**Chemical Reactions**

Now I’d like to consider chemical reactions. In particular I’ll do an example pertaining to nuclear synthesis after the Big Bang. So say we have protons, electrons, in a thermal bath at temperature T. And these can join to form Hydrogen atoms, with a binding energy of 13.6eV. Would like to know the ratio of proton/H-atom and electrons/H-atom, etc., as a function of T. So I guess we will presume our mixture lies within the universe at some volume V, and temperature T. Then we want to minimize the Free energy,



The chemical reaction relating the three species is:



and in terms of the number of reactions that have taken place, R, and the initial values of these species, we can say:



Then we’d minimize F w/r to the free variable,



Now let’s consider the number density for particles, including their rest energy so E = mc2 + (1/2)k2/2m. The only thing that changes is the addition of the rest mass to the chemical potential:



Now let’s say that T is rather low. Well, it should be about 3000K, assuming we’re in the recombination era of the universe. Under such circumstances, μ should be positive. But I guess we’re considering that T isn’t so low that μ is around mc2? Rather that T is large enough so that μ is somewhat small (because recall μ decreases with T and even eventually goes negative)? In this case z would be small, and it might be appropriate to neglect the 1 in the denominator and say:



This is just the classical result (times 2 for spin d.o.f.), which makes sense because as we argued in the original Fermion file, we can apply classical statistics to electrons here since the spacing between them is much larger than their thermal wavelength. So we have,



Hydrogen gets a factor of four because, I think, the electron/proton comprising each can occupy a spin up/down state. We can solve for the chemical potential then, and fill this into the chemical balance equation:



Let’s solve for nH:



and so we have:



The exponent numerator is just the binding energy EB = 13.6eV, and we can approximate mH as mp as well. We would also presume, by charge conservation, that the initial number of electrons and protons equal. And so they should continue to equal. Then we have a well known equation:



Let’s now say that we start in a universe with no initial H’s, and a bunch of e’s/p’s. We’ll recall from above that we must have nH = n0H + r = 0 + r, ne = n0e – r (where r = R/V, the number of reactions per unit volume). Filling these in,



When T = ∞, we have r = 0, as we’d expect. When T = 0, we have r = n0e, as we’d also expect. And so intermediate temperatures will give us something intermediate. Let’s keep going. We’ll introduce the thermal wavelength,



and let’s define a thermal binding volume,



And now let’s multiply both sides of our equation by it:



Then let’s define,



Then we can write,



Now let’s proceed with the solution,



And so,



and solving for r,



As N0e,TB goes from 0 to ∞, RTB goes from 0 to N­oe,TB. The kind of ‘critical’ value would be when N0e,TB = 1. This is when,



It’s basically when the thermal binding volume and the spatial volume per particle are the same. The recombination era would have started when this factor was ~ 1.

**Example**

In the early universe, at the beginning of the recombination era, the temperature was about 3000K, and the size of the universe was about 80 million light years. Assuming that then, as now, we had about 1080 electrons, and 1080 protons, what fraction of them would’ve combined into a neutral H atom?

So we will just solve for r and then divide by n0e,



So just have to calculate the numbers,



And we find,

