Transport Phenomena in Einstein-Bose and Fermi-Dirac Gases. II

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In this paper the general theory of transport phenomena in simple gases is concluded, and numerical values of the gas coefficients for heat conductivity and viscosity are obtained as a function of the temperature and density for the particular case of molecules acting as rigid elastic spheres. In the Introduction will be found a qualitative discussion of the principal results obtained and an interpretation of these results according to elementary considerations. In Section 1 the method of solution of the integral equations with which the formal theory of Part I was concluded is given together with the resulting general equations for the heat conductivity and viscosity coefficients. Since the integral equations can be solved only by a method of successive approximations, the expressions for the gas coefficients are in the form of infinite series the rapidity of convergence of which depends on a suitable choice of a complete set of auxiliary functions. In Section 2 all of the integrals appearing in the first two terms of the infinite series are evaluated. That only two terms are required is due to the fact that one is able to make an excellent choice of functions to represent the auxiliary set. In the evaluation of these integrals restriction is made in the application of the theory to small values of the degeneracy parameter A, since only terms in the zeroth and first power of A are retained. This restriction is only slightly greater than that imposed by the fundamental postulates of the general theory which restrict its applicability to moderately rare gases. In Section 3 the final equations for the gas coefficients are applied to gases consisting of molecules which interact quantum-mechanically as rigid elastic spheres of diameters and masses associated with the gases helium and hydrogen.

INTRODUCTION

IT has been shown in Part I[1] that the method of Lorentz, Hilbert and Enskog for the treatment of transport phenomena can be extended to take into account the modifications introduced by the quantum theory. In this paper the explicit solution of the integral equations will be obtained, and the general formulae for viscosity and heat conductivity will be developed. Numerical results for the case of the elastic sphere model will then be given. As already mentioned in Part I the quantum theory introduces two modifications into the classical kinetic theory of gases.

(a) The collision between two gas molecules which is the elementary process in all transport phenomena must be treated according to the quantum theory of collisions. Deviations from the classical theory may be expected, therefore, if the de Broglie wave-length corresponding to the mean temperature motion: $\lambda = \hbar/(mkT)^{\frac{1}{2}}$ is comparable to or larger than the diameter s of the molecule. Just as in the classical treatment, the mean free path l is inversely proportional to the density ρ, but the proportionality factor is now dependent on the temperature even for the

case of elastic spheres. In fact $l \sim 1/\rho f(\lambda/s)$, where for small values of λ/s, f approaches the classical value. Thus, the temperature dependence of the gas coefficients will be different than in the classical treatment. For light gases like H_2 and He, λ/s is already as large as 0.1 at room temperatures, so that considerable deviations even at high temperatures may be expected. Massey and Mohr[2] have recently taken this effect into account by introducing the quantum theoretically determined differential cross-sectional area into the classical expressions of Chapman for the gas coefficients. The complete justification of this procedure for temperatures which are not *too* low will be given in this paper.

(b) For temperatures which are very low the second modification becomes important. This effect is a consequence of the change in the Stosz-zahlansatz, which is equivalent to a change in the equilibrium distribution function from the Maxwell-Boltzmann to the Einstein-Bose or Fermi-Dirac distribution law. Due to this modification the mean free path l, even for an ideal gas, will be no longer strictly inversely proportional to the density. Instead $l \sim 1/\rho(1 + \alpha\rho\lambda^3)$, where α is a numerical factor, the sign of which depends on the statistics. Thus one

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[1] E. A. Uehling and G. E. Uhlenbeck, Phys. Rev. 43, 552 (1933).

[2] Massey and Mohr, Proc. Roy. Soc. A141, 434 (1933); A144, 188 (1934).

observes that the deviation from the inverse proportionality of l and ρ depends on the magnitude of λ/d where d is the mean distance between the molecules. In contrast with the first quantum effect the second will be small at ordinary temperatures, and will become important only at very low temperatures or very high densities. The ordinary reasoning, therefore, by which one shows in the classical kinetic theory the independence of the gas coefficients on the density is no longer strictly valid. At low temperatures the viscosity and heat conductivity coefficients become density dependent and the direction of the dependence is different for the two statistics.

That the latter effect depends on the magnitude of the parameter λ/d and therefore on the density as well as on the temperature requires that one consider also other possible contributions to the density dependence. Such an additional effect is the modification in the Stoss-zahlansatz due to the extension of the molecules, a modification which again is equivalent to a departure from the strict inverse proportionality in the classical theory of l and ρ. Thus, even when considered classically, there will be a small density correction to the gas coefficients which becomes important for sufficiently high densities. In fact, one can write for the case of elastic spheres $l \sim 1/\rho(1+\beta\rho s^3)$, where β is a numerical factor, and s is the diameter of the molecule. This correction, which has been carefully estimated by Enskog,[3] will be used as a criterion for the estimation of the importance of the rare gas density correction of the quantum theory, and as a criterion, furthermore, for an estimate of the possibility of an experimental test of the statistics. Since the magnitude of the quantum correction depends on the parameter λ/d, and the correction due to the extension of the molecules depends on the parameter s/d which is temperature independent in the case of elastic spheres, there will exist a temperature sufficiently low for which the latter is negligible in comparison with the former at any density.

Applying the general formulae developed in this paper to the rigid elastic sphere model, one finds that only below about 15°A does the

[3] Kungl. Svenska Vetenskapsakademien Handlungar. **63**, 5 (1921).

quantum theoretical density correction, which, depending on λ^3 varies as the inverse three-halves power of the temperature, have a magnitude greater than the classical density correction of the Enskog theory. In the case of helium, for example, one can expect at temperatures slightly greater than its critical temperature a correction of about $2\frac{1}{2}$ percent in the viscosity coefficient per atmosphere of pressure compared with the value of this coefficient in the limiting case of zero density, whereas the classical density correction due to the extension of the molecules should be about 0.5 percent. Assuming the Einstein-Bose statistics these corrections are of opposite sign. In this case the possibility of an experimental test of the statistics seems to be a favorable one. It is less favorable in the case of the heat conductivity coefficient for which the classical corrections are larger and the quantum corrections are smaller than for the viscosity coefficient. It is less favorable, also, in the case of other gases, hydrogen, for example, for which the range of temperatures and densities which lie well within the vapor phase are less suitable than in the case of helium for a test of this kind.

2. Solution of the Integral Equations

The formal theory of transport phenomena has given the following expressions for the heat conductivity and viscosity coefficients, κ and η

$$\kappa = \frac{3k}{2m} \frac{(mkT)^{\frac{1}{2}}}{s^2} \frac{2}{3}[\pi_i, \pi_i], \qquad (43)$$

$$\eta = \frac{(mkT)^{\frac{1}{2}}}{s^2} \frac{3}{2}[\pi_{ij}, \pi_{ij}], \qquad (46)$$

where m is the mass of the molecule, s is a quantity having the dimensions of length, or in the case of elastic sphere molecules may be taken as representing the molecular diameter, and $\pi_i = \xi_i \chi_a(\tau)$ and $\pi_{ij} = (\xi_i\xi_j - \tau^2/3\delta_{ij})\chi_b(\tau)$ are solutions of the inhomogeneous integral equations:

$$\left.\begin{aligned}
\frac{f^{(o)2}}{A^2 e^{-\tau^2}}\xi_i\left(\tau^2 - \frac{5}{2}\frac{p}{nkT}\right) &= J(\pi_i), \quad \text{a} \\[2ex]
\frac{f^{(o)2}}{A^2 e^{-\tau^2}}\left(\xi_i\xi_j - \frac{\tau^2}{3}\delta_{ij}\right) &= J(\pi_{ij}), \quad \text{b}
\end{aligned}\right\}(34)$$

so determined that they fulfill the auxiliary conditions:

$$\int \psi_k f^{(o)}(1+\theta f^{(o)})\pi d\omega = 0 \quad (k=1, 2, \cdots 5), \quad (36)$$

$\psi_k = m$, $m\xi_1$, $m\xi_2$, $m\xi_3$ and $m\tau^2$ being the five solutions (spoken of henceforth as null solutions) of the homogeneous equation: $J(\psi) = 0$ where, furthermore

$$J(F) = \frac{1}{s^2 A^2} \int d\omega_1 \int d\Omega \cdot \gamma I(\vartheta\gamma)$$

$$\cdot (F+F_1-F'-F_1') \cdot f^{(o)} f_1^{(o)}$$

$$\times (1+\theta f^{(o)\prime}(1+\theta f_1^{(o)\prime}), \quad (32)$$

$$[F, G] = \int d\omega \cdot GJ(F). \quad (32a)$$

For the remainder of the notation reference should be made to Part I.[4]

Eqs. (34a and b) will be solved by the Enskog method of successive approximations.[5] If one has a complete set of functions $h^{(r)}$ which fulfill the following conditions:

(a) $\displaystyle\int \psi_k f^{(o)}(1+\theta f^{(o)})h^{(r)}d\omega = 0 \quad \left\{\begin{array}{l} k=1, 2, \cdots 5 \\ r=1, 2, \cdots \end{array}\right\}$

(b) Linear independence,

(c) The integrals $[h^{(r)}, h^{(s)}]$ and $[h^{(r)}, \pi]$ have finite definite values,

a function $\pi^{(n)}$ may be constructed as a linear combination of the functions $h^{(r)}$ ($r=1, 2, \cdots n$), and the n constants of $\pi^{(n)}$ may be so determined as to minimize the integral $[\pi - \pi^{(n)}, \pi - \pi^{(n)}]$. According to the fourth of the properties of this operator discussed in Part I:[6]

$[F, G] = [G, F]$,

$[F, G+H] = [F, G] + [F, H]$,

$[F, cG] = c[F, G]$, where c is independent of all variables of integration,

$[F, F] \geq 0$

the integral $[\pi - \pi^{(n)}, \pi - \pi^{(n)}]$ can never be negative. Should one succeed in minimizing it to the value zero, the function $\pi^{(n)}$ for which this condition exists becomes the sought for solution. This result is a consequence of the fact that $\pi - \pi^{(n)}$ under this condition can be only a null solution. It satisfies, however, the auxiliary conditions since π as well as $\pi^{(n)}$ (which is only a linear combination of the $h^{(r)}$) separately satisfy these conditions. A function satisfying the auxiliary conditions, and which is itself a null solution can only be zero. Consequently $\pi = \pi^{(n)}$.

The values of the constants c_r in the function

$$\pi^{(n)} = \sum_{r=1}^{n} c_r h^{(r)} \quad (62)$$

are now determined by applying the condition for an extreme of $H^{(n)} = [\pi - \pi^{(n)}, \pi - \pi^{(n)}]$. This condition is

$$\partial H^{(n)}/\partial c_r = -2\left[h^{(r)}, \pi - \sum_{s=1}^{n} c_s h^{(s)}\right] = 0$$

or defining $a_{rs} = [h^{(r)}, h^{(s)}]$ and $\alpha_s = [h^{(s)}, \pi]$ the set of equations determining the extreme of $H^{(n)}$ is:[7]

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[4] The operator previously designated as $I(F)$ is now written $J(F)$, and the primes attached to the operators $[F, G]$ and which were used to distinguish them from analogous operators which also appeared in the formal theory are here omitted since no confusion can arise. The differential cross-sectional area previously designated by $w(\vartheta\gamma)$ is now written as $I(\vartheta\gamma)$ to conform to the more usual notation.

[5] Dissertation, Uppsala, 1917, p. 43; Courant-Hilbert, *Methoden der Mathematischen Physik* I, chapter 3.

[6] That this operator has these properties becomes immediately obvious from the fact that $\int d\omega \cdot GJ(F)$ is unchanged if G is replaced by G_1, $-G'$, of G_i'. One may show also that the analogous operator

$$[F, G] = \int F(\xi_i)G(\xi_i)d\omega - \int\int F(\xi_i)G(\xi_i')K(\tau\tau'\epsilon)d\omega d\omega'$$

obtained from the homogeneous part of the integral equation in its more usual form

$$f(\xi_i) = \pi(\xi_i) - \int \pi(\xi_i')K(\tau\tau'\epsilon)d\omega'$$

into which form Eqs. (34a and b) may be put (Eq. (37), Part I) has these properties in general if the kernel is symmetrical and is positive definite with a first eigen value greater than or equal to unity. The kernel of Eqs. (34a and b) when the equations are written in the standard form has these properties.

[7] That the extreme of $H^{(n)}$ thus determined is actually a minimum and not a maximum is shown by obtaining the second differential quotients and developing $H^{(n)}$ for values of c_r slightly different than those determined by Eq. (63) in a Taylor series. One obtains, since $H^{(n)}$ is a quadratic function of the $h^{(r)}$

$$\frac{\partial^2 H^{(n)}}{\partial c_r \partial c_s} = 2[h^{(r)}, h^{(s)}], \qquad H^{(n)} = H_0^{(n)} + [\Sigma_r c_r' h^{(r)}, \Sigma_r c_r' h^{(r)}],$$

where $c_r' = c_r - c_{r0}$, the c_{r0} are the constants determined by Eqs. (63), and $H_0^{(n)}$ is the corresponding value of $H^{(n)}$. According to the fourth property of the square bracket operator the first variation of $H^{(n)}$ is positive. Furthermore, $H^{(n)}$ is equal to $H_0^{(n)}$ *only* when the c_r' are zero, since $\Sigma_r c_r' h^{(r)}$ cannot be a null solution consistently with the requirement that the $h^{(r)}$ be linearly independent and at the same time satisfy the auxiliary conditions.

$$\sum_{s=1}^{n} c_s a_{rs} - \alpha_r = 0 \qquad r = 1, 2, \cdots n. \quad (63)$$

From Eqs. (62) and (63) the nth approximation function $\pi^{(n)}$ then becomes

$$\pi^{(n)} = \sum_{s=1}^{n} (A_s{}^{(n)}/A^{(n)})h^{(s)}, \quad (64)$$

where $A^{(n)}$ is the determinant $||a_{ij}||$ of n rows and columns, and $A_s{}^{(n)}$ is the determinant $A^{(n)}$ with the sth column a_{is} replaced by α_i. In order to make the character of the successive approximations of $\pi^{(n)}$ to the true solution π apparent in Eq. (64), this equation will be transformed so that the difference between $\pi^{(n)}$ and $\pi^{(n-1)}$ appears only in the last (the nth) term of $\pi^{(n)}$. Written in this manner Eq. (64) becomes

$$\pi^{(n)} = \sum_{s=1}^{n} [A_s{}^{(s)}D_s{}^{(s)}/(A^{(s-1)}A^{(s)})], \quad (65)$$

where $D_s{}^{(s)}$ is the determinant $A^{(s)}$ with the last (the sth) row a_{sj} replaced by $h^{(i)}$, or since the elements a_{ij} are symmetrical, $D_s{}^{(s)}$ is the determinant $A^{(s)}$ with the last column a_{is} replaced by $h^{(i)}$.

One can show now that the following relations exist:

$$\begin{array}{ll} [h^{(r)}, D_s{}^{(s)}] = A^{(s)} & r = s \\ \qquad\qquad\quad = 0 & r < s \end{array}\Big\}, \quad (66)$$

$$\begin{array}{ll} [D_s{}^{(s)}, D_r{}^{(r)}] = A^{(s-1)}A^{(s)} & r = s \\ \qquad\qquad\qquad = 0 & r \neq s \end{array}\Big\}, \quad (67)$$

$$[\pi, D_s{}^{(s)}] = A_s{}^{(s)} \quad (68)$$

and that as a consequence

$$[\pi^{(n)}, \pi^{(n)}] = [\pi, \pi^{(n)}] \quad (69)$$

$$= \sum_{s=1}^{n} [A_s{}^{(s)2}/A^{(s-1)}A^{(s)}]. \quad (70)$$

From Eq. (66) $A^{(1)} = a_{11}$ is a positive quantity since $h^{(1)}$ is not a null solution. Similarly from Eq. (67) using the result that $A^{(1)} > 0$, the fact that $D_s{}^{(s)}$ cannot be a null solution because of the linear independence of the $h^{(i)}$ and the existence for $h^{(i)}$ of the auxiliary conditions, and the fourth property of the operator $[F, F]$, one can show that $A^{(s)}$ for each successive value of s cannot be negative or zero. Consequently, each term of $[\pi^{(n)}, \pi^{(n)}]$ (Eq. 69) is positive. That

$[\pi^{(n)}, \pi^{(n)}]$ is also bounded is proven from the relation

$$[\pi - \pi^{(n)}, \pi - \pi^{(n)}] \geq 0$$
$$[\pi, \pi] - 2[\pi, \pi^{(n)}] + [\pi^{(n)}, \pi^{(n)}] \geq 0 \quad (71)$$

and the result of Eq. (69) from which Eq. (71) becomes

$$[\pi, \pi] - \sum_{s=1}^{n} \frac{A_s{}^{(s)2}}{A^{(s-1)}A^{(s)}} \geq 0.$$

Thus $[\pi^{(n)}, \pi^{(n)}]$ is bounded provided Eqs. (34a and b) have solutions such that the integral $[\pi, \pi]$ is finite. That $[\pi^{(n)}, \pi^{(n)}]$ actually converges to this upper limit as n approaches infinity may be proven in a manner analogous to that used by Enskog in the classical case. One may write then

$$[\pi, \pi] = \lim_{n \to \infty} \sum_{s=1}^{n} \frac{A_s{}^{(s)2}}{A^{(s-1)}A^{(s)}},$$

which, when introduced into Eq. (43) gives for the heat conductivity coefficient

$$\kappa = \frac{3k}{2m} \frac{(mkT)^{\frac{1}{2}}}{s^2} \frac{2}{3} \sum_{s=1}^{\infty} \frac{A_s{}^{(s)2}}{A^{(s-1)}A^{(s)}}. \quad (72)$$

The solution of Eq. (34b) is obtained in a similar manner using functions $k^{(r)}$ satisfying conditions analogous to those of $h^{(r)}$ which involve now the solutions π_{ii} instead of π_i. Defining as before the quantities $b_{rs} = [k^{(r)}, k^{(s)}]$ and $\beta_r = [k^{(r)}, \pi]$, constructing the function $\pi^{(n)}$ and the integral $H^{(n)}$ which is then minimized to completely determine $\pi^{(n)}$, one obtains finally for the viscosity coefficient from Eq. (46)

$$\eta = \frac{(mkT)^{\frac{1}{2}}}{s^2} \frac{3}{2} \sum_{s=1}^{\infty} \frac{B_s{}^{(s)2}}{B^{(s-1)}B^{(s)}}, \quad (73)$$

where $B^{(i)}$ and $B_i{}^{(i)}$ are determinants analogous to $A^{(i)}$ and $A_i{}^{(i)}$ defined as before, but with the functions $k^{(r)}(b_{rs}$ and $\beta_r)$ instead of $h^{(r)}(a_{rs}$ and $\alpha_r)$.

We will now make a choice of the functions $h^{(r)}$ and $k^{(r)}$. The analysis of Part I (§8 and note 4) has shown that the solutions of Eqs. (34a and b) are of the form: $\pi_i = \xi_i \chi_a(\tau^2)$, $\pi_{ii} = (\xi_i{}^2 - \tau^2/3)\chi_b(\tau^2)$. These functions are ac-

cordingly chosen so as to be proportional to ξ_i and $(\xi_i^2 - \tau^2/3)$, respectively, and to depend otherwise only on τ^2 in such a way that the $\pi^{(n)}$ constructed from these functions represent power series in τ^2. Using now further the fact that they must satisfy the auxiliary conditions one obtains as a suitable choice:

$$\left.\begin{aligned} h^{(r)} &= \xi\left[\tau^{2r} - \frac{\Gamma(r+5/2)}{\Gamma(5/2)}\frac{F_{r+\frac{1}{2}}}{F_{\frac{1}{2}}}\right] \quad \text{a} \\ k^{(r)} &= (\xi^2 - \tau^2/3)\tau^{2r-2} \quad \text{b} \end{aligned}\right\} \quad (74)$$

where

$$F_{r+\frac{1}{2}} = \frac{1}{\Gamma(r+3/2)}\int_0^\infty \frac{z^{r+\frac{1}{2}}dz}{(1/A)\exp z - \theta}. \quad (75)$$

3. EVALUATION OF THE INTEGRALS

§ 1. The functions α_r and β_r

Introducing the expression for $h^{(r)}$ into the definition of α_r, and making the substitutions:[8]

$$\frac{f^{(o)2}}{A^2 e^{-\tau^2}} = -\frac{1}{2\tau}\frac{\partial f^{(o)}}{\partial \tau}, \qquad p/nkT = F_{3/2}/F_{1/2},$$

$$\int_0^\infty \frac{\partial f^{(o)}}{\partial \tau}\tau^m d\tau = -m\int_0^\infty f^{(o)}\tau^{m-1}d\tau = -\frac{m}{2}\Gamma\left(\frac{m}{2}\right)F_{m/2-1},$$

one obtains

$$\alpha_r = \frac{2\pi}{3A}\Gamma\left(\frac{2r+7}{2}\right)\left[F_{(2r+3)/2} - \frac{5}{2r+5}\frac{F_{(2r+1)/2}F_{3/2}}{F_{1/2}}\right]. \quad (76)$$

But for $A < 1$, to which all future considerations will be restricted

$$F_\rho = A\left[1 + \frac{\theta A}{2^{\rho+1}} + \frac{(\theta A)^2}{3^{\rho+1}} + \cdots + \frac{(\theta A)^{n-1}}{n^{\rho+1}} + \cdots\right].$$

Accordingly, for $A \ll 1$

$$\alpha_r = \frac{2\pi r}{3}\Gamma\left(\frac{2r+5}{2}\right)\left[1 + \frac{\theta A}{2^{r+5/2}}\left\{\frac{2r+5}{2r} + \frac{5}{r}(2^{r-1}-1)\right\}\right]. \quad (77)$$

Similarly, introducing the expression for $k^{(r)}$ into the definitions of β_r

$$\beta_r = \frac{8\pi}{45A}\Gamma\left(\frac{2r+5}{2}\right)F_{(2r+1)/2} \quad (78)$$

and for $A \ll 1$

$$\beta_r = \frac{8\pi}{45}\Gamma\left(\frac{2r+5}{2}\right)\left[1 + \frac{\theta A}{2^{r+\frac{3}{2}}}\right]. \quad (79)$$

§ 2. The functions a_{rq} and b_{rq}

These functions will be evaluated only for the case of $A \ll 1$. They have been defined in Section 2 in the following manner:

$$a_{rq} = [h^{(r)}, h^{(q)}] = \frac{1}{4s^2A^2}\int d\omega\int d\omega_1\int d\Omega \cdot \gamma I(\vartheta\gamma)(h^{(r)} + h_1^{(r)} - h^{(r)\prime} - h_1^{(r)\prime})$$

$$\times (h^{(q)} + h_1^{(q)} - h^{(q)\prime} - h_1^{(q)\prime})f^{(o)}f_1^{(o)}(1 + \theta f^{(o)\prime})(1 + \theta f_1^{(o)\prime}) \quad (80)$$

with an analogous expression for b_{rq} using $k^{(r)}$ and $k^{(q)}$ for $h^{(r)}$ and $h^{(q)}$. It is convenient now to introduce a transformation of variables from $\xi\eta\zeta\xi_1\eta_1\zeta_1$ to $\gamma\lambda\theta\delta\alpha\epsilon$ where $\gamma = g(m/4kT)^{\frac{1}{2}}$ as previously defined; $\lambda = l(m/kT)^{\frac{1}{2}}$, l being the actual velocity of motion of the center of gravity of the interacting

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[8] *Transport Phenomena* I, Eq. (60).

molecules; θ and δ are the polar and azimuthal angles respectively describing the direction of the vector l; and α and ϵ are the polar and azimuthal angles respectively describing the direction of the vector g with respect to the vector l. In collision the only variables of this system which undergo alteration are α and ϵ which after collision become α' and ϵ', and then describe the direction of the vector g' with respect to the vector l. Introducing the considerations of the velocity pyramid, one obtains for the function $h^{(r)}$ in terms of the new variables

$$h^{(r)} = 2^{-r-\frac{1}{2}}[\lambda \cos \theta - \gamma(\cos \alpha \cos \theta - \sin \alpha \sin \theta \cos \epsilon)](\lambda^2 + \gamma^2 - 2\gamma\lambda \cos \alpha)^r, \tag{81}$$

$$h_1^{(r)} = 2^{-r-\frac{1}{2}}[\lambda \cos \theta + \gamma(\cos \alpha \cos \theta - \sin \alpha \sin \theta \cos \epsilon)](\lambda^2 + \gamma^2 + 2\gamma\lambda \cos \alpha)^r \tag{82}$$

plus terms which contribute nothing to the expression a_{rq}. Similarly, for the function $k^{(r)}$ one obtains

$$k^{(r)} = 2^{-r}[(\cos^2 \theta - \tfrac{1}{3})(\lambda^2 + \gamma^2 - 2\gamma\lambda \cos \alpha)^r + (\gamma^2 \sin^2 \theta \sin^2 \alpha \cos^2 \epsilon - \gamma^2 \cos^2 \theta \sin^2 \alpha$$

$$+ 2\gamma\lambda \sin \theta \cos \theta \sin \alpha \cos \epsilon + \gamma^2 \sin \theta \cos \theta \sin 2\alpha \cos \epsilon)(\lambda^2 + \gamma^2 - 2\gamma\lambda \cos \alpha)^{r-1}], \tag{83}$$

$$k_1^{(r)} = 2^{-r}[(\cos^2 \theta - \tfrac{1}{3})(\lambda^2 + \gamma^2 + 2\gamma\lambda \cos \alpha)^r + (\gamma^2 \sin^2 \theta \sin^2 \alpha \cos^2 \epsilon - \gamma^2 \cos^2 \theta \sin^2 \alpha$$

$$- 2\gamma\lambda \sin \theta \cos \theta \sin \alpha \cos \epsilon - \gamma^2 \sin \theta \cos \theta \sin 2\alpha \cos \epsilon)(\lambda^2 + \gamma^2 + 2\gamma\lambda \cos \alpha)^{r-1}]. \tag{84}$$

Analogous expressions exist for the primed functions in which α' and ϵ' appear everywhere for α and ϵ. The differential product in the new variable becomes, furthermore

$$d\omega d\omega_1 = \lambda^2 \gamma^2 \sin \theta d\theta d\delta \sin \alpha d\alpha d\epsilon d\gamma d\lambda. \tag{85}$$

Before introducing the new variables into the distribution function $f^{(o)}$, this function is to be expanded in ascending powers of A for values of $A < 1$. One obtains finally after retaining only powers of A up to and including the first:

$$f^{(o)} f_1^{(o)}(1 + \theta f^{(o)\prime})(1 + \theta f_1^{(o)\prime}) = A^2 e^{-(\lambda^2 + \gamma^2)}[1 + 2\theta A e^{-\frac{1}{2}(\lambda^2 + \gamma^2)} \cdot \{\cosh (\gamma\lambda \cos \alpha) + \cosh (\gamma\lambda \cos \alpha')\}]. \tag{86}$$

The function a_{rq} then becomes

$$a_{rq} = \frac{1}{2s^2} \int_0^\infty \int_0^\infty e^{-(\lambda^2 + \gamma^2)} r^3 \lambda^2 d\gamma d\lambda \int_0^\pi \int_0^{2\pi} \sin \theta d\theta d\delta \int_0^\pi \int_0^{2\pi} \sin \alpha d\alpha d\epsilon \cdot \int_0^\pi \int_0^{2\pi} I(\vartheta\gamma) \sin \vartheta d\vartheta d\varphi$$

$$\cdot (h^{(r)} + h_1^{(r)} - h^{(r)\prime} - h_1^{(r)\prime})(h^{(q)} + h_1^{(q)}) + \frac{\theta A}{s^2} \int_0^\infty \int_0^\infty e^{-\frac{3}{2}(\lambda^2 + \gamma^2)} \gamma^3 \lambda^2 d\gamma d\lambda \int_0^\pi \int_0^{2\pi} \sin \theta d\theta d\delta$$

$$\times \int_0^\pi \int_0^{2\pi} \sin \alpha d\alpha d\epsilon \cdot \int_0^\pi \int_0^{2\pi} I(\vartheta\gamma) \sin \vartheta d\vartheta d\varphi \cdot (h^{(r)} + h_1^{(r)} - h^{(r)\prime} - h_1^{(r)\prime})(h^{(q)} + h_1^{(q)})$$

$$\cdot \{\cosh (\gamma\lambda \cos \alpha) + \cosh (\gamma\lambda \cos \alpha')\}, \tag{87}$$

the function b_{rq} being an analogous expression with $k^{(r)}$ and $k^{(q)}$ appearing everywhere for $h^{(r)}$ and $h^{(q)}$.

Integration over all values of the variable φ, the azimuthal collision parameter, is accomplished with the help of the Maxwell theorem of spherical harmonics.[9] The following notation is used in the development of the various functions of the integrand considered as functions of $\alpha\epsilon$ and $\alpha'\epsilon'$ in spherical harmonics: The development coefficients in the functions

$$(h^{(r)} + h_1^{(r)}) \qquad\qquad \text{are} \quad c_{lp}^{(r)\prime}, c_{lp}^{(r)\prime\prime}$$

$$(h^{(r)} + h_1^{(r)})(h^{(q)} + h_1^{(q)}) \qquad\qquad d_{lp}^{(r, q)\prime}, d_{lp}^{(r, q)\prime\prime}$$

[9] Maxwell, *Sc. Papers* II, 681; Boltzmann, *Gastheorie* I, 171.

$$\cosh (\gamma \lambda \cos \alpha) \qquad\qquad \text{are} \quad e_{lp}{}', e_{lp}{}''$$

$$(h^{(r)}+h_1{}^{(r)}) \cosh (\gamma \lambda \cos \alpha) \qquad\qquad f_{lp}{}^{(r)'}, f_{lp}{}^{(r)''}$$

$$(h^{(r)}+h_1{}^{(r)})(h^{(q)}+h_1{}^{(q)}) \cosh (\gamma \lambda \cos \alpha) \qquad\qquad g_{lp}{}^{(r,\ q)'}, g_{lp}{}^{(r,\ q)''}$$

where a typical development is

$$(h^{(r)}+h_1{}^{(r)}) = \sum_{l=o}^{\infty} \sum_{p=o}^{l} (c_{lp}{}^{(r)'} \cos \epsilon + c_{lp}{}^{(r)''} \sin \epsilon) P_l{}^{(p)}(\cos \alpha).$$

Integrating then over φ with the aid of the Maxwell theorem, adding and subtracting suitable series involving $\int_0^\pi I(\vartheta\gamma) \sin \vartheta d\vartheta$, using relations existing among the coefficients to show that the sum of all terms which then do not involve $\int_0^\pi [1-P_l(\cos \vartheta)]I(\vartheta\gamma) \sin \vartheta d\vartheta$ is identically zero, integrating over α and ϵ, and defining a function

$$\theta^{(l)}(\gamma) = \frac{1}{s^2} \int_0^\pi [1-P_l(\cos \vartheta)]I(\vartheta\gamma) \sin \vartheta d\vartheta, \tag{88}$$

where the cross-sectional area effective in transport will be defined then as

$$Q_T{}^{(l)}(\gamma) = 2\pi s^2 \theta^{(l)}(\gamma) \tag{89}$$

one obtains finally

$$a_{rq} = 2\pi^3 \sum_{l=1}^{\infty} \frac{2}{2l+1} \Bigg[\int_0^\infty \int_0^\infty e^{-(\lambda^2+\gamma^2)} r^3 \lambda^2 \theta^{(l)}(\gamma) d\gamma d\lambda \int_0^\pi \sin \theta d\theta \cdot \Bigg\{ 2 c_{lo}{}^{(r)'} c_{lo}{}^{(q)'}$$

$$+ \sum_{m=1}^{l} \frac{(l+m)!}{(l-m)!}(c_{lm}{}^{(r)'} c_{lm}{}^{(q)'} + c_{lm}{}^{(r)''} c_{lm}{}^{(q)''})\Bigg\} + 2\theta A \int_0^\infty \int_0^\infty e^{-\frac{1}{2}(\lambda^2+\gamma^2)} \gamma^3 \lambda^2 \theta^{(l)}(\gamma) d\gamma d\lambda$$

$$\times \int_0^\pi \sin \theta d\theta \cdot \Bigg\{ 2(c_{lo}{}^{(r)'} f_{lo}{}^{(q)'} + c_{lo}{}^{(q)'} f_{lo}{}^{(r)'} - d_{lo}{}^{(r,\ q)'} e_{lo}{}') + \sum_{m=1}^{l} \frac{(l+m)!}{(l-m)!}$$

$$\times (c_{lm}{}^{(r)'} f_{lm}{}^{(q)'} + c_{lm}{}^{(r)''} f_{lm}{}^{(q)''} + c_{lm}{}^{(q)'} f_{lm}{}^{(r)'} + c_{lm}{}^{(q)''} f_{lm}{}^{(r)''} - d_{lm}{}^{(r,\ q)'} e_{lm}{}' - d_{lm}{}^{(r,\ q)''} e_{lm}{}'')\Bigg\}\Bigg]. \tag{90}$$

Similarly, one finds for b_{rq} an analogous function in which the various coefficients represent the development in spherical harmonics of the expressions just described in which $k^{(r)}$ and $k^{(q)}$ appear everywhere instead of $h^{(r)}$ and $h^{(q)}$.

We restrict our considerations now to the second approximation to the solution of the integral equations. Besides α_r and β_r for $r = 1$, 2 one requires for this purpose (Eqs. 72 and 73) the six quantities a_{rq} and b_{rq} with r, $q = 1$, 2. Determining then, all of the coefficients required in the various developments in spherical harmonics, integrating over θ and λ and defining

$$P^{(l,\ p)}(\alpha) = \int_0^\infty e^{-\alpha\gamma^2} \gamma^p \theta^{(l)}(\gamma) d\gamma \tag{91}$$

one obtains the expressions for the a_{rq} and b_{rq} which are given in Appendix 1.

The heat conductivity and viscosity coefficients, κ and η, then become (Eqs. 72 and 73):

$$\kappa = \frac{25}{32\pi^{\frac{1}{2}}} \frac{3k}{2m} \frac{\hbar}{\lambda} \frac{3}{2s^2 P^{(2,\ 7)}(1)}(1+\epsilon_1) \Bigg[1 + \frac{\pi^{\frac{1}{2}}}{4} n\lambda^3 \Bigg\{ 7 - \frac{128}{3^{\frac{3}{2}}} \frac{P^{(2,\ 9)}(4/3)+6P^{(2,\ 7)}(4/3)}{9P^{(2,\ 7)}(1)} + \epsilon_1' \Bigg\} \Bigg], \tag{92}$$

$$\eta = \frac{5}{16\pi^{\frac{1}{2}}} \frac{\hbar}{\lambda} \frac{3}{2s^2 P^{(2,7)}(1)} (1+\epsilon_2)\left[1 + \frac{\pi^{\frac{3}{2}}}{4} n\lambda^3\left\{4 - \frac{128}{3^{\frac{3}{2}}}\frac{P^{(2,7)}(4/3)}{P^{(2,7)}(1)} + \epsilon_2'\right\}\right],$$ (93)

where, as defined in the introduction, λ is the de Broglie wave-length corresponding to the mean temperature motion, and n is the number of molecules per unit volume. The small quantities ϵ_1 and ϵ_2 are given by the following equations:

$$\epsilon_1 = \frac{[7/2 P^{(2,7)}(1) - P^{(2,9)}(1)]^2}{P^{(2,11)}(1)P^{(2,7)}(1) - [P^{(2,9)}(1)]^2 + 7[P^{(2,7)}(1)]^2},$$

$$\epsilon_2 = \frac{[7/2 P^{(2,7)}(1) - P^{(2,9)}(1)]^2}{P^{(2,11)}(1)P^{(2,7)}(1) - [P^{(2,9)}(1)]^2 + 77/6[P^{(2,7)}(1)]^2}.$$

The small quantities ϵ_1' and ϵ_2' involve $P^{(r,q)}(\alpha)$ with values of α equal to 4/3 in addition to those with α equal to unity; with $r=4$ in addition to those with r equal to 2; and with q having the series of values 13, 11, 9, and 7. These expressions need not be given since their numerical magnitude is always small compared with the principal term of the density correction, which is already small, and except for light gases at low temperatures negligibly small, compared with the term independent of density. The order of magnitude of ϵ_1' and ϵ_2' will be discussed in connection with the application of these formulae to elastic sphere molecules.

Eqs. (92) and (93) for the gas coefficients have been written only for the case of the Einstein-Bose statistics for which the parameter θ of all previous equations has been put equal to +1. In the Fermi-Dirac statistics the equations for κ and η are similar to these with the opposite sign for the term depending on density and with the understanding that the integrals $P^{(r,q)}(\alpha)$ will then be evaluated according to these statistics. The term independent of density in these equations is exactly equivalent to the classical expressions of Enskog and Chapman when in the integrals $P^{(r,q)}(\alpha)$ classical cross-sectional areas are introduced instead of the quantum-mechanically determined areas.

It is of interest to consider the ratio of κ and η in connection with the well-known proportionality in the classical theory of this ratio to the specific heat. Neglecting the second approximation quantities ϵ, this ratio becomes, for the case of rigid elastic spheres, when the classical expression for the differential cross-sectional area is introduced $\kappa/\eta = (5/2)(\partial\epsilon/\partial T)_P$, where ϵ is the energy per unit mass, an expression which degenerates to proportionality with the specific heat only in the classical statistics. In the strict quantum theory, however, for the elastic sphere model as well as for a general force law, the coefficient of $n\lambda^3$ is temperature dependent and there are deviations from this simple result.

4. Application to the Rigid Sphere Model

In order to obtain an indication of the magnitude of the effects introduced by the quantum theory, the viscosity and heat conductivity equations will be applied to the case of the rigid elastic sphere molecule. The procedure is to evaluate first of all the differential cross-sectional area $I(\vartheta\gamma)$, then the function $\theta^{(l)}(\gamma)$ given by Eq. (88), and finally the function $P^{(l,p)}(\alpha)$ given by Eq. (91). The general expression for the differential cross-sectional area is:[10]

[10] Faxen and Holtzmark, Zeits. f. Physik 45, 307 (1927); Massey and Mohr, Proc. Roy. Soc. A141, 434 (1933); Mott and Massey, *The Theory of Atomic Collisions*.

$$I(\vartheta g) = (1/4K^2)\,|f(\vartheta g)|^2,$$ (94)

where

$$f(\vartheta g) = \sum_l (2l+1)(e^{2i\delta_l}-1)P_l(\cos\vartheta),$$ (95)

$$K = 2\pi mg/h.$$

g is the relative velocity, m the reduced mass of the molecule, and the δ_l are phase angles determined in the asymptotic solution for large values of r of the radial wave equation. Since Eq. (94) is valid only if the molecules may be considered as similar but not identical, one obtains the correct function in the Einstein-Bose statistics by multiplying by a factor 2 and

summing over even values of l. Similarly, in the Fermi-Dirac statistics one would sum over only the odd values of l. In all further considerations only the Einstein-Bose statistics will be used.

Having determined $I(\vartheta\gamma)$ one may next evaluate the function $\theta^{(l)}(\gamma)$ and with it the transport cross-sectional area. The latter has been defined by Eq. (89). Putting l equal to 2 one obtains the second order transport cross-sectional area, which becomes simply

$$Q_T^{(2)}(\gamma) = 3\pi \int_0^\pi I(\vartheta\gamma) \sin^3 \vartheta d\vartheta, \qquad (96)$$

whereas the scattering cross-sectional area is defined by the equation

$$Q_s(\gamma) = 2\pi \int_0^\pi I(\vartheta\gamma) \sin \vartheta d\vartheta. \qquad (97)$$

Introducing Eqs. (94) and (95) into Eq. (88) and using the recurrence relations for the Legendre functions one obtains for the second order function in the Einstein-Bose statistics

$$\theta^{(2)}(\gamma) = \frac{12}{K^2 s^2} \sum_l \left[\frac{16l^3 + 12l^2 - 2l - 1}{(4l-1)(4l+3)} \sin^2 \delta_{2l} \right.$$

$$- \frac{(2l+2)(2l+1)}{4l+3} \cos (\delta_{2l} - \delta_{2l+2})$$

$$\left. \times \sin \delta_{2l} \sin \delta_{2l+2} \right], \qquad (98)$$

where s, as throughout the theory, is an arbitrary quantity having the dimensions of length. In the Fermi-Dirac statistics one would have a similar expression with $2l$ everywhere replaced by $2l+1$.

Our considerations will be restricted now to the case of the rigid elastic sphere model, and the quantity s will be specialized to represent the molecular diameter. The phase angles δ_l are now determined[2] by the equation:

$$\delta_l = \arctan (-1)^l \frac{J_{l+\frac{1}{2}}(Ks)}{J_{-l-\frac{1}{2}}(Ks)}. \qquad (99)$$

Thus, in the particular case of the elastic sphere model the phase angles and therefore $\theta^{(l)}(\gamma)$ are functions of only the single variable $y = Ks$. Consequently, the function $P^{(l, p)}(\alpha)$ defined by Eq. (91) can be a function only of the ratio λ/s where $\lambda = \hbar/(mkT)^{\frac{1}{2}}$. This result follows from the fact that $\gamma = g(m/4kT)^{\frac{1}{2}} = K\lambda = y \cdot \lambda/s$, where $K = \frac{1}{2}mg/\hbar$, m being the actual mass and not the reduced mass of the molecule. One obtains, therefore, from Eq. (91)

$$P^{(l, p)}(\alpha) = \left(\frac{\lambda}{s}\right)^{p+1} \int_0^\infty e^{-\alpha(\lambda/s)^2 v^2} v^p \theta^{(l)}(y) dy. (100)$$

Thus, besides an explicit dependence of κ and η on λ and s there is an implicit dependence on these quantities only through the ratio of λ and s.

In order to make the results susceptible of comparison with experiment, the integrals will be evaluated for values of s and m corresponding to hydrogen and helium, of which the masses are 1.66189 and 3.2998×10^{-24} gram per molecule, respectively. The diameter of these molecules will be taken as 2.75 and 2.10×10^{-8} cm, respectively. The phase angles have been determined from Eq. (99) for twelve values of $y = Ks$ between 0.25 and 30.0, and from these phase angles the function $\theta^{(2)}(y)$ of Eq. (97) was determined. The results of this calculation are given in Table I, and a curve showing the

TABLE I.		TABLE II.	
$y = Ks$	$\theta^{(2)}(y)$	λ/s	$P^{(2, \eta)}(1)$
0.000	4.000	∞	12.000
0.25	3.91	1.77	7.98
0.5	3.67	1.02	4.26
1.0	2.77	0.79	3.24
1.5	1.78	.56	2.61
2.0	1.14	.45	2.37
3.0	0.88	.39	2.27
4.0	.80	.21	1.95
5.0	.74	.188	1.90
7.0	.67	.136	1.82
10.0	.61	.125	1.81
20.0	.58	.112	1.77
30.0	.53	.107	1.76
∞	.500	.103	1.74
		.0000	1.500

dependence of the transport cross-sectional area measured in units of the diameter squared as a function of y is given in Fig. 1. It will be observed that $\theta^{(2)}(y)$ and $Q_T^{(2)}(y)$ approach their classical values as y approaches infinity and a value equal to 8 times the classical values as y
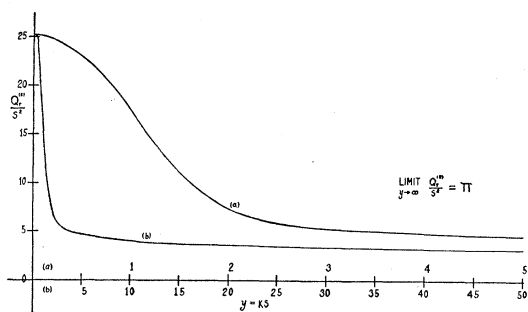
FIG. 1. $Q_T^{(2)}/s^2$ as a function of Ks.

approaches zero. In this respect the transport cross-sectional area differs from the scattering cross section, since the latter, due to the influence of small angle scattering, fails to approach the classical value as y becomes indefinitely large. In the Fermi-Dirac statistics one would find that $\theta^{(2)}(y)$ and $Q_T^{(2)}(y)$ approach the limiting value zero as y approaches zero.

The functions $P^{(l, p)}(\alpha)$ are now determined by numerical integration for a series of values of λ/s (a series of values of the temperature). Actually only the integrals with $l = 2$, $p = 7, 9$ and $\alpha = 1, 4/3$ have been evaluated. The remaining integrals appearing in the four ϵ's have not been determined, since it is certain from the form of these expressions that they are somewhat temperature insensitive, and that, consequently, their classical values may be used. These small quantities, when evaluated quantum-mechanically, approach their classical values for $\lambda/s \ll 1$ and $\lambda/s \gg 1$ (limiting case of very high and very low temperatures), and have a slight maximum or minimum at some intermediate temperature depending on the gas. In the case of hydrogen and helium this temperature is in the neighborhood of 1–3° Abs. The quantities ϵ_1 and ϵ_2, for example, exhibit minima equal to zero for s/λ about equal to $\frac{1}{2}$ (T less than 1° Abs. for H_2 and He) and increase monotonously in both directions achieving their classical values of 0.02273 and 0.01485 for s/λ very large and very small. Also the ratio of integrals appearing directly in Eqs. (92) and (93) are temperature insensitive, but in this particular case it is the difference between these ratios and a constant quantity of the same order of magnitude which is of consequence. The direction of the temperature dependence is such as to make the absolute

magnitude of this difference increase with decreasing temperature, so that, whereas the ratio of the integrals by themselves vary only by a factor 0.3 between either end of the absolute temperature scale and the temperature at which the maximum is reached, this difference in the case of the heat conductivity coefficient varies by a factor 4.0. Thus, the temperature dependence of the density term in κ and η is by no means confined solely to the appearance of λ^3 in these expressions.

Since the four ϵ's are the quantities coming from the second approximation in the solution of the integral equations, their magnitudes give some idea regarding the nature of convergence of the resulting series. The values of ϵ_1 and ϵ_2 have already been given. Classically, and quantum-mechanically for the case of very high and very low temperatures, ϵ_1' and ϵ_2' add corrections to the density term of about 1.4 and 3.0 percent, respectively. Their temperature dependence has not been investigated, but, as already mentioned, this dependence is certainly small. All of the second approximation corrections are therefore small; in fact, they are of the same order of magnitude as the probable errors in the numerical integrations. In the final numerical results these corrections are, therefore, not included. Various analytical relations exist among the integrals $P^{(l, p)}(\alpha)$ which have been helpful as a criterion of the accuracy with which the numerical integration was performed. This accuracy is certainly as good as 3 percent, and is probably somewhat better. Values of all the integrals will not be given, but merely to illustrate the behavior of these functions a set of values of $P^{(2, 7)}(1)$ is given in Table II, and a curve showing the dependence of $P^{(2, 7)}(1)$ on s/λ is given in Fig. 2.

The results of the numerical integration are now introduced into Eqs. (92) and (93), and numerical values of κ and η are found as functions of the temperature and density. These results are tabulated as follows: (a) To show the temperature dependence of the principal term. Actually these results should correspond to the limiting case of small densities. For the sake of comparison the best of the available experimental data are also given, most of the experimental data available having been obtained at
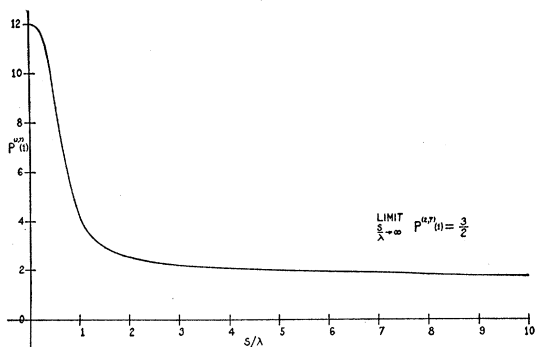
FIG. 2. $P^{(2, \eta)}(1)$ as a function of s/λ.

a pressure of about one atmosphere. These results for the heat conductivity and viscosity coefficients of hydrogen and helium, respectively, appear in Tables III, IV, V and VI. In the case of the viscosity coefficient the calculations leading to these results are a duplication of the published work of Massey and Mohr.[2] These

TABLE III. *Heat conductivity coefficient of hydrogen, κ in ergs cm^{-2} $sec.^{-1}$ $(°C$ $cm^{-1})^{-1}$.*

$T°K$	Experiment	Classical theory	Quantum theory $(\rho=0)$
3.0		1.33×10^3	0.47×10^3
5.0		1.72	0.80
10.0		2.43	1.40
15.4		3.02	1.92
20.9	1.06×10^3	3.52	2.38
73.1	4.83	6.58	5.12
123.1	8.12	8.54	6.91
173.1	11.02	10.13	8.36
223.1	13.6	11.50	9.59
273.1	15.9	12.72	10.86
323.1	17.96	13.83	11.97
373.1	20.04	14.53	

TABLE IV. *Heat conductivity coefficient of helium, κ in ergs cm^{-2} $sec.^{-1}$ $(°C$ $cm^{-1})^{-1}$.*

$T°K$	Experiment	Classical theory	Quantum theory $(\rho=0)$
3.0		1.62×10^3	0.62×10^3
5.0		2.09	1.03
10.0		2.96	1.76
15.0		3.63	2.31
20.9	2.14×10^3	4.28	2.85
73.1	5.55	8.01	6.22
123.1	8.24	10.39	8.31
173.1	10.4	12.32	10.19
223.1	12.3	13.99	11.87
273.1	13.9	15.48	13.49
323.1	15.4	16.83	14.81
373.1	16.7	18.09	

TABLE V. *Viscosity coefficient of hydrogen, η in micropoise.*

$T°K$	Experiment	Classical theory	Quantum theory $(\rho=0)$
3.0		8.7	3.0
5.0		11.2	5.1
10.0		15.8	9.0
15.4	5.7	20.0	12.4
20.6	8.5	23.0	14.9
70.9	31.9	43.0	32.2
89.6	39.2	48.0	37.2
170.2	60.9	66.0	53.4
273.1	84.2	84.0	70.2
296.1	88.2	88.0	73.6

TABLE VI. *Viscosity coefficient of helium, η in micropoise.*

$T°K$	Experiment	Classical theory	Quantum theory $(\rho=0)$
3.0		20.8	7.96
5.0		26.8	13.2
10.0		37.9	22.6
15.0	29.46	46.0	29.6
20.2	35.03	52.0	35.7
75.1	81.5	101.0	81.5
88.8	91.8	110	89.7
170.5	139.2	152	129.4
203.1	156.4	167	142.6
250.3	178.8	184	163.4
273.1	187.0	193	173.3
294.5	199.4	200	180.5

results are given again, however, because they differ from those of Massey and Mohr by an amount exceeding the probable error of the numerical integration. (b) To show the density dependence of the gas coefficients. The results of these calculations appear in Tables VII and VIII for both H_2 and He at temperatures close to the critical temperature. They are tabulated only for one value of the density since the magnitude of the density effect is in first approximation directly proportional to the density. The value of the density chosen corresponds to a value of the degeneracy parameter A equal to 0.1 except at temperatures below the critical value when lower values have been given corresponding to the existence of the vapor phase. Above the critical temperature somewhat higher values of the density than those corresponding to $A=0.1$ may be considered without violating seriously the applicability of the theory. Also, in these tables, for the purpose of comparison with the quantum corrections, appear

TABLE VII. *Density dependence of the viscosity coefficient.*

$T°K$	A	p (atmos.)	$\left(\dfrac{\eta_0-\eta_p}{\eta_0}\right)$ Quantum	$\left(\dfrac{\eta_p-\eta_0}{\eta_0}\right)$ Non-ideal
		Hydrogen		
15.4	0.001	0.068	0.0004	0.0003
20.6	.003	.44	.001	.001
34.0	.1	49.8	.04	.08
		Helium		
3.0	0.03	0.097	0.017	0.0008
5.0	.1	1.15	.05	.006
6.0	.1	1.82	.043	.008
10.0	.1	6.53	.039	.016
15.0	.1	18.0	.037	.03
20.2	.1	37.9	.037	.05

TABLE VIII. *Density dependence of the heat conductivity coefficient.*

$T°K$	A	p (atmos.)	$\left(\dfrac{\kappa_0-\kappa_p}{\kappa_0}\right)$ Quantum	$\left(\dfrac{\kappa_p-\kappa_0}{\kappa_0}\right)$ Non-ideal
		Hydrogen		
20.9	0.003	0.44	0.0003	0.004
34.0	.1	49.8	.009	.27
		Helium		
3.0	0.03	0.096	0.007	0.0026
5.0	.1	1.15	.014	.019
6.0	.1	1.82	.013	.025

the Enskog classical non-ideality corrections discussed in the introduction.

CONCLUSION

Eqs. (92) and (93) are general expressions for the heat conductivity and viscosity coefficients as given by the Einstein-Bose statistics applicable to any gas consisting of molecules whose interaction function is spherically symmetrical. The application of these equations to the rigid sphere type of molecule leads to the following conclusions: (a) As already remarked by Massey and Mohr,[2] the temperature coefficient of viscosity and heat conductivity is not correctly given by the rigid sphere model though the agreement with experiment is considerably better than that given by the classical equations. This improvement is due directly to the increase in the total transport cross-sectional area with

decrease in the relative velocity of the molecules, and can be attributable only in very small part to the density correction. The latter acts in the right direction, but is effective only at extremely low temperatures. At higher temperatures the quantum density correction is not only negligibly small but is more than compensated by the classical non-ideality correction which acts in the opposite direction. (b) The numerical values of κ and η have been calculated for only one value of the diameter s. One can easily show that a somewhat smaller value of s than that used would in the case of both H_2 and He give temperature coefficients in better agreement with experiment, but that the numerical values would at nearly all temperatures be somewhat too large. This result follows from the fact that the principal parts of κ and η depend on s and T only through s^3 and s/λ, and that at a particular temperature the derivative of $s^2P^{(2,\,7)}(1)$ with respect to s is always less than $2sP^{(2,\,7)}(1)$, its value at the two extremes of the temperature scale. A series development in powers of s/λ would be of interest in determining the exact dependence on s, but such a development has not been obtained. (c) The density correction is by no means negligible under suitable conditions, and seems to be susceptible to experimental test. Such a test leading to an experimental verification of the predictions, would be, also, an experimental verification of the statistics.

It is hoped, now, that the general theory may be extended to include mixtures of gases as well as the simple gases. In concluding this paper I wish to gratefully acknowledge my appreciation and indebtedness to Professor W. Heisenberg for the privilege of working in his Institute where the greater part of this study was made, and for his interest in the problem and the consultations which helped so materially in its eventual solution, and to Professor G. E. Uhlenbeck of the University of Michigan who originally suggested the problem, contributed considerably to the formal portions of the theory, and who was throughout a continual source of valuable criticisms and suggestions.

APPENDIX 1

The results of the integration in Part 3, §2 are as follows:

$$a_{11}=\frac{8\pi^3\sqrt{\pi}}{9}\left[P^{(2,\ 7)}(1)+\theta A\frac{8}{3}\sqrt{\frac{2}{3}}\left\{\frac{1}{9}P^{(2,\ 9)}\left(\frac{4}{3}\right)+\frac{2}{3}P^{(2,\ 7)}\left(\frac{4}{3}\right)\right\}\right],$$

$$b_{11}=\frac{16\pi^3\sqrt{\pi}}{45}\left[P^{(2,\ 7)}(1)+\theta A\frac{8}{3}\sqrt{\frac{2}{3}}P^{(2,\ 7)}\left(\frac{4}{3}\right)\right],$$

$$a_{21}=\frac{8\pi^3\sqrt{\pi}}{9}\left[P^{(2,\ 9)}(1)+\frac{7}{2}P^{(2,\ 7)}(1)+\theta A\frac{8}{3}\sqrt{\frac{2}{3}}\left\{\frac{26}{189}P^{(2,\ 11)}\left(\frac{4}{3}\right)+\frac{31}{27}P^{(2,\ 9)}\left(\frac{4}{3}\right)+\frac{14}{9}P^{(2,\ 7)}\left(\frac{4}{3}\right)\right.\right.$$
$$\left.\left.-\frac{4}{945}P^{(4,\ 11)}\left(\frac{4}{3}\right)\right\}\right],$$

$$b_{21}=\frac{8\pi^3\sqrt{\pi}}{45}\left[P^{(2,\ 9)}(1)+\frac{7}{2}P^{(2,\ 7)}(1)+\theta A\frac{8}{3}\sqrt{\frac{2}{3}}\left\{\frac{4}{3}P^{(2,\ 9)}\left(\frac{4}{3}\right)+\frac{7}{3}P^{(2,\ 7)}\left(\frac{4}{3}\right)\right\}\right],$$

$$a_{22}=\frac{8\pi^3\sqrt{\pi}}{9}\left[P^{(2,\ 11)}(1)+7P^{(2,\ 9)}(1)+\frac{77}{4}P^{(2,\ 7)}(1)+\theta A\frac{8}{3}\sqrt{\frac{2}{3}}\left\{\frac{124}{729}P^{(2,\ 13)}\left(\frac{4}{3}\right)+\frac{3260}{1701}P^{(2,\ 11)}\left(\frac{4}{3}\right)\right.\right.$$
$$\left.\left.+\frac{463}{81}P^{(2,\ 9)}\left(\frac{4}{3}\right)+\frac{154}{27}P^{(2,\ 7)}\left(\frac{4}{3}\right)-\frac{4}{405}P^{(4,\ 13)}\left(\frac{4}{3}\right)-\frac{44}{945}P^{(4,\ 11)}\left(\frac{4}{3}\right)\right\}\right],$$

$$b_{22}=\frac{8\pi^3\sqrt{\pi}}{45}\left[\frac{1}{2}P^{(2,\ 11)}(1)+\frac{7}{2}P^{(2,\ 9)}(1)+\frac{301}{24}P^{(2,\ 7)}(1)+\theta A\frac{8}{3}\sqrt{\frac{2}{3}}\left\{\frac{1528}{1701}P^{(2,\ 11)}\left(\frac{4}{3}\right)\right.\right.$$
$$\left.\left.+\frac{320}{81}P^{(2,\ 9)}\left(\frac{4}{3}\right)+\frac{301}{54}P^{(2,\ 7)}\left(\frac{4}{3}\right)-\frac{8}{2835}P^{(4,\ 11)}\left(\frac{4}{3}\right)\right\}\right].$$

Errata: On the Paramagnetic Rotation of Tysonite

J. H. Van Vleck and M. H. Hebb, *University of Wisconsin*
(Phys. Rev. **46**, 17, 1934)

I N the first line of the second column of the abstract column, and everywhere on pages 26–32, the word *trigonal* should be substituted for *triclinic*.