THE FORMAL NONEQUILIBRIUM THEORY OF PARTIALLY IONIZED AND/OR NONUNIFORM GAS MIXTURES

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Summary

Starting from Boltzmann-like equations, moment equations for a general gas mixture are developed. The equations are closed, and the collision integrals evaluated, by using Grad's 13-moment approximations for the velocity distribution functions. The collision integrals are determined for all possible types of binary encounters, which include recombination and attachment, spontaneous fission and natural decay, charge exchange and elastic collisions, and excitation and fission- and fusion-like processes. The derivation of transport relationships is considered, while the extension of the results to include such direct radiative phenomena as absorption, photo-ionization, stimulated emission, and Compton scattering is also briefly discussed.

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I. Introduction

In deriving equations for a partially ionized or nonuniform gas a multitude of collision phenomena must be taken into account. Of these the most important are elastic and inelastic collisions, including collisions of the second kind and fission- and fusion-like processes, recombination and attachment, and charge exchange. Furthermore, in any exact treatment the natural decay and spontaneous fission of excited states, the absorption of radiation, and a multitude of other radiative phenomena must also be included. Add to this the nonequilibrium properties of such a mixture and the interaction with electric and magnetic fields and the problem becomes extremely complex.

Fortunately, in a relatively dilute mixture all collision phenomena are essentially of a binary nature, so-called three-body processes being simply a single two-body collision followed by another such collision in competition with a spontaneous fission. Because of this all the processes mentioned in the first paragraph are mathematically similar and may be dealt with in an identical manner. Furthermore, in developing equations of change for the system each excited state of an atom, molecule, or ion may be treated as a particular particle type, the equations for each particle type being formally the same. Therefore, at least mathematically, the development of equations for a relatively dilute gas is a well-defined and logical problem. Ignoring the direct interaction of radiation with particles, the object of this paper is to develop such equations. However, primarily due to notational complications and the multitude of physical phenomena possible, the reduction of these equations to useful practical forms is extremely difficult. Nevertheless, conservation-type equations and transport relationships may be formally obtained and these aspects are also discussed.

General equations for monatomic gas mixtures have been developed by various authors (Kolodner 1950; Herdan and Liley 1960; Liley 1963). However, in such treatments elastic collisions only were considered. On the other hand, certain authors have studied the effects of inelastic processes on transport phenomena for a variety of special cases. For instance, Engelhardt and Phelps (1963) have studied the effects in a Townsend-type discharge, while Wang-Chang and Uhlenbeck (1951) have investigated the effects in a polyatomic nonionized simple gas. However, in addition to being more general, the approach in the present paper to inelastic collision phenomena is entirely different to that of other authors. In essence the method is to extend the analysis of Herdan and Liley (and Kolodner) for monatomic gas mixtures to the case in which inelastic processes are of importance. In particular, equations of change for various moments of the particle velocity distribution functions are generated. In principle, the associated collision integrals are evaluated by expanding the distribution functions in terms of multidimensional Hermite polynomials, although in practice only the first few terms of these integrals, corresponding to Grad's (1949) 13-moment approximations are determined. These equations are then closed by using Grad's 13-moment approximation to express otherwise physically indeterminate moments in terms of significant physical quantities. In carrying this analysis through, the effects of electric and magnetic fields, spatial gradients, and differences in particle temperatures are taken into account.

Since the general form of the equations is essentially identical with that developed by Herdan and Liley for a simple monatomic mixture, as is the form of the elastic collision integrals, the prime object of this paper is to determine general expressions for the inelastic integrals. Unfortunately, the derivation of these is somewhat tedious and therefore only an outline of the method and the final results are presented here, the details being given elsewhere (Bydder and Liley 1967). In Section II the derivation of the relevant equations of change is briefly summarized and the notation employed adequately defined. In Section III the collision integrals are evaluated, while in Section IV special and limiting cases of these are derived. Practical forms of the results, including conservation equations, transport relationships, Ohm's law, and equilibrium solutions are briefly discussed in Section V.

II. General Equations

(a) *Basic Equations and Definitions*

Each particle present in a general gas mixture is typed according to its mass, charge, and internal energy (assumed quantized). For each such particle type j a velocity distribution function $f_j(\boldsymbol{x}, \boldsymbol{c}, t)$, may be defined. Ignoring subscripts, these distribution functions satisfy the "Maxwell–Boltzmann" equations

$$\frac{\partial f}{\partial t}+\boldsymbol{c}.\frac{\partial f}{\partial \boldsymbol{x}}+(\boldsymbol{a}+\boldsymbol{c}\times\boldsymbol{b}).\frac{\partial f}{\partial \boldsymbol{c}}=\frac{\delta f}{\delta t}, \tag{1}$$

where

$$\boldsymbol{a}=(e/m)\boldsymbol{E}+\boldsymbol{g}, \qquad \boldsymbol{b}=(e/m)\boldsymbol{B},$$

$\boldsymbol{c}$ is the velocity vector, $\boldsymbol{x}$ the position vector, t the time, e the particle charge, m the particle mass, $\boldsymbol{g}$ any non-electromagnetic body force, $\boldsymbol{E}$ the electric field vector, $\boldsymbol{B}$ the magnetic induction vector, $\delta f/\delta t$ the "collision" term, $\partial/\partial\boldsymbol{z}\equiv\boldsymbol{e}^{\lambda}\,\partial/\partial z^{\lambda}$ the gradient operator, and $\boldsymbol{e}^{\lambda}$ an appropriate set of base vectors.

There is one such equation for each particle type present. In developing equations of change it is convenient to define a "peculiar" velocity $\boldsymbol{w}_j$ by the equation

$$\boldsymbol{w}_j=\boldsymbol{c}-\boldsymbol{v}_j,$$

where $\boldsymbol{v}_j$ is a function of $\boldsymbol{x}$ and t but may be otherwise unspecified. In practice, however, it is usual to take $\boldsymbol{v}_j$ equal to $\boldsymbol{v}_0$, the mean mass velocity of the system as a whole. Multiplying equation (1), applicable to particles type j, by any tensor (absolute) function $\psi_j(\boldsymbol{w}_j)$ and integrating over velocity space, a general equation of change is obtained. Ignoring subscripts, this equation may be written in the form (cf. Chapman and Cowling 1952, Ch. 18 and p. 49)

$$\frac{\partial n\langle\psi\rangle}{\partial t}+\frac{\partial}{\partial \boldsymbol{x}}.n\langle\boldsymbol{c}\psi\rangle-n\langle\left(\boldsymbol{f}+\boldsymbol{w}\times\boldsymbol{b}-\boldsymbol{w}.\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{x}}\right).\frac{\partial\psi}{\partial \boldsymbol{w}}\rangle=I(\psi), \tag{2}$$

where

$$n\langle\psi\rangle=\int f(\boldsymbol{x},\boldsymbol{c},t)\,\psi(\boldsymbol{w})\,\mathrm{d}\boldsymbol{c}, \tag{3}$$

$$\boldsymbol{f}=\boldsymbol{a}+\boldsymbol{v}\times\boldsymbol{b}-\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}, \qquad \frac{\mathrm{d}}{\mathrm{d}t}\equiv\frac{\partial}{\partial t}+\boldsymbol{v}.\frac{\partial}{\partial \boldsymbol{x}},$$

$$\frac{\partial}{\partial \boldsymbol{x}}\cdot \equiv \boldsymbol{e}^{\lambda}\cdot\frac{\partial}{\partial x^{\lambda}}, \qquad I(\psi) \equiv \int \psi \frac{\delta f}{\delta t}\,\mathrm{d}\boldsymbol{c},$$

n is the particle number density, and $\frac{\partial}{\partial \boldsymbol{x}}\cdot$ the divergence operator.

The velocity space averaged functions $n\langle\psi\rangle$ are referred to as moments of f. Those moments of interest in the subsequent analysis are

$\rho \equiv n\langle m\rangle$	particle mass density;
$U \equiv n\langle \mathscr{E}\rangle$	internal energy density, $\mathscr{E}$ being the internal energy per particle;
$\boldsymbol{u} \equiv \langle \boldsymbol{w}\rangle$	"mean" particle velocity;
$\boldsymbol{p} \equiv n\langle m\boldsymbol{w}\boldsymbol{w}\rangle$	"stress" tensor;
$p \equiv n\langle \frac{1}{3}mw^2\rangle$	"hydrostatic" pressure;
$\{\boldsymbol{p}\} \equiv n\langle m\{\boldsymbol{w}\boldsymbol{w}\}\rangle$	"nonhydrostatic" component of the "stress" tensor;
$\boldsymbol{q} \equiv n\langle \frac{1}{2}m\boldsymbol{w}w^2\rangle$	"thermal energy" flux vector;
$\boldsymbol{H} \equiv n\langle m\boldsymbol{w}\boldsymbol{w}\boldsymbol{w}\rangle$	un-named;
$\boldsymbol{h} \equiv n\langle m\boldsymbol{w}\{\boldsymbol{w}\boldsymbol{w}\}\rangle$	un-named;
$\boldsymbol{l} \equiv n\langle \frac{1}{2}mw^2\boldsymbol{w}\boldsymbol{w}\rangle$	un-named.

Inverted commas are used in naming these moments since they are defined with respect to a frame moving with an arbitrary velocity $\boldsymbol{v}_j$, and do not, therefore, necessarily correspond to the true physical quantities.

The bracket symbol { } used in the definition of the "nonhydrostatic" component of the "stress" tensor is of general significance. If $\boldsymbol{T}$ is any second rank tensor then

$$\{\boldsymbol{T}\} \equiv \tfrac{1}{2}(\boldsymbol{T}+\overline{\boldsymbol{T}})-\tfrac{1}{3}\boldsymbol{I}\boldsymbol{I} : \boldsymbol{T},$$

where $\boldsymbol{I} \equiv \boldsymbol{e}^{\lambda}\boldsymbol{e}_{\lambda}$ is a unit tensor (or idemfactor), $\boldsymbol{e}^{\lambda}$ and $\boldsymbol{e}_{\lambda}$ being an appropriate set of reciprocal base vectors,

$$\boldsymbol{T} = T^{\lambda\mu}\boldsymbol{e}_{\mu}\boldsymbol{e}_{\lambda}, \qquad \text{and} \qquad \overline{\boldsymbol{T}} = T^{\mu\lambda}\boldsymbol{e}_{\mu}\boldsymbol{e}_{\lambda}.$$

In particular,

$$\{\boldsymbol{w}\boldsymbol{w}\} \equiv \boldsymbol{w}\boldsymbol{w}-\tfrac{1}{3}\boldsymbol{I}w^2.$$

Other general definitions of interest are

$\boldsymbol{v}_0 = \rho^{-1}\sum_j \rho_j\langle \boldsymbol{c}_j\rangle$	mean mass velocity,
$\rho = \sum_j \rho_j$	mass density,
$\boldsymbol{r} = \boldsymbol{q}-\frac{5}{2}p\boldsymbol{u}$	heat flux vector.

We have also

$$p = nkT,$$

where k is Boltzmann's constant and T is the kinetic "temperature" as defined by this relationship,

$$\boldsymbol{p} = \{\boldsymbol{p}\}+p\boldsymbol{I}, \qquad \text{and} \qquad \boldsymbol{H} = \boldsymbol{h}+\tfrac{2}{3}\boldsymbol{q}\boldsymbol{I}.$$

Concerning other aspects of the tensor notation employed, the dot product between two tensors $\boldsymbol{A}$ and $\boldsymbol{T}$ is

$$\boldsymbol{A}.\boldsymbol{T} = A^{\alpha\ldots\beta\gamma\delta}T^{\zeta\rho\nu\ldots\epsilon}\boldsymbol{e}_\alpha\ldots\boldsymbol{e}_\gamma(\boldsymbol{e}_\delta.\boldsymbol{e}_\zeta)\boldsymbol{e}_\rho\ldots\boldsymbol{e}_\epsilon$$

and the double dot product is

$$\boldsymbol{A}:\boldsymbol{T} = A^{\alpha\ldots\beta\gamma\delta}T^{\zeta\rho\nu\ldots\epsilon}\boldsymbol{e}_\alpha\ldots{}_\beta(\boldsymbol{e}_\gamma.\boldsymbol{e}_\rho)(\boldsymbol{e}_\delta.\boldsymbol{e}_\zeta)\boldsymbol{e}_\nu\ldots\boldsymbol{e}_\epsilon.$$

The cross product between a vector $\boldsymbol{V}$ and a tensor $\boldsymbol{T}$ is determined as

$$\begin{aligned}\boldsymbol{V}\times\boldsymbol{T} &= T^{\alpha\beta\gamma\ldots}(\boldsymbol{V}\times\boldsymbol{e}_\alpha)\boldsymbol{e}_\beta\boldsymbol{e}_\gamma\ldots\\ &\neq \boldsymbol{T}\times\boldsymbol{V} = T^{\ldots\alpha\beta\gamma}\ldots\boldsymbol{e}_\alpha\boldsymbol{e}_\beta(\boldsymbol{e}_\gamma\times\boldsymbol{V}).\end{aligned}$$

It should also be noted that Greek suffixes are used to denote tensor components, a double suffix summation convention applying. On the other hand, Roman suffixes are used to denote particle type, any associated summation being explicity indicated.

(b) *Fundamental Equations of Change*

Taking ψ equal to m, $m\boldsymbol{w}$, $\frac{1}{2}mw^2$, and $\mathscr{E}$ respectively, equation (2) becomes alternatively the continuity, momentum, translational thermal energy, and internal heat energy equation. Ignoring subscripts, the equations are

$$\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial\boldsymbol{x}}.(\rho\boldsymbol{u}+\rho\boldsymbol{v}) = I(m), \tag{4}$$

$$\frac{\partial\rho\boldsymbol{u}}{\partial t}+\frac{\partial}{\partial\boldsymbol{x}}.(\rho\boldsymbol{v}\boldsymbol{u}+\boldsymbol{p})-\rho\boldsymbol{f}-\rho\boldsymbol{u}\times\boldsymbol{b}+\rho\boldsymbol{u}.\frac{\partial\boldsymbol{v}}{\partial\boldsymbol{x}} = I(m\boldsymbol{w}), \tag{5}$$

$$\frac{\partial\frac{3}{2}p}{\partial t}+\frac{\partial}{\partial\boldsymbol{x}}.(\tfrac{3}{2}p\boldsymbol{v}+\boldsymbol{q})-\rho\boldsymbol{f}.\boldsymbol{u}+\boldsymbol{p}:\frac{\partial\boldsymbol{v}}{\partial\boldsymbol{x}} = I(\tfrac{1}{2}mw^2), \tag{6}$$

$$\frac{\partial U}{\partial t}+\frac{\partial}{\partial\boldsymbol{x}}.(U\boldsymbol{u}+U\boldsymbol{v}) = I(\mathscr{E}). \tag{7}$$

The derivation of these equations is straightforward and needs no comment. Again, taking ψ equal to $m\{\boldsymbol{w}\boldsymbol{w}\}$ and $\frac{1}{2}m\boldsymbol{w}w^2$, equations for the "nonhydrostatic" component of the "stress" tensor and the "thermal" energy flux vector may be obtained. These are

$$\frac{\partial\{\boldsymbol{p}\}}{\partial t}+\frac{\partial}{\partial\boldsymbol{x}}.(\boldsymbol{v}\{\boldsymbol{p}\}+\boldsymbol{h})-2\rho\{\boldsymbol{f}\boldsymbol{u}\}-2\{\{\boldsymbol{p}\}\times\boldsymbol{b}\}+2\left\{\boldsymbol{p}.\frac{\partial\boldsymbol{v}}{\partial\boldsymbol{x}}\right\} = I(m\{\boldsymbol{w}\boldsymbol{w}\}), \tag{8}$$

$$\frac{\partial\boldsymbol{q}}{\partial t}+\frac{\partial}{\partial\boldsymbol{x}}.(\boldsymbol{v}\boldsymbol{q}+\boldsymbol{l})-\boldsymbol{f}.\boldsymbol{p}-\tfrac{3}{2}p\boldsymbol{f}-\boldsymbol{q}\times\boldsymbol{b}+\boldsymbol{q}.\frac{\partial\boldsymbol{v}}{\partial\boldsymbol{x}}+\boldsymbol{H}:\frac{\partial\boldsymbol{v}}{\partial\boldsymbol{x}} = I(\tfrac{1}{2}m\boldsymbol{w}w^2). \tag{9}$$

In terms of physically significant variables, equations (4)–(9) are the basic equations governing the behaviour of the gas mixture, there being an identical set for each particle type present. However, in certain instances various combinations of these equations may be of more use. In particular, an equation for $\boldsymbol{r}$, derived by subtracting $\frac{5}{2}kT/m$ times equation (5) from equation (9), is of more direct value than (9) in the derivation of transport relationships.

(c) *Collision Integrals*

For the equations of the preceding subsection to be of value the "collision" terms must be determined explicitly. As implied in the Introduction, and as discussed further in the next two sections, only binary collisions need be considered. Consider a collision between two particles of types k and l such that

$$k+l \rightarrow k'+l' .$$

Let the differential cross section for such a collision be $\mathrm{d}\sigma_{kl}^{k'l'}$. Then the number of such collisions per unit volume per unit time involving those particles with velocities in the ranges $(\boldsymbol{c}_k, \boldsymbol{c}_k+\mathrm{d}\boldsymbol{c}_k)$, $(\boldsymbol{c}_l, \boldsymbol{c}_l+\mathrm{d}\boldsymbol{c}_l)$ is

$$f_k(\boldsymbol{c}_k)\, f_l(\boldsymbol{c}_l)\, g_{kl}\, \mathrm{d}\sigma_{kl}^{k'l'}\, \mathrm{d}\boldsymbol{c}_k\, \mathrm{d}\boldsymbol{c}_l \qquad \text{where} \qquad g_{kl} = |\boldsymbol{c}_k - \boldsymbol{c}_l| .$$

If $\Delta_{kl}^{k'l'}(\psi_j)$ denotes the change in ψ_j due to such a collision then the total rate of change, per unit volume, of ψ_j due to collisions between particles of types k and l is

$$I_{kl}(\psi_j) = \sum_{(k'l')} I_{kl}^{k'l'}(\psi_j), \tag{10}$$

where

$$I_{kl}^{k'l'}(\psi_j) = \int f_k\, f_l\, \Phi_{kl}^{k'l'}(\psi_j)\, \mathrm{d}\boldsymbol{c}_k\, \mathrm{d}\boldsymbol{c}_l , \tag{11}$$

with

$$\Phi_{kl}^{k'l'}(\psi_j) = \int \Delta_{kl}^{k'l'}(\psi_j)\, g_{kl}\, \mathrm{d}\sigma_{kl}^{k'l'} . \tag{12}$$

The integrations are over all parameters of the differential cross section and over all velocity space $\boldsymbol{c}_k$, $\boldsymbol{c}_l$. The summation over $(k'l')$ applies to all possible combinations of k' and l', ensuring, however, that no such combination is counted twice.

Finally, the total rate change of ψ_j due to collisions between all particle types is

$$I(\psi_j) = \tfrac{1}{2} \sum_k \sum_l I_{kl}(\psi_j), \tag{13}$$

where for symmetry the I_{kl} are summed over both k and l.

To evaluate the integrals (11), the distribution functions must be given explicitly in terms of the $\boldsymbol{c}$ or the $\boldsymbol{w}_k$, etc. If the latter are chosen, then to have uniformity and consistency in presentation it is advisable to make all $\boldsymbol{v}_j$ the same. In particular, it is convenient to take $\boldsymbol{v}_j$ equal to $\boldsymbol{v}_0$, where $\boldsymbol{v}_0$ is the mean mass velocity as defined in Section II(a). In general, to express f explicitly in terms of, say, $\boldsymbol{w}$ it is necessary to expand f in terms of known functions of $\boldsymbol{w}$. For a gas mixture in which the various components may have different temperatures, the most suitable of all such possible expansions is that originally proposed by Grad (1949), namely, an expansion in terms of multidimensional Hermite polynomials. However, in order to make the problem tractable it is necessary to approximate to this expansion by a finite number of terms. The resulting expression for f is known as Grad's 13-moment approximation. Ignoring subscripts, in terms of $\boldsymbol{w}$ (with $\boldsymbol{v}_j = \boldsymbol{v}_0$) this is

$$f = f^0[a^0 + \boldsymbol{a}^1 . \boldsymbol{w} + \boldsymbol{a}^2 : \boldsymbol{w}\boldsymbol{w} + \boldsymbol{a}^3 . \boldsymbol{w}(\alpha w^2 - \tfrac{5}{2})], \tag{14}$$

where

$$f^0 = n(\alpha/\pi)^{3/2}\exp(-\alpha w^2).$$

Using this expression for f in the defining equation (3) to determine $\langle 1\rangle$, $\langle \boldsymbol{w}\rangle$, $\langle \frac{1}{2}mw^2\rangle$, $\langle m\{\boldsymbol{w}\boldsymbol{w}\}\rangle$, and $\langle \frac{1}{2}m\boldsymbol{w}w^2\rangle$, it is found that

$$\alpha = m/2kT, \qquad \begin{array}{ll} a^0 = 1, & \boldsymbol{a}^1 = 2\alpha\boldsymbol{u}, \\ \boldsymbol{a}^2 = (\alpha/p)\{\boldsymbol{p}\}, & \boldsymbol{a}^3 = \frac{4}{5}(\alpha/p)\boldsymbol{r}. \end{array}$$

Using the approximations (14) for the distribution functions in (11), knowing the differential cross sections and the dynamics of a collision, the collision integrals may be determined. These integrations are carried out in Section III and in the associated references. It is, however, important to note at this stage that the product $f_k f_l$ contains both linear and quadratic terms in the $\boldsymbol{a}_k$ and $\boldsymbol{a}_l$. In evaluating the integrals the quadratic terms are ignored. It follows therefore, from considerations of tensorial rank alone, that

$$I_j(m_j\boldsymbol{w}) = \sum_s (c_{js}^{uu}\rho_s\boldsymbol{u}_s + c_{js}^{ur}\boldsymbol{r}_s), \tag{15}$$

$$I_j(m_j\{\boldsymbol{w}\boldsymbol{w}\}) = \sum_s c_{js}^{pp}\{\boldsymbol{p}_s\}, \tag{16}$$

$$I_j(\tfrac{1}{2}m_j\boldsymbol{w}w^2) = \sum_s (c_{js}^{qu}\rho_s\boldsymbol{u}_s + c_{js}^{qr}\boldsymbol{r}_s). \tag{17}$$

In principle, the object of the following Sections III and IV is to explicitly determine the coefficients c and corresponding scalar terms for the continuity and energy equations.

(d) *Closure of Equations of Change*

Even with the collision integrals evaluated, equations (4)–(9) do not form a closed set of equations. The moments $\boldsymbol{h}$ and $\boldsymbol{l}$ are still undetermined. In general it is necessary to express these higher moments in terms of the lower moments before a closed set is obtained. Since the collision integrals are to be evaluated subject to (14), an obviously consistent method of closing these equations is to use the same expression for f to determine $\boldsymbol{h}$ and $\boldsymbol{l}$. Doing this, it is found (cf. Grad 1949; Liley 1963) that

$$\boldsymbol{l} = \tfrac{7}{2}(kT/m)\{\boldsymbol{p}\} + \tfrac{5}{2}(kT/m)p\boldsymbol{I}$$

and, referred to a rectangular system of unit base vectors $\boldsymbol{i}_\lambda$,

$$\boldsymbol{H} = \tfrac{2}{5}(q_\lambda\,\delta_{\sigma\mu} + q_\sigma\,\delta_{\lambda\mu} + q_\mu\,\delta_{\sigma\lambda})\boldsymbol{i}_\lambda\boldsymbol{i}_\sigma\boldsymbol{i}_\mu,$$

where the δ's are the usual Kronecker delta functions. In particular, it follows from this expression for $\boldsymbol{H}$ that

$$\frac{\partial}{\partial \boldsymbol{x}}.\boldsymbol{h} = \frac{4}{5}\left\{\frac{\partial \boldsymbol{q}}{\partial \boldsymbol{x}}\right\},$$

$$\boldsymbol{H}:\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{x}} = \frac{2}{5}\left(\boldsymbol{q}.\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{x}}+\boldsymbol{q}\frac{\partial}{\partial \boldsymbol{x}}.\boldsymbol{v}+\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{x}}.\boldsymbol{q}\right).$$

III. Collision Integrals

(a) *Collision Dynamics*

Before the collision integrals can be evaluated the parameters of the differential cross section must be specified and the $\Delta(\psi_j)$'s expressed in terms of the integration variables. To do this the relevant parameters of a collision must be first determined. As in Section II(c), consider a collision between two particles k and l such that

$$k+l \rightarrow k'+l'.$$

With respect to the mean mass velocity $\boldsymbol{v}_0$, the centre of mass velocity is

$$\boldsymbol{G} = M_k\,\boldsymbol{w}_k + M_l\,\boldsymbol{w}_l, \tag{18}$$

where $\boldsymbol{w}_k$ and $\boldsymbol{w}_l$ are the peculiar velocities prior to a collision and

$$M_k = m_k/m_0, \qquad M_l = m_l/m_0, \qquad m_0 = m_k + m_l.$$

Again, define a relative velocity

$$\boldsymbol{g} \equiv \boldsymbol{g}_{kl} = \boldsymbol{w}_k - \boldsymbol{w}_l = -\boldsymbol{g}_{lk}. \tag{19}$$

Then it follows that

$$\boldsymbol{w}_k = \boldsymbol{G} + M_l\,\boldsymbol{g}, \tag{20}$$

$$\boldsymbol{w}_l = \boldsymbol{G} - M_k\,\boldsymbol{g}. \tag{21}$$

Similarly, subsequent to the collision,

$$\boldsymbol{w}_{k'} = \boldsymbol{G}' + M_{l'}\,\boldsymbol{g}', \tag{22}$$

$$\boldsymbol{w}_{l'} = \boldsymbol{G}' - M_{k'}\,\boldsymbol{g}', \tag{23}$$

the primes, in general, denoting variables after a collision. However, from the conservation of mass and momentum

$$m_0' = m_0, \qquad \boldsymbol{G}' = \boldsymbol{G}, \tag{24}$$

while from the conservation of energy

$$\tfrac{1}{2}m_0'\,G'^2 + \tfrac{1}{2}m_{k'l'}\,g'^2 = \tfrac{1}{2}m_0\,G^2 + \tfrac{1}{2}m_{kl}\,g^2 - \Delta E_{kl,k'l'}, \tag{25}$$

where

$$m_{kl} = m_k\,m_l/m_0, \qquad m_{k'l'} = m_{k'}\,m_{l'}/m_0,$$

and

$$\Delta E_{kl,k'l'} \equiv \mathscr{E}_{k'} + \mathscr{E}_{l'} - \mathscr{E}_k - \mathscr{E}_l + \delta E_{kl,k'l'}.$$

$\mathscr{E}_{k'}$, $\mathscr{E}_k$, ... are the internal energies and $\delta E_{kl,k'l'}$ is the loss in kinetic energy due to immediate radiation or any other such cause.

Defining

$$\lambda^2_{kl,k'l'} = (m_{kl}/m_{k'l'})(1-2\Delta E_{kl,k'l'}/m_{kl}\, g^2)\,, \tag{26}$$

it follows from (24) and (25) that

$$g' = \lambda g\,,$$

subscripts being ignored. Therefore, in particular,

$$\boldsymbol{g}' = \lambda \boldsymbol{g}\cos\chi + \lambda g \sin\chi\cos\epsilon\, \boldsymbol{i}_1 + \lambda g\sin\chi\sin\epsilon\, \boldsymbol{i}_2\,, \tag{27}$$

where $\boldsymbol{i}_1$ and $\boldsymbol{i}_2$ are two mutually orthogonal unit vectors both being perpendicular to $\boldsymbol{g}$, and χ and ϵ are the polar and azimuthal "scattering" angles. (It is important to note that as defined $\chi \equiv \chi_{k'l'} \neq \chi_{l'k'} = \pi - \chi_{k'l'}$.)

It follows that the parameters of the collision are $\boldsymbol{G}$, $\boldsymbol{g}$, λ, χ, and ϵ, or to be more exact $\boldsymbol{G}$, $\boldsymbol{g}$, χ, ϵ, the particle types k, l, k', l', and the energy loss δE. This means that the differential cross section, referred to a centre of mass system, must be expressed in the form

$$\mathrm{d}\sigma^{k'l'}_{kl} = \sigma^{k'l'}_{kl}(g, \chi, \epsilon, \delta E)\sin\chi\,\mathrm{d}\chi\,\mathrm{d}\epsilon\,\mathrm{d}(\delta E)\,, \tag{28}$$

the dependence on particle type being implicit in the sub- and super-script notation.

The $\Delta(\psi_j)$ must now be determined in terms of these same parameters. Obviously, collisions between particles of types k and l only contribute to particles of type j if one or more of the k, l, k', l' are of type j. That is, in particular, the $\Delta(\psi_j)$ are given by

$$\Delta^{k'l'}_{kl}(\psi_j) = \psi_{k'}\,\delta_{k'j} + \psi_{l'}\,\delta_{l'j} - \psi_k\,\delta_{kj} - \psi_l\,\delta_{lj}\,, \tag{29}$$

where the δ's are the usual Kronecker delta functions and the $\psi_{k'}, \ldots$ are given in terms of the $\boldsymbol{G}$, $\boldsymbol{g}$, λ, χ, and ϵ.

For example, take $\psi_j = m_j\,\boldsymbol{w}_j$. Then from (20)

$$m_k\,\boldsymbol{w}_k\,\delta_{kj} = m_k(\boldsymbol{G}+M_l\,\boldsymbol{g})\delta_{kj} \equiv m_j\,\delta_{kj}\,\boldsymbol{G} + m_{jr}\,\delta_{jk}\,\boldsymbol{g}\,,$$

where

$$m_{jr} = m_j(m_0 - m_j)/m_0\,,$$

with similar terms for $m_{k'}\,\boldsymbol{w}_{k'}\,\delta_{k'j}, \ldots$. Using (28) and (29) it follows that

$$\begin{aligned}\Delta^{k'l'}_{kl}(m_j\,\boldsymbol{w}_j) = {} & m_j(\delta_{k'j}+\delta_{l'j}-\delta_{kj}-\delta_{lj})\boldsymbol{G} + m_{jr}(\delta_{k'j}-\delta_{l'j})\boldsymbol{g}(1-\lambda\cos\chi)\\ & + m_{jr}(\delta_{k'j}-\delta_{l'j})\lambda g\sin\chi\,(\cos\epsilon\,\boldsymbol{i}_1 + \sin\epsilon\,\boldsymbol{i}_2) + m_{jr}(\delta_{k'j}-\delta_{l'j}-\delta_{kj}+\delta_{lj})\boldsymbol{g}\,,\end{aligned} \tag{30}$$

there being corresponding, but in general more complicated, expressions for other values of ψ_j (see, in particular, Bydder and Liley 1967).

(b) *Transformations*

Since the Φ's of equations (11) and (12) are to be expressed in terms of $\boldsymbol{G}$ and $\boldsymbol{g}$, it is necessary to transform the integrals (11) from integrations over velocity space $\boldsymbol{c}_k$, $\boldsymbol{c}_l$ to integrations over velocity space $\boldsymbol{G}$, $\boldsymbol{g}$. Noting that $\boldsymbol{w}_k = \boldsymbol{c}_k - \boldsymbol{v}_0$, $\boldsymbol{w}_l = \boldsymbol{c}_l - \boldsymbol{v}_0$, with equations (20) and (21) giving $\boldsymbol{w}_k$ and $\boldsymbol{w}_l$ in terms of $\boldsymbol{G}$ and $\boldsymbol{g}$, the Jacobian of the transformation is unity and

$$I_{kl}^{k'l'}(\psi_j) = \int f_k f_l \Phi_{kl}^{k'l'}(\psi_j)\, \mathrm{d}\boldsymbol{G}\, \mathrm{d}\boldsymbol{g}. \tag{31}$$

On expressing the $f_k f_l$ in terms of $\boldsymbol{G}$ and $\boldsymbol{g}$ and noting that σ is independent of $\boldsymbol{G}$, that is, $\boldsymbol{G}$ only occurs in simple algebraic sums in the Φ's (i.e. in the $\Delta(\psi)$'s), integration over $\boldsymbol{G}$ should be immediately possible. Unfortunately, this is not the case. Due primarily to the fact that the different particle types concerned may have different kinetic temperatures, the exponential term in the product $f_k f_l$ inhibits direct integration. Therefore, a further transformation is necessary. This involves the definition of two dimensionless velocities:

$$\boldsymbol{x} = \beta(\boldsymbol{G}+\zeta\boldsymbol{g}), \tag{32}$$

$$\boldsymbol{y} = \gamma\boldsymbol{g}, \tag{33}$$

where

$$\beta^2 \equiv \alpha_k+\alpha_l, \qquad \gamma^2 \equiv \alpha_k\alpha_l/\beta^2, \qquad \zeta \equiv \zeta_{kl} = (\alpha_k M_l - \alpha_l M_k)/\beta^2 = -\zeta_{lk}. \tag{34}$$

In terms of these velocities, (20) and (21) become

$$\boldsymbol{w}_k = \beta^{-1}\boldsymbol{x}+\gamma^{-1}(M_l-\zeta)\boldsymbol{y}, \tag{35}$$

$$\boldsymbol{w}_l = \beta^{-1}\boldsymbol{x}-\gamma^{-1}(M_k+\zeta)\boldsymbol{y}. \tag{36}$$

From (32) and (33) the Jacobian of the transformation from $\boldsymbol{G}$, $\boldsymbol{g}$ to $\boldsymbol{x}, \boldsymbol{y}$ is such that

$$\mathrm{d}\boldsymbol{G}\,\mathrm{d}\boldsymbol{g} = (\alpha_k\alpha_l)^{-3/2}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{y},$$

and on using (35) and (36) in the expressions for the distribution functions the collision integral (31) becomes

$$I_{kl}^{k'l'}(\psi_j) = n_k n_l \pi^{-3} \int d(\boldsymbol{x},\boldsymbol{y}) \exp(-x^2-y^2)\, \Phi_{kl}^{k'l'}(\psi_j)\, \mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{y}. \tag{37}$$

$d(\boldsymbol{x},\boldsymbol{y})$ has a leading term equal to unity and, besides being a function of $\boldsymbol{x}$ and $\boldsymbol{y}$, is also a function of terms that are both linear and quadratic in the moments of f_k and f_l. The integral form (37) is of course generally true. Not only is it obtained when the distribution functions are given by the approximations (14), but it is also obtained when the complete expansions in terms of multidimensional Hermite polynomials are used. (Using (14) and ignoring the quadratic terms, the exact expression for $d(\boldsymbol{x},\boldsymbol{y})$ in terms of the $\boldsymbol{u}$, $\{\boldsymbol{p}\}$, and $\boldsymbol{r}$ is given by Bydder and Liley (1967).)

(c) *Integration over the Azimuth*

Using (32) and (33) to express the $\Delta(\psi)$'s in terms of the $\boldsymbol{x}$ and $\boldsymbol{y}$, and noting that σ is independent of $\boldsymbol{x}$, integration over $\boldsymbol{x}$ is immediately possible. However, in performing such integrations many terms containing the azimuthal angle ϵ are involved. In most cases of practical interest σ is independent of ϵ and such terms are superfluous. (Of course, in the case of various asymmetric molecules it is to be expected that for given orientations individual cross sections will be functions of ϵ. However, in the absence of an external polarizing agent it is also to be expected that suitably averaged values over all possible orientations will be independent of ϵ.) Therefore, on the assumption that σ is independent of ϵ, it is logical to integrate over this parameter first. In fact it is convenient to carry out such integrations at a level characterized by equation (30), i.e. prior to the transformation from $\boldsymbol{G}, \boldsymbol{g}$ to $\boldsymbol{x}, \boldsymbol{y}$. The results are such that the Φ's of equation (12) may be expressed in terms of a general integral function ϕ defined by

$$\phi_{kl}^{k'l'}(\mu,\nu) = \int (1-\lambda_{kl,k'l'}^{\mu}\cos^{\nu}\chi) g_{kl}\,\sigma_{kl}^{k'l'}\sin\chi\,\mathrm{d}\chi\,\mathrm{d}(\delta E)\,, \tag{38}$$

where the μ and ν are power indices. The integration limits are from 0 to π for χ and embrace all possible values of δE. In order to maintain a uniform notation, this equation is also used to define a function $\phi(-\infty,0)$. The associated term involving λ and χ is $\lambda^{-\infty}\cos^0\chi$ and this term is always taken to be zero no matter what the magnitude of λ, that is, $\lambda^{-\infty}\equiv 0$.

As an example, on inserting (30) in (12) and integrating over ϵ from 0 to 2π,

$$\begin{aligned}\Phi_{kl}^{k'l'}(m_j\,\boldsymbol{w}_j) = {} & 2\pi m_j(\delta_{k'j}+\delta_{l'j}-\delta_{kj}-\delta_{lj})\,\phi_{kl}^{k'l'}(-\infty,0)\,\boldsymbol{G} \\ & +2\pi m_{jr}(\delta_{k'j}-\delta_{l'j}-\delta_{kj}+\delta_{lj})\,\phi_{kl}^{k'l'}(1,1)\,\boldsymbol{g} \\ & -2\pi m_{jr}(\delta_{k'j}-\delta_{l'j})\,\phi_{kl}^{k'l'}(-\infty,0)\,\boldsymbol{g}\,,\end{aligned} \tag{39}$$

there being corresponding expressions for other values of ψ_j (Bydder and Liley 1967).

(*d*) *Integration over* $\boldsymbol{x}$ *Velocity Space*

Having determined the Φ's in terms of the ϕ's, $\boldsymbol{G}$, and $\boldsymbol{g}$, these may be rewritten in terms of the ϕ's, $\boldsymbol{x}$, and $\boldsymbol{y}$. The ϕ's become functions of the scalar y and not of $\boldsymbol{x}$ or $\boldsymbol{y}$. Limiting the subsequent integrations to the case for which $d(\boldsymbol{x},\boldsymbol{y})$ is given by only the linear terms in the product $f_k f_l$, the f's being given by (14), integration over $\boldsymbol{x}$ is therefore straightforward. However, the associated algebra is extremely tedious and only the results are quoted, the details being contained in the previously mentioned report by Bydder and Liley (1967). In carrying out these integrations it is also possible to reduce the integrals over velocity space $\boldsymbol{y}$ to integrals over the scalar y, the latter integrals being expressible in the common form

$$\Omega_{kl,k'l'}^{\mu,\nu}(r) \equiv \pi^{\frac{1}{2}} \int_0^\infty \exp(-y^2)\,y^{2r+2}\,\phi_{kl}^{k'l'}(\mu,\nu)\,\mathrm{d}y\,. \tag{40}$$

The Ω's and ϕ's as used here are in fact generalizations of similar functions defined by Chapman and Cowling (1952). They are, apart from a particle number density factor, essentially collision frequencies.

In order to avoid subsequent confusion, certain definitions will be restated before the final results are presented. The reduced mass m_{jr} is defined by

$$m_{jr} = m_j(m_0-m_j)/m_0\,,$$

where m_j is the mass of particle type j. With respect to particle types k and l the parameter α is given by

$$\alpha_k = m_k/2kT_k\,, \qquad \alpha_l = m_l/2kT_l\,.$$

k is Boltzmann's constant and T the kinetic temperature. β, γ, and ζ are as defined by equation (34), it being important to remember that ζ is equivalent to $\zeta_{kl} = -\zeta_{lk}$. ρ is the particle mass density and n, $\boldsymbol{u}$, $\{\boldsymbol{p}\}$, and $\boldsymbol{r}$ are as defined in Section II(a).

Since certain combinations of the δ functions repeatedly occur it is notationally convenient to replace these by single functions. In particular, it is convenient to define

$$\left.\begin{aligned} \delta_{kl}(1) &\equiv \delta_{k'j}+\delta_{l'j}-\delta_{lj}-\delta_{kj}\,, \qquad & \delta_{kl}(2) &\equiv \delta_{k'j}-\delta_{l'j}-\delta_{kj}+\delta_{lj}\,,\\ \delta_{kl}(3) &\equiv \delta_{k'j}-\delta_{l'j}\,, & \delta_{kl}(4) &\equiv \delta_{k'j}+\delta_{l'j}\,. \end{aligned}\right\} \tag{41}$$

Again, for notational convenience, the subscripts $kl, k'l'$ associated with the Ω's will be ignored, as will the superscripts associated with the I's and the subscripts associated with the $\delta_{kl}(1)$, $\delta_{kl}(2)$, ...

(i) *The Scalar* $I_{kl}(\psi_j)$

The integrals associated with the mass continuity, internal energy, and translational kinetic energy are all scalar functions and are given by

$$I_{kl}(m_j) = n_k\, n_l\, m_j\, \delta(1)\, 8\Omega^{-\infty,0}(0)\,,$$

$$I_{kl}(\mathscr{E}_j) = n_k\, n_l\, \mathscr{E}_j\, \delta(1)\, 8\Omega^{-\infty,0}(0)\,,$$

$$I_{kl}(\tfrac{1}{2}m_j\, w_j^2) = \frac{4n_k\, n_l}{\gamma^2}\Big[m_j\, \delta(1)\Big(\Big[\Big(\frac{m_{jr}}{m_j}\Big)^2+\zeta^2\Big]\Omega^{-\infty,0}(1)+\frac{3\gamma^2}{2\beta^2}\Omega^{-\infty,0}(0)\Big)$$
$$-m_{jr}\,\delta(2)\,2\zeta\Omega^{-\infty,0}(1)+m_{jr}\,\delta(3)\,2\zeta\Omega^{1,1}(1)-\frac{(m_{jr})^2}{m_j}\,\delta(4)\,\Omega^{2,0}(1)\Big]\,.$$

(ii) *The Momentum Integral*

This integral may be written in the form

$$I_{kl}(m_j\, \boldsymbol{w}_j) = n_k\, n_l[c_1^{uu}(\alpha_k)+c_2^{uu}(\alpha_k)]\boldsymbol{u}_k+n_k\, n_l[c_1^{uu}(\alpha_l)-c_2^{uu}(\alpha_l)]\boldsymbol{u}_l$$
$$+n_k\, n_l[c_1^{ur}(\alpha_k)+c_2^{ur}(\alpha_k)]\boldsymbol{r}_k/\rho_k+n_k\, n_l[c_1^{ur}(\alpha_l)-c_2^{ur}(\alpha_l)]\boldsymbol{r}_l/\rho_l\,,$$

where

$$c_1^{uu}(\alpha) = 8(\alpha/\beta^2)m_j\,\delta(1)\,\Omega^{-\infty,0}(0)\,,$$

$$c_2^{uu}(\alpha) = \tfrac{16}{3}[-m_j\,\delta(1)\,\zeta\Omega^{-\infty,0}(1)+m_{jr}\,\delta(2)\,\Omega^{-\infty,0}(1)-m_{jr}\,\delta(3)\,\Omega^{1,1}(1)]\,,$$

$$c_1^{ur}(\alpha) = \tfrac{32}{3}(\gamma^2\alpha/\beta^2)m_j\,\delta(1)\big(\Omega^{-\infty,0}(1)-\tfrac{3}{2}\Omega^{-\infty,0}(0)\big)\,,$$

$$c_2^{ur}(\alpha) = \tfrac{32}{3}\gamma^2[m_j\,\delta(1)\,\zeta\big(\Omega^{-\infty,0}(1)-\tfrac{2}{5}\Omega^{-\infty,0}(2)\big)+m_{jr}\,\delta(2)\,\big(\tfrac{2}{5}\Omega^{-\infty,0}(2)-\Omega^{-\infty,0}(1)\big)$$
$$+m_{jr}\,\delta(3)\,\big(\Omega^{1,1}(1)-\tfrac{2}{5}\Omega^{1,1}(2)\big)]\,.$$

It is to be appreciated that the subscripts j and $kl, k'l'$ should also be associated with these coefficients; that is, for example

$$c_1^{uu}(\alpha) \equiv c_{1,j,kl,k'l'}^{uu}(\alpha)\,.$$

(iii) *The Stress Equation Integral*

This integral is given by

$$I_{kl}(m_j\{\boldsymbol{w}_j\,\boldsymbol{w}_j\}) = n_k n_l[c_1^{pp}(\alpha_k) + c_2^{pp}(\alpha_k)]\{\boldsymbol{p}_k\}/\rho_k + n_k n_l[c_1^{pp}(\alpha_l) - c_2^{pp}(\alpha_l)]\{\boldsymbol{p}_l\}/\rho_l,$$

where

$$\begin{aligned} c_1^{pp}(\alpha) = \frac{16}{3}\Bigg[& m_j\,\delta(1)\left(\frac{3\alpha^2}{2\beta^4}\,\Omega^{-\infty,0}(0) + \frac{2}{5}\left[\zeta^2 + \left(\frac{m_{jr}}{m_j}\right)^2\right]\Omega^{-\infty,0}(2)\right) \\ & - m_{jr}\,\delta(2)\tfrac{4}{5}\zeta\Omega^{-\infty,0}(2) + m_{jr}\,\delta(3)\tfrac{4}{5}\zeta\Omega^{1,1}(2) \\ & + \frac{(m_{jr})^2}{m_j}\,\delta(4)\left(\tfrac{1}{5}\Omega^{2,0}(2) - \tfrac{3}{5}\Omega^{2,2}(2)\right)\Bigg], \end{aligned}$$

$$c_2^{pp}(\alpha) = \frac{16}{3}\left[-m_j\,\delta(1)\frac{2\zeta\alpha}{\beta^2}\,\Omega^{-\infty,0}(1) + m_{jr}\,\delta(2)\frac{2\alpha}{\beta^2}\,\Omega^{-\infty,0}(1) - m_{jr}\,\delta(3)\frac{2\alpha}{\beta^2}\,\Omega^{1,1}(1)\right].$$

(iv) *The Thermal Energy Flux Integral*

Like the momentum integral this integral may be presented in the form

$$\begin{aligned} I_{kl}(\tfrac{1}{2}m_j\,\boldsymbol{w}w^2) = {} & n_k n_l[c_1^{qu}(\alpha_k) + c_2^{qu}(\alpha_k)]\boldsymbol{u}_k + n_k n_l[c_1^{qu}(\alpha_l) - c_2^{qu}(\alpha_l)]\boldsymbol{u}_l \\ & + n_k n_l[c_1^{qr}(\alpha_k) + c_2^{qr}(\alpha_k)]\boldsymbol{r}_k/\rho_k + n_k n_l[c_1^{qr}(\alpha_l) - c_2^{qr}(\alpha_l)]\boldsymbol{r}_l/\rho_l, \end{aligned}$$

where

$$\begin{aligned} c_1^{qu}(\alpha) = {} & m_j\,\delta(1)\left[\frac{10\alpha}{\beta^4}\,\Omega^{-\infty,0}(0) + \frac{20\alpha}{3\beta^2\gamma^2}\left(\zeta^2 + \left(\frac{m_{jr}}{m_j}\right)^2\right)\Omega^{-\infty,0}(1)\right] \\ & - m_{jr}\,\delta(2)\frac{40\alpha\zeta}{3\beta^2\gamma^2}\,\Omega^{-\infty,0}(1) \\ & + m_{jr}\,\delta(3)\frac{40\alpha\zeta}{3\beta^2\gamma^2}\,\Omega^{1,1}(1) \\ & - \frac{(m_{jr})^2}{m_j}\,\delta(4)\frac{20\alpha}{3\beta^2\gamma^2}\,\Omega^{2,0}(1), \end{aligned}$$

$$\begin{aligned} c_2^{qu}(\alpha) = {} & -m_j\,\delta(1)\left[\frac{20\zeta}{3\beta^2}\,\Omega^{-\infty,0}(1) + \frac{8\zeta}{3\gamma^2}\left(\zeta^2 + 3\left(\frac{m_{jr}}{m_j}\right)^2\right)\Omega^{-\infty,0}(2)\right] \\ & + m_{jr}\,\delta(2)\left[\frac{20}{3\beta^2}\,\Omega^{-\infty,0}(1) + \frac{8}{\gamma^2}\left(\zeta^2 + \frac{1}{3}\left(\frac{m_{jr}}{m_j}\right)^2\right)\Omega^{-\infty,0}(2)\right] \\ & - m_{jr}\,\delta(3)\left[\frac{20}{3\beta^2}\,\Omega^{1,1}(1) + \frac{8\zeta^2}{\gamma^2}\,\Omega^{1,1}(2) + \frac{8}{3\gamma^2}\left(\frac{m_{jr}}{m_j}\right)^2\Omega^{3,1}(2)\right] \\ & + \frac{(m_{jr})^2}{m_j}\,\delta(4)\left[\frac{8\zeta}{3\gamma^2}\left(\Omega^{2,0}(2) + 2\Omega^{2,2}(2)\right)\right], \end{aligned}$$

$$c_1^{qr}(\alpha) = m_j\,\delta(1)\left[-\frac{20\alpha^2}{\beta^4}\left(1-\frac{7\alpha}{5\beta^2}\right)\Omega^{-\infty,0}(0)+\frac{40\alpha}{3\beta^2}\left(\frac{\gamma^2}{\beta^2}-\zeta^2-\left(\frac{m_{jr}}{m_j}\right)^2\right)\Omega^{-\infty,0}(1)\right.$$
$$\left.+\frac{176\alpha}{15\beta^2}\left(\left(\frac{m_{jr}}{m_j}\right)^2+\zeta^2\right)\Omega^{-\infty,0}(2)\right]$$
$$+m_{jr}\,\delta(2)\left[\frac{80\alpha}{3\beta^2}\,\zeta\left(\Omega^{-\infty,0}(1)-\frac{22}{25}\,\Omega^{-\infty,0}(2)\right)\right]$$
$$-m_{jr}\,\delta(3)\left[\frac{80\alpha}{3\beta^2}\,\zeta\left(\Omega^{1,1}(1)-\frac{22}{25}\,\Omega^{1,1}(2)\right)\right]$$
$$-\frac{(m_{jr})^2}{m_j}\,\delta(4)\left[-\frac{40\alpha}{3\beta^2}\,\Omega^{2,0}(1)+\frac{16\alpha}{15\beta^2}\left(7\Omega^{2,0}(2)+4\Omega^{2,2}(2)\right)\right],$$

$$c_2^{qr}(\alpha) = m_j\,\delta(1)\,\zeta\left[\frac{8\alpha}{3\beta^2}\left(5-\frac{11\alpha}{\beta^2}\right)\Omega^{-\infty,0}(1)+\frac{16}{3}\left(\zeta^2-\frac{\gamma^2}{\beta^2}+3\left(\frac{m_{jr}}{m_j}\right)^2\right)\Omega^{-\infty,0}(2)\right.$$
$$\left.-\frac{32}{15}\left(\zeta^2+3\left(\frac{m_{jr}}{m_j}\right)^2\right)\Omega^{-\infty,0}(3)\right]$$
$$+m_{jr}\,\delta(2)\left[-\frac{8\alpha}{3\beta^2}\left(5-\frac{11\alpha}{\beta^2}\right)\Omega^{-\infty,0}(1)+\frac{16}{3}\left(\frac{\gamma^2}{\beta^2}-3\zeta^2-\left(\frac{m_{jr}}{m_j}\right)^2\right)\Omega^{-\infty,0}(2)\right.$$
$$\left.+\frac{32}{15}\left(3\zeta^2+\left(\frac{m_{jr}}{m_j}\right)^2\right)\Omega^{-\infty,0}(3)\right]$$
$$+m_{jr}\,\delta(3)\left[\frac{8\alpha}{3\beta^2}\left(5-\frac{11\alpha}{\beta^2}\right)\Omega^{1,1}(1)-\frac{16}{3}\left(\frac{\gamma^2}{\beta^2}-3\zeta^2\right)\Omega^{1,1}(2)\right.$$
$$\left.-\frac{32}{5}\,\zeta^2\Omega^{1,1}(3)+\frac{16}{3}\left(\frac{m_{jr}}{m_j}\right)^2\Omega^{3,1}(2)-\frac{32}{15}\left(\frac{m_{jr}}{m_j}\right)^2\Omega^{3,1}(3)\right]$$
$$-\frac{(m_{jr})^2}{m_j}\,\delta(4)\left[\frac{16}{3}\,\zeta\left(\Omega^{2,0}(2)+2\Omega^{2,2}(2)\right)-\frac{32}{15}\,\zeta\left(\Omega^{2,0}(3)+2\Omega^{2,2}(3)\right)\right].$$

(e) *The Coefficients* c_{js}

To obtain the $I_j(\psi_j)$'s the integrals of the preceding subsection must be summed over all $(k'l')$ and over all k and l. For a real physical situation this is likely to be a complex process. However, in the case of the momentum, the stress, and the thermal flux equations formal simplifications are possible. On summing over $(k'l')$, and ignoring superscripts, define

$$c_{1,j,kl}(\alpha) = \sum_{(k'l')} c_{1,j,kl,k'l'}(\alpha), \tag{42}$$

with a corresponding definition for $c_{2,j,kl}$. Furthermore, by identifying the order of the subscripts kl with the argument of these coefficients, a further notational simplification is possible. In particular, define

$$c_{j,kl}(\alpha_k) \equiv c_{1,j,kl}(\alpha_k)+c_{2,j,kl}(\alpha_k), \qquad c_{j,kl}(\alpha_l) \equiv c_{1,j,kl}(\alpha_l)-c_{2,j,kl}(\alpha_l)\,; \tag{43}$$

then it follows, as inspection of the results of the preceding subsection confirms, that formally

$$I_{kl}(\psi_j) = \sum_{d} n_k n_l \left(c^{\alpha d}_{j,kl}(\alpha_k) \frac{d_k}{\rho_k} + c^{\alpha d}_{j,kl}(\alpha_l) \frac{d_l}{\rho_l} \right), \tag{44}$$

where $\boldsymbol{d}$ represents any one of the moments $\rho\boldsymbol{u}$, $\{\boldsymbol{p}\}$, or $\boldsymbol{r}$, and $\alpha \equiv n\langle\psi\rangle$.

Since I_{kl} must equal I_{lk}, on interchanging k and l in (44) and comparing the coefficients of the $\boldsymbol{d}$'s in these two different forms of the integral, it is immediately apparent that

$$c_{j,kl}(\alpha_k) = c_{j,lk}(\alpha_k), \qquad c_{j,kl}(\alpha_l) = c_{j,lk}(\alpha_l). \tag{45}$$

(Noting that

$$\zeta_{kl} = -\zeta_{lk}, \qquad \begin{matrix} \delta_{kl}(1) = \delta_{lk}(1), & \delta_{kl}(2) = -\delta_{lk}(2), \\ \delta_{kl}(3) = -\delta_{lk}(3), & \delta_{kl}(4) = \delta_{lk}(4), \end{matrix}$$

inspection of the results of the preceding subsection confirms that

$$c_{1,j,kl} = c_{1,j,lk}, \qquad c_{2,j,kl} = -c_{2,j,lk}.$$

Hence, on interchanging k and l in (43), equation (45) immediately follows, thus giving a direct confirmation of this result.)

On summing the I_{kl}, as given by (44), over both k and l,

$$I_j(\psi_j) = \sum_{d} \left[\sum_{k} \frac{n_k}{2\rho_k} \left(\sum_{l} n_l c^{\alpha d}_{j,kl}(\alpha_k) \right) \boldsymbol{d}_k + \sum_{l} \frac{n_l}{2\rho_l} \left(\sum_{k} n_k c^{\alpha d}_{j,kl}(\alpha_l) \right) \boldsymbol{d}_l \right]. \tag{46}$$

However, the summations over k and l are independent. Hence on changing subscripts, in particular putting $k = s$ and $l = k$ in the first summation and $l = s$ in the second,

$$I_j(\psi_j) = \sum_{d} \sum_{s} c^{\alpha d}_{js} \boldsymbol{d}_s,$$

where

$$c_{js} = \frac{1}{2m_s} \sum_{k} n_k \big(c_{j,sk}(\alpha_s) + c_{j,ks}(\alpha_s) \big).$$

Or, on using (43) and (45),

$$c_{js} = \frac{1}{m_s} \sum_{k} n_k c_{j,ks}(\alpha_s) \tag{47}$$

with

$$c_{j,ks}(\alpha_s) = c_{1,j,ks}(\alpha_s) - c_{2,j,ks}(\alpha_s).$$

Therefore, on using the subscripts k and s rather than k and l in the coefficients of the preceding subsection and summing over all k, the c_{js}'s of equations (15), (16), and (17) are explicitly determined.

IV. Special Cases

To complete the integrals the Ω's must be determined. In general this is not a simple task. An explicit knowledge of the differential cross sections is required, while each particular process, such as elastic, fission, recombination, etc., must be considered separately. Numerous calculations have been carried out, for different laws of interaction, for the elementary case of elastic collisions (e.g. Chapman and Cowling 1952; Hirschfelder, Curtiss, and Bird 1954). On the other hand, since the generalized Ω's as defined in Section III(d) are peculiar to this paper (and the associated references) few calculations have been performed for the general inelastic case. Bydder has considered those cases of importance involved in the formation of a hydrogenic-like plasma. However, the practical usefulness of his results is questionable since in order to obtain analytically tractable expressions certain approximations were made, the nature of which are only truly applicable to a very high temperature gas. Nevertheless, the results are extremely interesting in that they show (and generally imply) that, for a specific process, only one or two of the total number of Ω's (20 for the general case) have to be determined explicitly, the others being related to these in a relatively simple manner. Bydder's (1967a) results have been published elsewhere and will not be reproduced here. Instead, various cases of more general interest will be discussed. The Ω's are not determined, but in certain instances the results of Section III are considerably simplified. This is possible since much of the physics of a particular process is already explicitly contained within the δ's.

In the following subsections the more important of the possible physical processes are briefly considered. These were mentioned in the Introduction, being natural decay and spontaneous fission, recombination and attachment, elastic collisions and charge exchange processes, and the general inelastic collision, including excitation and fission- and fusion-like processes. As already implied, the integrals of Section III have been evaluated for the most general case possible, namely, the complete destruction of particles k and l and the creation of two entirely new particles k' and l'. Clearly, there are many possible combinations of k, l, k', and l', as well as various interpretations of ΔE (or to be more exact δE) that can lead to marked simplifications. Again, there are certain approximations and even certain limiting cases that also reduce the general results to simpler forms. For instance, if $T_k \simeq T_l$ then $\zeta \simeq 0$ and many terms may be ignored, while if $m_k \ll m_l$ or $m_{k'} \ll m_{l'}$ other approximations are possible. It is, however, beyond the scope of this paper to consider such cases in detail and only general aspects of those physical processes already mentioned will be discussed.

Before considering these various cases explicitly several points of a general nature should be noted. The collision integrals involve both "loss" (δ_{kj}, δ_{lj}) and "gain" ($\delta_{k'j}, \delta_{l'j}$) terms. The loss terms are only associated with the $\delta(1)$ and $\delta(2)$ terms and as such only involve the $\Omega^{-\infty,0}(r)$. Defining a "partial" cross section

$$Q_{kl}^{k'l'}(g) \equiv \int \sigma_{kl}^{k'l'} \sin\chi \,\mathrm{d}\chi \,\mathrm{d}(\delta E)\,\mathrm{d}\epsilon\,,$$

it follows from the definition (38) that

$$\phi_{kl}^{k'l'}(-\infty,0) = g\,Q_{kl}^{k'l'}(g)/2\pi\,, \tag{48}$$

or, on summing over all $(k'l')$, the loss terms only involve total cross sections.

Furthermore, if for any particular process $\lambda = 0$ then by definition

$$\phi(\mu,\nu) = \phi(-\infty,0)\,, \tag{49}$$

and again only the $\Omega^{-\infty,0}(r)$ are involved. However, in this latter case summation over $(k'l')$ will not necessarily lead to explicit expressions in terms of a total cross section.

(a) *Natural Decay and Spontaneous Fission*

In spontaneous fission a particle type k changes into particle types k' and l', l being a hypothetical particle of mass zero. Such a process only occurs if k is in an excited state, the excitation energy appearing as kinetic energy. In the limit $m_l \to 0$ it follows from (26) and (33) that

$$\lambda^2 = -2\Delta E\,\gamma^2/m_{k'l'}\,y^2,$$

ΔE being a negative (i.e. a gain) term.

Assuming that the hypothetical particles of type l have a Maxwellian distribution,

$$\boldsymbol{u}_l = \{\boldsymbol{p}_l\} = \boldsymbol{r}_l = 0\,;$$

while, since $\zeta \sim m_{kl}$, $\gamma^2 \sim m_{kl}$, on taking the limit as $m_l \to 0$ the integrals of Section III reduce to basically trivial forms. The loss terms are

$$I_{kl}(m_k) = -n_k m_k/\tau, \qquad I_{kl}(\mathscr{E}_k) = -n_k \mathscr{E}_k/\tau,$$
$$I_{kl}(\tfrac{1}{2}m_k w_k^2) = -\tfrac{3}{2}n_k kT_k/\tau, \qquad I_{kl}(m_k \boldsymbol{w}_k) = -n_k m_k \boldsymbol{u}_k/\tau,$$
$$I_{kl}(m_k\{\boldsymbol{w}_k \boldsymbol{w}_k\}) = -\{\boldsymbol{p}_k\}/\tau, \qquad I_{kl}(\tfrac{1}{2}m_k \boldsymbol{w}_k w_k^2) = -\boldsymbol{q}_k/\tau,$$

where τ is the decay time, being given by

$$\tau^{-1} \equiv n_l\, 8\Omega^{-\infty,0}(0) = 8n_l \pi^{\frac{1}{2}} \int_0^\infty \exp(-y^2) y^2 \phi_{kl}(-\infty, 0)\, \mathrm{d}y, \tag{50}$$

with

$$\phi(-\infty, 0) = g\, Q_{kl}(g)/2\pi, \tag{51}$$

the summation over $(k'l')$ having been implicitly carried out. Subject to this approach, however, τ^{-1} must also equal $n_l gQ_{kl}$ since the lifetime of an excited state is independent of particle speed. On substituting (51) in (50) and integrating, such an identity is obtained, thus confirming the adequacy of the limiting process adopted.

Similarly, on letting $m_l \to 0$ the gain terms are

$$I_{kl}(m_j) = n_k m_j\, \delta(4)/\tau, \qquad I_{kl}(\mathscr{E}_j) = n_k \mathscr{E}_j\, \delta(4)/\tau,$$
$$I_{kl}(\tfrac{1}{2}m_j w_j^2) = \big(\tfrac{3}{2}(m_j/m_k)n_k kT_k - (m_{jr}/m_j)n_k \Delta E\big)\delta(4)/\tau,$$
$$I_{kl}(m_j \boldsymbol{w}_j) = n_k m_j \boldsymbol{u}_k\, \delta(4)/\tau, \qquad I_{kl}(m_j\{\boldsymbol{w}_j \boldsymbol{w}_j\}) = (m_j/m_k)\{\boldsymbol{p}_k\}\delta(4)/\tau,$$
$$I_{kl}(\tfrac{1}{2}m_j \boldsymbol{w}_j w_j^2) = \big((m_j/m_k)\boldsymbol{q}_k - \tfrac{5}{3}(m_{jr}/m_j)n_k \boldsymbol{u}_k \Delta E\big)\delta(4)/\tau,$$

where subscripts associated with ΔE have been ignored, while in this case τ is an abbreviation for $\tau_{k,k'l'}$, the summation over $(k'l')$ being necessarily explicit.

As a limiting case of these results let $m_{l'} \to 0$; then $m_j \to m_k$ and $m_{jr} \to 0$. To within the approximation of ignoring the momentum associated with photons, the results are those appropriate to natural decay.

(b) *Recombination and Attachment*

In this case two particles k and l combine to form a single particle j. This process may or may not be accompanied by the emission of radiation, while the particle j will usually be left in an excited state. The surplus energy will be either radiated, converted into kinetic energy in a subsequent collision (a collision of the second kind), or the excited particle will subsequently undergo a spontaneous fission or natural decay.

The correct physical approach to this problem is to put g', and hence λ, equal to zero, summing together the separate gain integrals for k' and l' to obtain the integrals for j. The loss terms may be obtained directly from the results of the preceding section, involving only the $\delta(1)$ and $\delta(2)$ terms and the $\Omega^{-\infty,0}(r)$. There is no real simplification. In the case of the gain terms, since $\lambda = 0$, only the $\Omega^{-\infty,0}(r)$ are again involved but all the δ terms must be considered. In particular, for $j = k'$,

$$\delta(1) = \quad \delta(2) = \quad \delta(3) = \delta(4) = 1,$$

while, for $j = l'$,

$$\delta(1) = -\delta(2) = -\delta(3) = \delta(4) = 1.$$

Using these relationships and the fact that

$$m_{k'} + m_{l'} = m_j = m_k + m_l,$$

on adding the separate integrals for k' and l', the gain integrals are

$$I_{kl}(m_j) = n_k n_l m_j 8\Omega^{-\infty,0}(0), \qquad I_{kl}(\mathscr{E}_j) = n_k n_l \mathscr{E}_j 8\Omega^{-\infty,0}(0),$$

$$I_{kl}(\tfrac{1}{2}m_j w_j^2) = \frac{4n_k n_l}{\gamma^2}\left(m_j \zeta^2 \Omega^{-\infty,0}(1) + \frac{3m_j \gamma^2}{2\beta^2}\Omega^{-\infty,0}(0)\right),$$

with

$$c_1^{uu}(\alpha) = \frac{8\alpha}{\beta^2} m_j \Omega^{-\infty,0}(0),$$

$$c_2^{uu}(\alpha) = -\frac{16}{3} m_j \zeta \Omega^{-\infty,0}(0),$$

$$c_1^{ur}(\alpha) = \frac{32}{3}\frac{\gamma^2\alpha}{\beta^2} m_j [\Omega^{-\infty,0}(1) - \tfrac{3}{2}\Omega^{-\infty,0}(0)],$$

$$c_2^{ur}(\alpha) = \frac{32}{3}\gamma^2 m_j \zeta[\Omega^{-\infty,0}(1) - \tfrac{2}{5}\Omega^{-\infty,0}(2)],$$

$$c_1^{pp}(\alpha) = 8m_j \frac{\alpha^2}{\beta^4}\Omega^{-\infty,0}(0) + \frac{32}{15} m_j \zeta^2 \Omega^{-\infty,0}(2),$$

$$c_2^{pp}(\alpha) = -\frac{16m_j}{3}\frac{2\zeta\alpha}{\beta^2}\Omega^{-\infty,0}(1),$$

$$c_1^{qu}(\alpha) = m_j \frac{10\alpha}{\beta^4}\Omega^{-\infty,0}(0) + \frac{20\alpha}{3\beta^2\gamma^2} m_j \zeta^2 \Omega^{-\infty,0}(1),$$

$$c_2^{qu}(\alpha) = -\frac{20m_j}{3}\frac{\zeta}{\beta^2}\Omega^{-\infty,0}(1) + \frac{8\zeta^3}{3\gamma^2}m_j\,\Omega^{-\infty,0}(2),$$

$$c_1^{qr}(\alpha) = -20m_j\frac{\alpha^2}{\beta^4}\left(1-\frac{7\alpha}{5\beta^2}\right)\Omega^{-\infty,0}(0)$$

$$+\frac{40m_j}{3}\frac{\alpha}{\beta^2}\left(\frac{\gamma^2}{\beta^2}-\zeta^2\right)\Omega^{-\infty,0}(1) + \frac{176m_j}{15}\frac{\alpha\zeta^2}{\beta^2}\Omega^{-\infty,0}(2),$$

$$c_2^{qr}(\alpha) = m_j\,\zeta\left[\frac{8\alpha}{3\beta^2}\left(5-\frac{11\alpha}{\beta^2}\right)\Omega^{-\infty,0}(1) + \frac{16}{3}\left(\zeta^2-\frac{\gamma^2}{\beta^2}\right)\Omega^{-\infty,0}(2) - \frac{32}{15}\zeta^2\Omega^{-\infty,0}(3)\right].$$

In these expressions,

$$\Omega_{kl,j}^{-\infty,0}(r) = \pi^{\frac{1}{2}}\int_0^\infty \exp(-y^2)\,y^{2r+2}\,\frac{g\,Q_{kl}^j(g)}{2\pi}\,\mathrm{d}y,$$

with

$$Q_{kl}^j(g) = \int \sigma_{kl}^j \sin\chi\,\mathrm{d}\chi\,\mathrm{d}\epsilon\,\mathrm{d}(\delta E).$$

For $\lambda = 0$, $\frac{1}{2}m_{kl}g^2 = \Delta E$ and this means, in particular, that g (or y) and (δE) are not, for given k, l, and j, independent variables. However, this fact is implicit within the σ and need not be considered further.

Although the coefficients are still somewhat complex it is immediately obvious that they simplify markedly for $\zeta = 0$.

An alternative approach to the one just adopted is to take $m_{l'} \to 0$. This leads to λ being an infinite quantity but automatically ensures that all terms involving m_{jr} are zero. The fact that this approach leads to exactly the same results as those just obtained is of prime importance. Since in the first approach many terms in m_{jr} (that is, $m_{k'r}$ and $m_{l'r}$) have to be considered, the fact that such terms cancel gives an extremely precise confirmation of the algebraic accuracy of the general results.

(c) *Charge Exchange and Elastic Collisions*

In an elastic collision the identities of the particles are unchanged. Here $\Delta E = 0$, hence $\lambda = 1$, while $\delta(1) = \delta(2) = 0$. The relevant integrals may be obtained quite simply by inspection of the general case and will not, therefore, be recorded here. However, it is worth while noting the extreme simplicity of the self-collision terms. For this particular case, besides $\delta(1) = \delta(2) = 0$, $\delta(3)$ is also zero, as is ζ, while $\delta(4) = 2$. The relevant integrals are

$$I_{jj}(m_j) = I_{jj}(\mathscr{E}_j) = I_{jj}(\tfrac{1}{2}m_j w_j^2) = I_{jj}(m_j\,\boldsymbol{w}_j) = 0,$$

$$I_{jj}(m_j\{\boldsymbol{w}_j\,\boldsymbol{w}_j\}) = -\tfrac{16}{5}n_j\,\Omega^{2,2}(2)\{\boldsymbol{p}_j\}, \qquad I_{jj}(\tfrac{1}{2}m_j\,\boldsymbol{w}_j\,w_j^2) = -\tfrac{32}{15}n_j\,\Omega^{2,2}(2)\,\boldsymbol{r}_j.$$

It must of course be remembered that in obtaining the $I_j(\boldsymbol{\psi}_j)$ these integrals are divided by two.

In the simplest and most common of the exchange processes (resonance charge exchange) particle k becomes particle l and particle l becomes particle k. However, in general it is possible that particles k' and l' are excited states of particles l and k and within the approach adopted here these are quite different particle types from l and k; that is, no simplification of the general results is possible. Nevertheless, returning to the case of resonant charge exchange, this is somewhat similar to the pure elastic case and a reduction of the various coefficients is possible. Since for the subscript order kl the scattering cross section refers to k' rather than l', consider l and k' as the identical particles. Then for

$$j = l = k' \neq k = l', \qquad \delta(1) = 0, \quad \delta(2) = 2, \quad \delta(3) = \delta(4) = 1.$$

(The case of $k = l$ is exactly the same as that for elastic collisions.) Unlike elastic collisions, however, δE need not be zero and hence λ may be different from unity. Therefore, for resonant charge exchange the integrals become

$$I_{kl}(m_l) = I_{kl}(\mathscr{E}_l) = 0,$$

$$I_{kl}(\tfrac{1}{2}m_l w_l^2) = \frac{4n_k n_l}{\gamma^2}\left[-2m_{kl}\,\zeta\left(2\Omega^{-\infty,0}(1) - \Omega^{1,1}(1)\right) - \frac{(m_{kl})^2}{m_l}\,\Omega^{2,0}(1)\right],$$

while

$$c_1^{uu}(\alpha) = 0,$$

$$c_2^{uu}(\alpha) = \tfrac{16}{3}m_{kl}(2\Omega^{-\infty,0}(1) - \Omega^{1,1}(1)),$$

$$c_1^{ur}(\alpha) = 0,$$

$$c_2^{ur}(\alpha) = \tfrac{32}{3}m_{kl}\gamma^2[(\tfrac{4}{5}\Omega^{-\infty,0}(2) - 2\Omega^{-\infty,0}(1)) + (\Omega^{1,1}(1) - \tfrac{2}{5}\Omega^{1,1}(2))],$$

$$c_1^{pp}(\alpha) = \frac{16}{3}\left[-\tfrac{4}{5}m_{kl}\,\zeta\left(2\Omega^{-\infty,0}(2) - \Omega^{1,1}(2)\right) + \frac{(m_{kl})^2}{m_l}\left(\tfrac{1}{5}\Omega^{2,0}(2) - \tfrac{3}{5}\Omega^{2,2}(2)\right)\right],$$

$$c_2^{pp}(\alpha) = \frac{16}{3}m_{kl}\frac{2\alpha}{\beta^2}\left(2\Omega^{-\infty,0}(1) - \Omega^{1,1}(1)\right),$$

with corresponding but appreciably more complicated expressions for the $c^{qu}(\alpha)$ and $c^{qr}(\alpha)$.

(d) *General Inelastic Collision*

In a general inelastic collision particles k' and l' are distinctly different particles from k and l and no precise simplification of the results of Section III is possible. Both loss and gain terms must be considered separately. On the other hand, if the identity of particle k remains unchanged throughout the collision, such as in the inelastic scattering of an electron, then considerable simplification is possible. However, before discussing this particular case several other aspects of the general inelastic collision will be briefly considered.

Besides simple excitation or de-excitation (a collision of the second kind), in an inelastic collision, fission-like or fusion-like processes are also possible. That is, instead of there being just two product particles k' and l' there may be more or only one. In the latter case the problem is similar to recombination and need not be reconsidered. If, however, there are more than two particles then the problem is different but as will be seen no new difficulties are introduced. If k' is the particle of interest then the other products of the collision may be regarded as a simple composite particle l', having an internal energy equal to the sum of the internal energies of the individual components plus their kinetic energies referred to the centre of mass of l'. The fact that the "internal" energy ceases to be a discrete quantity is of no consequence, since this has already been allowed for by the inclusion of a continuum energy δE in the definition of the cross sections. Thus a fission- or fusion-like process may be essentially regarded as excitation to the continuum. In particular, on writing $l' \equiv \sum_s l'_s$,

$$m_{l'} = \sum_s m_{l'_s}, \qquad \mathscr{E}_{l'} = \sum_s \mathscr{E}_{l'_s},$$

while

$$\delta E_{kl,k'l'} \equiv \delta E_{l'} = \sum_s \tfrac{1}{2} m_{l'_s} g^2_{l'l'_s},$$

where

$$\boldsymbol{g}_{l'l'_s} = \boldsymbol{w}_{l'} - \boldsymbol{w}_{l'_s}.$$

In the case of simple ionization $\delta E_{l'}$ is readily identified with the energy of the ejected electron. In a more general case the problem need be no more difficult. It should always be possible to specify a cross section $\sigma(\ldots, \delta E_{k'})$ appropriate to the production of a particle k' with given energy $\delta E_{k'}$, the latter being referred (say) to the centre of mass velocity $\boldsymbol{G}$. Then since

$$\tfrac{1}{2} m_{k'l'} g^2_{k'l'} + \mathscr{E}_{k'} + \mathscr{E}_{l'} + \delta E_{kl,k'l'} = \tfrac{1}{2} m_{kl} g^2_{kl} + \mathscr{E}_k + \mathscr{E}_l,$$

while from (19) and (22)

$$\delta E_{k'} \equiv \tfrac{1}{2} m_{k'} g^2_{Gk'} = \tfrac{1}{2} m_{k'l'} M_{l'} g^2_{k'l'},$$

it follows that

$$\delta E_{k'} = M_{l'}[(\mathscr{E}_k + \mathscr{E}_l - \mathscr{E}_{k'} - \mathscr{E}_{l'}) + \tfrac{1}{2} m_{kl} g^2_{kl} - \delta E_{l'}].$$

Therefore the differential cross section

$$2\pi\sigma^{k'l'}_{kl}(g, \chi, \delta E_{k'}) \sin\chi \, \mathrm{d}\chi \, \mathrm{d}(\delta E_{k'})$$

may be readily transformed to the form adopted in the preceding sections, namely,

$$2\pi\sigma^{k'l'}_{kl}(g, \chi, \delta E) \sin\chi \, \mathrm{d}\chi \, \mathrm{d}(\delta E),$$

δE being equivalent to $\delta E_{l'}$. Again since

$$M_{l'} = (m_0 - m_{k'})/m_0 \equiv (m_0 - m_j)/m_0,$$

while λ, which only occurs in the gain terms, is "operated" on by $\delta_{k'j}$ leading to

$$\lambda^2_{kl,k'l'} = \frac{m_{kl}}{m_{k'l'}}\left(1 - \frac{2\Delta E_{kl,k'l'}}{m_{kl} g^2}\right) \equiv \frac{m_{kl}}{m_{jr}}\left(1 - \frac{2\Delta E_{kl,jl'}}{m_{kl} g^2}\right),$$

it follows that m_j ($\equiv m_{k'}$) and m_{jr} ($\equiv m_{k'r}$) are the only masses involved, and the determination of the ϕ's and the Ω's proceeds as in the case of simple excitation.

The final expression given above for λ^2 introduces a further point of general interest. This is that, provided $k' \neq l'$, the summations of the integrals over $(k'l')$ may be reduced to simple summations over l'. In fact such summations may be more succinctly included within the Ω's, the ϕ's being the only functions involved. In order to emphasize this conclusion consider the previously mentioned case of inelastic scattering of particle k. This corresponds to, with $k \neq l$, $k' \neq l'$:

$$k = j = k', \qquad \delta(1) = \delta(2) = 0, \quad \delta(3) = \delta(4) = 1.$$

Hence, from the results of Section III, the collision integrals are

$$I_{kl}(m_k) = I_{kl}(\mathscr{E}_k) = 0,$$

$$I_{kl}(\tfrac{1}{2}m_k w_k^2) = \frac{4n_k n_l}{\gamma^2}\left(2\zeta m_{kl}\,\Omega_{kl}^{1,1}(1) - \frac{(m_{kl})^2}{m_k}\,\Omega_{kl}^{2,0}(1)\right),$$

while

$$c_1^{uu} = c_1^{ur} = 0,$$

$$c_2^{uu} = -\tfrac{16}{3}m_{kl}\,\Omega_{kl}^{1,1}(1),$$

$$c_2^{ur} = \tfrac{32}{3}\gamma^2 m_{kl}(\Omega_{kl}^{1,1}(1) - \tfrac{2}{5}\Omega_{kl}^{1,1}(2)),$$

$$c_1^{pp} = \tfrac{64}{15}m_{kl}\,\zeta\Omega_{kl}^{1,1}(2) + \frac{16}{3}\frac{(m_{kl})^2}{m_k}\left(\tfrac{1}{5}\Omega_{kl}^{2,0}(2) - \tfrac{3}{5}\Omega_{kl}^{2,2}(2)\right),$$

$$c_2^{pp} = -\tfrac{32}{3}(\alpha/\beta^2)m_{kl}\,\Omega_{kl}^{1,1}(1),$$

with corresponding but somewhat more complicated expressions for the c^{qu} and c^{qr}. In these expressions the summation over $(k'l')$ is contained within the Ω's, these being defined by (cf. equation (40))

$$\Omega_{kl}^{\mu,\nu}(r) = \pi^{\frac{1}{2}}\int \exp(-y^2)\,y^{2r+2}\,\phi_{kl}(\mu,\nu)\,\mathrm{d}y,$$

with

$$\phi_{kl}(\mu,\nu) = \sum_{(k'l')}\phi_{kl}^{k'l'}(\mu,\nu) = \sum_{l'}\phi_{kl}^{kl'}(\mu,\nu),$$

and

$$\lambda^2_{kl,k'l'} = \lambda^2_{kl,kl'} = (1 - 2\Delta E_{kl,kl'}/m_{kl}\,g^2),$$

$$\Delta E_{kl,kl'} = \mathscr{E}_l - \mathscr{E}_{l'} - \delta E_{l'}.$$

In fact, for this case, a further notational simplification is possible. Redefining

$$\delta E \equiv \mathscr{E}_{l'} + \delta E_{l'},$$

the summation over l' may be implicitly contained within the cross section σ, using Dirac δ functions to account for discrete energies of excitation (including the purely elastic case) and step functions to account for the relevant continuum levels. Of course, at any level of description, σ also contains implicitly a step function of λ, since λ^2 must be greater than or equal to zero.

Finally, it should be noted that if, for instance, the above case corresponded to the inelastic scattering of electrons, then other integrals accounting for any ejected electron must also be evaluated in order to determine $I_e(\psi_e)$. This particular case for electrons has been discussed in detail by Bydder (1967*b*).

V. Reduction of Equations to Practical Forms

In this section the reduction of the equations of the preceding sections to more practical forms is briefly discussed. Such forms include transport relationships, conservation equations, the generalized Ohm's law, and equilibrium solutions.

The derivation of transport relationships is straightforward. These relationships are essentially "solutions" of equations (5), (8), and (9) for the $\boldsymbol{u}$, $\{\boldsymbol{p}\}$, and $\boldsymbol{q}$ (or $\boldsymbol{r}$) in terms of all other variables such as n, T (or p), $\boldsymbol{v}, \boldsymbol{f}, \ldots$. These solutions may be obtained by a method of successive approximation, being valid provided the collision or Larmor times and mean free paths or Larmor radii (or hybrids of these) are small compared with the characteristic times or dimensions of the system as a whole. Following the method of Herdan and Liley (1960), on using equations (15), (16), (17), and the expressions for $\boldsymbol{l}$, $\boldsymbol{h}$, and $\boldsymbol{H}$ given in Section II(*d*), equations (5), (8), and (9) may be written in the form

$$A_j(\boldsymbol{u}_j)+\frac{\partial p_j}{\partial \boldsymbol{x}}-\rho_j\boldsymbol{f}_j^0-\rho_j\boldsymbol{u}_j\times\boldsymbol{b}_j=\sum_s\left(c_{js}^{uu}\,\rho_s\boldsymbol{u}_s+c_{js}^{ur}\,\boldsymbol{r}_s\right),$$

$$A_j(\{\boldsymbol{p}_j\})+2p_j\left\{\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{x}}\right\}-2\rho_j\{\boldsymbol{f}_j^0\,\boldsymbol{u}_j\}-2\{\{\boldsymbol{p}_j\}\times\boldsymbol{b}_j\}=\sum_s c_{js}^{pp}\{\boldsymbol{p}_s\},$$

$$A_j(\boldsymbol{q}_j)-\boldsymbol{f}_j^0.\{\boldsymbol{p}_j\}-\frac{5}{2}p_j\boldsymbol{f}_j^0+\frac{5}{2}\frac{\partial}{\partial \boldsymbol{x}}\left(\frac{kT_j}{m_j}p_j\right)-\boldsymbol{q}_j\times\boldsymbol{b}_j=\sum_s\left(c_{js}^{qu}\,\rho_s\boldsymbol{u}_s+c_{js}^{qr}\,\boldsymbol{r}_s\right),$$

where

$$\boldsymbol{f}_j^0\equiv\boldsymbol{f}_j+\mathrm{d}\boldsymbol{v}/\mathrm{d}t=\boldsymbol{a}_j+\boldsymbol{v}\times\boldsymbol{b}_j\,.$$

The exact form of the A_j's may be determined by comparing these equations with those given in Section II(*b*), it being important to note, however, that they are primarily functions of the derivatives of $\boldsymbol{u}$, $\{\boldsymbol{p}\}$, and $\boldsymbol{q}$. A somewhat more convenient equation than that given for $\boldsymbol{q}$ is one for $\boldsymbol{r}$. This is obtained by subtracting $\frac{5}{2}kT_j/m_j$ times equation (3) from equation (5), leading to

$$A_j(\boldsymbol{r}_j)-\boldsymbol{f}_j^0.\{\boldsymbol{p}_j\}+\frac{5}{2}\frac{kp_j}{m_j}\frac{\partial T_j}{\partial \boldsymbol{x}}-\boldsymbol{r}_j\times\boldsymbol{b}_j=\sum_s\left(c_{js}^{ru}\,\rho_s\boldsymbol{u}_s+c_{js}^{rr}\,\boldsymbol{r}_s\right),$$

where

$$c^{r\alpha}=c^{q\alpha}-\tfrac{5}{2}(kT/m)c^{u\alpha}\,.$$

On neglecting the A_j's these equations determine the first approximations for the $\boldsymbol{u}$'s, $\{\boldsymbol{p}\}$'s, and $\boldsymbol{r}$'s (or $\boldsymbol{q}$'s). Using these first approximations to obtain first approximations for the A_j's and on retaining these latter terms, the equations then yield second approximations for the $\boldsymbol{u}$'s, $\{\boldsymbol{p}\}$'s, and $\boldsymbol{r}$'s. This process is repeated until the desired degree of accuracy is achieved. In practice, however, there is little value in proceeding beyond the first approximation since the higher order expressions are usually so complex that they are analytically unusable. Therefore, if the first approximations should be inadequate a different method of approximation from that described must be sought.

Coupled with the transport relationships are the continuity (n_j) and the energy (p_j or T_j and U_j) equations and an equation for $\boldsymbol{v}$. If $\boldsymbol{v}$ is equivalent to $\boldsymbol{v}_0$, the mean mass velocity of the mixture, then an equation for this variable is readily obtained. On summing equations (5) over all j, the usual momentum conservation equation is derived, namely,

$$\frac{\partial \rho \boldsymbol{v}_0}{\partial t} = \rho \boldsymbol{g} + \sigma \boldsymbol{E} + \boldsymbol{j} \times \boldsymbol{B} - \frac{\partial}{\partial \boldsymbol{x}} \cdot (\boldsymbol{p} + \rho \boldsymbol{v}_0 \, \boldsymbol{v}_0) ,$$

where $\boldsymbol{j}$ is the current density and σ the charge density, given by

$$\boldsymbol{j} = \sum_j n_j e_j (\boldsymbol{u}_j + \boldsymbol{v}_0) , \qquad \sigma = \sum_j n_j e_j ,$$

while

$$\rho = \sum_j \rho_j , \qquad \boldsymbol{p} = \sum_j \boldsymbol{p}_j .$$

Similarly, a conservation equation for ρ may be obtained by summing equations (4), the result being

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \boldsymbol{x}} \cdot \rho \boldsymbol{v}_0 = 0 .$$

On the other hand, on summing equations (6) and (7), a true conservation equation is not obtained since radiation losses (and gains) have to be taken into account. It is, however, possible to establish a continuity equation for the radiation energy density D, this being of the form

$$\frac{\partial D}{\partial t} + \frac{\partial}{\partial \boldsymbol{x}} . \boldsymbol{R} = - \sum_j \left(I_j(\mathscr{E}_j) + I_j(\tfrac{1}{2} m_j w_j^2) \right) ,$$

$\boldsymbol{R}$ being the radiation flux vector. (The absorption of radiation etc. is discussed in Section VI.) On summing over all j and adding the three types of energy equations the following equation is obtained

$$\frac{\partial (\frac{3}{2} p + U + D)}{\partial t} + \frac{\partial}{\partial \boldsymbol{x}} \cdot \left((\tfrac{3}{2} p + U) \boldsymbol{v}_0 + \boldsymbol{Q} + \boldsymbol{R} \right) + \boldsymbol{p} : \frac{\partial \boldsymbol{v}_0}{\partial \boldsymbol{x}} = \boldsymbol{E} . \boldsymbol{j} ,$$

where

$$p = \sum_j p_j , \qquad U = \sum_j U_j , \qquad \boldsymbol{Q} = \sum_j (\boldsymbol{q}_j + U_j \boldsymbol{u}_j) ,$$

$\boldsymbol{Q}$ being the total thermal flux vector.

The final basic equation for the system is the generalized Ohm's law. This is obtained by multiplying equations (5) throughout by e_j/m_j and summing over all j. However, due to differences in mass this equation is basically nothing more than an equation for the electrons. Furthermore, for $\boldsymbol{v} = \boldsymbol{v}_0$,

$$\boldsymbol{u}_j \leqslant \boldsymbol{u}_{\mathrm{e}} \quad (j \neq \mathrm{e}) \qquad \text{and} \qquad \boldsymbol{j} \simeq n_{\mathrm{e}} e_{\mathrm{e}} \boldsymbol{u}_{\mathrm{e}}.$$

Therefore, from equations (5), (16), and (47) the Ohm's law for the mixture is

$$\frac{m_{\mathrm{e}}}{n_{\mathrm{e}}e^2}\left(\frac{\partial \boldsymbol{j}}{\partial t}+\frac{\partial}{\partial \boldsymbol{x}}\cdot(\boldsymbol{v}_0\boldsymbol{j})+\boldsymbol{j}\cdot\frac{\partial \boldsymbol{v}_0}{\partial \boldsymbol{x}}\right)-\frac{1}{n_{\mathrm{e}}e}\frac{\partial}{\partial \boldsymbol{x}}\cdot\boldsymbol{p}_{\mathrm{e}}$$
$$+(n_{\mathrm{e}}e)^{-1}\boldsymbol{j}\times\boldsymbol{B}-(\boldsymbol{E}+\boldsymbol{v}_0\times\boldsymbol{B}) = -\eta\boldsymbol{j}-\alpha\boldsymbol{r}_{\mathrm{e}},$$

where

$$\eta = -(n_{\mathrm{e}}e^2)^{-1}\sum_k n_k\, c^{uu}_{\mathrm{e},k\mathrm{e}}(\alpha_{\mathrm{e}}), \qquad \alpha = (n_{\mathrm{e}}em_{\mathrm{e}})^{-1}\sum_k n_k\, c^{ur}_{\mathrm{e},k\mathrm{e}}(\alpha_{\mathrm{e}}),$$

and $e = |e_{\mathrm{e}}|$. Again, due to mass differences the $c_{\mathrm{e},k\mathrm{e}}$ coefficients may be reduced to relatively simple forms (e.g. see Bydder 1967*b*).

Without considering specific cases it is not possible to reduce these basic equations further. It would, of course, be convenient to define gross coefficients of thermal conductivity and viscosity. In general, however, this is not practicable. On adding together, say, the $\boldsymbol{q}_j$'s, terms other than a simple temperature gradient are involved, while the problem is further complicated by the fact that the various components of the mixture may have different temperatures. Again, since $\boldsymbol{Q}$ involves $U_j\boldsymbol{u}_j$ it is obvious that a density gradient could perhaps be of equal importance. However, in certain particular cases various simplifications should be possible. For instance, in a polyatomic gas mixture it should be possible to relate U to $\frac{3}{2}p$ by the introduction of the ratio of specific heats. In fact, it should even be possible to define a temperature characteristic of the internal energy of a particle and express the appropriate collision terms in such a manner that they exhibit the relaxation of energy between internal and translational degrees of freedom. Results of this nature have been obtained by Wang-Chang and Uhlenbeck (1951) using a Chapman–Enskog approach to the inelastic collision problem. So far, of course, the possibility of a number of internal degrees of freedom has been avoided, a particle being characterized solely by its total internal energy $\mathscr{E}_j$. To adequately account for this possibility the notation must be modified. One way of doing this is to put the subscript

$$j \equiv j_1+j_2+j_3+\ldots,$$

leading to

$$\mathscr{E}_j = \mathscr{E}_{j_1}+\mathscr{E}_{j_2}+\mathscr{E}_{j_3}+\ldots,$$

where $j_1, j_2, j_3, \ldots$ characterize the internal degrees of freedom. In general, this notational modification in no way alters the results of the preceding sections. However, for specific problems it can introduce additional notational complexity, since implicit within the summations over j, k, l, etc. there are also summations over $j_1, j_2, \ldots, k_1, k_2, \ldots$, etc.

Finally, referring to the equilibrium solutions, in the absence of spatial gradients and applied forces these are determined by

$$I_j(\psi_j) = 0, \qquad \text{for all} \quad \psi_j.$$

From (16), (17), and (18) these equations immediately yield

$$\boldsymbol{u}_j = \{\boldsymbol{p}_j\} = \boldsymbol{q}_j = \boldsymbol{r}_j = 0,$$

and the distribution functions become Maxwellian. On the other hand, the solutions of

$$I_j(m_j) = 0\,, \qquad I_j(\mathscr{E}_j) = 0\,, \qquad I_j(\tfrac{1}{2}m_j w_j^2) = 0$$

are not so obvious. In the absence of radiation it is to be expected that the appropriate solutions will be of the form

$$T_j = T\,, \qquad n_j \propto \exp(-\mathscr{E}_j/kT)\,, \qquad \text{for all } j\,.$$

However, this has not been proved and the problem of finding the correct equilibrium solutions has still to be solved.

VI. Discussion

Inevitably, this paper has been primarily mathematical in character and little of the physics associated with the results has been discussed. In particular, it has not been possible to discuss the various effects implied by the collision integrals. For instance, it is interesting to note the coupling between the momentum and thermal (or heat) flux equations. In the case of simple monatomic gases such coupling leads to thermal diffusion effects, anisotropic diffusion and resistivity coefficients, and other effects. These are well known and in general well understood. However, what is interesting is the implication that such effects are a peculiarity of particle type and not simply particle mass. That is, for instance, it is possible that these effects (thermal diffusion in particular) associated with inelastic collisions could lead to spatial separation of excited states of the same atom. Only an exact evaluation of the relevant coefficients involved, however, will prove or disprove this conjecture. Another interesting observation concerns the energy integrals. Even if the collision is inelastic there is still an "elastic" exchange of energy. On reflection this is an obvious result, but it is particularly well emphasized by the exact form of the energy integrals.

As already remarked, with one notable omission, all important collision phenomena in a relatively dilute gas have been accounted for. The omission concerns the direct interaction of radiation with the gas particles. The various emission processes such as bound–bound (excitation and natural decay), free–bound (recombination and natural decay), and free–free (bremsstrahlung, via the δE term) have all been included. On the other hand, absorption, stimulated emission, photo-ionization, and Compton scattering have been ignored. However, on regarding a photon as a particular particle type, these processes are analogous to recombination, ionization, a general inelastic collision, and a general inelastic collision respectively. In one sense, therefore, the physics of these processes has also been dealt with in the preceding sections. In fact, because of this, it is interesting to speculate on whether or not the results of this paper may also be applied to such direct photon interactions.

A photon of frequency ν is equivalent to a particle of mass $h\nu/c^2$. If in addition the energy of the photon is divided into a translational component of $\frac{1}{2}h\nu$ $(= \frac{1}{2}mc^2)$ and an internal energy of $\frac{1}{2}h\nu$, then on ignoring relativistic effects the basic dynamics of a collision between a photon and a gas particle are the same as for any other two particles. Therefore, on associating a velocity distribution function $f_\nu(\boldsymbol{x}, \boldsymbol{w}, t)$ with photons of frequency ν, these may be regarded as a particular particle type characterized by a mass m_ν, internal energy $\mathscr{E}_\nu$, and charge e_ν, where

$$m_\nu = h\nu/c^2\,, \qquad \mathscr{E}_\nu = \tfrac{1}{2}h\nu\,, \qquad e_\nu = 0\,.$$

It follows that an effective kinetic temperature T_ν may be defined by

$$\tfrac{3}{2}kT_\nu = \tfrac{1}{2}h\nu,$$

leading, in particular, to an α_ν given by

$$\alpha_\nu \equiv m_\nu/2kT_\nu = 3/2c^2\,,$$

c being, of course, the speed of light. Thus all parameters such as β, γ, and ζ that were introduced in Section III are well-defined functions. On the other hand, the final form for the collision integrals given in Section III(d) depended on using the expressions (14) for the distribution functions. Obviously these functions as such cannot be used directly to describe the velocity distribution of photons. However, for a given speed $\boldsymbol{w}$ they do specify the angular distribution in velocity space. Therefore, for $f \equiv f_\nu$, on replacing f^0 in equations (14) by

$$f^0 \equiv f^0_\nu N\,\delta(c-g)\,,$$

where $\delta(c-g)$ is a *Dirac* delta function, g being any relevant relative or "peculiar" speed, these functions may also be used to describe the photon velocity distributions, with

$$f^0_\nu = n_\nu(\alpha_\nu/\pi)^{3/2}\exp(\alpha_\nu w^2)$$

and N defined by

$$\int \boldsymbol{w}\, f_\nu\, \mathrm{d}\boldsymbol{w} = n_\nu\,.$$

n_ν is the number density per unit frequency range for photons of frequency ν and N is a dimensional normalizing factor. Using the previously determined value for α_ν it may be confirmed that

$$N = (\tfrac{2}{3}\pi c^2)^{3/2}\exp(\tfrac{3}{2})/4\pi c^2 \simeq c\,.$$

It then follows that provided the term

$$N\,\delta(c-g) \equiv N\,\delta(\gamma c - y)$$

is included within the Ω's, the results of Section III(d) can be applied directly to photon–particle interactions. Of course, in general the inclusion of photons introduces a continuum of particle types (i.e. a continuum of ν or m_ν) and hence various of the summations over k, l, and $(k'l')$ must be replaced by integrations over ν. Again, various equations of change for the photons must be developed in order to determine, in particular, the n_ν. With $\boldsymbol{\nu}$ set equal to zero this poses no problem since such equations will be the same as those given in Section II(b). However, for $\boldsymbol{\nu}$ equal to say $\boldsymbol{\nu}_0$, the relevant equations may be somewhat more complex since it is possible that a relativistic-like summation of velocities may be involved. This particular aspect has not been pursued. Again, no rigorous confirmation or proof of the various statements and conjectures made in this discussion has been sought. Nevertheless, even if some or all of these statements and conjectures should ultimately prove to be false, it is clear that it should be possible to arrive at a kinetic theory for the photons which is perfectly consistent with the analysis of the preceding sections.

VII. References

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