Physical Chemistry of Materials 2

Due date: October 10, 2012

Homework #3

1. Consider an ensemble of units in which the first excited electronic state at energy ε_1 is m_1-fold degenerate, and the energy of the ground state is m_0-fold degenerate with energy ε_0.

   (a) Demonstrate that if ε_0=0, the expression for the electronic partition function is

$$q_E = m_0\left(1+\frac{m_1}{m_0}e^{-\varepsilon_1/kT}\right)$$

   (b) Determine the expression for the internal energy U of an ensemble of N such units. What is the limiting value of U as the temperature approaches zero and infinity?

2. Determine the vibrational contribution to C_V for HCN where $\tilde{\nu}_1 = 2041 cm^{-1}$, $\tilde{\nu}_2 = 712\, cm^{-1}$ (doubly degenerate), *and* $\tilde{\nu}_3 = 3369\, cm^{-1}$ at T= 298, 500, and 1000 K.

3. The speed of sound is given by the following relationship

$$c_{sound} = \left(\frac{\frac{C_p}{C_V}RT}{M}\right)^{\frac{1}{2}}$$

   where C_p is the constant pressure heat capacity (equal to C_V+R), R is the ideal gas constant, T is the temperature, and M is molar mass.

   (a) What is the expression for the speed of sound for an ideal monatomic gas?

   (b) What is the speed of sound in air at 298 K, assuming that air is mostly made up of nitrogen ($B = 2.00\, cm^{-1}$ and $\tilde{\nu} = 2359\ cm^{-1}$)?

4. The fraction of molecules in the Jth rotational level is given by

$$P_J = \frac{(2J+1)e^{-\Theta_{rot}J(J+1)/T}}{q_{rot}} = (2J+1)\left(\Theta_{rot}/T\right)e^{-\Theta_{rot}J(J+1)/T}$$

   Show that the values of J at the maximum of a plot of P_J versus J is given by

$$J_{\max} \approx \left(\frac{T}{2\Theta_{rot}}\right)^{1/2} - \frac{1}{2}$$

5. $NO_2(g)$ is a bent triatomic molecule. The following data determined from spectroscopic measurements are
   $\tilde{\nu}_1 = 1319.7\,cm^{-1}, \tilde{\nu}_2 = 749.8\,cm^{-1}, \tilde{\nu}_3 = 1617.75\,cm^{-1}, B_A = 8.0012\,cm^{-1}, B_B = 0.43304\,cm^{-1}, B_C = 0.41040\,cm^{-1}$.
   Determine the three characteristic vibrational temperatures and the characteristic rotational temperatures for each of the principle axes of $NO_2(g)$ at 1000 K. Calculate the molar heat capacity C_V at 1000 K.

6. Solve the 9^{th} edition Atkin's problems: 15.18, 16.6, 16.12, 16.14.