Physical Chemistry II
Problem Set 6
Due Monday, May 12, 2008 (when you come to the final)
Total Number of Points = 60

Notes: (1) Write all numbers with the correct number of significant figures and units. Avoid rounding errors by writing intermediate results with additional subscripted non-significant figures. (2) Assume all zeroes to the left of the decimal place are significant (unless told otherwise). For example, 100 V has three significant figures (and should therefore have been written by Atkins and de Paula as 100. V or 1.00×10^2 V). (3) The answers to most of these problems are in the back of the book. However, you must justify your answers to receive credit.

1. (15 points) (Based on Atkins and de Paula Exercise 14.11b)
   (a) Write the ground state valence electron configurations of F_2 and F_2^+, and predict their bond orders.
   (b) The potential energy curve of which species, F_2 or F_2^+, will be deeper and possess a minimum at a smaller value of R? Briefly explain.
   (c) The potential energy curve of which species, F_2 or F_2^+, will be lower at all values of R? Briefly explain. (Note/hint: The answer to part (c) will not necessarily be the same as the answer to part (b).)
   (d) Based on your answers to parts (b) and (c), draw on a common set of axes the potential energy curves for F_2 and F_2^+. Label the species formed in the limit of large R for both curves.
   (e) Would you expect the $v' = 2 \leftarrow v = 0$ transition to be weaker or stronger than the $v' = 0 \leftarrow v = 0$ transition? Explain.

2. (7 points) Atkins and de Paula Problem 14.1

3. (7 points) Let us try to redeem my egregious math error in class on April 25: As we did in class that day, consider 100 particles distributed into two boxes. It is the case that the most probable distribution is when there are 50 particles in each box.
   (a) For every 100 times we observe the most probable distribution, how many times (on average) will we observe the distribution when there are 45 particles in one box and 55 particles in the other box?
   (b) For every 100 times we observe the most probable distribution, how many times (on average) will we observe the distribution when there are 40 particles in one box and 60 particles in the other box?
   (c) Say we observe the distribution when there are 99 particles in one box and 1 particle in the other box. How many times can we expect to observe the most probable distribution before we observe the "99 and 1" distribution again? (Give your answer to three significant figures.)

   Justify your above answers briefly on paper, using the Excel FACT() function whenever necessary.

Problem Set 6 continues on the back.

4. (6 points) Starting with the expression for the frequency of a distribution,

$$W = \frac{N!}{n_0!n_1!n_2!\cdots n_m!}$$

prove that

$$\ln W = N \ln N - \sum_{i=0}^{m} n_i \ln n_i$$

5. (4 points) Atkins and de Paula Exercise 16.1b.

6. (8 points) Atkins and de Paula Exercise 16.4b. Briefly discuss why the value of q you calculate is reasonable.

7. (5 points) Atkins and de Paula Exercise 16.5b

8. (3 points) Calculate the molar entropy (in units of J mol^{-1} K^{-1}) at 2000. K for a sample composed of the atoms specified in Exercise 16.4b.

9. (5 points) Atkins and de Paula Exercise 16.11b. Report your answer in units of J $mol^{-1}K^{-1}$