

NP-14536

Quarterly Technical Summary Report

on

DIRECT ENERGY CONVERSION SYSTEMS

Supplement 2

TRANSPORT PROPERTIES OF PARTIALLY IONIZED
MONATOMIC GASES

Prepared for
Advanced Research Projects Agency

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For the period
1 June - 31 August 1964

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ARPA Order Number: 246, Amendment 6
 Program Code Number: 3980
 Name of Contractor: Board of Trustees of the Leland
 Stanford Junior University
 Date of Contract: 1 November 1961
 Contract Number: AF 49(638)-1123
 Contract Expiration Date: 31 August 1964

September 30, 1964
Stanford, California

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SUMMARY

This report is concerned with special problems which arise in connection with calculations of the transport properties of partially ionized monatomic gases. The most serious problem concerns the lack of agreement of the usual thermal conductivity expression in the limit of full-ionization with other results derived explicitly for this case. It is shown that satisfactory agreement can be obtained in this limit if one uses the third rather than the second approximation in the Chapman-Enskog theory. Expressions for the fourth and lower approximations to the thermal conductivity, the thermal diffusion coefficient, and the ordinary diffusion coefficient of multicomponent gases are derived. The viscosity of this mixture is considered to the second approximation. It is shown that the thermal diffusion plays a very important role in an ionized gas. Neglect of this effect can cause the thermal conductivity to be seriously overestimated. An expression is presented which approximates the effect of the thermal diffusion on the thermal conductivity. The charged particle cross-section is considered with the screened Coulomb potential. Cross-sections derived with this potential should be accurate for denser plasmas that can be accurately considered with the usual Debye cut-off cross-section. Convergence of the higher approximation is checked by applying the formulas to the calculation of the properties of several special mixtures where the molecules obey the Coulomb and other inverse-power interaction potentials.

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NOTATION

Symbols are listed in alphabetical order. Some of the common symbols (e.g. p , T , ρ) have their usual meaning and are not listed.

<u>Symbols</u>	<u>Meaning</u>	<u>Page where first occurs</u>
$a_{im}, b_{im}, c_{im}^{hk}$	coefficients in the expansions of A_i, B_i, C_i^j	7
$A^{(l)}(\)$	related to the cross-section $Q^{(l)}$ for inverse-power potentials	42
$A_i, B_i, C_i^j (W_i)$	coefficients for φ_i expressions	7
b	impact parameter	4
b_0	mean distance of closest approach for the Coulomb potential	5
d	Debye length for complete screening by electrons and ions; also coefficient for inverse-power potential	5
d_e	Debye length for screening by electrons alone	34
\vec{d}_j	diffusion "force"	7
$d_{v_1}^{3\rightarrow}$	volume elements in the velocity space of the i -th species	4
D_{ij}	binary diffusion coefficient	36
D_{ij}	multicomponent diffusion coefficient	8
D_i^T	thermal diffusion coefficient	8
e	charge on electron = 4.80298×10^{-10} esu	5

NOTATION (Continued)

$\underline{E}(E_{ij})$	inverse of matrix $\underline{D}_m (D_{ij}m_j)$	16
f_i, f_i'	distribution function of i-th species	4
$f_i^{[0]}$	Maxwellian distribution function	6
g_{ij}	$= \vec{v}_i - \vec{v}_j $ relative speed of species i and j	4
h	$(= n_e^{-1/3})$ interelectron distance	30
$h_i (h_i^0)$	enthalpy per mass of species i (reactive energy)	19
\vec{I}	unit diagonal 2nd order tensor	7
\vec{J}_i	electric current carried by i-th species	26
\vec{J}	total electrical current	28
k	Boltzmann constant = 1.38054×10^{-16} erg/ $^{\circ}$ K	5
k_T	thermal diffusion ratio	46
K'	coefficient of $\partial T / \partial \vec{r}$ in expression for \vec{q} in electric field	27
$K (= \epsilon K')$	true thermal conductivity in presence of electrical field	29
m_i	mass of i-th species	4
n_i	number density of species i	5
\vec{q}	energy flux	16
$q_{ij}^{mm'} (q_{ij}^{00}, q_{ij}^{mm'})$	$= \sqrt{\frac{2\pi m_i}{kT}} q_{ij}^{mm'}$	9
$Q_{ij}^{(l)}(g)$	gas-kinetic cross-sections	11

NOTATION (Continued)

$Q_{ij}^{mm'}, \hat{Q}_{ij}^{OO} (\hat{Q}_{ij}^{mm'})$	coefficients of equations to be solved for $a_{ij}, c_{j0}^{hk} (b_{ij})$	9
r_{im}^{hk}	$= \sqrt{\frac{2\pi m_i}{kT}} R_{im}^{hk}$	9
R_{im}^{hk}	right hand side of equations to be solved for $a_{ij}, c_{j0}^{hk}, b_{ij}$	9
s, l	integers	
$S_n^m (W_i^2)$	Sonine polynomials of order n	7
\vec{v}_i	velocity of i -th species	4
\vec{v}_0	mean gas velocity	6
\vec{V}_i	$= \vec{v}_i - \vec{v}_0$	7
\vec{W}_i	$= \sqrt{\frac{m_i}{2kT}} \vec{v}_i$	7
$\vec{\bar{W}}_i$	$= \vec{W}_i \vec{W}_i - 1/3 W_i^2 \vec{1}$	23
$x (x_0)$	$= 2L \frac{\frac{1}{2} \mu_{ij} g^2}{Z_i Z_j e^2}$	31
\vec{X}_i	external force on the i -th species	4
y	$= \frac{\frac{1}{2} \mu_{ij} g^2}{kT}$	32
Z_i	charge multiple on i -th species	5
α	coefficient of $\partial T / \partial \vec{r}$ in expression for total electrical current	26
β	coefficient of \vec{E} in energy flux expression in presence of electrical field	27

NOTATION (Continued)

γ_{ij}^2	$= \frac{1}{2} \mu_{ij} g^2$	11
δ	exponent for inverse power-potential	42
δ_{ij}	Kronecker delta = $\begin{cases} 1 & \text{if } i=j \\ 0 & \text{if } i \neq j \end{cases}$	11
ζ	total number of ions in a mixture	25
η	viscosity	22
$\lambda, \lambda' (\lambda_p)$	thermal conductivity (frozen)	16, 17
Λ	$= \frac{2d}{b_0} =$ plasma parameter	34
μ_{ij}	$= \frac{m_i m_j}{m_i + m_j}$, reduced mass	11
ν	total number of species in a mixture	4
ϵ	level of approximation + 1	7
σ	electrical conductivity	26
σ_{ij}	collision-diameter	11
$\sigma_{ij}(\chi, g)$	differential cross-section for i-j species collisions	4
τ	$= \frac{Z_i Z_j e^2}{\frac{1}{2} \mu_{ij} g^2 d}$	32
φ_i	perturbation of distribution function	6
$\varphi_{ij}(r)$	potential between two particles	30
χ	angle of deflection during a collision	4
$\Omega_{ij}^{(l, s)*}$	factor measuring deviation of cross-section from hard-sphere model	11

ACKNOWLEDGMENTS

The author gratefully acknowledges the guidance and assistance of his advisor Professor Daniel Bershader. Professors I-Dee Chang, Charles Kruger and M. Mitchner have offered many helpful suggestions throughout the course of this work. The author has also benefited from stimulating discussions with Drs. W. C. Marlowe and H. Wong. Thanks are also due to Zuki for her careful typing of the manuscript. The support of the Ford Foundation through a graduate fellowship during part of this work is also gratefully acknowledged.

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1. INTRODUCTION

In the past several years there has been increased reliance on computed rather than measured values of transport properties of gases. This has come about because of difficulties in measuring these coefficients with any accuracy at the higher temperatures presently of interest. The calculations start from potentials of interaction between molecules, usually determined from molecular beam scattering experiments, and use theoretical or approximate formulas for the computations. The theoretical methods are usually the first or second approximations in the Chapman-Enskog theory [Chapman and Cowling, 1952; Hirschfelder, Curtiss and Bird, 1964]*). The approximate formulas [Wilke, 1950; Mason and Saxena, 1958; Brokaw, 1958] are usually derived from the theoretical formulas by making certain approximations. The approximations are ultimately justified by comparison of calculations made with the resulting formulas with those made with the theoretical formulas. The agreement is fairly good for most low temperature gases.

Both the theoretical and approximate formulas have been applied recently to the calculation of properties of dissociating hydrogen [Vanderslice et al, 1962] and nitrogen and oxygen [Yun et al, 1962]. Later these formulas have been applied to gases in which ionization is also important. Eastlund [1963] calculated the transport properties of partly ionized cesium vapor at temperatures up to 10000° K. Yos [1963] extended the computations of the properties of hydrogen, nitrogen, oxygen and air into the ionization regime. Fay [1962] has suggested an approximate mixture rule which was used by Camac, Fay, Feinberg and Kemp [1963] to compute the properties of argon in the ionized region. Other results and references are given in Pallone and van Tassell [1963] and Ahtye [1964].

A defect of the formulas used in the calculations mentioned above is the lack of a priori agreement of the thermal conductivity in the limit of complete ionization with the results of Spitzer and Härm [1953] or Landshoff [1951] for the fully ionized plasma. This defect has been

*). These two books will hereafter be denoted by CC and MTGL respectively.

realized by each of the authors and they have modified their formulas to obtain proper agreement in the fully ionized limit. Thus Fay [1962] and Yos [1963] adjust the value of the charged particle (Coulomb) cross-section in their approximate formulas to obtain agreement. Eastlund [1963], who used the theoretical formulas of MTGL, inserts some constants to insure the proper limiting values. Though the results of these calculations should then be accurate for very low or very high degrees of ionization, there is no certainty that they will be accurate in the intermediate partially ionized region. The probable accuracy can only be determined by comparison of calculations of a number of cases with results from rigorous theoretical formulas which give the correct results at low and high ionization without any ad hoc adjustment of constants.

The nature of this difficulty has apparently also been realized by Ahtye [1964], who used the theoretical formulas of MTGL to compute the transport coefficients of partially ionized argon. We will see later that these formulas, which are really just the second (and first) approximation to the exact solutions, need to be extended to higher approximations to obtain accurate values of the thermal conductivity (and viscosity) for partially ionized gases.

This report will be concerned explicitly with the calculation of transport properties of partially and multiply ionized monatomic gases, though some of the formulas can probably be used with success for polyatomic and dissociating gases. In this report expressions for the thermal conductivity, thermal diffusion and the multi-component diffusion coefficients of monatomic gas mixtures will be extended to the fourth approximation in the Chapman-Enskog theory. The viscosity will be extended to the second approximation. This level of approximation has been considered previously only for the binary gas mixture [Mason, 1957a; Saxena and Joshi, 1963]. After some discussion of the charged particle cross-sections these expressions will be applied to the electron-singly charged ion plasma. We will see here that it is necessary to use at least the third approximation for some of the transport properties for the fully ionized gas. The viscosity also is in error by at least 15% if only the first approximation is used. At this point we can examine the convergence

of the approximations for several other inverse-power potentials for some simple mixtures. In a later paper these expressions will be applied to the calculation of the transport properties of singly and multiply ionized argon plasma.

2. HIGHER APPROXIMATIONS IN THE CHAPMAN-ENSKOG THEORY

In this section the general expressions for the transport properties for multicomponent monatomic gases will be extended to higher approximations. Since the basic theory is already well covered in the books of Chapman and Cowling [1952] and Hirschfelder, Curtiss and Bird [1964], only a cursory review will be given in this section. The general formulation of the latter reference will be followed in this report, as will the majority of their notation. *) The numbers in brackets will refer to equations taken directly from that book.

The starting point for the Chapman-Enskog theory is the multicomponent Boltzmann equation for the distribution function of the i th species $[f_i(\vec{r}, \vec{v}_i, t)]$ [7.1-25, 10.1-5]

$$\begin{aligned} \frac{\partial f_i}{\partial t} + \vec{v}_i \cdot \frac{\partial f_i}{\partial \vec{r}} + \frac{\vec{X}_i}{m_i} \cdot \frac{\partial f_i}{\partial \vec{v}_i} &= \sum_{j=1}^v \iint (f_i' f_j' - f_i f_j) g_{ij} \cdot d\Omega d\epsilon d^3 \vec{v}_j \\ &= \sum_{j=1}^v \iint (f_i' f_j' - f_i f_j) \sigma_{ij}(g_{ij}, X) g_{ij} \sin X d\Omega d\epsilon d^3 \vec{v}_j \end{aligned} \quad (2.1)$$

The right side of this equation represents the rate of change of f_i due to collisions (or encounters) between the i th species and itself and the other $v-1$ species of the gas. It has been written here in two equivalent forms. Either form may be used when collisions are being treated classically, but only the second is valid when quantum mechanics is used. The general theory follows in the same way for either case. The quantum mechanical formulation is used most often in treating electron-atom collisions where the differential cross-section σ_{ij} is obtained in terms of partial wave phase shifts.

*) A list of symbols is given on page vii.

We note that this equation makes no provision for either chemical reactions or excitation of internal degrees of freedom during a collision. The theory is then strictly applicable to non-reacting monatomic gases with no internal degrees of freedom. The rare gases at temperatures below about 5000°K and above those temperatures where quantum degeneracy is important come closest to fulfilling these requirements. When ionization takes place the theory is no longer strictly applicable since chemical reaction and excitation of electronic states are important processes taking place during collisions. However, only a very small percentage of the collisions involve excitation or chemical reaction, so it appears justifiable to neglect these effects. Except in the case of the thermal conductivity, neglect of these effects has been successful for lower temperature polyatomic gases where rotational and vibrational internal states are important. Further consideration will be given to the effect of chemical reaction and electronic excitation on this coefficient in a later section.

We should note here another assumption implicit in the use of the Boltzmann equation. It is assumed, namely, that it is possible to represent encounters adequately within the framework of this equation. It has long been recognized that the Boltzmann collision term is valid for close encounters among charged particles, i.e. for those for which the impact parameter b is of the order of the mean distance of closest approach

$$b_0 = \frac{Z_i Z_j e^2}{2kT} \quad (2.2)$$

here written for the encounter of two particles of absolute charge $Z_i e$ and $Z_j e$. For more distant encounters, where the impact parameter is of the order of or greater than the Debye length

$$d^2 = \frac{kT}{4\pi e^2 \sum_i n_i Z_i} \quad (2.3)^*$$

*) This definition of the Debye length allows for complete screening by ions as well as by electrons.

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the Fokker-Planck collision operator is valid. This latter form has been used by Cohen, Spitzer and Routely [1950], and Spitzer and Härm [1953] to derive certain of the transport properties of fully-ionized plasmas. Grad [1960, 1961a, 1961b] has discussed in some detail the problem of the collision term for charged particles and concluded that, at least to dominant order, i.e. to order $\ln \Lambda$, where $\Lambda \sim d/b_0$, the Fokker-Planck part of the collision term may be replaced by the Boltzmann term if integrations over the impact parameter b are cut off at the Debye length. In cases where $\ln \Lambda \gg 1$ this approach is satisfactory, because the neglected terms are of order unity. However, a large number of plasmas which are presently being studied do not satisfy this criterion. For example, cesium vapor at 1 mm and 5000°K would be about 90% ionized with $d \sim 1.11 \times 10^{-5}$ cm, $n_e \sim 9.6 \times 10^{14}$ /cc and $\Lambda \sim 5$. Argon at 1 atm and 15000°K has about 60% ionization with $d \sim 1.42 \times 10^{-6}$ cm, $n_e \sim 9.6 \times 10^{14}$ /cc and $\Lambda \sim 36$. Thus we see that terms of order unity should really be included in considerations of the charged particle interactions for these cases. In a remarkable paper Kihara and Aono [1963] have accomplished just this step, neglecting only terms of order Λ^{-2} or smaller. Their method appears rather difficult to apply without going into considerable detail, but we can use an approximate treatment which, for the cases considered by Kihara, Aono and Itikawa [1963], gives almost the same results. In place of the Coulomb potential, for small angles of deflection we will use the spherically symmetric shielded potential. This potential has been considered earlier by Liboff [1959] and Kihara [1959]. Further details will be given in Section 3.

2.1 Review of the Chapman-Enskog Method

The first step in the Chapman-Enskog theory is to assume that each distribution function can be written in the form

$$f_i = f_i^{[0]} (1 + \phi_i + \dots) \quad (2.4)$$

where $f_i^{[0]}$ turns out to be the Boltzmann distribution [7.3-13]

$$f_i^{[0]} = n_i \left(\frac{m_i}{2\pi kT} \right)^{3/2} \exp \left[-m_i (\vec{v}_i - \vec{v}_0)^2 / 2kT \right] \quad (2.5)$$

Here n_1, m_1 and v_1 are, respectively, the number density, the mass, and the velocity of the i th species, \vec{v}_0 is the mean gas velocity and the T is the gas temperature. Upon substitution of (2.5) in the Boltzmann equation (2.1), it is found that the perturbation function ϕ_1 must be of the form [7.3-29, 35, 36, 37]

$$\phi_1 = A_1(W_1) \vec{W}_1 \cdot \frac{\partial \ln T}{\partial \vec{r}} - B_1(W_1) (\vec{W}_1 \vec{W}_1 - \frac{1}{3} W_1^2 \vec{I}) : \frac{\partial \vec{v}_0}{\partial \vec{r}} + n \sum_{j=1}^v c_1^j(W_1) \vec{W}_1 \cdot \vec{d}_j \quad (2.6)$$

where \vec{d}_j will be defined in Section 2.2.

The problem of determining the distribution function, and hence the transport properties, has now been reduced to one of determining the scalars A_1 , B_1 and C_1^j which are functions of the magnitude of the reduced velocity $\vec{W}_1 = \sqrt{\frac{m_1}{2kT}} \vec{V}_1$ where $\vec{V}_1 = \vec{v}_1 - \vec{v}_0$. The next step is to expand each of these scalar functions in a series of Sonine (or associated Laguerre) polynomials of W_1^2 [7.3-57]. The A_1 and C_1^j functions are expanded in terms of polynomials of order $3/2$ and the B_1 in polynomials of order $5/2$ [7.3-61],

$$\begin{aligned} A_1(W_1) &= \sum_{m=0}^{\xi-1} a_{1m} S_{3/2}^m(W_1^2) \\ B_1(W_1) &= \sum_{m=0}^{\xi-1} b_{1m} S_{5/2}^m(W_1^2) \\ C_1^h - C_1^k &= \sum_{m=0}^{\xi-1} c_{1m}^{hk} S_{3/2}^m(W_1^2) \end{aligned} \quad (2.7)$$

The number of terms retained in these series (i.e. $\xi-1$) will be called the level of approximation.* Usually one or two terms are sufficient

* This convention agrees with Chapter 7 of MGL but disagrees with Chapter 8 of that book.

to give accurate results for the transport coefficients. This is fortunate because the formulas become quite complicated at only the second approximation. We will see later that it is necessary to use at least the third approximation when computing the thermal conductivity and thermal diffusion coefficient of partially ionized gases, though the second approximation appears to be quite adequate for the other properties. We will now proceed to develop the formulas for the transport coefficients. Again free use will be made of equations already given in MTGL.

2.2 Diffusion Coefficients

The general expression for the diffusion velocity of the i th species relative to the mass average velocity is given by [7.4-3]

$$\langle \vec{v}_i \rangle = \frac{n^2}{n_i \rho} \sum_{\substack{j=1 \\ j \neq i}}^v m_j D_{ij} \vec{d}_j - \frac{1}{n_i m_i} D_i^T \frac{\partial \ln T}{\partial \vec{r}} \quad (2.8)$$

D_{ij} and D_i^T are the multicomponent diffusion and the thermal diffusion coefficients, respectively. \vec{d}_j is the sum of the concentration, pressure and external driving forces for diffusion [7.3-27],

$$\vec{d}_j = \frac{\partial}{\partial \vec{r}} \left(\frac{n_j}{n} \right) + \left(\frac{n_j}{n} - \frac{z_j m_j}{\rho} \right) \frac{\partial \ln p}{\partial \vec{r}} - \left(\frac{n_j m_j}{\rho p} \right) \left[\frac{\rho}{m_j} \vec{X}_j - \sum_{\ell=1}^v n_\ell \vec{X}_\ell \right] \quad (2.9)$$

where \vec{X}_ℓ is the external force acting on the ℓ th species of the gas. In terms of the coefficients of expansion of the distribution function (2.7), the diffusion coefficients are given by [7.4-8,9]

$$D_{ij} = \frac{\rho n_i}{2 n m_j} \sqrt{\frac{2kT}{m_i}} c_{i0}^{ji} \quad (2.10)$$

$$D_i^T = \frac{n_i m_i}{2} \sqrt{\frac{2kT}{m_i}} a_{i0} \quad (2.11)$$

We can now examine in some detail the solution of the equations for the higher approximations to the multicomponent diffusion coefficient.

The formula for this coefficient to the first approximation has already been given in MTGL, and the same general procedure will be followed as was used there.

The coefficients c_{k0}^{hk} are determined from the set of $4v$ equations [7.3-75]

$$\sum_{j=1}^v \left[Q_{1j}^{m0} c_{j0}^{hk} + Q_{1j}^{m1} c_{j1}^{hk} + Q_{1j}^{m2} c_{j2}^{hk} + Q_{1j}^{m3} c_{j3}^{hk} \right] = -R_{1m}^{hk} = \frac{3}{2} \sqrt{\frac{2kT}{m_1}} (\delta_{ik} - \delta_{ih}) \delta_{m0} \quad (2.12)$$

where $m=0,1,2,3$ (for the fourth approximation) and $i=1,2,3,\dots,v$. The solution of these equations may be obtained with the aid of Cramer's rule [Hildebrand, 1952] as the ratio of two $2v \times 2v$ determinants. The denominator is the determinant of the coefficients $Q_{1j}^{mm'}$, and the numerator involves the coefficients with one column replaced by the right-hand side of Eq. (2.12). A more convenient form, equivalent to that obtained with Cramer's rule, has been introduced in MTGL. Before proceeding to the explicit expression, it is convenient to define new elements different from those used in MTGL. In this way the number of operations performed in the calculation of the various coefficients will be materially reduced. We let

$$Q_{1j}^{mm'} = \sqrt{\frac{2\pi}{kT}} Q_{1j}^{mm'} \quad , \quad (2.13)$$

$$r_{10}^{hk} = \sqrt{\frac{2\pi m_1}{kT}} R_{10}^{hk} = 3\sqrt{\pi} (\delta_{ih} - \delta_{ik})$$

and the solution for the fourth approximation to the multicomponent diffusion coefficients is then

$$[D_{hk}]_4 = \frac{3\rho n_h}{2nm_h} \sqrt{\frac{2\pi kT}{m_h}} \frac{1}{|q|}$$

q_{1j}^{00}	q_{1j}^{01}	q_{1j}^{02}	q_{1j}^{03}	r_{10}^{hk}
---	---	---	---	---
q_{1j}^{10}	q_{1j}^{11}	q_{1j}^{12}	q_{1j}^{13}	0
---	---	---	---	---
q_{1j}^{20}	q_{1j}^{21}	q_{1j}^{22}	q_{1j}^{23}	0
---	---	---	---	---
q_{1j}^{30}	q_{1j}^{31}	q_{1j}^{32}	q_{1j}^{33}	0
---	---	---	---	---
δ_{hi}	0	0	0	0

(2.14)

where $|q|$ is the determinant formed from the numerator by deleting the last row and last column. (For convenience of notation the symbol $q_{1j}^{mm'}$ represents a block of elements with both i and j ranging from 1 to v .) To obtain the first, second and third approximations to D_{ij} we simply delete all q "blocks" except those with $m=m'=0$; $m, m' \leq 1$; $m, m' \leq 2$ respectively, from both the numerator and denominator.

Before proceeding to explicit formulas for the $q_{1j}^{mm'}$ elements, we can easily derive the form of the thermal diffusion coefficient. For the fourth approximation the a_{i0} are solutions of the $4v$ equations [7.3-75]

$$\sum_{j=1}^v \left[q_{1j}^{m0} a_{j0} + q_{1j}^{m1} a_{j1} + q_{1j}^{m2} a_{j2} + q_{1j}^{m3} a_{j3} \right] = -R_{im}$$

where $i=1,2,\dots,v$, and $m=0,1,2,3$. Here $R_{im} = \frac{15n_i}{4} \sqrt{\frac{2kT}{m_i}} \delta_{lm}$. We

can solve for a_{i0} as in the previous case and write the thermal diffusion coefficient as

$$[D_{\ell}^T]_4 = \frac{15}{4} \frac{\sqrt{2\pi m_{\ell} kT}}{|q|}$$

$$\begin{array}{c|c|c|c|c} \hline q_{1j}^{00} & q_{1j}^{01} & q_{1j}^{02} & q_{1j}^{03} & 0 \\ \hline q_{1j}^{10} & q_{1j}^{11} & q_{1j}^{12} & q_{1j}^{13} & n_1 \\ \hline q_{1j}^{20} & q_{1j}^{21} & q_{1j}^{22} & q_{1j}^{23} & 0 \\ \hline q_{1j}^{30} & q_{1j}^{31} & q_{1j}^{32} & q_{1j}^{33} & 0 \\ \hline \delta_{\ell j} n_j & 0 & 0 & 0 & 0 \\ \hline \end{array} \quad (2.15)$$

To obtain the third and second approximations to the thermal diffusion coefficient we simply delete all blocks containing $q_{1j}^{mm'}$ with, respectively, m or $m'=3$ and m or $m' \geq 2$. In the first approximation D_1^T is identically zero.

The general expression for the determinant elements occurring in the above relations is [7.3-71]

$$q_{1j}^{mm'} = \sqrt{\frac{2\pi m_1}{kT}} n_1 \sum_{\ell=1}^{\nu} n_{\ell} \left\{ \delta_{1j} [\vec{W}_1 S_{3/2}^m(W_1^2); \vec{W}_1 S_{3/2}^{m'}(W_1^2)]_{1\ell} + \delta_{j\ell} [\vec{W}_1 S_{3/2}^m(W_1^2); \vec{W}_{\ell} S_{3/2}^{m'}(W_{\ell}^2)]_{1\ell} \right\} \quad (2.16)$$

Here the $S_{3/2}^m(W_1^2)$ are the Sonine polynomials of W_1^2 mentioned earlier and defined in [7.3-57]. The expressions in brackets are defined in [7.3-43]. These "bracket integrals" can be reduced to a simpler form in terms of the integrals [8.2-8]

$$\pi \sigma_{1j}^2 \Omega_{1j}^{(\ell, s)*} = \frac{4(\ell+1)}{(s+1)! [2\ell+1 - (-1)^{\ell}] } \int_0^{\infty} e^{-\gamma^2} \gamma^{2s+3} Q_{1j}^{(\ell)}(\gamma) d\gamma \quad (2.17)$$

$$Q_{1j}^{(\ell)}(\gamma) = 2\pi \int_0^{\pi} \sigma_{1j}(\chi) (1 - \cos^{\ell} \chi) \sin \chi d\chi = 2\pi \int_0^{\infty} (1 - \cos^{\ell} \chi) bdb \quad (2.18)$$

Here $\sigma_{ij}(\chi)$ is the differential cross-section, χ is the angle of deflection during a collision, and $\gamma^2 = 1/2 (\mu_{ij} g^2 / kT)$, μ_{ij} being the reduced mass of the two species i and j .

General formulas for this reduction have been given in CC. Some of the explicit formulas are given in CC and MTGL. Others have been derived from the work of Mason [1957a]. Relations for obtaining the bracket expressions from his work are collected in the appendix. With the aid of these formulas and after some algebraic manipulation, the following expressions for the $q_{ij}^{mm'}$ elements may be derived:

$$\tilde{q}_{ij}^{00} = q_{ij}^{00} - \frac{n_j}{n_i} \sqrt{\frac{m_j}{m_i}} q_{ij}^{00} = 8 \sum_{\ell=1}^{\nu} \frac{n_{\ell} m_i^{1/2}}{(m_i + m_{\ell})^{1/2}} \pi \sigma_{i\ell}^2 \Omega_{i\ell}^{(1,1)*} \left[n_i \sqrt{\frac{m_{\ell}}{m_j}} (\delta_{ij} - \delta_{j\ell}) - n_j \frac{\sqrt{m_{\ell} m_j}}{m_i} (1 - \delta_{i\ell}) \right] \quad (2.19a)$$

$$q_{ij}^{01} = + 8 n_i \left(\frac{m_i}{m_j} \right)^{3/2} \sum_{\ell=1}^{\nu} \frac{n_{\ell} m_{\ell}^{3/2}}{(m_i + m_{\ell})^{3/2}} \pi \sigma_{i\ell}^2 \left[\frac{5}{2} \Omega_{i\ell}^{(1,1)*} - 3 \Omega_{i\ell}^{(1,2)*} \right] (\delta_{ij} - \delta_{j\ell}) \quad (2.19b)$$

$$q_{ij}^{10} = \left(\frac{m_j}{m_i} \right) q_{ij}^{01} \quad (2.19c)$$

$$q_{ij}^{11} = 8 n_i \left(\frac{m_i}{m_j} \right)^{3/2} \sum_{\ell=1}^{\nu} \frac{n_{\ell} m_{\ell}^{1/2}}{(m_i + m_{\ell})^{5/2}} \pi \sigma_{i\ell}^2 \left[(\delta_{ij} - \delta_{j\ell}) \cdot \left[\frac{5}{4} (6m_j^2 + 5m_{\ell}^2) \Omega_{i\ell}^{(1,1)*} - 15m_{\ell}^2 \Omega_{i\ell}^{(1,2)*} + 12m_{\ell}^2 \Omega_{i\ell}^{(1,3)*} \right] + (\delta_{ij} + \delta_{j\ell}) 4m_j m_{\ell} \Omega_{i\ell}^{(2,2)*} \right] \quad (2.19d)$$

$$q_{ij}^{02} = 8 n_i \left(\frac{m_i}{m_j} \right)^{5/2} \sum_{\ell=1}^{\nu} \frac{n_{\ell} m_{\ell}^{5/2}}{(m_i + m_{\ell})^{5/2}} \pi \sigma_{i\ell}^2 (\delta_{ij} - \delta_{j\ell}) \cdot \left(\frac{35}{8} \Omega_{i\ell}^{(1,1)*} - \frac{21}{2} \Omega_{i\ell}^{(1,2)*} + 6 \Omega_{i\ell}^{(1,3)*} \right) \quad (2.19e)$$

$$q_{1j}^{20} = \left(\frac{m_j}{m_1}\right)^2 q_{1j}^{02} \quad (2.19f)$$

$$q_{1j}^{12} = 8n_1 \left(\frac{m_1}{m_j}\right)^{5/2} \sum_{\ell=1}^v \frac{n_{\ell} m_{\ell}^{3/2}}{(m_1 + m_{\ell})^{7/2}} \pi c_{1\ell}^2 \left\{ (\delta_{1j} - \delta_{j\ell}) \cdot \right. \\ \cdot \left[\frac{35}{16} (12m_j^2 + 5m_{\ell}^2) \Omega_{1\ell}^{(1,1)*} - \frac{63}{2} (m_j^2 + \frac{5}{4} m_{\ell}^2) \Omega_{1\ell}^{(1,2)*} + \right. \\ \left. + 57 m_{\ell}^2 \Omega_{1\ell}^{(1,3)*} - 30m_{\ell}^2 \Omega_{1\ell}^{(1,4)*} \right] + \\ \left. + (\delta_{1j} + \delta_{j\ell}) \left[14m_j m_{\ell} \Omega_{1\ell}^{(2,2)*} - 16m_j m_{\ell} \Omega_{1\ell}^{(2,3)*} \right] \right\} \quad (2.19g)$$

$$q_{1j}^{21} = \left(\frac{m_j}{m_1}\right) q_{1j}^{12} \quad (2.19h)$$

$$q_{1j}^{22} = 8n_1 \left(\frac{m_1}{m_j}\right)^{5/2} \sum_{\ell=1}^v \frac{n_{\ell} m_{\ell}^{1/2}}{(m_1 + m_{\ell})^{9/2}} \pi \sigma_{1\ell}^2 \left\{ (\delta_{1j} - \delta_{j\ell}) \cdot \right. \\ \cdot \left[\frac{35}{64} (40m_j^4 + 168m_j^2 m_{\ell}^2 + 35 m_{\ell}^4) \Omega_{1\ell}^{(1,1)*} - \right. \\ - \frac{21}{8} m_{\ell}^2 (84m_j^2 + 35m_{\ell}^2) \Omega_{1\ell}^{(1,2)*} + \frac{3}{2} m_{\ell}^2 (108m_j^2 + 133m_{\ell}^2) \Omega_{1\ell}^{(1,3)*} - \\ - 210m_{\ell}^4 \Omega_{1\ell}^{(1,4)*} + 90m_{\ell}^4 \Omega_{1\ell}^{(1,5)*} + 24m_j^2 m_{\ell}^2 \Omega_{1\ell}^{(3,3)*} \left. \right] + \\ + (\delta_{1j} + \delta_{j\ell}) \left[7m_j m_{\ell} (4m_j^2 + 7m_{\ell}^2) \Omega_{1\ell}^{(2,2)*} - \right. \\ \left. - 112m_j m_{\ell}^3 \Omega_{1\ell}^{(2,3)*} + 80m_j m_{\ell}^3 \Omega_{1\ell}^{(2,4)*} \right] \left. \right\} \quad (2.19i)$$

$$q_{1j}^{03} = 8n_1 \left(\frac{m_1}{m_j} \right)^{7/2} \sum_{\ell=1}^{\nu} \frac{n_{\ell} m_{\ell}^{7/2}}{(m_1 + m_{\ell})^{7/2}} \pi \sigma_{1\ell}^2 \left\{ (\delta_{1j} - \delta_{j\ell}) \cdot \right. \\ \left. \cdot \left[\frac{105}{16} \Omega_{1\ell}^{(1,1)*} - \frac{189}{8} \Omega_{1\ell}^{(1,2)*} + 27 \Omega_{1\ell}^{(1,3)*} - 10 \Omega_{1\ell}^{(1,4)*} \right] \right\} \quad (2.19j)$$

$$q_{1j}^{30} = \left(\frac{m_j}{m_1} \right)^3 q_{1j}^{03} \quad (2.19k)$$

$$q_{1j}^{13} = 8n_1 \left(\frac{m_1}{m_j} \right)^{7/2} \sum_{\ell=1}^{\nu} \frac{n_{\ell} m_{\ell}^{5/2}}{(m_1 + m_{\ell})^{9/2}} \pi \sigma_{1\ell}^2 \left\{ (\delta_{1j} - \delta_{j\ell}) \cdot \right. \\ \left. \cdot \left[\frac{105}{32} (18m_j^2 + 5m_{\ell}^2) \Omega_{1\ell}^{(1,1)*} - \frac{63}{4} (9m_j^2 + 5m_{\ell}^2) \Omega_{1\ell}^{(1,2)*} + \right. \right. \\ \left. \left. + 81 (m_j^2 + 2m_{\ell}^2) \Omega_{1\ell}^{(1,3)*} - 160 m_{\ell}^2 \Omega_{1\ell}^{(1,4)*} + 60 m_{\ell}^2 \Omega_{1\ell}^{(1,5)*} \right] + \right. \\ \left. + (\delta_{1j} + \delta_{j\ell}) m_j m_{\ell} \left[\frac{63}{2} \Omega_{1\ell}^{(2,2)*} - 72 \Omega_{1\ell}^{(2,3)*} + 40 \Omega_{1\ell}^{(2,4)*} \right] \right\} \quad (2.19l)$$

$$q_{1j}^{31} = \left(\frac{m_j}{m_1} \right)^2 q_{1j}^{13} \quad (2.19m)$$

$$q_{1j}^{23} = 8n_1 \left(\frac{m_1}{m_j} \right)^{7/2} \sum_{\ell=1}^{\nu} \frac{n_{\ell} m_{\ell}^{3/2}}{(m_1 + m_{\ell})^{11/2}} \pi \sigma_{1\ell}^2 \left\{ (\delta_{1j} - \delta_{j\ell}) \cdot \right. \\ \left. \cdot \left[\frac{105}{128} (120m_j^4 + 252m_j^2 m_{\ell}^2 + 35m_{\ell}^4) \Omega_{1\ell}^{(1,1)*} - \right. \right. \\ \left. \left. - \frac{63}{64} (120m_j^4 + 750m_j^2 m_{\ell}^2 + 175m_{\ell}^4) \Omega_{1\ell}^{(1,2)*} + \frac{9}{4} m_{\ell}^2 (450m_j^2 + 217m_{\ell}^2) \Omega_{1\ell}^{(1,3)*} - \right. \right. \\ \left. \left. - \frac{5}{2} m_{\ell}^2 (198m_j^2 + 301m_{\ell}^2) \Omega_{1\ell}^{(1,4)*} + 615m_{\ell}^4 \Omega_{1\ell}^{(1,5)*} - 210m_{\ell}^4 \Omega_{1\ell}^{(1,6)*} + \right. \right. \\ \left. \left. + 108m_j^2 m_{\ell}^2 \Omega_{1\ell}^{(3,3)*} - 120m_j^2 m_{\ell}^2 \Omega_{1\ell}^{(3,4)*} \right] + \right. \\ \left. + (\delta_{1j} + \delta_{j\ell}) m_j m_{\ell} \left[\frac{63}{2} \Omega_{1\ell}^{(2,2)*} - 72 \Omega_{1\ell}^{(2,3)*} + 40 \Omega_{1\ell}^{(2,4)*} \right] \right\}$$

$$\begin{aligned}
& + (\delta_{1j} + \delta_{j\ell}) \left[\frac{63}{4} m_j m_\ell (8m_j^2 + 7m_\ell^2) \Omega_{1\ell}^{(2,2)*} - \right. \\
& - 18 m_j m_\ell (8m_j^2 + 21m_\ell^2) \Omega_{1\ell}^{(2,3)*} + 500 m_j m_\ell^3 \Omega_{1\ell}^{(2,4)*} - \\
& \left. - 240 m_j m_\ell^3 \Omega_{1\ell}^{(2,5)*} \right] \quad (2.19n)
\end{aligned}$$

$$q_{1j}^{32} = \left(\frac{m_j}{m_1} \right) q_{1j}^{23} \quad (2.19o)$$

$$\begin{aligned}
q_{1j}^{33} = & 8n_1 \left(\frac{m_1}{m_j} \right)^{7/2} \sum_{\ell=1}^{\nu} \frac{n_\ell m_\ell^{1/2}}{(m_1 + m_\ell)^{13/2}} m_{1\ell}^2 \left\{ (\delta_{1j} - \delta_{\ell j}) \cdot \right. \\
& \cdot \left[\frac{105}{256} (112m_j^6 + 1080m_j^4 m_\ell^2 + 1134m_j^2 m_\ell^4 + 105m_\ell^6) \Omega_{1\ell}^{(1,1)*} - \right. \\
& - \frac{567}{64} m_\ell^2 (120m_j^4 + 252m_j^2 m_\ell^2 + 35m_\ell^4) \Omega_{1\ell}^{(1,2)*} + \\
& + \frac{27}{16} m_\ell^2 (440m_j^4 + 2700m_j^2 m_\ell^2 + 651m_\ell^4) \Omega_{1\ell}^{(1,3)*} - \\
& - \frac{15}{2} m_\ell^4 (594m_j^2 + 301m_\ell^2) \Omega_{1\ell}^{(1,4)*} + \frac{135}{2} m_\ell^4 (26m_j^2 + 41m_\ell^2) \Omega_{1\ell}^{(1,5)*} - \\
& - 1890m_\ell^6 \Omega_{1\ell}^{(1,6)*} + 560m_\ell^6 \Omega_{1\ell}^{(1,7)*} + 18m_j^2 m_\ell^2 (10m_j^2 + 27m_\ell^2) \Omega_{1\ell}^{(3,3)*} - \\
& \left. - 1080m_j^2 m_\ell^4 \Omega_{1\ell}^{(3,4)*} + 720m_j^2 m_\ell^4 \Omega_{1\ell}^{(3,5)*} \right] + \\
& + (\delta_{1j} + \delta_{j\ell}) \left[\frac{189}{16} m_j m_\ell (8m_j^4 + 48m_j^2 m_\ell^2 + 21m_\ell^4) \Omega_{1\ell}^{(2,2)*} - \right. \\
& - 162m_j m_\ell^3 (8m_j^2 + 7m_\ell^2) \Omega_{1\ell}^{(2,3)*} + 10m_j m_\ell^3 (88m_j^2 + 225m_\ell^2) \Omega_{1\ell}^{(2,4)*} - \\
& \left. - 2160m_j m_\ell^5 \Omega_{1\ell}^{(2,5)*} + 840m_j m_\ell^5 \Omega_{1\ell}^{(2,6)*} + 64m_j^3 m_\ell^3 \Omega_{1\ell}^{(4,4)*} \right] \left. \right\} \quad (2.19p)
\end{aligned}$$

2.3 Energy Flow and Thermal Conductivity

The general expression for the energy flux in a monatomic, non-reacting gas with no internal degrees of freedom is given by [7.4-30]

$$\vec{q} = \frac{5}{2} kT \sum_{j=1}^v n_j \langle \vec{V}_j \rangle - \lambda' \frac{\partial T}{\partial \vec{r}} - nkT \sum_{j=1}^v \frac{1}{n_j m_j} D_j^T \vec{d}_j \quad (2.20)$$

The first term in this expression represents the translational enthalpy carried by each species as it diffuses relative to the mass-average velocity of the gas mixture. The last term represents a coupling between diffusion forces and heat flow. It is conventional to eliminate the explicit occurrence of \vec{d}_j in this expression by using the formula for the diffusion velocity (2.8) which can be rewritten in the following form

$$\sum_{j=1}^v m_j D_{ij} \vec{d}_j = \frac{n_i \rho \langle \vec{V}_i \rangle}{n^2} + \frac{\rho D_i^T}{n^2 m_i T} \frac{\partial T}{\partial \vec{r}} \quad (D_{jj}=0) \quad (2.21)$$

In order to eliminate the \vec{d}_j from (2.20) we can consider (2.21) as a set of linear equations to be solved for the unknowns \vec{d}_j . Defining E_{ij} as an element of the inverse of the matrix whose general element is $m_j D_{ij}$ we can write a formal solution for \vec{d}_j as

$$\vec{d}_j = \frac{\rho}{n^2} \sum_{i=1}^v E_{ji} n_i \langle \vec{V}_i \rangle + \frac{\rho}{n^2 T} \sum_{i=1}^v E_{ji} \frac{D_i^T}{m_i} \frac{\partial T}{\partial \vec{r}} \quad (2.22)$$

Then we have

$$\begin{aligned} -nkT \sum_{j=1}^v \frac{D_j^T \vec{d}_j}{n_j m_j} &= -\frac{\rho kT}{n} \sum_{j=1}^v \sum_{i=1}^v \frac{E_{ji} n_i D_j^T}{n_j m_j} \langle \vec{V}_i \rangle - \\ &\quad - \frac{\rho k}{n} \sum_{i=1}^v \sum_{j=1}^v \frac{E_{ji} D_i^T D_j^T}{n_j m_i m_j} \frac{\partial T}{\partial \vec{r}} \end{aligned}$$

The energy flux then becomes

$$\vec{q} = \frac{5}{2} kT \sum_{j=1}^v \left[1 - \frac{2}{5} \frac{\rho}{n} \sum_{i=1}^v \frac{E_{ij} D_i^T}{n_i m_i} \right] n_j \langle \vec{v}_j \rangle - \lambda \frac{\partial T}{\partial r} \quad (2.23)$$

where the coefficient of thermal conductivity is given by

$$\lambda = \lambda' + \frac{\rho k}{n} \sum_{i=1}^v \sum_{j=1}^v \frac{E_{ij} D_i^T D_j^T}{n_i m_i m_j} \quad (2.24)$$

Since no chemical reactions or internal transport of energy are considered in this expression, this λ is often called the frozen thermal conductivity and is sometimes denoted by λ_f .

The solution above for \vec{d}_j has been called a formal solution since no explicit formula has been given for finding the inverse matrix \underline{E} in terms of the elements $q_{ij}^{mm'}$. In actual calculations the diffusion coefficients D_{ij} will be calculated and then $\underline{E} = (\underline{D} \underline{m})^{-1}$ [written here in matrix form] may be found from a standard algorithm. If the calculations are done on a computer such as the IBM 7090, which is used for such calculations at Stanford, then there is generally a library procedure available which can be used to accomplish the inversion.

Expressions for D_i^T and D_{ij} were given in the last section. λ' is given in terms of the expansion coefficients of the scalar function $A_1(w_1)$ by [7.4-33]

$$\lambda' = - \frac{5}{4} k \sum_{j=1}^v n_j \sqrt{\frac{2kT}{m_j}} a_{j1} \quad (2.25)$$

where a_{j1} is obtained from the equations [7.3-33] already given in connection with the thermal diffusion coefficients. We can solve for the a_{j1} just as in that section, λ' then being given by a sum of such expressions. The final result is

$$[\lambda']_4 = - \frac{75k}{8} \frac{\sqrt{2m_i T}}{|q|}$$

$$\begin{vmatrix} q_{1j}^{00} & q_{1j}^{01} & q_{1j}^{02} & q_{1j}^{03} & 0 \\ \hline q_{1j}^{10} & q_{1j}^{11} & q_{1j}^{12} & q_{1j}^{13} & n_i \\ \hline q_{1j}^{20} & q_{1j}^{21} & q_{1j}^{22} & q_{1j}^{23} & 0 \\ \hline q_{1j}^{30} & q_{1j}^{31} & q_{1j}^{32} & q_{1j}^{33} & 0 \\ \hline 0 & n_j/\sqrt{m_j} & 0 & 0 & 0 \end{vmatrix} \quad (2.26)$$

This is the formula for λ' in the fourth approximation, and to obtain the third or second approximation we simply delete the blocks involving $q_{ij}^{mm'}$ with, respectively, m or $m'=3$ and m or $m' \geq 2$. This is the same prescription as given in the section on the diffusion coefficients. Trouble arises when we attempt to obtain a first approximation by deleting also the $q_{ij}^{mm'}$'s involving m or $m'=1$, for then the determinant in the numerator vanishes. This is equivalent to retaining only the first term in the expansion of $A_i(W_i)$. We can define a first approximation to the thermal conductivity as that obtained when we keep only the second term in the expansion of $A_i(W_i)$. [See Eq. (2.7).] The formula for the first approximation can then be obtained from (2.26) by deleting all q blocks except those with $m=m'=1$.

Muckenfuss and Curtiss [1958] have shown that the first approximation obtained in this way is identical with the total thermal conductivity to the second approximation. This arises in part because in the first approximation $[D_i^T]_1 = 0$ so $[\lambda]_1 = [\lambda']_1$. From irreversible thermodynamics it is always true that $\lambda \leq \lambda'$ and they show that the difference is sufficient to make $[\lambda]_2 = [\lambda]_1$. The complete formula to the second approximation is then

$$[\lambda]_2 = [\lambda]_1 = -\frac{75k}{8} \sqrt{\frac{2\pi kT}{|q|}} \begin{vmatrix} q_{11}^{11} & - & q_{1v}^{11} & n_1 \\ - & - & - & - \\ q_{v1}^{11} & - & q_{vv}^{11} & n_v \\ n_1/\sqrt{m_1} & - & n_v/\sqrt{m_v} & 0 \end{vmatrix} \quad (2.27)$$

This form is considerably simpler than the one given earlier for the second approximation and is usually used in "rigorous" calculations of the thermal conductivity. We will see later that this approximation gives answers which are much too low for the fully ionized gas, and presumably also for the partially ionized gas. It is necessary then to go to the third approximation for accurate values of this coefficient. Unfortunately no reduction similar to the above exists at present for the third or higher approximations.

The form (2.23) of the heat flux is most convenient when the thermal conductivity is defined as the coefficient of the temperature gradient in the expression for the flux when no diffusion is taking place. In (2.23) we recognize λ as the true thermal conductivity. However, (2.23) is really a mixed type of expression in that the heat flux is given in terms of a force, the temperature gradient, and other fluxes. If we wish to compute the total heat flux at a point in the gas and are not concerned with the "true" thermal conductivity, then this expression is often not the most convenient form. It is often more practical to write the expression for the heat flux from the outset solely in terms of the forces \vec{d}_j^* and $\partial T/\partial \vec{r}$. This is the convention followed in irreversible thermodynamics.

To write the heat flux in terms of forces we use Eq. (2.8) to eliminate the number fluxes from (2.20). After some manipulation we arrive at

$$\vec{q} = \sum_{j=1}^v \left[\frac{n^2}{\rho} m_j \sum_{\substack{i=1 \\ i \neq j}}^v m_i h_i D_{ij} - nkT \frac{D_j^T}{n_j m_j} \right] \vec{d}_j - \left(\lambda' + \sum_{i=1}^v \frac{h_i D_i^T}{T} \right) \frac{\partial T}{\partial \vec{r}} \quad (2.28)$$

^{*)} \vec{d}_j actually has the dimensions of L^{-1} but it is convenient to refer to it as a force.

where h_i is the total enthalpy of the i th species (see below). The disadvantage of this form may be seen if we try to find the usual coefficient of thermal conductivity. To do so we must set the diffusion fluxes equal to zero in (2.8), solve for the diffusion forces \vec{d}_j , and eliminate the \vec{d}_j in (2.28) with the resultant expressions. Clearly (2.23) and (2.24) are more convenient forms for this purpose, even though they require finding the inverse of \underline{D}_m .

The formulas above for the energy or heat flux vector apply still only to a non-reacting, monatomic gas with no internal degrees of freedom. Neglecting the effect of the chemical reactions on the distribution functions f_i , their only effect is to add an energy of formation h_i^0 to the translational enthalpy carried by each species as it diffuses relative to the mean gas motion. Thus we replace $5/2 kT$ in (2.23) by $[(5/2)(kT/m_j) + h_j^0]m_j$ and bring it inside the summation over j ,

$$\vec{q} = \sum_{j=1}^v \left(\frac{5}{2} \frac{kT}{m_j} + h_j^0 \right) n_j m_j \langle \vec{v}_j \rangle - \lambda \frac{\partial T}{\partial \vec{r}} \quad (2.29)$$

In this expression the second term multiplying the diffusion velocities in (2.23) has been dropped. Calculations show this term to be negligible compared to the first term.

Butler and Brokaw [1957; also, Brokaw, 1960] have carried out a reduction of (2.29) in the case of chemical equilibrium to give a much simpler form

$$\vec{q} = - (\lambda_f + \lambda_{\text{react}}) \frac{\partial T}{\partial \vec{r}} \quad (2.30)$$

To derive this relation they neglect thermal diffusion and use only the first approximation to the diffusion coefficients. We will see later that the latter can be in error up to almost a factor of 2 in the ionized gas. Also the thermal diffusion does play an important role when free electrons are present and probably cannot be neglected in this case. It thus appears that, even if chemical equilibrium did exist, the formula which they derive would not be applicable to the partially ionized gas.

It seems best, then, to leave the expression for the heat flow in the form of (2.23), which is also more general than the expression they derive since it applies equally to situations with chemical non-equilibrium.

The monatomic gases are generally considered to be without internal degrees of freedom for purposes of calculations of thermal conductivity. For argon, for example, at temperatures below about 15000°K this turns out to be a very good approximation. Results of Drellishak, Knopp, and Cambel [1963] show that at about this temperature the population of the excited states is sufficient to cause the atom partition function to begin to deviate from the unexcited value of 1. Similar deviations would be expected for alkali metal vapors at a much lower temperature. When electronic excitation becomes important, the possibility of heat transport by excited states must be considered. A similar problem arises in polyatomic gases at lower temperatures where energy transport by rotational and vibrational states must be considered. This latter case has been handled with moderate success by the Eucken factor, which is an approximate correction to account for this form of energy transport.

The first step in allowing for excitation of electronic states is to rewrite (2.29) as

$$\vec{q} = \sum_{j=1}^v n_j m_j h_j \langle \vec{v}_j \rangle - \lambda \frac{\partial T}{\partial r} \quad (2.29a)$$

where the total enthalpy of each species h_j now includes the translational enthalpy $(5/2)(k/m_j)T$, the energy of formation h_j^0 , and the energy stored in excited electronic states. In practice, the energy of formation (reactive energy) will probably swamp the other two forms.

Now because excited species can diffuse relative to the unexcited species, thus transporting energy of excitation, a correction must generally be applied to the coefficient of thermal conductivity. For polyatomic gases this correction takes the form of an Eucken-type correction [Mason and Monchick, 1962; Hirschfelder, 1957a,b]. However, Hirschfelder has pointed out that the diffusion coefficient for an electronically excited atom through atoms in the ground state is

probably very small. He arrives at this conclusion from estimates of the collision diameter for excited species. For example, argon in the first excited state would have a collision diameter about 3 times that of the ground state. Mason, Vanderslice and Yos [1959] have pointed out that the diffusion cross-section would be further reduced because of resonance exchange collisions which can occur with atoms in the ground state. It seems likely, then, that we can neglect altogether the effect of excited electronic states on the coefficient of thermal conductivity of monatomic gases.

2.4 Viscosity

In terms of the coefficients of expansion of $B_i(W_i)$ [see Eq. (1.7)], the viscosity is given by [7.4-20]

$$\eta = \frac{1}{2} kT \sum_{j=1}^v n_j b_{j0} \quad (2.31)$$

Since the convergence of the series for the viscosity is typically quite rapid, we will consider only the second approximation. The equations to solve for b_{j0} are [7.3-76]

$$\sum_{j=1}^v \left[\hat{Q}_{ij}^{00} b_{j0} + \hat{Q}_{ij}^{01} b_{j1} \right] = -R_{i0} = 5n_i \quad (2.32)$$

$$\sum_{j=1}^v \left[\hat{Q}_{ij}^{10} b_{j0} + \hat{Q}_{ij}^{11} b_{j1} \right] = 0$$

where $i=1, 2, \dots, v$.

The solution to these equations can be obtained just as it was for λ' occurring in the thermal conductivity. As before we define new determinant elements to simplify calculations

$$\hat{q}_{ij}^{mm'} = \sqrt{\frac{2mm'}{kT}} \hat{Q}_{ij}^{mm'} \quad (2.33)$$

and arrive at the formula

$$[\eta]_2 = -\frac{5}{2} \frac{\sqrt{2mkT}}{|q|} \begin{vmatrix} \hat{q}_{ij}^{00} & \hat{q}_{ij}^{01} & n_1 \sqrt{m_1} \\ \hat{q}_{ij}^{10} & \hat{q}_{ij}^{11} & 0 \\ n_j & 0 & 0 \end{vmatrix} \quad (2.34)$$

To obtain the first approximation from this expression we delete the blocks with m or $m'=1$. The general expression for the determinant elements is [7.3-71]

$$\hat{q}_{ij}^{mm'} = \sqrt{\frac{2mm_1}{kT}} n_1 \sum_{l=1}^v n_l \left\{ \delta_{ij} \left[\vec{W}_i S_{5/2}^m (w_1^2) ; \vec{W}_i S_{5/2}^{m'} (w_1^2) \right]_{1l} + \right. \\ \left. + \delta_{jl} \left[\vec{W}_i S_{5/2}^m (w_1^2) ; \vec{W}_l S_{5/2}^{m'} (w_l^2) \right]_{1l} \right\} \quad (2.35)$$

with

$$\vec{W}_i = \vec{W}_1 \vec{W}_i - \frac{1}{3} w_1^2 \vec{I} \quad (2.36)$$

As for the determinant elements occurring in the expressions for the other transport coefficients, these may be written entirely in terms of the $\Omega^{(l,s)*}$ integrals. Making use of the formulas given in MTGL and in Saxena and Joshi [1963] we find

$$\hat{q}_{ij}^{00} = 8n_1 \left(\frac{m_1}{m_j} \right) \sum_{l=1}^v \frac{n_l m_l^{1/2}}{(m_1 + m_l)^{3/2}} \pi \sigma_{il}^2 \left\{ \frac{10}{3} \Omega_{il}^{(1,1)*} (\delta_{ij} - \delta_{jl}) m_j + \right. \\ \left. + 2m_l \Omega_{il}^{(2,2)*} (\delta_{ij} + \delta_{jl}) \right\} \quad (2.37a)$$

$$\hat{q}_{ij}^{01} = 8n_i \left(\frac{m_i}{m_j}\right)^2 \sum_{\ell=1}^v \frac{n_{\ell} m_{\ell}^{3/2}}{(m_i + m_{\ell})^{5/2}} \pi \sigma_{i\ell}^2 \left\{ (\delta_{ij} - \delta_{j\ell}) \cdot \right. \\ \left. \cdot m_j \left(\frac{35}{3} \Omega_{i\ell}^{(1,1)*} - 14 \Omega_{i\ell}^{(1,2)*} \right) + m_{\ell} (\delta_{ij} + \delta_{j\ell}) \left(7 \Omega_{i\ell}^{(2,2)*} - 8 \Omega_{i\ell}^{(2,3)*} \right) \right\} \quad (2.37b)$$

$$\hat{q}_{ij}^{10} = \left(\frac{m_j}{m_i}\right) \hat{q}_{ij}^{01} \quad (2.37c)$$

$$\hat{q}_{ij}^{11} = 8n_i \left(\frac{m_i}{m_j}\right)^2 \sum_{\ell=1}^v \frac{n_{\ell} m_{\ell}^{1/2}}{(m_i + m_{\ell})^{7/2}} \pi \sigma_{i\ell}^2 \left\{ (\delta_{ij} - \delta_{j\ell}) \cdot \right. \\ \cdot \left[\frac{1}{6} m_j (140 m_j^2 + 245 m_{\ell}^2) \Omega_{i\ell}^{(1,1)*} - 98 m_j m_{\ell}^2 \Omega_{i\ell}^{(1,2)*} + \right. \\ \left. + 64 m_j m_{\ell}^2 \Omega_{i\ell}^{(1,3)*} + 24 m_j m_{\ell}^2 \Omega_{i\ell}^{(3,3)*} \right] + \\ \left. + (\delta_{ij} + \delta_{j\ell}) \left[\frac{1}{6} m_{\ell} (154 m_j^2 + 147 m_{\ell}^2) \Omega_{i\ell}^{(2,2)*} - 56 m_{\ell}^3 \Omega_{i\ell}^{(2,3)*} + \right. \right. \\ \left. \left. + 40 m_{\ell}^3 \Omega_{i\ell}^{(2,4)*} \right] \right\} \quad (2.37d)$$

2.5 Electrical Properties

The equations and properties given in the previous sections are sufficient to completely specify the mass (or number), momentum, and energy fluxes in a mixture of monatomic gases. It is worthwhile to examine the special form which these equations take when electrons and ions are present and when there is an external electric field.* In this way we will derive an explicit expression for the electrical conductivity. Without loss of generality we can consider for the moment a mixture without concentration or pressure gradients. Equation (2.9) for

*) No magnetic fields are considered in the present treatment.

the diffusion forces^{*)} becomes

$$\vec{d}_j = - \frac{n_j m_j}{nkT} \left[\frac{\rho}{m_j} \vec{X}_j - \sum_{k=1}^{\nu} n_k \vec{X}_k \right] \quad (2.38)$$

Let species 1 be the electron, species 2 through ζ be ions, each with charge eZ_i , and the remaining $\nu - \zeta$ particles be neutral. Then the external forces are

$$\vec{X}_1 = -e\vec{E}$$

$$\vec{X}_i = eZ_i \vec{E} \quad 2 \leq i \leq \zeta \quad (2.39)$$

$$\vec{X}_i = 0 \quad i > \zeta$$

and

$$\sum_{k=1}^{\nu} n_k \vec{X}_k = -n_1 e \vec{E} + e \vec{E} \sum_{i=2}^{\zeta} n_i Z_i = 0$$

since, for a neutral plasma, $n_1 = \sum_{i=2}^{\zeta} n_i Z_i$. The diffusion forces^{*)} are

$$\vec{d}_1 = \frac{n_1 e \vec{E}}{nkT}$$

$$\vec{d}_i = \begin{cases} 0 & i > \zeta \\ - \frac{n_i Z_i e \vec{E}}{nkT} & 2 \leq i \leq \zeta \end{cases} \quad (2.40)$$

Using these expressions in Eq. (2.8) the electron and ion contributions to the current are

^{*)} \vec{d}_j is really not a force. See footnote on page 19.

$$\vec{j}_1 = -en_1 \langle \vec{v}_1 \rangle = \frac{ne^2 \vec{E}}{\rho kT} \sum_{j=2}^{\zeta} n_j m_j D_{1j} Z_j + \frac{eD_1^T}{m_1 T} \frac{\partial T}{\partial \vec{r}} \quad (2.41)$$

$$\vec{j}_1 = en_1 \langle \vec{v}_1 \rangle Z_1 = \frac{Z_1 ne^2 \vec{E}}{\rho kT} \left[n_1 m_1 D_{11} - \sum_{\substack{j=2 \\ j \neq 1}}^{\zeta} n_j m_j Z_j D_{1j} \right] - \frac{Z_1 e D_1^T}{m_1 T} \frac{\partial T}{\partial \vec{r}}$$

The electrical conductivity is defined as the coefficient of \vec{E} in the expression for the total current,

$$\sigma = \frac{e^2 n}{\rho kT} \sum_{j=2}^{\zeta} \left\{ n_j n_j Z_j D_{1j} + n_1 m_1 Z_j D_{j1} - Z_j \sum_{\substack{i=2 \\ i \neq j}}^{\zeta} n_i m_i Z_i D_{ji} \right\} \quad (2.42)$$

Now $m_1 \ll m_j$ so we can examine this expression for terms of various orders of m_1/m_j . The diffusion coefficients D_{ij} are of order

$(n_i + m_j/m_i m_j)^{1/2}$ so $D_{1j} \propto (1/m_1^{1/2})$, $D_{j1} \propto (1/m_1^{1/2})$. Thus the first term in this expression is of order $m_j/m_1^{1/2}$, the second of order $m_1^{1/2}$ and the third of order $Z_j m_j^{1/2}$. Except in cases of large Z_j , only the first term is important and we make the approximation

$$\sigma \approx \frac{e^2 n}{\rho kT} \sum_{j=2}^{\zeta} n_j m_j Z_j D_{1j} \quad (2.42a)$$

The coefficient of the temperature gradient in (2.41) is also of interest. The complete expression is

$$\alpha = \frac{e}{T} \left[\frac{D_1^T}{m_1} - \sum_{j=2}^{\zeta} \frac{Z_j D_j^T}{m_j} \right] \quad (2.43)$$

and to highest order in the masses,

$$\alpha \approx \frac{e D_1^T}{T m_1} \quad (2.43a)$$

For the heat flux in the presence of an electric field we start with Eq. (2.28) and again neglect concentration and pressure gradients.

Using Eqs. (2.40) for the diffusion forces, (2.28) becomes

$$\vec{q} = \left[\left(\frac{n}{\rho k T} n_1 m_1 \sum_{i=2}^{\nu} m_i h_i D_{i1} - \frac{D_1^T}{m_1} \right) - \sum_{j=2}^{\xi} \left(\frac{n}{\rho k T} n_j m_j \sum_{\substack{i=1 \\ i \neq j}}^{\nu} m_i h_i D_{ij} - \frac{D_j^T}{m_j} \right) \right] e \vec{E} - \left(\lambda' + \sum_{i=1}^{\nu} \frac{h_i D_i^T}{T} \right) \frac{\partial T}{\partial r} \quad (2.44)$$

Let

$$K' = \lambda' + \sum_{i=1}^{\nu} \frac{h_i D_i^T}{T} \quad (2.45)$$

and denote the coefficient of the electric field by β

$$\beta = e \left\{ \sum_{j=2}^{\xi} \left[\frac{n}{\rho k T} n_j m_j \left(m_1 h_1 D_{1j} + \sum_{\substack{i=2 \\ i \neq j}}^{\nu} m_i h_i D_{ij} \right) - \frac{D_j^T}{m_j} \right] - \left(\frac{n}{\rho k T} n_1 m_1 \sum_{i=2}^{\nu} m_i h_i D_{i1} - \frac{D_1^T}{m_1} \right) \right\} \quad (2.46)$$

Again we examine the order of the various terms in these expressions.

In (2.45) we would be tempted to say that $n_1^T \propto m_1^{1/2}$ and $h_1 \propto (1/m_1)$ so that all of these terms except for the one corresponding to the electrons can be neglected. However, if chemical reactions are possible - and ionization or recombination are always possible when electrons are present - then h_1 might also include a very large ionization energy. Only in the case of a flow situation so rapid that the chemical composition is essentially frozen would this type of reduction by order in mass be permissible without more careful examination of each h_i . With this reservation in mind we go ahead and make the reduction to get

$$K' \approx \lambda' + \frac{5}{2} \frac{k}{m_1} D_1^T \quad (2.45a)$$

The reduction of (2.46) follows in the same manner with the above noted reservation. The first term is of order $m_j/m_1^{1/2}$, the second of order $m_j^{1/2}$, and the fourth of order $m_1^{1/2}$. In the terms involving the thermal diffusion coefficient, the electron term is still dominant. The simplified form of (2.46) is

$$\beta = \frac{5}{2} \frac{en}{\rho} \sum_{j=2}^{\zeta} n_j m_j D_{1j} + \frac{eD_1^T}{m_1} \quad (2.46a)$$

The expressions for the heat and current flow in the presence of the electric field are now

$$\vec{j} = \sigma \vec{E} + \alpha \frac{\partial T}{\partial r} \quad (2.47)$$

$$\vec{q} = -\beta \vec{E} - K' \frac{\partial T}{\partial r}$$

To get the true thermal conductivity K , we set $\vec{j}=0$ and solve for \vec{E} to get

$$K = \epsilon K' \quad , \quad \epsilon = 1 - \frac{\alpha \beta}{\sigma K'} \quad (2.48)$$

The modification of these expressions to include concentration and pressure diffusion forces follows in a straightforward manner from (2.9). The complete formulas will not be given here.

3. APPLICATIONS

We are now in a position to compute the transport properties to the fourth approximation for all except the viscosity, and this to the second approximation. We note that the complexity of the formulas is increased manifold with each increase in level of approximation. Further, each added level requires the computation of a kinetic cross-section $Q^{(l)}$ for a new l , and two new integrals, $\pi \sigma_{\Omega}^{2(l,s)*}$, for each lower value of l . Before attempting to calculate the properties of a real mixture then, it is important to have an idea of the level of approximation necessary to obtain reasonably accurate results. For the laws of force effective in low temperature gas mixtures, the second approximation for the thermal conductivity is quite adequate and the thermal diffusion is usually ignored. For the ordinary diffusion coefficient and the viscosity, the first approximation is accurate enough. These are just the levels of approximation for which expressions are given in MTGL.

In the case of a partially ionized plasma there are several forces operative between the various pairs of particles, and it is difficult to examine the convergence for this mixture without some particular gas in mind. We can, however, examine the convergence of the limiting case of a fully-ionized binary gas, since only one force law is needed here. This special case has already been treated with various simplifying assumptions by several other workers, and we can compare their results with those obtained with the expressions of this report. Before proceeding to this example, we should examine the charged particle interaction with the idea of retaining higher order terms in the cross-section. In the first section, expressions for the cross-sections necessary for up to the fourth approximation will be developed following the method used by Liboff [1959]. In the present report only the dominant log term in these cross-sections will be used, since the effect of the higher order term of order unity depends on the temperature and charged particle density. Hence its effect on the transport properties must be judged in particular cases.

Two methods for calculating the properties of the binary plasma suggest themselves. One would be to consider the special form that the general expressions take in this case, and to neglect terms of low order in the mass ratio to simplify the calculations. Landshoff [1949, 1951] has essentially used this method, starting from the somewhat different but equivalent formulation of CC for the binary gas. In the present case it was decided not to consider the reductions possible in special cases. Rather, the formulas were programmed for a computer in their most general form and special cases were computed with this general program. The program has been written in Subalgol, a version of Algol developed at Stanford for the IBM 7090. As input to the program it is necessary to specify the masses and number densities of each species, and procedures for computing the various cross-sections.

After the results for the binary plasma have been compared with those from other sources, convergence will be examined for three other special mixtures. Consideration of these cases is fruitful in two ways. Most important, it demonstrates the range of rates of convergence which can be expected for real gas mixtures. Also, it offers a check on the expressions of Section I and their translation to the computer program. In some of the cases to be considered the results may be compared with the exact answer; in other cases the rate of convergence has been derived by different methods.

3.1 Charged Particle Cross-Sections

The usual procedure for the charged particle cross-section is to take the Coulomb law of interaction

$$\phi_{ij} = \frac{z_i z_j e^2}{r} \quad (3.1)$$

as valid up to a finite distance, either the Debye length d [Grad, 1961b] or the interelectron distance $h = n_e^{-1/3}$ [CC, p. 179], and to neglect all interactions beyond this distance. From the discussion of Section II, it is apparent that for a large variety of plasmas the next higher order term beyond the dominant $\ln x/b_0$ where $x=d$ or h ,

should be considered. This could be accomplished with the usual cut-off procedure, but a more realistic method would be to use the Coulomb potential for close encounters and a shielded Coulomb potential

$$\varphi_{1j} = \frac{Z_1 Z_j e^2}{r} e^{-r/d} \quad (3.2)$$

for the more distant encounters. Liboff [1959] has evaluated some of the necessary integrals with this method. We can follow his method to compute the additional integrals necessary for the level of approximation considered here. Later some of the results will be compared with the more exact results of Kihara, Aono and Itikawa [1963].

The cross-section integral of (2.18) is separated into two parts

$$Q_{1j}^{(l)}(g) = 2\pi \int_0^L (1 - \cos^l \chi) b db + 2\pi \int_L^\infty (1 - \cos^l \chi) b db \quad ,$$

the first to be computed using the Coulomb potential (3.1) and the second with the shielded potential (3.2). L is some distance satisfying $b_0 \ll L \ll d$ where b_0 and d are defined in (2.2) and (2.3). For the Coulomb potential the angle of deflection is related to the impact parameter b by

$$\cos \chi = \frac{x^2 - 1}{x^2 + 1} \quad (3.3)$$

where

$$x = 2b \frac{\frac{1}{2} \mu_{1j} g^2}{Z_1 Z_j e^2}$$

Substituting this form into the cross-section integral for the cases $l=3,4$ we get

$$Q_c^{(3)} = \frac{3\pi}{2} (\tau d)^2 \left[\ln(1+x_0^2) - \frac{2}{3} \frac{x_0^2(2x_0^2+1)}{(x_0^2+1)^2} \right] \quad (3.4)$$

$$Q_c^{(4)} = 2\pi (\tau d)^2 \left[\ln(1+x_0^2) - \frac{5}{3} x_0^2 \frac{x_0^4 + \frac{6}{5} x_0^2 + \frac{3}{5}}{(x_0^2+1)^3} \right]$$

with

$$\tau = \frac{Z_1 Z_j e^2}{\frac{1}{2} \mu_{1j} g^2 d}$$

and

$$x_0 = \frac{2L}{\tau d}$$

Now the average value of x_0 is

$$\langle x_0 \rangle = \frac{2L}{d} \frac{\langle \frac{1}{2} \mu_{1j} g^2 \rangle}{Z_1 Z_j e^2} \approx 2 \frac{L}{b_0} \gg 1 \quad (3.5)$$

so we can expand $Q_c^{(\ell)}(g)$ and neglect terms of order $1/x_0^2$ or less.

$$Q_c^{(3)}(g) \approx 3\pi (\tau d)^2 \left[\ln \left(\frac{2L}{\tau d} \right) - \frac{2}{3} \right] \quad (3.6)$$

$$Q_c^{(4)}(g) \approx 4\pi (\tau d)^2 \left[\ln \left(\frac{2L}{\tau d} \right) - \frac{5}{6} \right]$$

For the shielded potential Liboff [1959] has shown that

$$\chi = \tau K_1 \left(\frac{b}{d} \right) \quad (3.7)$$

where K_1 is the modified Bessel function of the second kind. Making the small angle approximation $\sin \chi \approx \chi$ we arrive finally at

$$Q_{sc}^{(3)} = 3\pi (\tau d)^2 \left[-\ln \frac{L}{d} - \frac{1}{2} - \gamma + \ln 2 \right] \quad (3.8)$$

$$Q_{sc}^{(4)} = \frac{4}{3} Q_{sc}^{(3)}$$

Letting

$$y = \frac{\frac{1}{2} \mu_{1j} g^2}{kT}$$

and

$$b_0 = \frac{z_1 z_j e^2}{2kT}$$

the cross-sections are (including those obtained by Liboff)

$$\begin{aligned} Q^{(1)} &= 4\pi \left(\frac{b_0}{y}\right)^2 \left[\ln\left(\frac{yd}{b_0}\right) - \frac{1}{2} - \gamma + \ln 2 \right] \\ Q^{(2)} &= 8\pi \left(\frac{b_0}{y}\right)^2 \left[\ln\left(\frac{yd}{b_0}\right) - 1 - \gamma + \ln 2 \right] \\ Q^{(3)} &= 12\pi \left(\frac{b_0}{y}\right)^2 \left[\ln\left(\frac{yu}{b_0}\right) - \frac{7}{6} - \gamma + \ln 2 \right] \\ Q^{(4)} &= 16\pi \left(\frac{b_0}{y}\right)^2 \left[\ln\left(\frac{yd}{b_0}\right) - \frac{4}{3} - \gamma + \ln 2 \right] \end{aligned} \quad (3.9)$$

We now need the average cross-sections $\pi \sigma_{1j}^2 \Omega^{(l,s)*}$ given by (2.17), which can be rewritten in the form

$$\pi \sigma_{1j}^2 \Omega_{1j}^{(l,s)*} = \frac{2(l+1)}{(s+1)! [2l+1 - (-1)^l]} \int_0^\infty e^{-y} y^{s+1} Q_{1j}^{(l)}(y) dy \quad (3.10)$$

Inserting the expressions for $Q^{(l)}(y)$ we arrive at integrals of the form (c=constant)

$$\int_0^\infty \left[\ln\left(\frac{yd}{b_0}\right) - c \right] y^{s-1} e^{-y} dy = \Gamma(s) \left[\psi(s) - c + \ln\left(\frac{d}{b_0}\right) \right] \quad (3.11)$$

where for s integer the Psi-function $\psi(s) = -\gamma + \sum_{n=1}^{s-1} \frac{1}{n}$ where $\gamma = 0.5772$

is Euler's constant. This first integral may be evaluated by integration by parts or located in Bierens de Haan [1957]. The general expressions for the average cross-sections are

$$\pi \sigma_{1j}^2 \Omega^{(l,s)*} = \frac{4\pi(s-1)!}{(s+1)!} b_0^2 \left[\ln \Lambda - \frac{1}{2} - 2\gamma + \sum_{n=1}^{s-1} \left(\frac{1}{n}\right) \right] \quad (3.12)$$

$$\begin{aligned}
\pi\sigma_{\Omega}^{2(2,s)*} &= \frac{12\pi(s-1)!}{(s+1)!} b_0^2 \left[\ell n \Lambda - 1 - 2\gamma + \sum_{n=1}^{s-1} \left(\frac{1}{n}\right) \right] \\
\pi\sigma_{\Omega}^{2(3,s)*} &= \frac{12\pi(s-1)!}{(s+1)!} b_0^2 \left[\ell n \Lambda - \frac{7}{6} - 2\gamma + \sum_{n=1}^{s-1} \left(\frac{1}{n}\right) \right] \\
\pi\sigma_{\Omega}^{2(4;s)*} &= \frac{16\pi(s-1)!}{(s+1)!} b_0^2 \left[\ell n \Lambda - \frac{4}{3} - 2\gamma + \sum_{n=1}^{s-1} \left(\frac{1}{n}\right) \right]
\end{aligned} \tag{3.12}$$

where

$$\Lambda = \frac{4kTd}{Z_1 Z_j e^2} = \frac{2d}{b_0} .$$

We now have the cross-sections necessary for the calculation of the transport properties of mixtures of charged particles to the levels of approximation considered in Section 2. To dominant order, i.e. when $\ell n \Lambda \gg 1$, these results, using a screened Coulomb potential, agree with those obtained by using the unscreened potential together with a cut-off of the integrals at the Debye length. We can now compare some of these expressions with those obtained by the more exact method of Kihara, Aono and Itikawa [1963]. They examine in detail several phenomena in a binary plasma and obtain expressions equivalent to the average cross-sections $\pi\sigma_{\Omega}^{2(l,s)*}$ with $l=s=1$ or 2. For the case of relaxation between electron and ion temperatures ($l=s=1$) they obtain the same expression as in (3.12) with a different screening constant

$$d_e^2 = \frac{kT}{4\pi n_e e^2} \tag{3.13}$$

where n_e is the number density of the electrons. This is equivalent to neglecting the shielding by the ions in the earlier definition of the Debye length (2.3). For the cases of attenuation of low frequency oscillations and diffusion across a magnetic field ($l=s=1$) they obtain a screening constant between (3.13) and (2.3), thus indicating that screening by ions is only partially effective. For the cases of the relaxation of an anisotropic distribution of ion velocities, and of thermal conductivity across a strong magnetic field ($l=s=2$) they again obtain

the same result as in (2.12) with the effective screening constant between (3.13) and (2.3). Thus, in those cases where comparison is possible, we see that the results obtained with the shielded potential are very close to the more exact results.

A difficulty in the above treatment arises in very dense plasmas when the Debye length d turns out to be less than the interelectron distance h . Thus argon at 1 atm pressure and 15000°K has only about five electrons in a Debye sphere. In this case the concept of the Debye length as a shielding distance is lost. The practice adopted in CC and Cohen et al [1950] is to use the cut-off procedure with the distance h rather than d . This appears to be the only alternative with the present state of the theory.

3.2 Binary Electron-Ion Plasma

This case has already been considered by several authors. The most accurate and detailed work seems to be that of Landshoff [1949, 1951] and Cohen et al [1950] and Spitzer and Härm [1953]. Landshoff used a reduced form of the Chapman-Enskog method out to the fifth approximation (in the notation of this report) for the properties in the absence of a magnetic field. Spitzer and co-workers derived their results by a numerical analysis of Eq. (2.1) with a Fokker-Planck rather than a Boltzmann collision term. Both treatments consider a plasma with no mean velocity, neutral in the large, and with no pressure gradients. They assume further that the ions have a Maxwellian velocity distribution and hence do not contribute to the heat and current fluxes. This assumption also reduces the number of terms in the linear equations which result from the Chapman-Enskog method used by Landshoff.

The results for the electron-singly charged ion plasma are generally presented as the coefficients of Eqs. (2.47) for the current and heat fluxes,

$$\begin{aligned}\vec{j} &= \sigma \vec{E} + \alpha \frac{\partial T}{\partial r} \\ \vec{q} &= -\beta \vec{E} - K' \frac{\partial T}{\partial r}\end{aligned}\tag{3.14}$$

The results of Spitzer and Härm for these coefficients can be written as follows:

$$\begin{aligned}\sigma &= 0.5908 \frac{(kT)^{3/2}}{\sqrt{m_e} e^2 \ln \Lambda} \\ \alpha &= 0.4155 \frac{k(kT)^{3/2}}{\sqrt{m_e} e^3 \ln \Lambda} \\ \beta &= 1.8904 \frac{(kT)^{5/2}}{\sqrt{m_e} e^3 \ln \Lambda} \\ K' &= 2.2873 \frac{k(kT)^{5/2}}{\sqrt{m_e} e^4 \ln \Lambda}\end{aligned}\tag{3.15}$$

As before the true thermal conductivity is obtained by setting the current equal to zero. They obtained

$$K = \epsilon K' (= \lambda) \quad , \quad \epsilon = 0.4189\tag{3.16}$$

Landshoff [1951] obtained equations of the same form as the above with slightly different numerical coefficients in his fifth approximation. His results will be presented later.

To approximate the model used by these workers with the computer program, we can perform the calculations for various ion/electron mass ratios. The more massive the ion, the smaller will be its average velocity and the less will be its contribution to the transport properties. Landshoff neglected the ion velocity in performing the integrations over the impact parameter. Further, to agree with these authors, we need to consider only terms of dominant order. The same definition of Λ must also be used, since this has been taken slightly differently in the papers referred to above.

Examination of the expressions (2.14), (2.15), (2.26) and (2.34) for D_{ij}^* , D_i^T , λ' and η in conjunction with formulas (2.42a), (2.43a),

*) In a binary mixture D_{ij} is denoted by D_{ij} following MTGL.

(2.45a) and (2.46a) shows that the coefficients must be of the same form as those of Spitzer and Härm with a different numerical coefficient depending on the level of approximation and on the ion/electron mass ratio. The various approximations will be given in the tables to follow after division by some standard quantity. Tables 1 and 2 give the results from the calculations of the thermal conductivities K' and K after division by the first approximation to the electron thermal conductivity. The latter may be determined from

$$[\lambda]_1 = \frac{75}{64} \frac{k \sqrt{\pi kT}}{\sqrt{m_e} \pi \sigma^2 \Omega(2,2)^*}, \quad (3.17)$$

with $\pi \sigma^2 \Omega(2,2)^*$ as given in (3.12). The results of the other authors, who essentially neglect terms of order $(m_e/m_i)^{1/2}$, are given in the last column marked ∞ . The level of the approximation in the notation of this report is given in the first column. Since the results of Spitzer are essentially exact to dominant order, they are given as the infinite approximation. We may note here that the first and second approximations of Marshall [1958] agree exactly with those of Landshoff [1951] after the correction by Vaughn-Williams and Haas [1961] is made. The first approximation as derived by Chapman [1954] also agrees with these results, but his remark that the higher approximations should increase his results by a factor of about 1.4 is not in agreement. An explicit formula for the third approximation to the binary plasma thermal conductivity has also been derived by Inshennik [1962]. For $\sqrt{m_i/m_e} = 42.9$ he says that his formula gives $[\lambda]_3 = 0.741 [\lambda_e]$, which also agrees with the results of this report.

The first and second approximations to the viscosity, after division by the first approximation to the ion viscosity, are given in Table 3. The first approximation to the ion viscosity is given by

$$[\eta]_1 = \frac{5}{16} \frac{\sqrt{\pi m k T}}{\pi \sigma^2 \Omega(2,2)^*} \quad (3.18)$$

with the average cross-section $\pi \sigma^2 \Omega(2,2)^*$ given in equation (3.12). In Tables 4 - 6 are listed the other coefficients, after division by the corresponding result of Spitzer and Härm.

TABLE 1. HIGHER APPROXIMATIONS FOR K' FOR THE FULLY-IONIZED PLASMA WITH IONS OF SINGLE CHARGE. $[K']_m / [\lambda_e]_1$

$m_1/m_e =$	1836	10^4	10^6	10^8	∞
$m = 1$	0.3242	0.3127	0.3042	0.3033	0.3032x
$m = 2$	1.4838	1.4737	1.4655	1.4646	1.4644x
$m = 3$	1.7461	1.7340	1.7239	1.7228	1.7227x
$m = 4$	1.7591	1.7471	1.7369	1.7358	1.7336x
$m = 5$					1.7321x
$m = \infty$					1.7301*
x Landshoff [1951]					
* Spitzer and Harm [1953]					

TABLE 2. HIGHER APPROXIMATIONS TO THE THERMAL CONDUCTIVITY $K (= \lambda)$ FOR A FULLY-IONIZED PLASMA WITH IONS OF SINGLE CHARGE. $[K]_m / [\lambda_e]_1$

$m_1/m_e =$	1836	10^4	10^6	10^8	∞
$m = 1$	0.3242	0.3127	0.3042	0.3033	0.3032x
$m = 2$	0.3242	0.3127	0.3042	0.3033	0.3032x
$m = 3$	0.7397	0.7269	0.7166	0.7155	0.7155x
$m = 4$	0.7404	0.7275	0.7172	0.7161	0.7160x
$m = 5$					0.7183x
$m = \infty$					0.7247*
Key as for Table 1.					

TABLE 3. HIGHER APPROXIMATIONS TO THE VISCOSITY η FOR A FULLY IONIZED PLASMA WITH IONS OF SINGLE CHARGE. $[\eta]_m / [\eta_1]_1$

$m_1/m_e =$	1836	10^4	10^6	10^8
$m = 1$	0.9580	0.9812	0.9931	0.9998
$m = 2$	1.0851	1.1214	1.1485	1.1514

TABLE 4. HIGHER APPROXIMATIONS TO THE ELECTRICAL CONDUCTIVITY FOR A FULLY-IONIZED PLASMA WITH IONS OF SINGLE CHARGE. $[\sigma]_m / [\sigma]_{\text{SPITZER}}$

$m_i/m_e =$	1836	10^4	10^6	10^8	∞
m = 1	0.5067	0.5064	0.5064	0.5064	0.5064x
m = 2	0.9773	0.9782	0.9784	0.9784	0.9784x
m = 3	0.9863	0.9872	0.9874	0.9874	0.9874x
m = 4	0.9933	0.9943	0.9945	0.9945	0.9934x
m = 5					0.9954x
m = ∞					1.0*
Key as for Table 1.					

TABLE 5. HIGHER APPROXIMATIONS TO β FOR A FULLY-IONIZED PLASMA WITH IONS OF SINGLE CHARGE. $[\beta]_m / [\beta]_{\text{SPITZER}}$

$m_i/m_e =$	1836	10^4	10^6	10^8	∞
m = 1	0.3958	0.3957	0.3957	0.3957	0.3957x
m = 2	1.0096	1.0102	1.0103	1.0103	1.0103x
m = 3	0.9903	0.9909	0.9910	0.9910	0.9909x
m = 4	0.9983	0.9989	0.9990	0.9990	0.9977x
m = 5					0.9987x
m = ∞					1.0*
Key as for Table 1.					

TABLE 6. HIGHER APPROXIMATIONS TO α FOR A FULLY-IONIZED PLASMA WITH IONS OF SINGLE CHARGE. $[\alpha]_m$

$m_i/m_e =$	1837	10^4	10^6	10^8	∞
m = 1	0	0	0	0	0
m = 2	1.1168	1.1181	1.1184	1.1184	1.1184x
m = 3	0.9971	0.9980	0.9982	0.9982	0.9981x
m = 4	1.0085	1.0094	1.0096	1.0096	1.0077x
m = 5					1.0050x
m = ∞					1.0*
Key as for Table 1.					

TABLE 7. HIGHER APPROXIMATIONS TO THE THERMAL CONDUCTIVITY λ' FOR A FULLY-IONIZED PLASMA WITH IONS OF SINGLE CHARGE. $[\lambda']_m / [\lambda']_{e1}$

$m_1/m_e =$	1837	10^4	10^6	10^8
$m = 1$	0.3242	0.3127	0.3042	0.3033
$m = 2$	0.6064	0.5891	0.5868	0.5859
$m = 3$	0.9627	0.9499	0.9397	0.9386
$m = 4$	0.9668	0.9511	0.9437	0.9426

In all of the results we note that, for any level of approximation, the coefficients are fairly independent of the ion/electron mass ratio. In the worst case, that of the viscosity, the difference is only about 7% between the viscosity of a hydrogen plasma and the hypothetical plasma whose ion has 10^8 times the mass of the electron. The corresponding difference for the thermal conductivity is about 4%, and less than 1% for the other coefficients! We thus have rigorous support for the simple arguments which show that we may neglect the electrons when computing viscosity, and neglect the ions (but not the electron-ion interaction) when computing the other coefficients.

We can now examine the convergence of the Chapman-Enskog formulas for the various coefficients. In no case does the first approximation give a satisfactory answer. The second approximation to σ and β agrees within a few per cent with the higher approximations, but it is necessary to go to the third approximation for satisfactory results for K and α . Since the third approximation has not been worked out for the viscosity, we cannot say with certainty how much the second approximation differs from the true result. From study of the rate of convergence and of the other coefficients it would appear that the second approximation would agree within a few per cent with the true value.

We noted earlier that the form (2.28) of the heat flux expression, which was used in this section to afford a comparison with the results of other authors, is not the most convenient form for computation of the

thermal conductivity of multi-component mixtures. In subsequent calculations the other form (2.23) will be used, so it is worthwhile to compute the contribution of the second term of (2.24) to the total thermal conductivity for the fully ionized gas. This is done in Table 7 where $[\lambda']_m$ is given, again after division by the first approximation to the electron thermal conductivity. We note that the thermal conductivity would be seriously overestimated if we neglected the second term of (2.24). This term is proportional to the thermal diffusion coefficients, and is normally taken as negligible. They are still quite small in this case, but the denominator contains the term $m_1 m_j$, which is also small when both 1 and j refer to the electron. The conclusion is that the contribution of the second term of (2.24), negligible for ordinary gas mixtures, is definitely not negligible for ionized gases. From the arguments given above, we can probably approximate (2.24) with good accuracy for the partially ionized case by

$$\lambda = \lambda' + \frac{\rho k}{n} \frac{E_{11} (D_1^T)^2}{n_1 m_1^2} \quad (3.19)$$

where the subscript 1 refers to the electron. In the special case of a binary ionized mixture,

$$E_{11} = D_{22}^{m_2} / \begin{vmatrix} D_{11}^{m_1} & D_{12}^{m_2} \\ D_{21}^{m_1} & D_{22}^{m_2} \end{vmatrix}$$

but $D_{22} = 0$ so $E_{11} = 0$ and only E_{12} and E_{21} are non-vanishing. But also $D_1^T = -D_2^T$ and $n_1 = n_2$ so

$$\lambda = \lambda' + \frac{\rho k}{n} \frac{E_{12} (D_1^T)^2}{n_1 m_1 m_2} (E_{12} + E_{21}) \approx \lambda' - \frac{\rho k}{n} \frac{(D_1^T)^2}{n_1 m_1^2 D_{12}} \quad (3.20)$$

This approximation for the case of more than 2 species will be examined in a subsequent paper for partially ionized argon.

3.3 Mixtures of Isotopes; Lorentzian Gas; Quasi-Lorentzian Gas.

As another application of the formulas derived in Section 2, we can consider three special gas mixtures. The mixture of isotopes of the same element, which will supposedly have the same force between molecules and nearly the same mass is the first case to be considered. We will take the masses to be equal so the results will be the same as for the pure gas, except that the additional coefficient of self diffusion will be considered. The thermal diffusion coefficient vanishes identically for this mixture. For the Lorentzian gas, in which one component of the binary mixture is taken to have very small mass and concentration, there are exact results with which to compare the Chapman-Enskog approximations. Only the diffusion coefficients will be considered here. The last mixture to be considered will be that of the quasi-Lorentzian gas, a binary mixture of a heavy and a light component, the former of which is in small concentration. For this mixture Mason [1957b] discovered the exact result for the binary diffusion coefficient. He has also considered these mixtures for certain of the inverse power potentials using the Chapman and Cowling formulation for the binary mixture.

For the inverse power potential

$$\varphi = dr^{-\delta} \quad (3.21)$$

the cross-sections take the form [8.3-4]

$$\pi \sigma_{\Omega}^{2,(\ell, s)*} = \frac{4\pi(\ell+1)}{(s+1)!(2\ell-1-(-1)^{\ell})} \left(\frac{\delta d}{kT}\right)^{2/\delta} \Gamma(s+2-\frac{2}{\delta}) \cdot A^{(\ell)}(\delta) \quad (3.22)$$

where

$$A^{(\ell)}(\delta) = \int_0^{\pi} (1 - \cos^{\ell} \chi) y_0 dy_0 \quad (3.23)$$

with

$$y_0 = b \left[\frac{\frac{1}{2} \mu_{1j} \delta^2}{\delta d} \right]^{1/\delta}$$

Here $A^{(\ell)}(\delta)$ is a pure number depending only on δ . The Coulomb case ($\delta=1$) has been considered earlier in a somewhat different formulation. In this section we will consider only terms of dominant order for this case. The case for $\delta=2$ for $\ell=1,2$ has been worked out exactly by Eliason, Stogryn and Hirschfelder [1956] in terms of sine integrals. We also need the cross-sections for $\ell=3,4$ for the level of approximation considered in this report. These can be worked out by the same method as used by Eliason et al. The results for all of the $A^{(\ell)}(2)$ are

$$\begin{aligned}
 A^{(1)}(2) &= -\frac{1}{2} - \frac{\pi}{8} [\text{Si}(2\pi) - 2\text{Si}(\pi)] \\
 A^{(2)}(2) &= -\frac{\pi}{8} [\text{Si}(4\pi) - 2\text{Si}(2\pi)] \\
 A^{(3)}(2) &= -\frac{1}{2} - \frac{3\pi}{32} [\text{Si}(2\pi) - 2\text{Si}(\pi) + \text{Si}(6\pi) - 2\text{Si}(3\pi)] \\
 A^{(4)}(2) &= -\frac{\pi}{16} [\text{Si}(8\pi) - 4\text{Si}(2\pi)]
 \end{aligned}
 \tag{3.24}$$

where $\text{Si}(x)$ is the sine integral

$$\text{Si}(x) = \int_0^x \frac{\sin Z}{Z} dZ
 \tag{3.25}$$

These expressions may be evaluated with the help of the sine integral tables [F.W.A., 1940]. The results are given in Table 8.

TABLE 8. THE QUANTITIES $A^{(\ell)}(2)$ OF EQ. (3.23) FOR $\ell=1,2,3,4$.

	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
$A^{(\ell)}(2)$	0.397601	0.527843	0.712619	0.812981

The case for $\delta=3$ has also been considered by Eliason et al with an approximate technique due to Mott-Smith. The $A^{(\ell)}(3)$ are written as a series

$$A^{(\ell)}(\delta) = -2^{-2/\delta} \sum_{\rho=0}^{\infty} D_{\rho} \sum_{n=1}^{\ell} (-1)^{n} 2^{n+1} \binom{\ell}{n} \left(\frac{\delta}{\delta\rho + 2\delta n - 2} \right) \quad (3.26)$$

with the D_{ρ} as pure numbers depending only on δ . They have been evaluated by Eliason et al for ρ up to 4. Their table, which evidently contains $2D_{\rho}$ rather than the D_{ρ} that they indicate, is reproduced here in Table 9 after division by 2. The values determined for $A^{(\ell)}(3)$ are given in Table 10 to four figures though, because of the slow convergence of this series, they are probably accurate only out to three places.

TABLE 9. THE COEFFICIENTS D_{ρ} FOR THE SERIES (3.26).

	$\rho = 0$	$\rho = 1$	$\rho = 2$	$\rho = 3$	$\rho = 4$
$D_{\rho} =$	0.12719	0.062435	0.005095	-0.00141	0.001585

TABLE 10. THE QUANTITIES $A^{(\ell)}(3)$ OF EQ. (3.23) FOR $\ell=1,2,3,4$.

	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
$A^{(\ell)}(3) =$	0.3116	0.3535	0.4724	0.5034

As the last force law we can consider the gas composed of hard-spheres of diameter σ . This is a special case of the inverse power potential where we take the limit of $\delta \rightarrow \infty$ with $d^{2/(1+\delta)} \rightarrow \sigma^2$. This case may be treated quite simply with the theory of Section 2 by letting $\Omega^{(\ell,s)*} = 1$ for all ℓ and s .

The results for the mixture of isotopes or mechanically similar molecules are given in Tables 11 and 12. The ratio of higher to the first approximation for the viscosity and thermal conductivity are given in Table 11 for $\delta=1,2,3,4$ and ∞ . The case of $\delta=4$ is known as

Maxwellian molecules and gives the exact result in the first approximation to all coefficients. This case was not computed (though it would be a good check on the accuracy of the program) but is merely listed for reference. Because of the exact result in the first approximation when $\delta=4$ we might expect the convergence to be poorest for $\delta=1$ or $\delta=\infty$. We see from the table that $\delta=1$ does indeed give the slowest convergence.

TABLE 11. HIGHER APPROXIMATIONS FOR THE THERMAL CONDUCTIVITY AND VISCOSITY OF A MIXTURE OF ISOTOPES FOR THE INVERSE POWER POTENTIAL.

	$[\lambda]_m/[\lambda]_1$		$[\eta]_2/[\eta]_1$
	$m = 2$	$m = 3$	
∞	1.02272	1.02483	1.01486
4	1.0	1.0	1.0
3	1.00269	1.00274	1.00172
2	1.02500	1.02508	1.01579
1	1.25000	1.26444	1.15169

We should note that, because of the vanishing of the thermal diffusion coefficient for this case, the first and second approximations must be identical, even without the results of Muckenfuss and Curtiss [1958] (See Section 2.3). For this reason two terms in the Sonine polynomial expansion generally are called the first approximation to the thermal conductivity. This convention is followed in Table 11.

In Table 12 are listed the self-diffusion coefficients for the same values of δ as well as for others which have been worked out by Mason [1957b]. Here again the slowest convergence is found for $\delta=1$.

it is necessary to use successively smaller ratios of these quantities in the computations until the coefficients appear to have reached their limiting values. Ratios of n_1/n_2 or m_1/m_2 which are smaller or larger than a certain size will cause exponent over- or underflow in the computer when certain of the determinant elements are evaluated, thus leading to unknown inaccuracies in the final results. Fortunately, convergence of the formulas occurred for ratios which the program could safely handle.

The results for Lorentzian gas are presented in Tables 13 and 14. Also listed are the mass and number ratios necessary to assure that the various approximations had converged to their Lorentzian values, and some results taken from Mason [1957b].

TABLE 13. HIGHER APPROXIMATIONS TO THE DIFFUSION COEFFICIENTS OF A LORENTZIAN GAS FOR INVERSE POWER POTENTIALS.
 $[D_{12}]_m/[D_{12}]_1$

	m = 2	m = 3	m = 4	exact	n_1/n_2	m_1/m_2
∞	1.0833	1.1068	1.1165	1.13177	10^{-5}	10^{-5}
12	1.039*	1.048*		1.05624	0	0
10	1.032*	1.039*		1.04528	0	0
8	1.023*	1.027*		1.03120	0	0
6	1.010*	1.012*		1.01373	0	0
4	1.0	1.0	1.0	1.0	0	0
3	1.0119	1.0131	1.0135	1.01373	10^{-7}	10^{-6}
2	1.1250	1.1302	1.1312	1.13177	10^{-7}	10^{-6}
1	3.2500	3.3906	3.3945	3.39531	10^{-6}	10^{-6}
* Taken from Mason [1957b].						

TABLE 14. HIGHER APPROXIMATIONS TO THE THERMAL DIFFUSION RATIO FOR A LORENTZIAN GAS FOR INVERSE POWER POTENTIALS.

$$[k_T]_m / [k_T]_{\text{exact}}$$

	m = 2	m = 3	m = 4	n_1/n_2	m_1/m_2
∞	0.7692	0.8941	0.9388	10^{-5}	10^{-5}
12	0.849*	0.939*	0.968*	0	0
10	0.865*	0.947*	0.972*	0	0
8	0.889*	0.959*	0.979*	0	0
6	0.928*	0.975*	0.998*	0	0
4	1.0	1.0	1.0	0	0
3	1.0588	1.0135	1.0054	10^{-7}	10^{-6}
2	1.1111	1.0138	1.0043	10^{-7}	10^{-6}
1	0.7692	1.0138	1.0012	10^{-6}	10^{-6}

* Taken from Mason [1957b].

We note that the error in the first approximation to the diffusion coefficient for this mixture is very large, but that the second approximation is quite close to the true value. The rate of convergence of the thermal diffusion ratio is quite slow for this case. Again the inverse single power potential demonstrates the slowest convergence. Fortunately this case cannot occur in practice since electrons and ions must be present in nearly equal densities at any point except near the boundaries in a real plasma. Note that the so-called Lorentzian gas for the fully-ionized plasma [see e.g. Spitzer and Härm, 1953] takes the limit $m_1/m_2=0$ but retains $n_1=n_2$. Thus the ions are at rest, but the electrons and ions are present in equal densities.

For the quasi-Lorentzian mixture Mason [1957b] has discovered that all approximations give the exact result for the binary diffusion coefficient. As a check on the computer program we verified that we could duplicate this result for the cases $\delta=\infty, 3, 2, 1$. Agreement was achieved out to better than six significant figures with the mass ratios listed in Table 15. The results for the thermal diffusion ratio are

also given in this table. No exact result exists for this coefficient.

TABLE 15. HIGHER APPROXIMATIONS TO THE THERMAL DIFFUSION RATIO FOR THE QUASI-LORENTZIAN GAS WITH THE INVERSE POWER POTENTIAL. $[k_T]_m/[k_T]_1$

	m = 3	m = 4	n_1/n_2	m_1/m_2
∞	1.0455	1.0515	10^{-5}	10^4
12	1.031*	1.034*	0	0
10	1.028*	1.031*	0	0
8	1.023*	1.026*	0	0
6	1.016*	1.017*	0	0
4	1.0	1.0	0	0
3	0.9839	0.9827	10^{-7}	10^6
2	1.0909	1.1098	10^{-7}	10^6
1	1.1360	1.1742	10^{-7}	10^6
* Taken from Mason [1957b].				

We note again the slowest convergence for the Coulomb potential, though again this case cannot exist in practice. The rate of convergence for this mixture is considerably better than for the Lorentzian gas.

4. DISCUSSION AND CONCLUSIONS

In this report the usual Chapman-Enskog formulation of the transport properties of multicomponent mixtures has been extended to higher approximations. The expressions derived are, strictly speaking, applicable only to non-reacting monatomic gases with no internal degrees of freedom. However, with the exception of the thermal conductivity, they can probably be used with success for gases in which reactions are taking place and even for polyatomic gases. The corrections necessary for the thermal transport in monatomic gases were given in Section 2.3.

We saw in Section 3.2 that it is necessary to use at least the third approximation to obtain accurate results for the thermal conductivity and thermal diffusion coefficients of ionized gases. The second approximations to the viscosity and to the diffusion coefficient of the electrons appear to give quite accurate results. The theoretical relations are quite complicated in this level of approximation and it would be worthwhile to derive simpler expressions which approximate the exact results. The accuracy of any approximate relations can only be judged by the agreement (or lack of agreement) with the accurate results obtained with the expressions given here. For extensive calculations of the properties of gases it would appear preferable to use the full expressions. In spite of complexity of the formulas, actual computations proceed quite rapidly on a typical computer. For example, the coefficients for argon at one atmosphere have been computed from 4000° to 22000° K in steps of 1000° K in only about 1-minute run time on the IBM 7090. These computations were performed with the general Balgol program mentioned earlier and the time includes that necessary to compute some of the average cross-sections. Ionized argon is a relatively simple mixture of only three components, and somewhat longer time would be required for a more complicated mixture.

Another difficulty in using the general expressions arises because not all of the average cross-sections $\pi_2^{(l,s)}$ necessary for the third approximation have been worked out for the potentials of interaction between species in more complicated mixtures. Even in argon we

are limited to the third approximation because the integrals necessary for the fourth approximation have not been calculated for the exponential potential which is used for the atom-atom and atom-ion elastic interaction. Here again the presence of high-speed computers should make it possible to carry through rapidly the cross-section calculations for various potentials. This is not done for the argon case because the third approximation is felt to be adequate. In cases where the cross-sections are lacking for even the third approximation it would certainly be worthwhile to set up a general program to compute the necessary cross-sections.

One additional problem not completely resolved concerns the proper charged-particle-cross section. When $\ln \Lambda \gg 1$, then the Coulomb potential with the Debye cut-off is adequate. When $\Lambda^2 \gg 1$ but $\ln \Lambda \not\gg 1$ then a more accurate method must be used. The best method at present appears to be that of Kihara and Aono [1963]. Because of the complexity of their method, the simple screened potential was used in this report. Where comparison was possible, the results agree very well with those of Kihara, Aono and Itikawa [1963]. It appears that no adequate theory has yet been given for the Coulomb cross-section when the inter-electron distance becomes greater than the Debye length.

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APPENDIX

In this appendix relations will be given for obtaining the bracket expressions from the article of Mason [1957a]. Also presented are two bracket expressions which are not available in either MTGL or Mason's article. We should note first that both editions of MTGL [1954, 1964] contain a misprint in Eq. [7.A-5]. The right hand side of this relation should be multiplied by 8.

Mason [1957a] has derived the higher approximations for the transport properties of binary gas mixtures with the formulation of Chapman and Cowling [1952]. However, he does not use exactly the same expressions that they present, so some cross-checking of formulas between his article and Section 9.8 of that book is necessary to obtain the bracket expressions. The final translation formulas are, replacing 1 by i and 2 by j in the expressions of Mason,

$$[\vec{w}_1; \vec{w}_1 S_{3/2}^{m'}(w_1^2)]_{ij} = \sqrt{\frac{kT}{\pi}} \frac{m_1 + m_j}{m_1 \sqrt{m_j}} \pi \sigma_{ij}^2 a_{0m'} \quad (m' > 0) \quad (A.1)$$

$$[\vec{w}_1 S_{3/2}^m(w_1^2); \vec{w}_1 S_{3/2}^{m'}(w_1^2)]_{ij} = \sqrt{\frac{2kT}{\pi}} \left(\frac{m_1 + m_j}{m_1 m_j} \right)^{1/2} \pi \sigma_{ij}^2 a'_{mm'} \quad (m, m' > 0) \quad (A.2)$$

$$[\vec{w}_1 S_{3/2}^m(w_1^2); \vec{w}_j S_{3/2}^{m'}(w_j^2)]_{ij} = \sqrt{\frac{2kT}{\pi}} \left(\frac{m_1 + m_j}{m_1 m_j} \right)^{1/2} \pi \sigma_{ij}^2 c_{mm'} \quad (m > 0 > m') \quad (A.3)$$

These same relations may also be used to derive from Mason [1954] some of the bracket expressions given in MTGL.

Two of the bracket expressions necessary for the third and fourth approximations in the MTGL formulation are not given in either that book or in Mason [1957a]. They may be derived from relations given in CC [p. 157, Eq. (1)]; see also the remarks in Section 9.5 of CC] and the bracket expressions already obtained.

The results are

$$[\vec{w}_1; \vec{w}_j s^{3/2} (w_j^2)]_{1j} = -8 \sqrt{\frac{kT}{2\pi}} \frac{m_1^2}{(m_1 + m_j)^{5/2}} \pi \sigma_{1j}^2 \left[\frac{35}{8} \Omega_{1j}^{(1,1)*} - \frac{21}{2} \Omega_{1j}^{(1,2)*} + 6 \Omega_{1j}^{(1,3)*} \right] \quad (A.4)$$

$$[\vec{w}_1; \vec{w}_j s^3 (w_j^2)]_{1j} = -8 \sqrt{\frac{kT}{2\pi}} \frac{m_1^3}{(m_1 + m_j)^{7/2}} \pi \sigma_{1j}^2 \left[\frac{105}{16} \Omega_{1j}^{(1,1)*} - \frac{189}{8} \Omega_{1j}^{(1,2)*} + 27 \Omega_{1j}^{(1,3)*} - 10 \Omega_{1j}^{(1,4)*} \right] \quad (A.5)$$