

# Chemistry 4000 Spring 2009 Final Examination

**Time:** 3 hours

**Marks:** 103

**Aids allowed:** One  $8.5 \times 11$ -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:** You can answer the questions in any order, but make sure that you clearly label each of your answers with the section and question number in your exam booklet(s).

If you use software to answer a question, explain what you did and show all relevant equations. 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. In multi-step calculations, it may help me mark your work if you show the results of intermediate steps when this is feasible. Note also that you do not need to reproduce every digit generated by your calculator or computer in numerical calculations. Just give me a few decimal places so that I can assess whether you have done the calculation correctly.

In section 2, you have a selection of questions. **Do not answer more than the required number of questions.** I will stop marking as soon as I have reached the required number of questions from this section. **Extra answers will not be marked.**

If you answer extra questions, make sure you cross out the ones you don't want me to mark.

## Data

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

$$h = 6.626\,068\,8 \times 10^{-34} \text{ J/Hz}$$

$$k = 1.380\,650\,3 \times 10^{-23} \text{ J/K or } 0.695\,035\,6 \text{ cm}^{-1}\text{K}^{-1}$$

$$N_A = 6.022\,142\,0 \times 10^{23} \text{ mol}^{-1}$$

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

$$1 \text{ bar} = 100\,000 \text{ Pa}$$

$$1 \text{ cm}^{-1} = 1.986\,455\,5 \times 10^{-23} \text{ J}$$

To convert degrees Celsius to Kelvin, add 273.15.

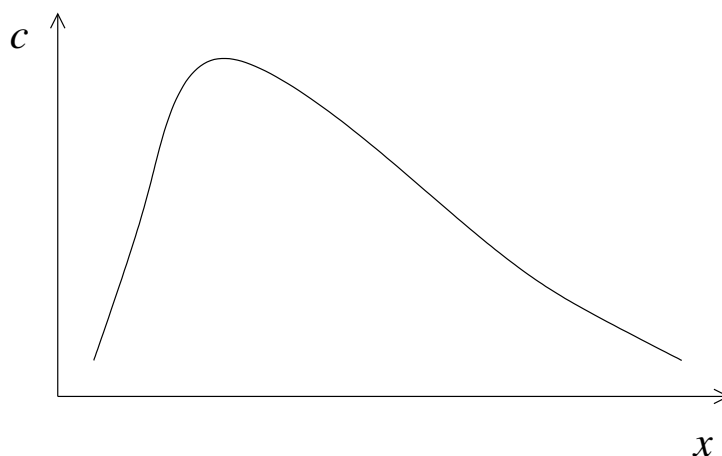
# 1 Answer *all* questions in this section.

Value of this section: 63 marks

1. What is the physical significance of the Boltzmann distribution? [1 mark]
2. You have bought a bottle of deuterium oxide in which, according to the manufacturer, 99.8% of the hydrogen atoms are of the deuterium isotope, and the rest are ordinary hydrogen. Hydrogen atoms exchange rapidly between water molecules, so the H and D isotopes should be randomly distributed. At any given time, what percentage of the molecules would you expect there to be of each of the three possible isotopomers ( $\text{D}_2\text{O}$ ,  $\text{HOD}$ ,  $\text{H}_2\text{O}$ )? [4 marks]

Hint: Imagine that you reach into the solution, pull out one molecule of water, and look at its hydrogens.

3. Consider the following concentration profile:



- (a) Reproduce this diagram in your exam booklet, and label the diagram with arrows to show the direction of the flux vectors in different regions of the profile. [2 marks]
  - (b) Where is the flux vector largest in magnitude? [1 mark]
  - (c) Explain briefly what Fick's second law says about what should happen at the maximum of the profile. [2 marks]
4. (a) Obtain an equation for the standard deviation of the molecular speed in a gas. [3 marks]
  - (b) What is the probability that the speed is within one standard deviation of the average? Does this quantity depend on the temperature? If not, give your answer to four decimal places. [6 marks]
- Maple notes: Don't forget that  $\pi$  is Pi in Maple. In this case, you are best off doing the main calculation without any assumptions, and then assuming that  $M$ ,  $R$  and  $T$  are positive only when you apply the `simplify()` function.

5. The lowest three electronic energy levels of  $\text{O}_2^+$  are as follows:

State ( $i$ )	$g_i$	$\epsilon_i/\text{cm}^{-1}$
1	2	0
2	2	197.3
3	4	32964

- Is state 3 of any relevance to the thermodynamics of  $\text{O}_2^+$  at normal temperatures? Give a quantitative argument. [3 marks]
  - Calculate the value of the electronic partition function at 298.15 K. What does this number mean? [4 marks]
  - Calculate the electronic contribution to the molar internal energy at 298.15 K. [4 marks]
- Note: Peek ahead to question 5d. You may want to do the algebra for both of these questions together before you enter any numbers.
- What is the electronic contribution to the molar heat capacity of  $\text{O}_2^+$  at 298.15 K? [4 marks]
  - It is possible to estimate the electronic contribution to the molar internal energy (or any other contribution to  $U$ , for that matter) using a simulation. To do this, we randomly generate the electronic states of an ensemble of molecules according to a Boltzmann distribution. We then get the average energy of the ensemble and multiply that by Avogadro's number to get the molar value. Carry out such a simulation at 298.15 K, and report both the molar electronic internal energy and the standard error in this quantity. Does your answer agree with the direct calculation in question 5c? Your brief report should also briefly describe how your simulation works. [15 marks]

You can use either Excel or Maple for this simulation. Excel doesn't have a built-in function for the standard error of the mean. You can calculate it by dividing the standard deviation by the square root of the number of samples. The following Excel functions are likely to be useful: `RAND()`; `IF(logical condition, value if true, value if false)`; `AVERAGE(range)`; `STDEV(range)`; `COUNT(range)`.

If you decide to use Maple, you will want to load the `RandomTools` and `Statistics` packages using the `with()` function. To generate a random number, use `MersenneTwister[GenerateFloat]()`. The following statistical functions may also be useful: `Mean( $x$ )` and `StandardError(Mean,  $x$ )`, where  $x$  is a `Vector`.

Note that I will be happy to provide *technical* assistance during the exam. You have to have a reasonably clear idea of what you are trying to accomplish, and ideally some code written that I can help you debug.

- The vibrational frequencies and rotational constants of the ground and first excited state are identical. They are  $\tilde{\nu} = 1904.8\text{ cm}^{-1}$ , and  $B = 1.6913\text{ cm}^{-1}$ . The molar mass of  $\text{O}_2^+$  is  $31.9983\text{ g/mol}$ . Calculate the standard molar entropy of  $\text{O}_2^+$ , and compare your value to the thermochemical value of  $206.22\text{ J K}^{-1}\text{ mol}^{-1}$ . Is the

agreement reasonable? If not, explain briefly where the major sources of error in your calculation are. [14 marks]

## 2 Answer any *four* questions in this section.

Value of this section: 40 marks

1. Explain how the microcanonical, canonical and grand canonical ensembles are related. [10 marks]
2. Discuss the similarities and differences between the lattice theories of small-molecule and of polymer solubility. [10 marks]
3. Discuss the assumptions of the lattice model of proteins. How reasonable are these assumptions? How could the model be improved? [10 marks]
4. Compare Lindemann's theory of gas-phase unimolecular reactions to RRK theory. [10 marks]
5. Explain how transition state theory can be used to predict rate constants for reactions. Make sure to explain what data are needed and how these data can be obtained. [10 marks]
6. Derive an equation for the average configurational entropy per lattice site of a surface with  $M$  sites on which  $N$  molecules are adsorbed. Give your answer in terms of the surface coverage,  $\theta$ . [10 marks]<sup>1</sup>
7. Derive the Einstein equation for the heat capacity of a solid. What is the major assumption of this theory? [10 marks]<sup>2</sup>

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<sup>1</sup>Leslie may not answer this question.

<sup>2</sup>Andrea may not answer this questions.