The Saha Equation

The Saha equation gives the fraction of an element in ionization state $i+1$ compared to state i. It requires that a gas be in thermodynanmic equilibrium (at least locally), and the densities be low enough so that the mean distance between atoms is larger than the size of an orbital associated with a high energy state. For instance, in the case of the hydrogen atom, the Bohr radius of level n is

$$a_n = (n+1)^2 \frac{\hbar^2}{m_e e^2} = 5.28 \times 10^{-9} (n+1)^2 \text{ cm} \tag{1}$$

Thus, if the particle density is

$$\rho \sim \frac{m_A}{4/3\pi(2a_0)^3} \sim 0.3\,\mu \text{ g cm}^{-3} \tag{2}$$

then all the hydrogen will be *pressure ionized.* In practice, the Saha equation begins to break down at distances of $\sim 10\,a_0$, which corresponds to $\sim 2.7 \times 10^{-3}$ g-cm^{-3}.

To derive the Saha equation, we start with the Boltzmann equation, which states that the number of atoms in level i relative to level j is

$$\frac{n_i}{n_j} = \frac{\omega_i}{\omega_j} e^{-\chi_{ij}/k\,T} \tag{3}$$

where ω_i is the statistical weight of the level i (*i.e.,* the number of separate, individual states that are degenerate in energy), and χ_{ij} is the difference in energy between the two levels. The number of atoms in level i relative to the number in *all levels* is thus

$$\frac{n_i}{n} = \frac{\omega_i}{\omega_0 e^{+\chi_{i0}/kT} + \omega_1 e^{+\chi_{i1}/kT} + \omega_2 e^{+\chi_{i2}/kT} + \ldots}$$

$$= \frac{\omega_i e^{-\chi_i/kT}}{\omega_0 + \omega_1 e^{-\chi_1/kT} + \omega_2 e^{-\chi_2/kT} + \ldots}$$

$$\frac{n_i}{n} = \omega_i \, \frac{e^{-\chi_i/kT}}{u} \tag{4}$$

where χ_i is the energy difference between the i^{th} level and the ground state. The variable u is the partition function for the atom (or ion). Because u is a function of temperature, it is usually written $u(T)$.

Now let's generalize this equation to electrons in the continuum. Let n_i be the number of atoms in all levels (defined as n above), and let state $i+1$ be that where an excited electron is in the continuum with momentum between p and $p + dp$. The Boltzmann equation then gives

$$\frac{dn_{i+1}}{n_i} = \frac{d\omega_{i+1}}{u_i} \exp\left(-\frac{\chi_i + p^2/2m_e}{k\,T}\right) \tag{5}$$

where χ_i is the energy needed to ionize the ground state of the atom, and $d\omega_{i+1}$ is the statistical weight of the ionized state. Now consider that $d\omega_i$ has two components: one from the ion (ω_{i+1}), and other from the free electron ($d\omega_e$). The former is just the statistical weight of the ground state of the ion, while the latter can be computed using the exclusion rule. Since each quantum cell in phase space can have only two electrons in it (spin up and spin down), then the number of degenerate states in a volume h^3 is

$$d\omega_e = 2\,\frac{d^3x\,d^3p}{h^3} = 2\,\frac{dV\,d^3p}{h^3} = \frac{2}{h^3}\,dV\,4\pi p^2 dp \tag{6}$$

Thus

$$\frac{dn_{i+1}}{n_i} = \frac{8\pi p^2}{h^3}\,\frac{\omega_{i+1}}{u_i(T)}\,\exp\left(-\frac{\chi_i + p^2/2m_e}{k\,T}\right) dV\,dp \tag{7}$$

The number of electrons in volume $\int dV = 1/n_e$, so the total number of electrons in all continuum states is therefore

$$\frac{n_{i+1}}{n_i} = \frac{\omega_{i+1}}{u_i(T)} \frac{8\pi}{n_e h^3} e^{-\chi_i/kT} \int_0^\infty p^2 \exp\left(-\frac{p^2}{2m_e kT}\right) dp \tag{8}$$

or, if we let $x^2 = p^2/2m_e kT$, then

$$\begin{aligned}
\frac{n_{i+1}}{n_i} &= \frac{\omega_{i+1}}{u_i(T)} \frac{8\pi}{n_e h^3} e^{-\chi_i/kT} \int_0^\infty (2m_e kT)\, x^2 \, e^{-x^2} \cdot (2m_e kT)^{1/2} \, dx \\
&= \frac{\omega_{i+1}}{u_i(T)} \frac{8\pi}{n_e h^3} e^{-\chi_i/kT} (2m_e kT)^{3/2} \int_0^\infty x^2 e^{-x^2} dx \\
&= \frac{\omega_{i+1}}{u_i(T)} \frac{8\pi}{n_e h^3} e^{-\chi_i/kT} (2m_e kT)^{3/2} \cdot \frac{\sqrt{\pi}}{4}
\end{aligned}$$

$$\frac{n_{i+1}}{n_i} = \frac{2}{n_e} \frac{\omega_{i+1}}{u_i(T)} \frac{(2\pi m_e kT)^{3/2}}{h^3} e^{-\chi_i/kT} \tag{9}$$

Finally, note that for the calculation above n_{i+1} represents those atoms of species n_i that have one electron in the continuum state, *i.e.,* ionized. It does not consider atoms of n_{i+1} that are themselves excited. (In other words, n_{i+1} in (9) only includes ionized atoms in their ground state.) To include all the excited states of n_{i+1}, we must again sum the contributions in exactly the same way as we did in (4). Thus, the statistical weight in (9) should be replaced by the partition function, and

$$\frac{n_{i+1}}{n_i} = \frac{2}{n_e} \frac{u_{i+1}(T)}{u_i(T)} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-\chi_i/kT} \tag{10}$$

This is the Saha equation, which relates the number of atoms in ionization state $i+1$ to the number in ionization state i. Note that if need be, we can substitute the electron pressure for the electron density using $P_e = n_e kT$, and write the Saha equation as

$$\frac{n_{i+1}}{n_i}\,P_e = 2\,\frac{u_{i+1}(T)}{u_i(T)}\,\left(\frac{2\pi m_e}{h^2}\right)^{3/2}\,(k\,T)^{5/2}\,e^{-\chi_i/kT} \qquad (11)$$

The sense of these equations is intuitive: the higher the temperature, the greater the ratio, but the higher the density (or pressure), the lower the ratio due to the greater possibility for recombinations).