Homework #8 Solutions

Question 1) K+K, Chapter 5, Problem 6 Gibbs sum for a 2-level system has the following list of states:

1) Un-occupied $N = 0$; $\varepsilon = 0$
2) Occupied with energy 0; $N = 1$, $\varepsilon = 0$
3) Occupied with energy ε; $N = 1$, $\varepsilon = \varepsilon$

a) The Gibbs sum can be written explicitely using the above list of all states.

$$\mathcal{Z}_g(T, \mu) = \sum_{N=0}^{\infty} \sum_{S(N)} e^{(N\mu - \varepsilon_s)/\tau} \tag{1}$$

$$= e^{(0\mu - 0)/\tau} + e^{(1\mu - 0)\tau} + e^{(1\mu - \varepsilon)/\tau} \tag{2}$$

$$= 1 + \lambda + \lambda e^{-\varepsilon/\tau} \tag{3}$$

where we have defined $\lambda \equiv e^{\mu/\tau}$ and $\mathcal{Z}_g$ denotes the grand canonical partition function.

b) Find the thermal average occupancy.

$$<N> = \lambda \frac{d}{d\lambda} \log \mathcal{Z}_g \tag{4}$$

$$= \lambda \frac{1}{\mathcal{Z}_g} \frac{d}{d\lambda} \mathcal{Z}_g \tag{5}$$

$$= \frac{\lambda + \lambda e^{-\varepsilon/\tau}}{\mathcal{Z}_g(T, \mu)} \tag{6}$$

c) Average thermal occupancy of state of energy ε.

$$P(1, \varepsilon) = \frac{\lambda e^{-\varepsilon/\tau}}{\mathcal{Z}_g}$$

This is the probability of occupancy of the state with $N = 1$ and energy ε.

d) The thermal average of the system is given by a weighted sum of energies and corresponding probabilities of occupation. In this case there is only one term

$$U = \frac{\varepsilon \lambda e^{-\varepsilon/\tau}}{\mathcal{Z}_g}$$

e) Now suppose that there can be an $N = 2$ state in which energy levels 0 and ε can be occupied simultaneously. This will add an $N = 2$ term to the sum:

$$e^{(2\mu - (0 + \varepsilon))/\tau} = \lambda^2 e^{-\varepsilon/\tau}$$

And the total Gibbs function becomes

$$\mathcal{Z}_g = 1 + \lambda + \lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-\varepsilon/\tau}$$

Question 2) K+K, Chapter 5, Problem 7 As usual we start by forming the partition function.

$$\mathcal{Z}_g = \sum_{N=0}^{2} \sum_{\varepsilon_s(N)} e^{(N\mu - \varepsilon_s)/\tau} \tag{7}$$

$$= e^{(0\mu + \delta/2)\tau} + e^{(\mu + \Delta/2)/\tau} + e^{(\mu - \Delta/2)/\tau} + e^{(2\mu - \delta/2)/\tau} \tag{8}$$

$$= e^{\delta/2\tau} + 2e^{\mu/\tau} \cosh\left(\frac{\Delta}{2\tau}\right) + e^{(2\mu - \delta/2)/\tau} \tag{9}$$

We can use eq(5) for $< N >$.

$$\mathcal{Z}_g = e^{\delta/2\tau} + 2\lambda \cosh\left(\frac{\Delta}{2\tau}\right) + \lambda^2 e^{-\delta/2\tau} \tag{10}$$

$$\frac{\partial \mathcal{Z}_g}{\partial \lambda} = 2\cosh\left(\frac{\Delta}{2\tau}\right) + 2\lambda e^{-\delta/2\tau} \tag{11}$$

$$< N > = \lambda \frac{1}{\mathcal{Z}_g}\left(2\cosh\left(\frac{\Delta}{2\tau}\right) + 2\lambda e^{-\delta/2\tau}\right) \tag{12}$$

Now enforce $< N >= 1$. Using the explicit form of $\mathcal{Z}_g$ we get

$$\mathcal{Z}_g = 2\lambda \cosh\left(\frac{\Delta}{2\tau}\right) + 2\lambda^2 e^{-\delta/2\tau} = e^{\delta/2\tau} + 2\lambda \cosh\left(\frac{\Delta}{2\tau}\right) + \lambda^2 e^{-\delta/2\tau} \tag{13}$$

$$\lambda^2 e^{-\delta/2\tau} = e^{\delta/2\tau} \tag{14}$$

$$\Rightarrow \lambda^2 = e^{\delta/\tau} \tag{15}$$

Since $\lambda = e^{\mu/\tau}$ we get $\boxed{\mu = \delta/2}$.

Question 3a) K+K, Chapter 5, Problem 8 First consider the case with O_2 only. In this case this is a two state system. The heme site can be occupied or unoccupied. The Gibbs sum has only two terms:

$$\mathcal{Z}_g = 1 + e^{(\mu - \varepsilon_A)/\tau} = 1 + \lambda e^{-\varepsilon_A/\tau} \tag{16}$$

We want to find ε_A such that $< N >= 0.9N$. Again using eq(5):

$$< N > = \lambda \frac{\partial}{\partial \lambda} \log \mathcal{Z}_g = \frac{\lambda}{\mathcal{Z}_g} e^{-\varepsilon_A/\tau} \tag{17}$$

$$= \frac{\lambda e^{-\varepsilon_A/\tau}}{1 + \lambda e^{-\varepsilon_A/\tau}} = \frac{1}{1 + \lambda^{-1} e^{\varepsilon_A/\tau}} = 0.9 \tag{18}$$

Note that in the last equality we used 0.9 instead of $0.9N$. The reason for this is the following. $\mathcal{Z}_g$ we used above is that for a single site (for N sites there would be more than 2 states). We are assuming that the heme sites are distinguishable and independent. Hence the average occupancy of N sites is just N times that of one site.

Now solve for ε_A to get:

$$\varepsilon_A = \tau \log\left(\frac{\lambda}{9}\right) \tag{19}$$

$$= 1.38 \times 10^{-23} \frac{J}{K}(273.16 + 37)K \log\left(\frac{10^{-5}}{9}\right) \tag{20}$$

$$= -5.87 \times 10^{-20} J = \boxed{-0.37eV} \tag{21}$$

This is the bonding energy of O_2 on Hb.

b) Now allow CO as well. The Gibbs sum now has 3 terms. The heme site can be un-occupied, occupied by O_2 or occupied by CO.

$$\mathcal{Z}_g = 1 + \lambda_{O_2} e^{-\varepsilon_A/\tau} + \lambda_{CO} e^{-\varepsilon_B/\tau} \tag{22}$$

We are looking for the condition on ε_B such that only 10% of the heme sites are occupied by O_2.

$$< N_{O_2} > = \frac{\lambda_{O_2} e^{-\varepsilon_A/\tau}}{\mathcal{Z}_g} = \frac{\lambda_{O_2} e^{-\varepsilon_A/\tau}}{1 + \lambda_{O_2} e^{-\varepsilon_A/\tau} + \lambda_{CO} e^{-\varepsilon_B/\tau}} = 0.1 \tag{23}$$

Again it is to be understood that this calculation is done for one heme site. Solving this for ε_B we get:

$$\varepsilon_B = -\tau \log\left(\frac{9\lambda_{O_2} e^{-\varepsilon_A/\tau} - 1}{\lambda_{CO}}\right) = \boxed{-0.548 \ eV = \varepsilon_B} \tag{24}$$

Discussion: An alternative method: N sites rather than one site

If we study the system with N sites for part a), the partition function will be:

$$Z = \sum_{l=0}^{l=N} \sum_{s} \lambda^l e^{-l\varepsilon_A/\tau} \tag{25}$$

$$= \sum_{l=0}^{l=N} \frac{N!}{l!(N-l)!}(\lambda e^{-\varepsilon_A/\tau})^l \tag{26}$$

$$= (\lambda e^{-\varepsilon_A/\tau} + 1)^N \tag{27}$$

Then, we can use the formula for average $< N >$:

$$< N > = \lambda \frac{1}{Z}\frac{\partial Z}{\partial \lambda} = 0.9N \tag{28}$$

The same method for part (b), but the math will be more complicated.

Question 4a) K+K, Chapter 5, Problem 10

$$<N> = \frac{\tau}{\mathcal{Z}_g} \frac{\partial \mathcal{Z}_g}{\partial \mu}\bigg|_{\tau,V} \tag{29}$$

$$\mathcal{Z}_g = \sum_N \sum_{\varepsilon_s(N)} e^{(\mu N - \varepsilon_s)/\tau} \tag{30}$$

$$\tau \frac{\partial \mathcal{Z}_g}{\partial \mu} = \sum_N \sum_{\varepsilon_s(N)} N e^{(\mu N - \varepsilon_s)/\tau} \tag{31}$$

$$\tau^2 \frac{\partial^2 \mathcal{Z}_g}{\partial \mu^2} = \sum_N \sum_{\varepsilon_s(N)} N^2 e^{(\mu N - \varepsilon_s)/\tau} \tag{32}$$

$$<N^2> = \frac{\sum_N \sum_{\varepsilon_s(N)} N^2 e^{(\mu N - \varepsilon_s)/\tau}}{\mathcal{Z}_g} = \frac{\tau^2}{\mathcal{Z}_g} \frac{\partial^2 \mathcal{Z}_g}{\partial \mu^2} \tag{33}$$

b) Consider

$$\frac{\partial <N>}{\partial \mu} = \frac{\partial}{\partial \mu} \frac{\sum_{ASN} N e^{(\mu N - \varepsilon_s)/\tau}}{\mathcal{Z}_g} \tag{34}$$

$$= \frac{-\frac{\partial \mathcal{Z}_g}{\partial \mu} \sum_{ASN} N e^{(\mu N - \varepsilon_s)/\tau}}{\mathcal{Z}_g^2} + \frac{1}{\mathcal{Z}_g \tau} \sum_{ASN} N^2 e^{(\mu N - \varepsilon_s)/\tau} \tag{35}$$

$$\tau \frac{\partial <N>}{\partial \mu} = -\left(\frac{\partial \mathcal{Z}_g}{\partial \mu}\right)^2 \frac{\tau^2}{\mathcal{Z}_g^2} + \frac{\tau^2}{\mathcal{Z}_g} \frac{\partial^2 \mathcal{Z}_g}{\partial \mu^2} = <(\Delta N)^2> \quad \text{(from above)} \tag{36}$$

Question 5) K+K, Chapter 5, Problem 12 Ascent of sap in trees.

Assume the water is in diffusive equilibrium in the tree. The vapor at the base has a chemical potential given by that of the ideal gas

$$\mu = \tau \log(n/n_Q)$$

$n = n_0$ at the pool.

$$\mu_{pool} = \tau \log(n_o/n_Q) \quad \text{(internal chem. pot. of water at the base)}$$

The external chemical potential due to gravity is Mgh, where M is the mass of the water molecule, and h is the height of the tree.

At the top of the tree, the total chemical potential of the water molecule is

$$\mu_{top} = \tau \log(rn_0/n_Q) + Mgh$$

where r is the relative humidity at the top of the tree.

In diffusive equilibrium, μ is uniform in the tree, so:

$$\mu_{pool} = \mu_{top} \tag{37}$$

$$\tau \log(n_o/n_Q) = \tau \log(rn_o/n_Q) + Mgh \tag{38}$$

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Solve for the maximum height of the tree

$$h = \frac{1}{Mg}\tau \log\left(\frac{n_0/n_Q}{rn_0/n_Q}\right) = \boxed{-\frac{\tau}{Mg}\log(r) = h} \tag{39}$$

For the mass of the water molecule we will use $M = 18$ amu $= 18 \times 1,66 \times 10^{-27}kg$ (Back inside cover of K+K). $r = 0.9$ is given in the problem. If you plug in everything in eq(39) you get

$$h = 1,480 \text{ meters}$$

That is one tall tree!

In practice trees rarely get over 100 meters in height, 110 meters is about the maximum.

This is an over-estimate because the tree does not grow in water, and there is often a temperature gradient between the roots and top. Other mechanical limitations may come into play as trees grow taller.

Question 6) K+K Chapter 6, Problem 1 FD Distribution $f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/\tau}+1}$.

$$-\frac{\partial f}{\partial \varepsilon} = \frac{1}{(e^{(\varepsilon-\mu)/\tau}+1)^2}\frac{1}{\tau}e^{(\varepsilon-\mu)/\tau}$$

Evaluate the derivative at the chemical potential:

$$-\frac{\partial f}{\partial \varepsilon}(\varepsilon = \mu) = \frac{\tau^{-1}e^0}{(e^0+1)^2} = \frac{1}{4\tau}$$

Question 7a) K+K Chapter 6, Problem 3 Suppose such a system is in thermal and diffusive contact with a reservoir at τ and μ. There are 3 distinct states:
1) Un-occupied with energy 0
2) Single occupancy with energy ε.
3) Double occupancy with energy 2ε.
The Gibbs sum is calculated as follows:

$$\mathcal{Z}_g = \sum_{N=0}^{2}\sum_{\varepsilon_s(N)}e^{(\mu N - \varepsilon_s(N))/\tau} \tag{40}$$

$$= e^{(0\mu-0)/\tau} + e^{(1\mu-\varepsilon)/\tau} + e^{(2\mu-2\varepsilon)/\tau} \tag{41}$$

$$= 1 + \lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-2\varepsilon/\tau} \tag{42}$$

We can calculate $< N >$ "by hand"

$$< N > = \frac{0 \times 1 + 1 \times \lambda e^{-\varepsilon/\tau} + 2 \times \lambda^2 e^{-2\varepsilon/\tau}}{\mathcal{Z}_g} \tag{43}$$

$$= \frac{\lambda e^{-\varepsilon/\tau}(1 + 2\lambda e^{-\varepsilon/\tau})}{1 + \lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-2\varepsilon/\tau}} \tag{44}$$

b) Note that this is a different case than part a). Now there are a total of 4 states.

1) No occupancy, 0 energy
2) Single occupancy, ε energy
3) Single occupancy, ε energy
4) Double occupancy, 2ε energy

In 2) and 3) only one of the degenerate states is occupied, the other one being un-occupied. In 4) both degenerate states are occupied. Keeping this in mind we can write down the partition function as:

$$\mathcal{Z}_g = e^{(0\mu-0)/\tau} + e^{(\mu-\varepsilon)/\tau} + e^{(\mu-\varepsilon)/\tau} + e^{(2\mu-2\varepsilon)/\tau} \tag{45}$$

$$= (1 + \lambda e^{-\varepsilon/\tau})^2 \tag{46}$$

Note that this is the product of two single-orbital Gibbs sums. Now calculate $< N >$ by hand

$$< N >= \frac{0 \times 1 + 2 \times (1 \times \lambda e^{-\varepsilon/\tau}) + 2 \times \lambda^2 e^{-2\varepsilon/\tau}}{\mathcal{Z}_g} \tag{47}$$

Using eq(46) for $\mathcal{Z}_g$ and after some math we obtain:

$$< N >= \frac{2\lambda e^{-\varepsilon/\tau}}{1 + \lambda e^{-\varepsilon/\tau}} = \frac{2}{e^{(\varepsilon-\mu)/\tau} + 1} \tag{48}$$

A factor of 2 greater than the Fermi distribution function. This arises from the double dgeneracy of the orbital.

Question8) K+K Chapter 6, Problem 5 For fixed N the thermodynamic identity reads :

$$d\sigma = \frac{dU}{\tau} + \frac{PdV}{\tau} \tag{49}$$

Write

$$dU = \left.\frac{\partial U}{\partial \tau}\right|_V d\tau + \left.\frac{\partial U}{\partial V}\right|_\tau dV$$

so

$$d\sigma = \left.\frac{\partial U}{\partial \tau}\right|_V d\tau + \left.\frac{\partial U}{\partial V}\right|_\tau dV + \frac{PdV}{\tau}$$

For the ideal gas we know that $U = 3N\tau/2$, so

$$\left.\frac{\partial U}{\partial \tau}\right|_V = \frac{3}{2}N \tag{50}$$

$$\left.\frac{\partial U}{\partial V}\right|_\tau = 0 \tag{51}$$

$$\tag{52}$$

Hence

$$d\sigma = \frac{3N}{2\tau}d\tau + \frac{N}{V}dV$$

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Now integrate both sides

$$\sigma - \sigma_1 = \int d\sigma = \frac{3N}{2} \int \frac{d\tau}{\tau} + N \int \frac{dV}{V} = \frac{3N}{2} \log(\tau) + N \log(V) \qquad (53)$$

Note that $C_V = 3N/2$, so

$$\sigma = C_V \log(\tau) + N \log(V) + \sigma_1$$

where σ_1 is a constant independent of τ and V.

Question 9) K+K Chapter 6, Problem 6 Entropy of Mixing.

Initially the two systems have the same temperature and volume and are made up of different species, but the same number of particles. Each has an entropy given by the ideal gas value:

$$\sigma_A = N \left[\log\left(\frac{n_{QA}}{n} \right) + \frac{5}{2} \right]$$

$$\sigma_B = N \left[\log\left(\frac{n_{QB}}{n} \right) + \frac{5}{2} \right]$$

where $n = N/V$ is the concentration of particles and $n_Q = (M\tau/2\pi\hbar^2)^{3/2}$ are the quantum concentration for particle A and B (they are different) . The entropies are additive:

$$\sigma_{initial} = \sigma_A + \sigma_B = N \left[\log\left(\frac{n_{QA}}{n} \right) + \frac{5}{2} + \log\left(\frac{n_{QB}}{n} \right) + \frac{5}{2} \right] \qquad (54)$$

After they are placed in diffusive contact and equilibrium is reached, we have the same temperature τ, twice the volume $2V$, and half the particle concentrations $n_A \to N/2V$ and $n_B \to N/2V$. The entropy after mixing can be obtained from eq(54) by making these changes.

$$\sigma_{final} = N \left[\log\left(\frac{n_{QA}}{(n/2)} \right) + \frac{5}{2} + \log\left(\frac{n_{QB}}{(n/2)} \right) + \frac{5}{2} \right]$$

The difference is easily calculated using the property of logarithm: $\log(ab) = \log(a) + \log(b)$:

$$\Delta\sigma = \sigma_{final} - \sigma_{initial} = \boxed{2N \log(2)} \qquad (55)$$

This is the change in entropy upon mixing.

Upon interdiffusion the A atoms have more accessible states than before, similarly for the B atoms (at the same temperature). This is the reason for the increase in entropy.

In the case of identical atoms we don't observe any increase in entropy. In this case the final state has 2N particles in a volume 2V.What's more, $\sigma_{QA} + \sigma_{QB}$

Hence the concentration is the same as before mixing. The entropy is then given by the standard formula

$$\sigma_{final} = 2N \left[\log\left(\frac{n_Q}{n}\right) + \frac{5}{2} \right]$$

I want to emphasize this is not the sum of two terms (as is the case before mixing for $A = B$ or in the case of $A \neq B$ before and after the mixing). It is simply the entropy of a gas of 2N particles in volume 2V.

This result is expected since macroscopically inserting/removing a partition in a box filled with a uniform gas does not change anything. This is called the Gibbs Paradox. The resolution lies in the indistinguashibility of identical particles. After mixing, the states per atom seems to have increased, but the indistinguahibility prevents us from overcounting (recall the 1/N! factors), and reduces the total amount of states to that of the case with two compartments.

Discussion : You can also use the formula as:

$$\sigma = N \log V + cons$$

But you should pay attention to the constant here:

$$\sigma = N[\log V + \log\frac{n_Q}{N} + 5/2]$$

$$cons = N[\log\frac{n_Q}{N} + 5/2]$$

which means the constant is also related with N, which will be useful in the case $A = B$.