

**Sample Exam II**  
Chemistry 448  
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1. Provide short answers to the following:

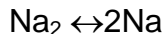
- (a) What is the probability for observing a closed thermally equilibrated system with a given energy  $E$ ?
- (b) What is the configuration integral?
- (c) What does the configuration integral reduce to for a system of non-interacting particles?
- (d) What is the average density of particles at position  $r$  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

$$q_{elec} = g_0 + g_1 \exp(-\beta \epsilon_1)$$

An example is NO molecule. In this case what would the quantities  $g_0$ ,  $g_1$ ,  $\epsilon_1$  correspond to?

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



making use of the following data:  $\omega = 159.23 \text{ cm}^{-1}$ ;  $r = 3.078 \times 10^{-8} \text{ cm}$ ;  $h = 6.624 \times 10^{-27} \text{ erg sec}$ ,  $c = 2.998 \times 10^{10} \text{ cm sec}^{-1}$ ,  $k = 1.3805 \times 10^{-16} \text{ erg deg}^{-1} \text{ molecule}^{-1}$ . The dissociation energy is 0.73 eV (1 eV = 8106  $\text{cm}^{-1}$ ).

4. Derive the heat capacity at constant volume and temperature  $T$  of a homonuclear diatomic gas in which the nuclei have spin  $\frac{1}{2}$  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



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  $\Delta \epsilon$  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

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

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

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

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  $N_B$ .