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

\[ \mu = \tau \log \left( \frac{n}{n_Q} \right) \]

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?

\[
\Delta E = \mu_2 - \mu_1, \\
= \tau \log \frac{n_2}{n_Q} - \tau \log \frac{n_1}{n_Q}, \\
= \tau \log \frac{n_2}{n_1}.
\]

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?

\[
\Delta W = \int_{V_1}^{V_2} -p \, dV, \\
= -N\tau \int_{V_1}^{V_2} \frac{dV}{V}, \\
= -N\tau \log \frac{V_2}{V_1}, \\
= N\tau \log \frac{V_1}{V_2}, \\
= N\tau \log \frac{N/V_2}{N/V_1}, \\
= N\tau \log \frac{n_2}{n_1}.
\]

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 (ZnSO$_4$) surrounding a zinc electrode and a copper sulfate (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

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}.$$ 

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
\[ \text{Zn} \rightarrow \text{Zn}^{++} + 2e^{-}. \]
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 CuSO\(_4\) dissociating into Cu\(^{++}\) and SO\(_4^{2-}\) at the positive electrode, the 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 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 $V_{cell} = 1.11$ 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!
Example: Magnetic Particles in a Magnetic Field

Recall the paramagnetic spin system we discussed in lecture 3. In this system, there are magnets with orientations parallel or antiparallel to a magnetic field. In the parallel orientation, the energy is \(-mB = -E\), where \(m\) is the magnetic moment and \(B\) is the magnetic field. In the antiparallel orientation the energy is \(+mB = +E\). In lecture 3, we worked out the relative numbers of parallel and antiparallel magnets and found that it depended on the ratio of thermal to magnetic energies.

Following the discussion in K&K, pages 127–129, suppose that we have the same kind of system, but in addition, the magnetic particles are free to move, so the aligned magnets will be attracted to regions of high field strength while the antiparallel magnets will be repelled from regions of high field strength. Of course, in the regions of high field, one would expect to find a greater fraction aligned even if the particles couldn’t move... Let \(n_{\uparrow}\) be the concentration of parallel and \(n_{\downarrow}\) be the concentration of antiparallel systems. Just as with an ideal gas, we expect that microscopic or internal contribution to the chemical potential should depend on the concentration,

\[
\mu_{\uparrow,\text{int}} = \tau \log \frac{n_{\uparrow}}{n_Q} \quad \text{and} \quad \mu_{\downarrow,\text{int}} = \tau \log \frac{n_{\downarrow}}{n_Q}.
\]

We assume that we can treat the parallel and antiparallel magnets as distinct kinds of “particles.” To the internal chemical potential must be added the external potential due the energy in the magnetic field,

\[
\mu_{\uparrow} = \tau \log \frac{n_{\uparrow}}{n_Q} - mB,
\]

\[
\mu_{\downarrow} = \tau \log \frac{n_{\downarrow}}{n_Q} + mB.
\]

Now, the parallel and antiparallel magnets are in thermal equilibrium with each other and can be changed into one another. That is, one can remove a particle from the parallel group and add it to the antiparallel group and vice-versa. When the system has come to equilibrium, at temperature \(\tau\), the free energy must be stationary with respect to changes in the particle numbers which means the chemical potentials of the two kinds of particles must be the same. Furthermore, we are allowing the particles to diffuse to regions of higher or lower field strength, and the chemical potential must be independent of field strength. So,

\[
\mu_{\uparrow} = \mu_{\downarrow} = \text{Constant}.
\]

This relation together with the previous equations are easily solved to yield

\[
n_{\uparrow}(B) = \frac{1}{2} n(0)e^{+mB/\tau} \quad \text{and} \quad n_{\downarrow}(B) = \frac{1}{2} n(0)e^{-mB/\tau},
\]
where we’re explicitly showing that the concentrations depend on $B$ and $n(0)$ is the combined concentration where $B = 0$. The combined concentration as a function of $B$ is

$$n(B) = n_\uparrow(B) + n_\downarrow(B) = n(0) \cosh(mB/\tau) = n(0) \left(1 + \frac{m^2 B^2}{2\tau^2} + \cdots\right).$$

These relations show both effects we mentioned earlier. The higher the field strength, the greater the fraction of aligned magnets (as we already knew from lecture 3) and the greater the concentration of magnets. The magnetic particles diffuse to regions of high field strength.

In figure 5.6, K&K show a plot of chemical potential versus concentration for several different field strengths. In problem 5 of chapter 5, we are asked for what value of $m/\tau$ was this figure drawn. The key datum to extract from the plot is that at a given chemical potential, the concentration increases by two orders of magnitude as $B$ is increased from 0 to 20 kG. We can plug this directly into the previous expression to get $m/\tau = 5.30/(20000 \text{ G}) = 0.000265 \text{ G}^{-1}$. Note that we had to use the cosh form of the expression, not the series, because $mB/\tau > 1$. Problem 5.5 also asks how many Bohr magnetons must be contained in each particle. A Bohr magneton (roughly the magnetic moment of an electron) is $\mu_B = e\hbar/2mc$ where $e$ and $m$ are the charge and mass of an electron. $\mu_B = 0.927 \times 10^{-20} \text{ erg G}^{-1}$. Doing the arithmetic, we obtain about 1200 magnetons. The particles must contain 1200 paramagnetic molecules with a spin of $\hbar/2$ and a magnetic moment of $\mu_B$. They could also contain a more or less arbitrary number of non-magnetic molecules.

**Example: Impurity Ionization**

In pages 143–144, K&K discuss an impurity atom in a semiconductor. The atom may lose a valence electron and become ionized. The energy required to remove an electron from the donor atom is $I$. The model for this impurity atom is a three state system: the ionized state has energy 0 and no electron is present. There are two bound states, both have energy $-I$ and both have one electron present. One has the electron with spin up along some axis and the other has the electron with spin down. The grand partition function is

$$Z = 1 + e^{(\mu + I)/\tau} + e^{(\mu + I)/\tau},$$

where the first term comes from the ionized state and the second and third terms account for the spin up and spin down bound states. The average number of (bound) electrons and the average energy are

$$\langle N \rangle = \frac{e^{(\mu + I)/\tau} + e^{(\mu + I)/\tau}}{1 + e^{(\mu + I)/\tau} + e^{(\mu + I)/\tau}} = \frac{2e^{(\mu + I)/\tau}}{1 + 2e^{(\mu + I)/\tau}},$$

$$\langle E \rangle = \frac{-Ie^{(\mu + I)/\tau} - Ie^{(\mu + I)/\tau}}{1 + e^{(\mu + I)/\tau} + e^{(\mu + I)/\tau}} = \frac{-2Ie^{(\mu + I)/\tau}}{1 + 2e^{(\mu + I)/\tau}}.$$
The probability that the impurity atom is ionized is

\[ P(N = 0) = \frac{1}{1 + 2e^{(\mu + I)/\tau}}. \]

If we don’t know the value of \( \mu \), we can’t actually calculate any of these averages or this probability. What sets the value of \( \mu \)? Answer: \( \mu \) is determined by the electron distribution in the rest of the semiconductor. (A subject we’ll get to in a few weeks!) Although we don’t know \( \mu \) at this point, we’re used to the idea that \( \mu \) increases with increasing concentration. In the above expressions we see that increasing \( \mu \) increases the mean number of particles in the system, decreases the mean energy (energy goes down for a bound particle), and decreases the probability of being ionized. All this is reasonable and might have been expected. The higher the concentration of electrons in the semiconductor, the harder it is for the atom to give an extra electron to the semiconductor and become ionized!

Example: K&K, Chapter 5, Problem 6

In this problem we are asked to work with a 3 state system. The states are: (1) no particle, energy is 0; (2) one particle, energy is still 0; (3) one particle, energy is \( \epsilon \), so a particle can be absent, present with zero energy, or present with energy \( \epsilon \). The grand partition function is

\[ Z = 1 + \lambda + \lambda e^{-\epsilon/\tau}, \]

where \( \lambda = \exp(\mu/\tau) \). The three terms in this sum correspond to the three states enumerated above. The thermal average occupancy is just the average number of particles in the system and is

\[ \langle N \rangle = \frac{1}{Z} \left( 0 \cdot 1 + 1 \cdot \lambda + 1 \cdot \lambda e^{-\epsilon/\tau} \right) = \frac{\lambda + \lambda e^{-\epsilon/\tau}}{1 + \lambda + \lambda e^{-\epsilon/\tau}}. \]

Of course, this result can also be obtained using \( \langle N \rangle = \lambda (\partial/\partial \lambda) \log Z \). Just as in the previous example, increasing \( \mu \) (\( \lambda \)) makes it harder for the system to give the particle to the reservoir (which determines \( \mu \)) and the system is more likely to contain a bound particle. The thermal average occupancy of the state with energy \( \epsilon \) is

\[ \langle N(E = \epsilon) \rangle = \frac{\lambda e^{-\epsilon/\tau}}{Z} = \frac{\lambda e^{-\epsilon/\tau}}{1 + \lambda + \lambda e^{-\epsilon/\tau}}. \]

Here we see that in the limit of very large \( \mu \) (\( \lambda \)) the system always contains a particle, and the relative probability that the particle is in the high energy state is just the Boltzmann factor, \( \exp(-\epsilon/\tau) \). The average energy is

\[ \langle E \rangle = \frac{\epsilon \lambda e^{-\epsilon/\tau}}{Z} = \frac{\epsilon \lambda e^{-\epsilon/\tau}}{1 + \lambda + \lambda e^{-\epsilon/\tau}}. \]
Finally, we are asked to calculate the grand partition function in the event that a particle can exist in both the zero energy state and the state with energy $\epsilon$ simultaneously. In other words, there is a fourth state of the system; it contains two particles and has energy $\epsilon$. We have

$$Z = 1 + \lambda + \lambda e^{-\epsilon/\tau} + \lambda^2 e^{-\epsilon/\tau} = (1 + \lambda) \cdot (1 + \lambda e^{-\epsilon/\tau}).$$

In this case, $Z$ can be factored. K&K point out that this means that the system can be treated as two independent systems. This is an example of a general rule that for independent (but weakly interacting) systems, the grand partition function is the product of the grand partition functions for each independent system, just as the partition function of independent systems is a product of the individual partition functions (Homework 2, problem 4).

**Fermi-Dirac and Bose-Einstein Distributions**

When we considered a low density gas in lecture 5, we considered the single particle states of a particle confined to a box. To treat more than one particle, we imagined that the particles were weakly interacting, so we could, to some level of approximation, treat each particle as though it occupied a single particle state. In the limit of no interactions between particles, this would be exact (but it might be hard to achieve thermal equilibrium!). For typical gases at room temperature and atmospheric pressure we found that the concentration was very low, so that the chance that any single particle state was occupied was very small, maybe one part in a million. We just didn’t have to worry about the chances of finding two particles in a state.

Now we want to consider the distribution when there’s a good chance of finding single particle states occupied. We are going to assume that we have non-interacting particles in which each particle in the system can be said to be in a single particle state. There are two kinds of particles, fermions, which have half integer spins (spin angular momentum is a half integer times $\hbar$), and bosons which have integral spins. fermions obey the Pauli exclusion principle: at most one particle may occupy a single state. On the other hand, an unlimited number of bosons may be placed in any given state. Since we have independent single particle states, the grand partition function for all the states is the product of the grand partition function for the individual states. So to start with, let’s calculate the grand partition function for an individual state of energy $\epsilon$.

In the case of fermions, there are two possibilities: no particle present with energy 0 and one particle present with energy $\epsilon$. Then

$$Z = 1 + e^{(\mu - \epsilon)/\tau}.$$
The average number of particles in this state of energy $\epsilon$ is denoted by $f(\epsilon)$

$$f(\epsilon) = \langle N \rangle = \frac{e^{(\mu - \epsilon)/\tau}}{1 + e^{(\mu - \epsilon)/\tau}} = \frac{1}{e^{(\epsilon - \mu)/\tau} + 1}.$$ 

This is called the Fermi-Dirac distribution and fermions are said to obey Fermi-Dirac statistics. If $\epsilon = \mu$, then the average number of particles in the state is $1/2$. If $\epsilon < \mu$, the average occupancy is bigger than $1/2$ and approaches $1$ as $\epsilon \to -\infty$. If $\epsilon > \mu$, the average occupancy is less than $1/2$ and approaches $0$ as $\epsilon \to +\infty$. This distribution starts at 1 at very low energies, winds up at 0 at very high energies and makes the transition from 0 to 1 in the neighborhood of $\mu$. The temperature controls the width of the transition. At very low temperatures the transition is sharp. At high temperatures, the transition is gradual.

For bosons, the possibilities are no particles present with energy 0, 1 particle present with energy $\epsilon$, 2 particles present with energy $2\epsilon$, 3 particles present with energy $3\epsilon$, and so on. The grand partition function is

$$Z = 1 + e^{(\mu - \epsilon)/\tau} + e^{2(\mu - \epsilon)/\tau} + e^{3(\mu - \epsilon)/\tau} + \ldots = \frac{1}{1 - e^{(\mu - \epsilon)/\tau}}.$$ 

Note that $\mu < \epsilon$ if the sum is to converge. The average occupancy is

$$f(\epsilon) = \tau \frac{\partial \log Z}{\partial \mu} = \frac{e^{(\mu - \epsilon)/\tau}}{1 - e^{(\mu - \epsilon)/\tau}} = \frac{1}{e^{(\epsilon - \mu)/\tau} - 1}.$$
This is called the Bose-Einstein distribution and bosons obey Bose-Einstein statistics. Again, note that \( \mu < \epsilon \) if the distribution function is to make sense. In fact, if we have weakly interacting particles occupying states of several different energies, they all have the same chemical potential which must therefore be less than the lowest energy of any available state. In other words
\[ \mu < \epsilon_{\text{minimum}}. \]

The minimum energy is often set to zero, and then \( \mu < 0 \), but the real constraint is just that \( \mu \) be lower than any accessible energy. The Bose-Einstein distribution diverges as \( \epsilon \to \mu \). As \( \epsilon \to +\infty \) the distribution goes exponentially to zero. The average occupancy is 1 when \( \epsilon - \mu = \tau \log 2 \). At lower energies there is more than one particle in the state and at higher energies there is less than one particle in the state.

The Bose-Einstein distribution, with \( \mu = 0 \), is exactly the occupancy we came up with for photons in blackbody radiation. Photons have spin 1, so they are bosons and obey Bose-Einstein statistics. There is no lower limit on the wavelength, so the lowest conceivable energy is arbitrarily close to zero which means \( \mu \leq 0 \).
At large energies both the Fermi-Dirac and Bose-Einstein distributions become

\[ f(\epsilon \to +\infty) \to e^{(\mu - \epsilon)/\tau}. \]

In this limit the average occupancy is small and quantum effects are negligible; this is the classical limit. The classical distribution is called the Maxwell-Boltzmann distribution.