J01T.2

Solution to J01T.2 — Solution of Biomolecules

The three possible states are an unbound molecule C, an A-C pair and a B-C pair with energies of ϵ_{AC} ,ϵ_{BC} , and 0 respectively. Starting with the expression for the grand canonical partition function

$$Z = \sum_{i}^{n} e^{-\beta\left(E_i - \mu_i N_i\right)} \tag{1}$$

and introducing the chemical potentials of the two molecule pairs μ_A and μ_B, our single particle partition function takes the form of

$$Z = 1 + e^{-\beta\left(-\epsilon_{AC} - \mu_A\right)} + e^{-\beta\left(-\epsilon_{BC} - \mu_B\right)} \tag{2}$$

We now take the product of all the single particle partition functions, of which there are N_C to find

$$Z = \left(1 + e^{-\beta\left(-\epsilon_{AC} - \mu_A\right)} + e^{-\beta\left(-\epsilon_{BC} - \mu_B\right)}\right)^{N_C} \tag{3}$$

To calculate the fraction of c molecules bound to A or B molecules, take the Gibbs factor for each AC and BC pair and divide by the single particle partition function

$$f_A = \frac{e^{\beta\left(\epsilon_{AC} + \mu_A\right)}}{1 + e^{\beta\left(\epsilon_{AC} + \mu_A\right)} + e^{\beta\left(\epsilon_{BC} + \mu_B\right)}} \tag{4}$$

$$f_B = \frac{e^{\beta\left(\epsilon_{BC} + \mu_B\right)}}{1 + e^{\beta\left(\epsilon_{AC} + \mu_A\right)} + e^{\beta\left(\epsilon_{BC} + \mu_B\right)}} \tag{5}$$

For part b, we can utilize

$$\frac{N_A}{V_A} = n_A = e^{\beta} \mu_A \tag{6}$$

and

$$\frac{N_B}{V_B} = n_B = e^{\beta}\mu_B \tag{7}$$

. The problem says that in the absence of molecule b, <u>every</u> c bonds to an A molecule which means the "unbound" state in our single particle partition function can be removed.

$$f_A = \frac{e^{\beta(\epsilon_{AC}+\mu_A)}}{e^{\beta(\epsilon_{AC}+\mu_A)} + e^{\beta(\epsilon_{BC}+\mu_B)}} \tag{8}$$

and with some algebra

$$f_A = \frac{e^{\beta(\epsilon_{AC}+\mu_A)}}{e^{\beta(\epsilon_{AC}+\mu_A)} + e^{\beta(\epsilon_{BC}+\mu_B)}} \cdot \frac{e^{-\beta(\epsilon_{AC}+\mu_A)}}{e^{-\beta(\epsilon_{AC}+\mu_A)}} \longrightarrow \frac{1}{1 + e^{\beta(\epsilon_{BC}+\mu_B-\epsilon_{AC}-\mu_A)}} \tag{9}$$

Substituting equations 5 and 6 into 8, we find that

$$f_A = \frac{1}{1 + \frac{n_B}{n_A} e^{\beta(\epsilon_{BC}-\epsilon_{AC})}} \tag{10}$$

For part c, insert the given parameters into the result of b to find

$$0.1 = \frac{1}{1 + 0.1e^{\beta\Delta E}} \tag{11}$$

where $\Delta E \equiv \epsilon_{BC} - \epsilon_{AC}$. Moving stuff around we find that our value of $\beta\Delta E = \ln 900 \approx 7$. Remembering that $k_B T \approx 25$ meV at room temperature gives us an energy difference between the two pairs of bound molecules of around 0.175 eV (using a calculator, the exact answer is 0.18 eV)

One thought on "J01T.2"

December 15, 2013 at 6:34 pm

Your answers in (a) and (b) seem to be correct (up to a typo in the denominator of (11)).

However, what you do in (a) doesn't look entirely consistent to me.
Notice that in the limit $\mu_B \to -\infty$ (no B molecules) your expression f_B indeed vanishes, while f_A doesn't go to 1 naively unless you make some assumptions about chemical potentials. I would say that the reason why it happens is because you've neglected the chemical potential μ_C of the C molecules in a somewhat unexplained way. μ_C is always negative and non-zero for bosons that are not in the Bose condensate phase. μ_C will indeed drop out of all final answers, but you should argue why. And after you consistently drop μ_C, your answer will be similar to (4).
Also notice that μ_A and μ_B given in the statement of the problem are not chemical potentials of AC and BC bound states. They are chemical potentials of A and B molecules.
Finally, the way you use the grand canonical ensemble looks somewhat unconventional to me. You compute the grand partition function only for C, AC and BC molecules with the total number of these molecules fixed and equal to N_C . I believe this will work if done correctly. But normally in the grand canonical ensemble we have fixed number of types of particles, but the number of particles of each type is not fixed (and is summed over). Then the average number of particles of each type is related to the chemical potential of the corresponding particles.
I think it would be more clear and transparent if you just considered the grand canonical ensemble of the system of A, B, C, AC, and BC particles (with the number of each particles not fixed). If you know the chemical potentials of A, B, C molecules and the binding energies, you'll find chemical potentials of AC and BC easily.