

## The Gibbs Factor

In lecture 5, we divided up a large object into a system and a heat reservoir and we considered what happens when the system and reservoir exchange energy. This led us to the Boltzmann factor and the partition function. Now let's consider the what happens if we divide up the large object into the system and a reservoir except this time we allow the exchange of particles as well as energy. The total energy is  $U_0$  and the total number of particles is  $N_0$  (which is not Avogadro's number during this discussion!). What is the probability that the system is in the single state 1 with  $N_1$  particles and energy  $E_1$  compared to the probability that it's in the single state 2 with  $N_2$  particles and energy  $E_2$ ? The ratio is

$$\frac{P(N_1, E_1)}{P(N_2, E_2)} = \frac{g(N_0 - N_1, U_0 - E_1) \times 1}{g(N_0 - N_2, U_0 - E_2) \times 1},$$

where  $g(N_R, U_R)$  is the number of states available to the reservoir when it contains  $N_R$  particles and has energy  $U_R$ . We are just applying our postulate that the probability is proportional to the number of available states. We have

$$\begin{aligned} P(N, E) &\propto g(N_0 - N, U_0 - E), \\ &\propto e^{\sigma(N_0 - N, U_0 - E)}, \\ &\propto e^{\left(\sigma(N_0, U_0) - N \frac{\partial \sigma}{\partial N} - E \frac{\partial \sigma}{\partial U}\right)}, \\ &\propto e^{(\sigma(N_0, U_0) + N\mu/\tau - E/\tau)}, \\ &\propto e^{\sigma(N_0, U_0)} \times e^{(N\mu/\tau - E/\tau)}, \\ &\propto e^{(N\mu/\tau - E/\tau)}, \end{aligned}$$

where we dropped the first factor since it's a constant for any given reservoir. The probability

$$P(N, E) \propto e^{(N\mu - E)/\tau},$$

is called the Gibbs factor. A probability distribution described by Gibbs factors is called the grand canonical distribution.

Consider the sum

$$\mathcal{Z} = \sum_{\text{All } N, E} e^{(N\mu - E)/\tau},$$

where the sum is over all numbers of particles  $N$ , and for each  $N$ , all possible states of  $N$  particles with energies  $E$ . Or, one can sum over all energies first, and then over all numbers of particles with that energy. Basically it's a sum over all possible states which are parameterized by number of particles and energy.  $\mathcal{Z}$  is called the *Gibbs sum*, the *grand sum*, or the *grand partition function*. K&K use a kind of cursive  $Z$  symbol for this sum. I don't seem to have that in my  $\text{\TeX}$  fonts, so we'll use  $\mathcal{Z}$ .

The grand partition function is used to normalize the probabilities:

$$P(N, E) = \frac{1}{\mathcal{Z}} e^{(N\mu - E)/\tau}.$$

With the normalized probability distribution, we can compute mean values. For example, the mean number of particles in the system is

$$\begin{aligned} \langle N \rangle &= \frac{1}{\mathcal{Z}} \sum_{\text{All } N, E} N e^{(N\mu - E)/\tau}, \\ &= \tau \frac{1}{\mathcal{Z}} \sum_{\text{All } N, E} \frac{N}{\tau} e^{(N\mu - E)/\tau}, \\ &= \tau \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu}, \\ &= \tau \frac{\partial \log \mathcal{Z}}{\partial \mu}. \end{aligned}$$

The mean energy is slightly more complicated. If we differentiate  $\mathcal{Z}$  with respect to  $1/\tau$ , it will pull down a term with the energy in it, but we'll also get the number of particles again.

$$\begin{aligned} \langle N\mu - E \rangle &= \frac{1}{\mathcal{Z}} \sum_{\text{All } N, E} (N\mu - E) e^{(N\mu - E)/\tau}, \\ &= \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial (1/\tau)}, \\ &= \frac{\partial \log \mathcal{Z}}{\partial (1/\tau)}, \\ \langle E \rangle &= \langle N\mu \rangle - \frac{\partial \log \mathcal{Z}}{\partial (1/\tau)}, \\ &= \mu \langle N \rangle - \frac{\partial \log \mathcal{Z}}{\partial (1/\tau)}, \\ &= \mu\tau \frac{\partial \log \mathcal{Z}}{\partial \mu} - \frac{\partial \log \mathcal{Z}}{\partial (1/\tau)}, \\ &= \mu\tau \frac{\partial \log \mathcal{Z}}{\partial \mu} + \tau^2 \frac{\partial \log \mathcal{Z}}{\partial \tau}. \end{aligned}$$

K&K define the *activity* as

$$\lambda = e^{\mu/\tau}.$$

The grand partition function can be rewritten in terms of the activity as

$$\mathcal{Z} = \sum_{\text{All } N, E} \lambda^N e^{-E/\tau},$$

from which it follows that the average number of particles is

$$\langle N \rangle = \lambda \frac{\partial \log \mathcal{Z}}{\partial \lambda}.$$

### Example: Binding of $N$ Molecules

This example is related to the myoglobin example discussed in K&K and also to K&K, chapter 5, problem 14. The example system is a hemoglobin molecule which can bind zero to four oxygen molecules. A hemoglobin molecule is similar to four myoglobin molecules, each of which can bind zero or one oxygen molecule.

We will work out an expression for the average number of molecules as a function of the partial pressure of oxygen in the atmosphere. We will assume that each successive molecule binds with same energy (relative to infinite separation),  $\epsilon < 0$ . This is not quite right as successive oxygen molecules are bound more tightly than the first oxygen molecule. Also, we will start by assuming that 0 to  $M$  molecules may be bound, and specialize to the case of four molecules later. Finally, we will assume that there is only one state in which  $N$  molecules are bound. This corresponds to assuming that the molecules are bound to hemoglobin in a definite order. We will let the activity be  $\lambda = \exp(\mu/\tau)$ . Then the grand partition function is,

$$\begin{aligned} \mathcal{Z} &= 1 + \lambda e^{-\epsilon/\tau} + (\lambda e^{-\epsilon/\tau})^2 + \dots + (\lambda e^{-\epsilon/\tau})^M, \\ &= \frac{1 - (\lambda e^{-\epsilon/\tau})^{M+1}}{1 - \lambda e^{-\epsilon/\tau}}, \\ \log \mathcal{Z} &= \log \left( 1 - (\lambda e^{-\epsilon/\tau})^{M+1} \right) - \log \left( 1 - \lambda e^{-\epsilon/\tau} \right). \end{aligned}$$

Now we differentiate with respect to  $\lambda$  in order to find the average number of bound molecules,

$$\begin{aligned} \langle N \rangle &= \lambda \frac{\partial \log \mathcal{Z}}{\partial \lambda}, \\ &= -\frac{(M+1) (\lambda e^{-\epsilon/\tau})^{M+1}}{1 - (\lambda e^{-\epsilon/\tau})^{M+1}} + \frac{\lambda e^{-\epsilon/\tau}}{1 - \lambda e^{-\epsilon/\tau}}, \\ &= \lambda e^{-\epsilon/\tau} \frac{1 - (M+1) (\lambda e^{-\epsilon/\tau})^M + M (\lambda e^{-\epsilon/\tau})^{M+1}}{\left( 1 - (\lambda e^{-\epsilon/\tau})^{M+1} \right) \left( 1 - \lambda e^{-\epsilon/\tau} \right)}. \end{aligned}$$

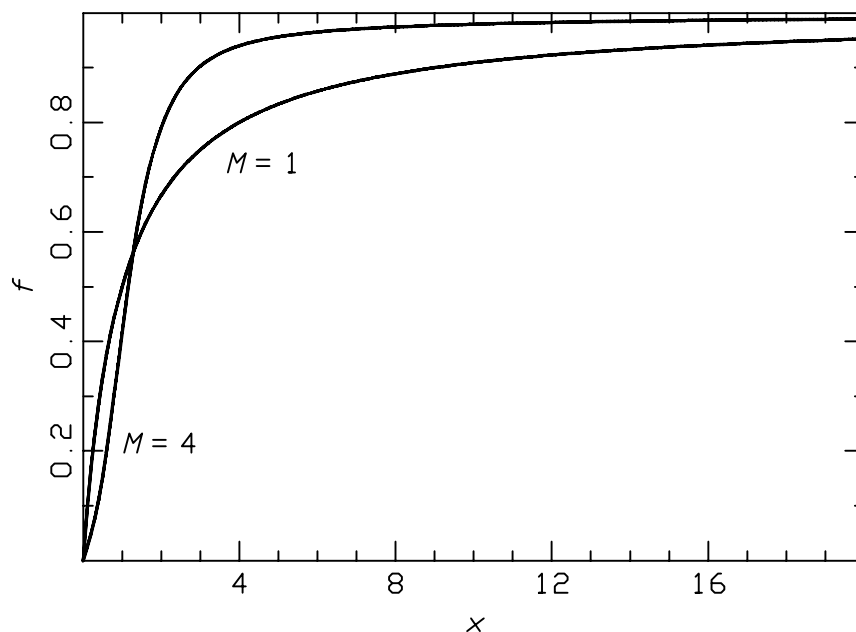
In the case that  $M = 1$ , which corresponds to myoglobin which can bind one molecule, the expression becomes

$$\langle N \rangle = \frac{\lambda e^{-\epsilon/\tau}}{1 + \lambda e^{-\epsilon/\tau}}.$$

Now,  $\lambda = \exp(\mu/\tau)$ , and in order for our system to be in equilibrium with atmospheric oxygen it must have the same chemical potential as atmospheric oxygen. This means that  $\lambda = n/n_Q = p/\tau n_Q$ , where  $p$  is the partial pressure of oxygen,  $\tau$  is the temperature of atmospheric oxygen (presumably room temperature), and  $n_Q$  is the quantum concentration evaluated at temperature  $\tau$  and for the mass of an  $O_2$  molecule. So  $\lambda$  can be evaluated numerically for any desired partial pressure of oxygen. If we look at the curve for myoglobin in figure 5.12 of K&K, it appears that the average number of bound molecules is about 1/2 when the partial pressure of oxygen is about 5 mm of Hg. (One atmosphere is 760 mm of Hg and oxygen is about 20% of the atmosphere, so the maximum partial pressure is roughly 150 mm of Hg. Let  $\lambda_{1/2}$  be the activity when the number of bound molecules is 1/2. From our expression above, we see that this means  $\lambda_{1/2} \exp(-\epsilon/\tau) = 1$  or  $\exp(-\epsilon/\tau) = 1/\lambda_{1/2}$ . Let's plug this into the formula for hemoglobin ( $M = 4$ ) and express the result as a fraction of the maximum number of bound molecules. The result is

$$f = \frac{\langle N \rangle}{4} = \frac{x}{4} \frac{1 - 5x^4 + 4x^5}{(1 - x^5)(1 - x)} = \frac{x}{4} \frac{1 + 2x + 3x^2 + 4x^3}{1 + x + x^2 + x^3 + x^4},$$

where  $x = \lambda/\lambda_{1/2}$ . This curve is shown in the figure. Binding more molecules, all with the



same binding energy, causes a sharper transition from “empty” to “full!”

## More on the Chemical Potential—Energy to Add a Particle

This section is based on the discussion in K&K in pages 250–252.

As you recall, the chemical potential is the amount of energy required to add one particle to a system. Also, we learned that the chemical potential for an ideal monatomic gas is  $\mu = \tau \log(n/n_Q)$  which is about  $-14$  to  $-11\tau$  for a typical gas under typical conditions. It appears that if we add one more particle to a gas, we're not required to spend energy, but we get back some energy! This must be wrong, but what's the explanation?

The answer has to do with where the particle came from. There's also an energy involved in removing the particle from its original location before we add it to the gas.

Suppose we have two containers of the same gas at the same temperature,  $\tau$ . Suppose the chemical potentials are different with  $\mu_2 > \mu_1$ . Then the concentrations must be different, or equivalently, the pressures are different with  $p_2 > p_1$ . If we remove a molecule from container 1 and add it to container 2, we receive energy  $\mu_1$  from container 1 but must give energy  $\mu_2$  to container 2. The total amount of energy that must be supplied by an external agent to move this molecule is  $\mu_2 - \mu_1 > 0$ . What does this turn out to be?

$$\begin{aligned}\Delta E &= \mu_2 - \mu_1, \\ &= \tau \log \frac{n_2}{n_Q} - \tau \log \frac{n_1}{n_Q}, \\ &= \tau \log \frac{n_2}{n_1}.\end{aligned}$$

Now suppose we have  $N$  molecules of a gas at temperature  $\tau$  and we isothermally compress it from volume  $V_1$  down to volume  $V_2$  or, equivalently, from concentration  $n_1$  up to concentration  $n_2$ . How much mechanical work is required?

$$\begin{aligned}\Delta W &= \int_{V_1}^{V_2} -p dV, \\ &= -N\tau \int_{V_1}^{V_2} \frac{dV}{V}, \\ &= -N\tau \log \frac{V_2}{V_1}, \\ &= N\tau \log \frac{V_1}{V_2}, \\ &= N\tau \log \frac{N/V_2}{N/V_1}, \\ &= N\tau \log \frac{n_2}{n_1}.\end{aligned}$$

So the energy per molecule required to isothermally change the concentration from  $n_1$  to  $n_2$  is just the energy required to move one molecule from a gas at concentration  $n_1$  to a gas at concentration  $n_2$ .

In fact, we could imagine doing the following: Isothermally compress the gas in container 1 from concentration  $n_1$  to concentration  $n_2$ . This requires spending an energy  $N\tau \log(n_2/n_1)$ . Move the molecule from container 1 to container 2. This requires no energy since the concentrations and the chemical potentials are now the same. Expand the gas in container 1 back to concentration  $n_1$ . This recovers an energy  $(N-1)\tau \log(n_2/n_1)$ , so the net expenditure of energy is  $\tau \log(n_2/n_1) = \mu_2 - \mu_1$ . Recall that the internal energy of an ideal monatomic gas depends only on its temperature ( $U = 3N\tau/2$ ). Before and after we moved the molecule from container 1 to container 2, the temperature of all the gas was  $\tau$ , so the internal energy of the gas did not change! Where did the energy  $\tau \log(n_2/n_1)$  go??? Hints: has the free energy of the combined systems changed? What about the entropy?

### Example: Chemical Potential and Batteries

Surprise: chemical potential might actually have something to do with chemistry! An example has to do with batteries—or better, voltaic cells. K&K have a discussion of the lead acid battery used in cars on pages 129–131. However, I’ve been told that this discussion is not quite right. In particular see Saslow, W., 1996, *PRL*, **76**, 4849.

By the way, did you know that Princeton subscribes to many of the on-line journals? This means if you access the web from a Princeton address, you’ll be allowed to read the journals on-line. In particular, you can find *Physical Review* and *Physical Review Letters* on-line and the article cited above can be downloaded and printed out.

Rather than discuss the lead acid battery, let’s look at a simpler (I hope) system: the Daniell cell. This is discussed by the same author in 1999, *AJP*, **67**, 574. (True confession: I have not read the article in the *American Journal of Physics*, but rather, the preprint that used to be on the author’s web site. But the TAMU physics web site has been revamped and I can’t find the preprint anymore!) The Daniell cell is also discussed in chemistry textbooks, such as the one I used many years ago, Pauling, L., 1964, *College Chemistry*, (San Francisco:Freeman), p. 354. The following discussion is based on both of these sources.

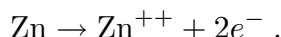
The figure shows a schematic of the cell. It has a solution of zinc sulfate ( $\text{ZnSO}_4$ ) surrounding a zinc electrode and a copper sulfate ( $\text{CuSO}_4$ ) solution surrounding a copper electrode. The two solutions are in contact. The zinc electrode is the negative electrode or cathode and the copper electrode is the positive electrode or anode.

Chemical reactions occur at the electrodes. At the copper electrode, the reaction is



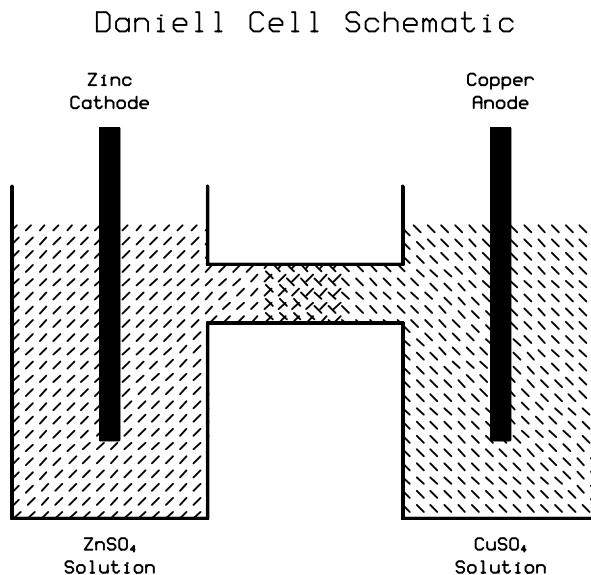
The copper ion was in solution and the electrons come from the electrode. The neutral copper atom “plates out” on the copper electrode.

At the zinc electrode, the reaction is



Zinc atoms in the electrode go into solution as zinc ions and leave behind two electrons on the cathode.

If a wire is connected between the two electrodes, the electrons left behind by the zinc can travel through the external circuit to the copper electrode where they join up with the copper ions to plate out the copper atoms. (Of course, electrons go in one end and different electrons come out the other end. . . .) Charge is transferred inside the cell, through the electrolyte, by sulfate ions. That is, one can think of  $\text{CuSO}_4$  dissociating into  $\text{Cu}^{++}$  and  $\text{SO}_4^{--}$  at the positive electrode, the  $\text{Cu}^{++}$  plates out leaving behind a spare sulfate ion which diffuses over to the negative electrode to join up with a zinc ion and form  $\text{ZnSO}_4$ . (Of course, sulfate ions don't go all the way across the electrolyte; ions go in one end and different ions come out the other end. . . .) Essentially all the current in the electrolyte is carried by the ions and none by electrons.



If we actually have a complete circuit, current will flow until one of the consumables is exhausted. If all the copper is plated out of solution or if the zinc electrode is completely dissolved, that will be the end of the cell. When operated in this mode, the cell converts chemical potential energy into electrical energy.

Our methods apply to equilibrium situations, so we'll discuss the situation when there is no current flowing in the external circuit and the system has reached equilibrium. (Actually, a non-uniform distribution of electrolytes is also not an equilibrium situation, so we are really assuming that the time for the electrolytes to diffuse is long compared to the time for the reactions at the electrodes to complete.) As zinc goes into solution and copper plates out, the electrodes acquire charges and electric potentials. When the potentials are large enough the reactions stop. When the reactions stop, the chemical potentials of the atoms/ions must be the same whether they are in solution or on the electrodes.

Let  $V_a$ ,  $V_s$ , and  $V_c$  be the electric potentials (voltages) of the anode, solutions, and cathode. Note that we assume the electrolytes (solutions) are equipotentials. If not, there would be a current flow until a uniform potential is established. The voltage of the cell (e.g., measured by a voltmeter placed across the anode and cathode) is

$$V_{\text{cell}} = V_a - V_c = (V_a - V_s) + (V_s - V_c) .$$

Consider a zinc ion in the cathode. When equilibrium has been established, the chemical potential of the zinc in the cathode must be the same as that of zinc in solution. The chemical potential is made of two parts: the internal chemical potential and the potential energy of the ion in macroscopic electric potential of the cathode or the solution:

$$\mu_{ci}(\text{Zn}^{++}) + 2eV_c = \mu_{si}(\text{Zn}^{++}) + 2eV_s ,$$

or

$$\mu_{ci}(\text{Zn}^{++}) - \mu_{si}(\text{Zn}^{++}) = 2e(V_s - V_c) ,$$

where  $e > 0$  represents the magnitude of the charge on an electron and  $\mu_{ci}$  and  $\mu_{si}$  represent the internal chemical potentials in the cathode and the solution. Note that I have shown the zinc as zinc ions on the cathode as well as in solution. This is mainly for clarity and can be justified by noting that the conduction electrons in a metal are not localized to any particular atom. The difference of internal chemical potentials is determined by the chemical reaction. It is customary to divide this by the magnitude of the electric charge and the number of charges involved and tabulate as a potential difference. So, for example, my 1962 edition of the *Handbook of Chemistry and Physics* has a table titled “Potentials of Electrochemical Reactions at 25° C in which one finds +0.7628 V listed for the reaction  $\text{Zn} \rightarrow \text{Zn}^{++} + 2e^-$ . This means that  $V_s - V_c$  is about 0.76 V.

At the anode, with no current flowing, we have

$$\mu_{ai}(\text{Cu}^{++}) - \mu_{si}(\text{Cu}^{++}) = -2e(V_a - V_s) .$$

The *Handbook* lists the electric potential of the reaction  $\text{Cu} \rightarrow \text{Cu}^{++} + 2e^-$  as  $-0.3460$  V. Thus  $V_a - V_s = 0.35$  V and the open circuit cell potential is  $V_{\text{cell}} = 1.11$  V.

Comments: the potentials associated with reactions that occur at the cathode or anode are called *half cell* potentials. If this reminds you of *redox* reactions in chemistry, it should! The *Handbook* contains a table titled “Electromotive Force and Composition of Voltaic Cells” which gives the composition and voltage of selected cells. The half cell voltages are determined by defining a standard half cell (a platinum electrode over which hydrogen ions are bubbled) as a standard with zero half cell potential. Then all other half cells are measured *relative* to the standard. Recall: only potential energy differences are important! Finally, by now you should be getting a feel for why it’s called the *chemical* potential!