Sample Exam II
Chemistry 448
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1. Provide short answers to the following:
(a) What is the probability for observing a closed thermally equilibrated system with a given energy *E*?
(b) What is the configuration integral?
(c) What does the configuration integral reduce to for a system of non-interacting particles?
(d) What is the average density of particles at position *r* given that a tagged particle is at the origin?
(e) What is the basis for the Metropolis sampling scheme?
(f) What is wrong with simple sampling?
(g) Why do we use periodic boundary conditions in a simulation of a physical system?

2. Derive the equation for the electronic contribution to the heat capacity for a gas whose electronic partition function is

$$q_{elec} = g_0 + g_1 exp(-\beta\varepsilon_1)$$

An example is NO molecule. In this case what would the quantities g_0 , g_1, ε_1 correspond to?

3. Compute the equilibrium constant at 1000 K of the dissociation

$$Na_2 \leftrightarrow 2Na$$

making use of the following data: ω= 159.23 cm^{-1}; *r*= 3.078x10^{-8} cm; *h* = 6.624x10^{-27} erg sec, *c* = 2.998x10^{10} cm sec^{-1}, *k* = 1.3805x10^{-16} erg deg^{-1} molecule^{-1}. The dissociation energy is 0.73 eV (1 eV = 8106 cm^{-1}).
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4. Derive the heat capacity at constant volume and temperature *T* of a homonuclear diatomic gas in which the nuclei have spin ½ and in contact with a paramagnetic solid. Derive the heat capacity at constant volume and temperature *T* of the same homonuclear diatomic gas which had been prepared and equilibrated at 4 K and then isolated from contact with any paramagnetic substances while being raised to temperature *T*.

5. Consider an isomerization process

$$A \leftrightarrow B$$

where A and B refer to the different isomer states of a molecule. Imagine that the process takes place in a dilute gas, and that $\Delta\varepsilon$ is the energy difference between state A and state B. According to the Boltzmann distribution law, the equilibrium ratio of A and B populations is given by

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{g_A}{g_B} \exp(-\beta \Delta\varepsilon)$$

where g_A and g_B are the degeneracies of states A and B, respectively. Show how this same result follows from the condition of chemical equilibria, $\mu_A = \mu_B$.

6. Consider the system described in problem 5. The canonical partition function is

$$Q = \frac{1}{N!} q^N$$

where N is the total number of molecules, and q is the Boltzmann-weighted sum over all single molecule states, both those associated with isomers of type A and those associated with isomers of type B.

(a) Show that one may partition the sum and write

$$Q = \sum_P \exp[-\beta A(N_A, N_B)]$$

where $\sum_P$ is over all the partitions of N molecules into N_A molecules of type A and N_B molecules of type B, the Helmholtz free energy $A(N_A,N_B)$

$$-\beta A(N_A, N_B) = \ln[(N_A! N_B!)^{-1} q_A^{N_A} q_B^{N_B}],$$

q_A is the Boltzmann-weighted sum over states of isomer A, and q_B is the Boltzmann-weighted sum over states of isomer B.

(b) Show that the condition of chemical equilibria is identical to finding the partitioning that minimizes the Helmholtz free energy,

$$\left(\frac{\partial A}{\partial \langle N_A \rangle}\right) = \left(\frac{\partial A}{\partial \langle N_B \rangle}\right) = 0$$

subject to the constraint that $\langle N_A \rangle + \langle N_B \rangle = N$ is fixed.

7. For the system described in problem 5 and 6, we have the canonical partition function

$$Q = \sum_{N_A, N_B} \left(q_A^{N_A} q_B^{N_B} / N_A! N_B!\right) = \left(q_A + q_B\right)^N / N!$$

with the double sum restricted to $N_A + N_B = N$.
Show that

$$\langle N_A \rangle = q_A \left(\frac{\partial \ln Q}{\partial q_A}\right)_{q_B, N} = N \frac{q_A}{q_A + q_B}$$

Use this result and the analogous formula for $\langle N_B \rangle$ to show that

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{q_A}{q_B}$$

Next, consider the fluctuations from these mean values. Express the average of the square fluctuation $[N_A - \langle N_A \rangle]^2$ as appropriately weighted sums over states.

Then, show that

$$\langle [N_A - \langle N_A \rangle]^2 \rangle = q_A \left(\frac{\partial \langle N_A \rangle}{\partial q_A}\right)_{q_B, N} = \frac{\langle N_A \rangle \langle N_B \rangle}{N}$$

Derive a similar expression for the fluctuations in N_B.