Sample Midterm Exam I
Chemistry 448
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Do any 4 of the following problems. As previously agreed, you may use your single 8.5"x11" sheet of notes with writing on both sides.

1. Calculate the probability of a state in a colloidal system of 2 cm^3 containing 5000 particles per cm^3 in which 10 particles have migrated spontaneously from one cm^3 to the other, relative to the probability of the state where each cubic centimeter contains 5000 particles.

2. Consider a system of N distinguishable independent (i.e., non-interacting particles each of which can exist in one of two states separated by an energy ε. We can specify the system quantum state j by listing the states of the individual particles,

j: (0,1,1,0,1,0,0,0,.......)

where $n_1 = 0$ means particle 1 is in the lower state

$n_2 = 1$ means particle 2 is in the upper state, etc.

(a) Write down the expression for E_j in terms of n_i and ε, assuming the ground state as the zero of energy.
(b) Derive the thermodynamic properties of this model. That is, first find Q, and then A, E, and lastly S.

3. (a) Consider a one-component system with N_1 molecules of type A in volume V. The concentration of molecules is $N_2 = N_1/V$. Consider a second system with N_2 molecules of type A in <u>unit volume</u>. What is the relation between the canonical partition functions $Q(N_1, T, V)$ and $Q(N_2, T, 1)$ of the two systems? [Hint: What function, related to Q is an extensive function?]
(b) In the same way, what is the relation between the grand partition functions $Z(\mu,T,V_1)$ and $Z(\mu,T,V_2)$ for two one-component systems which have the same chemical potential and the same temperature, but different volumes V_1 and V_2?

4. This problem is a very simple illustration of the application of the grand partition function in adsorption problems. Let each system in the grand ensemble consist of four distinguishable adsorption sites 1, 2, 3, and 4 in the shape of a square. There is a gas composed of atoms, A. The energy of adsorption at a site is $-\varepsilon$. There is an energy of interaction ω between atoms adsorbed on neighboring sites. Thus, the enumeration of the possible states of the system begins as follows:

One atom adsorbed at site 1, 2, 3, or 4	energy = $-\varepsilon$
Two atoms adsorbed at neighboring sites, such as (1,2), (2,3), etc.	energy = $-\varepsilon + \omega$
Two atoms adsorbed at opposite sites, such as (1,3), etc.	energy = -2ε

And so on, for three atoms adsorbed or four atoms adsorbed.

The activity λ of the gas is prescribed by the partial pressure of the gas. The temperature is T.

Set up the grand partition function $Z(\lambda,N, T)$ for this system. Use the general statistical thermodynamic formulas to calculate the average number of particles adsorbed at a given λ .

5. Consider the adsorption model in which molecules can be adsorbed on top of each other so that adsorption to the depth of many layers can occur. The total number N of adsorbed molecules is given by

$$N = n_1 + n_2 + n_3 + ... + ...$$

where the subscripts indicate the number of the layer, e.g., the first, second, or third layer, etc.

How many ways can n_1 molecules be adsorbed on a surface that has s sites?

How many ways can n_2 molecules be adsorbed on the n_1 molecules in the first layer to make the second layer?

How many ways can n_3 molecules be adsorbed on the n_2 molecules in the second layer to make the third layer?

Let q_1 be the molecular partition function of any molecule that is in the first layer, q_2 be the molecular partition function of any molecule that is in the second layer, etc. What is the partition function $Q(N,V,T)$?

Since the total number of adsorbed particles N changes from time to time, what then is the partition function $Z(\mu,T,V)$ for multilayer adsorption?