4. Reaction equilibria

4.1 The Saha equation

If particles and radiation are in equilibrium with themselves and each other, we call their state Thermodynamic Equilibrium, and the spectra are given by a Planckian for the radiation and a Fermi distribution (a Maxwellian if the density is not too high) for the particles. If the particles are only in equilibrium with themselves, but not with the radiation, we speak of Local Thermodynamic Equilibrium (LTE), in which the radiation spectrum is not a priori known, but the particle spectrum is still a Fermi, resp. a Maxwellian, distribution.

In Local Thermodynamic Equilibrium the distribution of atoms with ionization state i over the various energy states m is proportional to $\exp(-\chi_{i,m}/kT)$, where $\chi_{i,m}$ is the excitation energy of state m relative to the ground state. Then

$$\frac{N_{i,m}}{N_{i,1}} = \frac{g_{i,m}}{g_{i,1}} \ \exp(-\frac{\chi_{i,m}}{kT}) \tag{4.1}$$

where $g_{i,m}$ are the statistical weights of state (i,m), that is the number of independent arrangements of the atomic electrons that give the same ionization state and energy level. After summing over all m we find

$$N_i = \sum_m \ N_{i,m} = \frac{N_{i,1}}{g_{i,1}} \sum_m N_{i,m} \ g_{i,m} \ \exp(-\frac{\chi_{i,m}}{kT}) = \frac{N_{i,1}}{g_{i,1}} \, u_i(T) \tag{4.2}$$

$$\Rightarrow \qquad \frac{N_{i,m}}{N_i} = \frac{g_{i,m}}{u_i(T)} \ \exp(-\frac{\chi_{i,m}}{kT}) \qquad \text{where} \quad u_i(T) = \sum_m g_{i,m} \ \exp(-\frac{\chi_{i,m}}{kT}) \tag{4.3}$$

is called the *level partition function*. We can extend this treatment to the continuity of states with positive energy, that means ionizations. We then have to consider the free electron that is liberated during the ionization, because it is part of the initial atom. The free electron no longer has discrete energy levels, but a continuum of states limited only by Pauli's principle and Heisenberg uncertainty relation, so we have to use differentials and state densities. We thus derive for the ratio of singly ionized atoms to neutral, both in ground state,

$$\frac{dN_{1,1}}{N_{0,1}} = 2\,\frac{g_{1,1}}{g_{0,1}} \ \exp(-\frac{\chi_0 + \frac{p^2}{2m_e}}{kT}) \ \frac{d^3x \, d^3p}{h^3} \tag{4.4}$$

where the factor 2 takes care of the two independent spin positions of a free electron. Integrating over momentum we derive

$$\frac{dN_{1,1}}{N_{0,1}} = 2\,\frac{g_{1,1}}{g_{0,1}} \ (2\pi \, m_e \, kT)^{3/2} \ \exp(-\frac{\chi_0}{kT}) \ \frac{d^3x}{h^3} \tag{4.5}$$

The electron shares the available volume with all electrons, and thus $d^3x = n_e^{-1}$. Hence we finally derive the *Saha* equation that, using the level partition sums, can be written as an equation for the ionization equilibrium.

$$\frac{N_{1,1}}{N_{0,1}}\, n_e = 2\,\frac{g_{1,1}}{g_{0,1}}\;\frac{(2\pi\, m_e\, kT)^{3/2}}{h^3}\;\;\exp(-\frac{\chi_0}{kT}) \tag{4.6}$$

$$\frac{N_{i+1}}{N_i}\, n_e = 2\,\frac{u_{i+1}}{u_i}\;\frac{(2\pi\, m_e\, kT)^{3/2}}{h^3}\;\;\exp(-\frac{\chi_i}{kT}) \tag{4.7}$$

The density of electrons is determined by the density of ionized atoms, of course. In the statistical sense, the Boltzmann (exponential) factor preferes the bound state, whereas the large phase space volume available to a free electron favors the ionized state. Let us see what we obtain for the ionization fraction of hydrogen in the solar photosphere, where

$$\chi = 13.6\ \mathrm{eV} \qquad T_{\mathrm{ion}} = \frac{\chi}{k} \simeq 160.000\ \mathrm{K} \qquad T_{\mathrm{gas}} \simeq 6.000\ \mathrm{K} \qquad n_H \simeq 10^{17}\ \mathrm{cm}^{-3} \tag{4.8}$$

So the actual gas temperature is much smaller than the temperature equivalent of the ionization energy. Naively one would expect a very low ionization fraction of hydrogen in the solar photosphere. Hydrogen is the dominating element, hence the electron density should be related to the hydrogen density by

$$n_e = \frac{N_{i+1}}{N_i + N_{i+1}}\, n_H \tag{4.9}$$

The ratio of level partition sums is approximately 0.5, because the first excited level of atomic hydrogen is high compared with the thermal energy. Inserting the numbers into Saha's equation then gives the ionization fraction

$$\xi = \frac{N_{i+1}}{N_i + N_{i+1}} \qquad \Rightarrow \qquad \frac{\xi^2}{1-\xi} \approx 10^{-7} \qquad \Rightarrow \qquad \xi \simeq 3 \cdot 10^{-4} \tag{4.10}$$

A slightly hotter star with photospheric temperature $T_* = 12.000$ K of the *same* photospheric gas density would have an ionization fraction $\xi(T_* = 12.000\ \mathrm{K}) \simeq 0.3$, much higher than what the ionisation energy would suggest.

4.2 General statistical equilibrium

The *Saha* equation works well, if the density is high enough, for example in the photosphere of the sun. It is inappropriate in lower-density media like the interstellar medium. Instead of the detailed equilibrium, we may find a stationary state in the statistical sense, such that gains and losses balance each other for all energy states. It would then be necessary to consider the various atomic processes, such as photoionization and radiative recombination (with rate R) or collisional excitation and three-body recombination (with rate C).

$$N_i\,(R_{i,i+1} + C_{i,i+1}) = N_{i+1}\,(R_{i+1,i} + C_{i+1,i}) \tag{4.11}$$

These transition rates depend on the density of free electrons and on the intensity of the ambient photon field.

$$N_i\,(J\,P_{i,i+1} + n_e Q_{i,i+1}) = N_{i+1}\,(n_e P_{i+1,i} + n_e^2 Q_{i+1,i}) \tag{4.12}$$

and so does the occupation of the ionization states. The three-body recombination is usually negligible on account of the low density.
Near a star-forming region in a galaxy the intensity of optical-to-UV photons is probably very high, for the volume density of luminous hot stars is high. In that case photoionization (the first term on the LHS of 4.12) likely dominates over collisional excitation (the second term). We then expect

$$\frac{N_{i+1}}{N_i}\,n_e = \frac{J\,P_{i,i+1}}{P_{i+1,i}} \tag{4.13}$$

Near a young massive star the RHS of Eq.4.14 is much larger than unity, so the star will ionize its surroundings and thus destroy the cold molecular gas clouds in which it formed. The intensity of ionizing radiation will fall of not only with the inverse square of the distance to the star, but also on account of the photoionization which from the standpoint of the photon is an absorption process (photoelectric absorption). Short of calculating how exactly the ionization eats through the neutral gas in what is called an ionization front, we can estimate the size of the final region of ionized gas, called an HII-region (the roman numeral indicates the ionization state of the element starting with "I" for neutral, "II" for singly ionized, etc.). In an equilibrium situation the total rate of ionization inside the HII-region of radius R and density of free electrons, n_e, equals the production rate of ionizing photons by the central star, L^*. The total rate of recombination must be identical to that:

$$\frac{4\pi}{3}\,R^3\,n_e\,n_{HII}\;P_{HII,HI} \simeq \frac{4\pi}{3}\,R^3\,n_e^2\;P_{HII,HI} = \alpha = L^* \quad \rightarrow\; R \simeq \left(\frac{3\,L^*}{4\pi\,n_e^2\;P_{HII,HI}}\right)^{1/3} \tag{4.14}$$

The final bubble of ionized gas blown by a star is called Strömgren sphere. The Strömgren sphere of our sun is only about 50 Pluto orbits in size, but very massive stars can singlehandedly ionize a thousand solar masses worth of interstellar gas. Far from hot stars, e.g. in the galactic halo, photoionization probably plays a negligible role. Then

$$\frac{N_{i+1}}{N_i} = \frac{Q_{i,i+1}}{P_{i+1,i}} \tag{4.15}$$

Apparently we can expect different lines to be prominent in these two cases. One can therefore use the intensity ratios of characteristic lines to infer the electron density and the intensity of ionizing or exciting photon field.