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 $W_{\text{total}}$ done by the gases;
4. the heat $Q$ that is transferred from vessel A to vessel B;
5. the total change in entropy $\Delta S_{\text{total}}$. 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 $\Delta S_{\text{total}}$ 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 $\mu_f$ and the change in the chemical potential $\mu_A$ 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:

   \[ Z = e^{-E_1/(kT)} + e^{-E_2/(kT)} + \ldots + e^{-E_M/(kT)}. \]  

   (1)

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

   \[ p_m = \frac{e^{-E_m/(kT)}}{Z}, \]  

   (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 $E_m$.


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

   \[ C(T) \propto \frac{1}{T}, \]  

   (3)

   for large temperatures $T$ if the energy levels $E_i$ lie in a finite range $[E_{\text{min}}, E_{\text{max}}]$. 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 $\sigma_E$ 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

   \[ \sigma_E^2 = \overline{(E - \overline{E})^2} = \overline{E^2} - \overline{E}^2. \]  

   (4)

   The first equality is the definition of the variance $\sigma_E^2$ (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

$$\overline{E} = \sum_s p_s E_s, \quad (5)$$

and so the variance can be calculated as follows

$$\overline{(E - \overline{E})^2} = \sum_s p_s (E_s - \overline{E})^2 \quad (6)$$

$$= \sum_s p_s \left( E_s^2 - 2 \overline{E} E_s + \overline{E}^2 \right) \quad (7)$$

$$= \sum_s p_s E_s^2 - 2 \overline{E} \left( \sum_s p_s E_s \right) + \overline{E}^2 \sum_s p_s \quad (8)$$

$$= \overline{E^2} - 2 \left( \overline{E} \right)^2 + \left( \overline{E} \right)^2 \quad (9)$$

$$= \overline{E^2} - \left( \overline{E} \right)^2. \quad (10)$$

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.


**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.