Exercise 9.1. Show that the total radiant energy density at a point is
\[ \mathcal{U}^R = \frac{1}{c} \int_0^\infty \int_{4\pi} I_\lambda(\Omega) d\Omega \, dv, \]
and that the radiant heat flux is
\[ q^R = \int_0^\infty \int_{4\pi} I_\lambda(\Omega) \Omega d\Omega \, dv. \]
(See Vincenti and Kruger, 1965, Chapter XI.)

Exercise 9.2. For transitions between adjacent high-lying hydrogen levels, show that the oscillator strength has the value
\[ f_{m, m+1} \approx 0.25m. \]

Exercise 9.3. As a function of \( m \), show that for hydrogen \( A_{nm} \) passes through a minimum when \( m = n \sqrt{3} \), and that
\[ A_{\text{min}} \approx \frac{4.2 \times 10^{10}}{n^6} \text{ sec}^{-1}. \]

Exercise 9.4. For transitions in hydrogen from a high-lying level \( n \) to a level \( m \ll n \), show that
\[ A_{nm} \approx \frac{1.6 \times 10^{10}}{n^7 m} \text{ sec}^{-1}. \]
For transitions to nearby levels with \( m = n - \Delta n, \Delta n \ll n \), show that
\[ A_{n, n-\Delta n} \approx \frac{0.8 \times 10^{10}}{n^5 \Delta n} \text{ sec}^{-1}. \]
(From the results of Exercises 9.3 and 9.4, one may conclude that the most probable spontaneous transitions from a high-lying level are either to the ground level or to the adjacent level.)

Exercise 9.5. Calculate the bound-bound absorption cross section and photon mean free path at the line center of the \( n = 1 \) to \( n = 2 \) transition of hydrogen. Assume the line is naturally broadened and that the hydrogen number density is \( 10^{10} \text{ cm}^{-3} \).

10. EQUILIBRIUM RELATIONS

When a gas is in thermodynamic equilibrium, it is possible to calculate the particle densities of all the species in terms of the thermodynamic state of the gas. It is not within the scope of this book to present any systematic discussion of this topic, but we do need to point out and have available
several important relations that pertain to a gas in thermodynamic equilibrium. The derivation of these relations falls within the province of statistical mechanics, and is discussed in texts by Vincenti and Kruger (1965), Rushbrooke (1949), Tolman (1938), and by many other authors.

The ratio of the number density \( n_l \) of particles of a particular species (molecule, atom, or ion) in an upper energy level \( l \) to the number density \( n_k \) in a lower level \( k \) is given by the Boltzmann relation

\[
\frac{n_l}{n_k} = \frac{g_l}{g_k} e^{-\epsilon_{kl}/kT}.
\]  

(10.1)

Here \( g_l \) and \( g_k \) denote the degeneracies of the \( l \)th and \( k \)th levels, respectively, and

\[
\epsilon_{kl} = |\epsilon_l - \epsilon_k|
\]

is the energy difference between the levels.

To relate \( n_l \) to the total number of particles of the species, \( n = n_1 + n_2 + \cdots \), we employ equation (10.1) and write

\[
\frac{n}{n_1} = \sum_{i=1}^{l_{\text{max}}} \frac{n_l}{n_1} = \frac{1}{g_1} \sum_{i=1}^{l_{\text{max}}} g_i e^{-\epsilon_i/kT} = \frac{Z(T)}{g_1},
\]

(10.2)

where

\[
Z(T) \equiv \sum_{i=1}^{l_{\text{max}}} g_i e^{-\epsilon_i/kT} = g_1 + g_2 e^{-\epsilon_2/kT} + \cdots
\]

(10.3)

is the partition function for the species under consideration. A completely free particle has an infinite number of energy levels, so that \( l_{\text{max}} \to \infty \) and the expression for \( Z(T) \) diverges. The reason for this behavior is that the exponential factor in equation (10.3) approaches a constant value near the series limit, whereas the degeneracies continue to increase indefinitely. (For hydrogen, \( g_l = 2l^2 \).) In a gas, interactions with neighboring particles serve to impose an effective finite upper limit \( l_{\text{max}} \) on the number of energy levels, so that \( Z \) is finite. The manner of determining the value of \( l_{\text{max}} \), or equivalently, the lowering of the ionization potential, is discussed by Griem (1964) and by Drawin and Felenbok (1965). For purposes of illustration, Fig. 15 shows the dependence of the partition function on temperature with the ionization potentials lowered by 0.1 eV for several atomic and ionic species. The data for this figure is taken from Drawin and Felenbok (1965). At lower temperatures, the value of \( Z \) is insensitive to the cutoff. At higher temperatures, increasing the pressure increases the lowering of the ionization potential, and therefore decreases \( Z \) (see Drellishak, Knopp, and Cambel, 1963; and Drellishak, Aeschliman, and Cambel, 1965).
Depending on the species, the approximation $Z \approx g_1$ is frequently useful for temperatures which are not too high. (Approximate values of $Z$ for moderate temperatures are given in Table 2 for several species.) Employing equation (10.2), we may write the Boltzmann relation in the alternative form

$$\frac{n_i}{n} = \frac{g_i}{Z} e^{-\epsilon_i/kT}.$$  \hspace{1cm} (10.4)
Because of the role played by the lowering of the ionization potential, the partition function depends in general not only on temperature, but on the complete thermodynamic state of the gas.

For each species, the number density of singly ionized positive ions in the ground level \( n_i^+ \) and the corresponding number density of neutral particles in the \( k \)th level \( n_k \) are related to the free electron number density \( n_e \) by the Saha equation

\[
\frac{n_e n_i^+}{n_k} = 2 \frac{g_i^+}{g_k} \left( \frac{2\pi m_e kT}{\hbar^2} \right)^{3/2} e^{-\varepsilon_i/kT}.
\] (10.5a)

Here \( g_i^+ \) is the degeneracy of the ground level of the ion. This relation may be viewed either as a statement of the law of mass action or as a consequence of the Boltzmann relation (10.1) applied to the continuum (see Menzel, 1933). Equation (10.5a) applies independently to each species present in the gas. Introducing the partition functions \( Z \) for the neutral species and \( Z_i \) for the ion and employing equation (10.2), we may also write the Saha equation in the form

\[
\frac{n_e n_i}{n} = 2 \frac{Z_i}{Z} \left( \frac{2\pi m_e kT}{\hbar^2} \right)^{3/2} e^{-\varepsilon_i/kT}.
\] (10.5b)

Here \( n_i = n_i^+ + n_2^+ + \cdots \) denotes the total number density of ions of the species in question. This form of the Saha equation is frequently used to calculate the electron number density in partially ionized gases. In MKS units

\[
\left( \frac{2\pi m_e kT}{\hbar^2} \right)^{3/2} = 2.42 \times 10^{21} \text{ m}^{-3} \text{ K}^{-3/2}.
\]

The Saha relation may be generalized to the case of multiply ionized species as follows: If we denote the stage of ionization of a particle by the superscript \( r \), then equations (10.5) take on the more general forms

\[
\frac{n_e n_i^{(r+1)}}{n_k^{(r)}} = 2 \frac{g_i^{(r+1)}}{g_k^{(r)}} \left( \frac{2\pi m_e kT}{\hbar^2} \right)^{3/2} e^{-\varepsilon_i^{(r)}}/kT,
\] (10.6a)

and

\[
\frac{n_e n_i^{(r+1)}}{n^{(r)}} = 2 \frac{Z_i^{(r+1)}}{Z^{(r)}} \left( \frac{2\pi m_e kT}{\hbar^2} \right)^{3/2} e^{-\varepsilon_i^{(r)}}/kT.
\] (10.6b)

Equations (10.5) correspond to the case \( r = 0 \). Negative ions are described by taking \( r = -1 \), in which case \( \varepsilon_i^{(-1)} \) corresponds to the electron affinity.
We have previously noted in Sec. 6, that in thermodynamic equilibrium the velocity distribution of each species in the gas is described by the *Maxwellian* function

\[ f^M(W) = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mW^2/2kT}. \quad (10.7) \]

Here \( m \) denotes the mass of the species under consideration, and \( W \) denotes the particle velocity relative to a nonmoving fluid.

The three preceding equilibrium relations associated with the names of Boltzmann, Saha, and Maxwell pertain to matter. When the photons (or radiation field) are also in thermodynamic equilibrium with the matter, then in analogy to equation (10.7) the photons have an equilibrium distribution. The corresponding equilibrium value of the specific intensity defined by equation (9.6) is given by the *Planck function*

\[ B_\nu(T) = \frac{2h\nu^3/c^2}{e^{h\nu/kT} - 1}. \quad (10.8) \]

Here \( c \) denotes the speed of light. This relation is derived in Sec. 11 of Chapter VI.

Partially ionized gases are rarely in complete thermodynamic equilibrium, but they may frequently be in a state of approximate *local thermodynamic equilibrium*, or LTE. A gas is said to be in a condition of LTE when the matter particles are in equilibrium with themselves, but when the photons are *not* in equilibrium with the matter. In most situations, a partially ionized gas is transparent in many frequency intervals, and some radiation therefore escapes from the gas, thus violating a condition necessary for complete thermodynamic equilibrium. In order that the matter be in LTE, it is necessary that the collisional rates that populate and depopulate the various energy levels of the matter exceed the corresponding radiative rates. For a gas in LTE it is still possible to employ the Boltzmann and Saha relations even though complete thermodynamic equilibrium does not prevail.

For collision-dominated gases the Boltzmann and Saha relations are often applicable even when other kinds of departure from complete thermodynamic equilibrium occur. For example, as indicated in Sec. 7, it is often possible for the electrons to have temperature \( T_e \) that differs from the heavy particle temperature \( T \). Both types of particles may still have Maxwellian velocity distributions, but at different temperatures. The conditions for such a situation are discussed in Sec. VIII 3. When it is primarily collisions with electrons which produce the transitions that
determine the population of some energy level or the degree of ionization, the “temperature” that appears in the corresponding Boltzmann or Saha relation should be interpreted as the electron temperature.

**Exercise 10.1.** Calculate the equilibrium electron number density in a mixture of potassium and sodium vapor at a pressure of $10^{-3}$ atm and temperature of 2000$^\circ$K. The mass ratio of K to Na before heating is ten to one. What are the number densities of K$^+$ and Na$^+$? What electron number density would result from pure cesium at the same conditions?

**Exercise 10.2.** An arc heater is used to produce partially ionized argon at a pressure of 1 atm. It may be assumed that the gas is in thermodynamic equilibrium, that the electron and ion number densities are equal, that each species obeys a perfect equation of state (i.e. $p_s = n_s kT$), and that Dalton’s law of partial pressures is applicable. At what temperature will the electrons collide as frequently with argon ions as with argon atoms? What is the ratio of electron number density to argon number density at this temperature?