VI. *On the Law of Distribution of Molecular Velocities, and on the Theory of Viscosity and Thermal Conduction, in a Non-uniform Simple Monatomic Gas.*

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Contents.

§ 1. Introduction.

The kinetic theory of gases can be developed accurately only after the distribution of the molecular velocities has been determined. This was done by Maxwell* in the case of a uniform gas, and by means of his well-known law of distribution the pressure and temperature can be precisely expressed in terms of the molecular data. His law does not suffice, however, for the investigation of diffusion, viscosity, or thermal conduction, since these occur only when the gas is *not* uniform in composition, mean velocity, or energy. An accurate theory of these phenomena must be based on the evaluation of the modified velocity-distribution function, a task which for many decades has constituted one of the classical unsolved problems of the kinetic theory.

* Maxwell, 'Scientific Papers,' I., p. 377, II., p. 23. The proofs were unsatisfactory, and have been improved by Boltzmann, Jeans, and others.

In one special case, as MAXWELL found, the actual determination of this function proves to be unnecessary for the purpose mentioned; this is the case of a gas composed of molecules which are point centres of force varying inversely as the fifth power of the distance. The reasons for the peculiarity in this instance are analytical and not physical, and unfortunately for the simplicity of the mathematical theory of gases, MAXWELL's results* for such a gas do not accord with the observed data of actual gases. This particular molecular model is therefore interesting chiefly on theoretical grounds, and it is important to develop the theory for molecules of other types, which may better represent the behaviour of real molecules.

Until recently no progress had been made towards the determination of the velocity-distribution function for a non-uniform gas, beyond a theorem by BOLTZMANN,† who proved that the function must satisfy a certain integral equation. In 1911, ENSKOG‡ applied the method of solution by series to this equation; he determined the form of the function, but without evaluating its coefficients, and his numerical approximations proved far from satisfactory. In 1912, HILBERT§ showed that if the molecules of the gas are rigid elastic spheres, BOLTZMANN's equation may be transformed into a linear orthogonal integral equation of the second kind with a symmetrical kernel, and deduced the existence of a unique solution. LUNN‖ and PIDDUCK¶ have since removed HILBERT's restriction to a special type of molecule, and by means of the transformed equation PIDDUCK has worked out a numerical solution of a special problem on diffusion. These researches are of much importance and interest, especially from the logical standpoint of the pure mathematician. The use of BOLTZMANN's equation, howevever, does not appear to be the best method of actually determining the formal solution; thus PIDDUCK states that the symmetrical kernel of the transformed equation shows no special properties in the case of Maxwellian molecules, and in the numerical solution it appears to be necessary to repeat all the calculations, which are very laborious, in every special case which is worked out.

In 1911, by the assumption of a simple form for the velocity-distribution function, I endeavoured to extend MAXWELL's accurate theory of a gas to molecules of the most general kind compatible with spherical symmetry.** Subsequent acquaintance with ENSKOG's work convinced me of the approximate nature of my results, and during the last few years I have given much thought to the determination of the general velocity-distribution function. By a method which is quite distinct from that based on

* MAXWELL, 'Scientific Papers,' II., p. 23. Molecules which are point centres of force varying inversely as the fifth power of the distance will, for the sake of brevity, be referred to as Maxwellian molecules.

† BOLTZMANN, 'Vorlesungen über Gastheorie,' I., p. 114.

‡ ENSKOG, 'Physikalische Zeitschrift,' XII., 58, 1911.

§ HILBERT, 'Math. Annalen,' 1912, or 'Linearen Integralgleichungen' (Teubner), 1912.

‖ LUNN, 'Bull. Amer. Math. Soc.,' 19, p. 455, 1913.

¶ PIDDUCK, 'Proc. Lond. Math. Soc.,' (2), 15, p. 89, 1915; cf. p. 95 for the statement quoted.

** CHAPMAN, 'Phil. Trans.,' A, vol. 211, p. 433, 1911.

BOLTZMANN'S equation, viz., by the use of the aggregate of the equations of transfer for certain infinite sequences of functions of the molecular velocities, an expression for the velocity-distribution function similar to that found by ENSKOG can be obtained, and general formulæ for the coefficients can be determined. The present paper contains the solution for a gas in which the mean velocity and the temperature vary from point to point, the results being worked out at all completely only for the case of a simple gas; in a later paper I hope to give the solution in the most general terms, so as to yield a complete theory of viscosity, thermal conduction, and diffusion in a composite gas formed of two kinds of spherically symmetrical molecules of any type.

The formulæ obtained by the present method lend themselves to numerical calculation, and are found to converge rapidly. The results for any particular molecular model can be calculated to any desired degree of accuracy; in this paper three special types of molecule have been considered, viz., point centres of force varying inversely as the nth power of the distance, rigid elastic spheres, and rigid elastic attracting spheres. It is found that, for such molecules, the errors in the approximate formulæ for viscosity and thermal conduction which were given in my first paper do not exceed two or three per cent. at most. The detailed numerical results, and comparison with observed data, are given in §§ 10–12.

§ 2. DEFINITION AND PRELIMINARY CONSIDERATION OF THE PROBLEM.

The Nature of the Gas.

§ 2 (A). The gas contemplated in our calculations is monatomic and nearly perfect, "monatomic" implying nothing more than spherical symmetry of the molecules, while "nearly perfect" denotes a certain state as regards density and temperature; this state is such that the molecular paths are sensibly rectilinear for the majority of the time, being altered by mutual encounters, the duration of which is a very small fraction of the average interval *between* two encounters. In these circumstances the number and effect of encounters in which more than two molecules are simultaneously engaged is negligible in comparison with the number and effect of binary encounters.

The gas is supposed to be acted upon by external forces, and the variations of these forces, and of the density, mean velocity, and temperature of the gas, with regard to space and time, are small quantities of the first order at most. In the present paper the density of the gas is supposed such that the mean length of path of a molecule between collisions is small compared with the scale of the space-variation of the above quantities; the modifications of the theory in the case of highly rarefied gases, where the mean free path becomes large, will be dealt with in a future paper. As we are not interested in the mass motion or acceleration of the gas as a whole, but only in the small variations with regard to space and time, it is convenient to imagine that, by the addition of a suitable uniform motion and field

of force to the whole gas, the mean velocity and acceleration at the particular point and time under consideration are reduced to zero, the velocity and acceleration at other points throughout the gas being small, though not actually zero.

Notation.

§ 2 (B) We shall denote the mass of a molecule by m, the number of molecules per unit volume at the point (x, y, z) by ν, the components of external force acting on a molecule at (x, y, z) by (X, Y, Z), the components of the velocity of a typical molecule by (u, v, w), and the components of the mean velocity of the gas at the point (x, y, z) by (u_0, v_0, w_0). The vector difference between the velocity of a typical molecule and the mean velocity (u_0, v_0, w_0) will be called the peculiar velocity of the molecule; we shall denote its components by (U, V, W), so that

$$(1) \qquad U = u - u_0, \quad V = v - v_0, \quad W = w - w_0.$$

The Distribution of Velocities.

§ 2 (C) The distribution of the molecular velocities may be specified by (u_0, v_0, w_0) together with a function $f(U, V, W)$, called the velocity-distribution function, which is defined by the following property: the number of molecules contained within a volume-element $dx\,dy\,dz$ about the point (x, y, z) which possess peculiar velocities whose three components lie respectively between (U, V, W) and $(U+dU, V+dV, W+dW)$ is

$$(2) \qquad \nu f(U, V, W)\, dU\, dV\, dW\, dx\, dy\, dz.$$

Besides being a function of U, V, W, f will depend on the mass m, the absolute temperature T and its space derivatives at the point (x, y, z), and on the space derivatives of (u_0, v_0, w_0), but not on the absolute magnitudes of the latter: for we may evidently impart an arbitrary additional velocity (u', v', w'), to the whole mass of gas without affecting the distribution of the *peculiar* velocities of the molecules at any point. It is therefore legitimate, and it will prove convenient, to suppose that, at the actual point under consideration, $u_0 = v_0 = w_0 = 0$; where u_0, v_0, w_0 occur in any expression which has to be differentiated, however, they must not be made equal to zero till after the differentiation has been performed.

In consequence of the definition of f and of U, V, W, f must satisfy the following equations :—

$$(3) \qquad \iiint f(U, V, W)\, dU\, dV\, dW = 1,$$

$$(4) \qquad \iiint U f(U, V, W)\, dU\, dV\, dW = \iiint V f(U, V, W)\, dU\, dV\, dW$$

$$= \iiint W f(U, V, W)\, dU\, dV\, dW = 0.$$

If Q denotes any function of the velocity components (u, v, w) of a typical molecule, while $\overline{Q}$ denotes its mean value at the point (x, y, z), we have

$$(5) \qquad \overline{Q} = \iiint Q f(\mathsf{U}, \mathsf{V}, \mathsf{W}) \, d\mathsf{U} \, d\mathsf{V} \, d\mathsf{W},$$

in which, for purposes of integration, Q would be expressed in terms of $u_0 + \mathsf{U}$, $v_0 + \mathsf{V}$, $w_0 + \mathsf{W}$ by (2). In the integrals (3) to (5), and elsewhere throughout the paper, integrations with respect to the velocity components are understood to be taken over all values of the variables, from $-\infty$ to $+\infty$.

The equations (4) may, in the notation just introduced, be expressed as follows :—

$$(6) \qquad \overline{\mathsf{U}} = \overline{\mathsf{V}} = \overline{\mathsf{W}} = 0.$$

The Velocity-distribution Function for a Uniform Gas.

§ 2 (D) When the gas is uniform, all the derivatives of T and of (u_0, v_0, w_0) are zero, and f must depend only on m, T, and $(\mathsf{U}, \mathsf{V}, \mathsf{W})$. It has, in fact, been shown by MAXWELL and others* that

$$(7) \qquad f = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2)},$$

where

$$(8) \qquad \frac{1}{2h} = \mathrm{RT},$$

and R is the universal gas constant in the characteristic equation of a gas :

$$(9) \qquad p = \mathrm{R}\nu\mathrm{T}.$$

The Distribution Function for a Non-uniform Gas.

§ 2 (E) When the gas is slightly non-uniform, f will differ slightly from the value given by (7), which we shall denote by f_0 : we may therefore write

$$(10) \quad f(\mathsf{U}, \mathsf{V}, \mathsf{W}) = f_0(\mathsf{U}, \mathsf{V}, \mathsf{W})\{1 + \mathrm{F}(\mathsf{U}, \mathsf{V}, \mathsf{W})\} = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2)}\{1 + \mathrm{F}(\mathsf{U}, \mathsf{V}, \mathsf{W})\}.$$

The function F will be of the same order of magnitude as the variations of temperature and velocity in the gas ; these space derivatives we shall regard as being of the first order, and as we shall neglect second order quantities throughout our work, no products of derivatives will occur in F. Hence, since F vanishes when the variations in the gas are zero, it must be a linear function of the space derivatives of T and (u_0, v_0, w_0), with no term independent of these derivatives. The coefficients will be functions of m, T, and U, V, W.

Clearly the form of F cannot depend upon any special choice of axes of reference (these are throughout taken to be mutually perpendicular), so that F is an invariant

* *Cf.* JEANS' 'Dynamical Theory of Gases.'

with respect to any orthogonal transformation of the co-ordinate axes. This places some restriction upon the possible modes of occurrence in F of (U, V, W) and of the space derivatives of T and (u_0, v_0, w_0), though not, of course, on the scalar quantities m and T. It is easy to see that the most general invariant function of the quantities involved in F must be compounded of the following elementary invariants :—

$$(11) \qquad\qquad C^2 \equiv U^2 + V^2 + W^2,$$

$$(12),\ (13) \qquad S \equiv \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}, \qquad \nabla^2 T \equiv \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) T,$$

$$(14) \qquad\qquad DT \equiv \left(U\frac{\partial}{\partial x} + V\frac{\partial}{\partial y} + W\frac{\partial}{\partial z}\right) T,$$

$$(15) \quad S' \equiv U^2\frac{\partial u_0}{\partial x} + V^2\frac{\partial v_0}{\partial y} + W^2\frac{\partial w_0}{\partial z} + VW\left(\frac{\partial w_0}{\partial y} + \frac{\partial v_0}{\partial z}\right) + WU\left(\frac{\partial u_0}{\partial z} + \frac{\partial w_0}{\partial x}\right) + UV\left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y}\right),$$

together with derivatives of the last four expressions formed by operating on them any number of times by the invariant differential operators ∇^2 and D, in the notation of (13) and (14).

[*January 15, 1916.*—Except in the case of highly rarefied gases, which were expressly excluded in § 2 (A), only the derivatives of the first *order* actually occur in F, to the present degree of accuracy. The reasons for this will perhaps be more clearly apparent after reading § 11, but the following considerations will elucidate the point. Whatever derivatives are contained in F must (§ 11) appear either in the equation of pressure or the equation of energy, so that, if the ordinary equations of viscosity and thermal conduction are to hold good, only the first-order space derivatives of temperature and mean velocity can be present; otherwise the ordinary coefficients of viscosity and conduction do not exist. In actual gases at normal densities the ordinary equations are shown by experiment to be valid; they fail, however, in highly rarefied gases because the terms in F which contain second-order differentials of T, u_0, v_0, w_0 are in this case comparable with those containing derivatives of the first order, as will be seen in detail in the future paper mentioned in § 2 (A). The coefficients of the first and second order derivatives respectively contain (λ/l) and $(\lambda/l)^2$, where λ is the mean free path of a molecule and l is comparable with the scale of length within which the temperature and mean velocity vary appreciably; except in rarefied gases $(\lambda/l)^2$ can be neglected in comparison with (λ/l). The same inferences can be made also (*cf.* § 6) from the equations of transfer of § 3.

For the present paper it is therefore sufficient (and it is convenient) to write down the following form of F forthwith :—

$$(16) \qquad F = \left(U\frac{\partial T}{\partial x} + V\frac{\partial T}{\partial y} + W\frac{\partial T}{\partial z}\right) P_1(C^2) + SP_2(C^2) + S'P_3(C^2),$$

this being the only way in which the first-order derivatives can occur in F, in order that F may be an invariant.

Here $P_1(C^2)$, $P_2(C^2)$, $P_3(C^2)$ denote certain undetermined functions of U, V,   in which these variables appear only in the form $U^2 + V^2 + W^2$ or C^2. The first term of F is evidently of odd degree in U, V, W combined, and the second and third are of even degree; it is convenient to denote them by O(U, V, W) and E(U, V, W), when we wish to refer to the odd or even part of F separately.]

It is easy to see that, in a uniform gas, f_0 satisfies the necessary conditions (3), (4). In the non-uniform case these conditions require F to satisfy the equations

$$(17) \qquad \iiint f_0 F \, dU \, dV \, dW = 0,$$

$$(18) \qquad \iiint U f_0 F \, dU \, dV \, dW = \iiint V f_0 F \, dU \, dV \, dW = \iiint W f_0 F \, dU \, dV \, dW = 0.$$

Clearly the odd part O(U, V, W) of F satisfies (17), and the even part E(U, V, W) satisfies (18), but not *vice versâ*, so that these equations place certain restrictions on O and E.

§ 3. The Equation of Transfer of Molecular Properties.

§ 3 (A) The rate of change of $\nu \overline{Q}$, the aggregate value of Q(u, v, w) per unit volume, may be analysed into three parts, viz., that due to molecular encounters (which we denote by ΔQ), that due to the passage of molecules in or out of the volume-element considered, and that due to the action of the external forces. The equation expressing this analysis may readily be shown* to be

$$(19) \qquad \frac{\partial}{\partial t}(\nu \overline{Q}) = \Delta Q - \sum_{x, y, z} \left[\frac{\partial}{\partial x}(\nu \overline{uQ}) - \frac{\nu}{m} X \left(\overline{\frac{\partial Q}{\partial u}} \right) \right].$$

We may define ΔQ by the statement that $(\Delta Q) \, dx \, dy \, dz \, dt$ is the change produced by molecular encounters during time dt in the sum ΣQ taken over all the molecules in the volume-element $dx \, dy \, dz$: evidently $\Sigma Q = \nu \overline{Q} \, dx \, dy \, dz$.

If in (19) we make Q equal to unity, in which case ΔQ is clearly zero, the equation becomes

$$\frac{\partial \nu}{\partial t} = -\left(\frac{\partial \nu u_0}{\partial x} + \frac{\partial \nu v_0}{\partial y} + \frac{\partial \nu w_0}{\partial z} \right)$$

$$= -\nu \left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right) - \left(u_0 \frac{\partial \nu}{\partial x} + v_0 \frac{\partial \nu}{\partial y} + w_0 \frac{\partial \nu}{\partial z} \right),$$

which is the equation of continuity.

* *Cf.* Jeans' 'Dynamical Theory of Gases.'

Except under the differential sign we shall write $u = \mathsf{U}$, $v = \mathsf{V}$, $w = \mathsf{W}$, since we are supposing that $u_0 = v_0 = w_0 = 0$ at the point (x, y, z). The last equation consequently reduces to

$$(20) \qquad \frac{1}{\nu}\frac{\partial \nu}{\partial t} = -\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right).$$

In taking mean values of functions of U, V, W, as in (5), we shall neglect the part F in the velocity-distribution function f, in cases where the mean value is to be differentiated or multiplied by a small factor, since the resulting error is only of the second order.* Thus, in such cases, we shall write

$$(21) \qquad \overline{\mathsf{U}^2\mathsf{C}^{2s}} = \tfrac{1}{3}\overline{\mathsf{C}^{2(s+1)}}, \quad \overline{\mathsf{U}^4\mathsf{C}^{2(s-1)}} = \tfrac{1}{5}\overline{\mathsf{C}^{2(s+1)}}, \quad \overline{\mathsf{V}^2\mathsf{W}^2\mathsf{C}^{2(s-1)}} = \tfrac{1}{15}\overline{\mathsf{C}^{2(s+1)}},$$

$$(22) \qquad \overline{\mathsf{C}^{2s}} = 1 . 3 . 5 \ldots (2s+1)\,(2hm)^{-s},$$

while, if either p, q or r is odd,

$$(23) \qquad \overline{\mathsf{U}^p\mathsf{V}^q\mathsf{W}^r} = 0.$$

Since the equation of transfer involves derivatives of the first order only, it is sufficient, whenever the mean value of a function of u, v, w is to be differentiated, to expand it by Taylor's theorem in terms of u_0, v_0, w_0, so far as the *first* degree only; if, then, the coefficient of u_0, v_0, w_0 is of type (23), the corresponding term may be omitted altogether.

$$\textit{Case I.} \quad \mathrm{Q} = u\,(u^2 + v^2 + w^2)^s.$$

§ 3 (B) When $\mathrm{Q} = u\,(u^2 + v^2 + w^2)^s$, according to the principles just laid down we have

$$\frac{\partial}{\partial x}(\nu u \overline{\mathrm{Q}}) = \frac{\partial}{\partial x}\,\nu\left(\overline{\mathsf{U}^2\mathsf{C}^{2s}} + 2u_0\overline{\mathsf{U}\mathsf{C}^{2s}} + 2s\overline{\mathsf{U}^2\,(u_0\mathsf{U} + v_0\mathsf{V} + w_0\mathsf{W})\,\mathsf{C}^{2(s-1)}} + \ldots\right)$$

$$= \tfrac{1}{3}\frac{\partial}{\partial x}(\nu\overline{\mathsf{C}^{2(s+1)}}) = \frac{1 . 3 . 5 \ldots (2s+3)}{3}\frac{\partial}{\partial x}\,\nu\left(\frac{1}{2hm}\right)^{s+1}$$

$$= \frac{1 . 3 . 5 \ldots (2s+3)}{3}\left(\frac{1}{2hm}\right)^s\left\{\frac{1}{2hm}\frac{\partial \nu}{\partial x} + \nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right) + s\nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right)\right\},$$

$$\frac{\partial}{\partial y}(\nu v \overline{\mathrm{Q}}) = 0, \qquad \frac{\partial}{\partial z}(\nu w \overline{\mathrm{Q}}) = 0,$$

* Except in gases of very low density.

neglecting in each case quantities of the second order. Since $\overline{Q}$ is of the first order, to the same degree of accuracy as in the above equations, we have

$$\frac{\partial}{\partial t}(\nu\overline{Q}) = 0.$$

Again, writing $u = \mathsf{U}$, $v = \mathsf{V}$, $w = \mathsf{W}$ after differentiation, we have

$$\overline{\left(\frac{\partial Q}{\partial u}\right)} = \overline{C^{2s}} + 2s\overline{U^2 C^{2(s-1)}} = \tfrac{1}{3}(2s+3)\overline{C^{2s}} = \frac{1 \cdot 3 \cdot 5 \ldots (2s+3)}{3}\left(\frac{1}{2hm}\right)^s.$$

Here we have omitted $\overline{UVC^{2(s-1)}}$ and $\overline{UWC^{2(s-1)}}$, since when multiplied by X, which is of the first order, the result is of the second order, and hence negligible. Similarly

$$\overline{\left(\frac{\partial Q}{\partial v}\right)} = 0, \qquad \overline{\left(\frac{\partial Q}{\partial w}\right)} = 0.$$

The equation of transfer consequently takes the form

$$(24) \quad \Delta\mathsf{U}C^{2s} = \frac{1 \cdot 3 \cdot 5 \ldots (2s+3)}{3}\left(\frac{1}{2hm}\right)^s\left\{\frac{1}{2hm}\frac{\partial \nu}{\partial x} + \nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right) - \frac{\nu}{m}X + s\nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right)\right\}.$$

When $s = 0$, this becomes

$$\Delta\mathsf{U} = \frac{1}{2hm}\frac{\partial \nu}{\partial x} + \nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right) - \frac{\nu}{m}X.$$

Now $m\Delta\mathsf{U}$ is the rate of change of momentum per unit volume due to the molecular encounters, and, since action and re-action are equal and opposite, this change is zero. Hence we have, remembering that $(2h)^{-1} = \mathsf{R}\mathsf{T} = p/\nu$,

$$(25) \qquad \nu X = \frac{1}{2h}\frac{\partial \nu}{\partial x} + \nu\frac{\partial}{\partial x}\left(\frac{1}{2h}\right) = \frac{\partial}{\partial x}\left(\frac{\nu}{2h}\right) = \frac{\partial p}{\partial x},$$

which is one of the equations of pressure of the gas.

On substituting the value of X given by (25) into (24), the latter may be written

$$(26) \qquad \frac{(2hm)^{s+1}}{1 \cdot 3 \cdot 5 \ldots (2s+3)s}\frac{3}{\nu}\Delta\mathsf{U}C^{2s} = \frac{1}{\mathsf{T}}\frac{\partial \mathsf{T}}{\partial x},$$

where we have used the equation (cf. 8)

$$2hm\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right) = \frac{1}{\mathsf{T}}\frac{\partial \mathsf{T}}{\partial x}.$$

There are two equations similar to (26) giving $\Delta\mathsf{V}C^{2s}$ and $\Delta\mathsf{W}C^{2s}$ in terms of $\partial \mathsf{T}/\partial y$ and $\partial \mathsf{T}/\partial z$.

Case II. $Q = u^2 (u^2 + v^2 + w^2)^s$.

§ 3 (C) Making approximations and reductions as in Case I., we have

$$\frac{\partial}{\partial t}(\nu \overline{Q}) = \frac{\partial}{\partial t}\left(\tfrac{1}{3}\nu \overline{C^{2(s+1)}}\right) = \frac{1 \cdot 3 \cdot 5 \ldots (2s+3)}{3}\frac{\partial}{\partial t}\nu\left(\frac{1}{2hm}\right)^{s+1}$$

$$= \frac{1 \cdot 3 \cdot 5 \ldots (2s+3)}{3}\nu\left(\frac{1}{2hm}\right)^{s+1}\left\{\frac{1}{\nu}\frac{\partial \nu}{\partial t} + (s+1)\frac{1}{T}\frac{\partial T}{\partial t}\right\},$$

$$\frac{\partial}{\partial x}(\nu \overline{uQ}) = \frac{\partial}{\partial x}\nu\left\{\overline{U^3 C^{2s}} + 3u_0\overline{U^2 C^{2s}} + 2s\overline{U^3(u_0 U + v_0 V + w_0 W)C^{2(s-1)}} + \ldots\right\}$$

$$= \frac{\partial}{\partial x}\nu u_0\left(\overline{C^{2(s+1)}} + \tfrac{2}{5}s\overline{C^{2(s+1)}}\right) = \frac{1 \cdot 3 \cdot 5 \ldots (2s+5)}{5}\nu\left(\frac{1}{2hm}\right)^{s+1}\frac{\partial u_0}{\partial x},$$

$$\frac{\partial}{\partial y}(\nu \overline{vQ}) = \frac{\partial}{\partial y}\nu\left\{\overline{U^2 V C^{2s}} + v_0\overline{U^2 C^{2s}} + 2s\overline{U^2 V(u_0 U + v_0 V + w_0 W)C^{2(s-1)}} + \ldots\right\}$$

$$= \frac{\partial}{\partial y}\nu v_0\left(\tfrac{1}{3}\overline{C^{2(s+1)}} + \tfrac{2}{15}s\overline{C^{2(s+1)}}\right) = \frac{1 \cdot 3 \cdot 5 \ldots (2s+5)}{15}\nu\left(\frac{1}{2hm}\right)^{s+1}\frac{\partial v_0}{\partial y},$$

$$\frac{\partial}{\partial z}(\nu \overline{wQ}) = \frac{1 \cdot 3 \cdot 5 \ldots (2s+5)}{15}\nu\left(\frac{1}{2hm}\right)^{s+1}\frac{\partial w_0}{\partial z}.$$

$$\left(\overline{\frac{\partial Q}{\partial u}}\right) = 2\overline{UC^{2s}} + 2s\overline{U^3 C^{2(s-1)}} = 0, \qquad \left(\overline{\frac{\partial Q}{\partial v}}\right) = 0, \qquad \left(\overline{\frac{\partial Q}{\partial w}}\right) = 0.$$

The equation of transfer may therefore be written

$$(27) \qquad \Delta \overline{U^2 C^{2s}} = \frac{1 \cdot 3 \cdot 5 \ldots (2s+3)}{15}\nu\left(\frac{1}{2hm}\right)^{s+1}\left[5\left\{\frac{1}{\nu}\frac{\partial \nu}{\partial t} + (s+1)\frac{1}{T}\frac{\partial T}{\partial t}\right\}\right.$$

$$\left. + (2s+5)\left(3\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right)\right].$$

When $s = 0$, this becomes

$$\Delta \overline{U^2} = \frac{\nu}{2hm}\left[\frac{1}{\nu}\frac{\partial \nu}{\partial t} + \frac{1}{T}\frac{\partial T}{\partial t} + 3\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right].$$

If to this be added two similar equations giving $\Delta \overline{V^2}$ and $\Delta \overline{W^2}$, on the left-hand side we have $\Delta(\overline{U^2 + V^2 + W^2})$, which is the rate of change of molecular energy due to encounters; by the principle of conservation of energy this is zero, so that

$$3\left(\frac{1}{\nu}\frac{\partial \nu}{\partial t} + \frac{1}{T}\frac{\partial T}{\partial t}\right) + 5\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right) = 0,$$

or, by (20),

$$(28) \qquad \frac{1}{T}\frac{\partial T}{\partial t} = -\tfrac{2}{3}\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right) = \tfrac{2}{3}\frac{1}{\nu}\frac{\partial \nu}{\partial t} = \tfrac{2}{3}\frac{1}{\rho}\frac{\partial \rho}{\partial t}.$$

On integration this gives $T\rho^{-2/3} = $ constant, or, since $p = R\nu T$, it is equivalent to $p\rho^{-5/3} = $ constant; this is the law of adiabatic expansion for a gas which possesses only translational energy.

Eliminating $\dfrac{1}{\nu}\dfrac{\partial \nu}{\partial t}$ and $\dfrac{1}{T}\dfrac{\partial T}{\partial t}$ from (27) by means of (20) and (28), we have

(29)
$$\Delta U^2 C^{2s} = \frac{1.3.5\ldots(2s+3)}{15}\nu\left(\frac{1}{2hm}\right)^{s+1}\left[-\tfrac{5}{3}(2s+5)\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)\right.$$
$$\left.+(2s+5)\left(3\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)\right]$$
$$= \frac{1.3.5\ldots(2s+5)}{45}2\nu\left(\frac{1}{2hm}\right)^{s+1}\left(2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z}\right),$$

or

(30)
$$\frac{(2hm)^{s+1}}{1.3.5\ldots(2s+5)}\frac{45}{2\nu}\Delta U^2 C^{2s} = 2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z}.$$

By transformation of axes, or otherwise, we may deduce the equation

(31)
$$\frac{(2hm)^{s+1}}{1.3.5\ldots(2s+5)}\frac{45}{2\nu}\Delta 2VWC^{2s} = 3\left(\frac{\partial v_0}{\partial z}+\frac{\partial w_0}{\partial y}\right).$$

§ 4. THE EFFECT OF MOLECULAR ENCOUNTERS.

§ 4 (A) In this paper our primary concern is with simple gases containing molecules of one kind only; the difficulties are much enhanced when molecules of two kinds are present, especially as regards the equations of transfer, and the final determination of the coefficients of F when ΔQ has been calculated. These matters will be dealt with in a future paper, on diffusion and the general theory of composite gases. In the calculation of ΔQ, however, there is scarcely any advantage in making the restriction to one kind of molecule only, and it is convenient to carry out the calculation for a composite gas in order that the results may be quoted without repetition in the later, more general, investigation.

The notation of § 2 may be adapted to the case of a composite gas without further change than the addition of suffixes 1, 2 to denote to which group of molecules a symbol such as ν, m, U, V, W, f, F refers. The mean velocity of the two groups will be supposed the same, so that (u_0, v_0, w_0) is the same for both, either separately or together; similarly, their temperature or mean energy, and their relative densities (ν_1/ν_2) are supposed constant. All the remarks made concerning f and F hold both for f_1 and F_1, and f_2 and F_2, these being functions respectively of (U_1, V_1, W_1) and (U_2, V_2, W_2); they may each now be expected to involve $\nu_1 : \nu_2$ and $m_1 : m_2$ in addition to the quantities mentioned in § 2. A further important consideration which did not arise there is that f_1 and f_2, or F_1 and F_2 are *similar*,

in the sense that either may be obtained from the other by interchanging the suffixes 1, 2.

Notation for an Encounter.

§ 4 (B) Before proceeding to the actual consideration of the dynamics of an encounter between two molecules m_1, m_2, it is convenient to explain the notation to be used. The symbols m_0, μ_1, μ_2, μ_{12}, and μ_{21} are defined as follows :—

$$(32) \qquad\qquad m_0 \equiv m_1 + m_2,$$

$$(33) \qquad\qquad \mu_1 = m_1/m_0, \qquad \mu_2 = m_2/m_0,$$

$$(34) \qquad \mu_{12} = m_1/m_2 = \mu_1/\mu_2, \qquad \mu_{21} = m_2/m_1 = \mu_2/\mu_1,$$

so that

$$(35) \qquad\qquad \mu_1 + \mu_2 = 1, \qquad \mu_1{}^2 + \mu_2{}^2 = 1 - 2\mu_1\mu_2,$$

$$(36) \qquad\qquad \mu_{12}\mu_{21} = 1.$$

Velocities will be represented either by their x, y, z components or in vector notation. The components of the actual velocities of the molecules will be written (U, V, W), while those of other velocities, such as the velocity of the mass-centre G, or the relative velocity, will be written (X, Y, Z). The amplitude of a velocity will be denoted by C, and the vector itself by the same symbol in small type with a bar beneath, viz., $\underline{c}$.

The velocities of the molecules m_1, m_2, and of G will be distinguished by the respective suffixes 1, 2, 0, while the suffix R, similarly, will indicate reference to the molecular velocities *relative* to G or to one another. As regards time, square brackets enclosing a symbol, such as $[X_0]$, $[\underline{c}_1]$, will indicate reference to some particular (arbitrary) instant during the encounter; a symbol without brackets but with an accent (') will refer to any instant after the encounter,* while when there is neither bracket nor accent it will refer to any instant before the encounter.

Analysis of the Motions in an Encounter.

§ 4 (C) In the above notation the initial and final molecular velocities are respectively $\underline{c}_1$, $\underline{c}_2$ and $\underline{c}'_1$, $\underline{c}'_2$, or (U_1, V_1, W_1), (U_2, V_2, W_2) and (U'_1, V'_1, W'_1), (U'_2, V'_2, W'_2); also

$$(37) \qquad\qquad C^2 = U^2 + V^2 + W^2,$$

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* That is, any instant after the molecules have separated beyond the distance (which in actual gases is, at most, very small) at which their inter-action is appreciable; the words "before the encounter" are to be interpreted in a similar sense. In this sense the velocities of the molecules before and after the encounter are definite and constant.

where C, U, V, W all have the same suffix 1 or 2, with or without an accent ($'$). Similarly, the mass-centre G has the velocity c_0 or (X_0, Y_0, Z_0), and since (by the principle of conservation of momentum) this remains invariable throughout the encounter,[*] we have

$$(38) \qquad c_0 = \mu_1 c_1 + \mu_2 c_2 = \mu_1 c'_1 + \mu_2 c'_2 = \mu_1 [c_1] + \mu_2 [c_2],$$

or

$$c_0 = c'_0 = [c_0].$$

Since, by (38),

$$(39) \qquad m_1 \{[c_1] - [c_0]\} = -m_2 \{[c_2] - [c_0]\} = m_0 \mu_1 \mu_2 \{[c_1] - [c_2]\} \equiv m_0 (\mu_1 \mu_2)^{1/2} [c_R],$$

where $[c_R]$ is *defined* by the equation

$$(40) \qquad [c_R] \equiv (\mu_1 \mu_2)^{1/2} \{[c_1] - [c_2]\},$$

we see that the momentum of the molecules, relative to G, is equal in magnitude but opposite in direction in the two cases, its value being $\pm m_0 (\mu_1 \mu_2)^{1/2} [c_R]$. The relative velocity of the two molecules is, by (40), equal to $(\mu_1 \mu_2)^{-1/2} [c_R]$; this varies throughout the encounter, owing to the inter-action of the molecules; its initial and final values are given by

$$(41) \qquad c_R = (\mu_1 \mu_2)^{-1/2} (c_1 - c_2), \qquad c'_R = (\mu_1 \mu_2)^{-1/2} (c'_1 - c'_2),$$

which are special cases of (40).

Equations (38), (41), and the reciprocal equations

$$(42) \qquad c_1 = c_0 + \mu_{21}^{1/2} c_R \qquad c_2 = c_0 - \mu_{12}^{1/2} c_R,$$

$$(43) \qquad c'_1 = c_0 + \mu_{21}^{1/2} c'_R \qquad c'_2 = c_0 - \mu_{12}^{1/2} c'_R,$$

indicate that c, c_2 or c'_1, c'_2 are equivalent to c_0, c_R or c_0, c'_R, as specifications of the initial or final velocities of the molecules. Hence the problem of determining the final velocities of two molecules after an encounter, in terms of the initial velocities and whatever further independent variables are necessary to define the encounter, is equivalent to the determination of c'_R in terms of c_R and the variables of the encounter. Thus, in consequence of the invariability of c_0, the velocity of the mass-centre, we need only consider the motion relative to G, *i.e.*, the motion referred to uniformly moving axes with G as origin.

* We here suppose that the effect of the external forces during the brief interval of encounter is negligible; this is legitimate if the gas is "nearly perfect" (*cf.* § 2).

The Motion Relative to the Mass-centre.

§ 4 (D) Relative to these axes the molecules are initially moving along parallel lines with equal and opposite momenta $\pm m_0 (\mu_1\mu_2)^{1/2} c_R$, by (39). The plane containing these two lines is clearly the plane in which the inter-action and motion of the molecules will take place during the encounter. It is parallel to c_R, but its orientation ϵ about this direction is independent of c_0, c_R, *i.e.*, it is one of the additional variables needed to specify the encounter, and, similarly, so also is the perpendicular distance p between the initial lines of relative motion. It is convenient to measure ϵ from the plane containing c_0 and c_R.

In the plane of relative motion so defined, the molecules describe orbits which are similar to one another (the origin G being the centre of similitude), and symmetrical about the line of apses (*i.e.*, points of closest approach). Each orbit has two asymptotes, one being the initial, the other the final line of motion ; the distance between the pair of final asymptotes is clearly equal to that, p, between the initial asymptotes. The angle χ_{12} between the two asymptotes of either orbit measures the deflection of the relative motion due to the encounter; for molecules of given types it is a function of p and C_R* only, the nature of the function depending on the law of inter-action between a molecule m_1 and a molecule m_2. We shall find it convenient, for the sake of generality as well as of brevity, to retain χ_{12} as an unspecified function of p and C_R in our equations ; the special properties of the molecules under consideration are, throughout our work, involved *only* through the dependence of χ_{12} on p and C_R.

It is easy to see that the *magnitude* of the relative velocity $(\mu_1\mu_2)^{-1/2} c_R$ is unaltered by the encounter, *i.e.*,

$$(44) \qquad\qquad C_R = C'_R :$$

for by the equation of energy we have

$$(45) \qquad \tfrac{1}{2}(m_1 C_1^2 + m_2 C_2^2) = \tfrac{1}{2}(m_1 C'^2_1 + m_2 C'^2_2) = \tfrac{1}{2}m_0(C_0^2 + C_R^2) = \tfrac{1}{2}m_0(C_0^2 + C'^2_R)$$

by (42) and (43).

The Velocities in Spherical Polar Co-ordinates.

§ 4 (E) The above analysis of a molecular encounter may be made clearer by the following figure, in which x, y, z, c_0, c_R, c'_R are the points in which a unit sphere

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* That is, on p and on the *amplitude* C_R of the vector c_R.

centred at O is cut by radii parallel respectively to the co-ordinate axes and to $\underline{c}_0$, $\underline{c}_R$, and $\underline{c}'_R$. Then we have

(45A)
$$\epsilon = c_0 c_R c'_R, \qquad \chi_{12} = c_R O c'_R.$$
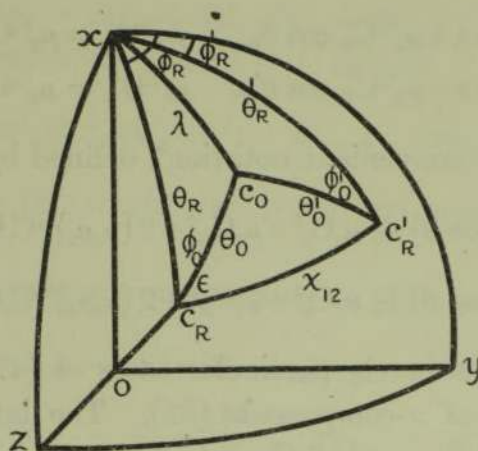
It is convenient also to use certain spherical polar co-ordinates, as follows, taking Ox, Oxy as initial line and plane for $\underline{c}_R$ and $\underline{c}'_R$, and Oc_R, $Oc_R x$, or Oc'_R, $Oc'_R x$ for $\underline{c}_0$. Thus we write

(46) $\qquad \theta_R = c_R Ox, \qquad \theta'_R = c'_R Ox, \qquad \theta_0 = c_0 Oc_R, \qquad \theta'_0 = c_0 Oc'_R, \qquad \lambda = c_0 Ox,$

(47) $\qquad\qquad \phi_R = c_R xy, \qquad \phi'_R = c'_R xy, \qquad \phi_0 = c_0 c_R x, \qquad \phi'_0 = c_0 c'_R x.$

Evidently we have

(48) $$\cos \theta'_0 = \cos \theta_0 \cos \chi_{12} + \sin \theta_0 \sin \chi_{12} \cos \epsilon,$$

(49) $$\cos \theta'_R = \cos \theta_R \cos \chi_{12} + \sin \theta_R \sin \chi_{12} \cos \overline{\epsilon + \phi_0},$$

(50) $$\cos \lambda = \cos \theta_0 \cos \theta_R + \sin \theta_0 \sin \theta_R \cos \phi_0,$$
$$= \cos \theta'_0 \cos \theta'_R + \sin \theta'_0 \sin \theta'_R \cos \phi'_0.$$

Expressions for the Velocities After an Encounter.

§ 4 (F) We have thus indicated how the final molecular velocities $\underline{c}'_1$, $\underline{c}'_2$ are to be determined (*cf.* 43) in terms of the initial velocities $\underline{c}_1$, $\underline{c}_2$ or $\underline{c}_0$, $\underline{c}_R$ together with p and ϵ (these being the eight independent variables of an encounter). This has been done by showing how $\underline{c}'_R$ depends upon $\underline{c}_R$, p and ϵ; it has in fact been shown that the spherical polar co-ordinates of $\underline{c}'_R$, referred to $\underline{c}_R$ and the plane $\underline{c}_0$, $\underline{c}_R$ as initial line and plane, are C_R, χ_{12} (a function of p and C_R) and ϵ. Hence we may at once write down

the expressions for the initial and final velocities and velocity components in terms of c_0, c_R, p and ϵ, as follows :—

$$(51) \quad \mu_1 C_1^2 = \Theta_{12}(\cos\theta_0), \quad \mu_2 C_2^2 = \Theta_{21}(\cos\theta_0), \quad \mu_1 C'^2_1 = \Theta_{12}(\cos\theta'_0), \quad \mu_2 C'^2_2 = \Theta_{21}(\cos\theta'_0),$$

$$(52) \quad \begin{cases} \mu_1^{1/2} U_1 = \mu_1^{1/2} C_0 \cos\lambda + \mu_2^{1/2} C_R \cos\theta_R, & \mu_2^{1/2} U_2 = \mu_2^{1/2} C_0 \cos\lambda - \mu_1^{1/2} C_R \cos\theta_R, \\ \mu_1^{1/2} U'_1 = \mu_1^{1/2} C_0 \cos\lambda + \mu_2^{1/2} C_R \cos\theta'_R, & \mu_2^{1/2} U'_2 = \mu_2^{1/2} C_0 \cos\lambda - \mu_1^{1/2} C_R \cos\theta'_R, \end{cases}$$

where we have adopted the convenient notation* defined by

$$(53) \quad \begin{cases} \Theta_{12}(\cos\theta) \equiv \mu_1 C_0^2 + \mu_2 C_R^2 + 2(\mu_1\mu_2)^{1/2} C_0 C_R \cos\theta, \\ \Theta_{21}(\cos\theta) \equiv \mu_2 C_0^2 + \mu_1 C_R^2 - 2(\mu_1\mu_2)^{1/2} C_0 C_R \cos\theta. \end{cases}$$

Equations (51) to (53) are merely particular cases of (42), (43), expressed in terms of amplitudes (51, 53) and of x-components (52). The latter might also have been written in terms of the components of C_0 and C_R, as, for example,

$$(54) \quad U'_1 = X_0 + \mu_{21}^{1/2} X'_R = X_0 + \mu_{21}^{1/2} \{ X_R \cos\chi_{12} + (Y_R^2 + Z_R^2)^{1/2} \sin\chi_{12} \cos(\epsilon + \phi_0) \},$$

by (49), writing (X_0, Y_0, Z_0), (X_R, Y_R, Z_R), (X'_R, Y'_R, Z_R'), for the components of c_0, c_R c'_R. Equations similar to (53), (54) may easily be written down also for the y and z components of the velocities.

The Dependence of U'_1, V'_1, W'_1 on χ_{12}.

§ 4 (G) From (51) and (54) it is clear that any function $Q_1(U'_1, V'_1, W'_1)$ of U'_1, V'_1, W' is a function of U_1, V_1, W_1, U_2, V_2, W_2, p and ϵ, or of U_1, V_1, W_1, U_2, V_2, W_2, χ_{12} and ϵ, since p is involved only through χ_{12} (though χ_{12} is not entirely independent of the preceding six variables, since it depends upon C_R). If $Q_1(U'_1, V'_1, W'_1)$ be regarded as a function of χ_{12}, when χ_{12} is made equal to zero it reduces to $Q_1(U_1, V_1, W_1)$ simply : this may be seen either from (51)–(54) or, still more readily, from the figure on p. 293, since when $\chi_{12} = 0$, c'_R becomes identical with c_R, and hence by (42), (43), so also does c'_1 with c_1.

Transformation of Co-ordinates.

§ 4 (H) In § 5 we require the Jacobian of transformation

$$J \equiv \frac{\partial(U'_1, V'_1, W'_1, U'_2, V'_2, W'_2)}{\partial(U_1, V_1, W_1, U_2, V_2, W_2)}$$

between the initial and final velocity components, p and ϵ being constant. Since the motion during an encounter is reversible, the relation between the two sets of velocity

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* In § 7, for the sake of brevity, we shall write Θ_{12}, Θ_{21}, Θ'_{12}, Θ'_{21} respectively for $\Theta_{12}(\cos\theta_0)$, $\Theta_{21}(\cos\theta_0)$, $\Theta_{12}(\cos\theta'_0)$, and $\Theta_{21}(\cos\theta'_0)$.

components is reciprocal, so that $J = \pm 1$. It may readily be seen that the positive sign is the correct one, by considering a particular case of variation, say $dU_1 = dU_2 = dU$, $dV_1 = dV_2 = dV$, $dW_1 = dW_2 = dW$. This is equivalent to the addition of a small velocity (dU, dV, dW) to the whole system; obviously this will reappear in the final velocities, so that also $dU'_1 = dU'_2 = dU$, $dV'_1 = dV'_2 = dV$, $dW'_1 = dW'_2 = dW$. In this case, and therefore always, we have $J = 1$, so that

$$(55) \qquad dU'_1\, dV'_1\, dW'_1\, dU'_2\, dV'_2\, dW'_2 = dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2.$$

With a little more trouble this might also be proved analytically from the equations of this section.

From the component equations corresponding to (42), (43), i.e., from

$$(56) \quad \begin{cases} U_1 = X_0 + \mu_{21}^{1/2} X_R, & V_1 = Y_0 + \mu_{21}^{1/2} Y_R, & W_1 = Z_0 + \mu_{21}^{1/2} Z_R, \\[2mm] U_2 = X_0 - \mu_{12}^{1/2} X_R, & V_2 = Y_0 - \mu_{12}^{1/2} Y_R, & W_2 = Z_0 - \mu_{12}^{1/2} Z_R, \end{cases}$$

$$(57) \qquad C_0^{\,2} = X_0^{\,2} + Y_0^{\,2} + Z_0^{\,2}, \qquad C_R^{\,2} = X_R^{\,2} + Y_R^{\,2} + Z_R^{\,2},$$

it is easy to prove that

$$(58) \qquad \frac{\partial\,(U_1,\, V_1,\, W_1,\, U_2,\, V_2,\, W_2)}{\partial\,(X_0,\, Y_0,\, Z_0,\, X_R,\, Y_R,\, Z_R)} = -(\mu_1\mu_2)^{-3/2}.$$

Hence, by further transformation to polar co-ordinates, we have

$$(59) \quad dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2 = -(\mu_1\mu_2)^{-3/2}\, dX_0\, dY_0\, dZ_0\, dX_R\, dY_R\, dZ_R$$
$$= -(\mu_1\mu_2)^{-3/2}\, C_0^{\,2} C_R^{\,2}\, dC_0\, dC_R\, d\cos\theta_0\, d\cos\theta_R\, d\phi_0\, d\phi_R.$$

Since $dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2$ is essentially positive, the negative sign on the right of (59) must be made positive, if the limits of C, $\cos\theta$, and ϕ in each case are taken as 0 to $+\infty$, -1 to $+1$, and 0 to 2π respectively; it may readily be seen that the negative sign corresponds to reversed limits of integration of one of the variables $\cos\theta$.

§ 5. The General Expression for ΔQ_1.

Definition of $\Delta_{11}Q_1$ and $\Delta_{12}Q_1$.

§ 5 (A) The rate of change of $\nu_1\overline{Q_1}$ due to molecular encounters, i.e., ΔQ_1, may be divided into the two parts $\Delta_{11}Q_1$, $\Delta_{12}Q_1$ due respectively to the encounters of the molecules m_1 among themselves, and those with molecules m_2. Thus

$$(60) \qquad \Delta Q_1 = \Delta_{11}Q_1 + \Delta_{12}Q_1.$$

We shall chiefly consider $\Delta_{12}Q_1$, whence $\Delta_{11}Q_1$ may be obtained by changing the suffix 2 into 1 throughout.

The Expression for $\Delta_{12}Q_1$.

§ 5 (B) The number of molecules m_1 having velocity components lying between the limits (U_1, V_1, W_1) and $(U_1+dU_1, V_1+dV_1, W_1+dW_1)$ is, by our definition of $f_1(U_1, V_1, W_1)$, equal to

$$\nu_1 f_1 (U_1, V_1, W_1)\, dU_1\, dV_1\, dW_1$$

per unit volume.   The number of encounters in time dt of any *one* of these, with a molecule m_2 having velocity components lying between the limits (U_2, V_2, W_2) and $(U_2+dU_2, V_2+dV_2, W_2+dW_2)$, the variables p, ϵ of the encounter lying between p and $p+dp$, ϵ and $\epsilon+d\epsilon$, is equal to the number of such molecules m_2 contained within a small cylinder of length $(\mu_1\mu_2)^{-1/2}C_R\, dt$ and of sectional area $p\, dp\, d\epsilon$, *i.e.*, to

$$\nu_2\, (\mu_1\mu_2)^{-1/2} f_2 (U_2, V_2, W_2)\, C_R p\, dp\, d\epsilon\, dU_2\, dV_2\, dW_2\, dt.$$

Thus the total number of encounters of the above type, per unit volume per unit time, is

(61) $$\nu_1\nu_2\, (\mu_1\mu_2)^{-1/2} f_1 (U_1, V_1, W_1)\, f_2 (U_2, V_2, W_2)\, C_R\, p\, dp\, d\epsilon\, dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2.$$

At each such encounter the change in the value of $Q_1 (U_1, V_1, W_1)$ is clearly

(62) $$Q_1 (U'_1, V'_1, W'_1) - Q_1 (U_1, V_1, W_1),$$

or $Q'_1 - Q_1$, as we shall write it for brevity.

We shall include the effect of all possible encounters per unit volume per unit time if we integrate the product of (61) and (62) over all values of ϵ (0 to 2π), p (0 to ∞) and (U_1, V_1, W_1), (U_2, V_2, W_2) (each from $-\infty$ to $+\infty$).   Such an integration will include encounters which are not binary, but our postulate that the gas is nearly perfect (§ 2) implies that our integral would be altered only inappreciably if the upper limit of integration for p were not infinity but equal to the very small distance at which two molecules cease to exercise any appreciable inter-action.   Hence, throughout this paper, where no limits of integration are specified, it is to be understood that they have the above values.   Thus we have

(63) $$\Delta_{12}Q_1 = \nu_1\nu_2\, (\mu_1\mu_2)^{-1/2} \iiiiiiiii (Q'_1 - Q_1) f_1 f_2 C_R\, p\, dp\, d\epsilon\, dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2.$$

The term $f_1 f_2$ in the integrand may be written

(64) $$\left(\frac{hm_1}{\pi}\right)^{3/2} \left(\frac{hm_2}{\pi}\right)^{3/2} e^{-h(m_1 C_1^2 + m_2 C_2^2)} \{1 + F_1(U_1, V_1, W_1) + F_2(U_2, V_2, W_2)\}$$

$$= (\mu_1\mu_2)^{3/2} \left(\frac{hm_0}{\pi}\right)^3 e^{-hm_0(C_0^2 + C_R^2)} (1 + F_1 + F_2),$$

where, in the first line, we have neglected $F_1 F_2$, which is a second-order quantity, while in the second line we have made use of (45).

The unit term in $(1+F_1+F_2)$ *may be omitted.*

§ 5 (C) It is easy to show that the part of (63) which arises from the unit term of $(1+F_1+F_2)$ in (64) is zero. For it may be written in the form

$$\iint \phi \nu_1 \nu_2 \mu_1 \mu_2 \, (hm_0/\pi)^3 \, C_R \, p \, dp \, d\epsilon,$$

where

$$\phi \equiv \iiiiii \{ Q_1 \, (U'_1, V'_1, W'_1) - Q_1 \, (U_1, V_1, W_1) \} \, e^{-hm_0 (C_0{}^2 + C_R{}^2)} \, dU_1 \, dV_1 \, dW_1 \, dU_2 \, dV_2 \, dW_2.$$

Now by (45) and (55) the latter is equal to

$$(65) \qquad \iiiiii Q_1 \, (U'_1, V'_1, W'_1) \, e^{-h(m_1 C'_1{}^2 + m_2 C'_2{}^2)} \, dU'_1 \, dV'_1 \, dW'_1 \, dU'_2 \, dV'_2 \, dW'_2$$

$$- \iiiiii Q_1 \, (U_1, V_1, W_1) \, e^{-h(m_1 C_1{}^2 + m_2 C_2{}^2)} \, dU_1 \, dV_1 \, dW_1 \, dU_2 \, dV_2 \, dW_2.$$

But the latter two integrals are equal, since they are definite integrals differing only in the symbols used to denote the variables. Hence (65) is zero, and the unit term in $(1+F_1+F_2)$ may be omitted from $\Delta_{12}Q_1$.

The same result can be seen also in another way: the part of $\Delta_{12}Q_1$ under consideration is that obtained by putting $F_1 = F_2 = 0$ in $f_1 f_2$, *i.e.*, it is equal to the value of $\Delta_{12}Q_1$ in a uniform gas. In a uniform gas, however, as we may see from the general equation of transfer (19), $\Delta_{11}Q_1 = \Delta_{12}Q_1 = 0$, whence the result follows at once.

If $Q(U, V, W)$ *is of odd degree, the even part of* $F(U, V, W)$ *contributes nothing to* $\Delta_{12}Q$, *and* vice versâ.

§ 5 (D) We may now, therefore, write $\Delta_{12}Q_1$ in the following form, transforming the variables (U_1, V_1, W_1), (U_2, V_2, W_2) to (X_0, Y_0, Z_0), (X_R, Y_R, Z_R), by (56), (58).

$$(66) \quad \Delta_{12}Q_1 = \nu_1 \nu_2 \mu_1 \mu_2 \left(\frac{hm_0}{\pi} \right)^3$$

$$\iiiiiiiii (Q'_1 - Q_1) \, e^{-hm_0 (C_0{}^2 + C_R{}^2)} \, (F_1 + F_2) \, C_R p \, dp \, d\epsilon \, dU_1 dV_1 dW_1 dU_2 dV_2 dW_2$$

$$= \nu_1 \nu_2 (\mu_1 \mu_1)^{-1/2} \left(\frac{hm_0}{\pi} \right)^3$$

$$\iiiiiiiii (Q'_1 - Q_1) \, e^{-hm_0 (C_0{}^2 + C_R{}^2)} \, (F_1 + F_2) \, C_R p \, dp \, d\epsilon \, dX_0 dY_0 dZ_0 dX_R dY_R dZ_R.$$

We here suppose the functions $Q(U, V, W)$ and $F(U, V, W)$ expressed in terms of the new variables and (in the case of Q'_1) of ϵ and χ_{12} (or p). We are concerned both as regards Q and F only with terms which are integral in the variables U, V, W; in reckoning their degree we shall make no distinction between U_1 and U_2, &c., or

between X_0 and X_R,* &c. Then since the equations of transformation (56) are linear, any term $U_1^l V_1^m W_1^n U_2^p V_2^q W_2^r$ in $Q_1 (F_1 + F_2)$ transforms into the sum of a number of terms $X_0^a Y_0^b Z_0^c X_R^d Y_R^e Z_R^f$ such that

$$l + p = a + d, \qquad m + q = b + e, \qquad n + r = c + f.$$

This is not true in the case of $Q_1' (F_1 + F_2)$, since (by 54) U_1', V_1', W_1' are not rational functions of the variables X, Y, Z, but it *is* true of $(F_1 + F_2) \int Q_1' d\epsilon$, since the integration with respect to ϵ causes all the irrational terms in Q_1' to disappear.† This may be proved quite generally, but it will be sufficient here to indicate the proof for the case $Q_1 = U_1 C_1^{2s}$, s being any positive integer. We may write

$$Q_1' = U_1' C_1'^{2s} = (X + a C_R \sin \theta_R \cos \overline{\epsilon + \phi_0}) (C^2 + 2a C_0 C_R \sin \theta_0 \cos \epsilon)^s,$$

where

$$a = \mu_{21}^{1/2} \sin \chi_{12}, \qquad X = X_0 + \mu_{21}^{1/2} X_R \cos \chi_{12},$$

$$C^2 = C_0^2 + \mu_{21} C_R^2 + 2\mu_{21}^{1/2} (X_0 X_R + Y_0 Y_R + Z_0 Z_R) \cos \chi_{12},$$

so that X is of the first degree in X_0 or X_R, and C^2 is of even degree in the variables $(X_0, X_R), (Y_0, Y_R), (Z_0, Z_R)$. The only terms in Q_1' which do not vanish on integration with respect to ϵ are of the form

$$X \{_s C_{2p} (C^2)^{s-2p} (2a C_0 C_R \sin \theta_0 \cos \epsilon)^{2p}\}$$

or

$$(C_0 C_R^2 \sin \theta_0 \sin \theta_R \cos^{2p+1} \epsilon \cos \overline{\epsilon + \phi_0}) \{2a^2 {}_s C_{2p+1} (C^2)^{s-2p-1} (2a C_0 C_R \sin \theta_0)^{2p}\}.$$

Now we have

$$(C_0 C_R \sin \theta_0)^2 = C_0^2 C_R^2 (1 - \cos^2 \theta_0) = \{C_0^2 C_R^2 - (X_0 X_R + Y_0 Y_R + Z_0 Z_R)^2\},$$

which is an even function of X, Y, Z, and can be included under the symbol C^2. Thus, on integration with respect to ϵ, the above expressions become (apart from a factor not involving X, Y, Z explicitly)

$$X C^{2s}, \quad (C_0 C_R^2 \sin \theta_0 \sin \theta_R \cos \phi_0) C^{2(s-1)}$$

and by (50) the latter may be written

$$C_0 C_R^2 (\cos \lambda - \cos \theta_0 \cos \theta_R) C^{2(s-1)} = [X_0 C_R^2 - X_R (X_0 X_R + Y_0 Y_R + Z_0 Z_R)] C^{2(s-1)}.$$

Both these expressions, and consequently $\int Q_1 (U_1', V_1', W_1') d\epsilon$ as a whole, are of the form $X C^{2s}$ in the sense above defined. Similarly it may be shown that $\int U_1'^2 C_1'^{2s} d\epsilon$ is even in all three variables $(X_0, X_R), (Y_0, Y_R), (Z_0, Z_R)$.

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* So that, for instance, x_0^2, $x_0 x_R$ and x_R^2 will all be regarded as even functions of x.

† The *explicit* occurrence of x, y, z in $\int Q_1' d\epsilon$ is here referred to; the latter may involve C_R irrationally through χ_{12}.

In the integrand of (66), the exponential term and C_R (whether occurring as an explicit factor or implicitly in χ_{12}) are even functions of X, Y, Z. Hence a term such as $X_0^a Y_0^b Z_0^c X_R^d Y_R^e Z_R^f$ in $\int (Q'_1 - Q_1)(F_1 + F_2)\, d\epsilon$ will contribute nothing to $\Delta_{12} Q_1$ unless a, b, c, d, e, f and *à fortiori* $a+d$, $b+e$, $c+f$ are all separately even. In view of what has been proved above, therefore, it appears that in $Q(U, V, W)\, F(U, V, W)$ only the terms which are even in U, V, W separately contribute anything to $\Delta_{12} Q_1$. Hence if Q is odd in U, only the part of F which is likewise odd in U need be considered, while if it is even in U, only the even part of F need be considered.

Introduction of $I_1(\chi_{12})$.

§ 5 (E) We now make the final transformation of $\Delta_{12} Q_1$ by adopting polar co-ordinates in place of (X_0, Y_0, Z_0), (X_R, Y_R, Z_R), as follows :—

$$(67) \qquad \Delta_{12} Q_1 = \nu_1 \nu_2 (\mu_1 \mu_2)^{-1/2} \left(\frac{hm_0}{\pi}\right)^3 \iiint e^{-hm_0(C_0^2 + C_R^2)} \{I_1(\chi_{12}) - I_1(0)\}\, C_0^2 C_R^3 p\, dp\, dC_0\, dC_R,$$

where

$$(68)\ \ I_1(\chi_{12}) = \iiiint\!\!\int Q_1(U'_1, V'_1, W'_1)\{F_1(U_1, V_1, W_1) + F_2(U_2, V_2, W_2)\}\, d\epsilon\, d\cos\theta_0\, d\cos\theta_R\, d\phi_0\, d\phi_R,$$

$$(69)\ \ I_1(0) = \iiiint\!\!\int Q_1(U_1, V_1, W_1)\{F_1(U_1, V_1, W_1) + F_2(U_2, V_2, W_2)\}\, d\epsilon\, d\cos\theta_0\, d\cos\theta_R\, d\phi_0\, d\phi_R.$$

Evidently (*cf.* § 4 (G)) the latter is obtained when χ_{12} is made zero in $I_1(\chi_{12})$, since χ_{12} is not concerned in the integrations of (68), (69), being a function of p and C_R only, while when $\chi_{12} = 0$ we have $Q_1(U'_1, V'_1, W'_1) = Q_1(U_1, V_1, W_1)$. Hence, in calculating $\Delta_{12} Q_1$ we shall concern ourselves only with $I_1(\chi_{12})$ until we come to the integration with respect to p, C_R, C_0. In so doing we shall, from the outset, omit from $F(U, V, W)$ those parts which, in accordance with § 5 (D), contribute nothing to the final result.

§ 6. THE FORM OF THE FUNCTION $F(U, V, W)$.

The two special forms of Q_1 which we consider are $U_1^2 C_1^{2s}$ and $U_1 C_1^{2s}$; the only parts of $F(U, V, W)$ which are relevant in these cases are respectively the part of $E_1 + E_2$, which is even in V and W_2, and $O_1 + O_2$; the notation here used is that of § 2 (E), p. 283. From (26) and (30) we see that $\Delta U_1 C_1^{2s}$ involves the space derivatives of mean properties of the gas only in the form $\dfrac{1}{T}\dfrac{\partial T}{\partial x}$, while $\Delta U_1^2 C_1^{2s}$ similarly involves only $2\dfrac{\partial u_0}{\partial x} - \dfrac{\partial v_0}{\partial y} - \dfrac{\partial w_0}{\partial z}$. We deduce from this that $O(U, V, W)$ must certainly include the term

$$(70) \qquad\qquad \frac{1}{T}\left(U\frac{\partial T}{\partial x} + V\frac{\partial T}{\partial y} + W\frac{\partial T}{\partial z}\right) P_1(C^2),$$

and that $E(U, V, W)$ must similarly include the term

(71) $$(c_{11}U^2 + c_{22}V^2 + c_{33}W^2 + c_{23}VW + c_{31}WV + c_{12}UV) \, P(C^2),$$

where

(72)
$$\begin{cases} c_{11} = 2\dfrac{\partial u_0}{\partial x} - \dfrac{\partial v_0}{\partial y} - \dfrac{\partial w_0}{dz}, & c_{23} = 3\left(\dfrac{\partial v_0}{\partial z} + \dfrac{\partial w_0}{\partial y}\right), \\[2ex] c_{22} = 2\dfrac{\partial v_0}{\partial y} - \dfrac{\partial w_0}{dz} - \dfrac{\partial u_0}{\partial x}, & c_{31} = 3\left(\dfrac{\partial w_0}{\partial x} + \dfrac{\partial u_0}{\partial z}\right), \\[2ex] c_{33} = 2\dfrac{\partial w_0}{\partial z} - \dfrac{\partial u_0}{\partial x} - \dfrac{\partial v_0}{\partial y}, & c_{12} = 3\left(\dfrac{\partial u_0}{\partial y} + \dfrac{\partial v_0}{\partial x}\right). \end{cases}$$

The factor of $P(C^2)$ in (71) is equal to $3S' - C^2S$, by (12) and (15), and is therefore an invariant with respect to an orthogonal transformation of axes.

Further since, by (26) and (30), no other derivatives of T and (u_0, v_0, w_0) occur in $\Delta U_1 C_1^{2s}$ or $\Delta U_1^2 C_1^{2s}$, we conclude that none such appear in $F(U, V, W)$—at any rate, to our degree of approximation; thus the other terms in (12)–(15), while they possess the invariant property, do not satisfy the other conditions which must be fulfilled by $F(U, V, W)$.

We therefore conclude that $F(U, V, W)$ is composed only of (70) and (71) to our order of accuracy, and we shall suppose that the two functions $P(C^2)$ are expansible as power series in C^2. Throughout this paper we shall assume that all convergency conditions necessary for the validity of our analysis are satisfied; the justification of this assumption would offer serious difficulty, and the investigation would lead us into regions of pure mathematics which are largely unexplored, and would be unsuitable in the present paper. In § 10 we shall see that numerical approximations for the most important molecular models confirm the assumption of convergence sufficiently for our purpose.

It is convenient to write our expression for $F(U, V, W)$ in the form

(73) $$F(U, V, W) = -B_0\frac{1}{T}\left(U\frac{\partial T}{\partial x} + V\frac{\partial T}{\partial y} + W\frac{\partial T}{\partial z}\right)\sum_{r=0}^{\infty}\frac{(2hm)^r}{1 \cdot 3 \cdot 5 \ldots (2r+3)\,r}\beta_{r-1}C^{2r}$$

$$-C_0 2hm\,(c_{11}U^2 + c_{22}V^2 + c_{33}W^2 + c_{23}VW + c_{31}WU + c_{12}UV)\sum_{r=0}^{\infty}\frac{(2hm)^r}{1 \cdot 3 \cdot 5 \ldots (2r+5)}\gamma_r C^{2r}.$$

In the first line, when $r = 0$, the factor r in the denominator is to be omitted. The suffix 1 or 2 must be added to m, U, V, W, C, β, γ when we wish to distinguish between $F_1(U_1, V_1, W_1)$ and $F_2(U_2, V_2, W_2)$.

Since, by (72),

(74) $$c_{11} + c_{22} + c_{33} = 0,$$

it is easy to see that (18) is satisfied by this form of F, while in order to satisfy (17) we must have

$$(75) \qquad \beta_{-1} + \overset{\infty}{\underset{0}{\Sigma}} \beta_r / (r+1) = 0.$$

The products $B_0 \beta_r$, $B_0 \gamma_r$ are quite definite, but B_0 and C_0 can evidently be assigned arbitrarily; we shall decide that their values, though unspecified for the present, are alike for F_1 and F_2.

The above expression for $F(U, V, W)$ is equivalent to that obtained by ENSKOG (§ 1), by an entirely different method. But the chief difficulty of our problem, and one hitherto unsolved, lies in the determination of the coefficients β and γ; this is effected in the present paper by means of ΔQ.

§ 7. THE CALCULATION OF ΔQ_1.

§ 7 (A) In calculating ΔQ_1 we shall deal chiefly with $\Delta_{12} Q_1$ (cf. § 5 (A) and (67)). The particular forms of Q_1 which we shall consider are

$$(76) \qquad Q_1 = (2hm_1)^{s+\frac{1}{2}} U_1 C_1^{2s} \equiv \mathfrak{B}_1^{(s)},$$

$$(77) \qquad Q_1 = (2hm_1)^{s+1} U_1^2 C_1^{2s} \equiv \mathbb{C}_1^{(s)}.$$

In accordance with § 5 (D), the only part of $F(U, V, W)$ which is relevant to $\Delta \mathfrak{B}_1^{(s)}$ is

$$(78) \qquad -B_0 \frac{1}{T} \frac{\partial T}{\partial x} U \overset{\infty}{\underset{0}{\Sigma}} \frac{(2hm)^r}{1 \cdot 3 \cdot 5 \ldots (2r+3) r} \beta_{r-1} C^{2r},$$

while that which alone concerns $\Delta \mathbb{C}_1^{(s)}$ is

$$(79) \qquad -2hm C_0 (c_{11} U^2 + c_{22} V^2 + c_{33} W^2) \overset{\infty}{\underset{0}{\Sigma}} \frac{(2hm)^r}{1 \cdot 3 \cdot 5 \ldots (2r+5)} \gamma_r C^{2r}.$$

As to the latter, since the remainder of the integrand of $\Delta \mathbb{C}_1^{(s)}$ is symmetrical with respect to V and W, the parts of this integral arising from V^2 and W^2 in (79) are equal, so that $c_{22} V^2 + c_{33} W^2$ can be replaced by $\frac{1}{2}(c_{22} + c_{33})(V^2 + W^2) = -\frac{1}{2} c_{11}(C^2 - U^2)$, by (74). Hence for our purpose (79) is equivalent to

$$(80) \qquad -\frac{1}{2}(2hm) C_0 c_{11} (3U^2 - C^2) \overset{\infty}{\underset{0}{\Sigma}} \frac{(2hm)^r}{1 \cdot 3 \cdot 5 \ldots (2r+5)} \gamma_r C^{2r}.$$

We shall denote by $b_{12}(r_1 s_1)$ the part of $\Delta_{12} \mathfrak{B}_1^{(s)}$ which arises from the term $-(2hm_1)^{r+\frac{1}{2}} U_1 C_1^{2r}$ in $F_1(U_1, V_1, W_1)$, and by $b_{12}(r_2 s_1)$ the part arising from the corresponding term of $F_2(U_2, V_2, W_2)$, in each case the numerical and other factors in F

being excluded.* The corresponding portions of $I_1(\chi_{12})$ will be denoted by $I(r_1s_1, \chi_{12})$ and $I(r_2s_1, \chi_{12})$ respectively. Then

$$(81) \quad I(r_1s_1, \chi_{12}) = \iiiint (2h\mu_1 m_0)^{r+s+1} U'_1 C'^{2s}_1 U_1 C^{2r}_1 \, d\epsilon \, d\cos\theta_0 \, d\cos\theta_R \, d\phi_0 \, d\phi_R,$$

$$(82) \quad I(r_2s_1, \chi_{12}) = \iiiint (2hm_0)^{r+s+1} \mu_1^{s+\frac{1}{2}} \mu_2^{r+\frac{1}{2}} U'_1 C'^{2s}_1 U_2 C^{2r}_2 \, d\epsilon \, d\cos\theta_0 \, d\cos\theta_R \, d\phi_0 \, d\phi_R,$$

$$(83) \quad b_{12}(r_1s_1) = -\nu_1\nu_2 (\mu_1\mu_2)^{-1/2} \left(\frac{hm_1}{\pi}\right)^3$$

$$\iiint e^{-hm_0(C_0^2+C_R^2)} \{I(r_1s_1, \chi_{12})-I(r_1s_1, 0)\} C_0^2 C_R^3 \, p \, dp \, dC_0 \, dC_R,$$

$$(84) \quad b_{12}(r_2s_1) = -\nu_1\nu_2 (\mu_1\mu_2)^{-1/2} \left(\frac{hm_0}{\pi}\right)^3$$

$$\iiint e^{-hm_0(C_0^2+C_R^2)} \{I(r_2s_1, \chi_{12})-I(r_2s_1, 0)\} C_0^2 C_R^3 \, p \, dp \, dC_0 \, dC_R.$$

The similar quantities relating to $\Delta_{12}\mathbb{C}_1^{(s)}$ will be denoted by $c_{12}(r_1s_1)$, $c_{12}(r_2s_1)$ and $J(r_1s_1, \chi_{12})$, $J(r_2s_1, \chi_{12})$ respectively, so that

$$(85) \quad J(r_1s_1, \chi_{12})$$
$$= \iiiint \tfrac{1}{2} (2h\mu_1 m_0)^{r+s+2} U'^2_1 C'^{2s}_1 (3U_1^2 - C_1^2) C_1^{2r} \, d\epsilon \, d\cos\theta_0 \, d\cos\theta_R \, d\phi_0 \, d\phi_R,$$

$$(86) \quad J(r_2s_1, \chi_{12})$$
$$= \iiiint \tfrac{1}{2} (2hm_0)^{r+s+2} \mu_1^{s+1} \mu_2^{r+1} U'^2_1 C'^{2s}_1 (3U_2^2 - C_2^2) C_2^{2r} \, d\epsilon \, d\cos\theta_0 \, d\cos\theta_R \, d\phi_0 \, d\phi_R,$$

$$(87) \quad c_{12}(r_1s_1) = -\nu_1\nu_2 (\mu_1\mu_2)^{-1/2} \left(\frac{hm_0}{\pi}\right)^3$$

$$\iiint e^{-hm_0(C_0^2+C_R^2)} \{J(r_1s_1, \chi_{12})-J(r_1s_1, 0)\} C_0^2 C_R^3 \, p \, dp \, dC_0 \, dC_R,$$

$$(88) \quad c_{12}(r_2s_1) = -\nu_1\nu_2 (\mu_1\mu_2)^{-1/2} \left(\frac{hm_0}{\pi}\right)^3$$

$$\iiint e^{-hm_0(C_0^2+C_R^2)} \{J(r_2s_1, \chi_{12})-J(r_2s_1, 0)\} C_0^2 C_R^3 \, p \, dp \, dC_0 \, dC_R.$$

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* We have here *included* a factor $(2hm)^{1/2}$ which does not occur in F; this will be allowed for subsequently.

The Integration with respect to θ_R, ϕ_R, ϕ_0.

§ 7 (B) In $I(rs, \chi_{12})$ and $J(rs, \chi_{12})$ it is clear from (48) to (53) that ϕ_R does not appear at all in the integrand, while θ_R and ϕ_0 occur only in the products $U'_1 U$ and $U'^2_1(3U^2 - C^2)$ respectively. We have

$$U'_1 U_1 = C_0^2 \cos^2 \lambda + \mu_{21} C_R^2 \cos \theta_R \cos \theta'_R + \mu_{21}^{1/2} C_0 C_R \cos \lambda (\cos \theta_R + \cos \theta'_R),$$

$$U'_1 U_2 = C_0^2 \cos^2 \lambda - C_R^2 \cos \theta_R \cos \theta'_R + C_0 C_R \cos \lambda (\mu_{21}^{1/2} \cos \theta'_R - \mu_{12}^{1/2} \cos \theta_R),$$

and, remembering the values of $\cos \lambda$ and $\cos \theta'_R$, we have

$$\iiint U'_1 U_1 \, d \cos \theta_R \, d\phi_0 \, d\phi_R = \tfrac{8}{3}\pi^2 \{C_0^2 + \mu_{21} C_R^2 \cos \chi_{12} - \mu_{21}^{1/2} C_0 C_R (\cos \theta_0 + \cos \theta'_0)\},$$

$$\iiint U'_1 U_2 \, d \cos \theta_R \, d\phi_0 \, d\phi_R = \tfrac{8}{3}\pi^2 \{C_0^2 - C_R^2 \cos \chi_{12} + C_0 C_R (\mu_{21}^{1/2} \cos \theta'_0 - \mu_{12}^{1/2} \cos \theta_0)\}.$$

In the notation of (53) the latter two equations may be conveniently re-written as follows :—

$$\mu_1 \iiint U'_1 U_1 \, d \cos \theta_R \, d\phi_0 \, d\phi_R = \tfrac{4}{3}\pi^2 \{\Theta_{12} (\cos \theta_0) + \Theta_{12} (\cos \theta'_0) - 2\mu_2 C_R^2 (1 - \cos \chi_{12})\}.$$

$$(\mu_1 \mu_2)^{1/2} \iiint U'_1 U_2 \, d \cos \theta_R \, d\phi_0 \, d\phi_R = \tfrac{4}{3}\pi^2 \{\mu_{12}^{1/2}\Theta_{21} (\cos \theta_0) + \mu_{21}^{1/2}\Theta_{12} (\cos \theta'_0)$$
$$+ 2 (\mu_1 \mu_2)^{1/2} C_R^2 (1 - \cos \chi) - (\mu_1 \mu_2)^{-1/2} C_R^2\}.$$

Substituting in (81) and (82), we thus have

$$(89) \quad I(r_1 s_1, \chi_{12}) = \tfrac{4}{3}\pi^2 (2hm_0)^{r+s+1} \iint \{\Theta_{12} + \Theta'_{12} - 2\mu_2 C_R^2 (1 - \cos \chi_{12})\} \, \Theta'^s_{12} \Theta^r_{12} \, d\epsilon \, d \cos \theta_0,$$

$$(90) \quad I(r_2 s_1, \chi_{12}) = \tfrac{4}{3}\pi^2 (2hm_0)^{r+s+1} \iint \{\mu_{12}^{1/2}\Theta_{21} + \mu_{21}^{1/2}\Theta'_{12} + 2 (\mu_1 \mu_2)^{1/2} C_R^2 (1 - \cos \chi_{12})$$
$$- (\mu_1 \mu_2)^{-1/2} C_R^2\} \, \Theta'^s_{12} \Theta^r_{12} \, d\epsilon \, d \cos \theta_0.$$

§ 7 (C) In the case of $J(rs, \chi_{12})$, we have

$$(91) \qquad \mu_1^2 U'^2_1 U_1^2 = (\mu_1^{1/4} C_0 \cos \lambda + \mu_2^{1/2} C_R \cos \theta_R)^2 (\mu_1^{1/2} C_0 \cos \lambda - \mu_2^{1/2} C_R \cos \theta'_R)^2,$$

in which (*cf.* the figure on p. 293) $\lambda = c_0 Ox$, $\theta_R = c_R Ox$, $\theta'_R = c'_R Ox$. In the integration over the sphere, with respect to θ_R and ϕ_0, since θ_0, ϵ, χ_{12} are constant the triangle $c_0 c_R c'_R$ preserves its form, so that we may, if we please, regard x as the variable point and $c_0 c_R c'_R$ as fixed. Now it may readily be proved, by the method of "poles" in the theory of harmonic functions, that if A, B, C are three fixed points on a unit sphere, and P a variable point, then the integral over the spherical surface of

$$\cos^2 PA \cos PB \cos PC$$

is

$$\tfrac{1}{15}\pi (2 \cos AB \cos AC + \cos BC).$$

Applying this result to (91), identifying A, B, C with one or more of the points c_0, c_R, c'_R, and P with x, we may with but little difficulty prove that

$$\mu_1^2 \iiint \mathsf{U}'_1{}^2 \mathsf{U}_1{}^2 \, d \cos \theta_R \, d\phi_0 \, d\phi_R = \tfrac{4}{15}\pi^2 \{\Theta_{12}{}^2 + 4\Theta_{12}\Theta'_{12} + \Theta'_{12}{}^2 - 4\mu_2 C_R{}^2 (\Theta_{12} + \Theta'_{12})(1 - \cos \chi_{12})$$
$$+ 4\mu_2{}^2 C_R{}^4 (1 - \cos \chi_{12})^2\}.$$

Similarly we may show that

$$\mu_1 \iiint \mathsf{U}'_1{}^2 \, d \cos \theta_R \, d\phi_0 \, d\phi_R = \tfrac{8}{3}\pi^2 \Theta'_{12},$$

so that

$$\mu_1^2 \iiint \mathsf{U}'_1{}^2 (3\mathsf{U}_1{}^2 - \mathsf{C}_1{}^2) \, d \cos \theta_R \, d\phi_0 \, d\phi_R = \tfrac{4}{5}\pi^2 \{\Theta_{12}{}^2 + \tfrac{2}{3}\Theta_{12}\Theta'_{12} + \Theta'_{12}{}^2$$
$$- 4\mu_2 C_R{}^2 (\Theta_{12} + \Theta'_{12})(1 - \cos \chi_{12}) + 4\mu_2{}^2 C_R{}^4 (1 - \cos \chi_{12})^2\}.$$

Hence we have

$$(92) \quad \mathrm{J}(r_1 s_1, \chi_{12}) = \tfrac{2}{5}\pi^2 (2 h m_0)^{r+s+2} \iint \{\Theta_{12}{}^2 + \tfrac{2}{3}\Theta_{12}\Theta'_{12} + \Theta'_{12}{}^2 - 4\mu_2 C_R{}^2 (\Theta_{12} + \Theta'_{12})(1 - \cos \chi_{12})$$
$$+ 4\mu_2{}^2 C_R{}^4 (1 - \cos \chi_{12})^2\} \, \Theta'_{12}{}^s \Theta_{12}{}^r \, d\epsilon \, d \cos \theta_0,$$

and it may be proved in a similar manner that

$$(93) \quad \mathrm{J}(r_2 s_1, \chi_{12}) = \tfrac{2}{5}\pi^2 (2 h m_0)^{r+s+2} \iint \Big[\mu_{12}\Theta_{21}{}^2 + \tfrac{2}{3}\Theta_{21}\Theta'_{12} + \mu_{21}\Theta'_{12}{}^2$$
$$+ 2 C_R{}^2 (\mu_{12}{}^{1/2}\Theta_{21} + \mu_{21}{}^{1/2}\Theta'_{12}) \{2 (\mu_1\mu_2)^{1/2} (1 - \cos \chi_{12}) - (\mu_1\mu_2)^{-1/2}\}$$
$$+ C_R{}^4 \{2 (\mu_1\mu_2)^{1/2} (1 - \cos \chi_{12}) - (\mu_1\mu_2)^{-1/2}\}^2 \Big] \Theta'_{12}{}^s \Theta_{21}{}^r \, d\epsilon \, d \cos \theta_0.$$

The Expansion of $(\rho^2 + \sigma^2 - 2\rho\sigma \cos \theta)^n$ in a LEGENDRE'S Series.

§ 7 (D) In order to effect the integration of I and J with respect to ϵ and θ_0, we must have recourse to the expansion of

$$(94) \qquad \mathrm{P}_n(\rho, \sigma, \cos \theta) \equiv (\rho^2 + \sigma^2 - 2\rho\sigma \cos \theta)^n$$

in a series of LEGENDRE'S functions. In a recent paper* I have shown that

$$(95) \qquad \mathrm{P}_n(\rho, \sigma, \cos \theta) = \sum_{k=0}^{n} (-1)^k (2k+1) \, {}^n\mathrm{A}^k(\rho^2, \sigma^2) \, \mathrm{P}_k(\cos \theta),$$

where $\mathrm{P}_k(\cos \theta)$ is the ordinary LEGENDRE'S function of $\cos \theta$, of type k, and†

$$(96) \qquad {}^n\mathrm{A}^k(\rho^2, \sigma^2) = \left(\frac{\rho}{\sigma}\right)^k \sum_{t=k}^{n} \frac{n_t}{(t+\tfrac{1}{2})_t} \frac{(n+\tfrac{1}{2})_{t-k}}{(t-k)_{t-k}} \rho^{2(r-t)} \sigma^{2t}$$
$$= \left(\frac{\sigma}{\rho}\right)^k \sum_{t=}^{n} \frac{n_t}{(t+\tfrac{1}{2})_t} \frac{(n+\tfrac{1}{2})_{t-k}}{(t-k)_{t-k}} \sigma^{2(r-t)} \rho^{2t}.$$

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* CHAPMAN, 'Quarterly Journal of Mathematics,' p. 16, 1916. The expansion is there not limited to integral values of n, though these are alone considered in the present paper.

† The constant k is necessarily a positive integer; if $k > n$, ${}^n\mathrm{A}^k = 0$.

In the last equation the symbol p_q, where q is integral, is defined thus :—

(97)
$$ p_q = p\,(p-1)\,(p-2) \ldots (p-q+1). $$

From (53) it is clear that

(98) $$ \{\Theta_{12}(\cos\theta)\}^n = \mathrm{P}_n(\mu_1 \mathrm{C}_0^2, \mu_2 \mathrm{C}_\mathrm{R}^2, -\cos\theta) = \sum_{k=0}^{n} (2k+1)\,{}^n\mathrm{A}^k_{12}\,\mathrm{P}_k(\cos\theta), $$

(99) $$ \{\Theta_{21}(\cos\theta)\}^n = \mathrm{P}_n(\mu_2 \mathrm{C}_0^2, \mu_1 \mathrm{C}_\mathrm{R}^2, \cos\theta) = \sum_{k=0}^{n} (-1)^k (2k+1)\,{}^n\mathrm{A}^k_{21}\,\mathrm{P}_k(\cos\theta), $$

where we have written, for brevity,

(100) $$ {}^n\mathrm{A}^k_{12} \equiv {}^n\mathrm{A}^k(\mu_1 \mathrm{C}_0^2, \mu_2 \mathrm{C}_\mathrm{R}^2) \qquad {}^n\mathrm{A}^k_{21} = {}^n\mathrm{A}^k(\mu_2 \mathrm{C}_0^2, \mu_1 \mathrm{C}_\mathrm{R}^2). $$

In our expressions for $\Delta\mathrm{Q}_1$, θ takes the values θ_0 and θ'_0, and the variable ϵ is involved only through the latter angle, which occurs in Θ'_{12} or $\Theta_{12}(\cos\theta'_0)$. In the expansion of the latter (*cf.* 98) in terms of $\mathrm{P}_k(\cos\theta'_0)$, or, by (48), of $\mathrm{P}_k(\cos\theta_0 \cos\chi_{12} + \sin\theta_0 \sin\chi_{12} \cos\epsilon)$, we shall make use of the following well-known formula in the theory of spherical harmonic functions :—

(101) $$ \mathrm{P}_k(\cos\theta'_0) = \mathrm{P}_k(\cos\theta_0 \cos\chi_{12} + \sin\theta_0 \sin\chi_{12} \cos\epsilon) $$

$$ = \mathrm{P}_k(\cos\theta_0)\,\mathrm{P}_k(\cos\chi_{12}) + 2 \sum_{l=1}^{k} \frac{(k-l)!}{(k+l)!}\,\mathrm{P}_k^l(\cos\theta)\,\mathrm{P}_k^l(\cos\chi_{12})\cos l\epsilon. $$

The Integration with respect to ϵ and θ_0.

§7 (E) Since the integral of $\cos l\epsilon$ with respect to ϵ, between 0 and 2π, is zero unless $l=0$, from (98) and (101) we deduce the result,

(102) $$ \int_0^{2\pi} \Theta'^n_{12}\, d\epsilon = 2\pi \sum_{k=0}^{n} (2k+1)\,{}^n\mathrm{A}^k_{12}\,\mathrm{P}_k(\cos\theta_0)\,\mathrm{P}_k(\cos\chi_{12}). $$

Now from (89), (90), and (92), (93), it is evident that as far as concerns integration with respect to ϵ and θ_0 we have to consider a number of terms such as

(103) $$ \iint \Theta^m \Theta'^n_{12}\, d\epsilon\, d\cos\theta_0, $$

where Θ^m may have the suffix 12 or 21, while Θ'^n always has the suffix 12.   Now Θ^m does not involve ϵ, so that (102) suffices for the integration with respect to ϵ, and leaves us with

(104) $$ 2\pi \int_{-1}^{1} \left\{ \sum_{k=0}^{m} (\pm 1)^k (2k+1)\,{}^m\mathrm{A}^k\,\mathrm{P}_k(\cos\theta_0) \right\} $$

$$ \left\{ \sum_{k=0}^{n} (2k+1)\,{}^n\mathrm{A}^k_{12}\,\mathrm{P}_k(\cos\theta_0)\,\mathrm{P}_k(\cos\chi_{12}) \right\} d\cos\theta_0 $$

in place of (103); in the first bracket the ambiguous sign is to be + in the case of $\Theta_{12}{}^m$, and − in that of $\Theta_{21}{}^m$.

By the theory of LEGENDRE's functions we have

$$(2k+1) \int_{-1}^{1} \mathrm{P}_k (\cos \theta_0) \, \mathrm{P}_l (\cos \theta_0) \, d \cos \theta_0 = 0 \qquad \text{if } k \neq l.$$

$$(2k+1) \int_{-1}^{1} \{ \mathrm{P}_k (\cos \theta_0) \}^2 \, d \cos \theta_0 = 2.$$

Consequently

$$(105) \qquad \iint \Theta_{12}{}^m \Theta'_{12}{}^n \, d\epsilon \, d \cos \theta_0 = 4\pi \sum_{k=0}^{m, n} (2k+1) \, {}^m \mathrm{A}^k_{12} {}^n \mathrm{A}^k_{12} \mathrm{P}_k (\cos \chi_{12}),$$

$$(106) \qquad \iint \Theta_{21}{}^m \Theta'_{12}{}^n \, d\epsilon \, d \cos \theta_0 = 4\pi \sum_{k=0}^{m, n} (-1)^k (2k+1) \, {}^m \mathrm{A}^k_{21} {}^n \mathrm{A}^k_{12} \mathrm{P}_k (\cos \chi_{12}),$$

where the upper limit of k is the lesser of the two integers m, n.

Applying these results to (89), (90), (92), (93), we have, therefore,

$$(107) \quad \mathrm{I} (r_1 s_1, \chi_{12}) = \tfrac{16}{3} \pi^3 (2hm_0)^{r+s+1}$$
$$\sum_{k=0}^{r+1, s+1} \{ {}^{r+1} \mathrm{A}^k_{12} {}^s \mathrm{A}^k_{12} + {}^r \mathrm{A}^k_{12} {}^{s+1} \mathrm{A}^k_{12}$$
$$- 2\mu_2 \mathrm{C}^2_{\mathrm{R}} {}^r \mathrm{A}^k_{12} {}^s \mathrm{A}^k_{12} (1 - \cos \chi_{12}) \} \, \mathrm{P}_k (\cos \chi_{12}),$$

$$(108) \quad \mathrm{I} (r_2 s_1, \chi_{12}) = \tfrac{16}{3} \pi^3 (2hm_0)^{r+s+1}$$
$$\sum_{k=0}^{r+1, s+1} (-1)^k [\mu^{1/2}_{12} {}^{r+1} \mathrm{A}^k_{21} {}^s \mathrm{A}^k_{12} + \mu^{1/2}_{21} {}^r \mathrm{A}^k_{21} {}^{s+1} \mathrm{A}^k_{12}$$
$$+ 2 \mathrm{C}^2_{\mathrm{R}} {}^r \mathrm{A}^k_{21} {}^s \mathrm{A}^k_{12} \{ (\mu_1 \mu_2)^{1/2} (1 - \cos \chi_{12})$$
$$- \tfrac{1}{2} (\mu_1 \mu_2)^{-1/2} \}] \, \mathrm{P}_k (\cos \chi_{12}),$$

$$(109) \quad \mathrm{J} (r_1 s_1, \chi_{12}) = \tfrac{8}{5} \pi^3 (2hm_0)^{r+s+2}$$
$$\sum_{k=0}^{r+2, s+2} [{}^{r+2} \mathrm{A}^k_{12} {}^s \mathrm{A}^k_{12} + \tfrac{2}{3} {}^{r+1} \mathrm{A}^k_{12} {}^{s+1} \mathrm{A}^k_{12} + {}^r \mathrm{A}^k_{12} {}^{s+2} \mathrm{A}^k_{12}$$
$$- 4\mu_2 \mathrm{C}^2_{\mathrm{R}} ({}^{r+1} \mathrm{A}^k_{12} {}^s \mathrm{A}^k_{12} + {}^r \mathrm{A}^k_{12} {}^{s+1} \mathrm{A}^k_{12}) (1 - \cos \chi_{12})$$
$$+ 4\mu_2^2 \mathrm{C}^4_{\mathrm{R}} {}^r \mathrm{A}^k_{12} {}^s \mathrm{A}^k_{12} (1 - \cos \chi_{12})^2] \, \mathrm{P}_k (\cos \chi_{12}),$$

$$(110) \quad \mathrm{J} (r_2 s_1, \chi_{12}) = \tfrac{8}{5} \pi^3 (2hm_0)^{r+s+2}$$
$$\sum_{k=0}^{r+2, s+2} (-1)^k [\mu_{12} {}^{r+2} \mathrm{A}^k_{21} {}^s \mathrm{A}^k_{12} + \tfrac{2}{3} {}^{r+1} \mathrm{A}^k_{21} {}^{s+1} \mathrm{A}^k_{12} + \mu_{21} {}^r \mathrm{A}^k_{21} {}^{s+2} \mathrm{A}^k_{12}$$
$$+ 2 \mathrm{C}^2_{\mathrm{R}} (\mu_{12}^{1/2} {}^{r+1} \mathrm{A}^k_{21} {}^s \mathrm{A}^k_{12} + \mu_{21}^{1/2} {}^r \mathrm{A}^k_{21} {}^{s+1} \mathrm{A}^k_{12}) \{ 2 (\mu_1 \mu_2)^{1/2} (1 - \cos \chi_{12}) - (\mu_1 \mu_2)$$
$$+ \mathrm{C}^4_{\mathrm{R}} {}^r \mathrm{A}^k_{21} {}^s \mathrm{A}^k_{12} \{ 2 (\mu_1 \mu_2)^{1/2} (1 - \cos \chi_{12}) - (\mu_1 \mu_2)^{-1/2} \}^2] \, \mathrm{P}_k (\cos \chi_{12}).$$

The Integration with respect to p.

§ 7 (F) On referring back to equations (81) to (88) it is clear that before executing the integration with respect to p, in the calculation of $b(rs)$ and $c(rs)$, we must subtract from $I(rs, \chi_{12})$ and $J(rs, \chi_{12})$, as given by (107) to (110), their values corresponding to $\chi_{12} = 0$. Now when $\chi_{12} = 0$, we have

$$1 - \cos \chi_{12} = 0, \qquad P_k(\cos \chi_{12}) = 1.$$

Thus where $P_k(\cos \chi_{12})$ occurs alone in (107) to (110), it must be replaced by $P_k(\cos \chi_{12}) - 1$ in the expressions for $b(rs)$ and $c(rs)$, the terms $P_k(\cos \chi_{12})(1 - \cos \chi_{12})$ and $P_k(\cos \chi_{12})(1 - \cos \chi_{12})^2$ remaining unchanged, since the corresponding terms in $I(rs, 0)$ and $J(rs, 0)$ vanish.

The variable p is involved in $b(rs)$ and $c(rs)$ only through $p\,dp$ and χ_{12}, the latter being also a function of C_R. We may therefore formally execute the integration with respect to p by writing

$$(111) \qquad \phi^k{}_{12}(C_R) \equiv (2k+1)(\mu_1\mu_2)^{-1/2} C_R \int_0^\infty \{1 - P_k(\cos \chi_{12})\}\, p\,dp,$$

$$(112) \qquad \phi'^k{}_{12}(C_R) \equiv (2k+1)(\mu_1\mu_2)^{-1/2} C_R \int_0^\infty (1 - \cos \chi_{12})\, P_k(\cos \chi_{12})\, p\,dp,$$

$$(113) \qquad \phi''^k{}_{12}(C_R) \equiv (2k+1)(\mu_1\mu_2)^{-1/2} C_R \int_0^\infty (1 - \cos \chi_{12})^2\, P_k(\cos \chi_{12})\, p\,dp.$$

The nature of these functions depends on the law of inter-action between molecules at collisions, and by keeping this law unspecified we retain the utmost generality in our theory, which implies no property of the molecules save that of spherical symmetry.

By means of the well-known equation

$$(114) \qquad (k+1)\, P_{k+1}(\cos \chi) - (2k+1)\cos \chi P_k(\cos \chi) + kP_{k-1}(\cos \chi) = 0$$

the function $\phi'^k{}_{12}(C_R)$ can be expressed in terms of $\phi^k{}_{12}(C_R)$, for different values of k, as follows :—

$$(115) \qquad \phi'^k{}_{12}(C_R) = \frac{k+1}{2k+3}\, \phi^{k+1}{}_{12}(C_R) - \phi^k{}_{12}(C_R) + \frac{k}{2k-1}\, \phi^{k-1}{}_{12}(C_R),$$

and by a repeated application of (114) we may obtain a similar expression (involving $\phi^l{}_{12}(C_R)$ for $l = k, k \pm 1, k \pm 2$) for $\phi''^k{}_{12}(C_R)$.

To avoid unnecessary formulæ, we shall not write down the forms taken by $b(rs)$ and $c(rs)$ on substitution of the results of this section till after we have considered the next step in the integration.

The Integration with respect to C_0 *and* C_R.

§ 7 (G) In the expressions for $b\,(rs)$ and $c\,(rs)$, integrated out with respect to all the variables save C_0 and C_R, it is now convenient to make the transformation

(116) $$x^2 = hm_0C_0^2, \qquad y^2 = hm_0C_R^2.$$

In connection with this we shall use the following notation :—

(117) $\mathrm{B}^k_{1212}\,(m,\,n) \equiv (2hm_0)^{m+n}\, {}^m\mathrm{A}^k_{12}\,{}^n\mathrm{A}^k_{12} = (2hm_0)^{m+n}\, .\, {}^m\mathrm{A}^k(\mu_1C_0^2,\,\mu_2C_R^2)\, .\, {}^n\mathrm{A}^k(\mu_1C_0^2,\,\mu_2C_R^2)$

$\qquad\qquad = {}^m\mathrm{A}^k(2\mu_1hm_0C_0^2,\,2\mu_2hm_0C_R^2)\, .\, {}^n\mathrm{A}^k(2\mu_1hm_0C_0^2,\,2\mu_2hm_0C_R^2),$

$\qquad\qquad = {}^m\mathrm{A}^k(2\mu_1x^2,\,2\mu_2y^2)\, .\, {}^n\mathrm{A}^k(2\mu_1x^2,\,2\mu_2y^2),$

(118) $\mathrm{B}^k_{2112}\,(m,\,n) = (2hm_0)^{m+n}\, .\, {}^m\mathrm{A}^k_{21}\,{}^n\mathrm{A}^k_{12},$

$\qquad\qquad = {}^m\mathrm{A}^k(2\mu_2x^2,\,2\mu_1y^2)\, .\, {}^n\mathrm{A}^k(2\mu_1x^2,\,2\mu_2y^2).$

We have here used the fact—cf. (96)–(100)—that ${}^n\mathrm{A}^k(\rho^2,\,\sigma^2)$ is a homogeneous polynomial of degree $2n$ in $\rho,\,\sigma$.

We now use equations (83), (84), (107), (108), in conjunction with § 7 (F), to write down the following expressions* for $b\,(r,\,s)$, taking particular note of the signs of the various terms :—

(119) $b_{12}\,(r_1s_1) = \tfrac{16}{3}\,\nu_1\nu_2 \displaystyle\iint e^{-(x^2+y^2)} \sum_{k=0}^{r+1,\,s+1} \big[\phi^k_{12}\,(\tau_{12}y)\,\{\mathrm{B}^k\,(r+1,\,s)+\mathrm{B}^k\,(r,\,s+1)\}$

$\qquad\qquad\qquad + 4\mu_2y^2\phi'^k_{12}\,(\tau_{12}y)\,\mathrm{B}^k\,(r,\,s)\big]_{1212}\,x^2y^2\,dx\,dy,$

(120) $b_{12}\,(r_2s_1) = \tfrac{16}{3}\nu_1\nu_2 \displaystyle\iint e^{-(x^2+y^2)} \sum_{k=0}^{r+1,\,s+1} (-1)^k\big[\phi^k_{12}(\tau_{12}y)\{\mu_{12}^{1/2}\mathrm{B}^k\,(r+1,\,s)$

$\qquad\qquad\qquad - 2\,(\mu_1\mu_2)^{-1/2}y^2\mathrm{B}^k\,(r,\,s)+\mu_{21}^{1/2}\mathrm{B}^k\,(r,\,s+1)\}$

$\qquad\qquad\qquad - 4\,(\mu_1\mu_2)^{1/2}y^2\phi'^k_{12}\,(\tau_{12}y)\,\mathrm{B}^k\,(r,\,s)\big]_{2112}\,x^2y^2\,dx\,dy.$

In a similar way, from (87), 88), (109), (110) we obtain the following expressions for $c\,(r,\,s)$:—

(121) $c_{12}(r_1s_1) = \tfrac{8}{5}\nu_1\nu_2 \displaystyle\iint e^{-(x^2+y^2)} \sum_{k=0}^{r+2,\,s+2} \big[\phi^k_{12}\,(\tau_{12}y)\,\{\mathrm{B}^k\,(r+2,\,s)+\tfrac{2}{3}\mathrm{B}^k\,(r+1,\,s+1)$

$\qquad\qquad\qquad + \mathrm{B}^k\,(r,\,s+2)\} + 8\mu_2y^2\phi'^k_{12}\,(\tau_{12}y)\,\{\mathrm{B}^k\,(r+1,\,s)$

$\qquad\qquad\qquad + \mathrm{B}^k\,(r,\,s+1)\} - 16\mu_2^2y^4\phi''^k_{12}\,(\tau_{12}y)\,\mathrm{B}^k\,(r,\,s)\big]_{1212}\,x^2y^2\,dx\,dy.$

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* In (119)–(122) the suffixes 1212 or 2112, which should be appended to the symbols $\mathrm{B}^k\,(m,\,n)$—the same for all those within any one square bracket—are for convenience of printing indicated only by being placed after the bracket itself.

$$(122) \quad c_{12}(r_2 s_1) = \tfrac{8}{5}\nu_1\nu_2 \iint e^{-(x^2+y^2)} \sum_{k=0}^{r+2,\,s+2} (-1)^k \big[\phi^k{}_{12}(\tau_{12}y)\{\mu_{12}B^k(r+2,\,s)+\tfrac{2}{3}B^k(r+1,\,s+1)$$

$$+\mu_{21}B^k(r,\,s+2)-4(\mu_1\mu_2)^{-1/2}y^2\Big(\mu_{12}{}^{1/2}B^k(r+1,\,s)$$

$$+\mu_{21}{}^{1/2}B^k(r,\,s+1)\Big)+4\mu_1\mu_2y^4B^k(r,\,s)\}$$

$$-8(\mu_1\mu_2)^{1/2}y^2\phi'^k{}_{12}(\tau_{12}y)\{\mu_{12}{}^{1/2}B^k(r+1,\,s)$$

$$-2(\mu_1\mu_2)^{-1/2}y^2B^k(r,\,s)+\mu_{21}{}^{1/2}B^k(r,\,s+1)\}$$

$$-16\mu_1\mu_2y^4\phi''^k{}_{12}(\tau_{12}y)B^k(r,\,s)\big]_{2112}\,x^2y^2\,dx\,dy.$$

The symbol τ in $\phi^k{}_{12}(\tau_{12}y)$ is defined by the equation

$$(123) \qquad \tau_{12} = \frac{1}{\sqrt{hm_0}}.$$

The integration with respect to x in the above expressions is of a quite elementary nature, but it will not be executed in general terms owing to the complexity of the polynomials $B^k(r,\,s)$, which are integral in x^2. Any individual term in the integrands of (119) to (122) is of the form (so far as concerns x)

$$(124) \qquad \int_0^\infty e^{-x^2}x^{2(m+1)}\,dx = \tfrac{1}{4}\pi^{1/2}(m+\tfrac{1}{2})_m.$$

The integration with respect to y will similarly not be executed in general; in any case, owing to the unspecified functions $\phi^k{}_{12}(\tau y)$, this integration could be only formally completed, and until we come to consider special types of molecular models we shall be content to leave $b(r,\,s)$ and $c(r,\,s)$ in the above form.

The Complete Expression for $\Delta_{12}Q_1$.

§ 7 (H) On referring back to § 7 (A), and the definition of $b(r,\,s)$, $c(r,\,s)$, it is clear that we are now able to write down the complete expressions for $\Delta_{12}Q_1$ in the two cases we have considered. This involves taking into account *all* the terms ($r = 0$ to ∞) in $F(U, V, W)$, with their appropriate coefficients, as in (78), (80); and in order to make the expressions more symmetrical, it is convenient to change the values of Q_1 slightly, by multiplying them by certain numerical factors (*cf.* 26, 30). Thus writing

$$(125) \qquad \lambda_{r-1,\,s-1} \equiv \frac{1}{1\,.\,3\,.\,5\,\ldots(2r+3)\,r\,.\,1\,.\,3\,.\,5\,\ldots(2s+3)\,s},$$

$$(126) \qquad \lambda'_{rs} \equiv \frac{1}{1\,.\,3\,.\,5\,\ldots(2r+5)\,.\,1\,.\,3\,.\,5\,\ldots(2s+5)},$$

we have the following equations for $\Delta_{12}Q_1$ in the two cases under consideration :—

$$(127) \quad \frac{(2hm_1)^{s+1}}{1 . 3 . 5 \ldots (2s+3)s} \Delta_{12}U_1C_1^{2s} = B_0 \frac{1}{T} \frac{\partial T}{\partial x} \sum_{r=0}^{\infty} \lambda_{r-1, s-1} \{ \beta_{r-1, 1} b_{12}(r_1s_1) + \mu_{12}^{1/2} \beta_{r-1, 2} b_{12}(r_2s_1) \},$$

$$(128) \quad \frac{(2hm_1)^{s+1}}{1 . 3 . 5 \ldots (2s+5)} \Delta_{12}U_1^2C_1^{2s} = C_0 c_{11} \sum_{r=0}^{\infty} \lambda'_{rs} \{ \gamma_{r, 1} c_{12}(r_1s_1) + \gamma_{r, 2} c_{12}(r_2s_1) \}.$$

The corresponding values of $\Delta_{11}Q_1$ in the two cases are obtainable from (127), (128) by replacing the suffix 2 by 1 throughout. We will write $b_{11}(r_1s_1)$ and $c_{11}(r_1s_1)$ respectively for the values taken by $b_{12}(r_1s_1) + b_{12}(r_2s_1)$ and $c_{12}(r_1s_1) + c_{12}(r_2s_1)$ when the distinction between the suffixes 2 and 1 in these expressions is abolished. In place of μ_1 and μ_2 we now write $\frac{1}{2}$, and $\mu_{12} = \mu_{21} = 1$, $m_0 = 2m_1$, while $B_{12}^k(m, n)$ and $B_{21}^k(m, n)$ become identical, and equal to

$$(129) \qquad {}^m A^k(x^2, y^2) \, {}^n A^k(x^2, y^2) \equiv B^k(m, n).$$

It is convenient to express $b_{11}(r_1s_1)$ and $c_{11}(r_1s_1)$ in terms of $\phi^k_{11}(\tau y)$ only, eliminating $\phi''^k_{11}(\tau y)$ and $\phi'''^k_{11}(\tau y)$ by means of (115) and a similar equation for $\phi'''^k_{11}(\tau y)$. When this is done it is found that the coefficient of $\phi^k_{11}(\tau y)$ vanishes for odd values of k, on account of the factor $(-1)^k$ in $b_{12}(r_2s_1)$ and $c_{12}(r_2s_1)$. The following are the results thus obtained* :—

$$(130) \quad b_{11}(r_1s_1) = \tfrac{3.2}{3} \nu_1^2 \iint e^{-(x^2+y^2)} \sum_{k=1}^{(r, s)} \phi^{2k}_{11}(\tau_{11}y) \Big[B^{2k}(r+1, s) + B^{2k}(r, s+1)$$

$$+ 2y^2 \Big\{ \frac{2k+1}{4k+1} B^{2k+1}(r, s) + \frac{2k}{4k+1} B^{2k-1}(r, s) - B^{2k}(r, s) \Big\} \Big] x^2 y^2 \, dx \, dy.$$

$$(131) \quad c_{11}(r_1s_1) = \tfrac{1.6}{5} \nu_1^2 \iint e^{-(x^2+y^2)} \sum_{k=1}^{[r, s]} \phi^{2k}_{11}(\tau_{11}y) \Big[B^{2k}(r+2, s) + \tfrac{2}{3} B^{2k}(r+1, s+1) + B^{2k}(r, s+2)$$

$$+ 4y^2 \Big\{ \frac{2k+1}{4k+1} \Big(B^{2k+1}(r+1, s) + B^{2k+1}(r, s+1) \Big)$$

$$+ \frac{2k}{4k+1} \Big(B^{2k-1}(r+1, s) + B^{2k-1}(r, s+1) \Big) - \Big(B^{2k}(r+1, s) + B^{2k}(r, s+1) \Big) \Big\}$$

$$+ 4y^4 \Big\{ \frac{(2k+2)(2k+1)}{(4k+3)(4k+1)} B^{2k+2}(r, s)$$

$$+ \Big(\frac{(2k+1)^2}{(4k+3)(4k+1)} + \frac{4k^2}{(4k+1)(4k-1)} + 1 \Big) B^{2k}(r, s)$$

$$+ \frac{2k(2k-1)}{(4k+1)(4k-1)} B^{2k-2}(r, s)$$

$$- 2 \Big(\frac{2k+1}{4k+1} B^{2k+1}(r, s) + \frac{2k}{4k+1} B^{2k-1}(r, s) \Big) \Big\} \Big] x^2 y^2 \, dx \, dy.$$

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* In these expressions $\phi^k_{11}(\tau_{11}y)$ is the equivalent, for an encounter between two molecules of the *same* kind, of $\phi^k_{12}(\tau_{11}y)$ for molecules of different kinds. Thus (*cf.* 111)

$$\phi^k_{11}(\tau_{11}y) \equiv 2(2k+1) C_R \int_0^\infty \{1 - P_k(\cos \chi_{11})\} p \, dp,$$

where the law connecting χ_{11} with p and C_R may differ from that for χ_{12}. Also τ_{11} now becomes $(2hm_1)^{-1/2}$.

The term corresponding to $k = 0$ is absent in both the above cases, since $\phi^0_{11}(\tau_{11}y)$ is itself zero, so that $\phi^2_{11}(\tau_{11}y)$ is the function $\phi_{11}(\tau_{11}y)$ of lowest order $(k = 2)$ in $b_{11}(r_1s_1)$ or $c_{11}(r_1s_1)$. The upper limit of k in the case of $b_{11}(r_1s_1)$ is equal to the integral part of the lesser of the two quantities $\frac{1}{2}(r+1)$ and $\frac{1}{2}(s+1)$; this is denoted by (r, s). Similarly the upper limit of k in the case of $c_{11}(r_1s_1)$ is the integral part of the lesser of the two quantities $\frac{1}{2}(r+2)$ and $\frac{1}{2}(s+2)$, which we denote by $[r, s]$. Thus, when $r = 0$ or $s = 0$, $b_{11}(r_1s_1) = 0$.

We can now write down the complete expressions for ΔQ, in the two cases above, as follows :—

$$(132) \quad \frac{(2hm_1)^{s+1}}{1 \cdot 3 \cdot 5 \ldots (2s+3)\,s} \Delta U_1 C_1^{2s}$$

$$= B_0 \frac{1}{T} \frac{\partial T}{\partial x} \sum_{r=0}^{\infty} \lambda_{r-1,\,s-1} [\beta_{r-1,\,1} \{ b_{11}(r_1s_1) + b_{12}(r_1s_1) \} + \mu_{12}^{1/2} \beta_{r-1,\,2} b_{12}(r_2s_1)],$$

$$(133) \quad \frac{(2hm_1)^{s+1}}{1 \cdot 3 \cdot 5 \ldots (2s+5)} \Delta U_1^2 C_1^{2s} = C_0 c_{11} \sum_{r=0}^{\infty} \lambda'_{rs} [\gamma_{r,\,1} \{ c_{11}(r_1s_1) + c_{12}(r_1s_1) \} + \gamma_{r,\,2} c_{12}(r_2s_1)].$$

In the present paper we are concerned with the application of these formulæ only to simple gases, in which $\nu_2 = 0$ and hence $b_{12}(r_1s_1) = b_{12}(r_2s_1) = c_{12}(r_1s_1) = c_{12}(r_2s_1) = 0$. It is convenient to write the reduced equations in the following form :—

$$(134) \quad \frac{(2hm)^{s+2}}{1 \cdot 3 \cdot 5 \ldots (2s+5)(s+1)} \frac{3}{\nu} \Delta U C^{2(s+1)} = \frac{1}{T} \frac{\partial T}{\partial x} \sum_{r=0}^{\infty} \beta_r b_{rs},$$

$$(135) \quad \frac{(2hm)^{s+1}}{1 \cdot 3 \cdot 5 \ldots (2s+5)} \frac{45}{2\nu} \Delta U^2 C^{2s} = c_{11} \sum_{r=0}^{\infty} \gamma_r c_{rs}.$$

In (134) we have substituted $r+1$, $s+1$ for r, s in (132), multiplied by $3/\nu$, and used the notation given by

$$(136) \quad b_{rs} \equiv \frac{3}{\nu} B_0 \lambda_{r,\,s} b_{11}(r+1, s+1);$$

the first term in (132), with factor β_{-1}, vanishes, since $b_{11}(0, s) = 0$. Similarly in (135) we have written

$$(137) \quad c_{rs} \equiv \frac{45}{2\nu} C_0 \lambda'_{rs} c_{11}(r_1s_1).$$

§ 8. The Expressions for the Coefficients in the Velocity-Distribution Functions.

§ 8 (A) We have now obtained expressions for ΔQ, the rate of change of a function of the molecular velocities due to encounters, in two different ways : in § 3 ΔQ was found from the equation of transfer, while in §§ 4–7 it has been determined by direct calculation. By comparison of (26) and (134)—substituting $s+1$ for s in the former —and of (30), (72) and (135), we deduce from these different expressions for ΔQ the

following linear equations connecting the unknown coefficients in the velocity-distribution function :—

$$(138) \qquad \sum_{r=0}^{\infty} \beta_r b_{rs} = 1,$$

$$(139) \qquad \sum_{r=0}^{\infty} \gamma_r c_{rs} = 1.$$

These are true for all values of s from 0 to ∞, the coefficients b_{rs} and c_{rs} being completely determined, in terms of the molecular data, by (130), (131),* and (136), (137).   If we assume that certain convergency conditions are satisfied (138) and (139) lead (in the way usual in the case of a *finite* system of linear equations) to the following expressions for β_r and γ_r :—

$$(140) \qquad \beta_r = \nabla_r (b_{rs})/\nabla (b_{rs}), \qquad \gamma_r = \nabla_r (c_{rs})/\nabla (c_{rs}),$$

where $\nabla (b_{rs})$ and $\nabla (c_{rs})$ denote the infinite determinants formed from the arrays (b_{rs}) and (c_{rs}), thus,

$$(141) \quad \nabla (b_{rs}) \equiv \begin{vmatrix} b_{00} & b_{10} & b_{20} & b_{30} & . & . \\ b_{01} & b_{11} & b_{21} & b_{31} & . & . \\ b_{02} & b_{12} & b_{22} & b_{32} & . & . \\ b_{03} & b_{13} & b_{23} & c_{33} & . & . \\ . & . & . & . & . & . \end{vmatrix} \qquad \nabla (c_{rs}) \equiv \begin{vmatrix} c_{00} & c_{10} & c_{20} & c_{30} & . & . \\ c_{01} & c_{11} & c_{21} & c_{31} & . & . \\ c_{02} & c_{12} & c_{22} & c_{32} & . & . \\ c_{03} & c_{13} & c_{23} & c_{33} & . & . \\ . & . & . & . & . & . \end{vmatrix}$$

and $\nabla_r (b_{rs})$, $\nabla_r (c_{rs})$ denote the determinants obtained by replacing each element of column (r) in $\nabla (b_{rs})$ and $\nabla (c_{rs})$ respectively by unity.

The General Expression for the Velocity Distribution Function.

§ 8 (B) This completes our solution of the fundamental problem of this paper, *i.e.*, the determination of the velocity-distribution function for a " nearly perfect " simple gas, composed of monatomic molecules of the most general type, and which is slightly non-uniform as regards temperature and mass-velocity.   The solution will be summarized as follows (*cf.* (10), (73)) :—

$$(142) \quad f(\mathsf{U}, \mathsf{V}, \mathsf{W}) = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2)}$$

$$\left\{ 1 - \mathrm{B}_0 \frac{1}{\mathrm{T}} \left(\mathsf{U}\frac{\partial \mathrm{T}}{\partial x} + \mathsf{V}\frac{\partial \mathrm{T}}{\partial y} + \mathsf{W}\frac{\partial \mathrm{T}}{\partial z} \right) \sum_{r=0}^{\infty} \frac{(2hm)^r}{1.3.5...(2r+3)r} \beta_{r-1} \mathrm{C}^{2r} \right.$$

$$- \mathrm{C}_0 (2hm) (c_{11}\mathsf{U}^2 + c_{22}\mathsf{V}^2 + c_{33}\mathsf{W}^2 + c_{23}\mathsf{V}\mathsf{W} + c_{31}\mathsf{W}\mathsf{U} + c_{12}\mathsf{U}\mathsf{V})$$

$$\left. \sum_{r=0}^{\infty} \frac{(2hm)^r}{1.3.5...(2r+5)} \gamma_r \mathrm{C}^{2r} \right\},$$

* The suffix 1 throughout these equations may now be omitted.

where c_{11}, c_{12}, &c., are given by (72). The coefficients β_r and γ_r, for $r = 0$ to $r = \infty$, are given by (140), where (*cf.* (136), (137), (130), (131)),

$$(143) \quad b_{rs} = 32\mathrm{B}_0\nu\lambda_{rs} \iint e^{-(x^2+y^2)} \overset{[r,s]}{\underset{k=1}{\Sigma}} \phi^{2k}(\tau y)\bigg[\mathrm{B}^{2k}(r+2, s+1) + \mathrm{B}^{2k}(r+1, s+2)$$

$$+2y^2\bigg\{\frac{2k+1}{4k+1}\mathrm{B}^{2k+1}(r+1, s+1) + \frac{2k}{4k+1}\mathrm{B}^{2k-1}(r+1, s+1)$$

$$-\mathrm{B}^{2k}(r+1, s+1)\bigg\}\bigg]x^2y^2\, dx\, dy,$$

$$(144) \quad c_{rs} = 72\mathrm{C}_0\nu\lambda'_{rs}\iint e^{-(x^2+y^2)}\overset{[r,s]}{\underset{k=1}{\Sigma}}\phi^{2k}(\tau y)\bigg[\mathrm{B}^{2k}(r+2, s) + \tfrac{2}{3}\mathrm{B}^{2k}(r+1, s+1) + \mathrm{B}^{2k}(r, s+2)$$

$$+4y^2\bigg\{\frac{2k+1}{4k+1}\Big(\mathrm{B}^{2k+1}(r+1, s) + \mathrm{B}^{2k+1}(r, s+1)\Big)$$

$$+ \frac{2k}{4k+1}\Big(\mathrm{B}^{2k-1}(r+1, s) + \mathrm{B}^{2k-1}(r, s-1)\Big) - \Big(\mathrm{B}^{2k}(r+1, s) + \mathrm{B}^{2k}(r, s+1)\Big)\bigg\}$$

$$+4y^4\bigg\{\frac{(2k+2)(2k+1)}{(4k+3)(4k+1)}\mathrm{B}^{2k+2}(r, s)$$

$$+\left(\frac{(2k+1)^2}{(4k+3)(4k+1)} + \frac{4k^2}{(4k+1)(4k-1)} + 1\right)\mathrm{B}^{2k}(r, s)$$

$$+\frac{2k(2k-1)}{(4k+1)(4k-1)}\mathrm{B}^{2k-2}(r, s)$$

$$-2\left(\frac{2k+1}{4k+1}\mathrm{B}^{2k+1}(r, s) + \frac{2k}{4k+1}\mathrm{B}^{2k-1}(r, s)\right)\bigg\}\bigg]x^2y^2\, dx\, dy$$

where (*cf.* (123))

$$(145) \qquad\qquad \tau = (2hm)^{-1/2},$$

and, by (111),

$$(146) \qquad \phi^{2k}(z) \equiv 2(4k+1)z\int_0^\infty \{1 - \mathrm{P}_{2k}(\cos\chi)\}\, p\, dp,$$

where $\mathrm{P}_k(\cos\chi)$ is the usual LEGENDRE's coefficient, and χ is a function of p and z which depends (§ 4 (D)) on the law of inter-action between two molecules at an encounter. The factors λ_{rs} and λ'_{rs} are defined by (125), (126), while the functions $\mathrm{B}^k(r, s)$, which are integral polynomials in x and y, with merely numerical coefficients, are defined by (129) and (96). In the upper limit of k, $[r, s]$ denotes the integral part of the lesser of the two quantities $\tfrac{1}{2}r+1$, $\tfrac{1}{2}s+1$.

The factors B_0, C_0 are, as yet, arbitrary; we now assign to them the values determined by the equations

$$(147) \qquad\qquad b_{00} = 1, \qquad c_{00} = 1.$$

This makes B_0 and C_0 each equal to ν^{-1} multiplied into a function of $(2hm)$, *i.e.*, of

the absolute temperature. The elements b_{rs}, c_{rs} and the coefficients β_r, γ_r, then become functions of the temperature only.

The coefficient β_{-1} is not determined by the above equations, but is given ($cf.$ (75)) by

$$(148) \qquad \beta_{-1} = - \sum_{r=0}^{\infty} \beta_r/(r+1).$$

Properties of the Determinants $\nabla(b_{rs})$, $\nabla(c_{rs})$.

§ 8 (C) On inspection of (143) and (144) it is evident that

$$(149) \qquad b_{rs} = b_{sr}, \qquad c_{rs} = c_{sr},$$

so that $\nabla(b_{rs})$ and $\nabla(c_{rs})$ are *symmetrical* determinants.

In expression (143) for b_{rs}, the variables of integration, x and y, are never negative, so that ($cf.$ (129), (96)) $^rA^k$, $^sA^k$ and $B^k(r, s)$ are essentially positive (or zero) for all integral values of r, s, and k; further, since $P_k(\cos \chi)$ never exceeds unity, $\phi^{2k}(\tau y)$ is also always positive. It is evident, therefore, that b_{rs} must be essentially positive if this can be proved true of

$$(150) \qquad B^{2k}(r+2, s+1) - 2y^2 B^{2k}(r+1, s+1) + B^{2k}(r+1, s+2).$$

Now

$$(151) \quad B^{2k}(r+2, s+1) - y^2 B^{2k}(r+1, s+1) = {}^{s+1}A^{2k}\left[{}^{r+2}A^{2k} - y^2\,{}^{r+1}A^{2k}\right]$$

$$= {}^{s+1}A^{2k}\left(\frac{y}{x}\right)^{2k}\left[\sum_{t=2k}^{r+2}\frac{(r+2)_t}{(t+\frac{1}{2})_t}\frac{(r+\frac{5}{2})_{t-2k}}{(t-2k)!}x^{2t}y^{2(r+2-t)} - \sum_{t=2k}^{r+1}\frac{(r+1)_t}{(t+\frac{1}{2})_t}\frac{(r+\frac{3}{2})_{t-2k}}{(t+2k)!}x^{2t}y^{2(r+2-t)}\right]$$

$$= {}^{s+1}A^{2k}\left(\frac{y}{x}\right)^{2k}\sum_{t=2k}^{r+2}\frac{(r+1)_{t-1}}{(t+\frac{1}{2})_t}\frac{(r+\frac{3}{2})_{t-2k-1}}{(t-2k)!}x^{2t}y^{2(r+2-t)}\{(r+2-t)(t-2k)+t(r+\frac{3}{2})\},$$

every term of which is positive. Interchanging r and s in (151), and adding the result to the latter, we obtain (150), which, with b_{rs} also, in consequence, is essentially positive.

From (151), moreover, it is clear that the numerical coefficients in (151) or (150) increase with r or s, and the same is readily seen to hold good also in the case of $B^k(r, s)$. As r or s increases, therefore, the numerical coefficients and the degree (in x and y) of the integrand of (143) increase, while if both r and s increase, new positive terms are added to the integrand. Hence, provided that the functions $\phi^{2k}(\tau y)$ satisfy certain simple conditions,* b_{rs} steadily increases with r or s, and the consideration of even a single term of (151) or the integrand of (143) shows that this increase is without limit, $i.e.$, b_{rs} tends steadily to infinity with r or s.

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* It is easy to see that the increase with y of $\phi^{2k}(\tau y)$ is less rapid than that of y; if $\phi^{2k}(\tau y)$ is constant or steadily increases, though less rapidly than y, b_{rs} will steadily increase with r or s. But much less restrictive conditions might be devised, $e.g.$, if $\phi^{2k}(\tau y)$ decreases like y^{-1}, the above result still holds good.

I have little doubt that, with rather more trouble, c_{rs} could be shown to share the above properties of b_{rs}, but I have not made any serious attempt to prove this; from the numerical calculations in § 10 (A) it appears probable that the increase of c_{rs} with r, s is more rapid than that of b_{rs}.

Properties of the First Row or Column of $\nabla(b_{rs})$ and $\nabla(c_{rs})$.

§ 8 (D) The numerical values of b_{rs} and c_{rs} obtained in § 10 suggest that many further general properties of these elements might be determined, with sufficient trouble, and that the convergence of the determinants $\nabla(b_{rs})$ and $\nabla(c_{rs})$ might thus be demonstrated.   Owing to the considerable algebraic difficulties involved, however, I have so far made little progress towards the proof of such properties, except for the case when r or s is zero, *i.e.*, for the elements of the first row or column of $\nabla(b_{rs})$ and $\nabla(c_{rs})$.   It will be shown that

$$(152) \qquad\qquad b_{r0} = b_{0r} = c_{r0} = c_{0r}$$

for all values of r.

This will be proved as a particular case of the more general result that

$$(152\text{A}) \quad (s+1)\, b_{rs}(k) = c_{rs}(k) \text{ when the lesser of } r \text{ and } s \text{ is even, and } k = [r,\, s],$$

where $b_{rs}(k)$, $c_{rs}(k)$ denote the parts of b_{rs} and c_{rs} respectively which are due to a particular value of k in (143), (144), while $[r,\, s]$ denotes the upper limit of k, as usual, *i.e.*, $k = \frac{1}{2}r+1$ or $\frac{1}{2}s+1$, whichever is the less.   Thus if we suppose that $r \gtreqqless s$, and that s is even, (152A) takes the form

$$(153) \qquad\qquad (s+1)\, b_{rs}\left(\tfrac{1}{2}s+1\right) = c_{rs}\left(\tfrac{1}{2}s+1\right).$$

When $s = 0$, this value of k is unity, and $b_{r0}(1)$, $c_{r0}(1)$, which usually form only a part of b_{rs}, c_{rs}, become the whole, so that (152) is the particular case of (153) corresponding to this value of s.

Since $\text{B}^k(r,\, s)$ is zero when either r or s is less than k, some of the terms in $b_{rs}\left(\tfrac{1}{2}s+1\right)$, $c_{rs}\left(\tfrac{1}{2}s+1\right)$ vanish.   In fact, as may readily be seen from (143), (144), we have

$$(154) \quad b_{rs}\left(\tfrac{1}{2}s+1\right) = 32\mathrm{B}_0\nu\lambda_{rs} \iint e^{-(x^2+y^2)}\phi^{s+2}(\tau y)\left\{\mathrm{B}^{s+2}(r+1,\, s+2)\right.$$

$$\left. + \frac{2(s+2)}{2s+5}\, y^2 \mathrm{B}^{s+1}(r+1,\, s+1)\right\} x^2 y^2 \, dx\, dy,$$

$$(155) \quad c_{rs}\left(\tfrac{1}{2}s+1\right) = 72\mathrm{C}_0\nu\lambda'_{rs} \iint e^{-(x^2+y^2)}\phi^{s+2}(\tau y)\left\{\mathrm{B}^{s+2}(r,\, s+2) + \frac{4(s+2)}{2s+5}\, y^2 \mathrm{B}^{s+1}(r,\, s+1)\right.$$

$$\left. + \frac{4(s+1)(s+2)}{(2s+3)(2s+5)}\, y^4 \mathrm{B}^s(r,\, s)\right\} x^2 y^2 \, dx\, dy$$

From (96) it is easy to see that

$$(156) \qquad {}^{k}A^{k} = \frac{k!}{(k+\frac{1}{2})_{k}} (xy)^{k},$$

so that

$$(157) \qquad B^{s+2}(r+1,\, s+2) + \frac{2(s+2)}{2s+5} y^{2}B^{s+1}(r+1,\, s+1)$$

$$= \frac{(s+2)!}{(s+\frac{5}{2})_{s+2}} \sum_{t=s+1}^{r+1} \frac{(r+1)_{t}\,(r+\frac{5}{2})_{t-s-1}}{(t+\frac{1}{2})_{t}\,(t-s-1)!} x^{2t}y^{2(r+s+3-t)}.$$

By putting r in place of $(r+1)$ in (157), and adding $\{2(s+2)y^{2}/(2s+5)\}$ times a similar expression in which r, s replace $r+1, s+1$ in (157), we also have

$$(158) \qquad B^{s+2}(r,\, s+2) + \frac{4(s+2)}{2s+5} y^{2}B^{s+1}(r,\, s+1) + \frac{4(s+1)(s+2)}{(2s+3)(2s+5)} y^{4}B^{s}(r,\, s)$$

$$= \frac{(s+2)!}{(s+\frac{5}{2})_{s+2}} \sum_{t=s}^{r} \frac{r_{t}}{(t+\frac{1}{2})_{t}} \frac{(r+\frac{5}{2})_{t-s}}{(t-s)!} x^{2t}y^{2(r+s+2-t)}.$$

We now substitute the expressions on the left of (157) and (158) into (154) and (155), and integrate with respect to x by means of the well-known formula

$$(159) \qquad \int_{0}^{\infty} e^{-x^{2}}x^{2(t+1)}\,dx = \tfrac{1}{4}\pi^{1/2}(t+\tfrac{1}{2})_{t};$$

we thus obtain the equations

$$(160) \quad b_{rs}(\tfrac{1}{2}s+1) = 8B_{0}\nu\pi^{1/2}\lambda_{rs}\int e^{-y^{2}}\phi^{s+2}(\tau y)\frac{(s+2)!}{(s+\frac{5}{2})_{s+2}} \sum_{t=s+1}^{r+1} \frac{(r+1)_{t}(r+\frac{5}{2})_{t-s-1}}{(t-s-1)!} y^{2(r+s+4-t)}\,dy,$$

$$(161) \quad c_{rs}(\tfrac{1}{2}s+1) = 18C_{0}\nu\pi^{1/2}\lambda'_{rs}\int e^{-y^{2}}\phi^{s+2}(\tau y)\frac{(s+2)!}{(s+\frac{5}{2})_{s+2}} \sum_{t=s}^{r} \frac{r_{t}(r+\frac{5}{2})_{t-s}}{(t-s)!} y^{2(r+s+3-t)}\,dy,$$

or, changing the notation so as to make the lower limit of t zero, and inserting the values of $\lambda_{rs}, \lambda'_{rs}$ according to (125), (126), i.e.,

$$(162) \qquad \lambda_{rs} = \frac{2^{-(r+s+4)}}{(r+1)(s+1)(r+\frac{5}{2})_{r+2}(s+\frac{5}{2})_{s+2}}, \qquad \lambda'_{rs} = \frac{2^{-(r+s+4)}}{(r+\frac{5}{2})_{r+2}(s+\frac{5}{2})_{s+2}},$$

we have

$$(163) \quad b_{rs}(\tfrac{1}{2}s+1)$$

$$= 2^{-(r+s+1)}B_{0}\nu\pi^{1/2}\frac{r_{s}}{(s+1)(r+\frac{5}{2})_{r+2}} \frac{(s+2)!}{\{(s+\frac{5}{2})_{s+2}\}^{2}}\int e^{-y^{2}}\phi^{s+2}(\tau y)\sum_{t=0}^{r-s} {}_{r-s}C_{t}(r+\tfrac{5}{2})_{t}\, y^{2(r+3-t)}\,dy,$$

$$(164) \quad c_{rs}(\tfrac{1}{2}s+1)$$

$$= 9\cdot 2^{-(r+s+3)}C_{0}\nu\pi^{1/2}\frac{r_{s}}{(r+\frac{5}{2})_{r+2}} \frac{(s+2)!}{\{(s+\frac{5}{2})_{s+2}\}^{2}}\int e^{-y^{2}}\phi^{s+2}(\tau y)\sum_{t=0}^{r-s} {}_{r-s}C_{t}(r+\tfrac{5}{2})_{t}\, y^{2(r+3-t)}\,dy.$$

The ratio of these two expressions is given by

$$\frac{b_{rs}\left(\tfrac{1}{2}s+1\right)}{c_{rs}\left(\tfrac{1}{2}s+1\right)} = \frac{A}{s+1},$$

where A is a quantity independent of r and s. When $s = 0$, as we have seen, $b_{rs}\left(\tfrac{1}{2}s+1\right)$ and $c_{rs}\left(\tfrac{1}{2}s+1\right)$ become identical with b_{rs} and c_{rs} respectively. Hence

$$\frac{b_{r0}}{c_{r0}} = A,$$

and since B_0 and C_0 have been chosen so that $b_{00} = 1$, $c_{00} = 1$, the value of A must be unity. Hence, when s is even and $r \geqq s$,

$$(s+1)\, b_{rs}\left(\tfrac{1}{2}s+1\right) = c_{rs}\left(\tfrac{1}{2}s+1\right),$$

with the consequence that

$$b_{r0} = c_{r0}$$

as a special case.

It is convenient to introduce the notation

$$(165) \qquad \int_0^\infty e^{-y^2}\phi^{2k}\left(\tau y\right) y^{2(m+1)}\, dy \equiv \tfrac{1}{4}\pi^{1/2}\left(m+\tfrac{1}{2}\right)_m K_{m-2k,\,k},$$

so that if $\phi^{2k}\left(\tau y\right)$ had the value unity, the value of $K_{m-2k,\,k}$ would also be unity, by (159). In terms of this notation (163) and (164) may be written as follows:—

$$(166) \qquad b_{rs}\left(\tfrac{1}{2}s+1\right) = 2^{-(r+s+3)} B_0 \nu\pi\, \frac{r_s}{s+1}\, \frac{(s+2)!}{\{(s+\tfrac{5}{2})_{s+2}\}^3}\, \sum_{t=0}^{r-s}{}_{r-s}C_t K_{r-s-t,\,\frac{1}{2}s+1},$$

$$(167) \qquad c_{rs}\left(\tfrac{1}{2}s+1\right) = 9\,.\,2^{-(r+s+5)} C_0 \nu\pi r_s\, \frac{(s+2)!}{\{(s+\tfrac{5}{2})_{s+2}\}^2}\, \sum_{t=0}^{r-s}{}_{r-s}C_t K_{r-s-t,\,\frac{1}{2}s+1}.$$

By writing $t = r-s-t'$ it is evident that

$$(168) \qquad \sum_{t=0}^{r-s}{}_{r-s}C_t K_{r-s-t,\,\frac{1}{2}s+1} = \sum_{t=0}^{r-s}{}_{r-s}C_t K_{t,\,\frac{1}{2}s+1}.$$

By giving to r and s in (166), (167) the value zero, we have

$$(169) \qquad b_{00} = \tfrac{4}{225} B_0 \nu\pi K_{0,1}, \qquad c_{00} = \tfrac{1}{25} C_0 \nu\pi K_{01},$$

whence, remembering that (cf. (147)) B_0 and C_0 are so defined as to make b_{00} and c_{00} each equal to unity, we have

$$(170) \qquad B_0 = \tfrac{225}{4}\, \frac{1}{\pi\nu K_{0,1}}, \qquad C_0 = 25\, \frac{1}{\pi\nu K_{0,1}}, \qquad B_0 = \tfrac{9}{4}C_0.$$

We will substitute these values into (166), (167), and write $s = 0$, in order to obtain expressions for b_{r0} and c_{r0} as follows :—

$$(171) \qquad b_{r0} = b_{0r} = c_{r0} = c_{0r} = \kappa_r / \kappa_0,$$

where we have written

$$(172) \qquad \kappa_r \equiv 2^{-r} \sum_{t=0}^{r} {}_rC_t K_{t,1},$$

so that

$$(173) \qquad \kappa_0 = K_{0,1} = \frac{16}{15\pi^{1/2}} \int_0^\infty e^{-y^2} \phi^2 (\tau y) y^6 \, dy.$$

It is of interest to examine also the rth successive difference of b_{r0} or c_{r0}, which we shall denote by $\delta_{r0}b_{r0}$ or $\delta_{r0}c_{r0}$.   We have

$$(174) \qquad \delta_{r0} f(r) = f(r) - {}_rC_1 f(r-1) + {}_rC_2 f(r-2) - \dots.$$

Then, from (172), it is easy to see that

$$\delta_{r0}\kappa_r = 2^{-r} \sum_{m=0}^{r} (-2)^m {}_rC_m \sum_{t=0}^{r-m} {}_{r-m}C_t K_{t,1}$$

$$= 2^{-r} \sum_{t=0}^{r} {}_rC_t K_{t,1} \sum_{m=0}^{r-t} (-2)^m {}_{r-t}C_m$$

$$= (-2)^{-r} \sum_{t=0}^{r} (-1)^t {}_rC_t K_{t,1},$$

since

$$\sum_{m=0}^{r-t} (-2)^m {}_{r-t}C_m = (1-2)^{r-t} = (-1)^{r-t}.$$

Hence

$$(175) \qquad \delta_{r0}b_{r0} = \delta_{r0}c_{r0} = (-2)^{-r} (\kappa_0)^{-1} \sum_{t=0}^{r} (-1)^t {}_rC_t K_{t,1}.$$

Similarly the rth difference of

$$2^{-r} \tau_s \sum_{t=0}^{r-s} {}_{r-s}C_t K_{t, 1/2 s+1},$$

which is the part of $b_{rs}(\tfrac{1}{2}s+1)$ or $c_{rs}(\tfrac{1}{2}s+1)$ which depends on r (s being even and $r \gtreqless s$) is equal to

$$(-1)^{r+s} \frac{\tau_s}{2^r} \sum_{t=0}^{r-s} (-1)^t {}_{r-s}C_t K_{t, 1/2 s+1}.$$

Symmetrical Expressions for $\displaystyle\sum_{r=0}^{\infty} \beta_r$ and $\displaystyle\sum_{r=0}^{\infty} \gamma_r$.

§ 8 (E) While $\nabla(b_{rs})$ and $\nabla(c_{rs})$ are symmetrical, the derived determinants $\nabla_r(b_{rs})$, $\nabla_r(c_{rs})$ are necessarily lacking in symmetry, and our expressions for β_r and γ_r, when we attempt to make successive numerical approximations to their values

for particular types of molecular models (*cf.* § 10), appear not to converge at all rapidly. Fortunately, in our applications of the velocity-distribution function to the theory of viscosity and thermal conductivity, we need to know not the individual values of the β's and γ's, but only the sums $\sum\limits_{r=0}^{\infty} \beta_r$ and $\sum\limits_{r=0}^{\infty} \gamma_r$; for these it is possible to determine symmetrical expressions which are found, in practice, to be highly convergent.

In what follows we shall use the symbol δ_{mn} placed before a function of the integral variables r, s (such as b_{rs} or c_{rs}) to denote the $(m, n)^{\text{th}}$ successive difference of this function with respect to r and s respectively. Thus

$$\delta_{m0} f(r, s) = f(r, s) - {}_m C_1 f(r-1, s) + {}_m C_2 f(r-2, s) - \dots$$

$$\delta_{0n} f(r, s) = f(r, s) - {}_n C_1 f(r, s-1) + {}_n C_2 f(r, s-2) - \dots$$

$$\delta_{mn} f(r, s) = \delta_{m0} f(r, s) - {}_n C_1 \delta_{m0} f(r, s-1) + {}_n C_2 \delta_{m0} f(r, s-2) - \dots$$

$$= \delta_{0n} f(r, s) - {}_m C_1 \delta_{0n} f(r-1, s) + {}_m C_2 \delta_{0n} f(r-2, s) - \dots$$

When we substitute b_{rs} or c_{rs} for $f(r, s)$ in the above formal expressions, any term with a negative suffix is to be omitted as being zero.

Since the value of a determinant is unaltered by subtracting from the elements of any one row or column the corresponding elements of any other row or column, and since this process can be repeated indefinitely often, it is clear that from (141), by subtracting the $(s-1)^{\text{th}}$ row from the sth, for all values of s from 1 onwards, we have[*]

(176) $$\nabla (b_{rs}) = \nabla (\delta_{01} b_{rs}), \qquad \nabla (c_{rs}) = \nabla (\delta_{01} c_{rs}).$$

The same process applied to $\nabla_r (b_{rs})$, $\nabla_r (c_{rs})$ leads to determinants identical with $\nabla (\delta_{01} b_{rs})$ and $\nabla (\delta_{01} c_{rs})$ respectively, save that in the rth column all the elements are zero except the one in the first row, which is unity. Evidently, therefore, $\nabla_r (b_{rs})$ and $\nabla_r (c_{rs})$ are the rth minors of determinants which are respectively identical with $\nabla (\delta_{01} b_{rs})$ and $\nabla (\delta_{01} c_{rs})$, except that in each case all the elements of the first row have the value unity. Consequently the sums $\sum\limits_{r=0}^{\infty} \nabla_r (b_{rs})$ and $\sum\limits_{r=0}^{\infty} \nabla_r (c_{rs})$ are equal to the sums of the minors of the two determinants just described, *i.e.*, they are equal to these determinants themselves. Thus, by (140),

(177) $$\sum\limits_{r=0}^{\infty} \beta_r = \frac{\nabla (\delta_{01} b'_{rs})}{\nabla (\delta_{01} b_{rs})}, \qquad \sum\limits_{r=0}^{\infty} \gamma_r = \frac{\nabla (\delta_{01} c'_{rs})}{\nabla (\delta_{01} c_{rs})},$$

where we have

(178) $$b'_{0s} = 1, \quad c'_{0s} = 1, \quad (s = 0 \text{ to } \infty), \quad b'_{rs} = b_{rs}, \quad c'_{rs} = c_{rs}, \quad (s = 0 \text{ to } \infty, \ r = 1 \text{ to } \infty).$$

[*] When $s = 0$, δ_{01} should be replaced by δ_{00}.

To the above determinants we now apply the same process of differencing by columns which has already been applied by rows, and we thus obtain the equations

$$(179) \qquad \sum_{r=0}^{\infty} \beta_r = \frac{\nabla\,(\delta_{11} b'_{rs})}{\nabla\,(\delta_{11} b_{rs})}, \qquad\qquad \sum_{r=0}^{\infty} \gamma_r = \frac{\nabla\,(\delta_{11} c'_{rs})}{\nabla\,(\delta_{11} c_{rs})}.$$

The determinants $\nabla\,(\delta_{11} b'_{rs})$ and $\nabla\,(\delta_{11} b_{rs})$ are identical save in their first rows; all the elements of the first row of the former are zero save the first, which is unity. Hence $\nabla\,(\delta_{11} b'_{rs})$ is equal to the *principal minor* of $\nabla\,(\delta_{11} b_{rs})$; we shall denote it by $\nabla'\,(\delta_{11} b_{rs})$. Hence, and with a similar notation for the principal minor of $\nabla\,(\delta_{11} c_{rs})$, we have*

$$\sum_{r=0}^{\infty} \beta_r = \frac{\nabla'\,(\delta_{11} b_{rs})}{\nabla\,(\delta_{11} b_{rs})}, \qquad\qquad \sum_{r=0}^{\infty} \gamma_r = \frac{\nabla'\,(\delta_{11} c_{rs})}{\nabla\,(\delta_{11} c_{rs})}$$

All these determinants have now regained a symmetrical form.

It is convenient, partly for the sake of elegance, and also because it imparts a highly convergent form to the elements of our determinants (*cf.* § 10) to continue this process of differencing still further, as follows. We repeat the whole of the above operation of differencing by rows and columns an indefinite number of times, beginning now at the second row and column (thus leaving unchanged the values both of ∇ and its principal minor), and afterwards successively at the next later row and column than on the previous occasion. The general element thus becomes $\delta_{rs} b_{rs}$ or $\delta_{rs} c_{rs}$, and we have

$$(180) \qquad \sum_{r=0}^{\infty} \beta_r = \frac{\nabla'\,(\delta_{rs} b_{rs})}{\nabla\,(\delta_{rs} b_{rs})}, \qquad\qquad \sum_{r=0}^{\infty} \gamma_r = \frac{\nabla'\,(\delta_{rs} c_{rs})}{\nabla\,(\delta_{rs} c_{rs})},$$

where the dash (') denotes the principal minor of the corresponding determinant. These expressions could, of course, have been obtained directly by a re-arrangement of the original equations of transfer, but it seems preferable to use the latter in the more simple, natural forms chosen, and to make this transformation by differencing in relation to the determinants formed by the elements b_{rs}, c_{rs}.

§ 9. Consideration of Particular Molecular Models.

§ 9 (A) While, as we have seen, certain general properties of the elements b_{rs}, c_{rs} can be demonstrated without the assumption of any property of the molecules save spherical symmetry, it is possible to carry our investigations much further when we represent the molecules by particular models of simple type, such as point centres of force, or rigid elastic spheres. This involves, primarily, the examination of the functions $\phi^{2k}\,(\tau y)$.

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* When r or s is zero, the corresponding suffix of δ_{11} should also be written as zero.

Molecules which are Point Centres of Force varying as r^{-n}.

§ 9 (B) When the molecules are point centres of force varying inversely as the nth power of the distance, the angle χ in the expression (146)—*cf.* § 4 (D)—is given by the following integral* :—

$$(181) \qquad \chi = 2 \int_0^{\eta_0} [1 - \eta^2 - (\eta/\alpha)^{n-1}]^{-1/2} \, d\eta.$$

Here η_0 is the least positive root of the equation $[1 - \eta^2 - (\eta/\alpha)^{n-1}] = 0$, and α is a multiple of p, thus,

$$(182) \qquad \alpha = p \left(\frac{n-1}{4 \mathrm{K} m}\right)^{\frac{1}{n-1}} (2 \mathrm{C_R})^{\frac{2}{n-1}} = p \left(\frac{n-1}{\mathrm{K} m}\right)^{\frac{1}{n-1}} \mathrm{C_R}^{\frac{2}{n-1}},$$

where K is a constant which measures the intensity of force between two molecules at unit distance. Hence (*cf.* (111))

$$
\begin{aligned}
(183) \qquad \phi^{2k}(\tau y) &= 2(4k+1)\left(\frac{\mathrm{K} m}{n-1}\right)^{\frac{2}{n-1}} \mathrm{C_R}^{1 - \frac{4}{n-1}} \int_0^\infty \{1 - \mathrm{P}_{2k}(\cos \chi)\} \, \alpha \, d\alpha \\
&= 2(4k+1)\left(\frac{\mathrm{K} m}{n-1}\right)^{\frac{2}{n-1}} \left(\frac{y^2}{2hm}\right)^{\frac{n-5}{2(n-1)}} \int_0^\infty \{1 - \mathrm{P}_{2k}(\cos \chi)\} \, \alpha \, d\alpha \\
&= {}_n \mathrm{A}_k \left(\frac{y^2}{2hm}\right)^{\frac{n-5}{2(n-1)}},
\end{aligned}
$$

where ${}_n \mathrm{A}_k$ is a constant depending on n and k, but not on y or h (*i.e.*, not on the absolute temperature).

When this value of $\phi^{2k}(\tau y)$ is substituted in our expressions for b_{rs} and c_{rs}, it becomes possible to execute the integration with respect both to x and to y in terms of gamma-functions. Thus (*cf.* (165))

$$
\begin{aligned}
(184) \qquad \int_0^\infty e^{-y^2} \phi^{2k}(\tau y) \, y^{2(m+1)} \, dy &= \tfrac{1}{4} \pi^{1/2} (m + \tfrac{1}{2})_m \mathrm{K}_{m-2k, \, k} \\
&= {}_n \mathrm{A}_k \left(\frac{1}{2hm}\right)^{\frac{n-5}{2(n-1)}} \int_0^\infty e^{-y^2} y^{2\left(m+1+\frac{1}{2}\frac{n-5}{n-1}\right)} \, dy \\
&= \tfrac{1}{2} {}_n \mathrm{A}_k \left(\frac{1}{2hm}\right)^{\frac{n-5}{2(n-1)}} \Gamma\left(m + 2 - \frac{2}{n-1}\right),
\end{aligned}
$$

so that

$$(185) \qquad \kappa_0 = \mathrm{K}_{0,1} = \tfrac{8}{15} \pi^{-1/2} {}_n \mathrm{A}_1 \left(\frac{1}{2hm}\right)^{\frac{n-5}{2(n-1)}} \Gamma\left(4 - \frac{2}{n-1}\right).$$

---

* *Cf.* § 14, p. 454, of my former memoir, 'Phil. Trans.,' A, vol. 211 (1911). The V_0 of the formula there given is the relative velocity of two molecules, which in our notation is $(\mu_1 \mu_2)^{-1/2} \mathrm{C_R} = 2 \mathrm{C_R}$ when the gas is simple.

and

$$(186) \qquad K_{t,1} = 2\pi^{-1/2} {}_n A_1 \left(\frac{1}{2hm}\right)^{\frac{n-5}{2(n-1)}} \{(t+\tfrac{5}{2})_{t+2}\}^{-1} \Gamma\left(t+4-\frac{2}{n-1}\right) = \frac{\left(t+3-\dfrac{2}{n-1}\right)_t}{(t+\tfrac{5}{2})_t} K_{0,1}.$$

Hence the values assumed by B_0 and C_0 in this special case are as follows (*cf.* (170), §8 (D)):—

$$(187) \qquad B_0 = \frac{15^3}{32} \frac{(2hm)^{1/2 \frac{n-5}{n-1}}}{\pi^{1/2} {}_n A_1 \Gamma\left(4-\dfrac{2}{n-1}\right)\nu}, \qquad C_0 = \frac{375}{8} \frac{(2hm)^{1/2 \frac{n-5}{n-1}}}{\pi^{1/2} {}_n A_1 \Gamma\left(4-\dfrac{2}{n-1}\right)\nu}.$$

From (186) we have

$$b_{r0} = c_{r0} = \kappa_r/\kappa_0 = 2^{-r} \sum_{t=0}^{r} {}_r C_t K_{t,1}/K_{0,1}$$

$$= 2^{-r} \sum_{t=0}^{r} \frac{r_t}{t!} \frac{\left(t+3-\dfrac{2}{n-1}\right)_t}{(t+\tfrac{5}{2})_t}$$

$$= 2^{-r} F\left(-r,\ 4-\frac{2}{n-1},\ \tfrac{7}{2},\ -1\right),$$

in the notation of the hypergeometric function. It may hence be shown, without much difficulty, that (if $n > 5$) b_{r0} and c_{r0} steadily increase to infinity with r, the rate of increase being comparable with that of $r^{\frac{n-5}{n-1}}$.

Since the functions $\phi^{2k}(\tau y)$ all depend on h in the same way, it is clear that, with the above values of B_0 and C_0, the elements b_{rs} and c_{rs} and consequently, also, the coefficients β_r and γ_r in the velocity-distribution function for molecules of this type, are independent of h, *i.e.*, they are independent of temperature. They are, indeed, pure numbers, depending only on the molecular mass and on the force constant of the molecules.

It is of interest to determine the value of the elements $\delta_{r0}b_{r0}$ (or $\delta_{r0}c_{r0}$) of the outer row or column of $\nabla(\delta_{rs}b_{rs})$, in this special case. We have, by (175),

$$\delta_{r0}b_{r0} = \delta_{r0}c_{r0} = (-2)^{-r} \sum_{t=0}^{r} (-1)^t {}_r C_t K_{t,1}/K_{0,1},$$

$$= (-2)^{-r} \sum_{t=0}^{r} (-1)^t \frac{r_t}{t!} \frac{\left(t+3-\dfrac{2}{n-1}\right)_t}{(t+\tfrac{5}{2})_t},$$

$$= (-2)^{-r} F\left(-r,\ 4-\frac{2}{n-1},\ \tfrac{7}{2},\ 1\right),$$

in the notation of hypergeometric functions, or, in terms of gamma-functions,

$$(188) \qquad \delta_{r0}b_{r0} = \delta_{r0}c_{r0} = (-2)^{-r} \frac{\Gamma\left(\tfrac{7}{2}\right)\Gamma\left(r-\tfrac{1}{2}+\dfrac{2}{n-1}\right)}{\Gamma\left(r+\tfrac{7}{2}\right)\Gamma\left(\dfrac{2}{n-1}-\tfrac{1}{2}\right)} = (-2)^{-r} \frac{\left(r-\tfrac{3}{2}+\dfrac{2}{n-1}\right)_r}{(r+\tfrac{5}{2})_r}.$$

As r tends to infinity, the last expression tends to zero more quickly that

$$2^{-r} r^{-\left(4-\frac{2}{n-1}\right)},$$

and also it is alternately of positive and negative sign, after the first two terms (both $\delta_{00} b_{r0}$ and $\delta_{10} b_{10}$ being positive).

Maxwellian Molecules: $n = 5$.

§9 (C) It is now easy to see what are the special properties of the fifth-power law ($n = 5$), the law obeyed by the molecules which we term Maxwellian, which enabled MAXWELL to work out the theory on this hypothesis with such great simplicity and accuracy.   When $n = 5$, we have from (186)

(189)
$$K_{t,1} = {}_5A_1,$$

which is independent of t.   Hence, by (170), (171), (172),

(190) $K_{t,1} = K_{0,1} = {}_5A_1, \quad \kappa_r = 2^{-r} \overset{r}{\underset{t=0}{\Sigma}} {}_rC_t K_{t,1} = 2^{-r} K_{0,1} \overset{r}{\underset{t=0}{\Sigma}} {}_rC_t = K_{0,1} = \kappa_0, \; b_{r0} = c_{r0} = 1 \;;$

(191) $\delta_{r,0} b_{r,0} = \delta_{r,0} c_{r0} = (-2)^{-r} \overset{r}{\underset{t=0}{\Sigma}} (-1)^t \, {}_rC_t = (-2)^{-r} (1-1)^r = 0, \quad (r>0)\;;$

(192) $B_0 = \tfrac{225}{4} (\nu_5 A_1)^{-1}, \quad C_0 = 25 (\nu_5 A_1)^{-1}.$

From (191) and the equation $b_{00} = c_{00} = 1$ we deduce that in this case the principal minors of $\nabla (\delta_{rs} b_{rs})$ and $\nabla (\delta_{rs} c_{rs})$ are equal to these determinants themselves, $i.e.$,

(193) $\overset{\infty}{\underset{r=0}{\Sigma}} \beta_r = 1, \qquad \overset{\infty}{\underset{r=0}{\Sigma}} \gamma_r = 1$ (Maxwellian molecules),

while from (190) it appears that all the elements of the first row and column of $\nabla (b_{rs})$ and $\nabla (c_{rs})$ are unity.   Hence in $\nabla_r (b_{rs})$ and $\nabla_r (c_{rs})$ the first column and column (r) are identical, so that we have

(194) $\nabla_r (b_{rs}) = 0, \qquad \nabla_r (c_{rs}) = 0, \qquad r > 0$ ⎫

(195) $\nabla_0 (b_{rs}) = \nabla (b_{rs}), \qquad \nabla_0 (c_{rs}) = \nabla (c_{rs})$ ⎬ (Maxwellian molecules),
⎭

whence also, by (140), we have

(196) $\beta_0 = 1, \qquad \gamma_0 = 1, \qquad \beta_r = \gamma_r = 0, \qquad (r > 0)$ (Maxwellian molecules),

and also, by (148),

(197) $\beta_{-1} = -\beta_0 = -1$ (Maxwellian molecules).

In the case of molecules which obey the fifth-power law, therefore, the velocity distribution function has the simple finite form (*cf.* (142))

$$(198) \quad f(\mathsf{U}, \mathsf{V}, \mathsf{W}) = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2)}$$

$$\left[1 - (\nu_5 \mathsf{A}_1)^{-1} \left\{ \tfrac{7.5}{4} \frac{1}{\mathsf{T}} \left(\mathsf{U}\frac{\partial \mathsf{T}}{\partial x} + \mathsf{V}\frac{\partial \mathsf{T}}{\partial y} + \mathsf{W}\frac{\partial \mathsf{T}}{\partial z}\right)(-1 + \tfrac{1}{5}2hm\mathsf{C}^2)\right.\right.$$

$$\left.\left. + \tfrac{5}{3}(2hm)(c_{11}\mathsf{U}^2 + c_{22}\mathsf{V}^2 + c_{33}\mathsf{W}^2 + 2c_{23}\mathsf{VW} + 2c_{31}\mathsf{WU} + 2c_{12}\mathsf{UV})\right\}\right]$$

(Maxwellian molecules),

where $\mathsf{C}^2 = \mathsf{U}^2 + \mathsf{V}^2 + \mathsf{W}^2$, c_{11}, c_{12}, &c., are given by (72), and (*cf.* (183))

$$(199) \qquad {}_5\mathsf{A}_1 = 10\left(\tfrac{1}{4}Km\right)^{1/2}\int_0^\infty \{1 - \mathrm{P}_2(\cos\chi)\}\,\alpha\,d\alpha = \tfrac{15}{2}(Km)^{1/2}\int_0^\infty \sin^2\chi\,.\,\alpha\,d\alpha.$$

MAXWELL[*] calculated the value of the integral $\int_0^\infty \sin^2\chi\,.\,\alpha\,d\alpha$, the forces being repulsive, by numerical quadrature, and found that

$$\pi\int_0^\infty \sin^2\chi\,.\,\alpha\,d\alpha = 1\cdot3682,$$

so that, for repulsive forces proportional to the inverse fifth power of the distance

$$(200) \qquad\qquad {}_5\mathsf{A}_1 = \frac{15}{2\pi}\,1\cdot3682\,(Km)^{1/2},$$

where Km^2 is the force between two molecules at unit distance.

Molecules which are Rigid Elastic Spheres.

§ 9 (D) We next consider molecules which behave at encounter like rigid elastic spheres of radius σ. This particular molecular model has been more used than any other, in researches on the kinetic theory, on account of its simplicity and concreteness, which aid the imagination in following or constructing "descriptive" theories of gaseous phenomena. As regards the analytical development of the theory, also, it is probably the simplest case after that of Maxwellian molecules. The difference between the two models in this respect is, however, enormous, the rigid elastic spherical molecule requiring the infinity of terms β_r, γ_r in the velocity-distribution function, just as in the case of the most general molecular model. The comparative simplicity of the present model lies in the moderately tractable expressions for b_{rs}, c_{rs} to which it leads. Apart from the methods of the present and my former paper,

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[*] MAXWELL, 'Collected Papers,' ii, p. 42. His constant A_2 equals $\pi\int_0^\infty \sin^2\chi\,.\,\alpha\,d\alpha$ in our notation.

however, it has not been found possible in the past to obtain any close numerical accuracy in calculations based on this molecular model, the errors resulting in previous theories (although these have been carefully constructed and closely scrutinized) ranging from 10 to 50 per cent. (*cf.* § 11 (F)).

It is readily seen* that in the present case

$$(201) \qquad \chi = 0 \quad (p > 2\sigma) \qquad \sin \tfrac{1}{2}\chi = p/2\sigma \quad (p \leqq 2\sigma)$$

so that

$$p\,dp = 2\sigma^2 \sin \tfrac{1}{2}\chi \cos \tfrac{1}{2}\chi\,d\chi = \sigma^2 \sin \chi\,d\chi = -\sigma^2\,d\cos\chi.$$

As p ranges from 0 to 2σ, χ ranges from 0 to 2π, and $-\cos\chi$ from -1 to 1. Hence (*cf.* (111))

$$(202) \qquad \phi^{2k}(\tau y) = 2(4k+1)\,\mathrm{C_R}\sigma^2 \int_{-1}^{1} \{1 - \mathrm{P}_{2k}(\cos\chi)\}\,d\cos\chi$$

$$= 4(4k+1)\,\sigma^2(2hm)^{-1/2}y,$$

since $\int_{-1}^{1} \mathrm{P}_{2k}(\mu)\,d\mu = 0$. Hence $\phi^{2k}(\tau y)$ depends on k only as regards the numerical factor $(4k+1)$, and the present case is, analytically, the same as that considered in § 8 (B) if we write (*cf.* (183))

$$(203) \qquad \frac{n-5}{n-1} = 1, \quad \text{or} \quad n = \infty, \quad \text{and} \quad {}_n\mathrm{A}_k = 4(4k+1)\,\sigma^2.$$

We may therefore quote from the formulæ of § 8 (B) as follows without further discussion :—

$$(204) \qquad \tfrac{1}{4}\pi^{1/2}(m+\tfrac{1}{2})_m\mathrm{K}_{m-2k,\,k} = 2(4k+1)\,\sigma^2(2hm)^{-1/2}\Gamma(m+2)$$

$$= 2(4k+1)(m+1)!\,\sigma^2(2hm)^{-1/2},$$

$$(205) \qquad \kappa_0 = \mathrm{K}_{0,1} = 64\pi^{-1/2}\sigma^2(2hm)^{-1/2}, \qquad \mathrm{K}_{t,1} = \mathrm{K}_{0,1}(t+3)_t/(t+\tfrac{5}{2})_t.$$

$$(206) \qquad \mathrm{B}_0 = \tfrac{225}{256}\frac{(2hm)^{1/2}}{\pi^{1/2}\sigma^2\nu}, \qquad \mathrm{C}_0 = \tfrac{25}{64}\frac{(2hm)^{1/2}}{\pi^{1/2}\sigma^2\nu},$$

$$(207) \qquad b_{r0} = c_{r0} = 2^{-r}\sum_{t=0}^{r}\frac{r_t}{t!}\frac{(t+3)_t}{(t+\tfrac{5}{2})_t} = 2^{-r}\mathrm{F}(-r,\,4,\,\tfrac{7}{2},\,-1),$$

$$(208) \quad \delta_{r0}b_{r0} = \delta_{r0}c_{r0} = (-2)^{-r}\frac{(r-\tfrac{3}{2})_r}{(r+\tfrac{5}{2})_r} = -(-\tfrac{1}{2})^r\frac{15}{(2r-1)(2r+1)(2r+3)(2r+5)}.$$

As in the case of molecules which are point centres of force varying inversely as

* *Cf.* § 13, p. 453, of my former paper, 'Phil. Trans.,' A, 211 (1911).

the nth power of the distance, the elements b_{rs} and c_{rs}, and the coefficients β_r and γ_r, are pure numbers, independent of the temperature (*i.e.*, of h).

Molecules which are Rigid Elastic Spheres which Exert Attractive Forces.

§ 9 (E) Experiments on the phenomena of actual gases, as, for example, on the variation of viscosity with temperature, indicate that none of the molecular models so far discussed in this chapter gives a really adequate representation of these phenomena. The best of all the simple models which have been used in the kinetic theory seems to be that considered by VAN DER WAALS and SUTHERLAND, viz., a rigid elastic sphere surrounded by a weak field of attractive force. This agrees with the known fact of slight cohesion in gases. The effect of this field of force on the velocity-distribution function, or on viscosity and thermal conductivity, may be referred mainly to the deflections of molecular paths for which it is responsible *indirectly*, through the collisions which it induces between molecules which would otherwise pass one another without mutual inter-action, rather than to its direct effect in the absence of collisions. The latter effect will be expressly neglected in our calculations, which will therefore be inapplicable to vapours in which the cohesion is large enough to render this neglect invalid.

A detailed account of the dynamics of collisions in these circumstances is given in § 15 of my former paper, from which the following results are quoted. If the potential of the force between two molecules in contact be denoted by $\frac{1}{2}b^2$ (reckoning this potential as zero when the separation is infinite), the condition that a collision may take place is

$$(209) \qquad p < p_0 \quad \text{where} \quad p_0 = 2\sigma \left(1 + \frac{b^2}{3C_R^2}\right)^{1/2}$$

(since the relative velocity, in my former paper written V_0, is here denoted by $2C_R$). The angle χ corresponding to such a collision is given by

$$(210) \qquad \sin \tfrac{1}{2}\chi = p/p_0.$$

The angle χ corresponding to larger values of p, which do not correspond to actual collisions, is given by (181) if the molecular forces obey the nth power law, but we will here make no assumption on this point, as the deflections produced by the inter-molecular forces alone will be rejected after equation (211). Consequently

$$(211) \quad \phi^{2k}(\tau y) = 2\,(4k+1)\,\sigma^2\,(1+b^2/4C_R^2)\,C_R + 2\,(4k+1)\,C_R \int_{p_0}^{\infty} \{1 - P_{2k}(\cos\chi)\}\,p\,dp$$

$$= 4\,(4k+1)\,\sigma^2\,(2hm)^{-1/2}y\,(1+2hmb^2/4y^2) + f_{2k}(y)$$

by analogy with (202) and (183). The latter term $f_{2k}(y)$ represents the negligible

deflecting effect of the forces alone, as above mentioned, and it will be omitted henceforward. Hence, corresponding to the equation (204) of §9 (D), we have

$$(212) \qquad \tfrac{1}{4}\pi^{1/2}(t+\tfrac{1}{2})_t \, \mathrm{K}_{t-2k,\,k} = 2\,(4k+1)\,\sigma^2\,(2hm)^{-1/2}\,\Gamma\,(t+2)\left(1+\frac{2hmb^2}{4\,(t+1)}\right)$$

$$= 2\,(4k+1)\,(t+1)!\,\sigma^2\,(2hm)^{-1/2}\left(1+\frac{3\mathrm{S}}{(t+1)\,\mathrm{T}}\right),$$

where we have written

$$(213) \qquad\qquad\qquad \mathrm{S} = \frac{b^2 m}{12\mathrm{R}}.$$

Similarly we have

$$(214) \qquad\qquad \kappa_0 = \mathrm{K}_{0,1} = 64\pi^{-1/2}\sigma^2\,(2hm)^{-1/2}\left(1+\frac{\mathrm{S}}{\mathrm{T}}\right),$$

$$(215) \qquad\qquad \mathrm{K}_{t,1} = 64\pi^{-1/2}\sigma^2\,(2hm)^{-1/2}\,\frac{(t+3)_t}{(t+\tfrac{5}{2})_t}\left(1+\frac{3}{t+3}\frac{\mathrm{S}}{\mathrm{T}}\right),$$

$$(216) \qquad \mathrm{B}_0 = \tfrac{225}{256}\frac{(2hm)^{1/2}}{\pi^{1/2}\sigma^2\nu}\frac{1}{1+\mathrm{S}/\mathrm{T}}, \qquad \mathrm{C}_0 = \tfrac{25}{64}\frac{(2hm)^{1/2}}{\pi^{1/2}\sigma^2\nu}\frac{1}{1+\mathrm{S}/\mathrm{T}}.$$

It will be seen later that S is the well-known "SUTHERLAND'S constant" (§ 11 (F)).

§ 10. NUMERICAL CALCULATIONS FOR PARTICULAR MOLECULAR MODELS.

Rigid Elastic Spheres.

§ 10 (A) In the last section we determined the complete expression for the velocity-distribution function for a gas composed of Maxwellian molecules. In the other cases there considered we must be content to make numerical approximations, which can, of course, be carried to any desired degree of accuracy. We shall consider in most detail the case of rigid elastic spherical molecules, for which we shall calculate b_{rs} and c_{rs} for $0 \leqq r \leqq 3$, $0 \leqq s \leqq 3$. These are chosen for the fullest treatment partly because of their simplicity, and partly as representing the limit between which, and the case of Maxwellian molecules, the molecules of actual gases appear to lie.

In making such numerical approximations the following table of expanded formulæ for $\mathrm{B}^k\,(r,\,s)$ is useful :—

TABLE I.—Expressions for $\mathrm{B}^k\,(r,\,s)$.

$\mathrm{B}^0(0,0) = 1$ $\quad \mathrm{B}^1(1,1) = \tfrac{2}{3}xy$ $\quad \mathrm{B}^2(2,2) = \tfrac{8}{15}x^2y^2$ $\quad \mathrm{B}^3(3,3) = \tfrac{16}{35}x^3y^3$ $\quad \mathrm{B}^4(4,4) = \tfrac{128}{315}x^4y^4$

$\mathrm{B}^0\,(1,\,0) = x^2+y^2$ $\quad \mathrm{B}^1\,(2,\,1) = \tfrac{4}{3}xy\,(x^2+y^2)$ $\quad \mathrm{B}^2\,(3,\,2) = \tfrac{8}{5}xy\,(x^2+y^2)$

$\mathrm{B}^3\,(4,\,3) = \tfrac{64}{35}x^3y^3\,(x^2+y^2)$ $\quad \mathrm{B}^4\,(5,\,4) = \tfrac{128}{63}x^4y^4\,(x^2+y^2)$

$\mathrm{B}^0\,(2,\,0) = x^4+\tfrac{10}{3}x^2y^2+y^4$ $\quad \mathrm{B}^1\,(3,\,1) = 2xy\,(x^4+\tfrac{14}{5}x^2y^2+y^4)$

$\mathrm{B}^2\,(4,\,2) = \tfrac{16}{5}x^2y^2\,(x^4+\tfrac{18}{7}x^2y^2+y^4)$

$\mathrm{B}^0\,(3,\,0) = x^6+7x^4y^2+7x^2y^4+y^6$ $\quad \mathrm{B}^1\,(4,\,1) = \tfrac{8}{3}xy\,(x^6+\tfrac{27}{5}x^4y^2+\tfrac{27}{5}x^2y^4+y^6)$

$\mathrm{B}^2\,(5,\,2) = \tfrac{16}{3}x^2y^2\,(x^6+\tfrac{33}{7}x^4y^2+\tfrac{33}{7}x^2y^4+y^6).$

It is useful also to recall that $B^k(r, s) = B^k(s, r)$, and that $B^k(r, s) = 0$ if $r < k$ or $s < k$.

By using these formulæ in connection with (143), (144), (147) and (204)–(208) the elements b_{rs}, c_{rs}, have been calculated,* as above mentioned, and are given in the following expressions :—

$$(217) \qquad \nabla(b_{rs}) = \begin{vmatrix} 1 & \dfrac{15}{2.7} & \dfrac{41}{2^2 3^2} & \dfrac{741}{2^7.11} & \cdot & \cdot \\[2ex] \dfrac{15}{2.7} & \dfrac{269}{2^2 7^2} & \dfrac{5993}{2^3 3^2 7^2} & \dfrac{7571}{2^{14} 3.7.11} & \cdot & \cdot \\[2ex] \dfrac{41}{2^2 3^2} & \dfrac{5993}{2^3 3^2 7^2} & \dfrac{152537}{2^{14} 3^4 7^2} & \dfrac{1517873}{2^5 3^7 7^2 11} & \cdot & \cdot \\[2ex] \dfrac{741}{2^7.11} & \dfrac{7571}{2^{14} 3.7.11} & \dfrac{1517873}{2^5 3^7 7^2 11} & \dfrac{50375871}{2^6 3^7 7^2 11^2} & \cdot & \cdot \end{vmatrix}$$

$$(218) \qquad \nabla(c_{rs}) = \begin{vmatrix} 1 & \dfrac{15}{2.7} & \dfrac{41}{2^2 3^2} & \dfrac{741}{2^7.11} & \cdot & \cdot \\[2ex] \dfrac{15}{2.7} & \dfrac{877}{2^2 3.7^2} & \dfrac{6893}{2^3 3^2 7^2} & \dfrac{3889}{2^{14} 3^2 11} & \cdot & \cdot \\[2ex] \dfrac{41}{2^2 3^2} & \dfrac{6893}{2^3 3^2 7^2} & \dfrac{193329}{2^4 3^4 7^2} & \dfrac{6202777\frac{2}{7}}{2^5 3^{14} 7^2 11} & \cdot & \cdot \\[2ex] \dfrac{741}{2^7.11} & \dfrac{3889}{2^{14} 3^2 11} & \dfrac{6202777\frac{2}{7}}{2^5 3^{14} 7^2 11} & \dfrac{225937695}{2^6 3^7 7^2 11^2} & \cdot & \cdot \end{vmatrix}$$

or, writing out the elements in decimals to six places,

$$(219) \qquad \nabla(b_{rs}) = \begin{vmatrix} 1{\cdot}000{,}000 & 1{\cdot}071{,}429 & 1{\cdot}138{,}889 & 1{\cdot}202{,}922 & \cdot & \cdot \\ 1{\cdot}071{,}429 & 1{\cdot}372{,}449 & 1{\cdot}698{,}696 & 2{\cdot}048{,}431 & \cdot & \cdot \\ 1{\cdot}138{,}889 & 1{\cdot}698{,}696 & 2{\cdot}402{,}006 & 3{\cdot}259{,}364 & \cdot & \cdot \\ 1{\cdot}202{,}922 & 2{\cdot}048{,}431 & 3{\cdot}259{,}364 & 4{\cdot}916{,}968 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

$$(220) \qquad \nabla(c_{rs}) = \begin{vmatrix} 1{\cdot}000{,}000 & 1{\cdot}071{,}429 & 1{\cdot}138{,}889 & 1{\cdot}202{,}922 & \cdot & \cdot \\ 1{\cdot}071{,}429 & 1{\cdot}491{,}497 & 1{\cdot}953{,}798 & 2{\cdot}455{,}177 & \cdot & \cdot \\ 1{\cdot}138{,}889 & 1{\cdot}953{,}798 & 3{\cdot}044{,}359 & 4{\cdot}439{,}790 & \cdot & \cdot \\ 1{\cdot}202{,}922 & 2{\cdot}455{,}177 & 4{\cdot}439{,}790 & 7{\cdot}350{,}929 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

* A considerable part of the computations of § 10 (A) have been made by Mr. J. MARSHALL, Scholar of Trinity College, Cambridge, who has thus been of much assistance in bringing the results into a useful form.

As explained in § 8 (E), however, the determinants $\nabla(\delta_{rs}b_{rs})$ and $\nabla(\delta_{rs}c_{rs})$ derived from the above by successive differencing are much more useful and suitable for numerical calculation.* They may conveniently be written as follows, where the factor above each column or before each row is to be multiplied into all the elements of that column or row as written (e.g., the right-hand element on the second row of $\nabla(\delta_{rs}b_{rs})$ is equal to $-59 \cdot \{2^3 3.7.11.2.7\}^{-1}$) :—

(221) $\nabla(\delta_{rs}b_{rs}) =$

	1	$(2.7)^{-1}$	$(2^2 3^2 7)^{-1}$	$(2^3 3.7.11)^{-1}$		
1	1	1	-1	1	.	.
$(2.7)^{-1}$	1	45	103	-59	.	.
$(2^2 3^2 7)^{-1}$	-1	103	5657	6783	.	.
$(2^3 3.7.11)^{-1}$	1	-59	6783	149749	.	.

(222) $\nabla(\delta_{rs}c_{rs}) =$

	1	$(2.7)^{-1}$	$(2^2 3^2 7)^{-1}$	$(2^3 3.7.11)^{-1}$		
1	1	1	-1	1	.	.
$(2.7)^{-1}$	1	$\frac{205}{3}$	163	$-\frac{287}{3}$	.	.
$(2^2 3^2 7)^{-1}$	-1	163	11889	$16798\frac{3}{7}$	.	.
$(2^3 3.7.11)^{-1}$	1	$-\frac{287}{3}$	$16798\frac{3}{7}$	$329573\frac{10}{21}$	.	.

As we are throughout concerned with ratios of determinants, the above fractional expressions for the elements, from which the column-factors or row-factors can for many purposes be omitted, are the most suitable for calculation. The following values of the elements in decimal notation (to six places) are of interest, however, as showing the relative magnitudes of the various terms :—

(223) $\nabla(\delta_{rs}b_{rs}) =$

1·000,000	0·071,429	$-0·003,968$	0·000,541	.	.
0·071,429	0·229,592	0·029,195	$-0·002,280$	.	.
$-0·003,968$	0·029,195	0·089,081	0·014,565	.	.
0·000,541	$-0·002,280$	0·014,565	0·043,849	.	.

(224) $\nabla(\delta_{rs}c_{rs}) =$

1·000,000	0·071,429	$-0·003,968$	0·000,541	.	.
0·071,429	0·348,639	0·046,202	$-0·003,698$	.	.
$-0·003,968$	0·046,202	0·187,216	0·036,072	.	.
0·000,541	$-0·003,698$	0·036,072	0·096,504	.	.

* This process of differencing renders the determinants much more convergent in appearance (cf. (219) and (220) with (223) and (224), without really altering in the least their value or the value of any of the partial determinants formed by the first n rows and columns.

By taking these determinants with one, two, three, and four columns we get successive approximations to ∇, ∇' (*cf.* § 8 (E)), and to the actual coefficients β and γ, as follows :—

TABLE II.—Rigid Elastic Spheres.

	$\nabla(b_{rs})$.	$\nabla(c_{rs})$.	$\Sigma\beta_r = \dfrac{\nabla'(\delta_{rs}b_{rs})}{\nabla(\delta_{rs}b_{rs})}$.	$\Sigma\gamma_r = \dfrac{\nabla'(\delta_{rs}c_{rs})}{\nabla(\delta_{rs}c_{rs})}$.
1st approximation	1·000,00	1·000,00	1·000,000	1·000,000
2nd ,,	0·224,49	0·343,54	1·022,727	1·014,851
3rd ,,	0·019,13	0·062,15	1·024,818	1·015,879
4th ,,	0·000,79	0·005,54	1·025,134	1·016,065

The determinants $\nabla(\delta_{rs}b_{rs})$, $\nabla(\delta_{rs}c_{rs})$ are obviously much more convergent in form than $\nabla(b_{rs})$, $\nabla(c_{rs})$. Table II. shows that in each case these determinants converge rapidly to the value zero, but that the principal minors of the former determinants converge also to the same value in nearly constant ratios. These ratios, the successive approximations to which are given in the two last columns of Table II., are the quantities $\Sigma\beta_r$ and $\Sigma\gamma_r$ which we require; they evidently converge rapidly, the successive differences being as follows :—

TABLE III.—Rigid Elastic Spheres.

	$\Sigma\beta_r$.	Differences.	$\Sigma\gamma_r$.	Differences.
1st approximation	1·000,00		1·000,00	
		2273		1485
2nd ,,	1·022,73		1·014,85	
		209		103
3rd ,,	1·024,82		1·015,88	
		31		29
4th ,,	1·025,13		1·016,07	

We may therefore conclude that, within a small fraction per cent., $\Sigma\beta_r$ and $\Sigma\gamma_r$ have the following values for rigid elastic spheres :—

$$(225) \qquad \overset{\infty}{\underset{0}{\Sigma}}\beta_r = 1\cdot026, \quad \overset{\infty}{\underset{0}{\Sigma}}\gamma_r = 1\cdot016, \quad \overset{\infty}{\underset{0}{\Sigma}}\beta_r / \overset{\infty}{\underset{0}{\Sigma}}\gamma_r = 1\cdot010.$$

It should be noticed that even the second approximations to these quantities give results which are very nearly accurate, owing to the rapid diminution of the successive differences.

While we may thus obtain a close approximation to the values of the series $\Sigma\beta_r$ and $\Sigma\gamma_r$ with little difficulty, the approximations to the values of the individual coefficients β and γ converge by no means quickly, as the following table shows :—

<div align="center">TABLE IV.—Rigid Elastic Spheres.</div>

	1st approximation.	2nd approximation.	3rd approximation.	4th approximation.
β_0	1·000,0	1·340,9	1·520,2	1·623,0
β_1	—	−0·318,2	−0·652,1	−0·943,2
β_2	—	—	0·156,7	0·432,8
β_3	—	—	—	−0·087,5
γ_0	1·000,0	1·222,8	1·309,4	1·366,3
γ_1	—	−0·207,9	−0·368,8	−0·526,3
γ_2	—	—	0·075,4	0·221,8
γ_3	—	—	—	−0·045,7

Evidently the β's and γ's alternate in sign, and successive terms do not seem to diminish quickly, at any rate near the beginning. To obtain an accurate estimate of the real values of these coefficients it is clearly necessary to carry the approximation much further than we have done, but for our purpose this is not required.

<div align="center">*Molecules which are Point Centres of Force varying as r^{-n}.*</div>

§ 10 (B) The next simplest case, analytically, to that which has just been discussed is the case of molecules which are point centres of force varying inversely as the nth power of the distance. By comparison of (186) and (205), in conjunction with the general expressions for b_{rs} and c_{rs}, it is easy to see that the difference between the values of b_{rs} or c_{rs} in the two cases consists of a power series in $\dfrac{1}{n-1}$, the constant term of which is zero, while the term of highest order is $(n-1)^{-(r+s)}$. Numerically the difference is small, as may easily be verified in any particular case ; it appears to be of constant sign, b_{rs} and c_{rs} being greatest for molecules which are rigid elastic spheres. The behaviour of the determinants $\nabla(b_{rs})$, $\nabla(c_{rs})$ or $\nabla(\delta_{rs}b_{rs})$, $\nabla(\delta_{rs}c_{rs})$ is similar in the two cases, the convergence being slightly the more rapid in the present instance. Since for rigid elastic spheres the second approximation to $\Sigma\beta_r$ and $\Sigma\gamma_r$ proved so satisfactory, we shall be content with a second approximation only, for molecules which are point centres of force ; this very materially lightens the labour

of numerical calculation. The following are the expressions found for the deter-
minants $\nabla(\delta_{rs} b_{rs})$, $\nabla(\delta_{rs} c_{rs})$ as far as regards the first four elements :—

$$(226) \quad \nabla(\delta_{rs} b_{rs}) = \begin{vmatrix} 1 & \left\{\dfrac{1}{14} - \dfrac{7}{2(n-1)}\right\} & \cdot & \cdot \\[2em] \left\{\dfrac{1}{14} - \dfrac{7}{2(n-1)}\right\} & \left\{\dfrac{45}{196} - \dfrac{4}{49(n-1)} + \dfrac{4}{49(n-1)^2}\right\} & \cdot & \cdot \\[2em] \cdot \quad \cdot \quad \cdot \quad \cdot & \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \end{vmatrix}$$

$$\nabla(\delta_{rs} c_{rs}) = \begin{vmatrix} 1 & \left\{\dfrac{1}{14} - \dfrac{7}{2(n-1)}\right\} & \cdot & \cdot \\[2em] \left\{\dfrac{1}{14} - \dfrac{7}{2(n-1)}\right\} & \left\{\dfrac{205}{588} - \dfrac{4}{49(n-1)} + \dfrac{4}{49(n-1)^2}\right\} & \cdot & \cdot \\[2em] \cdot \quad \cdot \quad \cdot \quad \cdot & \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \end{vmatrix}$$

When n is made infinite these become identical with (221), (222); it is interesting
to notice that the additional terms are the same in the two determinants, though
whether this is true for other values of r and s is not clear.

The first approximations to $\Sigma\beta_r$, $\Sigma\gamma_r$ are, of course, unity; the second are found
to be approximately as follows :—

$$(227) \quad \Sigma\beta_r = \frac{45}{44} \frac{1 - \dfrac{16}{45}\dfrac{n-2}{(n-1)^2}}{1 - \dfrac{2}{11}\dfrac{1}{n-1}}, \qquad \Sigma\gamma_r = \frac{205}{202} \frac{1 - \dfrac{48}{205}\dfrac{n-2}{(n-1)^2}}{1 - \dfrac{12}{101}\dfrac{1}{n-1}}.$$

From § 9 (C), (196), we know that when $n = 5$ the values of $\overset{\infty}{\underset{0}{\Sigma}}\beta_r$ and $\overset{\infty}{\underset{0}{\Sigma}}\gamma_r$ are

unity, and this is also true of any approximation to their values made in the present
manner. From § 10 (A), however, we know that for $n = \infty$ the second approxi-
mations are slightly too small, by 0·003 and 0·001 very nearly. In the following
table, therefore, which gives the approximate values of $\Sigma\beta_r$ and $\Sigma\gamma_r$ for various
values of n lying between 5 and ∞, the results obtained from (227) have been
increased by 0·001, 0·002, or 0·003, as seemed most appropriate in each case.

TABLE V.—Molecules which are Point Centres of Force varying as r^{-n}.

	Maxwell's case, $n = 5$.	$n = 9$.	$n = 15$.	$n = 25$.	$n = \infty$, rigid elastic spheres.
$\overset{\infty}{\underset{0}{\Sigma}}\beta_r$	1	1·007	1·013	1·018	1·026
$\epsilon_c \equiv \overset{\infty}{\underset{0}{\Sigma}}\gamma_r$	1	1·004	1·007	1·011	1·016
$\delta_c \equiv \overset{\infty}{\underset{0}{\Sigma}}\beta_r / \overset{\infty}{\underset{0}{\Sigma}}\gamma_r$	1	1·003	1·006	1·007	1·010

Rigid Elastic Attracting Spherical Molecules.

§ 10 (C) Considering next the case of rigid elastic spherical molecules which exert attractive forces, as in § 9 (E), we shall neglect the effect of the attractions in producing deflections without actual collisions, and, as in § 10 (B), we shall content ourselves with a second approximation to $\Sigma\beta_r$ and $\Sigma\gamma_r$. The difference between this case and that of rigid elastic spheres without attraction is small. The expressions for $\nabla(\delta_{rs}b_{rs})\ \nabla(\delta_{rs}c_{rs})$, as far as regards the first four elements, are as follows :—

$$(228) \qquad \nabla(\delta_{rs}b_{rs}) = \begin{vmatrix} 1 & \left\{\frac{1}{14}\frac{1-S/T}{1+S/T}\right\} & \cdot & \cdot \\ \left\{\frac{1}{14}\frac{1-S/T}{1+S/T}\right\} & \left\{\frac{45}{196}\frac{1+\frac{3}{5}S/T}{1+S/T}\right\} & \cdot & \cdot \\ & & & \\ & & & \end{vmatrix}$$

$$\nabla(\delta_{rs}c_{rs}) = \begin{vmatrix} 1 & \left\{\frac{1}{14}\frac{1-S/T}{1+S/T}\right\} & \cdot & \cdot \\ \left\{\frac{1}{14}\frac{1-S/T}{1+S/T}\right\} & \left\{\frac{205}{588}\frac{1+\frac{133}{205}S/T}{1+S/T}\right\} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix}.$$

When $S = 0$, *i.e.*, when there is no attraction, these reduce to (221), (223).

The second approximations to $\Sigma\beta_r$ and $\Sigma\gamma_r$ are hence found to be as follows :—

$$(229) \qquad \overset{\infty}{\underset{0}{\Sigma\beta_r}} = \frac{45\,(1+\frac{3}{5}S/T)}{45\,(1+\frac{3}{5}S/T)-(1-S/T)^2\,(1+S/T)^{-1}}, \text{ approximately,}$$

$$(230) \qquad \overset{\infty}{\underset{0}{\Sigma\gamma_r}} = \frac{205\,(1+\frac{133}{205}S/T)}{205\,(1+\frac{133}{205}S/T)-3\,(1-S/T)^2\,(1+S/T)^{-1}}, \text{ approximately.}$$

Since S/T is never negative, it is clear from (229), (230) that the second approximations to $\Sigma\beta_r$ and $\Sigma\gamma_r$ are never less than unity. Their values, without any estimated correction for the error of approximation, are given in the following table, for various values of S/T. The correction as estimated is appended as a suffix, and is to be added to the last digit of the corresponding number.

TABLE VI.—Rigid Elastic Attracting Spherical Molecules.

$\frac{S}{T}$.	Low temperatures.						Moderate temperatures.		High temperatures.		
	∞.	5.	4.	3.	2.	1.	0·7.	0·4.	0·2.	0·1.	0.
$\overset{\infty}{\underset{0}{\Sigma\beta_r}}$	1·038	1·015$_2$	1·012$_2$	1·008$_1$	1·004$_0$	1	1·001$_0$	1·005$_1$	1·011$_2$	1·016$_2$	1·023$_3$
$\epsilon_a \equiv \overset{\infty}{\underset{0}{\Sigma\gamma_r}}$	1·016	1·009$_1$	1·007$_1$	1·005$_1$	1·002$_0$	1	1·001$_0$	1·004$_0$	1·009$_1$	1·013$_1$	1·015$_1$
$\delta_a \equiv \overset{\infty}{\underset{0}{\Sigma\beta_r}}/\overset{\infty}{\underset{0}{\Sigma\gamma_r}}$	1·022	1·006$_1$	1·005$_1$	1·003$_0$	1·002$_0$	1	1·000$_0$	1·001$_1$	1·002$_1$	1·003$_1$	1·008$_2$

In the case of the actual gases for which S has been determined, it has an extreme range from about 50 to 250, while the range of absolute temperature over which experiments are usually made is from about 50° C. to 500° C. Thus the limits 5 and $\frac{1}{5}$ are rather extreme values of S/T, but from the above table it appears that the variation in $\Sigma\beta_r$, $\Sigma\gamma_r$ or their quotient hardly exceeds 1 per cent. over this range. The variation is especially slow in the neighbourhood of S/T = 1.

§ 11. Viscosity and Thermal Conduction.

We now proceed to apply the expression for the velocity-distribution function (§ 8 (B)) to the determination of the coefficients of viscosity and thermal conduction. We shall first obtain general formulæ for these coefficients, true for any monatomic gas, afterwards considering special molecular models in conjunction with the results of §§ 9, 10.

The Coefficient of Viscosity.

§ 11 (A) The system of pressures at any point of a gas is given by the equation

$$(231) \qquad \mathrm{P}_{xx} = \rho\overline{\mathrm{U}^2}, \quad \mathrm{P}_{xy} = \rho\overline{\mathrm{UV}}, \ \&\mathrm{c}.$$

By means of (5) and the velocity-distribution function (142), we find that

$$(232) \qquad \mathrm{P}_{xx} = \rho\overline{\mathrm{U}^2} = \tfrac{1}{3}\rho\overline{\mathrm{C}^2} + \tfrac{1}{3}\rho\overline{3\mathrm{U}^2 - \mathrm{C}^2},$$

$$= \frac{\rho}{2hm} - \frac{\rho}{15hm}c_{11}\mathrm{C}_0\overset{\infty}{\underset{0}{\Sigma}}\gamma_r.$$

$$(233) \qquad \mathrm{P}_{xy} = -\frac{\rho}{30hm}c_{12}\mathrm{C}_0\overset{\infty}{\underset{0}{\Sigma}}\gamma_r.$$

Since, by (74),

$$c_{11} + c_{22} + c_{33} = 0,$$

we have

$$(234) \qquad \mathrm{P}_{xx} + \mathrm{P}_{yy} + \mathrm{P}_{zz} = 3\,\frac{\rho}{2hm} = p,$$

p being the hydrostatic pressure as usually defined.

By comparing (232), (233) with the equations giving the system of pressures in a viscous fluid having a coefficient of viscosity μ, viz., with

$$(235) \qquad \mathrm{P}_{xx} = p - \tfrac{2}{3}\mu\left(2\,\frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z}\right),$$

$$= p - \tfrac{2}{3}\mu c_{11}.$$

$$(236) \qquad \mathrm{P}_{xy} = -\mu\left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y}\right) = -\tfrac{1}{3}\mu c_{12}$$

(remembering the meaning of c_{11}, c_{12}, &c., as defined in (72)), it appears that the two are identical if we write

$$(237) \qquad \mu = \tfrac{1}{10} \frac{\rho}{hm} C_0 \overset{\infty}{\underset{0}{\Sigma}} \gamma_r.$$

Hence, according to the kinetic theory, a gas behaves like an ordinary viscous fluid having a coefficient of viscosity defined in terms of the molecular data by (237). By (170), (173) we have

$$(238) \qquad C_0 = \frac{25}{\pi \nu \kappa_0},$$

whence, also,

$$(239) \qquad \mu = \frac{5}{2\pi} \frac{1}{h\kappa_0} \overset{\infty}{\underset{0}{\Sigma}} \gamma_r.$$

As we have seen in § 8 (B), κ_0 and $\overset{\infty}{\underset{0}{\Sigma}} \gamma_r$ are functions of the temperature (or h) only, and ν does not appear at all in the formula for μ. Hence, within the limits of applicability of our theory (cf. § 2), the coefficient of viscosity of a gas is independent of its density, varying only with the temperature. The law of this variation depends on the law of inter-action between two molecules at encounter, this being involved through $\phi^k (\tau y)$. As this function has remained unspecified, the expression in (237) is perfectly general and valid for any nearly perfect monatomic gas.

The Equation of Energy for a Simple Monatomic Gas.

§ 11 (B) In the discussion of the equation of transfer in § 3, we consistently neglected such second order quantities as products of differentials, or differentials of small quantities like $\overline{UV}$, $\overline{C^2 - 3U^2}$, and so on. In this way we have obtained an expression for the velocity-distribution function which is correct to the first order. By means of this function we can now determine the values of $\overline{UV}$, $\overline{C^2 - 3U^2}$, $\overline{UC^2}$, and similar expressions which are of the first order of small quantities, and by substitution in the equation of transfer obtain this in a form accurate to the second order. This we shall do for the special case $Q = (u)^2 + (v)^2 + (w)^2$, in order to get a second approximation to the equation of energy.

From the velocity-distribution function, using the formula (237) for the coefficient of viscosity, we have

$$(240) \qquad C^2 = 3 (hm)^{-1} = 3R_\nu T/m.$$

$$(241) \qquad \overline{3U^2 - C^2} = -2 (\mu/\rho) \left(2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right)$$

$$(242) \qquad \overline{UV} = - (\mu/\rho) \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right).$$

In finding $\overline{UC^2}$ it is convenient to write

(243)
$$f = \tfrac{5}{2} \sum_0^\infty \beta_r \Big/ \sum_0^\infty \gamma_r$$

and to recall (*cf.* (170)) that

(244)
$$B_0 = \tfrac{9}{4} C_0.$$

Thus we have

(245)
$$\overline{UC^2} = -\tfrac{2}{3} B_0 (2hm)^{-2} \frac{1}{T} \frac{\partial T}{\partial x} \sum_0^\infty \frac{r+\tfrac{5}{2}}{r} \beta_{r-1}$$

$$= -\tfrac{2}{3} B_0 (2hm)^{-2} \frac{1}{T} \frac{\partial T}{\partial x} \sum_0^\infty \beta_r = -3f \frac{\mu}{\rho} \frac{R}{m} \frac{\partial T}{\partial x},$$

where we have eliminated β_{-1} by means of (148).

Again, if $Q = (u)^2 + (v)^2 + (w)^2$, we have

$$Q = u_0^2 + v_0^2 + w_0^2 + 2(u_0 U + v_0 V + w_0 W) + C^2,$$

$$\overline{Q} = u_0^2 + v_0^2 + w_0^2 + \overline{C^2},$$

$$\overline{(u) Q} = u_0 (u_0^2 + v_0^2 + w_0^2) + u_0 \overline{C^2} + 2(u_0 \overline{U^2} + v_0 \overline{UV} + w_0 \overline{UW}) + \overline{UC^2}.$$

$$\frac{\partial Q}{\partial (u)} = (u), \qquad \overline{\left(\frac{\partial Q}{\partial (u)} \right)} = u_0.$$

Hence, putting $u_0 = v_0 = w_0 = 0$ except in differential coefficients, we have

$$\frac{\partial}{\partial t} (\nu \overline{Q}) = 3 \frac{\partial}{\partial t} \left(\frac{\nu}{2hm} \right) = \frac{3}{2hm} \frac{\partial \nu}{\partial t} + 3\nu \frac{\partial}{\partial t} \left(\frac{1}{2hm} \right)$$

$$= -3 \frac{R\nu T}{m} \left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right) + 3 \frac{R\nu}{m} \frac{\partial T}{\partial x}.$$

$$\Sigma \frac{\partial}{\partial x} (\nu \overline{(u) Q}) = \nu \Sigma \left(\overline{C^2 + 2U^2} \frac{\partial u_0}{\partial x} + 2\overline{UV} \frac{\partial v_0}{\partial x} + 2\overline{UW} \frac{\partial w_0}{\partial x} \right) + \Sigma \frac{\partial}{\partial x} (\nu \overline{UC^2})$$

$$= \nu \Sigma \left\{ \tfrac{5}{3} \overline{C^2} \frac{\partial u_0}{\partial x} + \tfrac{2}{3} \overline{3U^2 - C^2} \frac{\partial u_0}{\partial x} + 2\overline{UV} \frac{\partial v_0}{\partial x} + 2\overline{UW} \frac{\partial w_0}{\partial x} \right\} + \Sigma \frac{\partial}{\partial x} (\nu \overline{UC^2})$$

$$= 5 \frac{R\nu T}{m} \left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right)$$

$$- \frac{\mu}{\rho} \left\{ 4 \Sigma \left(\frac{\partial u_0}{\partial x} \right)^2 - \tfrac{4}{3} \left(\Sigma \frac{\partial u_0}{\partial x} \right)^2 - 2\Sigma \left(\frac{\partial v_0}{\partial z} + \frac{\partial w_0}{\partial y} \right)^2 \right\} + \Sigma \frac{\partial}{\partial x} (\nu \overline{UC^2}),$$

$$\frac{\nu}{m} \Sigma X \left(\overline{\frac{\partial Q}{\partial (u)}} \right) = 0.$$

Also, since no energy is gained or lost in molecular encounters,

$$\Delta Q_1^1 = 0.$$

The equation of transfer becomes, consequently, after a little reduction,

$$(246) \qquad \rho \frac{\partial T}{\partial t} = \Sigma \frac{\partial}{\partial x}\left(f\mu \frac{\partial T}{\partial x}\right) - \tfrac{2}{3}\rho T\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right)$$

$$+ \tfrac{2}{3}\frac{\mu m}{R\nu}\left\{2\Sigma\left(\frac{\partial u_0}{\partial x}\right)^2 - \tfrac{2}{3}\left(\Sigma \frac{\partial u_0}{\partial x}\right)^2 - \Sigma\left(\frac{\partial v_0}{\partial z} + \frac{\partial w_0}{\partial y}\right)^2\right\}.$$

which is the equation of energy.

The Thermal Conductivity of a Gas.

§ 11 (C) In the equation of energy which we have just obtained, the second term on the right-hand side represents the change of heat per unit volume due to the variation in density at the point considered, while the third term may be proved equal to the heat produced by internal friction. The first term, by comparison with FOURIER's equation of conduction of heat (ϑ being the thermal conductivity and C_v the specific heat at constant volume), $i.e.$, with

$$C_v\rho \frac{\partial T}{\partial t} = \Sigma \frac{\partial}{\partial x}\left(\vartheta \frac{\partial T}{\partial x}\right),$$

is seen to represent the change of heat by conduction, and to indicate that the coefficient of thermal conductivity of a gas is given by

$$(247) \qquad \vartheta = f\mu C_v.$$

The value of f in this well-known formula is, for a general monatomic gas, given by (243), $i.e.$,

$$(248) \qquad f = \tfrac{5}{2}\overset{\infty}{\underset{0}{\Sigma}}\beta_r \Big/ \overset{\infty}{\underset{0}{\Sigma}}\gamma_r.$$

In general f is a function of the temperature only.

Formulæ for μ and ϑ for Particular Molecular Models.

§ 11 (D) By substitution of the values of C_0 and $\Sigma\beta_r/\Sigma\gamma_r$ given in §§ 9, 10, for the particular molecular models there discussed, we obtain the following special cases of (237) and (248) :—

(249)　Rigid elastic spheres,

$$\mu = 1 \cdot 016 \frac{5m}{64\pi^{1/2}\sigma^2}\left(\frac{R}{m}T\right)^{1/2} \qquad\qquad f = \tfrac{5}{2} \cdot 1 \cdot 010 = 2 \cdot 525,$$

(250)　Attracting spheres,

$$\mu = (1+\epsilon_a)\frac{5m}{64\pi^{1/2}\sigma^2}\left(\frac{R}{m}T\right)^{1/2}\frac{1}{1+S/T} \qquad\qquad f = \tfrac{5}{2}(1+\delta_a),$$

(251)   Centres of force r^{-n},

$$\mu = (1+\epsilon_c)\,\frac{75m}{8\pi^{1/2}{}_nA_1\Gamma\left(4-\dfrac{2}{n-1}\right)}\left(\frac{R}{m}T\right)^{\frac{n+3}{2(n-1)}}\qquad f = \tfrac{5}{2}(1+\delta_c).$$

In these formulæ ϵ_a and ϵ_c denote the values of $\overset{\infty}{\underset{0}{\Sigma}}\gamma_r$ in the cases respectively when the molecules are attracting spheres and centres of force, and δ_a and δ_c similarly denote $\Sigma\beta_r/\Sigma\gamma_r$; their values are given in Tables V. and VI., and in no case differ from unity by more than two per cent.

The mode of variation of μ with the temperature affords a guide to the law of interaction between the molecules of actual gases. By comparison with experimental determinations of μ at various temperatures it is thus found that of the above models the one which most closely represents the behaviour of actual molecules in this respect, at ordinary temperatures, is the second, *i.e.*, a rigid elastic attracting sphere.*

Comparison of the present formulæ for μ and δ with those of my previous paper.

§ 11 (E) The general formulæ (237) and (248) for viscosity and thermal conductivity agree with those of my former paper,† except that the factors $\overset{\infty}{\underset{0}{\Sigma}}\beta_r$ and $\overset{\infty}{\underset{0}{\Sigma}}\beta_r/\overset{\infty}{\underset{0}{\Sigma}}\gamma_r$ were there omitted. This was in consequence of the assumption on which the analysis of that investigation was based, that $F(U, V, W)$ is sufficiently represented by the terms of the first three degrees in U, V, W. We have seen in § 9 (C) that this is true for a gas composed of Maxwellian molecules, but not otherwise. It seems of interest to consider why the neglect of all the coefficients β_r, γ_r after $r = 0$ led to results of such accuracy; for the errors arising from the assumption are represented in the special cases (249)–(251) of (237) and (248) by the factors $1\cdot016$, $1\cdot010$, $1+\epsilon_a$, $1+\delta_a$, $1+\epsilon_c$, $1+\delta_c$, so that the necessary corrections to my previous formulæ do not exceed one or two per cent. ENSKOG, on the other hand, after deducing formulæ similar to (237), (248), but without evaluating the coefficients β_r, γ_r, made a first approximation by neglect of all these coefficients after $r = 0$, and arrived at the result $f = 5$ for rigid elastic spheres.‡ This was due to the fact that such a use of (237), (248), as they stand, involves not only the neglect of all the coefficients after $r = 0$, but also requires an assumption as to the values of β_0, γ_0 themselves, as, for instance, that they are approximately the same as for Maxwellian molecules; a comparison of (196) with Table IV. (p. 331) will show that this is far from being the case.

It may readily be seen, however, that the method of my former paper required no

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* At very low temperatures, however, the nth power centre of force is the molecular model which gives by far the best representation of the relation between μ and T, in the case of helium; *cf.* KAMERLINGH ONNES and SOPHUS WEBER, 'Comm. Phys. Lab. Leyden,' 134B, p. 18, or JEANS' 'Dynamical Theory of Gases,' 2nd ed., §§ 405, 407.

† CHAPMAN, 'Phil. Trans.,' A, vol. 211, p. 433, *et seq.*

‡ ENSKOG, 'Phys. Zeit.,' XII., p. 58, 1911.

hypothesis as to the values of β_0, γ_0, which were determined from ΔUC^2 and ΔU^2 as in this paper ; in effect, the later coefficients were neglected, while β_0 and γ_0 were obtained from the equations (138), (139) corresponding to $s = 0$. Viewed otherwise, my previous formulæ were equivalent to (237), (248) divided respectively by $\overset{\infty}{\underset{0}{\Sigma}}\kappa_r\gamma_r/\kappa_0$ and $\overset{\infty}{\underset{0}{\Sigma}}\kappa_r\beta_r/\overset{\infty}{\underset{0}{\Sigma}}\kappa_r\gamma_r$. Thus the neglected factors in μ and f were

$$\frac{\overset{\infty}{\underset{0}{\Sigma}}\kappa_0\gamma_r}{\overset{\infty}{\underset{0}{\Sigma}}\kappa_r\gamma_r} \quad \text{and} \quad \frac{\overset{\infty}{\underset{0}{\Sigma}}\beta_r}{\overset{\infty}{\underset{0}{\Sigma}}\gamma_r} \cdot \frac{\overset{\infty}{\underset{0}{\Sigma}}\kappa_r\gamma_r}{\overset{\infty}{\underset{0}{\Sigma}}\kappa_r\beta_r},$$

which evidently reduce to unity if we neglect all the β'_0 and γ', after $r = 0$, without any assumption as to the values of β_0 and γ_0.

One of the main results of the former paper was that $f = \frac{5}{2}$ for all monatomic gases, and not only for those composed of Maxwellian molecules. This is now seen to require modification, but the values here found for f in the special cases which have been considered in §§ 9, 10 show that the correction needed to make the equation accurate is very small ; it appears probable that for all likely molecular models f is very slightly greater than 2·5, and that it is nearly but not quite constant with change of temperature (except when the molecules are elastic spheres or centres of force proportional to r^{-n}).

Comparison of the Formulæ for μ and ϑ with the Results of other Theories.

§ 11 (F) The only kinetic theory of viscosity and thermal conductivity which could hitherto lay claim to numerical accuracy (within the limits imposed by the initial postulates) is MAXWELL'S theory* of a gas composed of molecules of the kind dealt with in § 9 (C). The results of his theory are special cases of the general formulæ of this paper.

The theory of a gas composed of molecules which are point centres of force varying inversely as the nth power of the distance had not been discussed in detail, previous to my own former paper. RAYLEIGH,[†] however, from considerations of dimensions alone, had deduced the law of variation of viscosity with temperature, and the same argument would also show that for such a gas f is an absolute constant (for any given value of n). Nothing was known as to the value of this constant, or of the numerical coefficient in the expression for μ, and it is a surprising result, which could hardly have been guessed *à priori*, that as n ranges from 5 to ∞ the value of f should vary only from 2·500 to 2·525 approximately.

The theory for molecules which are rigid elastic spheres exerting attractive forces was equally undeveloped. SUTHERLAND‡ had taken an important step, however, in

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* MAXWELL, 'Collected Papers,' vol. II., p. 23.

† RAYLEIGH, 'Roy. Soc. Proc.,' vol. 6, p. 68, 1900.

‡ SUTHERLAND, 'Phil. Mag.,' (5), 31, 1893.

deducing the correction to the law connecting μ and T (*i.e.*, $\mu \propto T^{1/2}$) for molecules which are rigid elastic spheres without attraction ; he showed, without attempting numerical accuracy, but by a method which is correct in its main outlines, that the attractive forces necessitate an additional factor $(1+S/T)^{-1}$, as in (249).   The law $\mu \propto T^{1/2}(1+S/T)^{-1}$ is more successful than any other in representing the observed relation between μ and T over a considerable range of temperature, and S is deservedly known as SUTHERLAND's constant.

The theory of a gas composed of molecules which are rigid elastic spheres, which was taken by SUTHERLAND as the basis of his modified formulæ, has been developed along lines different from those of this paper by CLAUSIUS, MAXWELL, BOLTZMANN, MEYER, STEFAN, JEANS, and others.   Their method was less analytical than the present one, and while it gave correctly the general relationships between μ, ϑ, p, ρ, and T, its results do not possess numerical precision.   JEANS* notably improved certain of the formulæ due to earlier authors by taking into account the tendency of a molecule to persist, after a collision, in the general direction of its original course. For this reason his expression for the viscosity, viz.,

$$(252) \qquad \mu = \frac{0 \cdot 88}{4\pi} \frac{m}{\pi^{1/2} \sigma^2} \left(\frac{R}{m}T\right)^{1/2}, \qquad \text{(JEANS)}$$

approaches more nearly to the correct expression (249) than does the formula of any other author†.   A comparison of (249) with (252) indicates that the latter is still too small by 12 per cent. ; the error of the original formula, without JEANS' correction, was 30 per cent.

The numerical inaccuracy of the earlier prevailing theory of conductivity, which was due to MEYER‡, was very great.   Its result was generally given as

$$\vartheta = f\mu C_v \qquad \text{where} \quad f = 1 \cdot 6027,$$

but Prof. L. V. KING, of McGill University, has pointed out to me by letter that MEYER's argument really leads to the result

$$f = 1 \cdot 4161,$$

a numerical mistake having crept into his work which had not previously been detected.   The correct value of f for rigid elastic spheres is given in (249), *i.e.*,

$$f = 2 \cdot 525.$$

This large error in MEYER's theory indicates the difficulty of arriving at numerically accurate formulæ by the older "mean free path" method, and diminishes

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* *Cf.* JEANS' ' Dynamical Theory of Gases.'

† Apart from that in my former paper, which was $1 \cdot 6$ per cent. too small.

‡ MEYER's ' Kinetic Theory of Gases,' 2nd English edition, chap. IX.

confidence in other parts of that theory where detection of error is less easy. Until recently MEYER's value of f received support from experimental data for diatomic gases, to which it does not really apply; only lately have data for monatomic gases been obtained, which, as we shall see, give values of f nearly equal to $\frac{5}{2}$.

§ 12. COMPARISON OF THE THEORY WITH EXPERIMENTAL DATA.

The Variation of Viscosity with Pressure.

§ 12 (A) The main objects of a comparison of a mathematical theory with experimental data are either to test whether the postulates underlying the theory are valid, or whether the theory is itself mathematically correct. The present theory being exact, within certain defined limits, our purpose in this chapter is to consider how far the hypotheses underlying the analysis are well founded. The general validity of the foundations of the kinetic theory is attested in many ways, one of the most striking being the independence of viscosity and pressure in a gas. This law, when first discovered by MAXWELL, seemed so improbable that it gave a great stimulus to experimental research on gases, and the constancy of μ, when T is kept constant, has been verified over a range of pressure extending from a few millimetres of mercury up to more than one atmosphere. WARBURG and VON BABO have found that, in the case of carbon dioxide, the law begins to fail when the pressure becomes so great as 30 to 120 atmospheres, μ rising appreciably. In very rarefied gases, on the other hand, the viscosity falls *below* the value appropriate to the existing temperature. This must be referred to the failure of the postulates of our theory to represent the facts in these extreme cases, the molecules becoming too few for our statistical method to apply, on the one hand, while on the other our assumption that the molecular paths are rectilinear for the major part of the time, and our neglect of multiple encounters, become illegitimate.

The Variation of Viscosity with Temperature.*

§ 12 (B) Over a wide range of pressure and temperature, undoubtedly, the general postulates of our theory are true for actual gases. We cannot discover directly, however, the nature of the molecules or their mode of collision, and it is important, therefore, to examine which molecular model yields formulæ most in accordance with experimental data. For this purpose we naturally choose those properties which are most affected by the nature of the molecule; the chief of these is the variation of viscosity with temperature. MAXWELL abandoned his theory of a gas composed of rigid elastic spherical molecules because it led to the relation $\mu \propto T^{1/2}$, while his experiments gave the result $\mu \propto T$. This caused him to develop the theory of a Maxwellian gas (§ 9 (C)), for which $\mu \propto T$, but later experimenters have failed to confirm this law, and we must conclude that the molecules of actual gases behave during encounters neither like elastic spheres nor like Maxwellian molecules. The observed relation

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* The reader may be referred with advantage to the discussion of this point by JEANS in the second edition of his 'Dynamical Theory of Gases,' §§ 399–407.

between μ and T agrees much more closely with SUTHERLAND'S law $\mu \propto T^{1/2}(1+S/T)^{-1}$ than with any other; for example, SCHMITT* has found that the law is valid for hydrogen and helium from $-60°$ C. to $185°$ C., and BARUS has shown that it holds good for air over a wide range of temperature. The law has not been tested, for the former gases, above $185°$ C.

This seems to indicate that for the kinetic theory of gases at ordinary temperatures the best molecular model is an attracting sphere, and it is interesting to notice that this model is the one used by VAN DER WAALS with such success in deducing his famous law. Further confirmation is supplied by the excellent agreement between the values of the molecular diameters deduced on this hypothesis from the constant b of VAN DER WAALS' law and from the viscosity by means of my formula (250)— $cf.$ § 12 (F).

At low temperatures SCHMITT*, BESTELMEYER†, VOGEL‡ and others have shown that the observed values of μ are greater than those predicted by SUTHERLAND'S law. This may be compared with the rise in the value of μ when the pressure is greatly increased, both effects probably having a like cause; in these states, when the mean free path of the molecule is much reduced, the molecular paths may cease to be approximately rectilinear between collisions, and multiple encounters will grow in importance. Since our theory rules out these contingencies, its results cease to be applicable, and a modification of the theory and its postulates is necessary if a proper account of these phenomena is to be given. In regard to this, one point which should be noticed is that in § 9 (E) a term $f_{2k}(y)$ in $\phi^{2k}(\tau y)$ was neglected ($cf.$ (211)) which, if retained, would cause the law connecting μ and T to take the form

$$\mu \propto \frac{T^{1/2}}{1+(S/T)+f(T)}$$

where $f(T)$ can be expanded in the form $AT^{-2}+BT^{-3}+\ldots$. This term is due to the effect of the attractive forces in producing deflections without the occurrence of collisions, and is probably always small; but it may readily be seen that it is always positive, and that this correction would lead to a *diminution* in the theoretical value of μ at low temperatures. Clearly, therefore, the observed discrepancies cannot be attributed to our neglect of this small quantity.§

* SCHMITT, 'Ann. d. Phys.,' 30, p. 399, 1909.

† BESTELMEYER, 'Munich dissertation,' 1903.

‡ VOGEL, 'Berlin dissertation,' 1914, where full references, and an interesting discussion of low temperature work on viscosity, are given.

§ VOGEL, in his dissertation, suggests as possible causes of the failure of the theory to represent the observed variation of μ with T at low temperatures (i.) a failure of the ordinary mechanics, such as is contemplated in PLANCK'S theory of quanta; (ii.) that the attracting sphere model no longer represents the molecule; (iii.) that $1+S/T$ should be replaced (according to my suggestion in 'Phil. Trans.,' A, vol. 211, p. 474, 1912) by $1+(S/T)\pm(C/T)^2$. By the latter means a better accordance with observation is obtained, but the new term has the *minus* sign, and is therefore illegitimate.

The Thermal Conductivity of Monatomic Gases.

§ 12 (C) It is convenient to discuss the thermal conductivity of gases in terms of the constant f in the formula $\vartheta = f\mu C_v$, as this eliminates the necessity for a separate discussion of the dependence of ϑ on pressure and temperature ; this is parallel with that of μ, and f is nearly or quite independent of pressure and temperature in normal conditions. As we have seen in § 11 (F), the value of f has been a matter of some uncertainty ; so long as its value for rigid elastic spheres was supposed to be 1·6027, while for Maxwellian molecules it was known to be $\frac{5}{2}$, it seemed to offer a means of testing the suitability of different molecular models. On the ground of the discrepancy between the theoretical and observed relation between μ and T, Maxwellian molecules were known to be unsatisfactory representations of actual molecules. Until about 1900 no reliable determinations of f had been made for monatomic gases, and those found for diatomic gases agreed fairly well with MEYER's value of f (*i.e.*, 1·6027 or, more accurately, 1·416) ; at the time this was regarded as a confirmation of the rigid elastic spherical model of the molecule, and as indicating that the internal molecular energy, which is not taken into account in these theories of a monatomic gas, is transmitted at the same rate as the translational energy. When, in 1902, SCHWARZE obtained the values of f for argon and helium, and found them nearly equal to $\frac{5}{2}$, the conclusion to be drawn was not obvious. It certainly contradicted MEYER's theory, but left the question open as to whether the analysis, or the assumption of the rigid elastic spherical model, was at fault ; also if $f = \frac{5}{2}$ indicated that the molecules are Maxwellian, the failure of the corresponding law connecting μ and T remained unexplained. It should be remembered, moreover, that the law $\mu \propto T^{1/2}$ for rigid elastic spherical molecules is equally contradictory to experiment.

These difficulties were removed by the theorem of my former paper, according to which f is an invariable constant $\frac{5}{2}$ for all monatomic molecules. This is now seen to be incorrect as a general theorem, but the deviations found for the various particular molecular models discussed leaves little room for doubt that f is very nearly equal to $\frac{5}{2}$ in the case of all likely models. The fact simply is, therefore, that f is very unsuitable as a means of discrimination between different models, and SCHWARZE's observations indicate some mathematical fallacy in MEYER's theory, without supporting any particular molecular model. The observed values of f are hardly known with sufficient accuracy to enable any conclusion to be drawn from a slight divergence from the value $\frac{5}{2}$, within the limits prescribed in (249) to (251). They are important, however, as confirming the general validity of the kinetic theory, apart from any hypothesis as to the nature of the molecules.

The following table contains all the available data concerning the value of f for monatomic gases. Only very recently has the conductivity of neon been determined, owing to the scarcity of the gas ; for krypton and xenon its value is still unknown.

TABLE VII.—Values of f for Monatomic Gases.

Gas.	Absolute temperature.	f.	Authority.
	° C.		
Helium	273 {	2·51	SCHWARZE*
		2·40	EUCKEN†
	81	2·23	EUCKEN
	21	2·02	EUCKEN
Argon	273 {	2·50	SCHWARZE
		2·49	EUCKEN
	91	2·57	EUCKEN
Neon	283	2·50	DORN‡

These results for argon and neon and, to a less extent, for helium at normal temperatures agree very well with the theoretical value of f, especially since the combined experimental errors in their determination may easily exceed one per cent. at ordinary temperatures, and much more at low temperatures.

The diminution in the value of f for helium at low temperatures, if confirmed by further experiment, is very interesting and important. Helium is peculiar at low temperatures also in the striking divergence of its viscosity from SUTHERLAND'S law. EUCKEN suggests as the explanation of the former phenomenon a partial failure of interchange of molecular energy at collision, but (cf. Table VI. of his paper) down to 81° C., at any rate, the value of C_v for helium remains constant and appropriate to a gas which possesses only translational energy. A failure in interchange of translational energy would contradict the ordinary dynamical laws, and it is certainly desirable to seek some other explanation, if this be at all possible.

The alternatives are not numerous, and will be examined in turn. We may rule out a numerical error in the theory, of more than one per cent., as being quite improbable; but though all the molecular models discussed in this paper lead to values of f equal to or slightly greater than 2·5, it is conceivable that for some peculiar model f may have rather different values and a wider temperature range. I think this is unlikely, and that it is probably possible to prove that f always exceeds 2·5, but this is only a speculation; helium agrees so well at high temperatures, however, with SUTHERLAND'S law connecting μ and T, that its molecules can hardly be supposed so different in behaviour from rigid elastic attracting spheres as to make f theoretically equal to 2·0 at low temperatures.

Again, molecular aggregation might seem to afford an explanation, since if part of the gas were polyatomic through clustering of the molecules, the value of f would

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* SCHWARZE, 'Halle dissertation, Ann. d. Phys.,' (4), 11, p. 303, 1903.

† EUCKEN, 'Phys. Zeit.,' 14, p. 324, 1913, Tables 3, 6. EUCKEN (footnote 4 to p. 328) states that SCHWARZE'S value of f for helium is too large owing to a miscalculation in determining C_v.

‡ This result was kindly communicated to me by Prof. DORN, of Halle, as an extract from 'Mitt. d. Naturf. Ges. z. Halle,' 4, 1914.

probably lie between 2·5 and the lower values characteristic of polyatomic gases. In this case, however, the value of C_v, the specific heat at constant volume, should rise to correspond with the internal energy of such molecules ; as the experiments indicate a constant value of C_v, the suggestion must be abandoned.

The only possible remaining hypothesis seems to be to attribute the fall in f to the neglect of multiple collisions between molecules, including also the effect of the attractive forces (in SUTHERLAND's case) in producing deflections without collisions ; at low temperatures the molecules may be too close together for these postulates of our theory to continue valid. If we determine ϑ for helium from the formula $2\cdot5\mu\,C_v$, using the value of μ calculated from SUTHERLAND's formula (which is less than the observed value at low temperatures, as we have seen), the result is less than that observed at low temperatures. Hence both ϑ and μ diminish with temperature less than is predicted by SUTHERLAND's law, the divergence being greater for μ than for ϑ, so that f also diminishes. We cannot enter here into a test, by calculation, of this suggested hypothesis, but some confirmation might be sought experimentally by examining whether f is less than 2·5 for helium at normal temperatures but under considerably increased pressure. The latter would bring the molecules closer together in the same way as would a diminution of temperature, and this is all that our suggestion requires. It is known that over a large range of pressure μ and ϑ are constant, but that at high pressures μ increases ; the independence of ϑ on pressure has usually been tested by *diminishing* the normal pressures,* and experiments under increased pressure might throw valuable light on the present phenomenon. Gases other than helium may be expected to behave similarly, though perhaps only with lower temperatures or higher pressures.

§ 12 (D) The case of mercury vapour may also be mentioned, as it was the first monatomic gas for which f was determined. KOCH† determined μ for mercury vapour at 203° C., 273° C., and 380° C., while SCHLEIERMACHER‡ determined ϑ at 203° C. These data, together with the theoretically calculated value of C_v, led to $f = 3\cdot15$. MEYER and others have raised objections to the determinations of μ (a) because the three values show an improbable amount of variation with temperature, and (b) because of the vitiating effect of condensed mercury on the walls of the capillary tube used in the experiments. VOGEL§ has made a re-calculation of μ for mercury from an interesting formula which he gives, and finds that at 573° C. absolute‖ μ should equal $593\cdot10^{-7}$; this, combined with SCHLEIERMACHER's result, reduces f to 2·80. But it is desirable that more accurate experiments should be made in order that a thoroughly reliable value of f may be obtained.

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* EUCKEN, ' Phys. Zeit.,' 12, p. 1103, 1911, Table 2.

† KOCH, ' Wied. Ann.,' 19, p. 857 (1883).

‡ SCHLEIERMACHER, ' Wied. Ann.,' 36, p. 346 (1889).

§ VOGEL, ' Berlin dissertation,' p. 57, 1914.

‖ So given by VOGEL; it may be a misprint for 473° C.

The Thermal Conductivity of Polyatomic Gases at Low Temperatures.

§ 12 (E) The formula $\vartheta = f\mu \, C_v$ is true for polyatomic as well as for monatomic gases, f being independent of pressure and temperature over a considerable range. Under normal conditions, however, its value is 2·0 or less, being greatest for diatomic gases and diminishing down to about 1·5 for complex molecules. Eucken* has made the interesting and important discovery, however, that diatomic gases show an increase in f at low temperatures, the conductivity varying with temperature in the sense opposite to that observed in the case of helium. This is apparent, to a slight extent, in nitrogen, but is most striking in the case of hydrogen. It is found that, simultaneously with the rise in f, the specific heat C_v progressively falls in value until at 21° C. absolute its amount is that appropriate to a monatomic gas of the same molecular weight. At these low temperatures the rotatory motion of the molecules seems to fail, for some reason as yet undiscovered, so that the gas behaves in certain respects as if its molecules were of the spherically symmetrical type discussed in this paper. It is highly interesting and significant that this approach to monatomicity is accompanied by an upward tendency of f towards the value (2·5 approximately) which is appropriate to monatomic gases. The same phenomenon may be expected in the case of the other diatomic gases, at lower temperatures corresponding to their lower boiling points. In the following table* the results for hydrogen alone are given; the number n in the third column represents the number of "degrees of freedom" of the molecule, as calculated from the observed values of C_v.

<center>VALUES for f for Hydrogen.</center>

Absolute temperature.	f.	n.
° C.		
273	1·96	4·80
195	2·09	4·41
81	2·25	3·16
21	2·37	2·98

The Diameter of the Molecule.

§ 12 (F) In my former paper tables were given showing the values of the molecular diameters for several gases, calculated on the hypothesis that the molecules are rigid spheres, with or without attractive force. These require a small correction to be strictly accurate, on account of the factor $(\Sigma \gamma_r)^{1/2}$ there omitted from the formula for

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* *Cf.* Eucken, 'Phys. Zeit.,' 14, p. 329, 1913, Table 6.

σ in terms of μ.   In this paper I shall give only a few values of σ, calculated from recent data and from the exact formula

$$\sigma^2 = (1+\epsilon_a)\frac{5m}{64\pi^{1/2}\mu\,(1+S/T)}\left(\frac{R}{m}T\right)^{1/2}$$

$$= \frac{0\cdot491\,(1+\epsilon_a)\rho\,\overline{C}}{2^{1/2}\pi\nu\mu\,(1+S/T)}$$

appropriate to attracting spherical molecules.   The values of S are determined from the variation of viscosity with temperature, $\overline{C}$ is the mean molecular velocity, while ϵ_a is found from Table VI. (in all the cases here considered it is quite negligible).

In the following table values of the diameters calculated from the constant b of VAN DER WAALS' law are also given for comparison.   The agreement between the two sets of values is in most cases remarkable, and the table as a whole is a testimony to the close numerical accuracy now attained by the kinetic theory ; where there is disagreement in the table there is in most cases uncertainty as to the data.

While exact agreement may be expected only for monatomic gases, the values for diatomic gases show that our theory gives a mean diameter, in other cases, which agrees with that found for b; the internal energy which prevents the application of our formulæ to the conductivity of polyatomic gases hardly affects viscosity.

TABLE VIII.— Molecular Diameters Calculated from Viscosity and VAN DER WAALS' Law.

Gas.	$\mu_0\cdot10^7$.	S.	$1+\epsilon_a$. (Table V.)	VAN DER WAALS' b.	$2\sigma_1\cdot10^8$ (viscosity).	$2\sigma_2\cdot10^8$ (VAN DER WAALS.)
Argon	2107	162	1·002	0·001347	2·84	2·85
Krypton	2334	182	1·001	0·001774	3·12	3·14
Xenon	2107	252	1·000	0·002304	3·47	3·42
Helium.	1885	75	1·006	0·000432	1·89	1·96
Oxygen	1923	130	1·005	—	2·93	2·89
Hydrogen	854	76	1·006	0·00096	2·36	[2·52]
Nitrogen	1672	112	1·003	0·00255	3·10	$\begin{cases}3\cdot54\\3\cdot08\end{cases}$
Air	1721	111	1·004	0·00209	3·08	3·30
Carbon dioxide . .	1388	249	1·000	0·00228	$\begin{cases}3\cdot27\\3\cdot20\end{cases}$	$\begin{array}{c}3\cdot40\\3\cdot20\end{array}$

REFERENCES.

Viscosity μ_0 at 273° C. absolute.—These values are taken from the table on p. 476 of my first memoir, where full references may be found.   They agree very well with the list given by EUCKEN (' Phys. Zeitschr.,' 14, Table 3, 1913), in which VOGEL's determinations are included with other recent values in taking means.

SUTHERLAND'S *constant* S.—These values are those given in the same table of my former memoir (what is called S in this paper was there, and is usually, denoted by C), where references to sources may be found.   The value for krypton was there given incorrectly ; I am indebted to Dr. G. RUDORF for the correction.

VAN DER WAALS' *b.*—The values for helium (KAMERLINGH ONNES), hydrogen, nitrogen, air (ROSE-INNES), and carbon-dioxide (VAN DER WAALS') are taken from JEANS' 'Dynamical Theory of Gases,' 2nd edition, § 194.   Those for argon, krypton, and xenon (RAMSAY and TRAVERS), from RUDORF, ' Phil. Mag.,' June, 1909, p. 795, are not direct experimental values, however, but are calculated from critical data.

Diameter $2\sigma_1$ *from viscosity.*—These are practically twice the values for the radii given on pp. 476, 481 of my former memoir, where, however, errors of calculation (here corrected) were made in the case of argon and krypton (as Dr. G. RUDORF kindly indicated to me).

Diameter $2\sigma_2$ *from* VAN DER WAALS' *b.*—The value for oxygen, and the second values for nitrogen and carbon-dioxide (as well as $2\sigma_1$ for the latter) are from Table 7 of EUCKEN'S paper ; he does not give his authorities, but his values are probably the most recent and reliable.   The value for hydrogen, he says, is doubtful.