Chemistry 322 | Spring 2004
Professor J. Daniel Gezelter | Due Mon. 2/16/2004

Problem Set 4

1. The vibrational partition function for a single vibrational mode is:

$$q_{vib} = \frac{e^{-\theta_{vib}/2T}}{1 - e^{-\theta_{vib}/T}}$$

where $\theta_{vib} = h\nu/k_B$, and ν is the frequency of the vibrational mode. Show that the average energy for this vibrational mode approaches $k_B T$ in the limit of large temperatures. Hint: you will need to expand the exponentials in the expression for the average energy to show this. Discuss what this tells you about the equipartition theorem.

2. The Sackur-Tetrode equation for the absolute entropy of an ideal gas:

Use the following expression for the entropy (S)

$$S = k_B \ln \left(\frac{q^N}{N!} \right) + \frac{U}{T}$$

to show that for a monatomic ideal gas, the entropy can be written as

$$S = N k_B \ln \left(\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{e^{5/2}}{N} \right) V \right)$$

3. Use the expression in problem 2 to estimate the molar entropy for argon and compare it to the experimentally measured value of 155 $JK^{-1}mol^{-1}$.

4. If the equipartion theorem is true, what should the heat capacity be for water at high temperatures? Compare this value to the heat capacity of steam (0.5 Cal / g / K at 460 C).

5. Do problem 19-7 in McQuarrie and Simon.

6. Do problem 19-13 in McQuarrie and Simon.