Chapter 8 - The Time of Recombination: The Formation ofAtoms

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1. Introduction

‘Recombination’ refers to the formation of neutral atoms when the nuclei created in the Big Bang capture electrons. The term ‘recombination’ is rather inappropriate since the nuclei and electrons have never previously been combined. Perhaps ‘first combination’ would be better. The nuclei which are present tem minutes or so after the Big Bang (see Chapter 6B) are:-

	Fraction by Mass	Fraction by Number
H	~75%	~92.3%
D	~0.014%	~0.009%
He4	~25%	~7.7%
He3	~0.003%	~0.001%
Li7	$\sim 10^{-7}\%$	$\sim 2 \times 10^{-8}\%$

The propensity for these nuclei to capture electrons depends upon their ionisation potentials (χ), i.e. the amount of energy released when a free electron is captured. If the typical photon energy ($\sim 2.7k_BT$) exceeds the ionisation potential, the neutral atoms will not be stable but will immediately be re-ionised. Taking the ionisation potential of hydrogen for example (13.6eV), there will be no stable hydrogen atoms above a temperature of $13.6\text{eV}/2.7k_B \sim 58{,}000^oK$.

However, there continues to be essentially no neutral hydrogen even at temperatures of only one-tenth of this. The reason is mostly due to the huge numerical preponderance of photons over nuclei and electrons. The argument is familiar from Chapter 6. In that case we saw that deuterons became stable only when the number of photons with energies sufficient to cause deuterons to fission (E_f) became less than the number deuterons. Since the number of deuterons can only be at most $\sim 10^{-10}$ times the total number of photons, it requires less than 1 in every 10^{10} photons to have the necessary energy to cause deuterons to be unstable. This occurs at temperatures far lower than given by $2.7k_BT \sim E_f$.

The same approach will be used here, in Section 3, to obtain a temperature substantially lower than $\chi/2.7k_B$ at which neutral hydrogen, helium and lithium atoms are still unstable. However, the temperature at which neutral atoms are stable is lower still. This is because it is not necessary for a ground state electron to be ionised by a single photon. It may occur from multiple photon interactions.

In Section 4 we derive an equilibrium value for the density of free electrons using the techniques of statistical thermodynamics. The method is a general one, applicable to a wide range of similar equilibrium phenomena. In fact, we have anticipated it already in Chapter 6B In the present application it is known as the Saha equation. Rather surprisingly it turns out to depend upon the electron mass as well as the ionisation potential.

2. The Ionisation Potentials

The ionisation potentials of these elements are as follows;

Element/Nucleus	Electron	χ = Recombination Potential, eV
H,D	First	13.6
He3,He4	First	54.4
He3,He4	Second	24.6
Li7	First	122.4
Li7	Second	75.6
Li7	Third	5.4

Our terminology differs from the usual convention. We have called the energy released when the first electron is captured by a bare nucleus the 'first recombination potential'. Usually, this would be called 'the last ionisation potential'. Similarly, the last recombination potential is the first ionisation potential.

The recombination (or ionisation) potential is insensitive to the nuclear mass, but sensitive to its charge.

Note that the first recombination potential for any atom is given simply by the first Bohr energy level (i.e. the ground state) for a one electron Schrodinger equation, i.e. $E_1 = Z^2 \frac{mc^2}{2}\alpha^2$ where $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$. Subsequent potentials are harder to calculate because they involve multiple electron states. It is clear that the second recombination potential must be smaller than the first due to partial shielding of the positive nuclear charge by the other electron. Similarly, the third recombination potential will be smaller still. The outer electron of a (neutral) Li atom has a particularly low ionisation potential, consistent with this 'valance' electron being weakly bound in an alkali metal. Conversely, the first ionisation potential of helium is relatively high, consistent with a full S orbital corresponding to low chemical reactivity.

3. The 'Number of High Energy Photons' Argument

In Chapter 6 we saw that, at temperature T, the fraction of photons with energy greater than E_1 is,

$$\frac{N_\gamma(E > E_1)}{N_\gamma(\text{all}\,E)} = 0.416\left[2 + 2x_1 + x_1^2\right]e^{-x_1} \qquad (1)$$

provided that $x_1 = \frac{E_1}{k_B T} >> 1$. Since there are 1.9 x 10^9 photons per nucleon, the ratios of the nuclear densities to the total photon density are,

$$N_H / N_\gamma = 0.75 \text{ x } 1 \text{ x } 1/1.9 \text{ x } 10^9 \quad = \quad 3.9 \text{ x } 10^{-10} \qquad (2)$$

$$N_D / N_\gamma = 0.00014 \text{ x } 1/(2\text{x}1.9 \text{ x } 10^9) = \quad 3.7 \text{ x } 10^{-14} \qquad (3)$$

$$N_{He3} / N_\gamma = 0.00003 \text{ x } 1/(3\text{x}1.9 \text{ x } 10^9) = \quad 5.3 \text{ x } 10^{-15} \qquad (4)$$

$$N_{He4} / N_\gamma = 0.25 \text{ x } 1/(4\text{x}1.9 \text{ x } 10^9) \quad = \quad 3.3 \text{ x } 10^{-11} \qquad (5)$$

$$N_{Li7} / N_\gamma = 10^{-7} \text{ x } 1/(7\text{x}1.9 \text{ x } 10^9) \quad = \quad 7.5 \text{ x } 10^{-18} \qquad (6)$$

Equating the nuclear densities with the photon density for photons with energies above E_1 (set to the ionisation potential, χ) gives the following solutions for $x_1 = E_1/k_BT$,

Nucleus	x_1	χ (eV)	$T = \chi/k_Bx_1$ (^oK)
H	27.5	13.6	5,730
D	37.3	13.6	4,230
He3	39.4	24.6	7,240
He4	30.1	24.6	9,480
Li7	46.3	5.4	1,350

We are interested in the final recombination potential (the first ionisation potential), since only after capture of the final electron is a neutral atom formed. The above Table also includes the value of this potential energy, and hence the derived temperature. At this temperature the corresponding nucleus is still ionised, although it may be just the last electron that is missing.

It is interesting that lithium remains ionised even at quite low temperatures. This is mainly due to its low first ionisation potential, but is exacerbated by its low number density (and hence large x_1). If we use the second ionisation potential of lithium (75.6eV), the corresponding temperature is very high (~19,000^{o}K). Hence, whilst the singly charged Li^+ ion is expected to exist still at 1,350^{o}K, the doubly and triply charged ions Li^{++} or Li^{+++} will have disappeared long before. The implications of the persistence of ionised lithium at temperatures as low as 1,350^{o}K (in fact, as low as ~850^{o}K $\approx$ 580^{o}C, see section 4.2) for the transparency of the universe will be discussed in Chapter 9, although we anticipate that the very low density of lithium will prevent it rendering the universe opaque.

Before proceeding to a more detailed theory to predict the temperature at which neutral atoms become stable, we note that an improved bound for hydrogen and deuterium is easily obtained. This is because the greatest photon energy required is not that to fully ionise the atom, but rather that needed to bridge the greatest gap between energy levels. For a hydrogenic atom the energy levels are proportional to $1/n^2$, where n is the principal quantum number. Hence the largest energy gap is that between the ground state and the first excited state, i.e. between n = 1 and n = 2, so the gap is just 75% of the full ionisation potential, i.e. 10.2eV. This yields temperatures of 4,300^{o}K and 3,170^{o}K respectively for hydrogen and deuterium. Hence we may anticipate that our final answer will be consistent with most protons remaining free at 4,300^{o}K, but most having recombined by 3,170^{o}K. The latter follows because of the numerical dominance of protons over deuterons. This prediction will turn out to agree very well with the results of a more precise methodology to be developed next.

4. The Equilibrium Concentration of Electrons

4.1 Consideration of Hydrogen Alone

At the time when neutral hydrogen is forming, the results of Section 3 suggest that all helium nuclei are already in the form of neutral helium atoms, whereas all lithium nuclei will remain in the singly ionised state (Li^+). Consequently we may consider the formation of hydrogen atoms separately from the formation of the other atoms. The reversible reaction in question is,

$$e + p \Leftrightarrow H + \gamma \tag{7}$$

At any given temperature, what determines the equilibrium concentration of free electrons? The concentration, and energy spectrum, of the photons is fixed by the black body equations. The total density of protons is also fixed, i.e. $N_p = N_p^{free} + N_H$, where, for the purposes of this Section, N_p includes only the protons in hydrogen atoms plus free protons, but not those in helium atoms/nuclei or in the other minority nuclei. Since all the nuclei are stable, this N_p is a constant. Moreover, N_p is known at any given temperature, i.e.,

$$N_p = (0.75/1.9 \text{ x } 10^9)N_\gamma \tag{8}$$

The density of free electrons equals the density of free protons, $N_p^{free} = N_e^{free}$ (because the excess electrons are already combined with helium – and the number required to ultimately combine with lithium is negligible). Consequently there is only one degree of freedom as regards particle numbers, which we take to be the number (density) of free electrons.

Imagine, then, a unit volume which contains N_e^{free} free electrons, the same number of free protons, plus N_p - N_e^{free} hydrogen atoms, where N_p is given by Equ.8, and finally N_γ photons, where,

$$N_\gamma = 0.2436\left(\frac{k_B T}{\hbar c}\right)^3 \tag{9}$$

What is the probability of any given value of N_e^{free} at a given temperature? We shall need to enumerate all states and find the probability of each. The state of the totality of particles in our unit volume is defined firstly by N_e^{free}, but also by the momenta of every particle. In this respect we can exclude the photons whose number density and energy spectrum is known (black body). The photons effectively constitute a heat bath within which the massive particles find equilibrium.

The validity of this treatment of the photons, as a heat bath unaffected by the extent to which neutral atoms have formed, is justified as follows. Reaction (7) releases 13.6eV of energy, which is greater than the prevailing value of $k_B T$ (<1eV). However, since the photons are $>10^9$ times more numerous than the atoms, the average photon energy is clearly negligibly changed. The same argument applies to the reactions forming the other neutral atoms, the ionisation energies being tens of eV, representing an average photon energy increase after atom formation of about a factor of 10^{-7}. Hence, the photon temperature is unchanged by the release of the ionisation energy, i.e. the photons act as a constant temperature heat bath.

To find the equilibrium density of free electrons we therefore consider a state of thermal equilibrium to exist at the prevailing temperature. Moreover, we are in effect considering a constant volume (i.e. a unit volume – all such unit volumes being equivalent, or, if this seems unsatisfactory, the whole universe). We therefore wish to find the equilibrium free electron density for a fixed temperature and volume. The system under consideration consists of the free electrons, the free protons and the neutral hydrogen atoms. The photons are not part of the system, but rather provide the constant temperature heat bath. The neutral helium atoms, which have formed at an earlier time, play no part in the process and hence are not considered as part of the system. Nor do the very small numbers of lithium-7 ions, which have captured their first two electrons much earlier and will not capture their final electron until much later. The small number of deuterium nuclei are ignored for the present.

The system defined in this way does not have a predetermined internal energy, because the system may take energy from, or reject energy into, the photon heat bath. This is what the reaction (7) does. The internal energy is determined by the position of the equilibrium, i.e. the equilibrium electron (and hence hydrogen) density.

The method for determining the equilibrium position of a system which has temperature and volume constrained is by minimisation of the Helmholtz free energy. In general, the Helmholtz free energy changes as follows;

$$dF = \left(\frac{\partial F}{\partial N}\right)_{V,T} dN + \left(\frac{\partial F}{\partial V}\right)_{N,T} dV + \left(\frac{\partial F}{\partial T}\right)_{V,N} dT \tag{10}$$

where the partial derivatives of the free energy, F, are the important quantities,

Chemical Potential: $$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \tag{11}$$

Pressure: $$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} \tag{12}$$

Entropy (dimensionless): $$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N} , \qquad \tau = k_B T \tag{13a}$$

Entropy (conventional): $$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k_B \sigma \tag{13b}$$

So that the change in free energy is written in more familiar form as,

$$dF = \mu dN - PdV - SdT \tag{14}$$

In passing, we note that the change of the internal energy of a system is generally,

$$\Delta U = \Delta Q + \Delta W + \Delta W_c \tag{15}$$

where the three terms on the RHS represent the heat <u>input</u> to the system, the mechanical work done <u>on</u> the system, and the chemical work done <u>on</u> the system. In the case of reversible changes this may be written,

$$dU = TdS - PdV + \mu dN \qquad (16)$$

and we identify, for reversible changes,

$$TdS = \text{the heat added to the system} \qquad (17)$$
$$PdV = \text{the work done by the system} \qquad (18)$$
$$\mu dN = \text{the chemical work done on the system} \qquad (19)$$

we note that the difference between internal energy, (16), and free energy, (14), is the replacement of TdS (heat input) in the former by –SdT in the latter. Consequently we have the following relation between internal energy and free energy,

$$F = U - TS \qquad (20)$$

The utility of the free energy lies in two properties:-

1) The free energy is related to the partition function by,

$$F = -k_B T \log Z \quad \textit{or equivalently} \quad Z = e^{-F/k_B T} \qquad (21)$$

where,
$$Z \equiv \sum_{\text{states,s}} e^{-\varepsilon_s / k_B T} \qquad (22)$$

2) The free energy is a minimum at equilibrium for systems held at constant temperature and constant volume.

Equ.(21) can be seen to be consistent with (20) by differentiating the latter with respect to temperature and using the relation between internal energy and the partition function, i.e.,

$$T\left(\frac{\partial F}{\partial T}\right)_{V,N} = -TS = -k_B T \log Z - \frac{\sum_{\text{states,s}} \varepsilon_s e^{-\varepsilon_s / k_B T}}{Z} = F - U \qquad (23)$$

(using Equ.13b), i.e. as per (20).

The property that the free energy is minimum for the most probable state (i.e. in equilibrium) is established as follows. Call the internal energy of the system U_s, and the total energy of the system and reservoir U (a constant). The energy of the reservoir, U_r, is thus such that $dU_s + dU_r = 0$. The total entropy of the system plus reservoir can thus be written as a function of energy as,

$$\sigma_s(U_s) + \sigma_r(U_r = U - U_s) = \sigma_s(U_s) + \sigma_r(U) - \frac{\partial \sigma_r}{\partial U} U_s \qquad (24)$$

because the energy of the system is very small compared with that of the reservoir. Recalling that the derivative of entropy with respect to energy is the definition of (reciprocal) temperature, and using (20) to substitute for the system’s entropy, (24) becomes,

$$\sigma_s(U_s)+\sigma_r(U_r)=\frac{U_s-F_s}{k_BT}+\sigma_r(U)-\frac{U_s}{k_BT}=\frac{-F_s}{k_BT}+\sigma_r(U) \qquad (25)$$

The last term (the entropy of the reservoir if it had all the energy) is just a constant. The most probable (equilibrium) configuration is the value of energy U_s which maximises the total entropy, and hence from (25) minimises the free energy, as claimed.

Being equipped with the theoretical tools, we are now in a position to start the calculation of the equilibrium free electron density. Firstly we note from (10) that, for changes at constant temperature and constant volume, the change in free energy is just,

Constant T and V: $$dF=\left(\frac{\partial F}{\partial N}\right)_{V,T}dN \qquad (26)$$

Hence, the requirement that the free energy be a minimum (dF=0) becomes,

Most probable state: $$\left(\frac{\partial F}{\partial N}\right)_{V,T}=0 \qquad (27)$$

and from (21) this requires: $$\left(\frac{\partial Z}{\partial N}\right)_{V,T}=0 \qquad (28)$$

We now need to find the partition function for our system, recalling that (22) is the basic definition. Let us label the possible one-electron states I_e, with corresponding (one electron) energies $E_e(I_e)$. The protons and hydrogen atom states/energies are similarly labelled. The state of the whole system requires specification of the states of each of the N_e^{free} electrons, N_e^{free} protons and N_p - N_e^{free} hydrogen atoms. The probability of this state is the product of the probabilities of the state of N_e^{free} electrons, N_e^{free} protons and N_p - N_e^{free} hydrogen atoms, i.e. $P_e(N_e^{free})P_p(N_e^{free})P_H(N_p-N_e^{free})$.

Considering a state in which the electrons have energies ε_1, ε_2, ε_3,… the probability of the N_e^{free} electron state is proportional to,

$$P_e(N_e^{free})=e^{-\varepsilon_1/k_BT}e^{-\varepsilon_2/k_BT}e^{-\varepsilon_3/k_BT}......etc \qquad (29)$$

Specifically, (29) is the contribution to the partition function for the multi-electron state. More accurately, the contribution to the overall partition function is given by the product of (29) with similar expressions for a given state of the multi-proton and multi-hydrogen systems. Thus, the partition function for our system is,

$$\tilde{Z} = \sum_{I_e}\sum_{I_p}\sum_{I_H} \left(e^{-\varepsilon^e_1/k_BT} e^{-\varepsilon^e_2/k_BT} e^{-\varepsilon^e_3/k_BT} ..... \right) . \left(e^{-\varepsilon^p_1/k_BT} e^{-\varepsilon^p_2/k_BT} e^{-\varepsilon^p_3/k_BT} ..... \right) \left(e^{-\varepsilon^H_1/k_BT} e^{-\varepsilon^H_2/k_BT} e^{-\varepsilon^H_3/k_BT} ..... \right)$$

where the sum over electron states sums over all possible single-electron states I_e of the first electron, and all possible single-electron states I_e of the second electron, etc., and the same for the protons and hydrogen atoms. Hence we can re-write the above as,

$$\tilde{Z} = \left(\sum_{I_e} e^{-\varepsilon^e_{I_e}/k_BT} \right)^{N_e^{free}} \left(\sum_{I_P} e^{-\varepsilon^p_{I_p}/k_BT} \right)^{N_e^{free}} \left(\sum_{I_H} e^{-\varepsilon^H_{I_H}/k_BT} \right)^{N_p - N_e^{free}} \qquad (30)$$

Recalling that the partition function for a one-electron system is,

$$Z_e = \sum_{I_e} e^{-\varepsilon_{I_e}/k_BT} \qquad (31)$$

and similarly for one proton and one hydrogen atom systems, (30) becomes simply,

$$\tilde{Z} = Z_e^{N_e^{free}} Z_p^{N_e^{free}} Z_H^{N_p - N_e^{free}} \qquad (32)$$

This would be the partition function for our multi-particle system were it not for one error. Implicit within the enumeration of states in (30) is that the electrons are distinguishable. In reality there is no distinction between a state in which electron 1 has energy E and electron 2 has energy E' and vice-versa. For the N_e^{free} electron system we have therefore over-counted the electron states by a factor of $N_e^{free}!$ The same is true of the proton and hydrogen atom states. Hence, the partition function for our system is actually,

$$Z = \frac{Z_e^{N_e^{free}}}{N_e^{free}!} \frac{Z_p^{N_e^{free}}}{N_e^{free}!} \frac{Z_H^{N_p - N_e^{free}}}{\left(N_p - N_e^{free}\right)!} \qquad (33)$$

We can now apply the equilibrium condition, Equ.(28). (We shall also drop the superscript 'free' on the electron number). Hence we get by equating the derivative of (33) with respect to N_e to zero, recalling that N_p is the constant total number of protons (free + hydrogen), and using the Stirling approximation $\log N! \approx N \log N - N$,

$$\frac{N_e^2}{N_p - N_e} = \frac{Z_e Z_p}{Z_H} \qquad (34)$$

Equ.(34) provides the basis for finding the equilibrium electron density in terms of the partition functions for one-particle states. The latter is,

$$Z_e = \frac{VN_s}{2\pi^2}\int_0^\infty k^2 dk e^{-\varepsilon_k / k_B T} = \frac{VN_s}{2\pi^2\hbar^3}\int_0^\infty p^2 dp e^{-\varepsilon_p / k_B T} \qquad (35)$$

We note that we are safely in the non-relativistic regime, the typical thermal energies being <1eV (compared to the electron mass of 0.511MeV). Hence, energies are given by,

$$\varepsilon_p = mc^2 + \frac{p^2}{2m} \qquad (36)$$

where m is the mass of the electron, proton or hydrogen atom, as required. For the electron and the proton, the number of spin states, N_s, is 2. For the hydrogen atom we are considering the orbital state to be 1S, i.e. the ground state (it is this state that the 13.6eV ionisation potential relates to). However, there are two distinct spectral lines, split by the hyperfine coupling between the electron and proton spins. The lowest energy state is the spin singlet state (spin quantum number zero), but the spin triplet state (spin quantum number 1) has almost the same energy. Hence, hydrogen with n = 1, L = 0 has four spin states, $N_s = 4$.

Substituting (36) and also $x = \sqrt{2mk_B T}$ into (35) gives,

$$Z_e = \frac{N_s V}{2\pi^2\hbar^3}(2mk_B T)^{3/2} e^{-mc^2/k_B T}\int_0^\infty x^2 e^{-x^2 dx} = \frac{V}{\pi^2\hbar^3}(2mk_B T)^{3/2} e^{-mc^2/k_B T}.\frac{\sqrt{\pi}}{4} \qquad (37)$$

and Z_p is the same with the electron mass, m, replaced by the proton mass, M. Similarly, Z_H is the same with m replaced by the hydrogen atom mass, M_H, and also multiplied by an additional factor of 2 because of the four spins states rather than just two.

Equ.(34) therefore gives,

$$\frac{y^2}{1-y} = \frac{(2\pi m k_B T)^{3/2}}{(2\pi\hbar)^3 N_p} e^{-\chi/k_B T} \qquad (38)$$

where $y = N_e/N_p$ is the ratio of electron density to the total proton density (these numbers being interpreted as densities because we have replaced V with unit volume). Note that we have replaced the mass difference $m + M - M_H$ with the recombination potential, χ (13.6eV) – noting that the sign is correct, i.e. the hydrogen atom is lighter than the sum of the electron and proton masses.

Equ.(38) is known as the Saha equation. It is merely the expression of the minimisation of the free energy for this system, i.e. equilibrium.

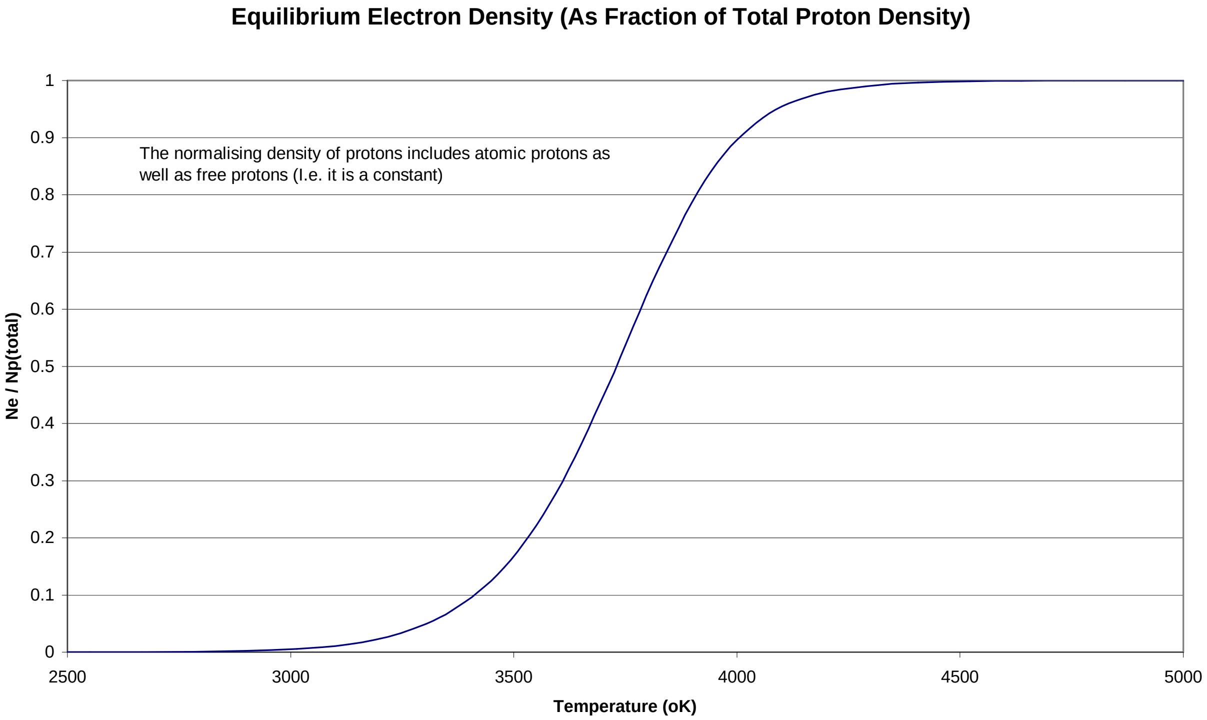
The rather surprising presence of the electron mass in Equ.(38) may be traced to the density of electron quantum states in k-space, (35), when coupled with the non-relativistic expression for kinetic energy, (36). The latter shows that, the larger is the electron mass, the smaller are the increments of energy between neighbouring states in k-space. Thus, larger m corresponds to a greater number of available one-particle states for a given energy interval. Hence, the greater predicted free electron density for larger masses, m, is a consequence of the greater number of available states resulting in a many electron system being more probable.

Why does the proton mass not appear in (38)? The reason is that, in (34), the ratio Z_p/Z_H occurs, which would lead to a factor $(M/M_H)^{3/2}$ in (38), but this is unity to an accuracy of about 0.05%. In other words, the density of states for the protons is essentially the same as the density of states for the hydrogen atoms. This issue is therefore balanced as regards the reaction $e + p \Leftrightarrow H + \gamma$. The phase-space factor favours the left hand side of this reaction because there are clearly far more two particle states (e plus p) than one particle states (H, recalling that the photon distribution is given).

Equ.(38) gives our prediction for the absolute electron density, recalling that Equs.(8) and (9) specify N_p. Making these substitutions gives,

$$\frac{y^2}{1-y} = 5.7\text{x}10^8 \left(\frac{mc^2}{k_B T}\right)^{3/2} e^{-\chi/k_B T} \tag{39}$$

Note that (39) has no dependence upon Planck’s constant. The value of $y = N_e/N_p$ is plotted against temperature below (using χ = 13.6eV),



Temperature can be translated into time using $T\sqrt{t} = 1.038 \times 10^{10}$. Thus, we find that 99% of the electrons are still free at a temperature of 4290°K (kT = 0.37eV), i.e. a time of ~185,000 years, but when the temperature has dropped to 3070°K (kT = 0.265eV), at time 363,000 years, there are just 1% of the electrons left. The recombination is not as rapid as some authors seem to imply, the age of the universe being about double at the ‘end’ (1%) compared with at the ‘beginning’ (99%). [NB:

In the preceding, “99% of electrons remaining” is with respect to the number of free electrons immediately prior to hydrogen recombination, i.e. after helium recombination]. We note that the temperature range over which recombination occurs is in very good agreement with the prediction at the end of Section 3.

4.2 Time and Temperatures for Atomic Helium Formation

We confine attention to the capture of the last electron that makes a neutral atom. Both lithium and helium will have captured the earlier electrons at much higher temperatures. On the basis of the crude scoping estimates of Section 3 we may anticipate that capture of the final electrons by helium and lithium will be at widely different temperatures, and also far from the 3,000°K – 4,300°K at which hydrogen recombines. So long as this turns out to be true, we can treat each in isolation from the others. The approach for each is the same as for hydrogen. Consider helium-4 firstly. The reaction in question is,

$$\mathrm{e} + \mathrm{He4}^{+} \Leftrightarrow \mathrm{He4} + \gamma \tag{40}$$

The number of helium-4 nuclei, whether as part of neutral atoms or as ions, is constant and equals 7.7% of the fraction $1/1.9\mathrm{x}10^{9}$ times the photon density given by Equ.(9). That is,

$$N_{He4} = 9.9x10^{-12}\left(\frac{k_B T}{\hbar c}\right)^3 \tag{41}$$

The number of helium-4 ions, denoted N_+, starts equal to N_{He4} and reduces to zero. Hence, in this case it is the ratio $y = N_+/N_{He4}$ that is of interest (starting at 1 and reducing to zero).

We cannot just use the same Saha equation as for hydrogen because the number of electrons does not equal the number of He4 ions, i.e. this differs from the hydrogen case for which the number of free electrons equalled the number of free protons. In this case only a small proportion of the electrons are used up by helium neutralisation, since most will still be left over for the later hydrogen recombination.

The total baryon number is $N_b = N_\gamma/1.9\mathrm{x}10^9$. Hence the total number of protons, whether as atoms or ions, is $N_p = 0.875N_b$ (since neutrons account for 12.5% of the baryons). The total number of electrons in all forms equals N_p. Now the helium nuclei have already captured one electron. This accounts for ~7.1% of the electrons, leaving the number of free electrons before helium recombination as $N_{e0} = 0.929N_p = 0.813N_b = 1.04\mathrm{x}10^{-10}\left(\frac{\mathrm{k_B T}}{\hbar \mathrm{c}}\right)^3$. After helium recombination is complete, the final number of free electrons is $N_{e1} = N_{e0} - N_{He4} = 0.96\mathrm{x}10^{-10}\left(\frac{\mathrm{k_B T}}{\hbar \mathrm{c}}\right)^3$. At an intermediate stage the number of free electrons is $N_e = N_{e1} + N_+$, where N_+ is the number of helium-4 ions. The number of helium ions, N_+, is the appropriate variable with respect to which the free energy should be minimised.

Thus, by the same method as lead to Equ.(33) we find,

$$Z = \frac{Z_e^{N_{e1}+N_+}}{(N_{e1}+N_+)!}\frac{Z_+^{N_+}}{N_+!}\frac{Z_a^{N_{He4}-N_+}}{(N_{He4}-N_+)!} \tag{42}$$

where the subscript $_+$ refers to the helium ions, and the subscript $_a$ to helium atoms. Recalling that N_{e1} and N_{He4} are constants, we may now find the stationary point of logZ with respect to variation in the ion number, N_+ (using the Stirling approximation $\log N! \approx N\log N - N$), thus,

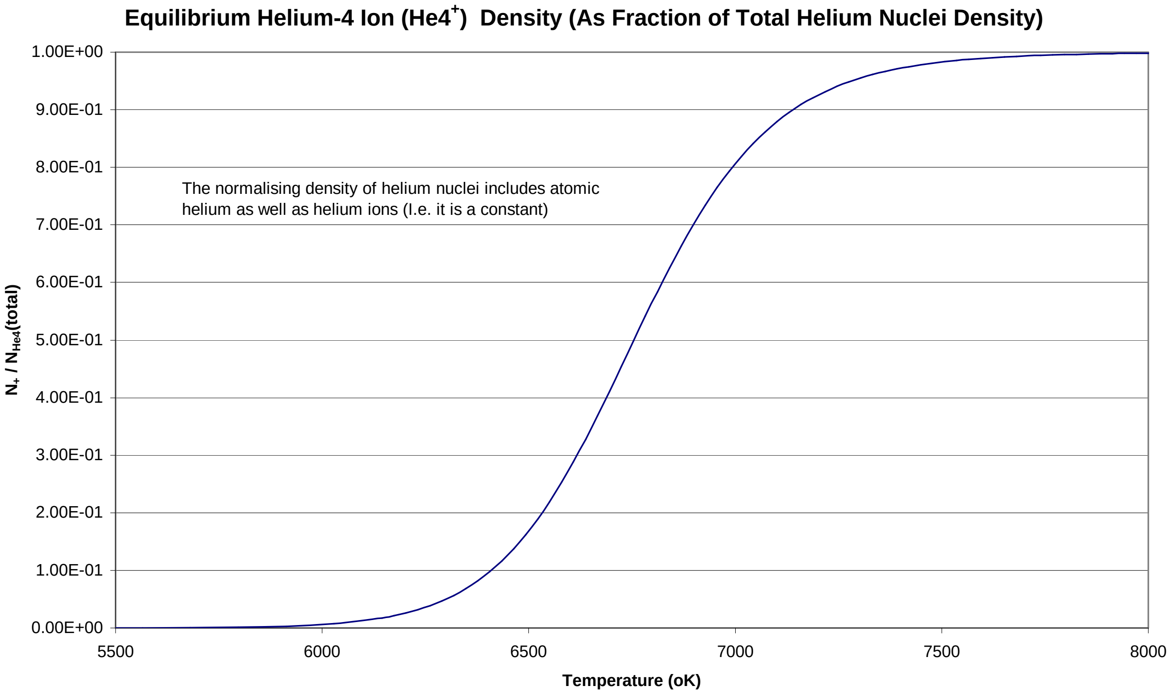
$$\frac{N_+(N_{e1}+N_+)}{N_{He4}-N_+} = \frac{Z_e Z_+}{Z_a} \tag{43}$$

Now N_+ is at most ~8% of N_{e1}, and so (unlike the hydrogen case) we may linearise this equation. In terms of the ratio $y = N_+/N_{He4}$ it becomes,

$$\frac{y}{1-y} = \frac{Z_e Z_+}{Z_a N_{e1}} \tag{44}$$

The evaluation of the single particle partition functions is identical to previously except for the spin states. In particular, the factor of the helium ion mass divided by the helium atom mass is essentially unity. On the other hand, the helium ion mass plus the electron mass minus the helium atom mass, which occurs in the exponent, is replaced by the recombination potential (χ = 24.6eV in this case). As regards the spin states, for hydrogen we had two spin states for the proton but four for the hydrogen atom, due to the ground state electron combining as a singlet or a triplet spin state with the nuclear (proton) spin. Hence, this gave a contribution to Z_p/Z_H of a factor of 2/4 =1/2. In contrast, in this case we have a zero-spin helium-4 nucleus together with a zero spin pair of ground state electrons (the electron spins must be anti-aligned, i.e. a singlet state, by the exclusion principle). Hence the spin factor for Za is unity. However, the helium-4 ion, having only a single electron, is a spin half particle, and hence there is a factor of two contribution to Z_+. Thus, there is a factor of four on the RHS compared with the hydrogen case, i.e.,

$$\frac{y}{1-y} = 4\frac{(2\pi m k_B T)^{3/2}}{(2\pi\hbar)^3 N_{e1}} e^{-\chi/k_B T} \tag{45}$$



Temperature can be translated into time using T√t = 1.038 x 10^{10}. Thus, we find that 99% of the helium-4 is still ionised at a temperature of 7620^oK (kT = 0.658), i.e. a time of ~59,000 years, but when the temperature has dropped to 6030^oK (kT = 0.52), at time ~94,000 years, there are just 1% of the helium ions left. From Section 4.1, the corresponding temperatures for hydrogen are 4290^oK and 3070^oK respectively, which occur in the epoch 185,000 to 363,000 years. Hence there is no overlap in time (or temperature) between the period when helium is recombining and the period when hydrogen is recombining, justifying our initial assumption to treat the two recombinations separately.

4.3 Atomic Lithium Recombination

We now turn to the recombination of lithium. We are not concerned with the early capture of the two S-shell electrons, but only with the capture of the third and last electron, which forms the neutral lithium atom. Recall that the nucleus in question is lithium-7 (3 protons, 4 neutrons). From the rough estimates of Section 3, we expect neutral atomic lithium to form only at much lower temperatures than both helium and hydrogen, perhaps around $1{,}000^o$K. The reaction in question, whose equilibrium we seek to establish at any given temperature, is,

$$e + Li_7^+ \Leftrightarrow Li_7 + \gamma \qquad (46)$$

The analysis is essentially the same as that for hydrogen, but different from that for helium. Denoting the electron density by N_e, we note that this must equal the number of lithium ions, N_{ions}. This is the direct equivalent of the position for hydrogen, in which the number of electrons was equated to the number of protons. (Note that we were entitled to equate the two for the hydrogen reaction only because the number of excess electrons, i.e. those left over for eventual neutralisation of the lithium ions, is such a very small fraction of the original number of free protons). The initial number of lithium ions (which equals the final number of neutral lithium atoms), N_{ions}^0, is known, namely a fraction ~2 x 10^{-8} times the number of baryons, and hence ~ 10^{-17} times the number of photons. Hence,

$$N_e = N_{ions} \quad \textit{and} \quad N_{Li} = N_{ions}^0 - N_{ions} \quad \textit{and} \quad N_{ions}^0 \approx 2x10^{-8} N_B \approx 10^{-17} N_\gamma \tag{47}$$

where N_{Li} is the number of neutral lithium atoms at any specified temperature. Using the same approach as for hydrogen we thus find the total partition function to be,

$$Z = \frac{Z_e^{N_e}}{N_e!} \frac{Z_{ions}^{N_e}}{N_e!} \frac{Z_{Li}^{N_{ions}^0 - N_e}}{\left(N_{ions}^0 - N_e\right)!} \tag{48}$$

The number of remaining free electrons is the only degree of freedom, with respect to which the free energy is minimised (Z is maximised), i.e. the equilibrium condition Equ.(28) applies. Hence we get, as before,

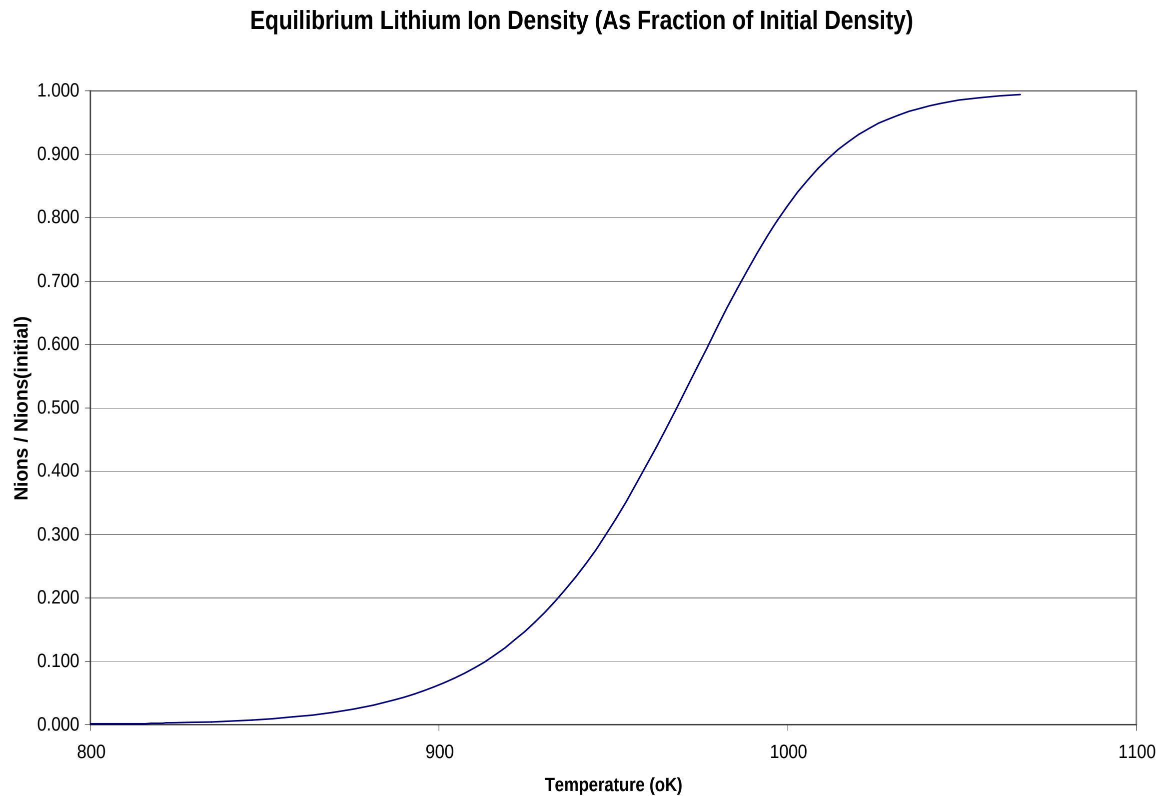
$$\frac{N_e^2}{N_{ions} - N_e} = \frac{Z_e Z_{ions}}{Z_{Li}} \tag{49}$$

where Z_{Li} related to the neutral lithium atoms. As previously, the virtual equality of the lithium ion mass and the lithium atom mass means that, from explicit expressions similar to (37), the ratio Z_{ions}/Z_{Li} is independent of the absolute lithium mass. However, dependence on the (very small) mass difference survives in the exponent in the form of the ionisation potential (which equals $m_e + M_{Li+} - M_{Li}$). The only other residual affect of the lithium partition functions in (49) is the ratio of the number of spin states.

Lithium-7 is a spin 3/2 nucleus. In the lithium ion, the two electrons form a spin zero, state with zero orbital angular momentum also. Hence, the lithium ion has four spin states (nuclear states). The neutral lithium atoms, however, has an additional valance electron, which is in an S orbital state (l=0) but has spin half. It will therefore form both a spin triplet (J = 1) state and a spin quintuplet (J = 2) state in combination with the spin 3/2 nucleus (analogous to hydrogen hyperfine splitting). Hence, a neutral lithium-7 atom has 8 spin states in total. Thus the spin state ratio contributes a factor of 4/8 = ½ to the RHS of (49), exactly the same as for the hydrogen case. Hence, the ‘Saha’ equation for lithium looks just the same as that for hydrogen except the normalising density is the original lithium ion density, N_{ions}^0, as given by (47)

$$\frac{y^2}{1-y} = \frac{(2\pi m k_B T)^{3/2}}{(2\pi\hbar)^3 N_{ions}^0} e^{-\chi/k_B T} \tag{50}$$

where $y = N_{ions} / N^0_{ions} = N_e / N^0_{ions} =$, i.e. the fraction of lithium ions left, starting at 1 and ending at 0. Hence we find,


Equilibrium Lithium Ion Density (As Fraction of Initial Density)

Temperature can be translated into time using $T\sqrt{t} = 1.038 \times 10^{10}$. (Note that this may not apply any longer to the neutral atoms, since they are now decoupled from the photon background. However, the temperature of the uncombined lithium nuclei is presumably still governed by that of the photons, even after hydrogen recombination). Thus, we find that 99% of the lithium-7 is still ionised at a temperature of 1055^oK (kT = 0.091eV), i.e. a time of ~3 million years, but when the temperature has dropped to 850^oK (kT = 0.074), at time ~4.7 million years, there are just 1% of the helium ions left. Note that these temperatures are consistent with the crude estimates of Section 2 (which implied that recombination of lithium would not occur until the temperature fell below ~$1{,}350^oK$). From Section 3.1, the corresponding temperatures for hydrogen are 4290^oK and 3070^oK respectively, which occur in the epoch 185,000 to 363,000 years. Hence there is no overlap in time (or temperature) between the period when lithium is recombining and the period when hydrogen is recombining, justifying our initial assumption to treat the two recombinations separately.

5. Summary

The results are summarised as follows, in chronological order,

Atom or Ion	1% Have Formed		99% Have Formed	
	Temperature, ^{o}K	**Time, years**	**Temperature, ^{o}K**	**Time, years**
He_4^{+}[*]	-	-	19,000	9,500
Li_7^{+}[*]	-	-	17,000	11,800
Helium-4	7,620	59,000	6,030	94,000
Hydrogen	4,290	185,000	3,070	363,000
Lithium-7	1,055	3,000,000	850	4,700,000

[*] these cases refer to the temperatures/times at which the doubly charged ions combine to form the singly charged ions, and are very approximate (obtained from the estimate of Section 3 by subtracting 2,000^{o}K).