# Chemistry 4000/5000/7001 Spring 2009 Test 1

**Time:** 50 minutes

**Marks:** 40

**Aids allowed:** One 8.5 × 11-inch formula sheet, calculator, computer

**The use of communications software or devices of any kind, including web browsers, is strictly prohibited.**

**You may not open any pre-existing files on your computer.**

**Instructions:** All answers should be written in the booklets provided.

If you use software to answer a question, explain what you did. You don't necessarily need to reproduce every command you entered, but someone who has used the software should have a good idea of how you solved the problem. For example, if you used software to solve an integral, it is generally enough to display the integral and answer, and indicate that you solved the integral using (e.g.) Maple. Note that you do not need to reproduce every digit generated by your calculator or computer. Just give me a few decimal places so that I can assess whether you have done the calculation correctly.

**Useful data:**

$c = 2.997\,924\,58 \times 10^{8}\,\mathrm{m/s}$

$h = 6.626\,068\,96 \times 10^{-34}\,\mathrm{J\,s}$

$k = 1.380\,650\,4 \times 10^{-23}\,\mathrm{J/K}$ or $0.695\,035\,6\,\mathrm{cm^{-1}K^{-1}}$

$N_A = 6.022\,141\,79 \times 10^{23}\,\mathrm{mol^{-1}}$

$R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$

To convert degrees Celsius to Kelvin, add 273.15.

1. For each of the following statements, state whether it is true or false, and **briefly** explain your reasoning. [2 marks each]

   (a) The heat capacity always tends toward zero at very low temperatures.

   (b) In a large ensemble of molecules, the ground-state population is always larger than the population of an excited energy level.

   (c) The molecular partition function of a gas can be exactly factored into translational, rotational, vibrational and electronic contributions.

   (d) The Boltzmann distribution is the only possible distribution of energy in a canonical ensemble.

   (e) We can calculate the canonical partition function of a dilute gas based on the molecular partition function because intermolecular forces are negligible in this case.

2. For LiF, the rotational constant $B = 1.345\,257\,6\,\mathrm{cm}^{-1}$.

   (a) Is it reasonable to use the integrated form of the rotational partition function at 100 K for LiF? [3 marks]

   (b) Calculate the probability than an LiF molecule in the gas phase occupies the $J = 3$ rotational level at 100 K. [4 marks]

3. The following are the first few electronic energy levels of a carbon atom:

| Level | Degeneracy | $\varepsilon/\mathrm{cm}^{-1}$ |
|---|---|---|
| 1 | 1 | 0 |
| 2 | 3 | 16.40 |
| 3 | 5 | 43.40 |
| 4 | 5 | 10 192.63 |

   You will be asked to calculate a few thermodynamic quantities in this problem. Read the whole question before you do anything. If you use Maple, do the algebra for all three parts *before* you substitute in any values. This will make it easier for you to write down the intermediate results, which in turn will make it easier for me to mark the question, especially if you make a mistake somewhere along the line.

   (a) Calculate the electronic partition function for a carbon atom at 25°C. Explain what your calculation tells us about the occupation of the energy levels at this temperature. [4 marks]

   (b) Calculate the molar internal energy of a gas of carbon atoms at 25°C.

   Maple hint: Use `simplify()` to clean up large expressions. [6 marks]

4. Suppose that you wanted to calculate the standard molar Gibbs free energy of fluorobenzene in the gas phase. What molecular data would you need? Be as specific as possible. [8 marks]

   **Bonus:** Thermodynamic tables give the standard Gibbs free energy of formation of a compound, not the Gibbs energy itself. Discuss briefly how you could calculate the standard free energy of formation. You need not go into the level of detail of the main part of this question. Instead, focus on any calculations that would differ in kind from those you have already described.

5. Suppose that we have a reaction $A \rightleftharpoons B$. Give an example of an arrangement of the energy levels of A and B that would tend to favor the formation of B. You can give your example in the form of a sketch. Make sure to explain why, based on statistical mechanical principles, your proposed arrangement favors B. [5 marks]