath), I show here that

$$\sigma_E^2 = \overline{\left(E - \overline{E}\right)^2} = \overline{E^2} - \left(\overline{E}\right)^2. \tag{4}$$

   The first equality is the definition of the variance σ_E^2 (standard deviation squared) as the average (overbar) of the square of the deviations $E - \overline{E}$ where $\overline{E}$ is the average value of E. The second equality is a commonly used equivalent[1] form. To obtain the second form from the first, assume that the

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[1] The two forms are mathematically equivalent but not numerically equivalent. It is possible in rare cases for the second expression to round to a negative number on a digital computer because of the quirks of floating point arithmetic.

variable E_s occurs with probability p_s where all the probabilities must add to one, $\sum_s p_s = 1$. Then by definition the average $\overline{E}$ is the expected value

$$\overline{E} = \sum_s p_s E_s, \tag{5}$$

and so the variance can be calculated as follows

$$\begin{aligned}
\overline{\left(E - \overline{E}\right)^2} &= \sum_s p_s \left(E_s - \overline{E}\right)^2 & (6)\\
&= \sum_s p_s \left(E_s^2 - 2\overline{E}E_s + \overline{E}^2\right) & (7)\\
&= \sum_s p_s E_s^2 - 2\overline{E}\left(\sum_s p_s E_s\right) + \overline{E}^2 \sum_s p_s & (8)\\
&= \overline{E^2} - 2\left(\overline{E}\right)^2 + \left(\overline{E}\right)^2 & (9)\\
&= \overline{E^2} - \left(\overline{E}\right)^2 . & (10)
\end{aligned}$$

In the above, I used the fact that a constant can be pulled out of a sum, e.g. $\sum_s p_s(-2\overline{E}E_s) = (-2\overline{E})\sum_s p_s E_s = -2\overline{E}^2$. The above derivation is the gist of Problem 6.17(c) on page 231 of Schroeder. You may want to work out this problem on your own if the above algebra is not fully familiar.

7. Problem 6.19 on page 231 of Schroeder. Hint: Einstein solids obey the equipartition theorem at high temperatures.

Problem 4: Time to Finish This Homework Assignment

Please tell me the approximate time in hours that it took you to complete this homework assignment.