Calculations of atom-atom ionization rates for the inverse process, based upon the method of detailed ionization balancing (see Sec. 11) applied to equation (V 9.11), agree to within an order of magnitude with the measurements on noble gases by Kelly (1966), although the dependence on temperature differs. Generalizations based on this comparison should be treated with care since the three-body (heavy particle) recombination rate may be sensitive to the species involved. It is evident that at the present time our understanding of the process (5.13) is quite incomplete.

The description of recombination in terms of the independent reaction processes represented by equations (5.11) to (5.15) is traditional, and frequently provides a useful approximation. In general, however, these processes may be coupled. This coupling has been demonstrated for the collisional and radiative processes (5.11) and (5.12) by Bates, Kingston, and McWhirter (1962) and is discussed in Chapter IX.

**Exercise 5.1.** Consider a mixture of helium and partially ionized potassium at a temperature of 2000°K. Above what He number density would the three-body process e + K + He → K + He have a larger recombination rate than the radiative process e + K → K + ?

**Exercise 5.2.** For the same mixture as in Exercise 5.1, above what electron number density would the three-body process e + K + e → K + e have a larger recombination rate than the radiative process?

**Exercise 5.3.** Slowly moving argon at an initial temperature of 2000°K and at a pressure of 4 atm is lightly seeded with potassium vapor so as to contain $10^{12}$ electrons/cm$^3$. This gas is then expanded through a supersonic converging-diverging nozzle 8 cm long to a velocity of 1000 m sec$^{-1}$. After the expansion the gas temperature is 1100°K and the pressure is 1 atm. Calculate the approximate electron number density just downstream of the nozzle. Show all necessary calculations.

**Exercise 5.4.** Using the random walk concept embodied in equation (5.9), obtain an approximate expression for the average distance $l_R$ traversed by an ion before it recombines. Calculate the value of $l_R$ for potassium ions in atmospheric pressure argon at 2000°K, assuming three-body (electron) recombination and an electron number density of $10^{12}$ cm$^{-3}$.

6. **THE VELOCITY DISTRIBUTION FUNCTION AND AVERAGES**

The fundamental kinetic description of a partially ionized gas is provided by the velocity distribution function for each species. If $n$ is the local number density of the species in question, then the distribution function $f(e)$ is defined through the statement that
denotes the average number of particles per unit volume with velocities
in the range between \( c \) and \( c + dc \). In general, the distribution function
depends on both space and time, as well as on particle velocity. As
defined, \( f(c) \) satisfies the normalization condition

\[
\int_{-\infty}^{\infty} f(c) \, d^3c = 1.
\]

Let us consider a differential volume element of gas \( d^3x \) located at
position \( x \), which is large enough to contain many particles but which
possesses dimensions small compared with the length scale of variation of
macroscopic properties of the gas. At any time, we may represent the velocity
coordinates of each particle in \( d^3x \) belonging to any particular species by a
point in velocity space, as indicated in Fig. 8. As time progresses, these
points will move about and some will disappear while others appear,
corresponding to particles which leave and enter \( d^3x \). Let us focus our
attention next on the velocity volume element \( d^3c \) centered about the vector
c. The velocity distribution function is defined such that \( nf(c) \, d^3c \, d^3x \)
represents the number of particles of the species in question contained in \( d^3c \),
averaged over a time which is long enough to allow many particles to leave
and enter \( d^3c \) but which is short compared with the time scale for
variation of macroscopic properties of the gas.

![Figure 8. The velocity distribution function.](image-url)
In the simplest possible model of a partially ionized gas, it is necessary to introduce as a minimum three species of particles, viz., electrons, positive ions, and neutrals. We shall frequently find it convenient to represent a partially ionized gas by such a model. Approximate results for more complicated gases consisting of several ionic and neutral species may be obtained by interpreting as suitably defined averages ion and neutral quantities appearing in the simple model.

For each species in the gas, one may define a species fluid (or average) velocity relative to some laboratory frame of reference. Thus, if $f_e(c)$ denotes the electron velocity distribution function with respect to the laboratory frame, the electron fluid velocity is

$$u_e = \int_{-\infty}^{\infty} cf_e(c) \, d^3c.$$  \hspace{1cm} (6.2)

In general $u_e = u_e(x, t)$ is a function of position and time. The ion fluid velocity $u_i(x, t)$ and the neutral fluid velocity $u_n(x, t)$ are defined in a completely analogous fashion. The electron, ion, and neutral mass densities are

$$\rho_e(x, t) = m_e n_e(x, t),$$  \hspace{1cm} (6.3a)
$$\rho_i(x, t) = m_i n_i(x, t),$$  \hspace{1cm} (6.3b)
$$\rho_n(x, t) = m_n n_n(x, t),$$  \hspace{1cm} (6.3c)

from which one may obtain the mass density of the fluid as a whole

$$\rho(x, t) = \rho_e + \rho_i + \rho_n.$$  \hspace{1cm} (6.4)

The mean mass velocity of the fluid as a whole is then defined by the equation

$$u(x, t) = \frac{\rho_e u_e + \rho_i u_i + \rho_n u_n}{\rho}.$$  \hspace{1cm} (6.5)

In a general situation, the species fluid velocities may be expected to differ from the mean mass velocity and from each other. The differences are conveniently represented by the diffusion velocities for each species. Thus, the electron diffusion velocity is defined by the difference

$$U_e(x, t) = u_e(x, t) - u(x, t),$$  \hspace{1cm} (6.6)

and similar relations apply for the other species. By virtue of the defining equation for the mean mass velocity, it follows that the diffusion velocities must satisfy the relation

$$\rho_e U_e + \rho_i U_i + \rho_n U_n = 0.$$  \hspace{1cm} (6.7)
For collision-dominated gases, it is usually more convenient to consider particle velocities with respect to a local frame of reference moving with the mean mass velocity of the fluid \( u(x, t) \), rather than with respect to a laboratory frame of reference, as was the case represented in Fig. 8. For this purpose, we may introduce the so-called peculiar velocity

\[
C = c - u(x, t),
\]

and regard the velocity distribution function as a function of \( C \), rather than \( c \). The average number of particles of any species per unit volume with peculiar velocities between \( C \) and \( C + dC \) will henceforth be written as \( n f(C) d^3C \). Corresponding to equation (6.2), we would then have

\[
U_s(x, t) = \int_{-\infty}^{\infty} C f_s(C) d^3C,
\]

where \( U_s \) denotes the diffusion velocity for the species \( s \). For a simple gas (i.e., a gas consisting of a single species), we would have \( U_s = 0 \). Results expressed relative to the mean mass velocity of the fluid correspond, in a sense, to first order deviations from a fluid at rest.

If we suppose that the species \( s \) in a partially ionized plasma carries a charge \( e_s \), then the flux density of charge associated with this species, relative to some laboratory frame of reference, is called the species current density and has the value

\[
j_s = e_s n_s u.
\]

Introducing the species diffusion velocity \( U_s \) and making the substitution \( u_s = u + U_s \), we may write

\[
j_s = e_s n_s u + J_s,
\]

where

\[
J_s = e_s n_s U_s
\]

is referred to as the species conduction current density, and where \( e_s n_s u \) is the species convection current density. In contrast to the convection current density the conduction current density is independent of the frame of reference. The current density for the fluid as a whole is obtained by summing over all species, \( j = \sum_s j_s \), and may be written

\[
j = \rho \dot{u} + J,
\]

where

\[
J = \sum_s e_s n_s U_s
\]
is the total *conduction current density*, and where

\[
\rho^c \equiv \sum_s e_s n_s
\]

(6.14)
is the *net charge density*. If we denote the charge carried by an electron as \(-e\), and suppose for our model that the ions are singly charged, then

\[
J = e(n_i U_i - n_e U_e),
\]

(6.15)
and

\[
\rho^c = e(n_i - n_e).
\]

(6.16)

In order to develop the analog of the reaction rate formula \(R_{\text{D}}^{(p)} = n_1 n_2 g Q_{\text{D}}^{(p)}(g)\) as given by equation (5.1b), but taking into account the distribution of particle velocities, we proceed as follows: In accord with the schematic representation of Fig. 7, we may regard the gas as being made up of a superposition of test-particle beams of infinitesimal strength, a typical beam being composed of particles belonging to the velocity class \(C\). In the frame of reference of the mean mass velocity of the fluid, the number of test particles per unit volume in such a beam is \(dn_1 = n_1 f_1(C) \, d^3C\). With respect to a field particle of velocity \(W\), each of these beam particles has the velocity \(g = C - W\). The number of beam particles passing per unit time through a unit area perpendicular to \(g\) is therefore equal to \(dn_1 g\), where

\[
g = |C - W|.
\]

(6.17)

Since the beam has the same direction as \(g\), the *differential flux density* (of test particles of velocity \(C\) relative to field particles of velocity \(W\)) can be written in vector form as

\[
d\Gamma_1 = [n_1 f_1(C) \, d^3C] \cdot (C - W),
\]

(6.18a)
and the magnitude can be written

\[
d\Gamma_1 = [n_1 f_1(C) \, d^3C] \cdot |C - W|.
\]

(6.18b)

From the definition of the cross section, the number of test particles in this beam of infinitesimal strength undergoing the process \(p\) per unit time with one field particle is

\[
n_1 f_1(C) \, d^3C \, |C - W| \, Q_{\text{D}}^{(p)}(|C - W|).
\]

Since there are \(n_2 f_2(W) \, d^3W\) field particles per unit volume with velocities between \(W\) and \(W + dW\), the average number of \(p\)-type processes per unit time and unit volume between test particles in the velocity class \(C\) and field particles in the velocity class \(W\), or what we may call the *differential reaction rate* for process \(p\), is

\[
dR_{\text{D}}^{(p)} = n_1 n_2 f_1(C) f_2(W) |C - W| Q_{\text{D}}^{(p)}(|C - W|) \, d^3C \, d^3W.
\]

(6.19a)
The total number of processes $p$ taking place per unit volume and unit time is

$$R[p]_2 = n_1 n_2 \int_{-\infty}^{\infty} f_1(C) f_2(W) |C - W| Q^{(p)}_{1/2}(|C - W|) \, d^3C \, d^3W. \quad (6.19b)$$

The integral in equation (6.19b) is nothing more than the average of the quantity $gQ_{12}(g)$. For a process with a threshold energy, it is apparent from the form of equation (6.19b), that the range of integration over velocities is correspondingly reduced to where $Q^{(p)}_{1/2} \neq 0$. When the test and field particles are identical, this calculation counts each collision twice, and so the right hand side of (6.19b) needs to be divided by two (see Vincenti and Kruger, 1965, p. 52, for more details).

To proceed further, we shall assume that $f_1$ and $f_2$ are Maxwellian functions at a temperature $T$ of the peculiar particle velocities, and therefore write

$$f_1(C) = f_1^M \equiv \left( \frac{m_1}{2\pi kT} \right)^{3/2} e^{-m_1C^2/2kT}, \quad (6.20)$$

and a similar expression for $f_2(W)$. Strictly, this form for the distribution function applies only under conditions of thermodynamic equilibrium, but in many nonequilibrium situations it provides an acceptable approximate description. The reaction rate of the process $p$ can then be written

$$R[p]_2 = n_1 n_2 \left( \frac{m_1 m_2}{2\pi kT} \right)^{3/2} \int_{-\infty}^{\infty} e^{-(m_1C^2 + m_2W^2)/2kT} |C - W| Q^{(p)}_{1/2}(|C - W|) \, d^3C \, d^3W. \quad (6.21)$$

Next, we transform to the center-of-mass and relative particle velocities. In the frame of reference of the mean mass velocity of the fluid, these are defined respectively, as follows:

$$G \equiv \frac{m_1 C + m_2 W}{(m_1 + m_2)}, \quad (6.22a)$$

$$g \equiv C - W. \quad (6.22b)$$

The inverse of this transformation is

$$C = G + \frac{m_1}{m_2} g, \quad (6.23a)$$

$$W = G - \frac{m_2}{m_1} g. \quad (6.23b)$$
where

$$m_{12} \equiv \frac{m_1 m_2}{(m_1 + m_2)} \quad (6.24)$$

is the reduced mass. It is not difficult to show that the Jacobian of this transformation is unity, and therefore

$$d^3 C d^3 W = d^3 G d^3 g. \quad (6.25)$$

Employing equations (6.23), the total kinetic energy of the two particles in the frame of reference of the mean mass velocity of the fluid is

$$\frac{m_1 C^2}{2} + \frac{m_2 W^2}{2} = \frac{(m_1 + m_2)}{2} G^2 + \frac{m_{12}}{2} g^2. \quad (6.26)$$

The first term on the right-hand side of equation (6.26) is the kinetic energy of the two-particle system moving as a whole at the speed of the center of mass in the mean-mass-velocity frame. The second term is the relative kinetic energy

$$\epsilon = \frac{m_{12}}{2} g^2. \quad (6.27)$$

The relative particle velocity $g = C - W = c - w$ is the same in the laboratory and in the mean-mass-velocity frames, and so $\epsilon$ is also the same in these two frames. The particle center-of-mass velocity in the laboratory frame has the value $G_u = G + u$.

In terms of spherical polar coordinates we may write $d^3 g = g^2 dg d\Omega_g$, where $d\Omega_g$ denotes the element of solid angle defined by the direction of $g$, and a similar expression may be written for $d^3 G$. Making the required substitutions in equation (6.21) and integrating over solid angle, we obtain

$$R_{12}^{(p)} = n_1 n_2 \left(\frac{4\pi}{2kT}\right)^{3/2} \int_0^\infty G^2 e^{-(m_1 + m_2)G^2/2kT} dG \times \int_0^\infty g^3 e^{-m_{12}g^2/2kT} Q_{12}(g) dg.$$

Using the result $\int_0^\infty y^2 e^{-y^2} dy = \sqrt{\pi}/4$, we have finally

$$R_{12}^{(p)} = n_1 n_2 \left(\frac{8kT}{\pi m_{12}}\right)^{1/2} \int_0^\infty xe^{-x} Q_{12}^{(p)}(\sqrt{\frac{2kT}{m_{12}}}x) dx, \quad (6.28)$$
where \( x = \frac{m_1 g^2}{2kT} \). This expression shows explicitly that the reaction rate is essentially a macroscopic quantity, depending on the thermodynamic state of the gas. For a process with a threshold, the lower limit of the integral in equation (6.28) will be determined by the threshold energy.

The exponential weighting factor appearing in the integrand of equation (6.28) reflects the assumed Maxwellian velocity distribution for the particles involved in the reaction under consideration. For certain situations the assumption of a Maxwellian is not justified, and use of equation (6.28) would lead to erroneous results. As an example, we may consider the case of the electron excitation reaction rate \( R_{12}^{(k-l)} \) in a gas at a temperature much less than the threshold energy. Only electrons in the high-energy tail of the electron velocity distribution function contribute to the integral in (6.28). Since the excitation process removes electrons from the tail, unless these electrons are replenished at an equal rate, it is quite possible for the bulk of the electrons to be approximately Maxwellian, but for the high-energy tail to be distributed quite differently. This situation, as discussed in Chapter IX, leads in effect to a weighting factor other than \( e^{-x} \) and can appreciably affect the value of the excitation rate.

As the last topic in this section, we may make some comments concerning the kinetic theory of transport coefficients. Historically, the first approach to the problem of relating the transport coefficients to the microscopic properties of the particles constituting a gas, was through the introduction of the concept of the mean free path, or equivalently, of the concept of the average collision frequency. This approach will be used in Sec. 12 to calculate the viscosity and thermal conductivity of a partially ionized gas, and in Sec. 13 to calculate the electrical conductivity. As we shall see, the "mean-free-path theory" is deficient in that it leads to expressions involving average collision frequencies (averaged over particle velocities), but it leaves unspecified the manner of averaging. Prescriptions for averaging may be given, and in most circumstances results are probably accurate to a factor of order two or three. To obtain higher accuracy, one must employ a more rigorous approach to kinetic theory based on the calculation of the velocity distribution function, as it is described by the Boltzmann equation. The latter approach is the subject of Chapters VII and VIII. As will be seen, this more rigorous approach makes no reference to the mean-free-path concept.

Under most circumstances, transport properties are dominated by elastic collisions with large scattering angles, and it is reasonable in this context to focus our attention on the momentum transfer collision frequency \( v_{12}^{(1)}(g) = n_2 g Q_{12}^{(1)}(g) \) defined by equation (5.6). To define an average momentum transfer collision frequency we employ a prescription suggested by the
first Chapman-Enskog approximation of the more rigorous theory, and write

$$\bar{v}_{12} \equiv n_2 \bar{\eta}_{12} \bar{Q}_{12},$$  \hspace{1cm} (6.29)

where the average momentum transfer cross section $\bar{Q}_{12}$ is defined as

$$\bar{Q}_{12} \equiv \frac{2}{3} \int_0^\infty x^2 e^{-\frac{x}{m_{12}}} x Q_{12}^{(1)} \left( \sqrt{\frac{2kT}{m_{12}}} x \right) dx,$$  \hspace{1cm} (6.30)

and where

$$\bar{g}_{12} \equiv \int_{-\infty}^{\infty} |C - W| f_1(C) f_2(W) d^3C d^3W = \left( \frac{8kT}{\pi m_{12}} \right)^{1/2},$$  \hspace{1cm} (6.31)

is the mean relative speed for particles with Maxwellian velocity distributions. The result expressed in equation (6.31) is obtained using equation (6.28). For cross sections which vary slowly in the vicinity of $\bar{g}_{12}$, one may frequently employ the approximation

$$\bar{Q}_{12} \approx \frac{4}{3} Q_{12}^{(1)}(\bar{g}_{12}) \approx Q_{12}^{(1)}(\bar{g}_{12}).$$  \hspace{1cm} (6.32)

Equations (6.29) and (6.30) may be interpreted as defining an energy-weighted average of the speed-dependent momentum transfer collision frequency, for as one may readily show,

$$\bar{v}_{12} = \int_0^\infty \left( \frac{m_{12} g^2/2}{3kT/2} \right) v_{12}^{(1)}(g) f_{M}^{(1)}(g) 4\pi g^2 dg.$$

Here $f_{M}^{(1)}$ denotes a Maxwellian distribution for a hypothetical particle having the reduced mass $m_{12}$. Some examples of energy-averaged cross sections, as defined by equation (6.30), are presented in Fig. 29.

The mean free path corresponding to equation (5.8), may now be defined more precisely as

$$l_{1} \equiv \frac{\bar{C}_1}{\bar{v}_1} = \frac{1}{\sum_s (m_s/m_{1s})^{1/2} n_s \bar{Q}_{1s}},$$  \hspace{1cm} (6.33)

where

$$\bar{C}_1 \equiv \int_{-\infty}^{\infty} C f_1(C) d^3C = \left( \frac{8kT}{\pi m_1} \right)^{1/2},$$  \hspace{1cm} (6.34)

is the mean speed of Maxwellian test particles relative to the local mean mass velocity of the fluid.
Exercise 6.1. Verify that the Jacobian of the transformation (6.22) or (6.23) equals unity and, therefore, that \( d^3C \ d^3W = d^3G \ d^3g \).

Exercise 6.2. If the relations (6.23) describe the velocities of two particles before a collision, then after the collision the particle velocities may be written

\[
\begin{align*}
C' &= G' + \frac{m_{12}}{m_1} g', \\
W' &= G' - \frac{m_{12}}{m_2} g'.
\end{align*}
\]

In an elastic collision the total momentum and total kinetic energy of the two particles are conserved. Prove that \( G' = G \) and that \( |g'| = |g| \).

Exercise 6.3. A particle of mass \( m \) and initial velocity \( C \) collides collinearly (so that the particles move on a straight line) with an atom of mass \( M \) initially at rest. The atom is excited and is raised from its ground level to an energy level \( \epsilon_{12} \) units above the ground level. The particle and atom have velocities \( C' \) and \( W' \), respectively, after the collision.

1. What are the conservation equations for this collision?
2. Obtain an expression for the final velocity of the particle of mass \( m \) in terms of \( C, m, M, \) and \( \epsilon_{12} \).
3. From this solution, determine the minimum initial kinetic energy the particle must have. What is this minimum kinetic energy for the case \( m = 2M \)? Discuss.

Exercise 6.4. Obtain an approximate equation for the ionization reaction rate by electron impact of a partially ionized cesium plasma. Assume the temperature of the plasma is much less than the ionization potential of Cs (3.89 eV).

Exercise 6.5. Show that the mean speed and mean square speed of test particles with a Maxwellian velocity distribution are \((8kT/\pi m_1)^{1/2}\) and \((3kT/m_1)\) respectively. Show that the mean relative speed and mean square relative speed are \( \bar{g}_{12} = (8kT/\pi m_{12})^{1/2} \) and \( \bar{g}_{12}^2 = (3kT/m_{12}) \), respectively. Show that \( \bar{g}_{12}^2 = m_{12}/kT \) and that \( \bar{g}_{12}^2 = (2m_{12}/\pi kT)^{1/2} \).

Exercise 6.6. Calculate the mean speeds of the following particles in a gas having a temperature of 2500°K:

1. an electron
2. a hydrogen atom
3. an argon atom
4. a cesium atom
At what temperature would the argon atoms have the same mean speed as the (2500°K) electrons?

**Exercise 6.7.** For a given recombination process, the approximate relation \( \alpha \approx \bar{g}_e Q^{(\text{recomb})} \) may be used to define a corresponding average recombination cross section. Using the data in Table 7, calculate a value for the average cross section for radiative recombination.

**Exercise 6.8.** In accordance with equation (6.18a), the vector differential flux density relative to the mean mass velocity of the fluid for any particle species may be written \( d\Gamma = n f(C) d^3C \). For particles with a Maxwellian velocity distribution, show that the total number of particles passing per unit time through a unit area (from one side to the other) is given by the expression

\[
\frac{n\bar{C}}{4},
\]

where \( \bar{C} = \left( \frac{8kT}{\pi m} \right)^{1/2} \).

**Exercise 6.9.** For the case where the type-1 particles have a Maxwellian distribution at a temperature \( T_1 \), and the type-2 particles are Maxwellian at a temperature \( T_2 \), show that instead of equation (6.28), one obtains

\[
\frac{n_1 n_2}{\pi} \int_0^\infty xe^{-x^2 Q_{12}(g)} dx.
\]

**Exercise 6.10.** The random current density for each species in a gas is defined as the charge carried by the species per unit time through a unit area (from one side to the other). Calculate the random electron and ion currents (in amperes per cm\(^2\)) in a gas containing partially ionized potassium at a temperature of .216 eV with \( n_e = n_i = 10^{13} \text{ cm}^{-3} \). Assume that the particles have Maxwellian velocity distributions.

### 7. ENERGY AND MOMENTUM TRANSFER IN ELASTIC COLLISIONS

In an elastic two-body collision, the total kinetic energy of the particles before and after the collision remains the same. However, in any reference frame other than the center-of-mass frame for the two particles (see Exercise 6.2), the speeds of the two particles will not remain unchanged. For example, a test particle incident on a field particle which is initially stationary will cause the field particle after the collision to exhibit motion. The test particle must therefore have lost some of its initial kinetic energy.

Consider a fluid in motion described by a macroscopic mean mass velocity field \( \mathbf{u} = \mathbf{u}(x, t) \). Let us consider a collision between two particles