CHM6461, Spring 2008,Homework #4

1. Calculate the entropy of Ar at 298 K and 1 atm. Compare this to the literature value of 36.98 J/K.

2. The quantum mechanical energy of a particle confined to a rectangular parallelpiped of lengths a,b, and c is:

$$\epsilon(n_x, n_y, n_z) = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Show that the translational partition function for this geometry is the same as that of a cube with the same volume.

3. Given that the quantum mechanical energy levels of a particle in a two-dimensional box are:

$$\epsilon(n_x, n_y) = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

a. First, calculate the density of states $\rho(\epsilon)d\epsilon$
b. Use $\rho(\epsilon)$ to find the translational partition function of a two-dimensional ideal gas.
c. Derive the partition function by another method.
d. Find the equation of state.
e. Find the thermodynamic energy, E.
f. Find the heat capacity.
g. Find the entropy.

4. Calculate the entropy of an arbitrary binary mixture of Ne and Ar at 500 K with total pressure of 10atm, assuing ideal behavior.

5. Many quantum mechanical systems have energy level expressions for which the lowest allowed energy,the zero point energy,is not zero.The derivation of the Maxwell-Boltzmann distribution assumed the zero-point energy was zero.Does a zero-point energy alter this distribution? Imagine each energy level in a system is shifted by zero-point energy that is simply added to each. Show that this change does not alter the distribution,and as a consequence,the zero-point energy can never influence observable quantities.

6. When a solid melts or a liquid boils, its partition function changes. Show that vaporization increases Q by a factor approximately equal to e^n. Follow these steps:

Use the equation : $S = k_B \ln Q + (\Delta_0 U)/T$ to write an expression $\Delta_{vap} S = S(g) - S(l)$.

Substitute $\Delta_0 U = \Delta_0 H - \Delta_0 (pV)$, and use $\Delta_{vap} S = \Delta_{vap} H / T_{vap}$.

Next, use the approximation $\Delta_{vap} V = V(g)$ and the ideal gas equation to complete the problem.

7. Derive an expression for the fluctuation in the pressure in a canonical ensemble.

8. Show that $\partial_N \mu |_{V,T} = -\frac{V^2}{N^2} \partial_V p |_{N,T}$

9. Show that the standard deviation of the energy in a grand canonical ensemble is:

$$\sigma_E{}^2 = k T^2 C_V + \mu \partial_N E |_{V,T} \sigma_N{}^2$$

where $\sigma_N{}^2 = k T \partial_\mu N |_{V,T}$

10. Show that in a two-component, open isothermal system, that

$$\overline{N_1 N_2} - \overline{N}_1 \overline{N}_2 = kT \partial_{\mu_2} \overline{N}_1 |_{V,T,\mu_1} = kT \partial_{\mu_1} \overline{N}_2 |_{V,T,\mu_2}$$