IONIZATION, SAHA EQUATION

Let the energies of two states, A and B, be E_A and E_B, and their statistical weights g_A and g_B, respectively. In LTE (Local Thermodynamic Equilibrium) the number of particles in the two states, N_A and N_B, satisfies Boltzman equation:

$$\frac{N_A}{N_B} = \frac{g_A}{g_B} \exp\left[-\left(E_A - E_B\right)/kT\right]. \tag{i.1}$$

Now, we shall consider two ions, "i" and "i+1", of the same element. The ionization potential, i.e. the energy needed to ionize "i" from the ground state is χ, and the statistical weights of the ground states of the two ions are g_i and g_{i+1}, respectively. The number densities, $[\,\mathrm{cm}^{-3}]$, of the two types of ions and free electrons are n_i, n_{i+1}, and n_e, respectively. We shall use the Boltzman equation (i.1) to estimate the number ratio n_{i+1}/n_i. The statistical weight of an ion in the lower ionization state to be used in the equation (i.1) is just g_i. The statistical weight of an ion in the upper ionization state is g_{i+1} multiplied by the number of possible states in which a free electron may be put. As we know, in every cell of a phase space with a volume h^3 there are two possible states for an electron, because there are two possible orientations of its spin. $h = 6.63 \times 10^{-27}\,\mathrm{erg\ s}$ is the Planck constant. The energy of a free electron with a momentum p with respect to the ground state of an ion in a lower ionization state is $E = \chi + p^2/2m$. The number of cells available for free electrons with a momentum between p and $p + dp$ is $V_e 4\pi p^2 dp/h^3$, where $V_e = 1/n_e$ is the volume in ordinary space available per electron, and n_e is the free electron number density. Now, we shall integrate over all available cells, taking the Boltzman factor into account

$$\frac{n_{i+1}}{n_i} = \frac{g_{i+1}}{g_i}\frac{2V_e}{h^3}\int_0^\infty e^{-\left(\chi + p^2/2m\right)/kT} 4\pi p^2 dp = \tag{i.2}$$

$$\frac{g_{i+1}}{g_i}\frac{1}{n_e}\frac{2}{h^3}\left(2mkT\right)^{3/2} e^{-\chi/kT} 2\pi \int_0^\infty e^{-x} x^{1/2} dx =$$

$$\frac{g_{i+1}}{g_i}\frac{1}{n_e}\frac{2}{h^3}\left(2\pi mkT\right)^{3/2} e^{-\chi/kT},$$

where we set $x = p^2/2mkT$, and the value of the last integral was $\pi^{1/2}/2$.

The last equation is usually written as the Saha equation

$$\frac{n_{i+1} n_e}{n_i} = \frac{\left(2\pi mkT\right)^{1.5}}{h^3}\frac{2g_{i+1}}{g_i} e^{-\chi/kT}. \tag{i.3}$$

It is customary to express the ionization energy in electron volts, $1\,\mathrm{eV} = 1.602 \times 10^{-12}$ *erg*. Ionization of the most abundant elements, hydrogen and helium, is important for the equation of state. For these elements we have:

ionization of hydrogen:	$\chi = 13.54\ eV$,	$2g_{i+1}/g_i = 1$,
first ionization of helium:	$\chi = 24.48\ eV$,	$2g_{i+1}/g_i = 4$,
second ionization of helium:	$\chi = 54.17\ eV$,	$2g_{i+1}/g_i = 1$.

Consider now pure, partly ionized hydrogen. Let n_H, n_{HI}, and n_{HII} be number density of all hydrogen, neutral hydrogen atoms, and hydrogen ions, respectively. We have $n_H = n_{HI} + n_{HII}$, $n_e = n_{HII}$, and $x \equiv n_{HII}/n_H$ is the degree of ionization. The density of gas is $\rho = H n_H$, where H is the mass of a hydrogen atom. We may write the Saha equation as

$$\frac{n_{HII}n_e}{n_{HI}} = \frac{\rho}{H}\frac{x^2}{1-x} = \frac{(2\pi mkT)^{1.5}}{h^3}\frac{2g_{i+1}}{g_i}e^{-\chi/kT}. \tag{i.4}$$

The constants in cgs units are: $H = 1.673 \times 10^{-24}$, $m = 9.11 \times 10^{-28}$, $k = 1.381 \times 10^{-16}$, $h = 6.63 \times 10^{-27}$. With these constants we have

$$\log\rho + \log\frac{x^2}{1-x} = \tag{i.5}$$

$$= 1.5\log T - \frac{5040}{T}\chi + \log\left[H(2\pi mk)^{1.5}h^{-3}\right] = 1.5\log T - \frac{68240}{T} - 8.394.$$

The pressure of partially ionized hydrogen gas is simply

$$P_g = (n_H + n_e)kT = (1+x)\frac{k}{H}\rho T. \tag{i.6}$$

The internal energy should now include not only kinetic, but also ionization energy:

$$U_g = 1.5(n_H + n_e)kT + n_e\chi = 1.5P + x\frac{\chi}{H}\rho. \tag{i.7}$$

In these equations the degree of ionization should be treated as a function of density and temperature, $x(\rho, T)$. Differentiating equation (i.4) we obtain

$$\left(\frac{\partial x}{\partial lnT}\right)_\rho = \frac{x(1-x)}{(2-x)}\left(1.5 + \frac{\chi}{kT}\right), \tag{i.8a}$$

$$\left(\frac{\partial x}{\partial\ln\rho}\right)_T = -\frac{x(1-x)}{(2-x)}. \tag{i.8b}$$

As an example of the thermodynamic properties of partially ionized hydrogen we shall calculate specific heat of hydrogen gas at constant volume:

$$c_{V,g} \equiv \left[\frac{\partial(U_g/\rho)}{\partial T}\right]_\rho = \frac{1.5}{\rho}\left(\frac{\partial P_g}{\partial T}\right)_\rho + \frac{\chi}{H}\left(\frac{\partial x}{\partial T}\right)_\rho = \tag{i.9a}$$

$$= \frac{k}{H}\left[1.5(1+x) + (1.5 + \chi/kT)^2\frac{x(1-x)}{(2-x)}\right].$$

When the hydrogen is 50% ionized, i.e. $x = 0.5$, then

$$c_{V,g} = \frac{k}{H}\left[2.25 + \frac{1}{6}(1.5 + \chi/kT)^2\right]. \tag{i.9b}$$

Typically, we have $\chi/kT \gg 1$, and therefore the specific heat for partly ionized gas is much higher than for neutral or fully ionized gas.

Let us consider now a mixture of partially ionized hydrogen with radiation. The equation of state is

$$P_g = (1+x)\frac{k}{H}\rho T, \qquad P_r = \frac{a}{3}T^4, \qquad P = P_g + P_r, \qquad \beta = P_g/P, \tag{i.10a}$$

$$P = (1+x)\frac{k}{H}\rho T + \frac{a}{3}T^4, \tag{i.10b}$$

$$U = 1.5(1+x)\frac{k}{H}\rho T + aT^4 + x\frac{\chi}{H}\rho, \tag{i.10c}$$

The equations in a differential form are:

$$d\ln P = (4-3\beta)\,d\ln T + \beta d\ln\rho + \frac{\beta}{1+x}dx \qquad \text{(equation of state)}, \tag{i.11a}$$

$$\frac{dU}{P} = (12 - 10.5\beta)\, d\ln T + \left(\frac{3}{2} + \frac{\chi}{kT}\right) \beta d\ln\rho + \left(\frac{3}{2} + \frac{\chi}{kT}\right) \frac{\beta}{1+x} dx, \tag{i.11b}$$

$$\frac{(2-x)}{x\,(1-x)} dx = \left(\frac{3}{2} + \frac{\chi}{kT}\right) d\ln T - d\ln\rho \qquad \text{(Saha equation).} \tag{i.11c}$$

From the Saha equation we obtain equations (i.8a) and (i.8b) . Those may be combined with the equations (i.11a) and (i.11b) to get

$$\left(\frac{\partial \ln P}{\partial \ln T}\right)_\rho = 4 - 3\beta + \frac{\beta}{(1+x)} \left(\frac{\partial x}{\partial \ln T}\right)_\rho , \tag{i.12a}$$

$$\left(\frac{\partial \ln P}{\partial \ln \rho}\right)_T = \beta + \frac{\beta}{(1+x)} \left(\frac{\partial x}{\partial \ln \rho}\right)_T , \tag{i.12b}$$

$$\frac{T}{P}\left(\frac{\partial U}{\partial T}\right)_\rho = 12 - 10.5\beta + \frac{\beta}{(1+x)} \left(1.5 + \frac{\chi}{kT}\right) \left(\frac{\partial x}{\partial \ln T}\right)_\rho . \tag{i.12c}$$

Now we have all the derivatives that are needed to calculate the adiabatic relations: γ, ∇_{ad}, and $(\partial \ln T / \partial \ln \rho)_S$, as well as the specific heats, c_V and c_P, for the mixture of partially ionized hydrogen and radiation.