

## Problem Set 10

*Due beginning of class on Wednesday, April 25th*

*(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)*

1. Atkins *Problem 15.14*. (Part (a) means put each molecule in the same state.) How will the result be different if we have  $N_A$  (Avogadro's number) molecules?
2. Consider a two-level system that has an energy separation of  $\epsilon$  between the two levels.
  - (a) Write the partition function.
  - (b) The total energy of the system as a function of temperature is  $E(T) = \sum_i N_i \epsilon_i$ . Rewrite this equation in a form that contains the derivative of  $q$  with respect to  $\beta$ .
  - (c) Plot  $E(T)$ . What is the value at  $T=0$ , and why? What is the value at  $T \rightarrow \infty$  and why?
3. The three normal modes of water are the symmetric stretch ( $\tilde{\nu}_1 = 3652 \text{ cm}^{-1}$ ), the antisymmetric stretch ( $\tilde{\nu}_3 = 3756 \text{ cm}^{-1}$ ), and the bend ( $\tilde{\nu}_2 = 1595 \text{ cm}^{-1}$ ). Each normal mode has a harmonic oscillator potential.
  - (a) Calculate the molecular vibrational partition function of water at 3000 K.
  - (b) (All at 3000 K.) What fraction of water molecules have the bend excited to  $v_2=1$ . What fraction of water molecules have the symmetric stretch excited to  $v_1=1$ ? Why do more molecules have the bend excited? What fraction of water molecules have both  $v_2=1$  and  $v_1=1$  excited?
  - (c) Recalculate the fractions when the temperature is raised to 5000 K. Comment on the changes.
4. We will not cover the subject material in this question explicitly until lecture on Monday.
  - (a) Determine the molecular rotational partition function for  $\text{H}^{35}\text{Cl}$  at 300 K. Numerically sum the first 1, 10, 20, and 100 terms in the rotational partition function equation. (See Example 15.1 for an equation. Use  $B = 10.591 \text{ cm}^{-1}$ ) To what value is the partition function converging? Give your answer to 5 significant figures.
  - (b) What is the value of the rotational partition function in the high temperature limit? (See Eqn 16.15.) Is this a good approximation at 300 K?
  - (c) Recall Problem Set 5, Question 4(e) where you were asked to sketch the pure rotational absorption spectrum of  $\text{H}^{35}\text{Cl}$ . In that problem, you were given the intensities. (Because those numbers were arbitrary, the results here may not match them.) Now we will calculate the relative intensities for the first seven transitions using the populations of the energy levels. (This approach omits some other factors). Make the intensities proportional to the probability of finding  $\text{H}^{35}\text{Cl}$  in the initial rotational level. Draw the spectrum quantitatively. Make your x-axis wavenumbers.