

6. RANGE OF APPLICATION OF THE MECHANISM

None of the discussion has involved the ratio of the concentration of holes to that of x atoms. Either of these may far outnumber the other. In particular, the concentration of impurity atoms may increase from zero up to the point where interactions among the impurity atoms become appreciable. The arguments, in short, apply to the same range as do the usual "infinite dilution" theories.

No use has been made of the periodicity of the lattice. For this reason it seems that the

foregoing considerations ought to apply without change to dilute liquid solutions, wherever the hole theory of diffusion is at all applicable. It is uncertain from the data³ whether the solute-hole molecule mechanism is commonly suitable for accounting for diffusion in liquids—that is, whether Q_0 commonly exceeds Q_x .

I am indebted to Dr. C. W. Hewlett, Mr. C. G. Found and Dr. W. Shockley for several discussions on this subject.

³H. S. Taylor, *J. Chem. Phys.* **6**, 331 (1938).

Transport Phenomena in Mixtures of Gases

E. J. HELLUND AND E. A. UEHLING
University of Washington, Seattle, Washington
(Received April 17, 1939)

The theory of transport in gases taking into account the full effect of quantum statistics is extended to include mixtures as well as one-component gases. The method of Lorentz, Hilbert, and Enskog, which was used previously in the development of the quantum theory of transport in a single component gas, is used again in this more general case. As is to be expected, all transport equations have formally the same dependence on velocity, temperature, and pressure gradients as in the classical statistics, the effects of diffraction and interference introduced by the

quantum statistics appearing only in the coefficients themselves. Expressions for the viscosity, heat conductivity, pressure diffusion, and thermal diffusion coefficients into which assumptions with regard to the interaction laws may be introduced have been obtained. It is expected that these expressions may form the basis for calculation based on plausible assumptions as to the interaction that will provide a relatively good test of these laws as well as of the theory itself.

INTRODUCTION

THE study of transport phenomena in gases has been recognized as a most promising field of investigation having as its objective the determination of intermolecular forces. The study of viscosity, heat conductivity and diffusion by numerous early investigators together with the rigorous analytical treatments of the subject given by Enskog and Chapman have demonstrated fully the sensitivity of the method and the practicality of the calculations which lead to the possibility of detailed comparisons between theoretical results and experimental observations.

With the introduction of the quantum statistics, the study of transport phenomena in gases took on a further significance, which was

to be found in the possibility of an experimental test of these statistics. Certain discrepancies between observational data and the results of calculations based on the classical theory of Chapman and Enskog had already appeared. These discrepancies, which were observed for all transport coefficients, were at first attributed to the assumption of incorrect interaction laws on the basis of which the theoretical results were obtained. That this interpretation of the discrepancies was inadequate was demonstrated by Massey and Mohr¹ for the case of viscosity and heat conductivity in single component gases. The considerable improvement in the theoretical results obtained by these authors when quantum-

¹H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc.* **A141**, 434 (1933); **A144**, 188 (1934).

theoretical cross sections were substituted for the classical cross sections in the expressions for the gas coefficients derived by Chapman was an indication of the importance of having a complete quantum-statistical treatment of transport.

Such a theory of transport in single component gases was given by Uehling and Uhlenbeck,² and calculations based on the theory applicable to the gases H₂ and He under the assumption of elastic sphere interaction were given by one of the present authors.³ The theory shows that the modifications due to the quantum statistics are of two kinds: (a) a diffraction effect, which for light gases of moderate density is appreciable even at room temperatures; and, (b) an interference effect due to modifications in the "Stoszzahlansatz," which is inappreciable even for the case of H₂ and He⁴ except at temperatures in the neighborhood of the critical values. The experiments of Itterbeek and Keesom⁵ on the viscosity of helium at low temperatures together with the results of previous experiments at higher temperatures demonstrate the importance of the diffraction effect. What discrepancies still remain in the temperature dependence of the viscosity coefficient are presumably attributable to the simplifying assumptions used with respect to the interaction laws. Numerical calculations of Massey and Mohr, Massey and Buckingham, and the authors⁶ based on Van der Waals types of interaction substantiate this conclusion.

The second of the two quantum-mechanical effects appears to be more difficult to detect. The theory shows a density dependence for the viscosity coefficient of He which is large compared with the nonideality correction in the neighborhood of 5°K.³ According to the experiments of Itterbeek and Keesom, this effect appears, however, to be too small for detection within the range of density variations in which the theory may be presumed to be valid, and the temperature dependence of the density effect

is difficult to separate from the temperature dependence of the diffraction effect.

For these reasons the development of a quantum theory of gas mixtures is undertaken. In addition to the phenomena of viscosity and heat conductivity, one now has also the phenomena of diffusion to consider. The introduction of diffusion processes into the problem leads to the following interesting considerations. There exist in general two types of diffusion; a pressure diffusion, and a thermal diffusion. As is the case with all transport coefficients, the diffusion coefficients will exhibit temperature and density variations which are characteristic of the diffraction effect and of the interference effect. Under certain conditions, however, only the ratio of these diffusion coefficients is important. This is true for any experimental arrangement in which a definite quantity of a mixture of gases is allowed to come to equilibrium under the influence of an impressed temperature gradient. Equilibrium is established under these conditions with variations in density of each component along the direction of the temperature gradient such that the processes of pressure diffusion in one direction are just balanced by the processes of thermal diffusion in the opposite direction. This equilibrium situation is described by the ratio of the pressure and thermal diffusion coefficients. Unlike all other transport coefficients this ratio does not depend on any single integral over transport cross sections, but only on the ratio of such integrals. One would expect, therefore, that in this particular case the importance of the diffraction effect is minimized, and that the interference effect in the quantum statistics is, in consequence, of relatively greater importance.

A test of this expectation seems to be of considerable importance from a theoretical point of view. As a test of interaction laws the transport process under consideration may be of considerable sensitivity, since the thermal diffusion process vanishes altogether in the classical statistics for a particular interaction law.⁷ Also, the temperature dependence of the ratio of thermal and pressure diffusion coefficients is of

² E. A. Uehling and G. E. Uhlenbeck, *Phys. Rev.* **43**, 552 (1933).

³ E. A. Uehling, *Phys. Rev.* **46**, 917 (1934).

⁴ Reference 3, Tables VII and VIII.

⁵ A. v. Itterbeek and W. H. Keesom, *Physica* **5**, 257 (1938).

⁶ H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc.* **A144**, 188 (1934). H. S. W. Massey and R. A. Buckingham, *Proc. Roy. Soc.* **A168**, 378 (1938). E. A. Uehling and E. J. Hellund, *Phys. Rev.* **54**, 479 (1938).

⁷ The inverse fifth-power law. See Sir James Jeans, *The Dynamical Theory of Gases* (Cambridge University Press, 1925), 4th ed., p. 324.

importance for any process of isotope separation which depends upon the establishment of an equilibrium state under the influence of a temperature gradient. In spite of the appearance of only ratios of cross section integrals in the description of this process, and the resulting complete lack of temperature dependence in the classical statistics for elastic sphere interaction, there is no *a priori* reason to believe that the temperature dependence in the quantum statistics is negligible for any interaction law.

From the point of view of isotope separation there is still another consideration which may be of importance. The ratios of cross sections which appear must involve, necessarily, similar and dissimilar molecules, and in a few cases, also, molecules of opposite statistics. The large effect arising from considerations of identity in the theory of collisions is, therefore, of importance in any consideration of separation of molecular species of approximately equal mass.

No numerical results are included in this paper, though preliminary calculations based on the elastic sphere model have been made in order to test the temperature sensitivity of the ratio of the thermal and pressure diffusion coefficients. In view of the known inadequacy of the elastic sphere model to even approximately describe the process of thermal diffusion these calculations are not included in this paper, though the results may be stated here. With this type of interaction the ratio of thermal and pressure diffusion coefficients shows a temperature dependence for the case of a mixture of helium and neon of approximately 20 percent between the temperatures of 10°K and 273°K as compared with a variation of approximately 30 percent in addition to the $T^{1/2}$ for each gas coefficient separately.

The formal theory of gas mixtures considered here is developed in three sections. The general theory of transport with a determination of the fundamental transport equations valid for a gas consisting of an arbitrary number of components is given in Section I. In Section II the differential integral equations for a gas of two components is solved according to usual methods valid for the case of infinitesimal deviations from the equilibrium state. In Section III an application

of the variation method is made in order to obtain explicit forms for the gas coefficients.

Numerical calculations based on the theory and on the assumption of a five-parameter type of interaction are in progress. These results will be obtained for cases of particular interest and published in a succeeding paper.

I. THE TRANSPORT EQUATIONS

The state of a gas consisting of N components is completely described by the distribution functions $f_i(x_\alpha, r_\alpha, t)$ which are solutions of the following differential integral equation:⁸

$$\begin{aligned} \frac{\partial f_i}{\partial t} + D_i(f_i) = & \sum_{j=1}^N \int d\phi_j \int g_{ij} w_{ij}(\vartheta \varphi) d\Omega \\ & \times \{ f_i' f_j' (1 + \theta_i f_i) (1 + \theta_j f_j) \\ & - f_i f_j (1 + \theta_i f_i') (1 + \theta_j f_j') \} \quad i=1, 2, \dots, N, \quad (1) \end{aligned}$$

where

$$D_i = r_{i\alpha} \partial / \partial x_\alpha + \bar{x}_{i\alpha} \partial / \partial r_{i\alpha},$$

$$d\phi_j = G_j (m_j / h)^3 dr_{j1} dr_{j2} dr_{j3}.$$

The distribution function f_i of these equations represents the number of particles of component i per cell of phase space of which the space part is taken to have the value unity. The notation adopted here is to use Latin letters as subscripts to designate the gas components, and to use Greek letters as subscripts to designate the components of vectors, with the repetition of a Greek letter as a subscript in the product of two quantities indicating a summation over the vector components. The meaning of the remaining quantities is as follows: $r_{i\alpha}$, the components of velocity of particles belonging to the i th specie; $\bar{x}_{i\alpha}$, the force components per unit mass; G_i , a weight factor; g_{ij} , the relative velocity of two particles belonging to the i th and j th species; $w_{ij}(\vartheta \varphi) d\Omega$ where $d\Omega = \sin \vartheta d\vartheta d\phi$, the differential cross section for scattering in which the direction of the relative velocity is changed through an angle ϑ and falls into an element of solid angle $d\Omega$ after collision; m_i , the particle mass; and h , Planck's constant representing the volume of a cell in phase space. The statistics are determined

⁸ Reference 3. See also R. H. Fowler, *Statistical Mechanics*, 2nd Ed. (Camb. Univ. Press, 1936), Chapter XVII.

by the value of θ_i , being Einstein-Bose if $\theta_i=1$ and Fermi-Dirac if $\theta_i=-1$. In this equation as in all succeeding equations in which collision integrals appear, primes are attached to functions of the velocity variables when the values of the variables after a collision are meant.

The general transport equations for the gas are obtained in the usual manner by multiplying Eq. (1) by a function $F_i(x_\alpha, r_\alpha, t)$, representing any additive property of the individual molecules, and integrating over all velocity space. Performing this operation, introducing new velocity variables $v_{i\alpha}=r_{i\alpha}-u_\alpha$, where u_α is any function of x_α, t possessing derivatives with respect to these variables, and defining

$$d/dt = \partial/\partial t + u_\alpha \partial/\partial x_\alpha$$

the general transport equation becomes

$$\begin{aligned} \frac{d}{dt} (n_i \langle F_i \rangle_{Av}) + n_i \langle F_i \rangle_{Av} \frac{\partial u_\alpha}{\partial x_\alpha} + \frac{\partial}{\partial x_\alpha} (n_i \langle v_{i\alpha} F_i \rangle_{Av}) \\ = n_i \left\{ \left\langle \frac{dF_i}{dt} \right\rangle_{Av} + \left\langle v_{i\alpha} \frac{\partial F_i}{\partial x_\alpha} \right\rangle_{Av} \right. \\ \left. + \left(\bar{x}_{i\alpha} - \frac{d u_\alpha}{dt} \right) \left\langle \frac{\partial F_i}{\partial v_{i\alpha}} \right\rangle_{Av} \right. \\ \left. - \left\langle v_{i\alpha} \frac{\partial F_i}{\partial v_{i\beta}} \right\rangle_{Av} \frac{\partial u_\beta}{\partial x_\alpha} \right\} + \sum_{j=1}^N \Delta_{ij}(F_i), \quad (2) \end{aligned}$$

where

$$\begin{aligned} \Delta_{ij}(F_i) = \int d\phi_i \int d\phi_j \int g_{ij} w_{ij} (\partial \varphi) d\Omega F_i \\ \times \{ f_i' f_j' (1 + \theta_i f_i) (1 + \theta_j f_j) \\ - f_i f_j (1 + \theta_i f_i') (1 + \theta_j f_j') \}. \quad (3) \end{aligned}$$

Average values are taken with the distribution function, and n_i denotes the total number of particles per unit volume of component i . Symmetry considerations lead to the following properties for $\Delta_{ij}(F_i)$

$$\begin{aligned} \Delta_{ij}(F_i) = \frac{1}{2} \int d\phi_i \int d\phi_j \int g_{ij} w_{ij} d\Omega \\ \times \{ F_i - F_i' \} \{ f_i' f_j' (1 + \theta_i f_i) (1 + \theta_j f_j) \\ - f_i f_j (1 + \theta_i f_i') (1 + \theta_j f_j') \} \\ \text{for } i \neq j, \quad (3a) \end{aligned}$$

$$\begin{aligned} \Delta_{ii}(F_i) = \frac{1}{4} \int d\phi_i \int d\phi_{i1} \int g_{ii} w_{i1} d\Omega \\ \times \{ F_i - F_i' + F_{i1} - F_{i1}' \} \\ \times \{ f_i' f_{i1}' (1 + \theta_i f_i) (1 + \theta_i f_{i1}') \\ - f_i f_{i1} (1 + \theta_i f_i') (1 + \theta_i f_{i1}') \}, \quad (3b) \end{aligned}$$

where for the case of $i=j$ a subscript 1 is attached to certain functions to distinguish the two velocity classes over which integration occurs.

The hydrodynamical equations are obtained from Eq. (2) by allowing the function F_i to assume in turn the character of mass, momentum, and kinetic energy. The function u_α is specialized to denote the components of mass velocity of the entire gas, and a variable $u_{i\alpha} = \langle r_{i\alpha} \rangle_{Av}$ is introduced to represent the same property for each of the gas components. The hydrodynamical equations then become

$$\frac{d\rho_i}{dt} + \rho_i \frac{\partial u_{i\alpha}}{\partial x_\alpha} + (u_{i\alpha} - u_\alpha) \frac{\partial \rho_i}{\partial x_\alpha} = 0, \quad (4a)$$

$$\begin{aligned} \frac{d j_{i\alpha}}{dt} + j_{i\alpha} \frac{\partial u_\beta}{\partial x_\beta} + \frac{\partial p_{i\alpha\beta}}{\partial x_\beta} = \rho_i \left(\bar{x}_{i\alpha} - \frac{d u_\alpha}{dt} \right) \\ - j_{i\beta} \frac{\partial u_\alpha}{\partial x_\beta} + \sum_{j=1}^N \Delta_{ij}(m_i v_{i\alpha}), \quad \alpha = 1, 2, 3 \quad (4b) \end{aligned}$$

$$\begin{aligned} \frac{d(Q_i/\rho_i)}{dt} + \frac{\partial q_{i\alpha}}{\partial x_\alpha} = \frac{Q_i}{\rho_i} \frac{\partial j_{i\alpha}}{\partial x_\alpha} + j_{i\alpha} \left(\bar{x}_{i\alpha} - \frac{d u_\alpha}{dt} \right) \\ - p_{i\alpha\beta} S_{\alpha\beta} + \sum_{j=1}^N \Delta_{ij} \left(\frac{1}{2} m_i v_{i\alpha} v_{i\alpha} \right), \quad (4c) \end{aligned}$$

where

$$\rho_i = n_i m_i, \quad \rho = \sum_{i=1}^N \rho_i, \quad \rho u_\alpha = \sum_{i=1}^N \rho_i u_{i\alpha},$$

$$j_{i\alpha} = \rho_i (u_{i\alpha} - u_\alpha) = - \frac{\rho_i}{\rho} \sum_{j=1}^N \rho_j (u_{i\alpha} - u_{j\alpha}), \quad \sum_{j=1}^N j_{j\alpha} = 0,$$

$$\begin{aligned} p_{i\alpha\beta} = \rho_i \langle v_{i\alpha} v_{i\beta} \rangle_{Av}, \quad p_{\alpha\beta} = \sum_{i=1}^N p_{i\alpha\beta}, \\ p_i = \frac{1}{3} \sum_{\alpha=1}^3 p_{i\alpha\alpha}, \quad p = \sum_{i=1}^N p_i, \quad (5) \end{aligned}$$

$$Q_i = \frac{1}{2} \rho_i \langle v_{i\alpha} v_{i\alpha} \rangle_{Av} = \frac{1}{2} \sum_{\alpha=1}^3 p_{i\alpha\alpha} = \frac{3}{2} p_i, \quad Q = \sum_{i=1}^N Q_i,$$

$$q_{i\alpha} = \frac{1}{2} \rho_i \langle v_{i\alpha} v_{i\beta} v_{i\beta} \rangle_{Av}, \quad q_\alpha = \sum_{i=1}^N q_{i\alpha},$$

$$S_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right).$$

Eqs. (4a, b and c) are, respectively, the continuity, hydrodynamical, and energy equations for the individual components of the gas mixture. The quantities $j_{i\alpha}$, $q_{i\alpha}$ and Q_i are, respectively, the mass current, heat current and kinetic energy density of the i th component in the gas, and $p_{\alpha\beta}$ and $S_{\alpha\beta}$ are, respectively, the stress and strain tensors for the gas as a whole.

The hydrodynamical equations for the gas mixture are now obtained by summing Eqs. (4) over all components. Using Eqs. (5) and the relations

$$\sum_{i,j}^N \Delta_{ij}(m_i v_{i\alpha}) = 0, \quad \sum_{i,j}^N \Delta_{ij}(\frac{1}{2}m_i v_{i\alpha} v_{i\alpha}) = 0,$$

which follow from (3a and b), one obtains for the entire mixture

$$\frac{d\rho}{dt} + \rho \frac{\partial u_\alpha}{\partial x_\alpha} = 0, \quad (6a)$$

$$\frac{\partial p_{\alpha\beta}}{\partial x_\beta} = -\rho \frac{du_\alpha}{dt} + \sum_{i=1}^N \rho_i \bar{x}_{i\alpha}, \quad \alpha = 1, 2, 3 \quad (6b)$$

$$\rho \frac{d(Q/\rho)}{dt} + \frac{\partial q_\alpha}{\partial x_\alpha} = -p_{\alpha\beta} S_{\alpha\beta} + \sum_{i=1}^N j_{i\alpha} \bar{x}_{i\alpha}. \quad (6c)$$

In the summation over i in Eq. (4c) two of the terms are conveniently grouped, and with the use of Eq. (4a) put in the form

$$\rho_i \frac{d(Q_i/\rho_i)}{dt} - \frac{Q_i}{\rho_i} \frac{\partial j_{i\alpha}}{\partial x_\alpha} = \frac{dQ_i}{dt} + Q_i \frac{\partial u_\alpha}{\partial x_\alpha}.$$

Equations (4) and (6) are exact. The form of these equations in zeroth approximation is of some interest. In this approximation all mean values quantities are evaluated for an equilibrium state of the gas. Since there are $N+4$ gas parameters, ρ_i , u_α and T ($i=1, 2, \dots, N$; $\alpha=1, 2, 3$), describing the equilibrium state of an N component gas, there must be just $N+4$ zero-order hydrodynamical equations. These equations may be obtained from (4a, 6b and 6c) by introducing the conditions of spherical symmetry into the evaluation of $p_{i\alpha\beta}$, $q_{i\alpha}$ and $j_{i\alpha}$. The form of the equations will be given in the next section in connection with the determination of the first approximation to the nonequilibrium distribution function.

II. SOLUTION OF THE BOLTZMANN EQUATION

§ 1. Principle of solution

Applying the method of Lorentz, Hilbert and Enskog to Eq. (1) we seek an approximate solution of the form

$$f_i = f_i^{(0)}(1 + \varphi_i), \quad (7)$$

where $f_i^{(0)}$ is the equilibrium distribution function, and φ_i is a function of the velocity, temperature, and pressure gradients within the gas, and expresses in first approximation the departure of the actual distribution function from that corresponding to the equilibrium state. The equilibrium distribution function is determined by the vanishing of the collision integral in Eq. (1). Multiplying this integral by $\ln f_i / (1 + \theta_i f_i) d\phi_i$, integrating, and using Eqs. (3a and b) one obtains in the manner familiar from the development of the H theorem

$$f_i^{(0)} = [A_i^{-1} \exp \{m_i(r_{i\alpha} - u_\alpha) \times (r_{i\alpha} - u_\alpha) / 2kT\} - \theta_i]^{-1}, \quad (8)$$

where the constants u_α are necessarily the same for all gas components.

Proceeding to the next approximation in the determination of f_i , its form given by (7) is substituted into Eq. (1), and second-order quantities are neglected. This corresponds to the introduction of $f_i^{(0)}$ into the left member and the neglect of products of the φ_i in the right member of Eq. (1). Defining

$$\chi_j = \varphi_j / (1 + \theta_j f_j^{(0)}), \quad (9)$$

one then obtains an integral equation for φ_i which is

$$\frac{\partial f_i^{(0)}}{\partial t} + D_i(f_i^{(0)}) = - \sum_{j=1}^N I_{ij}(\chi), \quad (10)$$

where

$$I_{ij}(\chi) = \int d\phi_j \int g_{ij} w_{ij}(\vartheta \varphi) d\Omega f_i^{(0)'} f_j^{(0)'} \times (1 + \theta_i f_i^{(0)})(1 + \theta_j f_j^{(0)}) [\chi_i + \chi_j - \chi_i' - \chi_j']. \quad (11)$$

Considering now the homogeneous part of Eq. (10), multiplying it by $\chi_i d\phi_i$ and integrating, one obtains

$$\sum_{j=1}^N [\chi, \chi]_{ij} = 0, \quad (12)$$

where for functions F and G of the velocity components

$$\begin{aligned}
 [F, G]_{ij} &= \int d\phi_i F_i I_{ij}(G) \\
 &= \int d\phi_i \int d\phi_j \int g_{ij} w_{ij} (\partial \varphi) d\Omega \\
 &\quad \times f_i^{(0)'} f_j^{(0)'} (1 + \theta_i f_i^{(0)}) (1 + \theta_j f_j^{(0)}) \\
 &\quad \times F_i [G_i + G_j - G_i' - G_j']. \quad (13)
 \end{aligned}$$

As in the derivation of Eqs. (3a and b) one may write

$$\begin{aligned}
 [F, G]_{ij} &= \frac{1}{2} \int d\phi_i \int d\phi_j \int g_{ij} w_{ij} (\partial \varphi) f_i^{(0)'} \\
 &\quad \times f_j^{(0)'} (1 + \theta_i f_i^{(0)}) (1 + \theta_j f_j^{(0)}) \\
 &\quad \times (F_i - F_i') (G_i + G_j - G_i' - G_j') \\
 &\quad \text{for } i \neq j, \quad (14a)
 \end{aligned}$$

$$\begin{aligned}
 [F, G]_{ii} &= \frac{1}{4} \int d\phi_i \int d\phi_{i1} \int g_{ii} w_{ii} (\partial \varphi) f_i^{(0)'} \\
 &\quad \times f_{i1}^{(0)'} (1 + \theta_i f_i^{(0)}) (1 + \theta_{i1} f_{i1}^{(0)}) \\
 &\quad \times (F_i + F_{i1} - F_i' - F_{i1}') \\
 &\quad \times (G_i + G_{i1} - G_i' - G_{i1}'). \quad (14b)
 \end{aligned}$$

Then

$$[F, F]_{ij} + [F, F]_{ji} \geq 0. \quad (15)$$

The solutions $\chi_i^{(0)}$ of Eq. (12) are null solutions of Eq. (10). In order that such solutions exist it follows necessarily from (12) that

$$\begin{aligned}
 \sum_{i,j} [\chi^{(0)}, \chi^{(0)}]_{ij} &= \sum_i [\chi^{(0)}, \chi^{(0)}]_{ii} \\
 &+ \sum_{i < j} \{ [\chi^{(0)}, \chi^{(0)}]_{ij} + [\chi^{(0)}, \chi^{(0)}]_{ji} \} = 0. \quad (16)
 \end{aligned}$$

Since, by Eq. (15), every term in this sum is positive definite, null solutions are those which fulfill the relation

$$\begin{aligned}
 \chi_i^{(0)} + \chi_j^{(0)} - \chi_i^{(0)'} - \chi_j^{(0)'} &= 0, \\
 i, j &= 1, 2, \dots, N, \quad (17)
 \end{aligned}$$

or

$$\chi_i^{(0)} = a_i + c_0 m_i v_{i\alpha} v_{i\alpha} + m_i c_{\alpha'} v_{i\alpha}, \quad (18)$$

containing five arbitrary constants which are functions of x_α and t , and of which only one may be different for the different components. The form (18) of $\chi_i^{(0)}$ follows strictly from (17) for spherically symmetric molecules without internal degrees of freedom to which the theory is

restricted. The existence of null solutions of Eq. (10) permits the imposition of auxiliary conditions on the solution χ_i which are taken to be of the following form

$$\int f_i^{(0)} \varphi_i d\phi_i = \int f_i^{(0)} (1 + \theta_i f_i^{(0)}) \chi_i d\phi_i = 0, \quad (19a)$$

$$\begin{aligned}
 \sum_{i=1}^N m_i \int (r_{i\alpha} - u_\alpha) f_i^{(0)} \varphi_i d\phi_i \\
 = \sum_{i=1}^N m_i \int (r_{i\alpha} - u_\alpha) f_i^{(0)} (1 + \theta_i f_i^{(0)}) \chi_i d\phi_i = 0, \\
 \alpha = 1, 2, 3, \quad (19b)
 \end{aligned}$$

$$\begin{aligned}
 \sum_{i=1}^N m_i \int (r_{i\alpha} - u_\alpha) (r_{i\alpha} - u_\alpha) f_i^{(0)} \varphi_i d\phi_i \\
 = \sum_{i=1}^N m_i \int (r_{i\alpha} - u_\alpha) (r_{i\alpha} - u_\alpha) f_i^{(0)} \\
 \times (1 + \theta_i f_i^{(0)}) \chi_i d\phi_i = 0. \quad (19c)
 \end{aligned}$$

The physical interpretation of these conditions is that the macroscopic description of the gas in terms of the $N+4$ parameters ρ_i , u_α and T is unaltered by the perturbation. Thus, from Eqs. (7) and (19)

$$\rho_i = m_i \int f_i d\phi_i = m_i \int f_i^{(0)} d\phi_i, \quad (20a)$$

$$\begin{aligned}
 \rho u_\alpha = \sum_{i=1}^N \rho_i u_{i\alpha} = \sum_{i=1}^N m_i \int r_{i\alpha} f_i d\phi_i \\
 = \sum_{i=1}^N m_i \int r_{i\alpha} f_i^{(0)} d\phi_i, \quad (20b)
 \end{aligned}$$

$$\begin{aligned}
 \rho \epsilon = \sum_{i=1}^N \rho_i \epsilon_i = \frac{1}{2} \sum_{i=1}^N m_i \int (r_{i\alpha} - u_\alpha) (r_{i\alpha} - u_\alpha) f_i d\phi_i \\
 = \frac{1}{2} \sum_{i=1}^N m_i \int (r_{i\alpha} - u_\alpha) (r_{i\alpha} - u_\alpha) f_i^{(0)} d\phi_i \\
 = \frac{3}{2} \sum_{i=1}^N p_i = \frac{3}{2} \sum_{i=1}^N \frac{RT}{M_i} \rho_i W_i (T \rho_i^{-3}), \quad (20c)
 \end{aligned}$$

where ϵ_i and ϵ are the kinetic energies per unit mass in component i and in the entire gas, respectively. The last two forms given in Eq. (20c) follow from the definitions given in Eqs. (5) and the well-known form of the equation of state for ideal gases.⁹

⁹ G. E. Uhlenbeck and E. A. Uehling, Phys. Rev. **39**, 1014 (1932).

If Eq. (10) is multiplied by $\chi_i^{(0)}d\phi_i$, integrated and summed over i , the right member vanishes by (14a and b and 17). Setting successively all but one of the $N+4$ arbitrary constants in $\chi_i^{(0)}$ equal to zero, one thus obtains $N+4$ equations representing the orthogonality conditions which must be fulfilled in order that Eq. (10) possess a solution. These conditions may be written in the form

$$\int m_i \left[\frac{\partial f_i^{(0)}}{\partial t} + D_i(f_i^{(0)}) \right] d\phi_i = 0, \quad i=1, 2, \dots, N, \quad (21a)$$

$$\sum_i \int m_i r_{i\alpha} \left[\frac{\partial f_i^{(0)}}{\partial t} + D_i(f_i^{(0)}) \right] d\phi_i = 0, \quad \alpha=1, 2, 3, \quad (21b)$$

$$\sum_i \int m_i r_{i\alpha} r_{i\alpha} \left[\frac{\partial f_i^{(0)}}{\partial t} + D_i(f_i^{(0)}) \right] d\phi_i = 0. \quad (21c)$$

One may readily show¹⁰ that these conditions are equivalent to the requirement that the parameters ρ_i , u_α and T of the equilibrium distribution function satisfy the hydrodynamical equations in zeroth approximation. Since this approximation is obtained by introducing the conditions for an equilibrium state, one evaluates the various mean value quantities of the transport equations under the assumption of a spherically symmetric velocity distribution. Thus, one has in this approximation

$$u_{i\alpha} = u_\alpha, \quad j_{i\alpha} = 0, \quad q_{i\alpha} = 0, \\ p_{i\alpha\beta} = p_i \delta_{\alpha\beta}, \quad \dot{p}_{\alpha\beta} = \dot{p} \delta_{\alpha\beta}.$$

Then from Eqs. (4a, 6b and c) the zeroth approximation to the hydrodynamical equations equivalent to the orthogonality conditions (21) are

$$\frac{d\rho_i}{dt} + \rho_i \frac{\partial u_\alpha}{\partial x_\alpha} = 0, \quad i=1, 2, \dots, N, \quad (22a)$$

$$\frac{\partial \dot{p}}{\partial x_\alpha} = -\rho \frac{du_\alpha}{dt} + \sum_{i=1}^N \rho_i \dot{x}_{i\alpha}, \quad \alpha=1, 2, 3, \quad (22b)$$

$$\rho \frac{d(Q/\rho)}{dt} = -\dot{p} \frac{\partial u_\alpha}{\partial x_\alpha}. \quad (22c)$$

As in the classical theory of the one component

¹⁰ Reference 2, note 2.

gas¹¹ one can now show that if a general solution χ of Eq. (10) is decomposed into a term satisfying the auxiliary conditions (19) and a term which is a null solution of the form (18) with constants a_i , c_0 and c_α ($i=1, 2, \dots, N$; $\alpha=1, 2, 3$), the constants can without loss of generality be chosen equal to zero at $t=t_0$, and they then remain equal to zero for all values of t . If a solution of Eq. (10) is obtained, then, subject to the condition that the gas parameters satisfy Eqs. (22), the auxiliary conditions (19) may be imposed and remain valid for all values of the time.

§ 2. Decomposition of the integral equation

Returning now to Eq. (10) the left member is transformed by the introduction of $f_i^{(0)}$ from Eq. (8) and the substitution of new velocity variables $\xi_{i\alpha}$ for $r_{i\alpha}$ according to the definition

$$\xi_{i\alpha} = (r_{i\alpha} - u_\alpha) c_i^{1/2}, \quad \tau_i^2 = \xi_{i\alpha} \xi_{i\alpha}, \quad (23)$$

where $c_i = m_i/2kT$. Then Eq. (10) becomes

$$\frac{f_i^{(0)2}}{A_i e^{-\tau_i^2}} \left[\frac{d \ln A_i}{dt} + \frac{\tau_i^2}{T} \frac{dT}{dt} \right. \\ \left. + \frac{\xi_{i\alpha}}{c_i^{1/2}} \left\{ \frac{\partial \ln A_i}{\partial x_\alpha} - 2c_i \left(\dot{x}_{i\alpha} - \frac{du_\alpha}{dt} \right) + \frac{\tau_i^2}{T} \frac{\partial T}{\partial x_\alpha} \right\} \right. \\ \left. + 2\xi_{i\alpha} \xi_{i\beta} \frac{\partial u_\alpha}{\partial x_\beta} \right] = - \sum_{j=1}^N I_{ij}(\chi). \quad (24)$$

The time derivatives in the left member of this equation may be eliminated by making use of the following relations:¹²

$$\frac{d \ln A_i}{dt} = \frac{dW_i}{dt} + W_i \left(\frac{1}{\rho_i} \frac{d\rho_i}{dt} - \frac{3}{2} \frac{1}{T} \frac{dT}{dt} \right), \quad (25a)$$

$$\frac{\partial \ln A_i}{\partial x_\alpha} = \frac{\dot{p}_i}{n_i k T} \left(\frac{1}{\dot{p}_i} \frac{\partial \dot{p}_i}{\partial x_\alpha} - \frac{5}{2} \frac{1}{T} \frac{\partial T}{\partial x_\alpha} \right), \quad (25b)$$

with $W_i(T\rho_i^{-3})$, the function defined in (20c), an adiabatic invariant. In accordance with the discussion of §1 all time derivatives of the gas parameters must fulfill the hydrodynamical equations in zeroth approximation. Then (25a) and (25b) must be evaluated subject to the conditions

¹¹ D. Enskog, *Kinetische Theorie der Vorgänge in mässig verdünnten Gasen*, Dissertation (Upsala, 1917).

¹² Reference 2, note 3; Phys. Rev. **39**, 1014 (1932).

given by Eqs. (22) and the vanishing of the total time derivative of W_i . For this purpose, Eq. (22c) is expressed in the form

$$dT/dt = -\frac{2}{3}T\partial u_\alpha/\partial x_\alpha, \quad (26)$$

which is obtained in the following manner:

$$Q = \frac{3}{2}p = \frac{3}{2}RT \sum_{i=1}^N \frac{\rho_i}{M_i} W_i (T\rho_i^{-3}),$$

$$\frac{d}{dt} \left(\frac{p}{\rho} \right) = \frac{p}{\rho T} \frac{dT}{dt} - \frac{p}{\rho^2} \frac{d\rho}{dt} + \frac{RT}{\rho} \sum_{i=1}^N \frac{W_i}{M_i} \frac{d\rho_i}{dt} + \frac{RT}{\rho} \sum_{i=1}^N \frac{\rho_i}{M_i} \frac{dW_i}{dt}.$$

The second and third terms of this equation vanish as a consequence of (22a) and the fourth as a consequence of the adiabatic invariance of W_i . Introducing Eqs. (22a, b and 26) into Eqs. (25a and b) one obtains

$$\frac{d \ln A_i}{dt} = 0, \quad (27a)$$

$$\frac{\partial \ln A_i}{\partial x_\alpha} - 2c_i \left(\bar{x}_{i\alpha} - \frac{du_\alpha}{dt} \right) = \frac{1}{n_i k T} \left[-\frac{5}{2} \frac{p_i}{T} \frac{\partial T}{\partial x_\alpha} + \frac{\partial p_i}{\partial x_\alpha} - \rho_i \bar{x}_{i\alpha} - \frac{\rho_i}{\rho} \sum_{j=1}^N \left(\frac{\partial p_j}{\partial x_\alpha} - \rho_j \bar{x}_{j\alpha} \right) \right]. \quad (27b)$$

Then the integral Eq. (24) becomes

$$\frac{f_i^{(0)2}}{A_i e^{-\tau_i^2}} \left[\frac{1}{c_i^{\frac{3}{2}}} \frac{1}{T} \xi_{i\alpha} \frac{\partial T}{\partial x_\alpha} \left(\tau_i^2 - \frac{5}{2} \frac{p_i}{n_i k T} \right) + \left(\xi_{i\alpha} \xi_{i\beta} - \frac{\tau_i^2}{3} \delta_{\alpha\beta} \right) \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) + \frac{2c_i^{\frac{3}{2}}}{\rho_i} \xi_{i\alpha} \left\{ \frac{\partial p_i}{\partial x_\alpha} - \rho_i \bar{x}_{i\alpha} \right\} - \frac{\rho_i}{\rho} \sum_{j=1}^N \left(\frac{\partial p_j}{\partial x_\alpha} - \rho_j \bar{x}_{j\alpha} \right) \right] = - \sum_{j=1}^N I_{ij}(\chi). \quad (28)$$

In the collision integrals $I_{ij}(\chi)$ it is convenient to introduce in addition to the variables $\xi_{i\alpha}$ a new relative velocity variable γ_{ij} for the g_{ij} defined by

$$g_{ij} = \gamma_{ij} \left(\frac{c_i + c_j}{c_i c_j} \right)^{\frac{1}{2}}.$$

Denoting $d\omega_i = d\xi_{i1} d\xi_{i2} d\xi_{i3}$, so that

$$d\phi_i = G_i \left(\frac{m_i}{h} \right)^3 c_i^{-3} d\omega_i,$$

the collision integral written out in full becomes

$$I_{ij}(\chi) = G_j \left(\frac{m_j}{h} \right)^3 \left(\frac{c_i + c_j}{c_i c_j} \right)^{\frac{3}{2}} c_j^{-3} \times F_{\frac{3}{2}}(A_i) F_{\frac{3}{2}}(A_j) J_{ij}(\chi), \quad (29)$$

where

$$J_{ij}(\chi) = F_{\frac{3}{2}}^{-1}(A_i) F_{\frac{3}{2}}^{-1}(A_j) \int d\omega_j \int \gamma_{ij} w_{ij} (\partial \varphi) d\Omega \times f_i^{(0)'} f_j^{(0)'} (1 + \theta_i f_i^{(0)}) \times (1 + \theta_j f_j^{(0)}) (\chi_i + \chi_j - \chi_i' - \chi_j') \quad (30)$$

and

$$F_S(A_i) = \frac{1}{\Gamma(S+1)} \int_0^\infty \frac{u^S du}{(1/A_i) \exp u - \theta_i} \quad (30a)$$

is the Sommerfeld integral.

Equation (28) with I_{ij} defined by Eqs. (29) and (30) must be solved now for χ_i in order to determine the distribution function to the first order of approximation. We consider here only a two-component gas and restrict all further considerations to this case. Writing out Eq. (28) in full one has then

$$\frac{f_1^{(0)2}}{A_1 e^{-\tau_1^2}} \left[\frac{1}{c_1^{\frac{3}{2}}} \frac{1}{T} \xi_{1\alpha} \frac{\partial T}{\partial x_\alpha} \left(\tau_1^2 - \frac{5}{2} \frac{p_1}{n_1 k T} \right) + \left(\xi_{1\alpha} \xi_{1\beta} - \frac{\tau_1^2}{3} \delta_{\alpha\beta} \right) \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) + \frac{2c_1^{\frac{3}{2}}}{\rho_1} \xi_{1\alpha} \left\{ \frac{\rho_2}{\rho} \frac{\partial p_1}{\partial x_\alpha} - \frac{\rho_1}{\rho} \frac{\partial p_2}{\partial x_\alpha} - \frac{\rho_1 \rho_2}{\rho} (\bar{x}_{1\alpha} - \bar{x}_{2\alpha}) \right\} \right] = -G_1 \left(\frac{m_1}{h} \right)^3 \frac{2^{\frac{3}{2}}}{c_1^2} F_{\frac{3}{2}}^2(A_1) J_{11}(\chi) - G_2 \left(\frac{m_2}{h} \right)^3 \left(\frac{c_1 + c_2}{c_1 c_2} \right)^{\frac{3}{2}} c_2^{-3} F_{\frac{3}{2}}(A_1) F_{\frac{3}{2}}(A_2) J_{12}(\chi), \quad (31a)$$

$$\frac{f_2^{(0)2}}{A_2 e^{-\tau_2^2}} \left[\frac{1}{c_2^{\frac{3}{2}}} \frac{1}{T} \xi_{2\alpha} \frac{\partial T}{\partial x_\alpha} \left(\tau_2^2 - \frac{5}{2} \frac{p_2}{n_2 k T} \right) + \left(\xi_{2\alpha} \xi_{2\beta} - \frac{\tau_2^2}{3} \delta_{\alpha\beta} \right) \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) + \frac{2c_2^{\frac{3}{2}}}{\rho_2} \xi_{2\alpha} \left\{ \frac{\rho_1}{\rho} \frac{\partial p_2}{\partial x_\alpha} - \frac{\rho_2}{\rho} \frac{\partial p_1}{\partial x_\alpha} - \frac{\rho_2 \rho_1}{\rho} (\bar{x}_{2\alpha} - \bar{x}_{1\alpha}) \right\} \right]$$

$$= -G_1 \left(\frac{m_1}{h} \right)^3 \left(\frac{c_1 + c_2}{c_1 c_2} \right)^{\frac{1}{2}} c_1^{-\frac{3}{2}} F_{\frac{3}{2}}(A_1) F_{\frac{3}{2}}(A_2) J_{21}(\chi) \\ - G_2 \left(\frac{m_2}{h} \right)^3 \frac{2^{\frac{3}{2}}}{c_2^2} F_{\frac{3}{2}}^2(A_2) J_{22}(\chi). \quad (31b)$$

The solution of these equations is to be obtained subject to the auxiliary conditions (19) which now take the form

$$\int f_i^{(0)} (1 + \theta_i f_i^{(0)}) \chi_i d\omega_i = 0, \quad i = 1, 2, \quad (32a)$$

$$G_1 m_1^2 \int \xi_{1\alpha} f_1^{(0)} (1 + \theta_1 f_1^{(0)}) \chi_{1\alpha} d\omega_1 \\ + G_2 m_2^2 \int \xi_{2\alpha} f_2^{(0)} (1 + \theta_2 f_2^{(0)}) \chi_{2\alpha} d\omega_2 = 0, \\ \alpha = 1, 2, 3. \quad (32b)$$

$$G_1 m_1^{\frac{3}{2}} \int \xi_{1\alpha} \xi_{1\alpha} f_1^{(0)} (1 + \theta_1 f_1^{(0)}) \chi_{1\alpha} d\omega_1 \\ + G_2 m_2^{\frac{3}{2}} \int \xi_{2\alpha} \xi_{2\alpha} f_2^{(0)} (1 + \theta_2 f_2^{(0)}) \chi_{2\alpha} d\omega_2 = 0. \quad (32c)$$

Since Eqs. (31) are linear, and all temperature, velocity and pressure gradients and the external forces are arbitrary, the solution χ_i may be decomposed into a linear combination of twelve functions $X_{i\alpha}$, $\Psi_{i\alpha}$ and $\Pi_{i\alpha\beta}$ ($\alpha, \beta = 1, 2, 3$; $\Pi_{i\alpha\beta} = \Pi_{i\beta\alpha}$) with coefficients depending on the gas constants and parameters together with their gradients. Thus, we may express

$$\chi_i = -\frac{\pi^{\frac{3}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \left[\frac{X_{i\alpha}}{kT} \left\{ \frac{\rho_2}{\rho} \frac{\partial p_1}{\partial x_\alpha} \right. \right. \\ \left. \left. - \frac{\rho_1}{\rho} \frac{\partial p_2}{\partial x_\alpha} + \frac{\rho_1 \rho_2}{\rho} (\bar{x}_{2\alpha} - \bar{x}_{1\alpha}) \right\} + \frac{\Psi_{i\alpha}}{T} \frac{\partial T}{\partial x_\alpha} \right. \\ \left. + \frac{\Pi_{i\alpha\beta}}{(2kT)^{\frac{1}{2}}} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \right], \quad i = 1, 2. \quad (33)$$

Introducing this form of χ_i into Eqs. (31) and using the relation

$$\rho_i = n_i m_i = m_i G_i \left(\frac{2\pi m_i kT}{h^2} \right)^{\frac{3}{2}} F_{\frac{3}{2}}(A_i),$$

which follows directly from (8) and (20a), one

obtains the following component equations for the individual functions

$$\frac{\xi_{1\alpha}}{m_1^{\frac{1}{2}}} \frac{f_1^{(0)2} e^{\tau_1^2}}{A_1 F_{\frac{3}{2}}(A_1)} = -\frac{n_1}{n_2} \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} J_{11}(X_\alpha) \\ + J_{12}(X_\alpha), \quad (34a)$$

$$\frac{\xi_{2\alpha}}{m_2^{\frac{1}{2}}} \frac{f_2^{(0)2} e^{\tau_2^2}}{A_2 F_{\frac{3}{2}}(A_2)} = J_{21}(X_\alpha) \\ + \frac{n_2}{n_1} \left(\frac{2m_1}{m_1 + m_2} \right)^{\frac{1}{2}} J_{22}(X_\alpha), \quad (34b)$$

$$\frac{n_1}{m_1^{\frac{3}{2}}} \xi_{1\alpha} \left(\tau_1^2 - \frac{5}{2} \frac{p_1}{n_1 kT} \right) \frac{f_1^{(0)2} e^{\tau_1^2}}{A_1 F_{\frac{3}{2}}(A_1)} \\ = -\frac{n_1}{n_2} \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} J_{11}(\Psi_\alpha) + J_{12}(\Psi_\alpha), \quad (34c)$$

$$\frac{n_2}{m_2^{\frac{3}{2}}} \xi_{2\alpha} \left(\tau_2^2 - \frac{5}{2} \frac{p_2}{n_2 kT} \right) \frac{f_2^{(0)2} e^{\tau_2^2}}{A_2 F_{\frac{3}{2}}(A_2)} \\ = J_{21}(\Psi_\alpha) + \frac{n_2}{n_1} \left(\frac{2m_1}{m_1 + m_2} \right)^{\frac{1}{2}} J_{22}(\Psi_\alpha), \quad (34d)$$

$$n_1 \left(\xi_{1\alpha} \xi_{1\beta} - \frac{\tau_1^2}{3} \delta_{\alpha\beta} \right) \frac{f_1^{(0)2} e^{\tau_1^2}}{A_1 F_{\frac{3}{2}}(A_1)} \\ = -\frac{n_1}{n_2} \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} J_{11}(\Pi_{\alpha\beta}) + J_{12}(\Pi_{\alpha\beta}), \quad (34e)$$

$$n_2 \left(\xi_{2\alpha} \xi_{2\beta} - \frac{\tau_2^2}{3} \delta_{\alpha\beta} \right) \frac{f_2^{(0)2} e^{\tau_2^2}}{A_2 F_{\frac{3}{2}}(A_2)} \\ = J_{21}(\Pi_{\alpha\beta}) + \frac{n_2}{n_1} \left(\frac{2m_1}{m_1 + m_2} \right)^{\frac{1}{2}} J_{22}(\Pi_{\alpha\beta}). \quad (34f)$$

As in the simple gas theory¹³ one can show from the form of these equations as linear integral equations of the second kind that the functions $X_{i\alpha}$, $\Psi_{i\alpha}$ and $\Pi_{i\alpha\beta}$ are necessarily of the form

$$X_{i\alpha} = \xi_{i\alpha} \chi_i(\tau^2), \quad (35a)$$

$$\Psi_{i\alpha} = \xi_{i\alpha} \psi_i(\tau^2), \quad (35b)$$

$$\Pi_{i\alpha\beta} = (\xi_{i\alpha} \xi_{i\beta} - \frac{1}{3} \tau_i^2 \delta_{\alpha\beta}) \pi_i(\tau^2). \quad (35c)$$

In terms of the solutions of Eqs. (34) a formal expression for the distribution function may now

¹³ D. Enskog, reference 11, p. 37.

be given. Using Eqs. (7), (8), (9), (33) and (35) one obtains

$$f_i = f_i^{(0)} \left[1 - \frac{\pi^{\frac{1}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \frac{f_i^{(0)} e^{\tau_i^2}}{A_i} \right. \\ \times \left\{ \frac{\xi_{i\alpha} \chi_i \left[\frac{\rho_2}{\rho} \frac{\partial p_1}{\partial x_\alpha} - \frac{\rho_1}{\rho} \frac{\partial p_2}{\partial x_\alpha} \right. \right. \\ \left. \left. + \frac{\rho_1 \rho_2}{\rho} (\bar{x}_{2\alpha} - \bar{x}_{1\alpha}) \right] + \frac{\xi_{i\alpha} \psi_i}{T} \frac{\partial T}{\partial x_\alpha} \right. \\ \left. \left. + \left(\xi_{i\alpha} \xi_{i\beta} - \frac{\tau_i^2}{3} \delta_{\alpha\beta} \right) \frac{\pi_i}{(2kT)^{\frac{1}{2}}} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \right\} \right], \\ i = 1, 2, \quad (36)$$

giving the distribution function in a form containing unknown functions which depend only on τ_i^2 . Using this form of the function all phenomena of transport may be considered, and the transport coefficients may be evaluated. The numerical values of these coefficients, in which we are particularly interested, may then be obtained by a variation method which will be discussed in succeeding sections.

§ 3. The diffusion coefficients

The gas coefficients which we now seek to evaluate are found as constants in the evaluation of the mean value quantities of the hydrodynamical equations. Referring to Eqs. (5) the quantities to be evaluated are

$$j_{1\alpha} = -j_{2\alpha} = (\rho_1 \rho_2 / \rho) (u_{1\alpha} - u_{2\alpha}),$$

$$p_{i\alpha\beta} = \rho_i \langle v_{i\alpha} v_{i\beta} \rangle_{Av},$$

$$q_{i\alpha} = \frac{1}{2} \rho_i \langle v_{i\alpha} v_{i\beta} v_{i\beta} \rangle_{Av},$$

the remaining quantities ρ_i , u_α and

$$Q_i = \frac{3}{2} p_i = \frac{1}{2} \sum_{\alpha=1}^3 p_{i\alpha\alpha}$$

remaining unchanged from their values as given by the equilibrium distribution function by virtue of the auxiliary conditions (20). Considering first the case of diffusion we evaluate the quantity $(u_{1\alpha} - u_{2\alpha})$ given by the equation

$$u_{1\alpha} - u_{2\alpha} = \frac{1}{n_1} \int f_1 v_{1\alpha} d\phi_1 - \frac{1}{n_2} \int f_2 v_{2\alpha} d\phi_2 \\ = \frac{G_1}{n_1 c_1^2} \left(\frac{m_1}{h} \right)^3 \int f_1 \xi_{1\alpha} d\omega_1 \\ - \frac{G_2}{n_2 c_2^2} \left(\frac{m_2}{h} \right)^3 \int f_2 \xi_{2\alpha} d\omega_2.$$

Introducing f_1 and f_2 as given by Eq. (36) one obtains

$$u_{1\alpha} - u_{2\alpha} = -\kappa \left[\frac{\rho_2}{\rho} \frac{\partial p_1}{\partial x_\alpha} - \frac{\rho_1}{\rho} \frac{\partial p_2}{\partial x_\alpha} \right. \\ \left. + \frac{\rho_1 \rho_2}{\rho} (\bar{x}_{2\alpha} - \bar{x}_{1\alpha}) + \nu \frac{\partial T}{\partial x_\alpha} \right], \quad (37)$$

where

$$\kappa = 2 \frac{(2kT)}{h^3} \frac{\pi^{\frac{1}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \left[\frac{G_1 m_1}{n_1 A_1} \int f_1^{(0)^2} e^{\tau_1^2} \right. \\ \left. \times \xi_1^2 \chi_1 d\omega_1 - \frac{G_2 m_2}{n_2 A_2} \int f_2^{(0)^2} e^{\tau_2^2} \xi_2^2 \chi_2 d\omega_2 \right], \quad (38a)$$

$$\kappa \nu = 2k \frac{(2kT)}{h^3} \frac{\pi^{\frac{1}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \left[\frac{G_1 m_1}{n_1 A_1} \int f_1^{(0)^2} e^{\tau_1^2} \right. \\ \left. \times \xi_1^2 \psi_1 d\omega_1 - \frac{G_2 m_2}{n_2 A_2} \int f_2^{(0)^2} e^{\tau_2^2} \xi_2^2 \psi_2 d\omega_2 \right]. \quad (38b)$$

In these integrals, which contain the square of a single vector component $\xi_{1\alpha}^2$, the distinguishing subscript α has been dropped. If we now multiply Eqs. (38a and b) by $\xi_1 \chi_1 d\omega_1 = X_1 d\omega_1$ and $\xi_2 \chi_2 d\omega_2 = X_2 d\omega_2$, respectively, and integrate, and then substitute the left member into Eqs. (38a) one obtains

$$\kappa = \frac{2}{(2kT)^{\frac{1}{2}}} \frac{1}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \\ \times \left[\frac{n_1}{n_2} \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \int X_1 J_{11}(X) d\omega_1 \right. \\ \left. + \int X_1 J_{12}(X) d\omega_1 + \int X_2 J_{21}(X) d\omega_2 \right. \\ \left. + \frac{n_2}{n_1} \left(\frac{2m_1}{m_1 + m_2} \right)^{\frac{1}{2}} \int X_2 J_{22}(X) d\omega_2 \right]. \quad (39a)$$

Similarly, multiplying Eqs. (34a and b) by $\xi_1\psi_1d\omega_1=\Psi_1d\omega_1$ and $\xi_2\psi_2d\omega_2=\Psi_2d\omega_2$, respectively, one obtains

$$\begin{aligned} \kappa\nu &= \frac{2k}{(2kT)^{\frac{1}{2}}} \frac{1}{n_1n_2} \left(\frac{m_1m_2}{m_1+m_2} \right)^{\frac{1}{2}} \\ &\times \left[\frac{n_1}{n_2} \left(\frac{2m_2}{m_1+m_2} \right)^{\frac{1}{2}} \int \Psi_1 J_{11}(X) d\omega_1 \right. \\ &+ \int \Psi_1 J_{12}(X) d\omega_1 + \int \Psi_2 J_{21}(X) d\omega_2 \\ &\left. + \frac{n_2}{n_1} \left(\frac{2m_1}{m_1+m_2} \right)^{\frac{1}{2}} \int \Psi_2 J_{22}(X) d\omega_2 \right]. \quad (39b) \end{aligned}$$

In a manner analogous to the definition of the operator $[F, G]_{ij}$ on functions F and G of the velocity variables $r_{i\alpha}$ and $r_{j\alpha}$ given by Eq. (13) we now define new operators on functions of the velocity variables $\xi_{i\alpha}$. With F_i and G_i functions of the variables $\xi_{i\alpha}$, F_j and G_j functions of $\xi_{j\alpha}$, we define

$$[F, G]_{ij} = \int F_i J_{ij}(G) d\omega_i, \quad (40)$$

where the operator $J_{ij}(G)$ is defined by Eq. (30). Since only operators on functions of the $\xi_{i\alpha}$ will now appear, no confusion with the operator previously defined by Eq. (13) will arise. Also, we define the operator

$$\begin{aligned} \{F, G\} &= \frac{n_1}{n_2} \left(\frac{2m_2}{m_1+m_2} \right)^{\frac{1}{2}} [F, G]_{11} + [F, G]_{12} \\ &+ [F, G]_{21} + \frac{n_2}{n_1} \left(\frac{2m_1}{m_1+m_2} \right)^{\frac{1}{2}} [F, G]_{22}. \quad (41) \end{aligned}$$

These operators have obviously the properties

$$[F, G]_{ii} = [G, F]_{ii}, \quad (42a)$$

$$[F, G+H]_{ij} = [F, G]_{ij} + [F, H]_{ij}, \quad (42b)$$

$$[F, cG]_{ij} = c[F, G]_{ij}, \quad (42c)$$

$$[F, F]_{ii} \geq 0, \quad (42d)$$

$$[F, G]_{12} + [F, G]_{21} = [G, F]_{12} + [G, F]_{21}, \quad (42e)$$

$$[F, F]_{12} + [F, F]_{21} \geq 0, \quad (42f)$$

where c is a constant. Also

$$\{F, G\} = \{G, F\}, \quad (43a)$$

$$\{F, G+H\} = \{F, G\} + \{F, H\}, \quad (43b)$$

$$\{F, cG\} = c\{F, G\}, \quad (43c)$$

$$\{F, F\} \geq 0. \quad (43d)$$

Other properties of this operator which will be required are the following. The equation

$$\{\chi, \chi\} = 0$$

can have only the solutions

$$\chi_i = a_i + c_0 \xi_{i\alpha} \xi_{i\alpha} + m_i^{\frac{1}{2}} c_\alpha \xi_{i\alpha}, \quad (44a)$$

where a_1, a_2, c_0, c_1, c_2 and c_3 are six arbitrary constants. But solutions of this form must vanish identically if they are to satisfy the auxiliary conditions (32). Secondly,

$$\{F, F\} \{G, G\} \geq \{F, G\}^2. \quad (44b)$$

The existence of this property may be shown as follows. Form a function H out of functions F and G in the manner

$$H = G\{F, F\} - F\{F, G\}.$$

Then

$$\{H, H\} = \{F, F\} [\{F, F\} \{G, G\} - \{F, G\}^2] \geq 0.$$

According to the above properties the result then follows immediately. Finally, if

$$\{F, F\} \{G, G\} - \{F, G\}^2 = 0,$$

where F and G are two functions satisfying the auxiliary conditions, it is necessarily true that

$$F = cG, \quad (44c)$$

where c is a constant. This result follows as a consequence of the property that if $\{H, H\} = 0$, H is of the form (44a). But G and F cannot be of this form and simultaneously satisfy the auxiliary conditions.

Returning now to the expressions for κ and $\kappa\nu$ one may express these coefficients in terms of the operators defined. Thus

$$\kappa = \frac{2}{(2kT)^{\frac{1}{2}}} \frac{1}{n_1n_2} \left(\frac{m_1m_2}{m_1+m_2} \right)^{\frac{1}{2}} \{X, X\}, \quad (45a)$$

$$\kappa\nu = \frac{2k}{(2kT)^{\frac{1}{2}}} \frac{1}{n_1n_2} \left(\frac{m_1m_2}{m_1+m_2} \right)^{\frac{1}{2}} \{\Psi, X\}, \quad (45b)$$

$$\nu = k \frac{\{\Psi, X\}}{\{X, X\}}. \quad (45c)$$

The method of evaluation of these coefficients and the determination of the unknown functions X , Ψ and Π may now be discussed. For the case of the function X let us define functions L which satisfy the auxiliary conditions (32) and which belong to a class defined by the equation

$$\{L, L\} = \frac{1}{m_1^{\frac{3}{2}}} \int \frac{\xi_1 f_1^{(0)^2} e^{\tau_1^2}}{A_1 F_1(A_1)} L_1 d\omega_1 - \frac{1}{m_2^{\frac{3}{2}}} \int \frac{\xi_2 f_2^{(0)^2} e^{\tau_2^2}}{A_2 F_1(A_2)} L_2 d\omega_2.$$

Using the integral Eqs. (34a and b) this condition is found to be equivalent to the equation

$$\{L, L\} = \{L, X\}. \quad (46)$$

Since the properties of this operator yield

$$\{X - L, X - L\} \geq 0,$$

it follows that

$$\{X, X\} - \{L, L\} \geq 0. \quad (47)$$

But, according to the discussion following Eq. (44a), there exists none but vanishing solutions of the equation $\{X - L, X - L\} = 0$, and, therefore, the equality sign of Eq. (47) is valid only for $L = X$. Then X may be determined as that function L satisfying the auxiliary conditions which maximizes $\{L, L\}$, and which gives, therefore, to the coefficient κ the largest possible value.

§ 4. The heat conductivity coefficient

In order to determine the heat conductivity coefficient one evaluates the heat current density. For each gas component

$$q_{i\alpha} = \frac{1}{2} \rho_i \langle v_{i\alpha} v_{i\beta} v_{i\beta} \rangle_N = \frac{1}{2} m_i \int f_i v_{i\alpha} v_{i\beta} v_{i\beta} d\phi_i \\ = \frac{m_i G_i}{2c_i^3} \left(\frac{m_i}{h} \right)^3 \int f_i \xi_{i\alpha} \tau_i^2 d\omega_i.$$

For the purpose of calculation it is convenient to consider the difference between this quantity and the quantity

$$\frac{5}{2} p_i \langle v_{i\alpha} \rangle_N = \frac{5}{2} p_i (u_{i\alpha} - u_\alpha) = \frac{5 p_i}{2 n_i} \int f_i v_{i\alpha} d\phi_i \\ = \frac{5 p_i G_i}{2 n_i c_i^2} \left(\frac{m_i}{h} \right)^3 \int f_i \xi_{i\alpha} d\omega_i.$$

Taking this difference and summing over the two components one obtains

$$q_\alpha - \frac{5}{2} [p_1(u_{1\alpha} - u_\alpha) + p_2(u_{2\alpha} - u_\alpha)] \\ = \frac{1}{2} \left(\frac{2kT}{h} \right)^3 \left[m_1 G_1 \int f_1 \xi_{1\alpha} \left(\tau_1^2 - \frac{5 p_1}{2 n_1 kT} \right) d\omega_1 \right. \\ \left. + m_2 G_2 \int f_2 \xi_{2\alpha} \left(\tau_2^2 - \frac{5 p_2}{2 n_2 kT} \right) d\omega_2 \right].$$

The distribution function (36) is now introduced into this expression giving the result

$$q_\alpha - \frac{5}{2} [p_1(u_{1\alpha} - u_\alpha) + p_2(u_{2\alpha} - u_\alpha)] \\ - \nu_1 \left[\frac{\rho_2}{\rho} \frac{\partial p_1}{\partial x_\alpha} - \frac{\rho_1}{\rho} \frac{\partial p_2}{\partial x_\alpha} \right. \\ \left. + \frac{\rho_1 \rho_2}{\rho} (x_{2\alpha} - x_{1\alpha}) \right] - \lambda_1 \frac{\partial T}{\partial x_\alpha}, \quad (48)$$

where

$$\nu_1 = \frac{(2kT)^2}{h^3} \frac{\pi^{\frac{3}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \\ \times \left[\frac{m_1 G_1}{A_1} \int f_1^{(0)^2} e^{\tau_1^2} \xi_1^2 \left(\tau_1^2 - \frac{5 p_1}{2 n_1 kT} \right) \chi_1 d\omega_1 \right. \\ \left. + \frac{m_2 G_2}{A_2} \int f_2^{(0)^2} e^{\tau_2^2} \xi_2^2 \left(\tau_2^2 - \frac{5 p_2}{2 n_2 kT} \right) \chi_2 d\omega_2 \right], \quad (49a)$$

$$\lambda_1 = k \frac{(2kT)^2}{h^3} \frac{\pi^{\frac{3}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \\ \times \left[\frac{m_1 G_1}{A_1} \int f_1^{(0)^2} e^{\tau_1^2} \xi_1^2 \left(\tau_1^2 - \frac{5 p_1}{2 n_1 kT} \right) \psi_1 d\omega_1 \right. \\ \left. + \frac{m_2 G_2}{A_2} \int f_2^{(0)^2} e^{\tau_2^2} \xi_2^2 \left(\tau_2^2 - \frac{5 p_2}{2 n_2 kT} \right) \psi_2 d\omega_2 \right]. \quad (49b)$$

Multiplying Eqs. (34c and d) by $\xi_1 \chi_1 d\omega_1 = X_1 d\omega_1$ and $\xi_2 \chi_2 d\omega_2 = X_2 d\omega_2$ respectively, integrating and

substituting into Eq. (49a) one obtains

$$\begin{aligned} \nu_1 &= \frac{(2kT)^{\frac{1}{2}} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \left[\frac{n_1}{n_2} \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \right. \\ &\quad \times \int X_1 J_{11}(\Psi) d\omega_1 + \int X_1 J_{12}(\Psi) d\omega_1 \\ &\quad + \int X_2 J_{21}(\Psi) d\omega_2 \\ &\quad \left. + \frac{n_2}{n_1} \left(\frac{2m_1}{m_1 + m_2} \right)^{\frac{1}{2}} \int X_2 J_{22}(\Psi) d\omega_2 \right] \\ &= \frac{(2kT)^{\frac{1}{2}} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \{X, \Psi\} = \kappa \nu T. \end{aligned} \quad (50a)$$

Similarly, multiplying Eqs. (34c and d) by $\xi_1 \psi_1 d\omega_1 = \Psi_1 d\omega_1$ and $\xi_2 \psi_2 d\omega_2 = \Psi_2 d\omega_2$, integrating and substituting into Eq. (49b) one obtains

$$\lambda_1 = \frac{(2kT)^{\frac{1}{2}} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \{\Psi, \Psi\}. \quad (50b)$$

Combining (37), (48) and (50a) one obtains finally

$$\begin{aligned} q_\alpha &= \frac{5}{2} [p_1(u_{1\alpha} - u_\alpha) + p_2(u_{2\alpha} - u_\alpha)] \\ &\quad + \nu T(u_{1\alpha} - u_{2\alpha}) - \lambda \frac{\partial T}{\partial x_\alpha}, \end{aligned} \quad (51)$$

where

$$\lambda = \lambda_1 - \kappa \nu^2 T. \quad (52a)$$

According to the property expressed in Eq. (43d), the coefficients κ and λ_1 are positive definite quantities. Also, evaluating $\kappa \lambda_1$ and $\kappa^2 \nu^2 T$ from (45a and b and 50b) and using (44b) one finds that the quantity $\lambda_1 - \kappa \nu^2 T$ is positive definite. The latter may never vanish, however, for according to (44c) the expression

$$\begin{aligned} \kappa \lambda_1 - \kappa^2 \nu^2 T &= \frac{2k}{(n_1 n_2)^2} \left(\frac{m_1 m_2}{m_1 + m_2} \right) \\ &\quad \times [\{X, X\} \{\Psi, \Psi\} - \{\Psi, X\}^2] \end{aligned}$$

can vanish only if $\Psi = cX$ where c is a constant. But such a relation cannot be fulfilled since Ψ and X must simultaneously satisfy Eqs. (34a, b, c

and d). Then

$$\left. \begin{aligned} \lambda_1 &> \kappa \nu^2 T, \\ \lambda &> 0, \\ \lambda &< \lambda_1 \text{ unless } \nu = 0. \end{aligned} \right\} \quad (52b)$$

Like X , the function Ψ may be determined by a variation process. Consider a class of functions M fulfilling the auxiliary conditions and defined by the equation

$$\begin{aligned} \{M, M\} &= \frac{n_1}{m_1^{\frac{3}{2}}} \int \xi_1 \left(\tau_1^2 - \frac{5}{2} \frac{p_1}{n_1 k T} \right) \frac{f_1^{(0)2} e^{\tau_1^2}}{A_1 F_1(A_1)} M_1 d\omega_1 \\ &\quad + \frac{n_2}{m_2^{\frac{3}{2}}} \int \xi_2 \left(\tau_2^2 - \frac{5}{2} \frac{p_2}{n_2 k T} \right) \frac{f_2^{(0)2} e^{\tau_2^2}}{A_2 F_1(A_2)} M_2 d\omega_2. \end{aligned}$$

According to Eqs. (34c and d) this condition is equivalent to

$$\{M, M\} = \{M, \Psi\}.$$

Since

$$\{\Psi - M, \Psi - M\} \geq 0,$$

it follows that

$$\{\Psi, \Psi\} - \{M, M\} \geq 0.$$

Thus, Ψ may be determined as that function M satisfying the above conditions which maximizes the coefficient λ_1 .

§ 5. The viscosity coefficient

We consider now the stress tensor and evaluate the quantities $p_{\alpha\beta}$ and $p_{\alpha\alpha} - p$. Since

$$\begin{aligned} p_{i\alpha\beta} &= \rho_i \langle v_{i\alpha} v_{i\beta} \rangle_{\Lambda_i} = m_i \int f_i v_{i\alpha} v_{i\beta} d\phi_i \\ &= G_i m_i \left(\frac{m_i}{h} \right)^3 c_i^{-5/2} \int f_i \xi_{i\alpha} \xi_{i\beta} d\omega_i, \end{aligned}$$

one obtains

$$\begin{aligned} p_{xy} &= \frac{(2kT)^{5/2}}{h^3} \left[G_1 m_1^{\frac{3}{2}} \int f_1 \xi_{1x} \xi_{1y} d\omega_1 \right. \\ &\quad \left. + G_2 m_2^{\frac{3}{2}} \int f_2 \xi_{2x} \xi_{2y} d\omega_2 \right], \end{aligned}$$

$$\begin{aligned} p_{xx} - p &= \frac{(2kT)^{5/2}}{h^3} \left[G_1 m_1^{\frac{3}{2}} \int f_1 \left(\xi_{1x}^2 - \frac{\tau_1^2}{3} \right) d\omega_1 \right. \\ &\quad \left. + G_2 m_2^{\frac{3}{2}} \int f_2 \left(\xi_{2x}^2 - \frac{\tau_2^2}{3} \right) d\omega_2 \right]. \end{aligned}$$

Introducing (36)

$$p_{xy} = -\mu \left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right), \quad (53a)$$

$$p_{xx} = p - \frac{2}{3} \mu \left[2 \frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y} - \frac{\partial u_z}{\partial z} \right], \quad (53b)$$

where

$$\begin{aligned} \mu = & 2 \frac{(2kT)^2}{h^3} \frac{\pi^{\frac{3}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \\ & \times \left[\frac{G_1 m_1^{\frac{3}{2}}}{A_1} \int f_1^{(0)2} e^{\tau_1^2} \xi_{1x}^2 \xi_{1y}^2 \pi_1 d\omega_1 \right. \\ & \left. + \frac{G_2 m_2^{\frac{3}{2}}}{A_2} \int f_2^{(0)2} e^{\tau_2^2} \xi_{2x}^2 \xi_{2y}^2 \pi_2 d\omega_2 \right], \\ = & \frac{3(2kT)^2}{2} \frac{\pi^{\frac{3}{2}}}{h^3} \frac{\pi^{\frac{3}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \\ & \times \left[\frac{G_1 m_1^{\frac{3}{2}}}{A_1} \int f_1^{(0)2} e^{\tau_1^2} \left(\xi_{1x}^2 - \frac{\tau_1^2}{3} \right) \pi_1 d\omega_1 \right. \\ & \left. + \frac{G_2 m_2^{\frac{3}{2}}}{A_2} \int f_2^{(0)2} e^{\tau_2^2} \left(\xi_{2x}^2 - \frac{\tau_2^2}{3} \right) \pi_2 d\omega_2 \right]. \end{aligned}$$

In the evaluation of this coefficient it will be sufficient to consider only the second form, and to restrict our considerations to the functions

$$\Pi_{i\alpha} = \left(\xi_{i\alpha}^2 - \frac{\tau_i^2}{3} \right) \pi_i.$$

Proceeding then as before with Eqs. (34e and f) one obtains finally

$$\mu = \frac{3(2kT)^{\frac{1}{2}}}{2} \frac{\pi^{\frac{3}{2}}}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \{ \Pi, \Pi \}. \quad (54)$$

As is the case with the other two functions, Π has a maximal property, such that of all functions N defined by the condition

$$\{ N, N \} = \{ \Pi, \Pi \}$$

and satisfying the auxiliary conditions, Π is that one which maximizes the coefficient μ . All of the gas coefficients may be evaluated, therefore, with the help of a variation method. Explicit expressions for the gas coefficients in terms of

known functions will be found in this manner, and discussed in the succeeding section.

III. DERIVATION OF EXPRESSIONS FOR THE GAS COEFFICIENTS IN TERMS OF KNOWN FUNCTIONS

§ 1. Method of solution

For the purpose of this section it is convenient to consider a slight change in notation. Hitherto, all functions of velocity variables have been regarded as defined in their respective spaces $\xi_{1\alpha}$ and $\xi_{2\alpha}$. We shall now regard each function as defined over the combined velocity space of two particles, and introduce a new operator on functions H and K defined in this six-dimensional space as follows:

$$\begin{aligned} [H, K] = & \frac{1}{2} F_i^{-1}(A_1) F_i^{-1}(A_2) \int d\omega_1 \int d\omega_2 \\ & \times \int \gamma_{12} w_{12} (\partial \varphi) d\Omega (H - H') (K - K') \\ & \times f_1^{(0)'} f_2^{(0)'} (1 + \theta_1 f_1^{(0)}) (1 + \theta_2 f_2^{(0)}). \quad (55) \end{aligned}$$

Then for two functions $H = F_1 + F_2$ and $K = G_1 + G_2$ where F_1 and G_1 are defined so as to vanish in the subspace 2, and F_2 and G_2 to vanish in the subspace 1, the operator defined by Eq. (41) becomes

$$\begin{aligned} \{H, K\} = & \frac{n_1}{n_2} \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} [F_1, G_1]_{11} \\ & + [F_1 + F_2, G_1 + G_2] \\ & + \frac{n_2}{n_1} \left(\frac{2m_1}{m_1 + m_2} \right)^{\frac{1}{2}} [F_2, G_2]_{22}, \quad (56) \end{aligned}$$

since, obviously, from a comparison of Eqs. (55) and (40)

$$[F_1 + F_2, G_1 + G_2] = [F, G]_{12} + [F, G]_{21}, \quad (56a)$$

where, in the left member each function appearing is regarded as defined over the combined space, and in the right member all functions are defined separately in both component spaces. The purpose of this change of notation is that we have now a notation for a portion of the operator $\{H, K\}$ which occurs when one term of H or K or both vanish over the entire space.

Conforming with this notation the solutions of the integral equations, X , Ψ and Π , must be regarded as functions of six variables; e.g.,

$$X = X_1 + X_2,$$

where X_1 vanishes in region 2 and X_2 vanishes in region 1. The quantities $\{F, G\}$ appearing in the expressions for the transport coefficients derived in the last section may be taken, then, as of the form given by Eq. (56) without altering their meaning.

The procedure now, as indicated in the previous discussion of the maximal properties of the solutions of the integral equations, is to choose complete sets of linearly independent functions which individually fulfill the auxiliary conditions (32), and from which linear combinations may be formed which belong to the proper functional class as defined, for example, in the case of the function X , by Eq. (46). The constants of this linear combination are then to be varied in order to satisfy the maximal property.¹⁴

Since both X and Ψ are proportional to ξ and depend otherwise only on τ^2 one set of $(2n+1)$ functions, $h^{(0)}, h_1^{(r)}, h_2^{(r)}$ ($r=1, 2, \dots, n$), may be used in the determination of these solutions. Similarly, we determine that solution Π which is proportional to $(\xi^2 - \frac{1}{3}\tau^2)$, and in terms of which the viscosity coefficient may be evaluated, by choosing a set of $2n$ functions, $k_1^{(r)}, k_2^{(r)}$ ($r=1, 2, \dots, n$), each of which is of this form. Sets of functions of this character, which satisfy also the auxiliary conditions may be chosen, then, as follows:

$$h^{(0)} = \frac{\rho_1 \rho_2}{\rho} \frac{\xi_1}{n_1(m_1)^{\frac{1}{2}}} \text{ in region 1;}$$

$$= -\frac{\rho_1 \rho_2}{\rho} \frac{\xi_2}{n_2(m_2)^{\frac{1}{2}}} \text{ in region 2;}$$

$$h_1^{(r)} = \xi_1 \left[\tau_1^{2r} - \frac{\Gamma(r+5/2)}{\Gamma(5/2)} \frac{F_{r+\frac{1}{2}}(A_1)}{F_{\frac{1}{2}}(A_1)} \right] \text{ in region 1;}$$

$$= 0 \text{ in region 2;}$$

$h_2^{(r)} = 0$ in region 1;

$$= \xi_2 \left[\tau_2^{2r} - \frac{\Gamma(r+5/2)}{\Gamma(5/2)} \frac{F_{r+\frac{1}{2}}(A_2)}{F_{\frac{1}{2}}(A_2)} \right] \text{ in region 2}$$

for the first set, and

$$k_1^{(r)} = (\xi_1^2 - \frac{1}{3}\tau_1^2) \tau_1^{2r-2} \text{ in region 1;}$$

$$= 0 \text{ in region 2;}$$

$k_2^{(r)} = 0$ in region 1;

$$= (\xi_2^2 - \frac{1}{3}\tau_2^2) \tau_2^{2r-2} \text{ in region 2}$$

for the second set. Since these functions satisfy the auxiliary conditions, any linear combination of them also satisfies these conditions.

§ 2. Series developments for the gas coefficients

In order to determine X we consider the function $X^{(n)}$ given by

$$X^{(n)} = \beta^{(0)} h^{(0)} + \sum_{r=1}^n (\beta_1^{(r)} h_1^{(r)} + \beta_2^{(r)} h_2^{(r)}) \quad (57)$$

and determine the coefficients β so as to minimize the quantity

$$H_n = \{X - X^{(n)}, X - X^{(n)}\}.$$

Differentiating H_n with respect to each of the β 's one obtains the following set of algebraic equations

$$\{h^{(0)}, X^{(n)}\} = \{h^{(0)}, X\},$$

$$(r=1, 2, \dots, n; s=1, 2): \quad (58)$$

$$\{h_s^{(r)}, X^{(n)}\} = \{h_s^{(r)}, X\}$$

It follows from (57) and (58) that

$$\{X^{(n)}, X^{(n)}\} = \{X^{(n)}, X\} \quad (58a)$$

and that

$$H_n = \{X, X\} - \{X^{(n)}, X^{(n)}\} \geq 0.$$

Solving Eqs. (58) for the β 's and introducing the results into Eq. (57) one obtains

$$X^{(n)} = -\frac{A^{(2n+2)}}{D^{(2n+1)}}, \quad (59)$$

where

¹⁴For a complete discussion of this procedure together with questions of convergence see Enskog, reference 11, pp. 71-87.

$$A^{(2j+2)} = \begin{vmatrix} \{h^{(0)}, h^{(0)}\} & \dots & \{h^{(0)}, h_1^{(j)}\} & \{h^{(0)}, h_2^{(j)}\} & \{h^{(0)}, X\} \\ \{h_1^{(j)}, h^{(0)}\} & \dots & \{h_1^{(j)}, h_1^{(j)}\} & \{h_1^{(j)}, h_2^{(j)}\} & \{h_1^{(j)}, X\} \\ \{h_2^{(j)}, h^{(0)}\} & \dots & \{h_2^{(j)}, h_1^{(j)}\} & \{h_2^{(j)}, h_2^{(j)}\} & \{h_2^{(j)}, X\} \\ h^{(0)} & \dots & h_1^{(j)} & h_2^{(j)} & 0 \end{vmatrix},$$

$$D^{(2i+1)} = \begin{vmatrix} \{h^{(0)}, h^{(0)}\} & \dots & \{h^{(0)}, h_1^{(i)}\} & \{h^{(0)}, h_2^{(i)}\} \\ \{h_1^{(i)}, h^{(0)}\} & \dots & \{h_1^{(i)}, h_1^{(i)}\} & \{h_1^{(i)}, h_2^{(i)}\} \\ \{h_2^{(i)}, h^{(0)}\} & \dots & \{h_2^{(i)}, h_1^{(i)}\} & \{h_2^{(i)}, h_2^{(i)}\} \end{vmatrix}.$$

The ratio of determinants occurring in Eq. (59) may be rewritten as a series, and takes the form

$$X^{(n)} = \frac{\{h^{(0)}, X\} h^{(0)}}{\{h^{(0)}, h^{(0)}\}} + \sum_{r=1}^n P^{(r)}, \quad (60)$$

where

$$P^{(r)} = \frac{A_{2r+2, 2r+1}^{(2r+2)} A_{\{2r+1, 2r+2\}^{(2r+2)}} - A_{2r+2, 2r}^{(2r+2)} A_{\{2r+1, 2r+2\}^{(2r+2)}}}{D^{(2r-1)} D^{(2r+1)}}$$

and $A_{k, l}^{(2j+2)}$ is the cofactor of the element in the k th row and l th column of $A^{(2j+2)}$. We now form the quantity $\{X^{(n)}, X^{(n)}\}$. In order to obtain this expression, we observe that if h is any of the functions $h^{(0)}, \dots, h_1^{(r-1)}, h_2^{(r-1)}$, then both of the quantities

$$\left\{ h, A_{\{2r+1, 2r+2\}^{(2r+2)}} \right\} \quad \text{and} \quad \left\{ h, A_{\{2r+1, 2r+2\}^{(2r+1)}} \right\}$$

vanish, since in both cases one obtains a determinant with two equal rows. Then

$$\{P^{(r)}, h^{(0)}\} = \{P^{(r)}, P^{(s)}\} = 0, \quad (r \neq s). \quad (61)$$

Using Eqs. (58), (60) and (61) one then obtains

$$\{P^{(s)}, X^{(n)}\} = \{P^{(s)}, P^{(s)}\} = \{P^{(s)}, X\}. \quad (62)$$

Now using Eqs. (58a) and (62) the result

$$\{X^{(n)}, X^{(n)}\} = \frac{\{h^{(0)}, X\}^2}{\{h^{(0)}, h^{(0)}\}} + \sum_{r=1}^n \{P^{(r)}, P^{(r)}\}$$

follows. The expression $\{P^{(r)}, P^{(r)}\}$ may be rewritten. From Eq. (62) it follows that $\{P^{(r)}, P^{(r)}\}$ is given by $P^{(r)}$ if each element $h^{(0)}, h_1^{(1)}, h_2^{(1)}, \dots, h_2^{(r)}$ in $P^{(r)}$ is replaced, respectively, by

$\{h^{(0)}, X\}, \{h_1^{(1)}, X\}, \dots, \{h_2^{(r)}, X\}$. Then

$$\{P^{(r)}, P^{(r)}\} = \frac{B_{2r+2, 2r+1}^{(2r+2)} B_{\{2r+1, 2r+2\}^{(2r+2)}} - B_{2r+2, 2r}^{(2r+2)} B_{\{2r+1, 2r+2\}^{(2r+2)}}}{D^{(2r-1)} D^{(2r+1)}},$$

where $B^{(2r+2)}$ is the determinant $A^{(2r+2)}$ in which this replacement has been made. But all of the elements $\{h_1^{(j)}, X\}$ and $\{h_2^{(j)}, X\}$ in $B^{(2r+2)}$ vanish. This may be shown as follows using Eqs. (56) and (56a)

$$\begin{aligned} \{h_1^{(j)}, X\} &= \frac{n_1}{n_2} \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} [h^{(j)}, X]_{11} \\ &\quad + [h_1^{(j)}, X_1 + X_2] \\ &= \frac{n_1}{n_2} \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} [h^{(j)}, X]_{11} + [h^{(j)}, X]_{12}. \end{aligned}$$

Using Eq. (34a) and the definition of $F_s(A_1)$ given by Eq. (30a)

$$\begin{aligned} \{h_1^{(j)}, X\} &= \frac{1}{m_1^{\frac{1}{2}} A_1 F_{\frac{1}{2}}(A_1)} \int \xi_1 f_1^{(0)^2} e^{\tau_1^2} h_1^{(j)} d\omega_1 \\ &= \frac{2\pi}{3m_1^{\frac{1}{2}} F_{\frac{1}{2}}(A_1)} \int_0^3 \int_0^\infty \frac{z^{\frac{1}{2}}}{(1/A_1)e^z - \theta_1} \\ &\quad \times \left\{ z^j - \frac{\Gamma(j+5/2)}{\Gamma(5/2)} \frac{F_{j+\frac{1}{2}}(A_1)}{F_{\frac{1}{2}}(A_1)} \right\} dz \\ &\quad + j \int_0^\infty \frac{z^{j+\frac{1}{2}}}{(1/A_1)e^z - \theta_1} dz = 0. \end{aligned}$$

The determinant $B^{(2r+2)}$ is now conveniently expressed in terms of the determinant $D^{(2r+1)}$.

One then obtains

$$\{P^{(r)}, P^{(r)}\} = \{h^{(0)}, X\}^2 \frac{D_{1, 2r}^{(2r+1)} D_{\{2r+1, 2r+1\}}^{(2r+1)} - D_{1, 2r+1}^{(2r+1)} D_{\{2r+1, 2r\}}^{(2r+1)}}{D^{(2r-1)} D^{(2r+1)}} \quad (63)$$

As in the one component gas theory one can show that if the integral equations (34a and b) possess finite and continuous solutions, the limit as n approaches infinity of $\{X^{(n)}, X^{(n)}\}$ is $\{X, X\}$. Therefore, from Eq. (45a) one obtains for the gas coefficient κ

$$\kappa = \frac{22}{(2kT)^{\frac{1}{2}}} \frac{1}{n_1 n_2} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \times \left[\frac{\{h^{(0)}, X\}^2}{\{h^{(0)}, h^{(0)}\}} + \sum_{r=1}^{\infty} \{P^{(r)}, P^{(r)}\} \right] \quad (64)$$

with $\{P^{(r)}, P^{(r)}\}$ given by (63). This coefficient is thus expressed completely in terms of known functions since the quantity $\{h^{(0)}, X\}$ may be evaluated by integration of Eqs. (34a and b).

In order to determine Ψ and the thermal

conductivity coefficient associated with it one considers as before a function $\Psi^{(n)}$ formed as a linear combination from the set $h^{(0)}, h_1^{(1)}, \dots, h_2^{(n)}$. One obtains then as in the case of $X^{(n)}$ the result

$$\Psi^{(n)} = - \frac{C^{(2n+2)}}{D^{(2n+1)}} = \frac{\{h^{(0)}, \Psi\} h^{(0)}}{\{h^{(0)}, h^{(0)}\}} + \sum_{r=1}^n Q^{(r)},$$

where $C^{(2n+2)}$ is the same determinant as $A^{(2n+2)}$ with Ψ replacing X and $Q^{(r)}$ is the same as $P^{(r)}$ with the same replacement. The quantity $\{h^{(0)}, \Psi\}$ unlike $\{h^{(0)}, X\}$ vanishes, as may be shown in a manner analogous to that used above to prove the vanishing of $\{h_s^{(j)}, X\}$, and using finally the relation $p/nkT = F_{3/2}(A)/F_{1/2}(A)$. Then

$$\Psi^{(n)} = \sum_{r=1}^n Q^{(r)}.$$

Of the two thermal conductivity coefficients, the coefficient λ given by Eq. (52a) is of the greater interest. In order to determine it the expressions $\{\Psi^{(n)}, \Psi\}$ and $\{\Psi^{(n)}, X\}$ must be evaluated in addition to $\{X^{(n)}, X\}$ already obtained. Denoting

$$F^{(2r+1)} = \begin{vmatrix} \{h_1^{(1)}, h_1^{(1)}\} & \dots & \{h_1^{(1)}, h_2^{(r)}\} & \{h_1^{(1)}, \Psi\} \\ \{h_2^{(r)}, h_1^{(1)}\} & \dots & \{h_2^{(r)}, h_2^{(r)}\} & \{h_2^{(r)}, \Psi\} \\ \{h_1^{(1)}, \Psi\} & \dots & \{h_2^{(r)}, \Psi\} & 0 \end{vmatrix}, \quad (66a)$$

$$G^{(2r)} = F_{2r+1, 2r+1}^{(2r+1)}, \quad (66b)$$

one finds

$$\{\Psi^{(n)}, \Psi\} - \frac{\{X, \Psi^{(n)}\}^2}{\{X^{(n)}, X\}} = - \frac{F^{(2n+1)}}{G^{(2n)}} = \sum_{r=1}^n \frac{F_{2r+1, 2r}^{(2r+1)} F_{\{2r-1, 2r-1\}}^{(2r+1)} - F_{2r+1, 2r-1}^{(2r+1)} F_{\{2r, 2r+1\}}^{(2r+1)}}{G^{(2r-2)} G^{(2r)}},$$

where $G^{(0)}$ is to be set equal to unity. Taking the limit of this expression as n approaches infinity,

and using Eqs. (52a), (50b), (45b and c) one obtains

$$\lambda = \frac{(2kT)^{\frac{1}{2}}}{2n_1 n_2 T} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \sum_{r=1}^{\infty} \frac{F_{2r+1, 2r}^{(2r+1)} F_{\{2r-1, 2r-1\}}^{(2r+1)} - F_{2r+1, 2r-1}^{(2r+1)} F_{\{2r, 2r+1\}}^{(2r+1)}}{G^{(2r-2)} G^{(2r)}} \quad (67)$$

Similarly, the function Π and the viscosity coefficient associated with it are evaluated by

introducing a function $\Pi^{(n)}$ expressed as a linear combination of the functions $k_1^{(1)}, k_2^{(1)}, \dots, k_2^{(n)}$.

Proceeding as before and denoting

$$L^{(2r+1)} = \begin{vmatrix} \{k_1^{(1)}, k_1^{(1)}\} & \dots & \{k_1^{(1)}, k_2^{(r)}\} & \{k_1^{(1)}, \Pi\} \\ \{k_2^{(r)}, k_1^{(1)}\} & \dots & \{k_2^{(r)}, k_2^{(r)}\} & \{k_2^{(r)}, \Pi\} \\ \{k_1^{(1)}, \Pi\} & \dots & \{k_2^{(r)}, \Pi\} & 0 \end{vmatrix}, \tag{68a}$$

$$K^{(2r)} = L_{2r+1, 2r+1}^{(2r+1)}, \tag{68b}$$

one obtains from Eq. (54)

$$\mu = -\frac{3(2kT)^{\frac{1}{2}}}{2n_1n_2} \left(\frac{m_1m_2}{m_1+m_2}\right)^{\frac{1}{2}} \sum_{r=1}^{\infty} \frac{L_{2r+1, 2r}^{(2r+1)} L_{\{2r-1, 2r-1\} \{2r, 2r+1\}}^{(2r+1)} - L_{2r+1, 2r-1}^{(2r+1)} L_{\{2r-1, 2r\} \{2r, 2r+1\}}^{(2r+1)}}{K^{(2r-2)} K^{(2r)}}. \tag{69}$$

Finally, the thermal diffusion coefficient may be developed from the relations already obtained. Referring to Eq. (45b) one finds that it is the limit of the expression $\{X^{(n)}, \Psi^{(n)}\}$ which is required for this purpose. This may be obtained from Eq. (60) for $X^{(n)}$ or from the corresponding equation for $\Psi^{(n)}$ to give

$$\begin{aligned} \{X^{(n)}, \Psi^{(n)}\} &= \sum_{r=1}^n \{P^{(r)}, \Psi^{(n)}\} = \sum_{r=1}^n \{Q^{(r)}, X^{(n)}\} \\ &= \sum_{r=1}^n \{P^{(r)}, \Psi\} = \sum_{r=1}^n \{Q^{(r)}, X\}. \end{aligned}$$

Passing to the limit in the summation over n and introducing the result into Eq. (45b) one obtains

$$\kappa\nu = \frac{2k}{(2kT)^{\frac{1}{2}}} \frac{1}{n_1n_2} \left(\frac{m_1m_2}{m_1+m_2}\right)^{\frac{1}{2}} \sum_{r=1}^{\infty} \frac{M_{2r+2, 2r+1}^{(2r+2)} M_{\{2r, 2r\} \{2r+1, 2r+2\}}^{(2r+2)} - M_{2r+2, 2r}^{(2r+2)} M_{\{2r, 2r+1\} \{2r+1, 2r+2\}}^{(2r+2)}}{D^{(2r-1)} D^{(2r+1)}}, \tag{70}$$

where

$$M^{(2r+2)} = \begin{vmatrix} \{h^{(0)}, h^{(0)}\} & \{h^{(0)}, h_1^{(1)}\} & \dots & \{h^{(0)}, h_2^{(r)}\} & 0 \\ \{h_1^{(1)}, h^{(0)}\} & \{h_1^{(1)}, h_1^{(1)}\} & \dots & \{h_1^{(1)}, h_2^{(r)}\} & \{h_1^{(1)}, \Psi\} \\ \{h_2^{(r)}, h^{(0)}\} & \{h_2^{(r)}, h_1^{(1)}\} & \dots & \{h_2^{(r)}, h_2^{(r)}\} & \{h_2^{(r)}, \Psi\} \\ \{h^{(0)}, X\} & 0 & \dots & 0 & 0 \end{vmatrix}. \tag{71}$$

The coefficients characterizing a mixture of two gases are thus completely determined and expressed in terms of known functions. The diffusion process depends on κ and ν , the heat conduction on λ and ν , and the viscosity on μ . In order to obtain numerical values of the coefficients there remains the evaluation of

integrals of the type $\{h_i^{(r)}, h_j^{(s)}\}$, $\{h_i^{(r)}, X\}$ and $\{k_i^{(r)}, \Pi\}$. Integrals involving the unknown functions are evaluated by direct substitution from the integral equations. These calculations with reference to particular gas coefficients will be given in a succeeding paper.