Chapter 14
Ionization

In Sect. 4.2 and Chap. 13 we assumed complete ionization of all atoms. This is a good approximation in the very deep interior, where T and P are sufficiently large, but the degree of ionization certainly becomes smaller if one approaches the stellar surface, where T and P are small. In the atmosphere of the Sun, for instance, hydrogen and helium atoms are neutral. When a gas is partially ionized the mean molecular weight and thermodynamic properties such as c_P depend on the degree of ionization. It is the aim of this section to show how this can be calculated and how it influences the properties of the stellar gas.

14.1 The Boltzmann and Saha Formulae

We consider the atoms of a chemical element in a certain state of ionization, contained in a unit volume of gas in thermodynamic equilibrium. They are distributed over many states of excitation, which we denote by subscript s, and these different states can be degenerate such that the state of number s consists in reality of g_s substates. The number g_s is the *statistical weight*. Consider in particular the atoms of a certain element in state s and in the ground state $s = 0$, separated by the energy difference ψ_s, and the transition between both, say, by emission and absorption of photons. In equilibrium, the rate of such upward transitions is equal to that of downward transitions. This gives as the ratio between the numbers of atoms in the two states:

$$\frac{n_s}{n_0} = \frac{g_s}{g_0}\,\mathrm{e}^{-\psi_s/kT}. \qquad (14.1)$$

Equation (14.1) is the well-known *Boltzmann formula*, which governs the distribution of particles over states of different energy.

Instead of referring to the atoms in the ground state, we want to compare the atoms of state s with the number n of *all* atoms of that element:

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$$n = \sum_s n_s \ . \tag{14.2}$$

From (14.1), multiplication by g_0 and summation over all states leads to

$$g_0 \frac{n}{n_0} = g_0 \sum_{s=0}^{\infty} \frac{n_s}{n_0} = g_0 + g_1 \, \mathrm{e}^{-\psi_1/kT} + g_2 \, \mathrm{e}^{-\psi_2/kT} + \ldots := u_\mathrm{p} \ , \tag{14.3}$$

where $u_\mathrm{p} = u_\mathrm{p}(T)$ is the so-called *partition function*. From (14.1) and (14.3) we obtain the Boltzmann formula in the form

$$\frac{n_s}{n} = \frac{g_s}{u_\mathrm{p}} \, \mathrm{e}^{-\psi_s/kT} \ . \tag{14.4}$$

We can also use the Boltzmann formula to determine the degree of ionization, but there are differences between excitation and ionization that require attention. Excitation concerns ions and bound electrons distributed over *discrete* states only. In the case of ionization the upper state consists of two separate particles, the ion and the electron; and the free electron has a *continuous* manifold of states. After ionization, say by absorption, the electron "thrown out" can have an arbitrary amount of kinetic energy, and recombination can occur with electrons of arbitrary kinetic energy.

We say an atom is in the rth state of ionization if it has already lost r electrons. The energy necessary to take away the next electron from the ground state is χ_r. After ionization this electron is in general not at rest, but has a momentum relative to the atom of absolute value p_e. Then $p_\mathrm{e}^2/(2m_\mathrm{e})$ is its kinetic energy; therefore relative to its original bound state the free electron has the energy $\chi_r + p_\mathrm{e}^2/(2m_\mathrm{e})$, while the state of ionization of the atom is now $r + 1$.

Let us consider as the lower state an r-times ionized ion in the ground state. The upper state may be that of the $(r + 1)$ times ionized ion plus the free electron with momentum in the interval $[p_\mathrm{e}, p_\mathrm{e} + dp_\mathrm{e}]$. The number densities of ions in these two states are n_r and dn_{r+1}. The statistical weight of the upper state is the product of g_{r+1} of the ion and of $dg(p_\mathrm{e})$, the statistical weight of the free electron. Transitions upwards and downwards occur between the two states with equal rates. In the case of thermodynamic equilibrium the Boltzmann formula (14.1) applies and gives

$$\frac{dn_{r+1}}{n_r} = \frac{g_{r+1} dg(p_\mathrm{e})}{g_r} \exp\left(-\frac{\chi_r + p_\mathrm{e}^2/(2m_\mathrm{e})}{kT} \right) . \tag{14.5}$$

What is the statistical weight $dg(p_\mathrm{e})$ of the electron in the momentum interval $[p_\mathrm{e}, p_\mathrm{e} + dp_\mathrm{e}]$? The Pauli principle of quantum mechanics tells us that in phase space a cell of volume $dq_1 \, dq_2 \, dq_3 \, dp_1 \, dp_2 \, dp_3 = dV \, d^3p$ can contain up to $2dV \, d^3p/h^3$ electrons, namely up to two electrons per quantum cell of volume h^3. Here the q's and the p's are the space and momentum variables of the (six-dimensional) phase space, while dV and d^3p are the (three-dimensional) "volumes" and h is the *Planck constant* ($h = 6.62620 \times 10^{-27}$ erg s). Then

$$dg(p_\mathrm{e}) = \frac{2\,dV\,d^3p_\mathrm{e}}{h^3}\ . \tag{14.6}$$

If the electron density in (three-dimensional) space is n_e then per electron the volume $dV = 1/n_\mathrm{e}$ is available, while the volume in (three-dimensional) momentum space containing all points belonging to the interval $[p_\mathrm{e}, p_\mathrm{e} + dp_\mathrm{e}]$ is $d^3p_\mathrm{e} = 4\pi p_\mathrm{e}^2 dp_\mathrm{e}$, since all these points are on a spherical shell of radius p_e and thickness dp_e. We then have

$$dg(p_\mathrm{e}) = \frac{8\pi p_\mathrm{e}^2 dp_\mathrm{e}}{n_\mathrm{e}h^3} \tag{14.7}$$

and (14.5) yields

$$\frac{dn_{r+1}}{n_r} = \frac{g_{r+1}}{g_r}\frac{8\pi p_\mathrm{e}^2 dp_\mathrm{e}}{n_\mathrm{e}h^3}\exp\left(-\frac{\chi_r + p_\mathrm{e}^2/(2m_\mathrm{e})}{kT}\right)\ . \tag{14.8}$$

All upper states (ions of degree $r + 1$ in the ground state and free electrons of all momenta) are then obtained by integration over p_e:

$$\frac{n_{r+1}}{n_r} = \frac{g_{r+1}}{g_r}\frac{8\pi}{n_\mathrm{e}h^3}\,\mathrm{e}^{-\chi_r/kT}\int_0^\infty p_\mathrm{e}^2\exp\left(-\frac{p_\mathrm{e}^2}{2m_\mathrm{e}kT}\right)dp_\mathrm{e}\ . \tag{14.9}$$

Since for $a > 0$

$$\int_0^\infty x^2\mathrm{e}^{-a^2x^2}dx = \frac{\sqrt{\pi}}{4a^3}\ , \tag{14.10}$$

we obtain

$$\frac{n_{r+1}}{n_r}n_\mathrm{e} = \frac{g_{r+1}}{g_r}f_r(T)\ , \quad \text{with} \quad f_r(T) = 2\frac{(2\pi m_\mathrm{e}kT)^{3/2}}{h^3}\,\mathrm{e}^{-\chi_r/kT}\ . \tag{14.11}$$

This is the *Saha equation* (named after the physicist Meghnad Saha) though it is still not yet in its final form, since we have considered only the ground states. Therefore, in order to be more precise, we now use the quantities $n_{r+1,0}, n_{r,0}, g_{r+1,0}, g_{r,0}$, where the second subscript indicates the ground state for which these quantities are defined. By $n_{r+1}, n_r, g_{r+1}, g_r$ we from now on mean number densities of ions and statistical weights for *all* states of excitation. A particular state of excitation is indicated by a second subscript such that $n_{i,k}$ is the number density of atoms in the stage i of ionization and in state k of excitation and $g_{i,k}$ is the corresponding statistical weight. The Saha equation (14.11) is then written more precisely as

$$\frac{n_{r+1,0}}{n_{r,0}}n_\mathrm{e} = \frac{g_{r+1,0}}{g_{r,0}}f_r(T)\ . \tag{14.12}$$

The number density of ions in the ionization state r (in *all* states of excitation) is

$$n_r = \sum_s n_{r,s} \ , \tag{14.13}$$

which corresponds to (14.2), and we now write the Boltzmann formula (14.1) for ions of state r as

$$\frac{n_{r,s}}{n_{r,0}} = \frac{g_{r,s}}{g_{r,0}} \, \mathrm{e}^{-\psi_{r,s}/kT} \ , \tag{14.14}$$

where $\psi_{r,s}$ is the excitation energy of state s; then (14.13) can be written in the form

$$\begin{aligned} \frac{g_{r,0}}{n_{r,0}} n_r &= g_{r,0} \sum_s \frac{n_{r,s}}{n_{r,0}} \\ &= g_{r,0} + g_{r,1}\mathrm{e}^{-\psi_{r,1}/kT} + g_{r,2}\mathrm{e}^{-\psi_{r,2}/kT} + \ldots := u_r \ , \end{aligned} \tag{14.15}$$

where $u_r = u_r(T)$ is the partition function for the ion in state r. With the help of $n_r \, g_{r,0} = n_{r,0} \, u_r$, which follows from (14.15), the Saha equation can be written for all stages of excitation as

$$\frac{n_{r+1}}{n_r} n_\mathrm{e} = \frac{u_{r+1}}{u_r} \, f_r(T) \ , \tag{14.16}$$

where $f_r(T)$ is given in (14.11). With $P_\mathrm{e} = n_\mathrm{e} kT$ one has

$$\frac{n_{r+1}}{n_r} P_\mathrm{e} = \frac{u_{r+1}}{u_r} \, 2 \frac{(2\pi m_\mathrm{e})^{3/2}}{h^3} \, (kT)^{5/2} \, \mathrm{e}^{-\chi_r/kT} \ . \tag{14.17}$$

14.2 Ionization of Hydrogen

In order to see the consequences of the Saha equation we shall apply it to a pure hydrogen gas. We define the *degree of ionization* x by

$$x = \frac{n_1}{n_0 + n_1} \ , \tag{14.18}$$

i.e. $n_1/n_0 = x/(1-x)$. If the gas is neutral, then $x = 0$; if it is completely ionized, $x = 1$. Also the left-hand side of (14.17) can be replaced by $xP_\mathrm{e}/(1-x)$, and if $n = n_0 + n_1$ is the total number of hydrogen atoms, then we can relate the partial pressure of the electrons to the total gas pressure:

$$P_\mathrm{e} = n_\mathrm{e} kT = (n + n_\mathrm{e})kT \, \frac{n_\mathrm{e}}{n + n_\mathrm{e}} = P_\mathrm{gas} \frac{n_\mathrm{e}}{n + n_\mathrm{e}} \ . \tag{14.19}$$

For each ionized atom there is just one electron ($n_\mathrm{e} = n_1$); therefore

$$P_\mathrm{e} = \frac{x}{1+x} P_\mathrm{gas} \tag{14.20}$$

and (14.17) can be written in the form

$$\frac{x^2}{1-x^2} = K_\mathrm{H} \,, \quad \text{with} \quad K_\mathrm{H} = \frac{u_1}{u_0}\frac{2}{P_\mathrm{gas}}\frac{(2\pi m_\mathrm{e})^{3/2}}{h^3}\,(kT)^{5/2}\,\mathrm{e}^{-\chi_\mathrm{H}/kT} \,. \tag{14.21}$$

Here $\chi_\mathrm{H} = 13.6\,\mathrm{eV}$ is the ionization energy of hydrogen. Now with (14.21) we have come up with a quadratic equation for the degree of ionization that can be solved if T and P_gas are given. If radiation pressure is important, it is sufficient to give T and the total pressure P, and then P_gas can be obtained from (13.2).

In order to compute the degree of ionization, the partition function has to be known. For this we need the statistical weights of the different states of excitation, which are given by quantum mechanics. Since the higher states contribute little to the partition function, we may approximate it by the weight of the ground state, $u_0 \approx g_{0,0} = 2$, while for ionized hydrogen, $u_1 = 1$ (see, for instance, Cox, 2000, pp. 2–34).

We now give some numerical examples. In the solar photosphere we have in cgs units $P_\mathrm{gas} = 1.01 \times 10^5, T = 5{,}779\,\mathrm{K}$, and we obtain $x = 5 \times 10^{-5}$, while in a deeper layer with $P_\mathrm{gas} = 3.35 \times 10^{12}, T = 7.17 \times 10^5\,\mathrm{K}$, hydrogen is almost completely ionized: $x = 0.985$.

Since in (14.21) K_H increases with T and decreases with P_gas, and since the left-hand side increases with x, one can see that the degree of ionization increases with temperature and decreases with the gas pressure. This can be easily understood: with increasing temperature, the collisions become more violent, the photons more energetic, and the processes of "kicking off" the electrons from the atoms more frequent. If, on the other hand, the temperature is kept constant but the pressure increases, then the probability grows that the ion meets an electron and recombines.

In Chap. 4 we have defined the mean molecular weight μ for a mixture of gases and have seen that it is different for ionized and non-ionized gases. Therefore mean molecular weights depend on the degree of ionization.

In order to determine μ for the hydrogen gas having the degree of ionization x, we define the number E of free electrons per atom (neutral or ionized), which is here simply

$$E = \frac{n_\mathrm{e}}{n} = x \,. \tag{14.22}$$

Remember that μm_u, $\mu_0 m_\mathrm{u}$, and $\mu_\mathrm{e} m_\mathrm{u}$ are defined as the average particle masses per free particle, per nucleus, and per free electron, respectively. This means that the density can be written as

$$\varrho = (n + n_\mathrm{e})\mu m_\mathrm{u} = n\mu_0 m_\mathrm{u} = n_\mathrm{e}\mu_\mathrm{e} m_\mathrm{u} \,. \tag{14.23}$$

Using (14.22) and $n = n_0 + n_1$, we solve (14.23) for the mean molecular weight and find

$$\mu = \frac{\varrho}{m_\mathrm{u} n} \frac{1}{1+E} = \frac{\mu_0}{1+E} = \mu_\mathrm{e} \frac{E}{1+E} \,, \tag{14.24}$$

where we have neither replaced μ_0 by its value 1 for hydrogen nor E by x, since (14.24) also holds for a mixture of gases.

14.3 Thermodynamical Quantities for a Pure Hydrogen Gas

Many thermodynamic properties depend on the degree of ionization. We here indicate roughly how the formulae can be derived for the relatively simple case of the pure hydrogen gas. This is not because of its importance, but rather because the treatment is quite analogous to that in the much more involved case of mixtures. The gas is supposed to be perfect, since partial ionization usually occurs only in the stellar envelope, where effects of degeneracy can be neglected.

In Sect. 4.1 we defined the quantity $\delta = -(\partial \ln\varrho / \partial \ln T)_P$. In the case of pure hydrogen obeying the perfect-gas equation we have $\delta = 1$ for $x = 0$ and $x = 1$, since μ is constant in both cases (Remember that we wished to incorporate in α and δ the changes of μ due to partial ionization, while φ should be reserved for changes of μ due to changing chemical composition.). For partial ionization, x varies with T, and therefore δ is given by a complicated expression. From the perfect-gas equation $\varrho \sim \mu P/T$ and (14.24) with μ_0 = constant we find

$$\delta = 1 + \frac{1}{1+E} \left(\frac{\partial E}{\partial \ln T} \right)_P \,, \tag{14.25}$$

which also holds for a mixture of gases. For pure hydrogen $E = x$ and we need the derivative of x, which can be obtained by differentiation of the Saha equation (14.21). This gives

$$\delta = 1 + \frac{1}{2} x (1-x) \left(\frac{5}{2} + \frac{\chi_\mathrm{H}}{kT} \right) \,. \tag{14.26}$$

While the mean molecular weight as given by (14.24) depends only on the degree of ionization, δ depends also on T, and if in addition radiation pressure is taken into account, one has to add terms proportional to $(1-\beta)/\beta$ to the right-hand sides of (14.25) and (14.26).

The definition (4.4) of c_P together with $P = \Re \varrho T/\mu$ gives

$$c_P = \left(\frac{\partial u}{\partial T} \right)_P + \frac{\Re}{\mu} \delta \,. \tag{14.27}$$

So we need the internal energy per mass unit

$$u = \frac{3}{2}\frac{\Re}{\mu_0}(1+E)T + u_{\mathrm{ion}} \ , \tag{14.28}$$

where the first term gives the kinetic energy of ions and electrons, and the second term u_{ion} means the energy that has been used for ionization and that again becomes available if the ions recombine. Again (14.27) and (14.28) also hold for mixtures. For pure hydrogen, $E = x$ and $u_{\mathrm{ion}} = x\chi_{\mathrm{H}}/(\mu_0 m_{\mathrm{u}}) = x\chi_{\mathrm{H}}/m_{\mathrm{u}}$, and after lengthy manipulations, one gets

$$c_P \frac{\mu_0}{\Re} = \frac{5}{2}(1+x) + \frac{\Phi_{\mathrm{H}}^2}{G(x)} \ , \tag{14.29}$$

with the abbreviations

$$\Phi_{\mathrm{H}} := \frac{5}{2} + \frac{\chi_{\mathrm{H}}}{kT} \quad \text{and} \quad G(x) := \frac{1}{x(1-x)} + \frac{1}{x(1+x)} = \frac{2}{x(1-x^2)} \ . \tag{14.30}$$

If radiation plays a role, it appears not only in the equation for the pressure, but also in the internal energy. The result for c_P is that in (14.29) the factor 5/2 has to be replaced by $5/2 + 4(1-\beta)(4+\beta)/\beta^2$.

We can now easily derive an expression for ∇_{ad}:

$$\nabla_{\mathrm{ad}} = \frac{P\delta}{T\varrho c_P} = \frac{2 + x(1-x)\Phi_{\mathrm{H}}}{5 + x(1-x)\Phi_{\mathrm{H}}^2} \ . \tag{14.31}$$

14.4 Hydrogen–Helium Mixtures

As a next step in the general problem we consider a gas of hydrogen and helium with weight fractions X, Y respectively. This is important for stellar envelopes and shows the difficulties which arise if mixtures are treated. We now have six types of particles: neutral and ionized hydrogen; neutral, ionized, and double ionized helium; and electrons. There are three types of ionization energy: χ_{H}^0 for hydrogen and $\chi_{\mathrm{He}}^0, \chi_{\mathrm{He}}^1$ for neutral and single ionized helium ($\chi_{\mathrm{H}}^0 = 13.598$ eV, $\chi_{\mathrm{He}}^0 = 24.587$ eV, $\chi_{\mathrm{He}}^1 = 54.418$ eV). Each ionized hydrogen atom contributes the energy χ_{H}^0 to the internal energy, each helium atom in the first stage of ionization the energy χ_{He}^0 and each helium atom completely stripped of its two electrons the energy $\chi_{\mathrm{He}}^0 + \chi_{\mathrm{He}}^1$. By $x_{\mathrm{H}}^0, x_{\mathrm{H}}^1, x_{\mathrm{He}}^0, x_{\mathrm{He}}^1, x_{\mathrm{He}}^2$ we define degrees of ionization, i.e. x_i^r gives the number of atoms of type i in ionization state r (= r electrons lost) divided by the total number of atoms of type i (irrespective of their state of ionization):

$$x_{\mathrm{H}}^{0}=\frac{n_{\mathrm{H}}^{0}}{n_{\mathrm{H}}}\,,\quad x_{\mathrm{H}}^{1}=\frac{n_{\mathrm{H}}^{1}}{n_{\mathrm{H}}}\,,\quad x_{\mathrm{He}}^{0}=\frac{n_{\mathrm{He}}^{0}}{n_{\mathrm{He}}}\,,$$
$$x_{\mathrm{He}}^{1}=\frac{n_{\mathrm{He}}^{1}}{n_{\mathrm{He}}}\,,\quad x_{\mathrm{He}}^{2}=\frac{n_{\mathrm{He}}^{2}}{n_{\mathrm{He}}}\,,\tag{14.32}$$

with $n_{\mathrm{H}}=n_{\mathrm{H}}^{0}+n_{\mathrm{H}}^{1}$ and $n_{\mathrm{He}}=n_{\mathrm{He}}^{0}+n_{\mathrm{He}}^{1}+n_{\mathrm{He}}^{2}$, where the n_i^r are number densities of ions of type i in ionization state r. Note that the degrees of ionization x_{H}^{0} and x_{H}^{1} correspond to $1-x$ and x in Sect. 14.2.

The contribution of the ionization energy to the internal energy per unit mass [cf. (14.28)] is

$$u_{\mathrm{ion}}=\frac{1}{m_{\mathrm{u}}}\left\{X x_{\mathrm{H}}^{1}\chi_{\mathrm{H}}^{0}+\frac{1}{4}Y\left[x_{\mathrm{He}}^{1}\chi_{\mathrm{He}}^{0}+x_{\mathrm{He}}^{2}\left(\chi_{\mathrm{He}}^{0}+\chi_{\mathrm{He}}^{1}\right)\right]\right\}\,,\tag{14.33}$$

since X/m_{u}, $Y/(4m_{\mathrm{u}})$ are the numbers of hydrogen and helium atoms (neutral and ionized) per unit mass. Correspondingly we have for the number E of electrons per atom (irrespective of ionization state and chemical type)

$$E=\left[X x_{\mathrm{H}}^{1}+\frac{1}{4}Y\left(x_{\mathrm{He}}^{1}+2x_{\mathrm{He}}^{2}\right)\right]\mu_0\,.\tag{14.34}$$

We now have three Saha equations:

$$\frac{x_{\mathrm{H}}^{1}}{x_{\mathrm{H}}^{0}}\frac{E}{E+1}=K_{\mathrm{H}}^{0}\,,\quad \frac{x_{\mathrm{He}}^{1}}{x_{\mathrm{He}}^{0}}\frac{E}{E+1}=K_{\mathrm{He}}^{0}\,,\quad \frac{x_{\mathrm{He}}^{2}}{x_{\mathrm{He}}^{1}}\frac{E}{E+1}=K_{\mathrm{He}}^{1}\,,\tag{14.35}$$

with

$$K_i^r=\frac{u_{r+1}}{u_r}\frac{2}{P_{\mathrm{gas}}}\frac{(2\pi m_{\mathrm{e}})^{3/2}(kT)^{5/2}}{h^3}\,\mathrm{e}^{-\chi_i^r/kT}\tag{14.36}$$

for i = H, He, and by definition

$$x_{\mathrm{H}}^{0}+x_{\mathrm{H}}^{1}=1\,,\quad x_{\mathrm{He}}^{0}+x_{\mathrm{He}}^{1}+x_{\mathrm{He}}^{2}=1\,.\tag{14.37}$$

We now consider X, Y, P_{gas}, and T to be given. Then (14.34), (14.35) and (14.37) are six equations for the six unknown quantities $x_{\mathrm{H}}^{0}, x_{\mathrm{H}}^{1}, x_{\mathrm{He}}^{0}, x_{\mathrm{He}}^{1}, x_{\mathrm{He}}^{2}, E$. The equations (14.35) are coupled to each other via E, which, for instance, means that the degree of ionization of hydrogen also depends on the degree of ionization of helium. But this is to be expected, since a hydrogen ion can also recombine with free electrons that originally came from helium, since it has no prejudices concerning the origin of a captured electron.

The coupling of the three Saha equations (14.35) makes an analytical treatment impossible: the degrees of ionization have to be obtained numerically. In general,

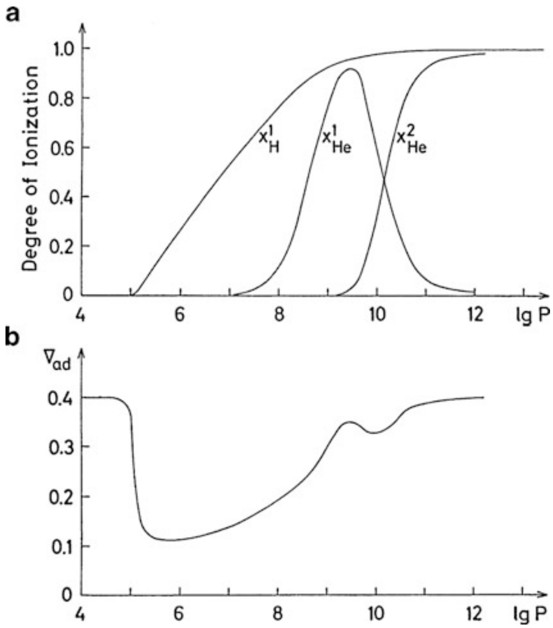

Fig. 14.1 Ionization in the outer layers of the Sun. (**a**) Degrees of ionization of hydrogen and helium. (**b**) The influence of ionization on ∇_{ad}

this is done by an iteration procedure, starting with a trial value of E, which is then gradually improved.

In Fig. 14.1 we give the degrees of ionization and ∇_{ad} for the outer layers of the Sun. One can see that the regions of partial ionization of H and He are almost separated. This is because the ionization energies χ_H^0, χ_{He}^1, χ_{He}^2 differ from each other appreciably. The second helium ionization does not start until the hydrogen is almost completely ionized. Therefore one may, for an approximative treatment, solve at most two of equations (14.35) simultaneously, which simplifies the situation. Each of the three ionization layers produces a lowering of ∇_{ad} where influences of hydrogen and first helium ionization overlap.

14.5 The General Case

If X_i is the weight fraction of the chemical element i with charge number Z_i and molecular weight μ_i, and if x_i^r are the degrees of ionization (the numbers of atoms of type i in ionization state r in units of the total number of atoms of type i), then

$$E = \sum_i \nu_i \sum_{r=0}^{Z_i} x_i^r = \sum_i \frac{\mu_0}{\mu_i} X_i \sum_{r=0}^{Z_i} x_i^r r \ , \tag{14.38}$$

where $\nu_i = n_i/n = X_i\mu_0/\mu_i$ is the relative number of particles of type i. Equation (14.34) is a special case of (14.38). Then the degrees of ionization are obtained from the set of Saha equations

$$\frac{x_i^{r+1}}{x_i^r}\frac{E}{E+1} = K_i^r \ , \quad i = 1, 2, \ldots, \quad r = 0, 1, \ldots Z_i \ , \tag{14.39}$$

where the K_i^r are given by (14.36). In addition we have the relations

$$\sum_{r=0}^{Z_i} x_i^r = 1 \ , \quad i = 1, 2, \ldots \ . \tag{14.40}$$

For a given type i of atoms, equations (14.39) in which E is replaced by (14.38) represent Z_i equations for the $Z_i + 1$ degrees r of ionization, and together with (14.40) one therefore has the same number of equations as of variables. The equations can be solved iteratively; thus the degrees of ionization can be used to determine the mean molecular weight according to $\mu = \mu_0/(1 + E)$. The kinetic part of the internal energy [cf. (14.28)] is

$$u_{\mathrm{kin}} = \frac{3}{2}\frac{\Re}{\mu}T = \frac{3}{2}\frac{\Re}{\mu_0}(1+E)T \ , \tag{14.41}$$

while the ionization energy per mass unit is

$$u_{\mathrm{ion}} = \sum_i \frac{X_i}{\mu_i m_{\mathrm{u}}} \sum_{r=0}^{Z_i} x_i^r \sum_{s=0}^{r-1} \chi_i^s \ , \tag{14.42}$$

which is the general form of (14.33).

For the determination of δ and c_P according to (14.25) and (14.27) we need derivatives of the degrees of ionization: $(\partial x_i^r/\partial \ln T)_P$. They can be computed numerically by evaluating the x_i^r for neighbouring arguments, though one has to be careful if the radiation pressure is not negligible. The derivatives of the x_i^r are needed for constant *total* pressure P, whereas the argument for evaluating the degrees of ionization is the *gas* pressure. One therefore has to choose the neighbouring arguments P_{gas} and T such that $P = P_{\mathrm{gas}} + P_{\mathrm{rad}}$ = constant. The general theory of ionization and, in particular, the influence on the thermodynamic functions for arbitrary mixtures are given in Baker and Kippenhahn (1962, Appendix A).

In modern stellar evolution calculations the equation of state is no longer computed online, but rather pre-calculated tables are used. These tables result from sophisticated models of the properties of stellar matter, which are too complicated to be integrated into the stellar evolution programs. Ionization is only one of the many physical effects treated in such models for many chemical elements, their number amounting to up to 20.

14.6 Limitation of the Saha Formula

In the derivation of the Saha formula we have assumed thermodynamic equilibrium. This is certainly fulfilled in the interior of stars, and the Saha formula is even a sufficient approximation for many atmospheres as long as one can assume so-called LTE (local thermodynamic equilibrium), which is the case when collisions dominate over radiative processes. One cannot apply it for non-LTE, as, for example, in the solar corona.

But even in the deep interior of a star, where local thermodynamic equilibrium is certainly a very good approximation, the naïve application of the Saha formula gives wrong results. For instance let us apply it to the centre of the Sun ($P_c \approx P_{gas} = 2.32 \times 10^{17}$ dyn/cm^2, $T_c = 1.57 \times 10^7$ K) and assume for simplicity pure hydrogen ($X = 1$); then (14.21) gives for the degree of ionization $x_H = 0.80$. This would mean that 20 % of the hydrogen atoms are neutral. Indeed, for sufficiently high temperatures, the exponential in the Saha formula can be replaced by 1, and x^1_H decreases inwards with K_H if $\nabla \equiv d \ln T / d \ln P_{gas} < 2/5$, as can be seen from (14.21).

The solution of this paradox has to do with the decrease of the ionization energy with increasing density. Let us consider ions at a distance d from each other: their electrostatic potentials have to be superimposed in order to obtain their total potential (Fig. 14.2). Obviously the higher quantum states of the ions are strongly disturbed, and the ionization energy is reduced for high density. This should be taken into account in the Saha formula, which would then give a higher degree of ionization. Furthermore, the neighbouring ions allow only a finite number of bound states. This has the consequence that in the partition function as given by (14.15) one has to sum over a finite number of excited states only.

In order to estimate roughly at which density these effects become important, we consider a pure hydrogen gas. If the mean distance between two atoms is d, then there will be no bound states if the orbital radius a of the electron is comparable with, or larger than, $d/2$. With

$$a = a_0 \nu^2 , \quad d \approx \left(\frac{3}{4\pi n_H} \right)^{1/3} , \tag{14.43}$$

where $a_0 = 5.3 \times 10^{-9}$ cm is the Bohr radius, ν the quantum, number and n_H the number density of the atoms, we obtain from the condition $a < d/2$ (which must be fulfilled for a bound state) that

$$\nu^2 < \left(\frac{3}{4\pi n_H} \right)^{1/3} \frac{1}{2a_0} . \tag{14.44}$$

This allows a rough estimate of the principal quantum number of the highest bound state. In the centre of the Sun, with $\varrho_c \approx 150$ g/cm^3, we have $n_H \approx \varrho_c / m_u \approx 10^{26}$ cm^{-3}, and therefore $\nu^2 < 0.13$, which means that even the ground state of hydrogen does not exist. Therefore all hydrogen atoms will be ionized.

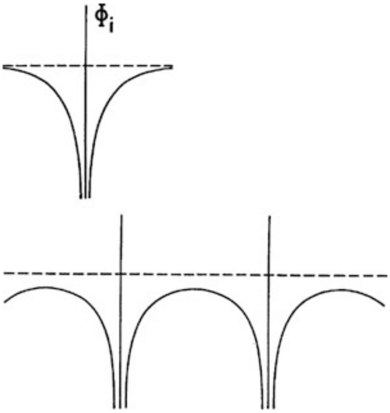

Fig. 14.2 Sketch of the electrostatic potential of an isolated ion (*above*) and the superposition of the potentials of neighbouring ions (*below*)

For this so-called *pressure ionization*, no perfect theory is at hand. The picture we have used above is a static one, since it does not take into account that the ions move relative to each other. It also ignores that at high densities electrons can tunnel from a bound state of one ion into a bound state of another ion in the neighbourhood. In the specialized computations of the equation of state for an astrophysical plasma, more elaborate models are used to solve this problem. An example is the hydrogen–helium equation of state by Saumon et al. (1995).

For simplified stellar-model calculations one may use the Saha formula for the outer layers of the stars and then switch to complete ionization when the Saha formula gives degrees of ionization which decrease again towards deeper layers. This switching normally does not produce a noticeable discontinuity in the run of ionization, since the maximum often occurs close to complete ionization.

If we assume that pressure ionization can be neglected as long as $d > 10a_0$, then the Saha formula would be valid only for densities:

$$\varrho = \mu_0 m_{\mathrm{u}} n_{\mathrm{ion}} < \frac{3\mu_0 m_{\mathrm{u}}}{4\pi(10a_0)^3} = 2.66 \times 10^{-3} \mu_0 \,\mathrm{g\,cm^{-3}} \ . \tag{14.45}$$