Baby Reif, Level 2 notes PhL 4.17.07

This is a second level review (see raw notes in separate document), followed by applications and other things of special interest to me right now.

********** **1. Baby Reif Review** **********

Chapter 1. This is mainly just introduction, with advanced warning of things to come. Conjecture is that A and A' each consisting of lots of small particles will be in equilibrium if average energy is same on both sides. Later we will learn that *temperatures* are the same, and in certain normal systems average energy is N kT where N is some number, so you get this result that average energies are the same. We have a few toy calculations for ideal gas.

Chapter 2. Here Reif talks about the **binomial distribution**. How is this connected to the story?

His first physical connection is given on page 74 in a small note. Break a box into two volumes V and V', then p = V/V* and q = V'/V* and then binomial P(N) of (14) tells you the probability distribution that N molecules are in the V side. We intuitively know that P(N) will have a strong peak at N = N*(V/V*) = n*V, but now we know details of the distribution around that peak and in fact everywhere. The binomial arises whenever you have an independent either-one-or-the-other situation for your "events", left side or right side, heads or tails, spin up or spin down, with probs p and q.

His second physical connection is on page 80 with a system of N spins. In this case, p = probability of spin up, and q of spin down, and spin magnitude (as a mag moment say) is μ_0.

Then later on page 84 he returns to the ideal gas case.

Somehow, I find this chapter to be disorganized and not presented in a logical order. I would rather see all the math first, and then see bang, bang, direct applications all in a row, so we don't mix the discussions together all the time.

Chapter 3. Here he introduces the state density $\mathbf{\Omega(E)} = \rho(E)dE$ and $\Phi(E)$ as its integral up to E. These quantities are computed for a quantum particle in a 1D and 3D box. We then get the idea that for a macro system with very large f, we have $\Phi(E) \sim \phi(\varepsilon)^f$ which generally leads to $\mathbf{\Omega(E) \sim (E-E_0)^f}$, and we get the notion that as you increase E, the number of accessible states dramatically increases by a huge power law. The term **"adiabatic"** is defined, two systems are insulated from each other so no heat transfer. Reif then states the rule $\mathbf{dE = dQ + dW}$ which just says that there are two ways the energy of system A can increase, you add heat from A', or A' does work on A. [This is the **First Law**.]

Chapter 4. This is the big central chapter of the book which gets the main results of interest.

As usual, systems $\mathbf{A^* = A + A'}$ and we get the famous result $\mathbf{\Omega^*(E) = \Omega(E)\,\Omega'(E^* - E)}$ where each is a strong power function for any macro system. This leads to the fact that $\Omega^*(E)$ has a very strong peak where the A and A' derivatives $\mathbf{\partial \ln\Omega(E)/\partial E}$ **are equal.** These derivatives in effect are called "temperature" and we conclude that $\Omega^*(E)$ has its strong maximum when the A and A' temperatures are equal. The final system A* will end up in this maximal state density region (with small fluctuations) when temperatures equalize for system starting non-equal. This state change is irreversible.

Temperature is exactly defined as $\mathbf{\partial \ln\Omega(E)/\partial E = \beta = 1/kT}$ (absolute T that is), and entropy is exactly defined as $\mathbf{S(E) = k \ln \Omega(E).}$ [then $\partial S(E)/\partial E = 1/T$ and so TdS = dE]

If you add a little heat to system A (no work), its energy increases and number of accessible states increases, and this comes out being expressed as $\mathbf{dS = dQ/T}$. [In this case, first law says dE = TdS + W]

The concept of A' being a huge **thermal reservoir** comes next and has major implications. If system A has energy $E_r << E^*$ (because most energy is in the large reservoir as E'), then you can expand $\ln\Omega'(E^* - E_r)$ in terms of very small E_r and you get $\ln \Omega'(E^* - E_r) = \ln \Omega'(E^*) - E_r \beta(E^*)$ which at once leads to the very famous and important **Boltzmann factor** result which says $\mathbf{P_r = const * \Omega'(E^*) \exp(-\beta E_r)}$. This says that as you steal more small energy E_r from E* for your A system, the number of states of the A' system drops off as $\exp(-\beta E_r)$. Up to know, we have associated $\Omega(E)$ with high power laws, but here for the first time we get an exponential appearing.

This Boltzmann factor idea is not just obscure theory, you use it directly to compute things. You take a system and assume $P_r = C \exp(-\beta E_r)$, you sum over all states r to determine C, then you have an exact probability distribution known as the **Boltzmann Distribution** written in (51). [This is the probability that system A in contact with heat reservoir A' at temperature T has energy E_r.]

First application is a A = single **magnetic dipole** in a B field, so there are only 2 states, and we know their two energies, and we assume this single dipole is in contact with a thermal reservoir A' that consists of all the other dipoles in a paramagnetic solid. With little ado we quickly derive result (59) which is the tanh law for mean dipole moment, and we get a simple Curie's Law formula for χ . In this example, it was very simple to do the Boltzmann sum since only 2 states.

Second application is the 3D **ideal gas** where we compute the mean energy $<\varepsilon_r>$. Again, A = one molecule, A' = reservoir of all other molecules. Reif replaces symbol E_r with ε_r as energy of system A. The Boltzmann distribution is (72) in general form. If you want to compute the mean energy $<\varepsilon_r>$, you can do a trick since this energy appears in the exponent. This trick leads to the definition of the **partition function Z** as just the sum of the exponentials, and the mean energy is a derivative of lnZ wrt β. Reif shows how to compute Z by replacing the discrete quantum 3D state space with a continuum to get an integral with result (82) for Z. The derivative for $<\varepsilon_r>$ then gives **(3/2)kT** and we learn that the $<\varepsilon_r>$ depends on nothing but T!

Still doing ideal gas, Reif shows how to compute the **mean pressure**. To get pressure into the picture, Reif lets a box wall move a little outward, it will do work $dW = p\, dV = F\, dL_z = d\varepsilon_r$ for average molecule. Here p is pressure, and F is entire force on the z wall. Reif sets out to compute <F> using the Boltzmann distribution, and he then gets to use $F = dL_z / d\varepsilon_r$. He is then able to change form so derivative again acts on the exponential factor (page 172 bottom): $d/dL_z [\exp(-\beta\varepsilon_r)] = \exp(-\beta\varepsilon_r)(d\varepsilon_r/dL_z)$ // chain rule. This allows us to use the same old partition function Z, and the desired force F comes out again as a certain derivative of Z. We already know Z for our ideal gas, so get result (90) at once and this leads at once to the idea that **p = nkT,** so we have derived the ideal gas law using the Boltzmann distribution. [Like all results, this result is only true for system A when things are in equilibrium, including quasi-static.]

Chapter 5. An interlude chapter about thermometers, fact that $S \to S_o$ as $T \to 0$, comments on work dW and quasi-static, some experiments. It then talks about heat capacity dQ/dT with some parameter held fixed. If that parameter is V, you get the ideal gas result for $C_V = 3/2\ R$ on page 209.

Chapter 6. Up to now, we used spin systems or quantum particle in a box to count states. It is useful however to apply our results to **"classical systems"** without worrying about quantum theory. The trick for doing this is that you "count states" by counting the volume of little squares in **"phase space"** which has the form dpdq for each of your particles. This notion arises from the Heisenberg notion and no doubt has more theory behind it than is presented here, but the notion seems very reasonable (recall phase space from Goldstein mechanics, for example, or scattering theory).

Big **ideal gas application:** we now write the **Boltzmann Distribution** as (14) then (15) using this phase space idea, and we take note that only the magnitude of particle velocity appears in the Boltzmann exponent in the ε_r factor. Integrating over the dq coordinates of the phase space just gives a V volume constant, so the real issue is the dp momentum or dv velocity coordinates. So we now write Boltzmann as (17) and the constant C is computed on the next page in terms of the basic gaussian integral.

Calculation #1: compute **distribution in v_x only**, result trivially is (24) which is of course just a **gaussian** or normal distribution peaked at $v_x = 0$, but we see the standard deviation and all that stuff.

Calculation #2: compute the **speed distribution in v**. Write $d^3v = v^2 dv\, d\Omega$ and get 4π and then the very famous result is just $v^2 \exp(-\beta m v^2/2)$ as shown in (30) called the **Maxwell speed distribution** which is plotted page 238 at various temperatures. It is easy to compute the **most probable speed** as in (32). For air at room temperature, this speed is 420 m/sec or which is 420*2.236 9 = 948.12 mph, faster than the speed of sound!

So what have we done here? Without knowing anything about quantum theory, assuming the simple phase space count method, we have derived the Maxwell type ideal gas distributions.

Now on page 246 we look more generally at computing $<\varepsilon_r>$ in a Boltzmann situation. If the energy of a particle or subsystem has the usual **quadratic** coordinate form, then you get **1/2kT for each degree of freedom** (ie, for each such quadratic contribution to energy) and this is the **equipartition theorem**. One particle in a 3D box gives 3/2 kT. **Harmonic oscillator** gives 2/2 kT. By modeling an elemental **solid of atoms** as an array of 3D harmonic oscillators, we can compute 6/2 kT for each one and we get heat capacity as $c_V = 3R$ instead of (3/2) R as it was for ideal gas.

Chapter 7. Now the notion of "work" is added to the picture. We know about dW = pdV work on a gas, and here we have the more general work as **dW = Xdx** where dx is a parameter, and X is a **generalized force**. This force can be expressed as a derivative of the state count as in (13) $\mathbf{-\beta X = (\partial \ln \Omega/\partial x)_E}$ which is similar in form to the temperature definition derivative $(\partial \ln \Omega(E)/\partial E) = \beta$.

In order to maximize the state count $\Omega^*(E^*)$, just as we had to have $\beta = \beta'$ for temperature for equilibrium, now we *also* have to have X = X' for each generalized force. For ideal gas with X = pressure p, we need to have p = p' for box divided into V + V' with a sliding divider.

Now, the general rule is that dE = dQ + dW with appropriate signs. dQ is heat added to A, dW is work done on A. You can write dQ = TdS. You solve little problems with this dE = dQ + dW equation, I remember doing this many times. (again, this is the first law).

Example: **adiabatic ideal gas expansion**. Set dQ = 0, then dE = dW or $c_V dT = pdV = RTdV/V$ for one mole, then have $c_V\, dT/T = RdV/V$. IF (!) you assume constant c_V, then can integrate to get the adiabatic gas law which is $T^{(cV/R)}V$ = constant. Usually written as pV^γ = constant with $\gamma = 1 + R/c_V$. We are allowed to use the p = nkT result as needed since always true in ideal gas.

This leads into a statement of the **"laws of thermodynamics"**, an epic point in any such class!

(0) If A eq B and B eq C, then A eq C thermo, so you can have the notion of a "**thermometer**".

(1) If A is isolated, E = constant. Otherwise $\Delta E = W + Q$ = work done on it + heat added to it. This is the **first law**, write as dE = dQ + dW perhaps. Conservation of energy, really.

(2) For quasi-static, dS = dQ/T, otherwise $\Delta S \geq 0$. This is the **second law**.

(3) As $T \rightarrow 0$, $S \rightarrow$ some small S_0.

(4) Here we get some new stuff.

Up to now, we have used A* to represent our total system and we assumed it was isolated. Now let's suppose that system A is isolated and get rid of the *. Notice that for **isolated system A** you can then write $P(y) \sim \Omega(E,y) = \exp(k \ln\Omega(E,y)/k) = \exp(S(E,y)/k)$. We maximize $\Omega(E,y)$ when we maximize $S(E,y)$ where y is some parameter. So consider two values of y called y and y_0:

$$P(y_0) = \exp(S(E,y_0)/k)$$
$$P(y) = \exp(S(E,y)/k) \quad \Rightarrow \quad P(y) / P(y_0) = \exp(\Delta S/k) \qquad \text{// p 287 (67)}$$

This is not the Boltzmann exponential, it is just the definition of S exponential.

Now we go back to A* = A + A' with A' being now both a temperature AND a pressure reservoir. We can claim that $P(y) / P(y_0) = \exp(\Delta S^*/k)$ for the A* total system as in (71).

Now, we want to compute $\Delta S^* = \Delta S + \Delta S'$. We can write $\Delta S' = dQ'/T'$ if we move some heat into the A' reservoir. But that heat must come from system A, so system A gains heat dQ = -dQ'. The rule for system A is dE = dQ + dW where dW work is done on system A and dQ is heat added to system A. We know that dW = -p'dV where dV is an increase in system A volume. Putting these pieces together, we have

$$\Delta S' = dQ'/T' = -dQ/T' = -(dE - dW)/T' = -(dE + p'dV)/T'$$

Therefore

$$\Delta S^* = \Delta S + -(dE + p'dV)/T' = (T'\Delta S - dE - p'dV)/T' = (T\Delta S - dE - pdV)/T$$

We retain T' and p' primes to remind us these are the reservoir values, but of course p = p' and T = T' since we are in equilibrium, so we can write the thing as on the far right above. Then define

$$G = E - TS + pV \qquad \text{so } \Delta G = \Delta E - T\Delta S + p\Delta V \qquad \text{then } \mathbf{\Delta S^* = -\Delta G/T}$$

The result $\Delta S^* = -\Delta G/T$ only obtains in the situation treated above where we are in contact with a constant T and constant p reservoir. But, this is the situation for all chemical reactions in solution, and that is **why Gibb's Free Energy G shows up in chemistry**. Now of course we can write:

$$P(y) / P(y_0) = \exp(\Delta S^*/k) = \exp(-\Delta G^*/kT) = \exp(-G(y)^*/kT) \exp(-G(y_0)^*/kT)$$

where 0 refers to some "standard state", then we can generally say:

$$P(y) \sim \exp(-G(y)^*/kT)$$

and minimizing G(y) is now what maximizes P(y).

Application: Suppose system A with a constant p and T reservoir has two phases. You quickly conclude that in equilibrium you will have $g_1 = g_2$ where g_i is the G for a molecule in a phase i at p and T. Reif then does more with multi-phase systems which I skip here for the moment. He then goes on to deal with the basics of thermo "engines" . This is where I stopped reading.

********** **2. Thermo Stuff appearing in Watson's cell book.** **********

Review of Watson panel page 668-9.

Reif says

$G = E - TS + pV$

and we can also separate out the TS part and say

$H = E + pV$ = "enthalpy" // but above $dQ = dE + pdV$ so $Q = E + pV$

so you can think of enthalpy as the same as the heat released in a system of constant pressure p. Watson notes that in biological reactions, volume changes are minimal, so roughly $H = E$ and $\Delta H = \Delta E$.

Watson quotes the **first law** as overall energy conservation of E* for A + A' systems.

He then quotes the **second law** as saying system spontaneously moves to region of most probable microstates. Order means low-probability states, so move to more randomness.

In his entropy section on page 669, we see this:

$\Delta S_{mole} = N_a \Delta S_{single} = N_a [k \ln\Omega_B - k \ln\Omega_A] = (N_a k) \ln [\Omega_B/\Omega_A] = R \ln [\Omega_B/\Omega_A]$

Watson also quotes $\Delta S_{sea} = Q/T$ for heat transferred out of the System A into System A'. A reservoir is a "sea".

Watson next writes $G = H - TS$ and derives Reif's result that $-\Delta G/T = \Delta S_{universe} = \Delta S^*$. To figure which way a reaction will go, compute ΔG for all species on both sides and see who wins. ΔG is indication of distance away from equilibrium.

Following our digression argument given below, we can write for a single reaction center that $\Omega_a(E) = V_a \ const_a = K_a / [a]$ and then we get something like $\Delta S_{mole} = \Delta S_0 + R \ln ([B]/[A])$ where we are now showing concentrations. But this version of the equation does not appear in the Watson panel.

Question: How do we relate the molarity concentration of a chemical species to parameters used in earlier discussion?

The number n_B is usually a density in number of molecules of type B per cm^3. [B] is the number of moles per liter (the molarity). So $n_B = N_B/V(cm^3) = (N_B/N_a) N_a /1000V(\ell) = N_{moles\ of\ B} / V(\ell) * (N_a/1000) = [B] * N_a/1000 = n_B\ (cm^{-3})$. So assume cgs units, then we have:

$[B] = (1000/N_a) N_B / V$

which of course says that [B] is proportional to N_B.

Question: How do we relate a concentration like [B] to a state density like Ω(E) ?

See digression below for a possible answer .

********** digression **********

I am trying to find a believable derivation of this equation:

$\Delta G = \Delta G^0 + RT \ln Q$ where Q is the usual ratio of concentrations

My problem is that I don't know the proper handle or name for this equation, so I cannot look it up well on the web! Q is called the **"reaction quotient"**. // More web minutes, still no name for this equation. It is not really the Nernst equation, you get Nernst from it!

OK, I will now attempt my own derivation which is a little weird but follows http://en.wikipedia.org/wiki/Nernst_equation pretty much.

Consider *a single reaction* that is going to occur at some point inside a reaction volume. The reaction is going to be a+b $\rightarrow$ c+d+c. We know that the number of states available to a single particle in a 3D box is proportional to the volume of the box. So we might say $\Omega_a(E) = V\ const_a$. However, for our single reaction of interest which involves exactly one "a" molecule, the relevant volume is that volume around our reaction center that contains on average 1 type-a molecule. That volume would be $V_a = const / [a]$. That is to say, as you double the concentration, you double density n_a, and you halve the average space which contains one type a molecule. So with this reinterpretation of "volume" for our particular reaction point in a container, we say $\Omega_a(E) = V_a\ const_a = K_a / [a]$ where K is some a-dependent constant. As we increase the density, we make the volume which contains only one "a" molecule smaller, and we get *fewer* states it can have. So we now write:

$S_{initial} = k\ln\Omega_a + k\ln\Omega_b$ // entropy for one initial reaction set (or first phase)
$S_{final} = k\ln\Omega_c + k\ln\Omega_d + k\ln\Omega_e$ // entropy for one final reaction set (or second phase)

Rewrite these as

$S_{initial} = k \ln \Omega_a\Omega_b$
$S_{final} = k \ln \Omega_c\Omega_d\Omega_e$

Then

$\Delta S_{single} = S_{final} - S_{initial} = k \ln [\ \Omega_c\Omega_d\Omega_e\ / \Omega_a\Omega_b\ ]$

Now at this point we finally use our idea that $\Omega_a = K_a / [a]$, so we then have:

$\Delta S_{single} = k \ln [\ K_cK_dK_e/K_aK_b * [a][b]/[c][d][e]\ ] = k \ln(\ K_cK_dK_e/K_aK_b\ ) + k \ln([a][b]/[c][d][e]\ )$

Now, we know that $\Delta G = \Delta H - T\Delta S$, where ΔH is a property of the specific reaction. So we get:

$\Delta G_{single} = \{\ \Delta H_{abcde} - kT \ln(\ K_cK_dK_e/K_aK_b\ )\ \} + kT \ln([c][d][e]/[a][b])$

$= \Delta G_{single}^0 + kT \ln Q$

where we define Q and Δ_{single}^0 as shown. But this is all for a single reaction remember. If we want to redefine ΔG to apply to a mole of reactions (just N_a reactions), then we multiply through by N_a to get

$$\Delta G_{mole} = N_a \Delta G_{single}^0 + nN_aT \ln Q$$
$$= \Delta G^0 + RT \ln Q$$

So, using the idea of a different "reaction volume" for each reactant near a specific single reaction center, such that each such volume contains only 1 reacting molecule, and using the fact that the number of states available to a molecule is proportional to the volume it lives in, I have derived this equation:

$$\Delta G = \Delta G^0 + RT \ln Q$$

Our "System A" in this case can be thought of as a two-phase system. In one phase the system has molecules a and b, in the other phase it has c and d and e. The System A' is the "reservoir" of all the other reaction centers and molecules in our reaction vessel. This is a constant temperature and pressure reservoir, so we can use the G function properly.

This equation appears on page 671 of Watson.

The above discussion does not assume the two phases are in equilibrium within the System A system. The function Q equals the equilibrium constant K expression only when the phases *are* in equilibrium. In that case, we know from Reif's two-phase discussion that we will have $g_a + g_b = g_c + g_d + g_e$ so ΔG = 0. We can then make the statement:

$$0 = \Delta G^0 + RT \ln K \quad \text{or} \quad \Delta G^0 = -RT \ln K \quad \text{or} \quad K = \exp(-\Delta G_0/kT)$$

Another fact is that when all concentrations are one molar, we have $\Delta G = \Delta G^0$ since Q = 1. So this concludes what we see on **Watson page 671.**

Let's just add these facts:

$Q = ([c][d][e]/[a][b])$ = a variable you can arrange to be anything you want with concentrations

$K = ([c]_{eq}[d]_{eq}[e]_{eq}/[a]_{eq}[b]_{eq})$ = a constant

Entropy unit - a non-S.I. unit of thermodynamic entropy, usually denoted "e.u." and equal to one calorie per kelvin.

I think in Reif's book, entropy S would be in joules/kelvin or ergs/kelvin.

Alternate to the above without my arm-waving about specific volume for each species.

Assume N_i of each type i, where N_i is a large number of course. Then

$$S_{initial} = k \ln \Omega_a^{Na} \Omega_b^{Nb} / Na!\, Nb!$$
$$S_{final} = k \ln \Omega_c^{Nc} \Omega_d^{Nd} \Omega_e^{Ne} / Nc!\, Nd!\, Ne!$$

where the factorials come from the identical molecules issue. Then we get

$$\Delta S_{single} = S_{final} - S_{initial} = k \ln [\Omega_c^{Nc} \Omega_d^{Nd} \Omega_e^{Ne} / Nc!\, Nd!\, Ne!] - k \ln [\Omega_a^{Na} \Omega_b^{Nb} / Na!\, Nb!]$$

Now split this into the two types of terms. The Ω terms give this:

$$k \ln [\Omega_c^{Nc} \Omega_d^{Nd} \Omega_e^{Ne} / \Omega_a^{Na} \Omega_b^{Nb}]$$

But now scale each count here so we get $N_i = b_i A$ where A = Avogadro and b_i is the number of molecules in the reaction, here all positive for the way I have done things. This term then becomes

$$- Ak \ln [\Omega_c^{bc} \Omega_d^{bd} \Omega_e^{be} / \Omega_a^{ba} \Omega_b^{bb}] = -R \ln [\Omega_c^{bc} \Omega_d^{bd} \Omega_e^{be} / \Omega_a^{ba} \Omega_b^{bb}]$$

and this entire term is then somehow a function of the specific chemical reaction.

Now look at the factorial term which is this:

$$- k \ln [Nc!\, Nd!\, Ne!] + k \ln [Na!\, Nb!]$$

$$= - k \ln Nc! - etc + k \ln Na! + etc$$

Since these numbers N are large, use Stirling which says ln N! = N(lnN-1) as shown Daddy Reif p322. Then the terms above are:

$$= - k\, Nc\, (\ln Nc - 1) + ... + k\, Na\, (\ln Na - 1) - ...$$

$$= - k \ln Nc^{Nc} + ... + k \ln Na^{Na} - ... + kNc + kNd.... - kNa - kNb$$

The rightmost terms give kA times a constant, so group with constant term that is reaction dependent. In the first terms, write $Nc = Ab_c$ and so on so they become

$$- kA \ln N_c^{bc} \text{ etc.}$$

Now use the fact that $[B] = (1000/N_a)\, N_B / V$ which for us is $[c] = (1000/A) N_c / V$ so we get

$$N_c = V[c]\, A/1000.$$

Then our terms become

$$- kA \ln \{ V[c]\, A/1000 \}^{bc} \text{ etc}$$

Now take all the logs for things other than concentrations and put them off into the constant term. You then have left

$$- kA \ln [c]^{bc} [d]^{bd} \text{ etc} = - kA \ln Q = - R \ln Q$$

Our result is then

$\Delta S_{\text{mole of reactions}} = \Delta S^0_{\text{mole of reactions}} - R \ln Q$

We then put this into the formula $\Delta G = \Delta H - T\Delta S$, put ΔH into the constant term, and we then have

$\Delta G_{\text{mole of reactions}} = \Delta G^0_{\text{mole of reactions}} + RT \ln Q$

Comments: In this method, I am not forced to think about a different size "volume" for each molecule type involved in the reaction. Instead, I set the volume V fixed, and instead of thinking about just one reaction, I think about a whole mole of them in this volume V, and the counts like N_d for each reactant are now different. I use two different replacements for N_d in different places:

$N_d = b_d A$ = count for one reaction * Avogadro // since mole of reactions assumed

$N_d = V[d] A/1000.$ = relates N_d to the molarity.

Now, it is the identical particles which leads to terms like $\ln(N_d!) \sim N_d \ln(N_d)$ Then I use $b_d A$ for the first N_d here and I use $V[d] A/1000$ for the second, and that is how we end up with $\ln [d]^{bd}$ and thus how we end up with the fancy Q thing!

Thus, the entire Q mass action term in the result is coming from the identical particles factorial! You see this also happening on the Daddy Reif derivation from my Daddy notes, Reif page 322 circa. These factorials are HUGE numbers (which is to say, 10^{23}!) and you have to expect them to play a role! We treat the molecules of type "d" as being identical when we count their states.

The lnQ term arises entirely from these factorials, and they in turn come from "state counting" for large numbers of indistinguishable particles. This term has nothing really to do with the details of the actual chemical reaction, that is all in the first term ΔG^0 . The lnQ is in effect a "driving term" from the molarity concentrations. And in equilibrium, as usual we will get $RT\ln Q = -\Delta G^0_{\text{mole of reactions}}$ and then Q will be the usual K constant.

So I think I have learned a lot from this alternative derivation. Notice that I don't need to use the fancy thing about F being related to lnZ as Reif uses, but that little think is where some of the N! action comes in I suspect. In fact, Reif shows the factorials in 8.10.7 and these appear top of page 322 and these cause the N_i to appear inside the logs. So same thing, I guess the F/Z connection is not the secret.

Interpretation:

Imagine a reaction $a + b \rightarrow c + d$. If you make [a] very large, we know we are going to increase the reaction rate going to the right, for a fixed amount of [b]. We could do this by adding some N_a molecules. This seems to increase the number of states available to the N_a molecule subsystem. Intuitively we feel this should shift the balance point of the reaction. But I don't really know how to follow this interpretive path exactly, and have no need to right now.

What I do have is this equation:

$\Delta G = \Delta G^0 + RT \ln Q$ where Q is the usual ratio of concentrations, final/initial

$$= \Delta G^0 + RT \ln \frac{[c][d]}{[a][b]}$$

Suppose, for some initial set of molarities of the molecules, the reaction wants to go to the right. That would be due to the overall ΔG being negative as computed above. This would start using up left side reactants and create more right side ones, so the term lnQ gets larger, more positive. This tends to make ΔG be smaller. Eventually, ΔG reaches 0 and we are in equilibrium, the concentrations stop changing.

This sounds very much like what happens in a battery as it wears down.

On the other hand, if you had a way to maintain all the original molarities, you could keep operating your battery forever with the same ΔG. Maybe this is what a fuel cell does. Such a battery is being operated far from equilibrium because it runs with $\Delta G \neq 0$.

********** **3.Nernst type equations and chem potentials** **********