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On the Kinetic Theory of a Gas. Part II: A Composite Monatomic Gas: Diffusion, Viscosity, and Thermal Conduction

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V. *On the Kinetic Theory of a Gas. Part II.—A Composite Monatomic Gas: Diffusion, Viscosity, and Thermal Conduction.*

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Communicated by Sir JOSEPH LARMOR, *F.R.S.*

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CONTENTS.

INTRODUCTION.*

THE present memoir was originally intended to deal only with the theory of diffusion, which still remains its chief subject. During the course of the work, however, it became clear that the theory of viscosity and thermal conduction could also be incorporated by a slight extension of the analysis. This has been done, and the paper now affords an account of all these three "ordinary" mean-free-path phenomena of a composite gas.

The treatment of viscosity and conduction is brief, partly because the theory for a composite gas is so much more complex and less important than that for

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* See Note F, p. 197.

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a simple gas.* For the same reason the results are not carried to a higher degree of approximation than that attained, in regard to the same phenomena, in an earlier memoir.† The present method, however, enables the approximation to be carried to any degree of accuracy, which was not formerly possible. Also a certain mistake in the previous investigation of the conductivity of a composite gas is indicated and corrected (*cf.* § 18).

By its very nature, the problem of diffusion requires the consideration of molecules of two kinds, a complication which is unnecessary in the construction of a theory of viscosity and conduction. Perhaps this circumstance largely explains the greater progress which had hitherto been made in the latter theory, as compared with the theory of diffusion. Until recently the only accurate expression which had been obtained for the coefficient of diffusion D_{12} was that deduced by MAXWELL in his second great memoir‡ on the dynamical theory; it referred exclusively to a gas whose molecules inter-act according to the inverse fifth-power law of force. The best available value of D_{12} for molecules of other kinds was due to LANGEVIN,§ but the formula, unlike MAXWELL'S, was only approximate. It was determined on the assumption that the distribution of velocities in each group of molecules, relative to the mean velocity of the group, was according to MAXWELL'S well-known law appropriate to a gas in the uniform steady state. The amount of error (if any) introduced by this assumption was unknown. In the present paper the true law of distribution is determined, and an exact expression is obtained for D_{12} which is applicable to the most general case of a composite monatomic gas. It is found on comparison that the error of the above approximate formula is as great as 13 per cent. in extreme cases (§ 13 (*e*)).

A particular case of LANGEVIN'S formula, relating to rigid elastic spherical molecules, had previously been deduced by STEFAN in 1871. The theories of MAXWELL,|| STEFAN,¶ BOLTZMANN,** and LANGEVIN, and my own earlier theory, all agreed in predicting no change in D_{12} with the relative proportion of the two sets of molecules. Another theory, originated by MEYER††, asserted that there would be a large variation in D_{12} as the proportion of either component varied from 0 to 1.

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* This has been dealt with in detail in my recent memoir, 'Phil. Trans.,' A, vol. 216, pp. 279–348, 1915.

† 'Phil. Trans.,' A, vol. 211, pp. 433–483, 1911.

‡ MAXWELL, 'Collected Works,' ii., p. 27. His formula for D_{12} is a special case of the general result (13·03) of this paper.

§ LANGEVIN, 'Ann. de Chimie et de Physique,' (8), v., 245 (1905); *cf.* also ENSKOG, 'Phys. Zeit.,' xii., 533 (1911). The same result was independently discovered by the present writer, 'Phil. Trans.,' A vol. 211, p. 499 (1911).

|| MAXWELL, 'Collected Works,' i., p. 392; ii., p. 57, p. 345.

¶ STEFAN, 'Wien. Sitzb.,' 63, (2), p. 63, 1871; 65, p. 323, 1872.

** BOLTZMANN, 'Wien. Sitzb.,' 66, p. 324, 1872; 78, p. 733, 1878; 86, p. 63, 1882; 88, p. 835, 1883; also 'Vorlesungen,' i., p. 96.

†† MEYER, 'Kinetic Theory of Gases,' p. 255 (English ed.); also GROSS, 'Wied. Ann.,' 40, p. 424, 1890.

The experimental data which were determined in order to test the point confirmed neither conclusion; a variation in D_{12} was observed, but it was so much smaller than that suggested by MEYER's formula that the experimental values of D_{12} were in closer numerical agreement with a *constant* expression than with MEYER's highly variable result. Recently KUENEN* has modified MEYER's theory by taking into account the tendency of a molecule to persist in its original direction after collision, a consideration the importance of which was brought into prominence by JEANS† in connection with the elastic-sphere theory of viscosity. As a result of this revision MEYER's theory is brought much more closely into accord with experiment (§ 13 (*i*)), though the discrepancies still exceed those between the observed values of D_{12} and a suitable constant mean.

In § 13 (*i*) the observations of D_{12} relating to the above variations are compared also with the results of the present theory, which affords a formula similar to that of LANGEVIN but multiplied by a correction factor which is a function of the relative proportions of the component gases. The agreement with experiment, while not exact, is perhaps as close as the degree of experimental errors, and the uncertainty as to the best molecular model, entitle us to expect.

The present theory of diffusion is compared also, in two particular cases, with exact results obtained theoretically by other writers. These cases are (*a*) that of a gas formed of two sets of molecules which are identical in their dynamical properties (as in the problem of the self diffusion of a gas), and (*b*) that of a gas in which the molecules of one kind are infinitesimal in size and mass compared with those of the other kind (as in electronic diffusion in gases). These problems have been dealt with respectively by PIDDUCK‡ and LORENTZ§; the corresponding special forms of the general expressions here deduced are in satisfactory accordance with their results (§ 13 (*e*), (*f*)).

Certain other phenomena connected with diffusion are also discussed which do not seem to have been investigated in any detail hitherto. In §§ 10, 14, 15 it is shown that diffusion may be produced by a gradient of pressure or temperature independently of the presence of a concentration gradient or of external forces; in §§ 14, 15 the amount of this effect is considered, with numerical illustrations relating to particular pairs of gases. Conversely, the absence of diffusion in a composite gas in which the temperature is non-uniform (the pressure being uniform and there being no external forces) implies the existence of a corresponding variation in the relative concentration of the two gases. This latter variation (*cf.* § 16) appears to be so large in amount

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* KUENEN, 'Supp. No. 8 to the Communications from the Leyden Physical Laboratory,' January, 1913; also 'Amsterdam Acad. Proc.,' 16, p. 1162, 1914.

† JEANS, 'Dynamical Theory of Gases' (2nd ed.), pp. 276, 292, 328.

‡ PIDDUCK, 'Proc. Lond. Math. Soc.' (2), 15, p. 89, 1915.

§ LORENTZ, 'Archives Néerlandaises,' 10, p. 336, 1905; 'Theory of Electrons,' p. 268. More general results obtained by JEANS, using LORENTZ's method, are given in his 'Dynamical Theory of Gases,' 2nd ed., §§ 314, *et seq.* *Cf.* also PIDDUCK, *loc. cit.*, p. 112.

as to suggest a doubt whether some compensating influence has not been overlooked in the theory, and it is desirable that the matter should be put to the test of experiment (see Note A, p. 196). In §§ 12, 19, it is shown that diffusion is necessarily accompanied by a transfer of thermal energy, and a new physical constant, the "specific energy of diffusion," is introduced and discussed.

The method used to determine the velocity-distribution function is similar to that published in my recent memoir on a simple gas; the details of the work are, of course, more complicated in the present case. The formulation of the equations of diffusion and energy for a composite gas, executed in §§ 10 and 12, embodies certain features which seem to be novel.

We may here remark also upon some by-products of the analysis which suggest interesting developments in the field of pure mathematics. The comparison of LORENTZ's solution of the problem of electronic diffusion with my own has led to expressions for π and $\sin \pi x$ of an altogether new form. LORENTZ used BOLTZMANN's integral equation for the velocity-distribution function, and obtained a solution in finite terms involving π; the solution arrived at in this paper is determined by the use of the aggregate of the equations of transfer (§ 2), which is really equivalent to BOLTZMANN's equation. The result is expressed, however, in terms of the quotient of a symmetrical infinite determinant by its principal minor, and formulæ of this kind are hence found for π (and also for $\sin \pi x$). The elements of the determinant are expressible simply, in terms of gamma functions. A further study of the subject from the analytical point of view would probably be fruitful in results of interest and importance (see Note B, p. 196).

I hope later to apply the present methods to the examination of the problems offered by rarefied gases. So far, however, as concerns the mean-free-path phenomena in monatomic gases under *normal* conditions, the investigation imperfectly attempted in my memoir of 1911 is completed by this and the second paper already referred to ('Phil. Trans.,' A, vol. 216).

It is a pleasure here to make grateful acknowledgment of my indebtedness to Sir JOSEPH LARMOR throughout these investigations, which were started under his influence, and would hardly have been carried to this stage but for the inspiration afforded by his continued encouragement and interest.

§ 1. ANALYSIS OF THE DYNAMICAL STATE OF A COMPOSITE GAS.

(a) *Notation.*[*]

The gas considered in this paper is one composed of molecules of two kinds, each having the property of spherical symmetry (or, in brief, each being "monatomic").

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[*] In numbering the equations I have adopted the decimal method introduced by PEANO. The number to the left of the decimal point is the number of the section, and within any section the numbers to the right, if read as decimals, are in numerical order. With this method it is possible, by the introduction of a third or even fourth figure, to number equations inserted between others already numbered, without having to alter the references to all succeeding equations.

The density of the gas is supposed to be such that the mean free path of a molecule is large compared with the distance at which molecules appreciably affect one another's trajectories: this we express concisely by terming the gas "nearly perfect."

Similar quantities relating to the two groups of molecules will be represented by similar symbols, with distinguishing suffixes 1, 2; it is convenient to adopt the convention that the first gas is that which has the greater molecular mass. The molecular masses will be denoted by m_1, m_2, while the notation for various other characteristics of the gas at (x, y, z, t)* is explained by the following list:

$\nu_1, \nu_2 \equiv$ the number of molecules of the first and second kinds per unit volume.

$\lambda_1, \lambda_2 \equiv$ the proportion of molecules of each kind at (x, y, z, t).

$\rho_1, \rho_2 \equiv$ the densities of the constituent gases.

$\mathrm{P}_1, \mathrm{P}_2 \equiv$ the external forces (in vector notation) acting on each molecule m_1, m_2.

$(\mathrm{X}_1, \mathrm{Y}_1, \mathrm{Z}_1), (\mathrm{X}_2, \mathrm{Y}_2, \mathrm{Z}_2) \equiv$ the same forces in Cartesian notation.

c_1, c_2 or $(u_1, v_1, w_1), (u_2, v_2, w_2) \equiv$ the mean velocities of the two groups of molecules in vector or Cartesian notation.

We define further quantities of the same nature, in terms of the above, as follows:—

$$(1{\cdot}01) \quad \nu_0 \equiv \nu_1+\nu_2, \quad \text{so that} \quad \lambda_1 = \nu_1/(\nu_1+\nu_2) = \nu_1/\nu_0, \quad \lambda_2 = \nu_2/(\nu_1+\nu_2) = \nu_2/\nu_0, \quad \lambda_1+\lambda_2 = 1.$$

$$(1{\cdot}02) \quad 2\lambda'_0 \equiv \lambda_1-\lambda_2, \qquad \lambda_{12} \equiv \lambda_1/\lambda_2, \qquad \lambda_{21} \equiv \lambda_2/\lambda_1, \qquad \text{so that} \qquad \lambda_{12}\lambda_{21} = 1.$$

$$(1{\cdot}03) \quad m_0 \equiv \lambda_1 m_1+\lambda_2 m_2, \qquad m'_0 \equiv \lambda_1(m_1-m_0) = -\lambda_2(m_2-m_0) = \lambda_1\lambda_2(m_1-m_2).$$

Now we have

$$(1{\cdot}04) \qquad \rho_1 = \nu_1 m_1, \qquad \rho_2 = \nu_2 m_2,$$

so that, by (1·01) and (1·03),

$$(1{\cdot}05) \qquad \rho_0 \equiv \rho_1+\rho_2 = \nu_1 m_1+\nu_2 m_2 = \nu_0 m_0, \qquad \rho'_0 \equiv \frac{\nu_0 m'_0}{\lambda_1\lambda_2} = \nu_0(m_1-m_2).$$

Also, in vector notation P, c, we shall write

$$(1{\cdot}06) \quad \mathrm{P}_0 \equiv \lambda_1\mathrm{P}_1+\lambda_2\mathrm{P}_2, \quad \mathrm{P}'_0 \equiv \lambda_1\left(\mathrm{P}_1-\frac{m_1}{m_0}\mathrm{P}_0\right) = -\lambda_2\left(\mathrm{P}_2-\frac{m_2}{m_0}\mathrm{P}_0\right) = \lambda_1\lambda_2\left(\frac{m_2}{m_0}\mathrm{P}_1-\frac{m_1}{m_0}\mathrm{P}_2\right).$$

$$(1{\cdot}07) \quad c_0 \equiv \lambda_1 c_1+\lambda_2 c_2, \qquad c'_0 \equiv \lambda_1(c_1-c_0) = -\lambda_2(c_2-c_0) = \lambda_1\lambda_2(c_1-c_2).$$

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* *I.e.*, at the point (x, y, z) and at time t.

The corresponding component equations, involving X, Y, Z or u, v, w with appropriate suffixes, are similar and will not be written down here.

By inverting the above equations we obtain the following expressions for the original in terms of the derived quantities:—

$$(1{\cdot}08) \qquad m_1 = m_0 + \frac{m'_0}{\lambda_1}, \qquad \mathrm{P}_1 = \frac{m_1}{m_0}\mathrm{P}_0 + \frac{\mathrm{P}'_0}{\lambda_1}, \qquad c_1 = c_0 + \frac{c'_0}{\lambda_1}.$$

$$(1{\cdot}09) \qquad m_2 = m_0 - \frac{m'_0}{\lambda_2}, \qquad \mathrm{P}_2 = \frac{m_2}{m_0}\mathrm{P}_0 - \frac{\mathrm{P}'_0}{\lambda_2}, \qquad c_2 = c_0 - \frac{c'_0}{\lambda_2}.$$

(*b*) *The Interpretation of the Derived Quantities.*

Corresponding to (1·08) and (1·09), the motion of the gas can be analysed into (*a*) a steady motion of the composite gas as a whole with velocity c_0, together with (*b*) a motion of interdiffusion in which the mean velocities of the two streams are respectively c'_0/λ_1 and $-c'_0/\lambda_2$. In this latter motion equal numbers of molecules are transferred per unit time in each direction, the number (per unit area normal to the direction of the vector c'_0) being $\nu_0 c'_0$, since by (1·01)

$$(1{\cdot}10) \qquad \nu_1 c'_0/\lambda_1 = \nu_2 c'_0/\lambda_2 = \nu_0 c'_0.$$

The momentum of the common motion (*a*) is clearly $\rho_0 c_0$ per unit volume, while that of the motion of interdiffusion is $\nu_0(m_1 - m_2)c'_0$ or, by (1·05), $\rho'_0 c'_0$; in general this is not zero, owing to the inequality of mass of the molecules, although the diffusing streams convey equal *numbers* of them in any interval of time. This analysis of momentum corresponds to the equation

$$(1{\cdot}11) \qquad \rho_1 c_1 + \rho_2 c_2 = \nu_1 m_1 c_1 + \nu_2 m_2 c_2 = \rho_0 c_0 + \rho'_0 c'_0.$$

The equations (1·06) differ from the others by involving the molecular masses as well as ν_1 and ν_2. This resolution of the forces P_1 and P_2 may be considered as follows: the first terms (*cf.* 1·08 and 1·09), viz., $\frac{m_1}{m_0}\mathrm{P}_0$ on m_1 and $\frac{m_2}{m_0}\mathrm{P}_0$ on m_2, represent forces which will impart a common acceleration P_0/m_0 to each group of molecules (we may regard this variation as affecting their common velocity of streaming, c_0); the remaining components, P'_0/λ_1 on m_1 and $-\mathrm{P}'_0/\lambda_2$ on m_2, when summed up over the ν_1, ν_2 molecules of the corresponding groups, afford equal and opposite *total* forces $\nu_0\mathrm{P}'_0$, $\nu_0\mathrm{P}'_0$. In connection with this we may remember that two such interdiffusing groups of molecules as we have considered will exert equal and opposite actions on one another, and that equal and opposite forces must be applied to the two groups if their motion of interdiffusion is to be maintained, or modified without imparting any *common* velocity to them.

As regards λ'_0, this is useful for the purpose of imparting a symmetrical form to some of our equations; if D denotes a differential operator of any kind with respect to (x, y, z, t), since $\lambda_1+\lambda_2 = 1$ we have, by (1·02),

$$(1\cdot12) \qquad D\lambda_1 = -D\lambda_2 = \tfrac{1}{2}D(\lambda_1-\lambda_2) = D\lambda'_0.$$

(*c*) *The "Peculiar" Motions of the Molecules.*

So far we have been concerned with the *mean* velocities of the constituents of the gas, without considering the actual motions of individual molecules. We shall denote the velocities of typical molecules of the two kinds by $(c)_1, (c)_2$ or $\{(u)_1, (v)_1, (w)_1\}$, $\{(u)_2, (v)_2, (w)_2\}$, when referred to the co-ordinate axes, or, when referred to axes moving with the velocity c_0 appropriate to the point and time in question, by C_1, C_2 or $(U_1, V_1, W_1), (U_2, V_2, W_2)$. Thus

$$(1\cdot13) \qquad C_1 = (c)_1-c_0, \qquad C_2 = (c)_2-c_0.$$

The velocities C_1, C_2 will be called the "peculiar" velocities of the molecules.

We have no means of determining the individual values of C_1, C_2 for the molecules near (x, y, z, t), but for a given state of the gas, as specified by its composition, mean motions, pressures, and temperature (these are expressible in terms of mean values of functions of C), there will be a certain frequency law, or function representing the distribution of various values of the velocity among the molecules. The determination of this velocity-distribution function is fundamental in the method of this paper. It will clearly involve C or its components as independent variables, together with certain parameters (*e.g.*, pressures or mean velocities) which are dependent on (x, y, z, t).

The mean value of any function of the molecular velocities will be denoted by placing a bar over the expression representing the function. Thus, for instance (*cf.* 1·07),

$$(1\cdot14) \quad \overline{(c)}_1 = c_1, \ \overline{(c)}_2 = c_2, \ \overline{C}_1 = \overline{(c)}_1-c_0 = c_1-c_0 = c'_0/\lambda_1, \ \overline{C}_2 = \overline{(c)}_2-c_0 = c_2-c_0 = -c'_0/\lambda_2.$$

It is convenient at this stage to modify the meaning of our symbols C_1, C_2, which have so far represented vector quantities; henceforward they will denote not the vectors themselves, but their amplitudes. These, of course, are essentially positive, scalar quantities. Thus

$$(1\cdot15) \qquad C_1^2 = U_1^2+V_1^2+W_1^2, \qquad C_2^2 = U_2^2+V_2^2+W_2^2.$$

The mean energy of peculiar motion per molecule is $\frac{1}{2}m\overline{C^2}$, and we shall write

$$(1\cdot16) \qquad m_1\overline{C_1^2} \equiv \frac{3}{2h_1} \equiv 3RT_1, \qquad m_2\overline{C_2^2} \equiv \frac{3}{2h_2} \equiv 3RT_2,$$

where R is the "universal gas constant." These equations define h and T; we shall call T_1, T_2 the absolute temperatures of the component gases. According to the theorem of equipartition of energy, in the uniform steady state of a gas they are equal. In the slightly disturbed states which we shall consider, the differences h_1-h_2, T_1-T_2 will be small.*

We further define p_1, p_2, p_0, the mean hydrostatic pressures of the separate components of the gas, and of the total gas, by the equations

$$(1\cdot17)\qquad p_1 \equiv \tfrac{1}{3}\nu_1 m_1 \overline{C_1^2} = \frac{\nu_1}{2h_1} = R\nu_1 T_1, \qquad p_2 \equiv \tfrac{1}{3}\nu_2 m_2 \overline{C_2^2} = \frac{\nu_2}{2h_2} = R\nu_2 T_2,$$

$$(1\cdot18)\qquad p_0 \equiv p_1+p_2 = \frac{\nu_1}{2h_1}+\frac{\nu_2}{2h_2} \equiv \frac{\nu_0}{2h_0} \equiv R\nu_0 T_0.$$

The last equation also defines h_0 and T_0; the latter will be called the absolute temperature of the composite gas. Clearly

$$(1\cdot181)\qquad T_0 = \lambda_1 T_1+\lambda_2 T_2, \qquad \frac{1}{h_0} = \frac{\lambda_1}{h_1}+\frac{\lambda_2}{h_2}.$$

We shall define T'_0, p'_0, h'_0 by the equations

$$(1\cdot182)\qquad T'_0 = \lambda_1(T_1-T_0) = -\lambda_2(T_2-T_0) = \lambda_1\lambda_2(T_1-T_2),$$

$$(1\cdot183)\qquad \frac{1}{h'_0} = \lambda_1\left(\frac{1}{h_1}-\frac{1}{h_0}\right) = -\lambda_2\left(\frac{1}{h_2}-\frac{1}{h_0}\right) = \lambda_1\lambda_2\left(\frac{1}{h_1}-\frac{1}{h_2}\right),$$

$$(1\cdot184)\qquad p'_0 = \frac{\nu_0}{2h'_0} = \lambda_1\lambda_2\left(\frac{p_1}{\lambda_1}-\frac{p_2}{\lambda_2}\right) = R\nu_0 T'_0.$$

The following equations are inverse to the above :—

$$(1\cdot185)\qquad T_1 = T_0+\frac{T'_0}{\lambda_1}, \qquad T_2 = T_0-\frac{T'_0}{\lambda_2},$$

$$(1\cdot186)\qquad p_1 = \lambda_2(p_0+\lambda_1 p'_0), \qquad p_2 = \lambda_1(p_0-\lambda_2 p'_0).$$

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* [In the paper as originally communicated, no account was taken of these differences, a preliminary examination having indicated that they do not materially affect the theory of diffusion. The distinction between T_1 and T_2 has been re-introduced at the suggestion of a referee, in order that its influence, if any, on the phenomenon of thermal diffusion might be made clear. It will appear that T_1-T_2 is a small multiple of the rate of change of λ'_0 (or λ_1) with *time*, so that in steady states of the gas it is a small quantity of the second order only; in particular, the phenomenon dealt with in § 16 is unaffected.

Throughout the paper, wherever a distinction is made between h_1 and h_2, T_1 and T_2, or wherever T'_0 (equation 1·182) appears, this has been introduced on revision (June, 1916). The original form of the equations may be found by making the difference zero. An appendix has also been added on account of this extension.—*June 2, 1916.*]

(*d*) *Some Convenient Limitations of the Problem.*

Our immediate aim is to determine functions $f_1(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1)$, $f_2(\mathsf{U}_2, \mathsf{V}_2, \mathsf{W}_2)$ which define the distribution of the peculiar velocities of the molecules, *i.e.*, which are such that the number of molecules of the group considered (the appropriate suffix 1 or 2 being added throughout), the components of whose velocities lie between $(\mathsf{U}, \mathsf{V}, \mathsf{W})$ and $(\mathsf{U}+d\mathsf{U}, \mathsf{V}+d\mathsf{V}, \mathsf{W}+d\mathsf{W})$ respectively, is

$$(1{\cdot}19) \qquad \nu f(\mathsf{U}, \mathsf{V}, \mathsf{W})\, d\mathsf{U}\, d\mathsf{V}\, d\mathsf{W}$$

per unit volume. Besides the independent variables U, V, W, these functions $f(\mathsf{U}, \mathsf{V}, \mathsf{W})$ will also involve such quantities as ν, λ, P, c, h and their derivatives, all of which are functions of (x, y, z, t). The distribution of the peculiar velocities is, however, clearly unaffected by the absolute magnitude of the mean velocity c_0 (though the same is not true of the derivatives of c_0). We may, therefore, legitimately make the simplifying convention that $c_0 = 0$ at the particular point and time under consideration. This merely amounts to a particular choice of uniformly moving axes of reference, a choice which the laws of dynamics leave quite unrestricted.

Our concern being with problems of *molecular* rather than *mass* motion, we shall suppose that the acceleration of the gas as a whole is of the first order only, which requires that the resultant force on unit mass of the gas, viz., P_0/m_0, shall be small. We shall also suppose throughout that the velocity c'_0 of interdiffusion, and the derivatives, with respect to space and time, of ν, λ, c, h, are all of the first order, at most*; consequently, since in this paper we shall neglect second order quantities, products and derivatives of any of the small quantities just mentioned will be omitted from our analysis.

§ 2. THE EQUATION OF TRANSFER OF MOLECULAR PROPERTIES.

(*a*) *The Equation of Continuity.*

The general equation of transfer for a function Q_1 of the velocity components $(u)_1$, $(v)_1$, $(w)_1$ of a molecule of the first kind is†

$$(2{\cdot}01) \qquad \Delta \mathrm{Q}_1 = \frac{\partial}{\partial t}\left(\nu_1 \overline{\mathrm{Q}_1}\right) + \sum_{x, y, z} \left[\frac{\partial}{\partial x}\left\{\nu_1 \overline{(u)_1 \mathrm{Q}_1}\right\} - \frac{\nu_1}{m_1} \mathrm{X}_1 \overline{\left\{\frac{\partial \mathrm{Q}_1}{\partial (u)_1}\right\}}\right],$$

where $\Delta \mathrm{Q}_1$ denotes the rate of change of $\nu_1 \overline{\mathrm{Q}_1}$ at (x, y, z, t) produced by the encounter of the molecules of the first kind with others of the same or the other kind.

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* [And likewise p'_0, T'_0, $1/h'_0$, when we are considering unsteady states in which $\mathrm{T}_1 \neq \mathrm{T}_2$.—*June 2, 1916.*]

† *Cf.* Chapter IX. of JEANS' 'Treatise' (2nd ed.), and also, for the details of the reduction of (2·01)–(2·02) and (2·09), 'Phil. Trans.,' A, vol. 216, p. 285.

If we write $Q = 1$, since $\Delta Q_1 = 0$, and $\dfrac{\partial Q_1}{\partial (u)_1} = 0$, the equation of transfer reduces to

$$(2{\cdot}011) \qquad \frac{\partial \nu_1}{\partial t} + \frac{\partial (\nu_1 u_1)}{\partial x} + \frac{\partial (\nu_1 v_1)}{\partial y} + \frac{\partial (\nu_1 w_1)}{\partial z} = 0,$$

which is the equation of continuity for the first component of the composite gas. By adding to this the corresponding equation for the second component, we obtain the equation of continuity for the gas as a whole, in the form

$$\frac{\partial (\nu_1 + \nu_2)}{\partial t} + \frac{\partial (\nu_1 u_1 + \nu_2 u_2)}{\partial x} + \frac{\partial (\nu_1 v_1 + \nu_2 v_2)}{\partial y} + \frac{\partial (\nu_1 w_1 + \nu_2 w_2)}{\partial z} = 0$$

or

$$(2{\cdot}012) \qquad \frac{\partial \nu_0}{\partial t} + \frac{\partial (\nu_0 u_0)}{\partial x} + \frac{\partial (\nu_0 v_0)}{\partial y} + \frac{\partial (\nu_0 w_0)}{\partial z} = 0.$$

If at the point under consideration the mean velocity of the gas is zero, the last equation may be written

$$(2{\cdot}013) \qquad \frac{1}{\nu_0}\frac{\partial \nu_0}{\partial t} = -\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right).$$

(*b*) $Q_1 = \mathsf{U}_1 C_1^{2s}$.

If in the equation of transfer (2·01) we assign to Q_1 the value $(u)_1 (c)_1^{2s}$, and omit all terms which in a gas of ordinary density are of the second order, we find that

$$(2{\cdot}02) \quad \Delta \mathsf{U}_1 C_1^{2s} = \frac{1.3.5\ldots(2s+3)}{3}\frac{\nu_1}{(2h_1 m_1)^s}\left[\frac{\partial u_0}{\partial t} + \frac{1}{2h_1 m_1}\frac{1}{\nu_1}\frac{\partial \nu_1}{\partial x} - \frac{1}{m_1}X_1 + (s+1)\frac{\partial}{\partial x}\left(\frac{1}{2h_1 m_1}\right)\right].$$

We have here used the convention that $c_0 = 0$ at this particular point and time, so that $(c)_1$ and C_1 are identical, and, except in differential coefficients, c_0 can be neglected.

If we multiply both sides of (2·02) by m_1, and add the corresponding equation for the second group of molecules, in the case when $s = 0$ we obtain the result

$$\begin{aligned}(2{\cdot}03) \quad \Delta (m_1 \mathsf{U}_1 + m_2 \mathsf{U}_2) &= (\nu_1 m_1 + \nu_2 m_2)\frac{\partial u_0}{\partial t} + \left(\frac{1}{2h_1}\frac{\partial \nu_1}{\partial x} + \frac{1}{2h_2}\frac{\partial \nu_2}{\partial x}\right) \\ &\quad - (\nu_1 X_1 + \nu_2 X_2) + \left\{\nu_1 \frac{\partial}{\partial x}\left(\frac{1}{2h_1}\right) + \nu_2 \frac{\partial}{\partial x}\left(\frac{1}{2h_2}\right)\right\} \\ &= \nu_0 m_0 \frac{\partial u_0}{\partial t} - \nu_0 X_0 + \frac{\partial}{\partial x}\left(\frac{\nu_1}{2h_1} + \frac{\nu_2}{2h_2}\right) \\ &= \nu_0 m_0 \frac{\partial u_0}{\partial t} - \nu_0 X_0 + \frac{\partial p_0}{\partial x},\end{aligned}$$

by (1·18). In this equation the left-hand side is the rate of change of the momentum per unit volume of the whole gas at (x, y, z, t) which is produced by encounters between the molecules. Since, however, an encounter between two molecules leaves their combined momentum unchanged, $\Delta(m_1\mathsf{U}_1+m_2\mathsf{U}_2)$ is zero, and consequently

$$(2\cdot04) \qquad \frac{\partial u_0}{\partial t} = \frac{1}{m_0}\mathrm{X}_0 - \frac{1}{\nu_0 m_0}\frac{\partial p_0}{\partial x}.$$

This and the two similar equations in y and z are the equations of mean motion of the gas.

We will now apply (2·04) to the elimination of $\frac{\partial u_0}{\partial t}$ from (2·02). At the same time we shall neglect the difference between h_1 and h_0, T_1 and T_0 in products or derivatives, since our equations are to be carried only to the first order of accuracy. Then (2·02) becomes

$$(2\cdot05) \qquad \frac{3\,(2h_0m_1)^s}{1.3.5\ldots(2s+3)}\frac{m_1}{\nu_1}\Delta\mathsf{U}_1\mathrm{C}_1^{2s} = \frac{1}{2h_0}\frac{1}{\nu_1}\frac{\partial \nu_1}{\partial x} + \frac{m_1}{m_0}\mathrm{X}_0 - \mathrm{X}_1 - \frac{m_1}{\nu_0 m_0}\frac{\partial p_0}{\partial x} + (s+1)\frac{\partial}{\partial x}\left(\frac{1}{2h_0}\right)$$

$$= \frac{1}{2h_0}\left(\frac{1}{\nu_1}\frac{\partial \lambda_1}{\partial x} + \frac{1}{\nu_0}\frac{\partial \nu_0}{\partial x}\right) + \frac{\partial}{\partial x}\left(\frac{1}{2h_0}\right) - \frac{1}{\lambda_1}\mathrm{X}'_0 - \frac{m_1}{\nu_0 m_0}\frac{\partial p_0}{\partial x} + s\frac{\partial}{\partial x}\left(\frac{1}{2h_0}\right)$$

$$= \frac{1}{\lambda_1}\left[\frac{1}{2h_0}\frac{\partial \lambda'_0}{\partial x} - \mathrm{X}'_0 - \frac{m'_0}{\nu_0 m_0}\frac{\partial p_0}{\partial x}\right] + \mathrm{R}s\frac{\partial \mathrm{T}_0}{\partial x}.$$

Thus, if we write

$$(2\cdot06) \qquad \xi'_0 \equiv \frac{1}{2h_0}\frac{\partial \lambda'_0}{\partial x} - \mathrm{X}'_0 - \frac{m'_0}{\nu_0 m_0}\frac{\partial p_0}{\partial x},$$

the equation (2·05) and the corresponding equation for the second set of molecules become

$$(2\cdot07) \qquad \frac{3\,(2h_0m_1)^s}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}m_1\Delta\mathsf{U}_1\mathrm{C}_1^{2s} = \nu_0\xi'_0 + \mathrm{R}s\nu_1\frac{\partial \mathrm{T}_0}{\partial x},$$

$$(2\cdot08) \qquad \frac{3\,(2h_0m_2)^s}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}m_2\Delta\mathsf{U}_2\mathrm{C}_2^{2s} = -\,\nu_0\xi'_0 + \mathrm{R}s\nu_2\frac{\partial \mathrm{T}_0}{\partial x}.$$

To this order of approximation, therefore, these equations do not involve T'_0.

(*c*) $\mathrm{Q}_1 = \mathsf{U}_1^2\mathrm{C}_1^{2s}$.

When $\mathrm{Q}_1 = \mathsf{U}_1^2\mathrm{C}_1^{2s}$, the equation of transfer takes the form (*cf.* § 3 (C) of my second paper, *loc. cit.*)

$$(2\cdot09) \qquad \frac{15\,(2h_1m_1)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}\Delta\mathsf{U}_1^2\mathrm{C}_1^{2s} = 5\nu_1\left\{\frac{1}{\nu_1}\frac{\partial \nu_1}{\partial t} + (s+1)\,2h_1\frac{\partial}{\partial t}\left(\frac{1}{2h_1}\right)\right\}$$

$$+ (2s+5)\,\nu_1\left(3\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right).$$

Now

$$(2{\cdot}10)\qquad 3\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z} = \tfrac{5}{3}\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)+\tfrac{2}{3}\left(2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z}\right)$$

$$= -\tfrac{5}{3}\frac{1}{\nu_0}\frac{\partial \nu_0}{\partial t}+\tfrac{2}{3}c_{xx}$$

by (2·013), where also we have used the notation indicated by

$$(2{\cdot}11)\qquad \left\{\begin{aligned} c_{xx} &= 2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z},\\ c_{yy} &= 2\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z}-\frac{\partial u_0}{\partial x},\\ c_{zz} &= 2\frac{\partial w_0}{\partial z}-\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}. \end{aligned}\right.$$

Evidently we have

$$(2{\cdot}12)\qquad c_{xx}+c_{yy}+c_{zz} = 0.$$

By substitution from (2·10) into (2·09), we find that

$$(2{\cdot}13)\qquad \frac{15\,(2h_0m_1)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}\,\Delta \mathrm{U}_1{}^2\mathrm{C}_1{}^{2s} = 5\nu_1\left\{\frac{1}{\nu_1}\frac{\partial \nu_1}{\partial t}+(s+1)\,2h_1\frac{\partial}{\partial t}\left(\frac{1}{2h_1}\right)-\tfrac{1}{3}\,(2s+5)\,\frac{1}{\nu_0}\frac{\partial \nu_0}{\partial t}\right\}$$

$$+\tfrac{2}{3}\,(2s+5)\,\nu_1 c_{xx}.$$

If we divide both sides of this equation by $10\,.\,2h_1$, and assign the zero value to s, it becomes

$$(2{\cdot}14)\qquad \Delta\tfrac{1}{2}m_1\mathrm{U}_1{}^2 = \tfrac{1}{2}\left\{\frac{1}{2h_1}\frac{\partial \nu_1}{\partial t}+\nu_1\frac{\partial}{\partial t}\left(\frac{1}{2h_1}\right)-\tfrac{5}{3}\,\frac{\nu_1}{2h_1}\frac{1}{\nu_0}\frac{\partial \nu_0}{\partial t}+\frac{\nu_1}{3h_1}\,c_{xx}\right\}.$$

On adding to this the corresponding y and z equations, the result is

$$(2{\cdot}15)\qquad \Delta\tfrac{1}{2}m_1\mathrm{C}_1{}^2 = \tfrac{3}{2}p_1\left(\frac{1}{p_1}\frac{\partial p_1}{\partial t}-\tfrac{5}{3}\,\frac{1}{\nu_0}\frac{\partial \nu_0}{\partial t}\right).$$

There is a similar equation for the second set of molecules, and by addition of the two we get

$$(2{\cdot}16)\qquad \Delta\left(\tfrac{1}{2}m_1\mathrm{C}_1{}^2+\tfrac{1}{2}m_2\mathrm{C}_2{}^2\right) = 0 = \tfrac{3}{2}p_0\left(\frac{1}{p_0}\frac{\partial p_0}{\partial t}-\tfrac{5}{3}\,\frac{1}{\nu_0}\frac{\partial \nu_0}{\partial t}\right),$$

the left-hand side being zero, since energy is conserved throughout molecular encounters. The integration of the last equation gives us the equation of state of the gas, viz.,

$$p_0\nu_0^{-5/3} = \text{constant}, \tag{2·17}$$

or

$$\mathrm{T}_0\nu_0^{-2/3} = \text{constant}. \tag{2·18}$$

We will now return to the general case of (2·13); on neglecting the difference between h_1 and h_0, T_1 and T_0, in derivatives and products, the equation becomes

$$\begin{aligned}\frac{3\,(2h_0m_1)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}\,\Delta \mathrm{U}_1^2\mathrm{C}_1^{2s} &= \nu_1\left[\frac{1}{\nu_1}\frac{\partial\nu_1}{\partial t}-\frac{1}{\nu_0}\frac{\partial\nu_0}{\partial t}+(s+1)\left\{2h_0\frac{\partial}{\partial t}\left(\frac{1}{2h_0}\right)-\tfrac{2}{3}\frac{1}{\nu_0}\frac{\partial\nu_0}{\partial t}\right\}\right] \\ &\qquad +\tfrac{2}{15}\,(2s+5)\,\nu_1 c_{xx} \\ &= \nu_0\frac{\partial\lambda'_0}{\partial t}+\tfrac{2}{15}\,(2s+5)\,\nu_1 c_{xx}\end{aligned} \tag{2·19}$$

by (2·18). The similar equation for the second set of molecules is

$$\frac{3\,(2h_0m_2)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}\,\Delta \mathrm{U}_2^2\mathrm{C}_2^{2s} = -\nu_0\frac{\partial\lambda'_0}{\partial t}+\tfrac{2}{15}\,(2s+5)\,\nu_2 c_{xx}. \tag{2·20}$$

(*d*) $\mathrm{Q}_1 = \mathrm{V}_1\mathrm{W}_1\mathrm{C}_1^{2s}$.

From (2·20), by transformation of rectangular co-ordinates, or by direct calculation, the equations of transfer in this case may readily be shown to have the form

$$\frac{3\,(2h_0m_1)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}\,\Delta \mathrm{V}_1\mathrm{W}_1\mathrm{C}_1^{2s} = \tfrac{2}{15}\,(2s+5)\,\nu_1 c_{yz}, \tag{2·21}$$

$$\frac{3\,(2h_0m_2)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}\,\Delta \mathrm{V}_2\mathrm{W}_2\mathrm{C}_2^{2s} = \tfrac{2}{15}\,(2s+5)\,\nu_2 c_{yz}, \tag{2·22}$$

where

$$c_{yz} \equiv \tfrac{3}{2}\left(\frac{\partial v_0}{\partial z}+\frac{\partial w_0}{\partial y}\right).$$

(*e*) $\mathrm{Q} = \mathrm{C}^{2s}$.

By the addition of the x, y, and z equations corresponding to (2·19), (2·20), and by changing s to $s-1$, we may obtain the following simple equations:—

$$\frac{(2h_0m_1)^s}{1\,.\,3\,.\,5\,\ldots\,(2s+1)}\,\Delta\mathrm{C}_1^{2s} = \nu_0\frac{\partial\lambda'_0}{\partial t} = -\frac{(2h_0m_2)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+1)}\,\Delta\mathrm{C}_2^{2s}. \tag{2·23}$$

§ 3. THE VELOCITY-DISTRIBUTION FUNCTION.

(*a*) *The Form of the Function.*

In the uniform undisturbed state of a gas, in which c_0, λ, h are constant, while c'_0, h'_0, P are zero, the velocity-distribution functions assume MAXWELL'S well-known form

$$(3\cdot01) \qquad (f_1)_0 = \left(\frac{h_0 m_1}{\pi}\right)^{3/2} e^{-h_0 m_1 \mathrm{C}_1{}^2}, \qquad (f_2)_0 = \left(\frac{h_0 m_2}{\pi}\right)^{3/2} e^{-h_0 m_2 \mathrm{C}_2{}^2}.$$

The suffix 0 appended to f_1 and f_2 is to indicate the special state to which these equations refer. They clearly satisfy the necessary conditions

$$(3\cdot02) \qquad \iiint_{-\infty}^{\infty} (f_1)_0 \, d\mathsf{U}_1 \, d\mathsf{V}_1 \, d\mathsf{W}_1 = 1, \qquad \iiint_{-\infty}^{\infty} (f_2)_0 \mathrm{C}_1{}^2 \, d\mathsf{U}_1 \, d\mathsf{V}_1 \, d\mathsf{W}_1 = \frac{3}{2h_0 m_1},$$

and similar equations with suffix 2.

In the general slightly disturbed state considered in this paper, $f(\mathsf{U}, \mathsf{V}, \mathsf{W})$ will differ from $(f)_0$ by an amount of the first order. From the equations of transfer (§ 2) it may be deduced* that f may be expressed as follows :—

$$\begin{aligned}(3\cdot03) \quad f_1(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1) = (f_1)_0 \Big[1 &- \tfrac{1}{3} 2h_0 m_1 \mathrm{A}_0 (\mathsf{U}_1 \xi'_0 + \mathsf{V}_1 \eta'_0 + \mathsf{W}_1 \zeta'_0) \, \mathrm{F}_1(\mathrm{C}_1{}^2) \\ &- \tfrac{1}{3} 2h_0 m_1 \mathrm{B}_0 \left(\mathsf{U}_1 \frac{\partial \mathrm{T}_0}{\partial x} + \mathsf{V}_1 \frac{\partial \mathrm{T}_0}{\partial y} + \mathsf{W}_1 \frac{\partial \mathrm{T}_0}{\partial z} \right) \mathrm{G}_1(\mathrm{C}_1{}^2) \\ &- \tfrac{2}{45} 2h_0 m_1 \mathrm{C}_0 (c_{xx} \mathsf{U}_1{}^2 + c_{yy} \mathsf{V}_1{}^2 + c_{zz} \mathsf{W}_1{}^2 + 2c_{yz} \mathsf{V}_1 \mathsf{W}_1 + 2c_{zx} \mathsf{W}_1 \mathsf{U}_1 + 2c_{xy} \mathsf{U}_1 \mathsf{V}_1) \, \mathrm{H}_1(\mathrm{C}_1{}^2) \\ &- \mathrm{D}_0 \frac{\partial \lambda'_0}{\partial t} \mathrm{J}_1(\mathrm{C}_1{}^2) \Big],\end{aligned}$$

$$\begin{aligned}(3\cdot04) \quad f_2(\mathsf{U}_2, \mathsf{V}_2, \mathsf{W}_2) = (f_2)_0 \Big[1 &- \tfrac{1}{3} 2h_0 m_2 \mathrm{A}_0 (\mathsf{U}_2 \xi'_0 + \mathsf{V}_2 \eta'_0 + \mathsf{W}_2 \zeta'_0) \, \mathrm{F}_2(\mathrm{C}_2{}^2) \\ &- \tfrac{1}{3} 2\mathrm{h}_0 m_2 \mathrm{B}_0 \left(\mathsf{U}_2 \frac{\partial \mathrm{T}_0}{\partial x} + \mathsf{V}_2 \frac{\partial \mathrm{T}_0}{\partial y} + \mathsf{W}_2 \frac{\partial \mathrm{T}_0}{\partial z} \right) \mathrm{G}_2(\mathrm{C}_2{}^2) \\ &- \tfrac{2}{45} 2h_0 m_2 \mathrm{C}_0 (c_{xx} \mathsf{U}_2{}^2 + c_{yy} \mathsf{V}_2{}^2 + c_{zz} \mathsf{W}_2{}^2 + 2c_{yz} \mathsf{V}_2 \mathsf{W}_2 + 2c_{zx} \mathsf{W}_2 \mathsf{U}_2 + 2c_{xy} \mathsf{U}_2 \mathsf{V}_2) \, \mathrm{H}_2(\mathrm{C}_2{}^2) \\ &- \mathrm{D}_0 \frac{\partial \lambda'_0}{\partial t} \mathrm{J}_2(\mathrm{C}_2{}^2) \Big].\end{aligned}$$

The constants A_0, B_0, C_0, D_0, and the functions $\mathrm{F}(\mathrm{C}^2)$, $\mathrm{G}(\mathrm{C}^2)$, $\mathrm{H}(\mathrm{C}^2)$, $\mathrm{J}(\mathrm{C}^2)$ remain to be determined. The latter involve (x, y, z, t) only through the occurrence

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* The argument is given in my second paper, *loc. cit.*, §§ 2, 6, and will not be repeated here.

of ν and h (but not their derivatives) as factors. We suppose them to be capable of expansion in power series as follows* (see Note C, p. 196):—

$$(3{\cdot}05)\qquad F_1(C_1^2)=\sum_{r=0}^{\infty}\alpha_r\frac{(2hm_1)^r}{1.3.5\ldots(2r+3)}C_1^{2r},\qquad F_2(C_2^2)=\sum_{r=0}^{\infty}\alpha_{-r}\frac{(2hm_2)^r}{1.3.5\ldots(2r+3)}C_2^{2r},$$

$$(3{\cdot}06)\qquad G_1(C_1^2)=\sum_{r=0}^{\infty}{}'\,\beta_r\frac{(2hm_1)^r}{1.3.5\ldots(2r+3)\,r}C_1^{2r},\quad G_2(C_2^2)=\sum_{r=0}^{\infty}{}'\,\beta_{-r}\frac{(2hm_2)^r}{1.3.5\ldots(2r+3)\,r}C_2^{2r},$$

$$(3{\cdot}07)\qquad H_1(C_1^2)=\sum_{r=0}^{\infty}\gamma_r\frac{(2hm_1)^r}{1.3.5\ldots(2r+5)}C_1^{2r},\qquad H_2(C_2^2)=\sum_{r=0}^{\infty}\gamma_{-r}\frac{(2hm_2)^r}{1.3.5\ldots(2r+5)}C_2^{2r},$$

$$(3{\cdot}071)\qquad J_1(C_1^2)=\sum_{r=0}^{\infty}\delta_r\frac{(2hm_1)^r}{1.3.5\ldots(2r+1)}C_1^{2r},\qquad J_2(C_2^2)=\sum_{r=0}^{\infty}\delta_{-r}\frac{(2hm_2)^r}{1.3.5\ldots(2r+1)}C_2^{2r}.$$

The dash (′) after the sign of summation in (3·06) is used to signify that the factor r in the denominator of the numerical coefficient is to be omitted in the first term ($r=0$). The choice of the notation $+r$ and $-r$ for the suffixes has a convenience which will become apparent later; we may remark, in passing, that for this purpose a distinction must be maintained between $+0$ and -0.

In (3·03) and (3·04) the constants A_0, B_0, C_0, D_0 can be chosen arbitrarily, but when this has been done, the remaining constants α, β, γ, δ all become perfectly definite.

(*b*) *Relations between the Coefficients.*

The velocity-distribution functions $f(U, V, W)$ must satisfy the three conditions expressed by the equations (with appropriate suffixes 1 or 2 throughout):—

$$(3{\cdot}08)\qquad \iiint f(U,V,W)\,dU\,dV\,dW=1,$$

$$(3{\cdot}09)\qquad \iiint f(U,V,W)\,C^2\,dU\,dV\,dW=\frac{3}{2hm}\qquad (h_1 \text{ or } h_2),$$

$$(3{\cdot}10)\qquad \iiint f_1(U_1,V_1,W_1)\,U_1\,dU_1\,dV_1\,dW_1=u_1-u_0=u'_0/\lambda_1,$$

$$\iiint f_2(U_2,V_2,W_2)\,U_2\,dU_2\,dV_2\,dW_2=u_2-u_0=-u'_0/\lambda_2.$$

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* [Here, and throughout the remainder of the paper, where h and T appear without any suffix, they are to be read as h_0 and T_0.—*June 2, 1916.*]

These yield the equations

(3·101) $$\sum_0^\infty \delta_r = 0,$$

(3·102) $$\sum_0^\infty \delta_{-r} = 0.$$

(3·103) $$\tfrac{1}{3}\mathrm{D}_0 \frac{\partial \lambda'_0}{\partial t} \sum_0^\infty (2r+3)\,\delta_r = -\frac{\mathrm{T}'_0}{\lambda_1 \mathrm{T}_0},$$

(3·104) $$\tfrac{1}{3}\mathrm{D}_0 \frac{\partial \lambda'_0}{\partial t} \sum_0^\infty (2r+3)\,\delta_{-r} = \frac{\mathrm{T}'_0}{\lambda_2 \mathrm{T}_0}.$$

(3·11) $$-\tfrac{1}{9}\left\{\mathrm{A}_0\xi'_0 \sum_0^\infty \alpha_r + \mathrm{B}_0 \frac{\partial \mathrm{T}}{\partial x} \sum_0^{\infty}{}' r^{-1}\beta_r\right\} = u'_0/\lambda_1,$$

(3·12) $$-\tfrac{1}{9}\left\{\mathrm{A}_0\xi'_0 \sum_0^\infty \alpha_{-r} + \mathrm{B}_0 \frac{\partial \mathrm{T}}{\partial x} \sum_0^{\infty}{}' r^{-1}\beta_{-r}\right\} = -u'_0/\lambda_2.$$

In each of the pairs (3·103)–(3·12) we will multiply the first equation by λ_1 and the second by λ_2 respectively, and add. We may separately equate the coefficients of ξ'_0 and $\frac{\partial \mathrm{T}}{\partial x}$ (in the second resulting equation) to zero, since these quantities are quite independent of one another, and of their coefficients. We thus obtain the conditions

(3·121) $$\lambda_1 \sum_0^\infty (2r+3)\,\delta_r = -\delta'_0 = -\lambda_2 \sum_0^\infty (2r+3)\,\delta_{-r},$$

or, by (3·101), (3·102),

(3·122) $$2\lambda_1 \sum_1^\infty r\,\delta_r = -\delta'_0 = -2\lambda_2 \sum_1^\infty r\,\delta_{-r}.$$

(3·13) $$\lambda_1 \sum_0^\infty \alpha_r = -\alpha'_0 = -\lambda_2 \sum_0^\infty \alpha_{-r},$$

(3·14) $$\lambda_1 \sum_0^{\infty}{}' r^{-1}\beta_r = -\beta'_0 = -\lambda_2 \sum_0^{\infty}{}' r^{-1}\beta_{-r},$$

where also we have introduced a convenient notation for the separate sums involved. Expressed in terms of this (3·101)–(3·12) are equivalent to

(3·15) $$u'_0 = \tfrac{1}{9}\left(\alpha'_0 \mathrm{A}_0 \xi'_0 + \beta'_0 \mathrm{B}_0 \frac{\partial \mathrm{T}}{\partial x}\right),$$

(3·151) $$\mathrm{T}'_0 = \tfrac{1}{3}\mathrm{D}_0 \mathrm{T}_0\, \delta'_0 \frac{\partial \lambda'_0}{\partial t}.$$

[Throughout the remainder of the paper we shall neglect $\frac{\delta \lambda'_0}{\delta t}$, *i.e.*, we shall practically assume that the ratio of mixture is not varying with respect to time. The values of α, β, γ determined in the succeeding sections will, however, hold good also in the general case; the determination of the δ's will be found in the Appendix. All the corrections to $(f)_0$ are of the first order, and hence are separately deducible; the complete value is obtained by adding to the series in α, β, γ, calculated in the body of the paper, the series in δ, determined in the Appendix.—*June 2, 1916.*]

§ 4. Completion of the Equations of Transfer.

(*a*) *The Values of* ΔQ.

We may now complete the equations of transfer (2·07)–(2·10) by the insertion of the values of ΔQ, calculated in terms of the constants in the expressions for $f(\mathsf{U}, \mathsf{V}, \mathsf{W})$ given in § 3. The calculation of ΔQ is a lengthy and elaborate operation which will not be described here, since a full account of it is to be found in my second memoir ('Phil. Trans.,' A, vol. 216, § 7, p. 301). It appears that only those terms in f which are of odd degree in U, V, W contribute to the resulting expression for $\Delta \mathsf{U} \mathrm{C}^{2s}$, and only the even terms, similarly, contribute to $\Delta \mathsf{U}^2 \mathrm{C}^{2s}$. The following results will be quoted forthwith :—

$$(4·01)\quad \frac{3\,(2hm_1)^s}{2^{s+1}\,(s+\frac{3}{2})_{s+1}} m_1 \Delta \mathsf{U}_1 \mathrm{C}_1^{\,2s} = \sum_{r=0}^{\infty} \Big[m_1 \Big(\mathrm{N}_{rs} \mathrm{A}_0 \xi'_0 \alpha_r + s \mathrm{N}'_{rs} \mathrm{B}_0 \frac{\partial \mathrm{T}}{\partial x} \beta_r \Big) \{ \rho_{11}(r_1 s_1) + \rho_{12}(r_1 s_1) \} \\ + m_2 \Big(\mathrm{N}_{rs} \mathrm{A}_0 \xi'_0 \alpha_{-r} + s \mathrm{N}'_{rs} \mathrm{B}_0 \frac{\partial \mathrm{T}}{\partial x} \beta_{-r} \Big) \rho_{12}(r_2 s_1) \Big],$$

$$(4·02)\quad \frac{3\,(2hm_2)^s}{2^{s+1}\,(s+\frac{3}{2})_{s+1}} m_2 \Delta \mathsf{U}_2 \mathrm{C}_2^{\,2s} = \sum_{r=0}^{\infty} \Big[m_1 \Big(\mathrm{N}_{rs} \mathrm{A}_0 \xi'_0 \alpha_r + s \mathrm{N}'_{rs} \mathrm{B}_0 \frac{\partial \mathrm{T}}{\partial x} \beta_r \Big) \rho_{21}(r_1 s_2) \\ + m_2 \Big(\mathrm{N}_{rs} \mathrm{A}_0 \xi'_0 \alpha_{-r} + s \mathrm{N}'_{rs} \mathrm{B}_0 \frac{\partial \mathrm{T}}{\partial x} \beta_{-r} \Big) \{ \rho_{22}(r_2 s_2) + \rho_{21}(r_2 s_2) \} \Big],$$

$$(4·03)\quad \frac{45\,(2hm_1)^{s+1}}{2^{s+2}\,(s+\frac{5}{2})_{s+2}} \frac{1}{2\nu_1} \Delta \mathsf{U}_1^{\,2} \mathrm{C}_1^{\,2s} = \frac{1}{\nu_1} \mathrm{C}_0 c_{xx} \sum_{r=0}^{\infty} \mathrm{N}''_{rs} [\gamma_r \{ \rho'_{11}(r_1 s_1) + \rho'_{12}(r_1 s_1) \} + \gamma_{-r} \rho'_{12}(r_2 s_1)],$$

$$(4·04)\quad \frac{45\,(2hm_2)^{s+1}}{2^{s+2}\,(s+\frac{5}{2})_{s+2}} \frac{1}{2\nu_2} \Delta \mathsf{U}_2^{\,2} \mathrm{C}_2^{\,2s} = \frac{1}{\nu_2} \mathrm{C}_0 c_{xx} \sum_{r=0}^{\infty} \mathrm{N}''_{rs} [\gamma_r \rho'_{21}(r_1 s_2) + \gamma_{-r} \{ \rho'_{22}(r_2 s_2) + \rho'_{21}(r_2 s_2) \}].$$

(*b*) *Explanation of the Notation.*

In the above equations r and s may take all positive integral values, including zero. We shall presently alter our notation so as to consider also negative integral values, but in the following definitions of N_{rs}, N'_{rs}, N''_{rs}, the positive numerical values of r and s are in every case to be used on the right-hand side :

$$(4·05)\qquad \mathrm{N}_{rs} = \{ 2^{r+s+2} (r+\tfrac{3}{2})_{r+1} (s+\tfrac{3}{2})_{s+1} \}^{-1}, \qquad \mathrm{N}'_{rs} = \frac{1}{rs} \mathrm{N}_{rs}, \qquad \mathrm{N}''_{rs} = \mathrm{N}_{r+1,\, s+1}.$$

In the case of N'_{rs}, the factor r is to be omitted from the denominator when $r = 0$; when $s = 0$, the value of $s\mathrm{N}'_{rs}$, in which form N'_{rs} occurs in (4·01), (4·02), is to be taken as $r^{-1}\mathrm{N}_{rs}$. The meaning of the symbols $(r+\frac{3}{2})_{r+1}$, $(s+\frac{3}{2})_{s+1}$ will be understood from the following definition, where q is a positive integer and p any number whatsoever :

$$(4\cdot06)\qquad p_q \equiv p\,(p-1)\,(p-2)\ldots(p-q+1), \qquad p_0 = 1.$$

We shall have frequent occasion to use this factorial symbol.

The following are the expressions found for $\rho\,(rs)$ and $\rho'\,(rs)$ in the various cases :—

$$(4\cdot07)\qquad \rho_{11}\,(r_1s_1) = \tfrac{32}{3}\nu_1^{\,2}\iint e^{-(x^2+y^2)}x^2y^2 \sum_{k=1}^{\frac{1}{2}(r+1,\,s+1)} \phi_{11}^{\,2k}(y)\Big[\mathrm{B}^{2k}(r+1,\,s)+\mathrm{B}^{2k}(r,\,s+1) + 2y^2\Big\{\frac{2k+1}{4k+1}\mathrm{B}^{2k+1}(r,\,s)+\frac{2k}{4k+1}\mathrm{B}^{2k-1}(r,\,s)-\mathrm{B}^{2k}(r,\,s)\Big\}\Big]dx\,dy,$$

$$(4\cdot08)\qquad \rho_{12}\,(r_1s_1) = \tfrac{16}{3}\nu_1\nu_2\iint e^{-(x^2+y^2)}x^2y^2 \sum_{k=0}^{(r+1,\,s+1)} \big[\phi_{12}^{\,k}(y)\,\{\mathrm{B}^k(r+1,\,s)+\mathrm{B}^k(r,\,s+1)\} + 4\mu_2y^2\psi_{12}^{\,k}(y)\,\mathrm{B}^k\,(r,\,s)\big]_{1212}\,dx\,dy.$$

$$(4\cdot09)\qquad \rho_{12}\,(r_2s_1) = \tfrac{16}{3}\nu_1\nu_2\mu_{12}^{\,1/2}\iint e^{-(x^2+y^2)}x^2y^2 \sum_{k=1}^{(r+1,\,s+1)}(-1)^k\big[\phi_{12}^{\,k}(y)\,\{\mu_{12}^{\,1/2}\mathrm{B}^k(r+1,\,s)-2\,(\mu_1\mu_2)^{-1/2}y^2\mathrm{B}^k\,(r,\,s) + \mu_{21}^{\,1/2}\mathrm{B}^k(r,\,s+1)\}-4\,(\mu_1\mu_2)^{1/2}y^2\psi_{12}^{\,k}(y)\,\mathrm{B}^k(r,\,s)\big]_{2112}\,dx\,dy.$$

$$\begin{aligned}(4\cdot10)\qquad \rho'_{11}\,(r_1s_1) = \tfrac{16}{5}\nu_1^{\,2}\iint e^{-(x^2+y^2)}x^2y^2 & \sum_{1}^{\frac{1}{2}(r+2,\,s+2)} \phi_{11}^{\,2k}(y)\Big[\mathrm{B}^{2k}\,(r+2,\,s)+\tfrac{2}{3}\mathrm{B}^{2k}(r+1,\,s+1)+\mathrm{B}^{2k}\,(r,\,s+2)\\ &+4y^2\Big\{\frac{2k+1}{4k+1}\Big(\mathrm{B}^{2k+1}(r+1,\,s)+\mathrm{B}^{2k+1}(r,\,s+1)\Big)\\ &-\Big(\mathrm{B}^{2k}\,(r+1,\,s)+\mathrm{B}^{2k}\,(r,\,s+1)\Big)\\ &+\frac{2k}{4k+1}\Big(\mathrm{B}^{2k-1}(r+1,\,s)+\mathrm{B}^{2k-1}(r,\,s+1)\Big)\Big\}\\ &+4y^4\Big\{\frac{(2k+2)\,(2k+1)}{(4k+3)\,(4k+1)}\mathrm{B}^{2k+2}(r,\,s)\\ &+\Big(\frac{(2k+1)^2}{(4k+3)\,(4k+1)}+\frac{(2k)^2}{(4k+1)\,(4k-1)}+1\Big)\,\mathrm{B}^{2k}\,(r,\,s)\\ &+\frac{2k\,(2k-1)}{(4k+1)\,(4k-1)}\mathrm{B}^{2k-2}\,(r,\,s)\\ &-2\Big(\frac{2k+1}{4k+1}\mathrm{B}^{2k+1}\,(r,\,s)+\frac{2k}{4k-1}\,\mathrm{B}^{2k-1}(r,\,s)\Big)\Big\}\Big]dx\,dy.\end{aligned}$$

$$(4{\cdot}11)\quad \rho'_{12}(r_1s_1) = \tfrac{8}{5}\nu_1\nu_2\iint e^{-(x^2+y^2)}x^2y^2 \sum_{k=0}^{(r+2,\,s+2)}\big[\phi_{12}{}^{k}(y)\{\mathrm{B}^k(r+2,s)+\tfrac{2}{3}\mathrm{B}^k(r+1,s+1)+\mathrm{B}^k(r,s+2)\}$$
$$+8\mu_2y^2\psi_{12}{}^{k}(y)\{\mathrm{B}^k(r+1,s)+\mathrm{B}^k(r,s+1)\}$$
$$-16\mu_2{}^2y^4\chi_{12}{}^{k}(y)\,\mathrm{B}^k(r,s)\big]_{1212}\,dx\,dy.$$

$$(4{\cdot}12)\quad \rho'_{12}(r_2s_1) = \tfrac{8}{5}\nu_1\nu_2\iint e^{-(x^2+y^2)}x^3y^2 \sum_{k=0}^{(r+2,\,s+2)}(-1)^k\big[\phi_{12}{}^{k}(y)\{\mu_{12}\mathrm{B}^k(r+2,s)+\tfrac{2}{3}\mathrm{B}^k(r+1,s+1)$$
$$+\mu_{21}\mathrm{B}^k(r,s+2)-4(\mu_1\mu_2)^{-1/2}y^2(\mu_{12}{}^{1/2}\mathrm{B}^k(r+1,s)+\mu_{21}{}^{1/2}\mathrm{B}^k(r,s+1))$$
$$+4\mu_1\mu_2y^4\mathrm{B}^k(r,s)\}-8(\mu_1\mu_2)^{1/2}y^2\psi_{12}{}^{k}(y)\{\mu_{12}{}^{1/2}\mathrm{B}^k(r+1,s)$$
$$-2(\mu_1\mu_2)^{-1/2}y^2\mathrm{B}^k(r,s)+\mu_{21}{}^{1/2}\mathrm{B}^k(r,s+1)\}$$
$$-16\mu_1\mu_2y^4\chi_{12}{}^{k}(y)\,\mathrm{B}^k(r,s)\big]_{2112}\,dx\,dy.$$

There are also six other equations, similar to the above, except that the suffixes 1 and 2 are interchanged; these need not be written down here.

The limits of integration of x and y throughout the above expressions are 0 and ∞. The upper limits of the summations are in each case indicated by two numbers, which are not necessarily integers; the upper limit is to be taken equal to the greatest integer which does not exceed either of these two numbers. The suffixes 1212 or 2112 on the right-hand of the main square brackets of (4·08), (4·09), (4·11), (4·12) are there placed only for convenience in printing: they should really be appended to each of the symbols $\mathrm{B}^k(m,n)$ contained within the brackets. These symbols are defined by the following equations:—

$$(4{\cdot}13)\qquad \mathrm{B}^k{}_{1212}(m,n) = {}^m\!\mathrm{A}^k(2\mu_1x^2, 2\mu_2y^2)\,.\,{}^n\!\mathrm{A}^k(2\mu_1x^2, 2\mu_2y^2),$$
$$\mathrm{B}^k{}_{2112}(m,n) = {}^m\!\mathrm{A}^k(2\mu_2x^2, 2\mu_1y^2)\,.\,{}^n\!\mathrm{A}^k(2\mu_1x^2, 2\mu_2y^2),\quad \mathrm{B}^k(m,n) = {}^m\!\mathrm{A}^k(x^2,y^2)\,{}^n\!\mathrm{A}^k(x^2,y^2),$$

where ${}^m\!\mathrm{A}^k(u,v)$ is a polynomial in powers of u, v defined thus:—

$$(4{\cdot}14)\qquad {}^m\!\mathrm{A}^k(u,v) = {}^m\!\mathrm{A}^k(v,u) = \left(\frac{u}{v}\right)^{1/2k}\sum_{t=k}^{m}\frac{m_t}{(t+\frac{1}{2})_t}\frac{(m+\frac{1}{2})_{t-k}}{(t-k)\,!}u^{m-t}v^t \qquad k \leqslant m.$$

When $k > m$, ${}^m\!\mathrm{A}^k(u,v)$ is zero. Also $\mu_1, \mu_2, \mu_{12}, \mu_{21}$, have the following values:—

$$(4{\cdot}15)\quad \mu_1 = m_1/(m_1+m_2),\quad \mu_2 = m_2/(m_1+m_2),\quad \mu_{12} = m_1/m_2 = \mu_1/\mu_2,\quad \mu_{21} = m_2/m_1 = \mu_2/\mu_1,$$

so that

$$(4{\cdot}16)\qquad \mu_1+\mu_2 = 1,\qquad \mu_{12}\mu_{21} = 1.$$

Finally we must define the functions $\phi^k(y)$, $\psi^k(y)$, $\chi^k(y)$; these are the only quantities in the expressions for $\rho(r, s)$ and $\rho'(r, s)$ which depend on the law of inter-action between molecules. If two molecules m_1, m_2 encounter one another, the direction of their relative velocity will be changed through a certain angle θ_{12} in a plane parallel to the initial relative velocity and to the perpendicular (of length p) between their initial and final lines of undisturbed rectilinear motion; denoting the magnitude of the initial or final relative velocity by $\left(\frac{m_1+m_2}{hm_1m_2}\right)^{1/2}y$, θ_{12} will be a function of p and y, the nature of the function being determined by the mode of inter-action between molecules in proximity to one another. Then we have

$$(4{\cdot}17) \qquad \phi_{12}{}^k(y) = (2k+1)\{\mu_1\mu_2 h(m_1+m_2)\}^{-1/2} y \int_0^\infty \{1-\mathrm{P}_k(\cos\theta_{12})\}\, p\, dp,$$

$$(4{\cdot}18) \qquad \psi_{12}{}^k(y) = (2k+1)\{\mu_1\mu_2 h(m_1+m_2)\}^{-1/2} y \int_0^\infty (1-\cos\theta_{12})\mathrm{P}_k(\cos\theta_{12})\, p\, dp,$$

$$(4{\cdot}19) \qquad \chi_{12}{}^k(y) = (2k+1)\{\mu_1\mu_2 h(m_1+m_2)\}^{-1/2} y \int_0^\infty (1-\cos\theta_{12})^2\mathrm{P}_k(\cos\theta_{12})\, p\, dp,$$

where $\mathrm{P}_k(\cos\theta_{12})$ denotes, as usual, the Legendre function of $\cos\theta_{12}$ of order k. By changing the suffix 1 *or* 2 throughout into 2 *or* 1 respectively, we obtain the corresponding expressions for $\phi_{22}{}^k$ or $\phi_{11}{}^k$, and so on; mere interchange of the suffixes does not affect the functions.

By means of the recurrence formula for the Legendre functions, viz.,

$$(4{\cdot}20) \qquad (k+1)\,\mathrm{P}_{k+1}-(2k+1)\cos\theta_{12}\mathrm{P}_k+k\mathrm{P}_{k-1} = 0,$$

we may express ψ and χ in terms of the function ϕ. Thus for $\psi^k(y)$ we have

$$(4{\cdot}21) \qquad \psi^k(y) = \frac{k+1}{2k+3}\,\phi^{k+1}(y)-\phi^k(y)+\frac{k}{2k-1}\,\phi^{k-1}(y).$$

In this way we may prove that

$$(4{\cdot}22) \quad \psi^0(y) = \tfrac{1}{3}\phi^1(y), \quad \chi^0(y) = \tfrac{2}{3}\phi^1(y)-\tfrac{2}{15}\phi^2(y), \quad \psi^1(y) = -\phi^1(y)+\tfrac{2}{5}\phi^2(y).$$

From the symmetry, with respect to r and s, of the expressions on the right hand of equations (4·07), (4·08), (4·10), (4·11) it is clear that

$$(4{\cdot}23) \quad \rho_{11}(r_1s_1) = \rho_{11}(s_1r_1), \quad \rho'_{11}(r_1s_1) = \rho'_{11}(s_1r_1), \quad \rho_{12}(r_1s_1) = \rho_{12}(s_1r_1), \quad \rho'_{12}(r_1s_1) = \rho'_{12}(s_1r_1).$$

(*c*) *Special Values of* $\rho(r, s)$ *and* $\rho'(r, s)$.

To facilitate the exposition of subsequent parts of the work it is convenient at this stage to write down certain special cases of the equations (4·07)–(4·12), after executing the integrations with respect to x and y. Owing to the generality of the functions

ϕ, ψ, χ (depending on the functional relation between θ_{12} and p, y) the integration with respect to y can only be made *formally*, however, and for this purpose we shall use the notation

$$(4{\cdot}24)\qquad \mathrm{K}^k(t) \equiv \frac{4\pi^{-1/2}}{(t+k+\frac{1}{2})_{t+k}} \int_0^\infty e^{-y^2} \phi^k(y)\, y^{2(t+k-1)}\, dy.$$

The suffix 11, 12, or 22 is to be appended to $\mathrm{K}^k(t)$ to correspond with the suffix of $\phi^k(y)$ on the right. The notation is chosen so as to make $\mathrm{K}^k(t)$ equal to $\phi^k(y)$ *when this is independent of* y, as in the case of molecules which obey MAXWELL's fifth-power law.*

For small values of r and s it is convenient to simplify our formulæ by writing also

$$(4{\cdot}25)\qquad k_t \equiv \frac{\mathrm{K}'_{12}(t)}{\mathrm{K}'_{12}(0)}, \quad k^t{}_{11} \equiv \frac{\mathrm{K}^2{}_{11}(t)}{\mathrm{K}'_{12}(0)}, \quad k^t{}_{12} \equiv \frac{\mathrm{K}^2{}_{12}(t)}{\mathrm{K}'_{12}(0)}, \quad k^t{}_{22} \equiv \frac{\mathrm{K}^2{}_{22}(t)}{\mathrm{K}'_{12}(0)}.$$

In terms of the above notation we may now give the following results:—

$$(4{\cdot}26)\qquad \rho_{11}(r_1 0_1) = \rho_{11}(0_1 s_1) = 0, \quad \rho_{11}(s_1 1_1) = \rho_{11}(1_1 s_1) = \tfrac{16}{45}\pi\nu_1{}^2 s(s+\tfrac{3}{2})_{s+1}\mathrm{K}'_{12}(0) \sum_0^{s-1}{}_{s-1}\mathrm{C}_t k^t{}_{11},$$

$$(4{\cdot}27)\qquad \rho_{12}(s_1 0_1) = \rho_{12}(0_1 s_1) = \tfrac{4}{9}\pi\nu_1\nu_2\mu_2 2^s(s+\tfrac{3}{2})_{s+1}\mathrm{K}'_{12}(0) \sum_0^{s}{}_s\mathrm{C}_t \mu_1{}^{s-t}\mu_2{}^t k_t,$$

$$(4{\cdot}28)\qquad \rho_{12}(r_2 0_1) = -\tfrac{4}{9}\pi\nu_1\nu_2\mu_1 2^r(r+\tfrac{3}{2})_{r+1}\mathrm{K}'_{12}(0) \sum_0^{r}{}_r\mathrm{C}_t \mu_2{}^{r-t}\mu_1{}^t k_t,$$

$$(4{\cdot}29)\qquad \rho_{12}(0_2 s_1) = -\tfrac{4}{9}\pi\nu_1\nu_2\mu_1 2^s(s+\tfrac{3}{2})_{s+1}\mathrm{K}'_{12}(0) \sum_0^{s}{}_s\mathrm{C}_t \mu_1{}^{s-t}\mu_2{}^t k_t,$$

$$(4{\cdot}30)\qquad \rho_{12}(s_1 1_1) = \rho_{12}(1_1 s_1) = \tfrac{8}{9}\pi\nu_1\nu_2\mu_2 2^s(s+\tfrac{3}{2})_{s+1}\mathrm{K}'_{12}(0)\Big[\tfrac{5}{2}\sum_0^{s}{}_s\mathrm{C}_t\mu_1{}^{s-t}\mu_2{}^t(\mu_1 k_t+\mu_2 k_{t+1})$$
$$+ s\sum_0^{s-1}{}_{s-1}\mathrm{C}_t\mu_1{}^{s-1-t}\mu_2{}^t(3\mu_1{}^2 k_t+\mu_2{}^2 k_{t+2}+\tfrac{4}{5}\mu_1\mu_2 k^t{}_{12})\Big],$$

$$(4{\cdot}31)\qquad \rho_{12}(1_2 s_1) = -\tfrac{8}{9}\pi\nu_1\nu_2\mu_1 2^s(s+\tfrac{3}{2})_{s+1}\mathrm{K}'_{12}(0)\Big[\tfrac{5}{2}\sum_0^{s}{}_s\mathrm{C}_t\mu_1{}^{s-t}\mu_2{}^t(\mu_2 k_t+\mu_1 k_{t+1})$$
$$+ s\mu_1\mu_2\sum_0^{s-1}{}_{s-1}\mathrm{C}_t\mu_1{}^{s-1-t}\mu_2{}^t(3k_t+k_{t+2}-\tfrac{4}{5}k^t{}_{12}\Big],$$

$$(4{\cdot}32)\qquad \rho'_{11}(0_1 s_1) = \rho'_{11}(s_1 0_1) = \tfrac{8}{75}\pi\nu_1{}^2(s+\tfrac{5}{2})_{s+2}\mathrm{K}'_{12}(0)\sum_0^{s}{}_s\mathrm{C}_t k^t{}_{11},$$

$$(4{\cdot}33)\qquad \rho'_{12}(0_1 s_1) = \rho'_{12}(s_1 0_1) = \tfrac{32}{45}\pi\nu_1\nu_2\mu_2 2^s(s+\tfrac{5}{2})_{s+2}\mathrm{K}'_{12}(0)\sum_0^{s}{}_s\mathrm{C}_t\mu_1{}^{s-t}\mu_2{}^t(\mu_1 k_t+\tfrac{3}{10}\mu_2 k^t{}_{12}),$$

$$(4{\cdot}34)\qquad \rho'_{12}(0_2 s_1) = \tfrac{32}{45}\pi\nu_1\nu_2\mu_2 2^s(s+\tfrac{5}{2})_{s+2}\mathrm{K}'_{12}(0)\sum_0^{s}{}_s\mathrm{C}_t\mu_1{}^{s-t}\mu_2{}^t(-\mu_1 k_t+\tfrac{3}{10}\mu_1 k^t{}_{12}).$$

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* *Cf.* 'Phil. Trans.,' A, vol. 216, § 9 (C), p. 323.

It may readily be deduced from the above equations that

$$(4{\cdot}35) \qquad \rho_{12}(r_1 0_1) = -\rho_{21}(r_1 0_2), \quad \rho_{12}(r_2 0_1) = -\rho_{21}(r_2 0_2),$$

$$(4{\cdot}36) \qquad \mu_1\rho_{12}(0_1 s_1) = -\mu_2\rho_{12}(0_2 s_1), \quad \mu_1\rho_{21}(0_1 s_2) = -\mu_2\rho_{21}(0_2 s_2).$$

Also, in the case of Maxwellian molecules, for which $k_t = 1$ and $k^t{}_{12} = k^0{}_{12}$ (whatever the value of t) we shall have

$$(4{\cdot}37) \qquad \rho_{12}(1_1 s_1) - 5\rho_{12}(0_1 s_1) = \tfrac{8}{9}\pi\nu_1\nu_2\mu_2 2^s s\,(s+\tfrac{3}{2})_{s+1}\,\mathrm{K}'_{12}(0)\,(3\mu_1{}^2 + \mu_2{}^2 + \tfrac{4}{5}\mu_1\mu_2 k^0{}_{12}),$$

$$(4{\cdot}38) \qquad \rho_{12}(1_2 s_1) - 5\rho_{12}(0_2 s_1) = -\tfrac{8}{9}\pi\nu_1\nu_2\mu_1\mu_2{}^2 2^s s\,(s+\tfrac{3}{2})_{s+1}\,\mathrm{K}'_{12}(0)\,(4 + \tfrac{4}{5}k^0{}_{12}).$$

§ 5. THE SYMBOLIC SOLUTION FOR THE COEFFICIENTS IN f (U, V, W).

(a) *The Linear Equations for α, β, γ.*

We now refer back to the two corresponding sets of equations (2·07)–(2·10) and (4·01)–(4·04). For the two members of each pair of corresponding equations the left-hand side is the same, so that we may equate the right-hand sides. Also, as regards the first two pairs, we may separately equate the parts which contain as factors the independent quantities ξ'_0 and $\dfrac{\partial \mathrm{T}}{\partial x}$. Thus we have

$$(5{\cdot}01) \qquad \frac{1}{\nu_0}\mathrm{A}_0 \sum_{r=0}^{\infty} \mathrm{N}_{rs}\left[m_1\alpha_r\left\{\rho_{11}(r_1 s_1) + \rho_{12}(r_1 s_1)\right\} + m_2\alpha_{-r}\rho_{12}(r_2 s_1)\right] = 1, \quad (s = 0 \text{ to } s = \infty),$$

$$(5{\cdot}02) \qquad -\frac{1}{\nu_0}\mathrm{A}_0 \sum_{r=0}^{\infty} \mathrm{N}_{rs}\left[m_1\alpha_r\rho_{21}(r_1 s_2) + m_2\alpha_{-r}\left\{\rho_{22}(r_2 s_2) + \rho_{21}(r_2 s_2)\right\}\right] = 1, \quad (s = 0 \text{ to } s = \infty),$$

$$(5{\cdot}03) \qquad \frac{1}{\mathrm{R}\nu_1}\mathrm{B}_0 \sum_{r=0}^{\infty} \mathrm{N}'_{rs}\left[m_1\beta_r\left\{\rho_{11}(r_1 s_1) + \rho_{12}(r_1 s_1)\right\} + m_2\beta_{-r}\rho_{12}(r_2 s_1)\right] = 1, \quad (s = 1 \text{ to } s = \infty),$$

$$(5{\cdot}04) \qquad \frac{1}{\mathrm{R}\nu_2}\mathrm{B}_0 \sum_{r=0}^{\infty} \mathrm{N}'_{rs}\left[m_1\beta_r\rho_{21}(r_1 s_2) + m_2\beta_{-r}\left\{\rho_{22}(r_2 s_2) + \rho_{21}(r_2 s_2)\right\}\right] = 1, \quad (s = 1 \text{ to } s = \infty),$$

$$(5{\cdot}05) \qquad \frac{1}{\mathrm{R}\nu_0}\mathrm{B}_0 \sum_{r=0}^{\infty} s\mathrm{N}'_{rs}\left[m_1\beta_r\rho_{12}(r_1 s_1) + m_2\beta_{-r}\rho_{12}(r_2 s_1)\right] = 0, \quad (s = 0),$$

$$(5{\cdot}06) \qquad \frac{1}{\nu_1}\mathrm{C}_0 \sum_{r=0}^{\infty} \mathrm{N}''_{rs}\left[\gamma_r\left\{\rho'_{11}(r_1 s_1) + \rho'_{12}(r_1 s_1)\right\} + \gamma_{-r}\rho'_{12}(r_2 s_1)\right\}\right] = 1, \quad (s = 0 \text{ to } s = \infty),$$

$$(5{\cdot}07) \qquad \frac{1}{\nu_2}\mathrm{C}_0 \sum_{r=0}^{\infty} \mathrm{N}''_{rs}\left[\gamma_r\rho'_{21}(r_1 s_2) + \gamma_{-r}\left\{\rho'_{22}(r_2 s_2) + \rho'_{21}(r_2 s_2)\right\}\right] = 1, \quad (s = 0 \text{ to } s = \infty).$$

By virtue of (4·26) and (4·35) the equations (5·01) and (5·02) are identical when $s = 0$, while (5·03) and (5·04) then assume the same special form (5·05); we may recall that in § 4 (b) the value of $s\mathrm{N}'_{rs}$ was defined to be $r^{-1}\mathrm{N}_{rs}$ when $s = 0$ (or N_{rs} when r is also zero). Moreover, from (4·26) and (4·36), it is clear that in (5·01)–(5·05) the ratio of the factors of α_0 and α_{-0}, or of β_0 and β_{-0} has the constant value -1. Consequently, the above equations do not enable us to determine the separate values of α_0 and α_{-0}, or β_0 and β_{-0}, but only of $\alpha_0-\alpha_{-0}$ and $\beta_0-\beta_{-0}$, which form single unknowns. When these and all the other values of α_r and β_r $(r \neq 0)$ have been determined, the separate coefficients α_0, α_{-0}, β_0, β_{-0} may be deduced with the aid of (3·13) and (3·14).

In order to simplify the notation of our formal solutions for the coefficients α, β, γ, it is convenient to re-write (5·01)–(5·07) in the form

$$(5{\cdot}08) \quad \sum_{r=-\infty}^{-1} a_{rs}\alpha_r + a_{0s}(\alpha_0-\alpha_{-0}) + \sum_{r=1}^{\infty} a_{rs}\alpha_r = 1 \quad (s = -\infty \text{ to } s = \infty, \text{ including } s = 0),$$

$$(5{\cdot}09) \quad \sum_{r=-\infty}^{-1} b_{r+1,s+1}\beta_r - b_s\frac{\beta'_0}{\lambda_1\lambda_2} + \sum_{r=1}^{\infty} b_{r-1,s-1}\beta_r = 1 \quad (s = -\infty \text{ to } s = \infty, \text{ excluding } s = 0),$$

$$(5{\cdot}10) \quad \sum_{r=-\infty}^{-1} b_{r+1}\beta_r - b\frac{\beta'_0}{\lambda_1\lambda_2} + \sum_{r=1}^{\infty} b_{r-1}\beta_r = 0,$$

$$(5{\cdot}11) \quad \sum_{r=-\infty}^{\infty} c_{rs}\gamma_r = 1 \quad (\pm r,\ \pm s \text{ range from 0 to } \infty).$$

In obtaining (5·09), (5·10) from (5·03)–(5·05) we have eliminated β_0 and β_{-0} by means of (3·14), and in order to preserve symmetry we have subtracted $1/s\lambda_1$ or $1/s\lambda_2$ times the equation (5·05) from (5·03) or (5·04) respectively. The new symbols are defined as follows:—

$$(5{\cdot}12) \quad s \geqslant 0 \quad a_{0s} = -a_{-0s} = \frac{m_1}{\nu_0}\mathrm{A}_0\mathrm{N}_{0s}\rho_{12}(0_1 s_1), \quad a_{rs} = \frac{m_1}{\nu_0}\mathrm{A}_0\mathrm{N}_{rs}\{\rho_{11}(r_1 s_1)+\rho_{12}(r_1 s_1)\} \quad r > 0,$$

$$(5{\cdot}13) \quad s \leqslant 0 \quad a_{0s} = -a_{-0s} = -\frac{m_1}{\nu_0}\mathrm{A}_0\mathrm{N}_{0s}\rho_{21}(0_1 s_2), \quad a_{rs} = -\frac{m_2}{\nu_0}\mathrm{A}_0\mathrm{N}_{rs}\{\rho_{22}(r_2 s_2)+\rho_{21}(r_2 s_2)\} \quad r < 0,$$

$$(5{\cdot}14) \quad r < 0,\ s \geqslant 0 \quad a_{rs} = \frac{m_2}{\nu_0}\mathrm{A}_0\mathrm{N}_{rs}\rho_{12}(r_2 s_1), \quad a_{rs} = -\frac{m_1}{\nu_0}\mathrm{A}_0\mathrm{N}_{rs}\rho_{21}(r_1 s_2) \quad r > 0,\ s \leqslant 0,$$

$$(5{\cdot}15) \quad r \geqslant 0 \quad b_r = \frac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\frac{1}{r+1}(a_{r+1,0}-a_{00}), \quad b = \frac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}a_{00}, \quad b_r = \frac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\frac{1}{r+1}(a_{r-1,0}-a_{-00}) \quad r \leqslant -0,$$

$$(5{\cdot}16) \quad s \geqslant 0 \quad b_s = \frac{1}{\lambda_1}\frac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\frac{1}{s+1}(a_{0,s+1}-a_{00}), \quad b_s = -\frac{1}{\lambda_2}\frac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\frac{1}{s+1}(a_{0,s-1}-a_{00}) \quad s \leqslant -0,$$

$$(5{\cdot}17) \quad s \geqslant 0 \quad \begin{cases} b_{rs} = \dfrac{1}{\lambda_1}\dfrac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\dfrac{1}{(r+1)(s+1)}\{a_{r+1,s+1}-a_{0,s+1}-a_{r+1,0}+a_{00}) & r \geqslant 0, \\[2ex] b_{rs} = \dfrac{1}{\lambda_1}\dfrac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\dfrac{1}{(r+1)(s+1)}\{a_{r-1,s+1}-a_{-0,s+1}-a_{r-1,0}+a_{-00}\} & r \leqslant -0, \end{cases}$$

$$(5\cdot18)\quad s \leqslant -0 \quad \begin{cases} b_{rs} = -\dfrac{1}{\lambda_2}\dfrac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\dfrac{1}{(r+1)(s+1)}\{a_{r+1,\,s-1}-a_{0,\,s-1}-a_{r+1,\,0}+a_{00}\} & r \geqslant 0, \\ b_{rs} = -\dfrac{1}{\lambda_2}\dfrac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\dfrac{1}{(r+1)(s+1)}\{a_{r-1,\,s-1}-a_{-0,\,s-1}-a_{r-1,\,0}+a_{-00}\} & r \leqslant -0 \end{cases}$$

$$(5\cdot19)\qquad r \geqslant 0,\, s \geqslant 0 \qquad c_{rs} = \frac{1}{\nu_1}\mathrm{C}_0\mathrm{N}''_{rs}\,\{\rho'_{11}(r_1s_1)+\rho'_{12}(r_1s_1)\}$$

$$c_{rs} = \frac{1}{\nu_1}\mathrm{C}_0\mathrm{N}''_{rs}\rho'_{12}(r_2s_1) \quad r \leqslant -0,\ s \geqslant 0,$$

$$(5\cdot20)\qquad r \leqslant -0,\, s \leqslant -0 \qquad c_{rs} = \frac{1}{\nu_2}\mathrm{C}_0\mathrm{N}''_{rs}\,\{\rho'_{22}(r_2s_2)+\rho'_{2\mathrm{f}}(r_2s_2)\}$$

$$c_{rs} = \frac{1}{\nu_2}\mathrm{C}_0\mathrm{N}''_{rs}\rho'_{21}(r_1s_2) \quad r \geqslant 0,\ s \leqslant -0.$$

On the right-hand sides of the above equations the positive numerical values of r and s are to be used (whatever their signs on the left-hand side) except when they are suffixed to a or b.

(*b*) *The Formal Solution of the Equations for* α, β, γ.

If we may solve the linear equations (5·08)–(5·11), each containing an infinite number of unknowns, as if they were finite, we arrive at the results

$$(5\cdot21)\ \begin{cases} \alpha_0-\alpha_{-0} = \dfrac{\nabla_0(a_{mn})}{\nabla(a_{mn})} \qquad \alpha_r = \dfrac{\nabla_r(a_{mn})}{\nabla(a_{mn})} & (r = -\infty \text{ to } r = \infty, \text{ excluding } r = 0), \\ \beta'_0 = -\lambda_1\lambda_2\dfrac{\nabla_0(b_{mn})}{\nabla(b_{mn})} \qquad \beta_r = \dfrac{\nabla_r(b_{mn})}{\nabla(b_{mn})} & (r = -\infty \text{ to } r = \infty, \text{ excluding } r = 0), \\ \gamma_r = \dfrac{\nabla_r(c_{mn})}{\nabla(c_{mn})} & (r = -\infty \text{ to } r = +\infty, \text{ including } r = \pm 0). \end{cases}$$

In these equations $\nabla(a_{mn})$, $\nabla(b_{mn})$, $\nabla(c_{mn})$ denote the determinants which have a_{mn}, b_{mn}, c_{mn} as their general element; in the two latter, $\pm m$, $\pm n$ range from 0 to ∞, there being also a central row and a central column in $\nabla(b_{mn})$ which are not enumerated by m or n. In $\nabla(a_{mn})$ the values ± 0 of m and n are not distinct from one another, so that this also has a central column ($m = 0$) and central row ($n = 0$); $\nabla(c_{mn})$ has not got either of these, since ± 0 correspond to different rows or columns. The determinant ∇_r denotes that obtained from the corresponding ∇ by replacing all the elements of the r^{th} column by unity or, in the case only of the central element of the r^{th} column of $\nabla_r(b_{mn})$, by zero. It may be remarked that all these determinants ∇ and ∇_r are infinite in both directions, covering the whole plane. In two quadrants (m, n both positive or both negative) the determinants ∇ possess symmetry (*cf.* (4·23)).

In order to make this investigation complete, from a purely mathematical standpoint, it would clearly be necessary to supplement the above formal solution by a discussion of the questions of convergence raised in the course of our analysis. The complexity of the problem, however, and the rudimentary condition of the theory of infinite determinants, may well absolve the author from an attempt at such a task, for the present. From the standpoint of mathematical physics there is, fortunately, sufficient *numerical* evidence (*cf.* § 13*e*, *f*, and 'Phil. Trans.,' A, vol. 216, p. 330, Table III.) to afford reasonable assurance that our expressions converge satisfactorily; this is especially so in regard to the formulæ actually used in the applications of $f(\mathsf{U}, \mathsf{V}, \mathsf{W})$, *i.e.*, (5·22)–(5·25).

(*c*) *On Certain Combinations of the Coefficients* α, β, γ.

For the purpose of the theory of diffusion, viscosity, and thermal conduction in composite gases, we require only certain combinations of α, β, γ, and never their individual values. The following expressions comprise all those we shall find necessary in this paper; in connection with them we may refer back to (3·13), (3·14), and the formulæ (3·03), (3·04) for $f(\mathsf{U}, \mathsf{V}, \mathsf{W})$:—

$$(5{\cdot}22) \qquad \alpha'_0 = -\lambda_1\lambda_2 \sum_0^\infty (\alpha_r - \alpha_{-r}),$$

$$(5{\cdot}23) \qquad \beta'_0 = -\lambda_1\lambda_2 \left\{(\beta_0 - \beta_{-0}) + \sum_1^\infty r^{-1}(\beta_r - \beta_{-r})\right\},$$

$$(5{\cdot}24) \qquad 2h\,(\nu_1 m_1 \overline{3\mathsf{U}_1^2 - \mathrm{C}_1^2} + \nu_2 m_2 \overline{3\mathsf{U}_2^2 - \mathrm{C}_2^2}) = -\tfrac{4}{225}\mathrm{C}_0 c_{xx} \sum_0^\infty (\nu_1\gamma_r + \nu_2\gamma_{-r}),$$

$$(5{\cdot}25) \quad 2h\,(\nu_1 m_1 \overline{\mathsf{U}_1\mathrm{C}_1^2} + \nu_2 m_2 \overline{\mathsf{U}_2\mathrm{C}_2^2}) = -\tfrac{2}{9}\mathrm{A}_0\xi'_0 \left\{\tfrac{5}{2}(\nu_1\alpha_0 + \nu_2\alpha_{-0}) + \sum_0^\infty (r + \tfrac{5}{2})(\nu_1\alpha_r + \nu_2\alpha_{-r})\right\}$$
$$-\tfrac{2}{9}\mathrm{B}_0 \frac{\partial \mathrm{T}}{\partial x}\left\{\tfrac{5}{2}(\nu_1\beta_0 + \nu_2\beta_{-0}) + \sum_0^\infty \frac{r + \frac{5}{2}}{r}(\nu_1\beta_r + \nu_2\beta_{-r})\right\}$$
$$= -\tfrac{2}{9}\left\{\mathrm{A}_0\xi'_0 \sum_1^\infty r(\nu_1\alpha_r + \nu_2\alpha_{-r}) + \mathrm{B}_0\frac{\partial \mathrm{T}}{\partial x}\sum_1^\infty (\nu_1\beta_r + \nu_2\beta_{-r})\right\}.$$

We therefore desire to obtain concise expressions for the following quantities:—

$$(5{\cdot}26) \qquad \sum_0^\infty (\alpha_r - \alpha_{-r}), \qquad \beta_0 - \beta_{-0} + \sum_1^\infty r^{-1}(\beta_r - \beta_{-r}),$$

$$(5{\cdot}27) \qquad \sum_1^\infty r\,(\nu_1\alpha_r + \nu_2\alpha_{-r}), \qquad \sum_1^\infty (\nu_1\beta_r + \nu_2\beta_{-r}), \qquad \sum_0^\infty (\nu_1\gamma_r + \nu_2\gamma_{-r}).$$

The denominators in the expressions (5·21) for α_r, β_r, γ_r are independent of r. Hence our problem consists in the combination of the *numerator* determinants ∇_r for an infinite number of values of r,

(*d*) *Difference-Transformations of Infinite Determinants.*

It is convenient at this stage to describe certain operations, by the application of which we are enabled to preserve the symmetry and increase the convenience of our determinantal formulæ. These operations will be termed "continued differencing" by rows, by columns, or by rows and columns, and we shall denote the corresponding symbolic operators by δ_{0s}, δ_{r0}, or δ_{rs} respectively. We shall first define them in relation to infinite determinants which cover only a quadrant of the infinite plane ($r \geqslant 0$, $s \geqslant 0$), and afterwards in relation to the more complicated type which occurs in this paper.

The operation of continued differencing by rows (δ_{0s}) or by columns (δ_{r0}), applied to the determinant $\nabla(f_{rs})$, where $r \geqslant 0$, $s \geqslant 0$, transforms it into the determinant $\nabla(\delta_{0s} f_{rs})$ or $\nabla(\delta_{r0} f_{rs})$ respectively, where

$$(5\cdot28) \qquad \delta_{0s} f_{rs} \equiv \sum_{n=0}^{s} (-1)^n {}_s\mathrm{C}_n f_{r,\,s-n}, \qquad \delta_{r0} f_{rs} \equiv \sum_{m=0}^{r} (-1)^m {}_r\mathrm{C}_m f_{r-m,\,s}.$$

We may effect the operation δ_{0s} as follows: from each element of row s we subtract the corresponding element of row $s-1$, for every row from $s = 1$ onwards: this done, we repeat the operation on the transformed determinant, except that we now begin at $s = 2$: and this process is continued without end, beginning each time with the row next after the initial row on the previous occasion. It may readily be seen that the result is as we have already stated, and that the value of the determinant is unaffected by the operation. Continued differencing by columns is strictly analogous, and need not be separately described. Continued differencing by rows *and* columns is performed by applying the two separate operations successively, the order being immaterial. Without alteration in value, the determinant is thus changed in form from $\nabla(f_{rs})$ to $\nabla(\delta_{rs} f_{rs})$, where (*cf.* (5·28))

$$(5\cdot29) \qquad \delta_{rs} f_{rs} = \delta_{r0}(\delta_{0s} f_{rs}) = \delta_{0s}(\delta_{r0} f_{rs}) = \sum_{m=0}^{n} \sum_{n=0}^{s} (-1)^{m+n} {}_r\mathrm{C}_m \,.\, {}_s\mathrm{C}_n f_{r-m,\,s-n}.$$

In the case of determinants which are infinite in both directions, the operation of continued differencing by rows and columns is effected by applying the process described above to each separate quadrant; thus the differencing by rows is performed by differencing outwards from the centre row in *both* directions (above and below), and likewise, by columns, both to right and left of the centre column. Neither of these partial operations, nor the complete process, alters the value of the determinant, a fact which we may express by the equation

$$(5\cdot30) \qquad \nabla(f_{rs}) = \nabla(\delta_{r0} f_{rs}) = \nabla(\delta_{0s} f_{rs}) = \nabla(\delta_{rs} f_{rs}),$$

where the notation is similar to that used in the former case. There, however, r, s, and consequently also m, n, were necessarily positive or zero, while our convenient notation for determinants of the present type involves also negative values of r and s.

In order to make the former definitions of δ_{r0}, δ_{0s}, δ_{rs} applicable to this case, we must adopt certain conventions as to the interpretation of (5·28), (5·29), to allow for negative quantities. These conventions are (a) that in ${}_{r}\mathrm{C}_{m,\,s}\mathrm{C}_{n}$ the positive numerical values of r and s, m and n[*] are to be used in all cases: and (b) that $r-m$ and $s-n$ retain the same signs as r and s respectively even when $m = r$, $n = s$. The latter rule preserves, in relation to f_{rs}, the distinction between $+0$ and -0 which in certain cases we desire to maintain.

(e) *A Symmetrical Expression for* $\sum\limits_{0}^{\infty}(\alpha_r - \alpha_{-r})$.

In discussing $\Sigma(\alpha_r - \alpha_{-r})$ it is convenient to change our notation for $\nabla_r(a_{mn})$' writing it in the form $\nabla({}_{r}a_{mn})$ to denote the determinant whose $(m, n)^{\text{th}}$ element is ${}_{r}a_{mn}$. If we define ${}_{r}a_{mn}$ by the equations

$$(5·31) \qquad {}_{r}a_{mn} \equiv a_{mn} \quad (m \neq r), \qquad {}_{r}a_{rn} = 1, \qquad {}_{r}a_{m0} \equiv {}_{r}a_{m,\,-0}$$

we make $\nabla({}_{r}a_{mn})$ identical with $\nabla_r(a_{mn})$ as defined in § 5 (b), and therefore, by (5·21),

$$(5·32) \qquad \alpha_0 - \alpha_{-0} = \frac{\nabla({}_{0}a_{mn})}{\nabla(a_{mn})}, \qquad \alpha_r = \frac{\nabla({}_{r}a_{mn})}{\nabla(a_{mn})}, \quad (r \neq 0).$$

By applying the operation of continued differencing by rows to $\nabla({}_{r}a_{mn})$ we transform it into $\nabla(\delta_{0n\,.\,r}a_{mn})$, where $\delta_{0n\,.\,r}a_{mn}$ is defined by (5·28) (putting $f_{mn} = {}_{r}a_{mn}$, and making no distinction between f_{m0} and $f_{m,\,-0}$—*cf.* the third equation of (5·31)). Now it is readily evident that

$$(5·33) \qquad \delta_{0n\,.\,r}a_{mn} = \delta_{0n}a_{mn} \quad (m \neq r), \qquad \delta_{0n\,.\,r}a_{rn} = 0 \quad (n \neq 0), \qquad \delta_{00\,.\,r}a_{r0} = 1,$$

so that $\nabla(\delta_{0n\,.\,r}a_{mn})$, and consequently, also, $\nabla_r(a_{mn})$, is equal to $\nabla'_r(\delta_{0n}\,.\,a_{mn})$, this being defined as identical with $\nabla(\delta_{0n}\,.\,a_{mn})$ except that in the r^{th} column the central element is unity, while all the others are zero. Hence $\nabla'_r(\delta_{0n}a_{mn})$ is clearly equal to the minor of the r^{th} element of the central row in $\nabla(\delta_{0n}a_{mn})$. If we replace the elements of this central row by $+1$ $(m \geqslant 0)$ or -1 $(m < 0)$, and denote the result by $\nabla'(\delta_{0n}a_{mn})$, we may evidently write (*cf.* (5·32))

$$(5·34) \qquad \sum_{0}^{\infty}(\alpha_r - \alpha_{-r}) = \frac{\nabla'(\delta_{0n}a_{mn})}{\nabla(a_{mn})} = \frac{\nabla'(\delta_{0n}a_{mn})}{\nabla(\delta_{0n}a_{mn})}$$

by (5·30).

We next apply to $\nabla(\delta_{0n}a_{mn})$ and $\nabla'(\delta_{0n}a_{mn})$ the operation of continued differencing by columns, so as to transform them into $\nabla(\delta_{mn}a_{mn})$ and $\nabla'(\delta_{mn}a_{mn})$. We make one slight difference of rule here, as compared with the former differencing by rows: that is, in (5·29) we shall preserve the distinction between $m = 0$ and $m = -0$, writing f_{0n}

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[*] The signs of m, n are the same, of course, as those of r, s respectively.

for the elements of the central column in ∇ or ∇', and defining f_{-0n} as equal to $-f_{0n}$. This means, in effect, that the elements of the central column are to be reversed in sign, for the purpose of differencing on the left (in <0).* Now, by definition, $\nabla'(\delta_{0n}a_{mn})$ differs from $\nabla(\delta_{0n}a_{mn})$ only in the central row, for which

$$f_{m0} = 1 \quad (m \geqslant 0), \qquad f_{m0} = -1 \quad (m < 0), \quad \text{and also} \quad f_{-00} \equiv -1,$$

so that

$$\delta_{m0}f_{m0} = 0 \quad \text{if} \quad m \neq 0, \qquad \delta_{00}f_{00} = 1.$$

Hence, when transformed into $\nabla'(\delta_{mn}a_{mn})$, it differs from $\nabla(\delta_{mn}a_{mn})$ only in the central row, all the elements of which are zero except the central one, which is unity. In other words, $\nabla'(\delta_{mn}a_{mn})$ is the principal minor of $\nabla(\delta_{mn}a_{mn})$, and the expression for $\sum\limits_0^\infty(\alpha_r - \alpha_{-r})$, viz.,

$$\sum_0^\infty(\alpha_r - \alpha_{-r}) = \frac{\nabla'(\delta_{mn}a_{mn})}{\nabla(\delta_{mn}a_{mn})} = -\frac{\alpha'_0}{\lambda_1\lambda_2} \tag{5·35}$$

has thus been reduced to a concise symmetrical form.

(*f*) *A Symmetrical Expression for* β'_0.

It appears from (5·21) that

$$\beta'_0 = -\lambda_1\lambda_2\frac{\nabla_0(b_{mn})}{\nabla(b_{mn})},$$

where ∇_0 is the same as ∇, except that all the elements of the central column are unity save the central one, which is zero. If we transform ∇ and ∇_0 by the operations described in § 5 (*d*), differencing by columns with $m = 1$ (for the right) and $m = -1$ (for the left) as starting points, and similarly for the rows, we leave the central column (not enumerated by m) untouched as regards the first part of the operation, and the central row untouched by the second part. Thus we obtain the result

$$\beta'_0 = -\lambda_1\lambda_2\frac{\nabla'_0(\delta_{mn}b_{mn})}{\nabla(\delta_{mn}b_{mn})}, \tag{5·36}$$

where $\nabla(\delta_{mn}b_{mn})$ is the determinant whose general element is $\delta_{mn}b_{mn}$ ($\pm m$, $\pm n$ ranging from 0 to ∞), and which has a central column $\delta_{0n}b_n$, a central row $\delta_{m0}b_m$, and b as the central element. From this determinant we obtain $\nabla'_0(\delta_{mn}b_{mn})$ by substituting zero for all the elements of the central column except those next to the centre on either side ($n = \pm 0$) which are replaced by unity.

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* We may note that the elements of the central column are the coefficients of α_0 in (5·01)–(5·05), while the elements reversed in sign are the coefficients of α_{-0}.

(*g*) *Symmetrical Expressions for* $\sum\limits_1^\infty r(\nu_1\alpha_r+\nu_2\alpha_{-r})$, $\sum\limits_1^\infty(\nu_1\beta_r+\nu_2\beta_{-r})$, $\sum\limits_0^\infty(\nu_1\gamma_r+\nu_2\gamma_{-r})$.

As in § 5 (*e*) we may prove that

$$\sum_1^\infty r(\nu_1\alpha_r+\nu_2\alpha_{-r}) = \frac{\nabla_0(\delta_{0n}a_{mn})}{\nabla(\delta_{0n}a_{mn})},$$

where $\nabla_0(\delta_{0n}a_{mn})$ is identical with $\nabla(\delta_{0n}a_{mn})$ except in the central row, the elements of which are equal to $r\nu_1\,(r \geqslant 0)$ or $r\nu_2\,(r \leqslant 0)$, the positive numerical value of r being taken in both cases. On applying the operation of continued differencing by columns we obtain the result

$$\sum_1^\infty r(\nu_1\alpha_r+\nu_2\alpha_{-r}) = \frac{\nabla_0(\delta_{mn}a_{mn})}{\nabla(\delta_{mn}a_{mn})}, \tag{5·37}$$

where $\nabla_0(\delta_{mn}a_{mn})$ differs from $\nabla(\delta_{mn}a_{mn})$ only in the central row, all the elements of which are zero save those on either side the centre ($r = 1$ and $r = -1$), which are respectively equal to ν_1 and ν_2. This follows from the fact that

$$\delta_{r0}r = 0 \quad (r \neq 1), \qquad \delta_{r0}r = 1 \quad (r = 1).$$

Again, from (5·21), we may prove in the usual way that

$$\beta_r = \frac{\nabla_r(\delta_{0n}b_{mn})}{\nabla(\delta_{0n}b_{mn})},$$

where ∇_r and ∇ are the same, except that in the r^{th} column of ∇_r all the elements are zero save those on either side the centre (*i.e.*, $n = \pm 0$) which are unity. If in ∇ and ∇_r we add half of each of the rows $n = \pm 0$ to the centre row, and subtract this new centre row from the rows $n = \pm 0$, ∇ becomes transformed into $\nabla(\delta_{0n}b'_{mn})$, where $b'_{mn} = b_{mn}$, except when $n = \pm 0$, while

$$b'_{m0} = \tfrac{1}{2}(b_{m0}-b_{m-0})-b_m, \quad b'_{m-0} = \tfrac{1}{2}(b_{m-0}-b_{m0})-b_m, \quad b'_m = b_m+\tfrac{1}{2}(b_{m0}+b_{m-0}). \tag{5·38}$$

Similarly, ∇_r becomes transformed into $\nabla_r(\delta_{0n}b'_{mn})$, identical with $\nabla(\delta_{0n}b'_{mn})$, except that in the r^{th} column all the elements are zero save the central one, which is unity.

Consequently we may write

$$\sum_1^\infty(\nu_1\beta_r+\nu_2\beta_{-r}) = \frac{\nabla_0(\delta_{0n}b'_{mn})}{\nabla(\delta_{0n}b'_{mn})},$$

where ∇_0 is the same as ∇ except that in the central row all the elements on the right of the centre ($m \geqslant 0$) are equal to ν_1, all those to the left ($m \leqslant -0$) are equal to ν_2, while the central element is zero. We now "difference" by columns, with the result

$$\sum_1^\infty(\nu_1\beta_r+\nu_2\beta_{-r}) = \frac{\nabla_0(\delta_{mn}b'_{mn})}{\nabla(\delta_{mn}b'_{mn})}. \tag{5·39}$$

The general element of ∇ is $\delta_{mn}b_{mn}$ or $\delta_{mn}b'_{mn}$, which are the same except when $n = \pm 0$; the general elements of these two rows are $\delta_{m0}b'_{m0}$, $\delta_{m-0}b'_{m-0}$ (*cf.* (5·38)), the general elements of the central row and column respectively are $\delta_{m0}b'_{m}$ and $\delta_{0n}b_{n}$, while the central element is b. From this we obtain ∇_0 if we replace all the elements of the central row by zero, except the two on either side the centre, which are $\nu_1 (m = 0)$ and $\nu_2 (m = -0)$.

Finally, we may prove that

$$(5·40) \qquad \sum_{0}^{\infty} (\nu_1\gamma_r + \nu_2\gamma_{-r}) = \frac{\nabla_0 (\delta_{mn}c_{mn})}{\nabla (\delta_{mn}c_{mn})},$$

where ∇ is defined as usual ($\pm m$, $\pm n$ ranging from 0 to ∞), while in ∇_0 all the elements are equal to the corresponding elements of ∇ except in the two central rows ($n = \pm 0$). In the row $n = 0$ all the elements are zero except the central two, which are $\nu_1 (m = 0)$ and $\nu_2 (m = -0)$. In the row $n = -0$ the general element is $c_{m-0} - c_{m0}$.

§ 6. THE COMPLETE SOLUTION FOR MAXWELLIAN MOLECULES.

In the case of Maxwellian molecules, *i.e.*, molecules which are point centres of force varying inversely as the fifth power of the distance, the solution reduces to finite terms. This arises from the fact (*cf.* § 9 (C), 'Phil. Trans.,' A, vol. 216, p. 323) that for such a law of inter-action the functions ϕ, ψ, χ are independent of y, with the result that for all values of t we have (*cf.* (4·25))

$$(6·01) \qquad k_t = 1, \qquad k^t_{11} = k^0_{11}, \qquad k^t_{12} = k^0_{12}, \qquad k^t_{22} = k^0_{22},$$

and consequently,

$$(6·02) \qquad \sum_{0}^{s} {}_sC_t \mu_1^{s-t} \mu_2^t k_t = \sum_{0}^{s} {}_sC_t \mu_1^{s-t} \mu_2^t = (\mu_1 + \mu_2)^s = 1.$$

From (5·12)–(5·14) and (4·27), (4·29), with the aid of (6·02), we deduce that

$$(6·03) \qquad \alpha_{00} = \alpha_{0s} = \alpha_{r0} = \tfrac{2}{27} \frac{m_1 m_2}{m_1 + m_2} \lambda_1 \lambda_2 \nu_0 A_0 K'_{12}(0),$$

independently of the value of r or s. From (5·21) and (3·13) we consequently have

$$(6·04) \qquad \alpha_r = 0 \quad (r \neq 0), \qquad \alpha_0 - \alpha_{-0} = \frac{1}{\alpha_{00}} = -\frac{\alpha'_0}{\lambda_1 \lambda_2}, \qquad \alpha_0 = -\frac{\alpha'_0}{\lambda_1}, \qquad \alpha_{-0} = \frac{\alpha'_0}{\lambda_2}.$$

Again, from (6·03) and (5·16), (5·17) we conclude that $b_r = 0 = b_s$ for all values of $\pm r$, $\pm s$ from 0 to ∞. Hence, by (5·36), or more simply from (5·21)—since in $\nabla_0 (b_{mn})$ *all* the elements of the central column are zero, instead of all except one, the central element, as in ∇—we have

$$(6·05) \qquad \beta'_0 = 0.$$

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Also in $\nabla(b_{mn})$ and $\nabla_r(b_{mn})$ we may in this case omit the central row and column, all the elements of which are zero (if $r \neq 0$) except the central element, which is the same in each (b); we suppose that this is done, so that ∇ and ∇_r become determinants which possess no single central row or column, just as with $\nabla(c_{mn})$. We will consider the two central columns of $\nabla(b_{mn})$ and $\nabla(c_{mn})_1$ corresponding to $m = \pm 0$. We have, by (5·12)–(5·18), (4·35)–(4·38), and (6·03),

$$(6{\cdot}06) \quad s > 0, \quad b_{0s} = \frac{1}{\lambda_1}\frac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}\frac{1}{s+1}(a_{1,s+1} - a_{0,s+1})$$

$$= \frac{64\pi m_1}{675\mathrm{R}}\mathrm{B}_0\mathrm{K}'_{12}(0)\{\nu_1 + 5\mu_2\nu_2(3\mu_1{}^2 + \mu_2{}^2 + \tfrac{4}{5}\mu_1\mu_2 k_{12}{}^0)\},$$

$$(6{\cdot}07) \quad s < 0, \quad b_{-0s} = -\frac{64\pi m_2}{675\mathrm{R}}\mathrm{B}_0\mathrm{K}'_{12}(0)\{\nu_2 + 5\mu_1\nu_1(3\mu_2{}^2 + \mu_1{}^2 + \tfrac{4}{5}\mu_1\mu_2 k_{12}{}^0)\},$$

$$(6{\cdot}08) \quad s > 0, \quad b_{-0s} = -\frac{16\pi m_2}{135\mathrm{R}}\mathrm{B}_0\mathrm{K}'_{12}(0)\,\mu_1\mu_2{}^2(1 + \tfrac{1}{5}k_{12}{}^0),$$

$$(6{\cdot}09) \quad s < 0, \quad b_{0s} = \frac{16\pi m_1}{135\mathrm{R}}\mathrm{B}_0\mathrm{K}'_{12}(0)\,\mu_1{}^2\mu_2(1 + \tfrac{1}{5}k^0{}_{12}),$$

$$(6{\cdot}10) \quad s > 0, \quad c_{0s} = \frac{32}{15^3}\pi\mathrm{C}_0\mathrm{K}'_{12}(0)\,[3\nu_1 k_{11}{}^0 + 2\mu_2\nu_2(10\mu_1 + 3\mu_2 k_{12}{}^0)],$$

$$(6{\cdot}11) \quad s > 0, \quad c_{-0s} = \frac{32}{15^3}2\pi\mu_2\nu_2\mathrm{C}_0\mathrm{K}'_{12}(0)\,(-10\mu_1 + 3\mu_1 k_{12}{}^0),$$

$$(6{\cdot}12) \quad s < 0, \quad c_{0s} = \frac{32}{15^3}2\pi\mu_1\nu_1\mathrm{C}_0\mathrm{K}'_{12}(0)\,(-10\mu_2 + 3\mu_2 k_{12}{}^0),$$

$$(6{\cdot}13) \quad s < 0, \quad c_{-0s} = \frac{32}{15^3}\pi\mathrm{C}_0\mathrm{K}'_{12}(0)\,[3\nu_2 k_{22}{}^0 + 2\mu_1\nu_1(10\mu_2 + 3\mu_1 k_{12}{}^0)].$$

All these quantities, it will be noticed, are independent of s; thus we see that in $\nabla(b_{mn})$ and $\nabla(c_{mn})$ the elements of the two centre columns take only four distinct values, all the elements of these columns which are in the same quadrant having the same value.

By using the method of differencing by rows it is easy to prove, as a consequence of the property of $\nabla(b_{mn})$ and $\nabla(c_{mn})$ which we have just established, that

$$(6{\cdot}14) \qquad \beta_r = 0 \quad (r \geqslant 2,\ r \leqslant -2), \qquad \gamma_r = 0 \quad (r \geqslant 1,\ r \leqslant -1),$$

while (*cf.* (6·05), (6·14), (3·14)),

$$(6{\cdot}15) \qquad \gamma_0 = \frac{c_{-00} - c_{-0-0}}{c_{-00}c_{0-0} - c_{00}c_{-0-0}}, \qquad \gamma_{-0} = \frac{c_{00} - c_{0-0}}{c_{00}c_{-0-0} - c_{0-0}c_{-00}},$$

$$(6{\cdot}16) \qquad \beta_0 = -\beta_1 = \frac{b_{-0-0} - b_{-00}}{b_{-00}b_{0-0} - b_{00}b_{-0-0}}, \qquad \beta_{-0} = -\beta_{-1} = \frac{b_{00} - b_{0-0}}{b_{0-0}b_{-00} - b_{00}b_{-0-0}}.$$

Consequently, in the case of Maxwellian molecules, $F(c^2)$ and $H(c^2)$ each reduce to their first terms, while $G(c^2)$ reduces to two terms only, the solution being quite finite.

§ 7. THE GENERAL SOLUTION WHEN $m_1 : m_2$ IS VERY LARGE.

When the mass m_1 of the heavier molecules is very large compared with that of the lighter molecules, so that m_2/m_1 may be supposed zero, an exact general solution may be obtained in simple terms. This was first proved by LORENTZ,* in connection with the theory of electrons. His method is much simpler than that of this paper, from which, however, his results may, with little difficulty, be deduced as a very special case. The deduction will be described in some detail, since the knowledge of the exact solution throws valuable light on the convergence of our successive approximations; it also leads to an expression for π which is of interest, as being in a form which, so far as my knowledge goes, is new.

We suppose that the effect of collisions between the molecules m_2 is negligible, so that ρ_{22} and ρ'_{22} may be omitted from our calculations; if the molecules are rigid elastic spheres of radii $\sigma_1 : \sigma_2$, this amounts to the neglect of $\sigma_2{}^2/\sigma_1{}^2$ (*cf.* § 9 (*f*)) or, in general, to ϕ_{22}/ϕ_{11}.

It may readily be seen from (4·13), (4·14) that if $m_2 = 0$ the value of $B^k(m, n)$, with whatever suffix, is zero except when $k = 0$, and that

$$(7{\cdot}01) \qquad \begin{cases} B^0{}_{1212}(m, n) = (2x^2)^{m+n}, & B^0{}_{2112}(m, n) = 2^{m+n}y^{2m}x^{2n}, \\ B^0{}_{2121}(m, n) = (2y^2)^{m+n}, & B^0{}_{1221}(m, n) = 2^{m+n}x^{2m}y^{2n}. \end{cases}$$

We also require $B^1(m, n)$ to the first order in m_2, as follows :—

$$(7{\cdot}02) \qquad \begin{cases} B^1{}_{1212}(m, n) = \tfrac{4}{9}mn\mu_2 2^{m+n}x^{2(m+n-1)}y^2, & B^1{}_{2112}(m, n) = \tfrac{4}{9}mn\mu_2 2^{m+n}y^{2m}x^{2n}, \\ B^1{}_{2121}(m, n) = \tfrac{4}{9}mn\mu_2 2^{m+n}y^{2(m+n-1)}x^2, & B^1{}_{1221}(m, n) = \tfrac{4}{9}mn\mu_2 2^{m+n}x^{2m}y^{2n}. \end{cases}$$

From these, by means of (4·07)–(4·12) we deduce the following expressions for $\rho(r, s)$, $\rho'(r, s)$, retaining only the terms of highest order :—

$$(7{\cdot}03) \qquad \rho_{12}(r_1 s_1) = \tfrac{4}{9}\pi\nu_1\nu_2\mu_2 2^{r+s}(2rs+r+s+\tfrac{3}{2})(r+s+\tfrac{1}{2})_{r+s}K'_{12}(0),$$

$$(7{\cdot}04) \qquad \rho_{12}(r_2 s_1) = -\tfrac{4}{9}\pi\nu_1\nu_2\mu_1 2^{r+s}(r+\tfrac{3}{2})_{r+1}(s+\tfrac{3}{2})_s k_r K'_{12}(0),$$

$$(7{\cdot}05) \qquad \rho_{21}(r_1 s_2) = -\tfrac{4}{9}\pi\nu_1\nu_2\mu_2 2^{r+s}(r+\tfrac{3}{2})_{r+1}(s+\tfrac{3}{2})_s k_s K'_{12}(0),$$

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* LORENTZ, 'Archives Néerlandaises,' 10, p. 336, 1905; 'Theory of Electrons,' p. 268. A more general form of LORENTZ'S theory is given in JEANS' 'Dynamical Theory of Gases,' 2nd ed., §§ 314, *et seq.* I am indebted to Mr. JEANS for pointing out the interest of a detailed comparison of LORENTZ'S theory with this special case of my own, and in consequence I have rewritten § 7 with greater fullness than at first.

$$(7{\cdot}06)\qquad \rho_{21}(r_2s_2) = \tfrac{4}{9}\pi\nu_1\nu_2\mu_1 2^{r+s}(r+s+\tfrac{3}{2})_{r+s+1}k_{r+s}\mathrm{K}'_{12}(0),$$

$$(7{\cdot}07)\qquad \rho'_{12}(r_1s_1) = \tfrac{32}{45}\pi\nu_1\nu_2\mu_2 2^{r+s}(rs+r+s+\tfrac{5}{2})(r+s+\tfrac{3}{2})_{r+s+1}\mathrm{K}'_{12}(0),$$

$$(7{\cdot}08)\qquad \begin{cases} \rho'_{12}(r_2s_1) = \tfrac{8}{45}\pi\nu_1\nu_2\mu_1 2^{r+s}rs(r+\tfrac{5}{2})_{r+2}(s+\tfrac{1}{2})_s k_{r+1}\mathrm{K}'_{12}(0), \qquad r>0,\ s>0. \\ \rho'_{12}(0_2s_1) = \tfrac{32}{45}\pi\nu_1\nu_2\mu_2 2^{s}(s+\tfrac{5}{2})_{s+2}(-k_0+\tfrac{3}{10}k_{12}{}^{0})\mathrm{K}'_{12}(0) = \rho'_{21}(s_10_2), \\ \rho'_{12}(r_20_1) = \tfrac{32}{45}\pi\nu_1\nu_2\mu_2 2^{r}(r+\tfrac{5}{2})_{r+2}(-k_r+\tfrac{3}{10}k^{r}{}_{12})\mathrm{K}'_{12}(0) = \rho'_{21}(0_1r_2), \end{cases}$$

$$(7{\cdot}09)\qquad \rho'_{21}(r_1s_2) = \tfrac{8}{45}\pi\nu_1\nu_2\mu_1 2^{r+s}rs(r+\tfrac{1}{2})_r(s+\tfrac{5}{2})_{s+2}k_{s+1}\mathrm{K}'_{12}(0), \qquad r>0,\ s>0,$$

$$(7{\cdot}10)\qquad \rho'_{21}(r_2s_2) = \tfrac{16}{75}\pi\nu_1\nu_2\mu_1 2^{r+s}(r+s+\tfrac{5}{2})_{r+s+2}k_{12}{}^{r+s+1}\mathrm{K}'_{12}(0).$$

For the particular values of r and s there dealt with, the expressions (4·26)-(4·34) reduce to the above in the present special case, as may readily be verified.

We now substitute from (7·03)-(7·10) in (5·12)-(5·20), retaining only the terms of the highest order, and neglecting quantities of order $m_2{}^2 : m_1{}^2$; the result is as follows:—

$$(7{\cdot}11)\quad s \geqslant 0,\ a_{0s} = \tfrac{2}{27}\pi\lambda_1\lambda_2\nu_0 m_1\mu_2\mathrm{A}_0\mathrm{K}'_{12}(0) = a_{00}, \qquad s \leqslant 0,\ a_{0s} = \tfrac{2}{27}\pi\lambda_1\lambda_2\nu_0 m_1\mu_2\mathrm{A}_0 k_s\mathrm{K}'_{12}(0),$$

$$(7{\cdot}12)\qquad\qquad r > 0,\ s \geqslant 0, \qquad a_{rs} = \frac{m_1}{\nu_0}\mathrm{N}_{rs}\rho_{11}(r_1s_1),$$

$$(7{\cdot}13)\qquad r<0,\ s\leqslant 0, \qquad a_{rs} = -\tfrac{2}{27}\pi\lambda_1\lambda_2\nu_0 m_2\mu_1\mathrm{A}_0\frac{(r+s+\frac{3}{2})_{r+s}}{(r+\frac{3}{2})_r(s+\frac{3}{2})_s}k_{r+s}\mathrm{K}'_{12}(0),$$

$$(7{\cdot}14)\qquad\qquad (r<0,\ s\geqslant 0), \qquad a_{rs} = -\tfrac{2}{27}\pi\lambda_1\lambda_2\nu_0 m_2\mu_1\mathrm{A}_0 k_r\mathrm{K}'_{12}(0),$$

$$(7{\cdot}15)\qquad\qquad (r>0,\ s\leqslant 0), \qquad a_{rs} = \tfrac{2}{27}\pi\lambda_1\lambda_2\nu_0 m_1\mu_2\mathrm{A}_0 k_s\mathrm{K}'_{12}(0),$$

$$(7{\cdot}16)\quad (r\geqslant 0),\ b_r = 0,\ b = \frac{\mathrm{B}_0}{\mathrm{A}_0\mathrm{R}}a_{00}, \quad b_r = -\tfrac{2}{27}\frac{\pi}{\mathrm{R}}\lambda_1\lambda_2\nu_0 m_1\mu_2\mathrm{B}_0\frac{k_{r+1}-1}{r+1}\mathrm{K}'_{12}(0), \quad (r\leqslant -0).$$

$$(7{\cdot}17)\quad (s\geqslant 0), \qquad b_s = 0, \qquad b_s = -\frac{1}{\lambda_2}\tfrac{2}{27}\frac{\pi}{\mathrm{R}}\lambda_1\lambda_2\nu_0 m_1\mu_2\mathrm{B}_0\frac{k_{s+1}-1}{s+1}\mathrm{K}'_{12}(0), \qquad (s\leqslant -0),$$

$$(7{\cdot}18)\qquad\qquad (r\leqslant -0,\ s\geqslant 0), \qquad b_{rs} = 0, \qquad (r\geqslant 0,\ s\leqslant -0),$$

$$(7{\cdot}19)\quad (r\geqslant 0,\ s\geqslant 0), \qquad b_{rs} = \frac{1}{\lambda_1}\tfrac{2}{27}\frac{\pi}{\mathrm{R}}\lambda_1\lambda_2\nu_0 m_2\mu_1\mathrm{B}_0\frac{1}{(r+1)(s+1)}$$
$$\left\{\frac{(r+s+\frac{7}{2})_{r+s}}{(r+\frac{5}{2})_r(s+\frac{5}{2})_s}k_{r+s+2}-k_{r+1}-k_{s+1}+1\right\}\mathrm{K}'_{12}(0).$$

Since, by (7·14), (7·15), $a_{rs}(r<0,\ s\geqslant 0)$ is independent of s, and $a_{rs}(r>0,\ s\leqslant 0)$ is independent of r, it is readily evident that in the alternate quadrants of the determinants $\nabla(\delta_{mn}a_{mn})$ and $\nabla'(\delta_{mn}a_{mn})$ all the elements vanish. Hence each ∇ becomes equal to the product of the two remaining quadrants; in the positive quadrant the determinants are the same ($r > 0$, $s > 0$). Consequently in this case (5·35) becomes

$$\alpha'_0 = -\lambda_1\lambda_2 \sum_0^\infty (\alpha_r - \alpha_{-r}) = -\frac{27}{2\pi\nu_0 m_2 \mathrm{A}_0 \mathrm{K}'_{12}(0)} \frac{\mathrm{D}_0}{\mathrm{D}} \tag{7·20}$$

where D is the determinant whose general element is

$$\delta_{rs} a_{rs} = \delta_{rs} \frac{(r+s+\frac{3}{2})_{r+s}}{(r+\frac{3}{2})_r (s+\frac{3}{2})_s} k_{r+s}, \qquad r \geqslant 0,\ s \geqslant 0, \tag{7·21}$$

and D_0 is its principal minor.

Similarly, it follows from (5·36) and (7·16)–(7·19) that β'_0 can be likewise expressed as the quotient by an infinite determinant (covering only a quadrant of the infinite plane) of its *second* minor, as follows:—

$$\beta'_0 = -\frac{27\mathrm{R}\lambda_2}{2\pi\nu_0 m_2 \mathrm{B}_0 \mathrm{K}'_{12}(0)} \frac{\mathrm{D}'_1}{\mathrm{D}'}. \tag{7·22}$$

Here D′ is the determinant whose general element d_{rs} is given by

$$(r > 0,\ s > 0) \quad d_{rs} = \delta_{r-1,s-1} \frac{1}{rs} \left\{ \frac{(r+s+\frac{3}{2})_{r+s}}{(r+\frac{3}{2})_r (s+\frac{3}{2})_s} k_{r+s} - k_r - k_s + 1 \right\}$$
$$= \frac{1}{rs} \delta_{rs} \frac{(r+s+\frac{3}{2})_{r+s}}{(r+\frac{3}{2})_r (s+\frac{3}{2})_s} k_{r+s}, \tag{7·23}$$

$$r > 0 \qquad d_{r0} = d_{0r} = \delta_{r-1} \frac{1}{r}(k_r - 1) = \frac{1}{r} \delta_r k_r \qquad d_{00} = 1. \tag{7·24}$$

Thus it is the same as the determinant D of (7·20) except that the r^{th} row and column ($r \geqslant 1$) are divided throughout by r. The determinant D'_1 is the second minor of D′, *i.e.*, the minor of the next element to the centre in the first row or column.

Again, from (5·37), we may prove that

$$\sum_1^\infty r(\nu_1 \alpha_r + \nu_2 \alpha_{-r}) = -\frac{27\nu_0}{2\pi\nu_1 m_2 \mathrm{A}_0 \mathrm{K}'_{12}(0)} \frac{\mathrm{D}_1}{\mathrm{D}}, \tag{7·25}$$

where D_1 is the second minor of D just as D'_1 is of D′. It is easy to see that*

$$\frac{\mathrm{D}_1}{\mathrm{D}} = \frac{\mathrm{D}'_1}{\mathrm{D}'}. \tag{7·26}$$

Likewise, from (5·39), we have

$$\sum_1^\infty (\nu_1 \beta_r + \nu_2 \beta_{-r}) = -\frac{27\nu_0}{2\pi\nu_1 m_2 \mathrm{B}_0 \mathrm{K}'_{12}(0)} \frac{\mathrm{D}''_1}{\mathrm{D}''}, \tag{7·27}$$

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* *Cf.* the footnote on p. 154, indicating that $\Sigma r(\nu_1\alpha_r + \nu_2\alpha_{-r})$ is, quite generally, a mere multiple of β'_0.

where D″ is the determinant which is identical with D′ except in its first two rows (for which *cf.* (5·38)), while D''_1 is the minor of the second element in the first *row* of D″.

§ 8. THE GENERAL SOLUTION FOR THE CASE OF SIMILAR MOLECULES.

Another instructive and specially simple particular case is that of a gas composed of two sets of molecules whose mechanical properties—mass and mode of inter-action during encounter—are identical. In this case all the symbols which we have distinguished by the suffixes 1 or 2, to indicate reference to one or other molecular group, now have the same value for either suffix, with the exception of ν_1, ν_2 or λ_1, λ_2, which denote the numbers or proportions of the two molecular groups. Moreover (*cf.* (4·01)–(4·04), (4·07)–(4·12), or, for a simpler and more general explanation, 'Phil. Trans.,' A, vol. 216, § 7 (H), p. 309), we have

$$\frac{1}{\nu_1^{\,2}}\,\rho_{11}(r_1 s_1) = \frac{1}{\nu_2^{\,2}}\,\rho_{22}(r_2 s_2) = \frac{1}{\nu_0^{\,2}}\,\rho(r,\ s), \tag{8·01}$$

$$\rho_{12}(r_1 s_1)+\rho_{12}(r_2 s_1) = \rho_{21}(r_2 s_2)+\rho_{21}(r_1 s_2) = \lambda_1\lambda_2\rho(r,\ s) \qquad \rho_{12}(r_2 s_1) = \rho_{21}(r_1 s_2), \tag{8·02}$$

$$\frac{1}{\nu_1^{\,2}}\,\rho'_{11}(r_1 s_1) = \frac{1}{\nu_2^{\,2}}\,\rho'_{22}(r_2 s_2) = \frac{1}{\nu_0^{\,2}}\,\rho'(r,\ s), \tag{8·03}$$

$$\rho'_{12}(r_1 s_1)+\rho'_{12}(r_2 s_1) = \rho'_{21}(r_2 s_2)+\rho'_{21}(r_1 s_2) = \lambda_1\lambda_2\rho'(r,\ s), \tag{8·04}$$

where $\rho(r,\ s)$ and $\rho'(r,\ s)$ are defined by (8·01) and (8·03).

By means of these relations we may reduce the expressions for α'_0 and β'_0 to a much simpler form. Our operations may be performed on the actual determinants which express the general solution, but they could, of course, be equally well described as transformations of the general equations (5·08)–(5·11).

First considering $\nabla(\delta_{rs} a_{rs})$, we add to the m^{th} column on the right $(m > 0)$ the corresponding column $(-m)$ on the left of the centre; the new element on the right is now given by the equations

$$\begin{aligned}(m > 0,\ n \geqslant 0) \quad \delta_{mn}(a_{mn}+a_{-mn}) &= \frac{m}{\nu_0}\,\mathrm{A}_0\delta_{mn}\mathrm{N}_{mn}\{\rho_{11}(m_1 n_1)+\rho_{12}(m_1 n_1)+\rho_{12}(m_2 n_1)\}, \\ &= \frac{m}{\nu_0}\,\mathrm{A}_0\delta_{mn}\mathrm{N}_{mn}(\lambda_1^{\,2}+\lambda_1\lambda_2)\,\rho(m,\ n) \\ &= \lambda_1\frac{m}{\nu_0}\,\mathrm{A}_0\delta_{mn}\mathrm{N}_{mn}\rho(m,\ n),\end{aligned} \tag{8·05}$$

$$(m > 0,\ s \leqslant 0) \qquad \delta_{mn}(a_{mn}+a_{-mn}) = -\lambda_2\frac{m}{\nu_0}\,\mathrm{A}_0\delta_{mn}\mathrm{N}_{mn}\rho(m,\ n). \tag{8·06}$$

We next add λ_2/λ_1 times the n^{th} row $(n > 0)$ to the $(-n)^{\text{th}}$ row; the elements of the negative rows $(n \leqslant 0)$ thus acquire the following values:—

$$(8{\cdot}07)\quad (m > 0,\ n \leqslant 0)\quad \delta_{mn}\left\{a_{mn}+a_{-mn}+\frac{\lambda_2}{\lambda_1}(a_{m-n}+a_{-m-n})\right\} = 0 \qquad a_{00} = -\frac{m}{\nu_0}\mathrm{A}_0\mathrm{N}_{00}\rho_{12}(0_1 0_1),$$

$$(8{\cdot}08)\qquad (m \leqslant 0,\ n \leqslant 0)\quad \delta_{mn}\left(a_{mn}+\frac{\lambda_2}{\lambda_1}a_{m-n}\right) = -\frac{m}{\nu_1}\mathrm{A}_0\delta_{mn}\mathrm{N}_{mn}\rho_{12}(r_1 s_1).$$

These transformations do not alter the value of $\nabla(\delta_{mn}a_{mn})$, nor of $\nabla'(\delta_{mn}a_{mn})$ when applied to this determinant, which continues to be identical with the principal minor of ∇ in its new form. Since in each of these determinants the elements of one entire quadrant $(m > 0,\ n \leqslant 0)$ are all zero, they may be expressed as the product of the two simply infinite determinants formed by the quadrants $(m > 0,\ n > 0)$ and $(m \leqslant 0,\ n \leqslant 0)$. The former quadrant, however, is the same for ∇ and ∇', so that (5·35) may be written (after a little reduction*) in the form

$$(8{\cdot}09)\qquad \alpha'_0 = -\lambda_1\lambda_2\sum_0^\infty(\alpha_r-\alpha_{-r}) = -\frac{27}{\pi\nu_0 m\mathrm{A}_0\mathrm{K}'_{12}(0)}\frac{\nabla'_0}{\nabla_0},$$

where ∇'_0 is the principal minor of ∇_0, the general elements a'_{mn} of which is given by the equations

$$(8{\cdot}10)\qquad a'_{mn} = \delta_{mn}\frac{27\rho_{12}(m,n)}{\pi\nu_1\nu_2 2^{m+n+2}(m+\frac{3}{2})_{m+1}(n+\frac{3}{2})_{n+1}\mathrm{K}'_{12}(0)},$$

so that

$$(8{\cdot}11)\qquad a'_{00} = 1 \qquad a'_{m0} = \delta_{m0}2^{-m}\sum_0^m {}_m\mathrm{C}_t k_t = a'_{0m}.$$

Here, since $m_1 = m_2$, the equation (4·08) takes the special form

$$(8{\cdot}12)\quad \frac{\rho_{12}(r_1 s_1)}{\nu_1\nu_2}$$
$$= \tfrac{16}{3}\iint e^{-x^2-y^2}x^2y^2\sum_0^{r+1,s+1}[\phi^k(y)\{\mathrm{B}^k(r+1,\ s)+\mathrm{B}^k(r,\ s+1)\}+2y^2\psi^k(y)\,\mathrm{B}^k(r,\ s)]\,dx\,dy,$$

whence it is clear that ∇_0, and consequently also α'_0, is independent of the ratio $\nu_1 : \nu_2$ (*i.e.*, ν_1 and ν_2 occur only in the form $\nu_1+\nu_2$ or ν_0).

It may readily be verified that a corresponding calculation in the case of $\nabla(\delta_{mn}b_{mn})$ leads to the result

$$(8{\cdot}13)\qquad \beta'_0 = 0.$$

In the same way we may determine the particular forms assumed by (5·37), (5·39), and (5·40) in this special case.

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* This reduction chiefly consists in cancelling out factors common to all the elements of corresponding rows of ∇_0 and ∇'_0.

§ 9. First and Second Approximations in the General Case.

(*a*) *General Remarks.*

In the general case there are no such simplifications as have been described in §§ 7–9, and for practical numerical purposes we have to be content with successive approximations to the complete solution. The approximate formulæ become increasingly complicated with each successive step, however, so that it is fortunate that a first or second approximation generally gives a close approach to accuracy. In the theory of viscosity and conduction in a simple gas ('Phil. Trans.,' A, vol. 216, § 11, p. 334) it was found that a first approximation gave a result not more than 2 or 3 per cent. too small, while the error after a second approximation was negligible. In the present theory of a composite gas the error of the first approximation may be much larger (up to 13 per cent.) in extreme cases where the masses, densities, or diameters of the two sets of molecules differ widely (*cf.* § 7). Such a case is worked out to a fifth approximation in § 13 (*e*), and as this is one in which an exact solution is possible by another method, the results there obtained throw much light on the general character of the convergence of our analysis. It would seem that (as in the previous memoir just cited) the successive approximations form a monatomic sequence, the first and second members of which give a good indication of the accurate limiting value. If the difference between these two members is about 2 per cent., the additional correction due to all further approximations is about $\frac{1}{4}$ per cent., while if the difference is so much as 8 per cent., the further correction is about 4 per cent., the additional correction being in an increasing ratio to the first difference as the value of the latter rises.

In this paper we shall not go beyond a first approximation in the general case, except in regard to α'_0, where we shall stop at the second approximation.

(*b*) *First Approximation to* α'_0.

If in our set of equations (5·08) we neglect all save the central one, and consider only the central term of that, we get the equation

(9·01) $$a_{00}(\alpha_0 - \alpha_{-0}) = 1, \quad \text{or} \quad a_{00}\alpha'_0 = -\lambda_1\lambda_2.$$

By (5·12) and (4·27) we have

(9·02) $$a_{00} = \mathrm{A}_0 \frac{2\pi\nu_1\nu_2 m_1 m_2 \mathrm{K}'_{12}(0)}{27\nu_0(m_1+m_2)}.$$

It is convenient to choose A_0 (which is quite arbitrary as yet) so as to make

(9·021) $$a_{00} = 1,$$

so that

(9·022) $$\mathrm{A}_0 = \frac{27(m_1+m_2)}{2\pi\lambda_1\lambda_2\nu_0 m_1 m_2 \mathrm{K}'_{12}(0)},$$

and so that the equation for the first approximation to α'_0 becomes (with this value of A_0)

$$\alpha'_0 = -\lambda_1\lambda_2. \tag{9·03}$$

(c) *Second Approximation to α'_0.*

We may conveniently obtain our second approximation by means of (5·35), taking the three rows and columns of ∇ and ∇' which contain a_{00} in the centre. From (5·12)–(5·14) it is easy to see that the elements have the following values (when $a_{00} = 1$):—

$$\delta_{01}a_{01} = \mu_2(k_1-1) = \delta_{10}a_{10} \equiv p_1, \quad \delta_{0-1}a_{0-1} = \mu_1(k_1-1) = -\delta_{-10}a_{-10} \equiv -p_2, \tag{9·04}$$

$$\delta_{11}a_{11} = \left\{\tfrac{6}{5}\mu_1^2+\mu_2^2(1-2k_1+\tfrac{7}{5}k_2)+\tfrac{8}{25}\mu_1\mu_2k_{12}^0+\tfrac{2}{25}\frac{\nu_1}{\nu_2\mu_2}k_{11}^0\right\} \equiv p_{11}, \tag{9·05}$$

$$\delta_{-1-1}a_{-1-1} = -\left\{\tfrac{6}{5}\mu_2^2+\mu_1^2(1-2k_1+\tfrac{7}{5}k_2)+\tfrac{8}{25}\mu_1\mu_2k_{12}^0+\tfrac{2}{25}\frac{\nu_2}{\nu_1\mu_1}k_{22}^0\right\} \equiv -p_{22}, \tag{9·06}$$

$$\delta_{1-1}a_{1-1} = -\delta_{-11}a_{-11} = \mu_1\mu_2\{\tfrac{11}{5}-2k_1+\tfrac{7}{5}k_2-\tfrac{8}{25}k_{12}^0\} \equiv -p_{12}. \tag{9·07}$$

Consequently, the third-order determinant for ∇ is given by

$$-\begin{vmatrix} p_{12} & p_1 & p_{11} \\ p_2 & 1 & p_1 \\ p_{22} & p_2 & p_{12} \end{vmatrix} = -\{p_{12}^2-p_{11}p_{22}-2p_1p_2p_{12}+p_{11}p_2^2+p_{22}p_1^2\} \equiv \tfrac{1}{25}\Delta_1, \tag{9·08}$$

and its principal minor by

$$-\begin{vmatrix} p_{12} & p_{11} \\ p_{22} & p_{12} \end{vmatrix} = -(p_{12}^2-p_{11}p_{22}). \tag{9·081}$$

It is easy to prove that

$$(p_{12}^2-p_{11}p_{22}) = -\tfrac{1}{25}\frac{1}{\nu_1\nu_2}(d_1\nu_1^2+2d_{12}\nu_1\nu_2+d_2\nu_2^2), \tag{9·082}$$

where

$$d_1 \equiv \frac{1}{\mu_2}k_{11}^0\{\tfrac{12}{5}(1-2\mu_1\mu_2)+\tfrac{16}{25}\mu_1\mu_2k_{12}^0-2(\tfrac{1}{5}+2k_1-\tfrac{7}{5}k_2)\mu_1^2\}, \tag{9·09}$$

$$d_2 \equiv \frac{1}{\mu_1}k_{22}^0\{\tfrac{12}{5}(1-2\mu_1\mu_2)+\tfrac{16}{25}\mu_1\mu_2k_{12}^0-2(\tfrac{1}{5}+2k_1-\tfrac{7}{5}k_2)\mu_2^2\}, \tag{9·10}$$

$$2d_{12} \equiv \tfrac{4}{25}\frac{1}{\mu_1\mu_2}k_{11}^0k_{22}^0+\tfrac{6}{5}(1-4\mu_1\mu_2)(1-2k_1+\tfrac{7}{5}k_2)+8\mu_1\mu_2k_{12}^0(\tfrac{11}{5}-2k_1+\tfrac{7}{5}k_2). \tag{9·11}$$

Also

$$(9{\cdot}12)\qquad 2p_1p_2p_{12}-p_{11}p_2^{\,2}-p_{22}p_1^{\,2} = -\frac{(k_1-1)^2}{25\nu_1\nu_2}(b_1\nu_1^{\,2}+2b_{12}\nu_1\nu_2+b_2\nu_2^{\,2}),$$

where

$$(9{\cdot}13)\qquad b_1 = 2\mu_1\mu_{12}k_{11}^{\,0},\qquad b_2 = 2\mu_2\mu_{21}k_{22}^{\,0},\qquad 2b_{12} = 30\,(1-4\mu_1\mu_2)+8\mu_1\mu_2k_{12}^{\,0}.$$

Consequently, if we write

$$(9{\cdot}14)\qquad \epsilon_0 \equiv \frac{2p_1p_2p_{12}-p_{11}p_2^{\,2}-p_{22}p_1^{\,2}}{p_{12}^{\,2}-p_{11}p_{22}} = (k_1-1)^2\,\frac{b_1\nu_1^{\,2}+2b_{12}\nu_1\nu_2+b_2\nu_2^{\,2}}{d_1\nu_1^{\,2}+2d_{12}\nu_1\nu_2+d_2\nu_2^{\,2}},$$

we have, as our second approximation to α'_0 by (5·35),

$$(9{\cdot}15)\qquad \alpha'_0 = -\lambda_1\lambda_2\frac{1}{1-\epsilon_0}\cdot$$

We may note that

$$(9{\cdot}16)\qquad \Delta_1 = \frac{1}{\nu_1\nu_2}\,\{d_1\nu_1^{\,2}+2d_{12}\nu_1\nu_2+d_2\nu_2^{\,2})-(k_1-1)^2\,(b_1\nu_1^{\,2}+2b_{12}\nu_1\nu_2+b_2\nu_2^{\,2})\}$$

$$= \frac{1}{\nu_1\nu_2}\,\{a_1\nu_1^{\,2}+2a_{12}\nu_1\nu_2+a_2\nu_2^{\,2}\},$$

where

$$(9{\cdot}161)\qquad a_1 = \frac{2}{\mu_2}\,k_{11}^{\,0}\,\{\tfrac{6}{5}\mu_2^{\,2}-\mu_1^{\,2}\,(k_1^{\,2}-\tfrac{7}{5}k_2)+\tfrac{8}{25}\mu_1\mu_2k_{12}^{\,0}\},$$

$$(9{\cdot}162)\qquad a_2 = \frac{2}{\mu_1}\,k_{22}^{\,0}\,\{\tfrac{6}{5}\mu_1^{\,2}-\mu_2^{\,2}\,(k_1^{\,2}-\tfrac{7}{5}k_2)+\tfrac{8}{25}\mu_1\mu_2k_{12}^{\,0}\},$$

$$(9{\cdot}163)\qquad a_{12} = d_{12}-(k_1-1)^2\,b_{12}.$$

The determinant $\nabla_0(\delta_{mn}a_{mn})$ of (5·37) is, to the same order of approximation as for $\nabla(\delta_{mn}a_{mn})$ in (9·08),

$$(9{\cdot}164)\qquad -\begin{vmatrix} p_{12} & p_1 & p_{11} \\ \nu_2 & 0 & \nu_1 \\ p_{22} & p_2 & p_{12} \end{vmatrix} = \nu_1\,(p_2p_{12}-p_1p_{22})+\nu_2\,(p_1p_{12}-p_2p_{11}) \equiv \tfrac{1}{25}\,(k_1-1)\,\epsilon_1$$

where

$$(9{\cdot}17)\qquad \epsilon_1 \equiv 30\,(\nu_1\mu_2+\nu_2\mu_1)\,(\mu_1-\mu_2)-8\mu_1\mu_2k^0{}_{12}\,(\nu_1-\nu_2)+2\,(\nu_1\mu_{12}k^0{}_{11}-\nu_2\mu_{21}k^0{}_{22}).$$

Hence we have, as a first approximation,

$$(9{\cdot}18)\qquad \sum_1^\infty r\,(\nu_1\alpha_r+\nu_2\alpha_{-r}) = \frac{k_1-1}{\Delta_1}\,\epsilon_1.$$

(*d*) *First Approximation to* β'_0 *and* $\Sigma(\nu_1\beta_r - \nu_2\beta_{-r})$.

In this case, owing to the fact that the central element in the numerator determinants of (5·36) and (5·39) is zero, we have to deal with the third order determinant in order to obtain a *first* approximation. From (5·15)–(5·18) it is easy to see that $\nabla(\delta_{mn}b_{mn})$ may be obtained from $\nabla(\delta_{mn}a_{mn})$, each being limited to the three central rows and columns, if we replace a_{00} by $\frac{B_0}{A_0R}a_{00}$, and divide the top and bottom rows respectively by λ_1 and $-\lambda_2$. Consequently the third order determinant obtained from $\nabla(\delta_{mn}b_{mn})$ is equal to $-\frac{1}{25}\frac{1}{\lambda_1\lambda_2}\left(\frac{B_0}{A_0R}\right)^3\Delta_1$. The value of $\nabla'_0(\delta_{mn}b_{mn})$ is similarly (*cf.* § 5 (*f*) for the definition of this determinant),

$$(9·19)\qquad \left(\frac{B_0}{A_0R}\right)^2\begin{vmatrix} \frac{p_{12}}{\lambda_1} & 1 & \frac{p_{11}}{\lambda_1} \\ p_2 & 0 & p_1 \\ \frac{p_{22}}{\lambda_2} & 1 & \frac{p_{12}}{\lambda_2} \end{vmatrix} = \frac{1}{\lambda_1\lambda_2\nu_0}\left(\frac{B_0}{A_0R}\right)^2\begin{vmatrix} p_{12} & \nu_1 & p_{11} \\ p_2 & 0 & p_1 \\ p_{22} & \nu_2 & p_{12} \end{vmatrix} = -\frac{k_1-1}{25\lambda_1\lambda_2\nu_0}\left(\frac{B_0}{A_0R}\right)^2\epsilon_1$$

by (9·17). Hence, by (5·36), we have

$$(9·20)\qquad \beta'_0 = -\frac{A_0R}{B_0}\frac{k_1-1}{\nu_0\Delta_1}\lambda_1\lambda_2\epsilon_1 = -\frac{A_0R}{B_0}\frac{\lambda_1\lambda_2}{\nu_0}\sum_1^\infty r(\nu_1\alpha_r + \nu_2\alpha_{-r})^*$$

by (9·18).

Again, the determinant $\nabla_0(\delta_{mn}b'_{mn})$ defined in § 5 (*g*) has the form

$$(9·21)\qquad \left(\frac{B_0}{A_0R}\right)^2\begin{vmatrix} \frac{1}{2}\left(\frac{p_{12}}{\lambda_1}-\frac{p_{22}}{\lambda_2}\right)-p_2 & \frac{1}{2}\left(\frac{p_1}{\lambda_1}-\frac{p_2}{\lambda_2}\right)-1 & \frac{1}{2}\left(\frac{p_{11}}{\lambda_1}-\frac{p_{12}}{\lambda_2}\right)-p_1 \\ \nu_2 & 0 & \nu_1 \\ -\frac{1}{2}\left(\frac{p_{12}}{\lambda_1}-\frac{p_{22}}{\lambda_2}\right)-p_2 & -\frac{1}{2}\left(\frac{p_1}{\lambda_1}-\frac{p_2}{\lambda_2}\right)-1 & -\frac{1}{2}\left(\frac{p_{11}}{\lambda_1}-\frac{p_{12}}{\lambda_2}\right)-p_1 \end{vmatrix}$$

$$= \left(\frac{B_0}{A_0R}\right)^2\begin{vmatrix} p_2 & 1 & p_1 \\ \nu_2 & 0 & \nu_1 \\ \frac{p_{12}}{\lambda_1}-\frac{p_{22}}{\lambda_2} & \frac{p_1}{\lambda_1}-\frac{p_2}{\lambda_2} & \frac{p_{11}}{\lambda_1}-\frac{p_{12}}{\lambda_2} \end{vmatrix}$$

$$= -\frac{\nu_0}{\nu_1\nu_2}\left(\frac{B_0}{A_0R}\right)^2\left[\nu_1^2(p_{22}-p_2^2)+2\nu_1\nu_2(p_{12}-p_1p_2)+\nu_2^2(p_{11}-p_1^2)\right]$$

$$= -\frac{\nu_0}{2\nu_1\nu_2}\left(\frac{B_0}{A_0R}\right)^2\left[\frac{\mu_2}{k_{11}^{\ 0}}a_1\nu_1^2+2a'_{12}\nu_1\nu_2+\frac{\mu_1}{k_{22}^{\ 0}}a_2\nu^2\right],$$

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* This last equation, here proved true only by comparing the first approximations to β'_0 and $\Sigma r(\nu_1\alpha_r + \nu_2\alpha_{-r})$, may easily be shown to be strictly accurate, by comparing the general expressions for these quantities.

where α_1 and α_2 are given by (9·161), (9·162) and α'_{12} by

(9·22) $$\alpha'_{12} = \mu_1\mu_2\left\{\tfrac{6}{5} - k_1{}^2 + \tfrac{7}{5}k_2 - \tfrac{8}{25}k_{12}{}^0 + \tfrac{1}{25}\left(\frac{k_{11}{}^0}{\mu_2} + \frac{k_{22}{}^0}{\mu_1}\right)\right\}.$$

Consequently, by (5·39), to this order of approximation we have

(9·23) $$\sum_1^\infty(\nu_1\beta_r + \nu_2\beta_{-r}) = \frac{25\mathrm{A}_0\mathrm{R}}{2\mathrm{B}_0\nu_0\nabla_1}\left\{\frac{\mu_2}{k_{11}{}^0}\alpha_1\nu_1{}^2 + 2\alpha'_{12}\nu_1\nu_2 + \frac{\mu_1}{k_{22}{}^0}\alpha_2\nu_2{}^2\right\}.$$

(*e*) *The First Approximation to* $\Sigma(\nu_1\gamma_r + \nu_2\gamma_{-r})$.

The two central terms of the two central equations of type (5·11) are

(9·24) $$\gamma_0\left\{1 + \tfrac{3}{10}\mu_{21}k_{12}{}^0 + \tfrac{3}{20}\frac{\nu_1}{\nu_2}\frac{1}{\mu_1\mu_2}k^0{}_{11}\right\} - \gamma_{-0}(1 - \tfrac{3}{10}k_{12}{}^0) = \frac{675\nu_1}{8\pi\nu_1\nu_2\mu_1\mu_2\mathrm{C}_0\mathrm{K}'_{12}(0)},$$

(9·25) $$-\gamma_0(1 - \tfrac{3}{10}k_{12}{}^0) + \gamma_{-0}\left\{1 + \tfrac{3}{10}\mu_{12}k_{12}{}^0 + \tfrac{3}{20}\frac{\nu_2}{\nu_1}\frac{1}{\mu_1\mu_2}k_{22}{}^0\right\} = \frac{675\nu_2}{8\pi\nu_1\nu_2\mu_1\mu_2\mathrm{C}_0\mathrm{K}'_{12}(0)},$$

which lead to the result (equivalent to that obtained as a first approximation from 5·40),

(9·26) $$\mathrm{C}_0\sum_0^\infty(\nu_1\gamma_r + \nu_2\gamma_{-r}) = \frac{1125}{2\pi\mathrm{K}'_{12}(0)}\frac{c_1\nu_1{}^2 + 2c_{12}\nu_1\nu_2 + c_2\nu_2{}^2}{k_{11}{}^0c_1\nu_1{}^2 + 2k_{12}{}^0c'_{12}\nu_1\nu_2 + \tfrac{3}{20}k_{22}{}^0c_2\nu_2{}^2},$$

where

(9·27), (9·28) $$c_1 \equiv 1 + \tfrac{3}{10}\mu_{12}k_{12}{}^0, \qquad c_2 = 1 + \tfrac{3}{10}\mu_{21}k_{12}{}^0,$$

(9·29) $$c_{12} = 1 - \tfrac{3}{10}k_{12}{}^0 + \tfrac{3}{40}\frac{1}{\mu_1\mu_2}(k_{11}{}^0 + k_{22}{}^0),$$

(9·30) $$c'_{12} = 1 + \tfrac{3}{40}\frac{1}{\mu_1\mu_2}\frac{k_{11}{}^0k_{22}{}^0}{k_{12}{}^0}.$$

A second approximation would replace the right-hand factor in (9·26), by the quotient of one quartic homogeneous polynomial in ν_1, ν_2 by another, and similarly each further approximation would increase the degree of both numerator and denominator by 2.

(*f*) *Values of* $\mathrm{K}'_{12}(0)$ *for Particular Molecular Models.*

In connection with the above approximate formulæ, and their subsequent applications, it is convenient here to write down the values taken by $\mathrm{K}'_{12}(0)$ and the other constants k, when certain particular characteristics are attributed to the molecules.

When the molecules are regarded as rigid elastic spheres of radii σ_1 and σ_2, it may readily be shown (*cf.* 'Phil. Trans.,' A, vol. 216, § 9, p. 320) that

$$\text{(9·31)} \qquad \mathrm{K}'_{12}(0) = 4(\sigma_1+\sigma_2)^2\left(\frac{m_1+m_2}{h\pi m_1 m_2}\right)^{1/2},$$

$$\text{(9·32)} \qquad k_t = \frac{(t+2)_t}{(t+\frac{3}{2})_t} \quad k_{11}{}^t = \left(\frac{2\sigma_1}{\sigma_1+\sigma_2}\right)^2 k_{12}{}^t \quad k_{22}{}^t = \left(\frac{2\sigma_2}{\sigma_1+\sigma_2}\right)^2 k_{12}{}^t \quad k_{12}{}^t = \tfrac{5}{3}\frac{(t+3)_{t+1}}{(t+\frac{5}{2})_{t+1}}.$$

When the molecules are point centres of force proportional to the inverse n^{th} power of the distance, the force at unit distance being $\mathrm{K}_{12}m_1m_2$, it may be shown* that

$$\text{(9·33)} \qquad \mathrm{K}'_{12}(0) = \frac{2}{\pi^{3/2}}\mathrm{I}_1(n)\left(\frac{hm_1m_2}{m_1+m_2}\right)^{\frac{2}{n-1}-1/2}\left[\mathrm{K}_{12}(m_1+m_2)\right]^{\frac{2}{n-1}}\Gamma\left(3-\frac{1}{n-1}\right),$$

where

$$\text{(9·34)} \qquad \mathrm{I}_1(n) \equiv 4\pi\int_0^\infty \sin^2\tfrac{1}{2}\theta\,.\,\alpha\,d\alpha$$

and

$$\text{(9·35)} \qquad \pi-\theta = 2\int_0^{\eta_0}\frac{d\eta}{\sqrt{\left\{1-\eta^2-\dfrac{2}{n-1}\left(\dfrac{\eta}{\alpha}\right)^{n-1}\right\}}},$$

η_0 being the root of the following equation in η:

$$\text{(9·36)} \qquad 1-\eta^2-\frac{2}{n-1}\left(\frac{\eta}{\alpha}\right)^{n-1} = 0.$$

Further,

$$\text{(9·37)} \qquad k_t = \frac{\Gamma\left(t+3-\dfrac{2}{n-1}\right)}{(t+\frac{3}{2})_t\,\Gamma\left(3-\dfrac{2}{n-1}\right)} \qquad k_{12}{}^t = 5\frac{\Gamma\left(t+4-\dfrac{2}{n-1}\right)}{(t+\frac{5}{2})_{t+1}\,\Gamma\left(3-\dfrac{2}{n-1}\right)}\frac{\mathrm{I}_2(n)}{\mathrm{I}_1(n)},$$

where

$$\text{(9·38)} \qquad \mathrm{I}_2(n) = \pi\int_0^\infty \sin^2\theta\,.\,\alpha\,d\alpha.$$

Also

$$\text{(9·39)} \qquad k_{11}{}^t = \left(\frac{\mathrm{K}_{11}}{\mathrm{K}_{12}}\right)^{\frac{2}{n-1}} k_{12}{}^t \qquad k_{22}{}^t = \left(\frac{\mathrm{K}_{22}}{\mathrm{K}_{12}}\right)^{\frac{2}{n-1}} k_{12}{}^t,$$

where K_{11}, K_{22} are the force constants appropriate to a pair of molecules of the first or second kind respectively; we here assume that the law of variation of force with distance is the same whether the molecules are like or unlike—if this be not so, n must

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* *Cf.* 'Phil. Trans.,' A, vol. 216, § 9, p. 320, or JEANS' 'Dynamical Theory of Gases' (2nd edit.), §§ 305 *et seq.* I have adopted the notation of the above equations in order to facilitate comparison with the corresponding equations in JEANS' treatise.

also have suffixes 11, 12, or 22, and the formulæ (9·37)–(9·39) will need to be modified in a manner sufficiently obvious.

When $n = 5$, *i.e.*, when the molecules are Maxwellian, it is clear that

$$(9\cdot40) \qquad \mathrm{K}'_{12}(0) = \frac{3}{2\pi}\,\mathrm{I}_1(5)\,[\mathrm{K}_{12}(m_1+m_2)]^{1/2},$$

$$(9\cdot41) \qquad k_t = 1 \qquad k_{12}{}^{t} = 5\,\frac{\mathrm{I}_2(5)}{\mathrm{I}_1(5)}.$$

§ 10. The Equation of Diffusion.

(*a*) *Definitions of the Various Coefficients of Diffusion.*

In our analysis of molecular motions (§ 1) the rate of inter-diffusion was expressed in terms of u'_0, which is defined by the equations

$$(10\cdot01) \qquad (\nu_1+\nu_2)\,u'_0 = \nu_1(u_1-u_0) = -\nu_2(u_2-u_0) = \frac{\nu_1\nu_2}{\nu_1+\nu_2}(u_1-u_2).$$

Further, by (3·15) and (2·06), we have, as the equation of diffusion,

$$(10\cdot02) \qquad u'_0 = \tfrac{1}{9}\mathrm{A}_0\alpha'_0\left(\frac{1}{2h}\frac{\partial\lambda'_0}{\partial x} - \mathrm{X}'_0 - \frac{m'_0}{\nu_0 m_0}\frac{\partial p_0}{\partial x}\right) + \tfrac{1}{9}\mathrm{B}_0\beta'_0\frac{\partial \mathrm{T}}{\partial x}.$$

Hence it appears that the agents effective in causing diffusion are (taking the terms of this equation in order) a concentration-gradient or variation in the relative proportions of the two component gases, external forces of unequal amounts per unit mass of the two gases, and variations in the total pressure or the temperature of the composite gas.

When the pressure and temperature are uniform, and the external forces are such as to make X'_0, Y'_0, Z'_0 zero, diffusion can take place only if there is a variation in the relative concentration of the component gases. In this case we may compare (10·02) which now has the special form

$$(10\cdot03) \qquad u'_0 = \tfrac{1}{9}\mathrm{A}_0\alpha'_0\frac{1}{2h}\frac{\partial\lambda'_0}{\partial x} = \frac{1}{9\nu_0}\mathrm{A}_0\alpha'_0\frac{1}{2h}\frac{\partial\nu_1}{\partial x} = -\frac{1}{9\nu_0}\mathrm{A}_0\alpha'_0\frac{1}{2h}\frac{\partial\nu_2}{\partial x},$$

with the ordinary equation of diffusion

$$(10\cdot04) \qquad \nu_0 u'_0 = \nu_1(u_1-u_0) = -\mathrm{D}_{12}\frac{\partial\nu_1}{\partial x} \qquad \nu_2(u_2-u_0) = -\mathrm{D}_{12}\frac{\partial\nu_2}{\partial x},$$

where D_{12} is the coefficient of diffusion. By comparison we have

$$(10\cdot05) \qquad \mathrm{D}_{12} = -\tfrac{1}{9}\mathrm{A}_0\mathrm{R}\mathrm{T}\alpha'_0.$$

When the pressure, temperature, and composition of the gas are uniform, a steady motion of diffusion may be produced by equal and opposite forces $\pm(\nu_0 X'_0, \nu_0 Y'_0, \nu_0 Z'_0)$ per unit volume on the two components. This will be termed forced diffusion, and we define the coefficient of forced diffusion D'_{12} by the equation

$$u'_0 = D'_{12}\nu_0 X'_0, \tag{10·06}$$

so that, by comparison with (10·02),

$$D'_{12} = -\tfrac{1}{9}\frac{1}{\nu_0}A_0\alpha'_0 = \frac{1}{p_0}D_{12}. \tag{10·07}$$

From (10·02) it is clear that diffusion will occur also when the relative proportion of the two gaseous components is uniform, and in the absence of external forces such as might produce diffusion, provided that the pressure or temperature varies. If we define coefficients of thermal diffusion D_T and of pressure diffusion D_p by the equation

$$u'_0 = D_p\frac{1}{p_0}\frac{\partial p_0}{\partial x} - D_T\frac{1}{T}\frac{\partial T}{\partial x}, \tag{10·08}$$

we have, by comparison with (10·02)

$$D_p = -\tfrac{1}{9}A_0\alpha'_0\frac{p_0 m'_0}{\nu_0 m_0} = -\tfrac{1}{9}A_0 RT\alpha'_0\frac{m'_0}{m_0} = \frac{m'_0}{m_0}D_{12}, \tag{10·09}$$

$$D_T = -\tfrac{1}{9}B_0\beta'_0 T. \tag{10·10}$$

(*b*) *The Equation of Diffusion.*

If we now substitute the various coefficients of diffusion in the equation of diffusion (10·02), this becomes

$$u'_0 = -D_{12}\frac{\partial\lambda'_0}{\partial x} + D'_{12}\nu_0 X'_0 + D_p\frac{1}{p_0}\frac{\partial p_0}{\partial x} - D_T\frac{1}{T}\frac{\partial T}{\partial x}. \tag{10·11}$$

In later sections, when we consider in detail the values of the four coefficients of diffusion, we shall see that they are all positive (the molecules 1 being the heavier—*cf.* § 1).* Hence from (10·11) we deduce that the direction of diffusion of the heavier component of a gas is (*a*) opposite to the direction of increasing concentration (*b*) in the direction of the diffusion-component of the external force (*c*) in the direction of increasing mean pressure and (*d*) opposite to the direction of increasing temperature.* This is fairly evident as regards (*a*) and (*b*). In case (*c*), the sign of D_p is the same as that of m'_0 (*cf.* (10·09), D_{12} being always positive), which is a multiple of $m_1 - m_2$; the physical reason is also not difficult to grasp—under the influence of a difference of pressure both components will tend to flow in the direction of diminishing pressure, so as to render the pressure uniform. The lighter molecules will travel

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* This statement is modified, with regard to D_T, in Note E, p. 197.

faster than the heavier, however, so that relative to the mean motion the heavier gas will be diffusing in the direction of increasing pressure. Such a process must go on, to some extent, during the passage of sound-waves in air or any mixed gas, and will influence the propagation of the disturbance to a degree which is probably comparable with that of the effects due to viscosity and thermal conduction. The effects of these latter have been examined by STOKES, KIRCHHOFF, and RAYLEIGH.*

It is rather more difficult to perceive, either analytically or physically, that D_T must be positive if the molecules 1 are the heavier (see Note E, p. 197). A discussion of this coefficient will be found in § 14.

If in (10·11) we assign to u'_0 the value zero, we get the equation of condition for a state without diffusion. Some special cases of this equation will be considered in § 16, after the relative magnitudes of the various coefficients of diffusion have been determined.

§ 11. THE EQUATION OF VISCOSITY.

The various pressure components p_{xx}, p_{xy}, *et cetera*, for the composite gas are given by the following and similar equations :—

(11·01)
$$p_{xx} = \nu_1 m_1 \overline{U_1^2} + \nu_2 m_2 \overline{U_2^2}, \qquad p_{xy} = \nu_1 m_1 \overline{U_1 V_1} + \nu_2 m_2 \overline{U_2 V_2}.$$

A reference to (5·24) or to our expressions for f (U, V, W) in § 3 hence enables us to deduce that

(11·02)
$$p_{xx} - p_0 = -\tfrac{4}{675} \frac{1}{2h} C_0 c_{xx} \sum_0^\infty (\nu_1 \gamma_r + \nu_2 \gamma_{-r}),$$

(11·03)
$$p_{xy} = -\tfrac{4}{675} \frac{1}{2h} C_0 c_{xy} \sum_0^\infty (\nu_1 \gamma_r + \nu_2 \gamma_{-r}),$$

We may compare these with the equations of pressure of a gas whose coefficient of viscosity is κ_{12} (*cf.* (2·11) and (2·14) for the values of c_{xx} and c_{xy}) :—

(11·04)
$$p_{xx} - p_0 = -\kappa_{12} \left[2 \frac{\partial u_0}{\partial x} - \tfrac{2}{3} \left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial 2} \right) \right] = -\tfrac{2}{3} \kappa_{12} c_{xx},$$

(11·05)
$$p_{xy} = -\kappa_{12} \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right) = -\tfrac{2}{3} \kappa_{12} c_{xy}.$$

It thus becomes evident that the composite gas behaves like a viscous fluid whose coefficient of viscosity is given by

(11·06)
$$\kappa_{12} = \tfrac{2}{225} \frac{C_0}{2h} \sum_0^\infty (\nu_1 \gamma_r + \nu_2 \gamma_{-r}).$$

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* STOKES, 'Cambridge Transactions,' 8, p. 287, 1845; KIRCHHOFF, 'Pogg. Ann.,' 134, p. 177, 1868; RAYLEIGH, 'Phil. Trans.,' 175, p. 1883, 'Theory of Sound,' II., ch. XIX.

§ 12. The Equation of Energy.

(*a*) *The Deduction of the Equation.*

In order to obtain the equation of energy we return to the consideration of the equation of transfer (2·01). Having determined the form of the velocity distribution function f (U, V, W) correct to the first order of small quantities, we can now make the equations of transfer accurate so far as the second order, and this is necessary in connection with the equation of energy. Also we need no longer suppose that the mean motion of the gas (u_0, v_0, w_0) at the point considered is zero.

We add to (2·01) the corresponding equation for the molecules of the second kind, with the result

$$(12·01)\quad \frac{\partial}{\partial t}(\nu_1\overline{Q_1}+\nu_2\overline{Q_2})+\sum_{xyz}\left[\frac{\partial}{\partial x}\{\nu_1\overline{(u)_1Q_1}+\nu_2\overline{(u)_2Q_2}\}-\left\{\frac{\nu_1}{m_1}X_1\overline{\left(\frac{\partial Q_1}{\partial(u)_1}\right)}+\frac{\nu_2}{m_2}X_2\overline{\left(\frac{\partial Q_2}{\partial(u)_2}\right)}\right\}\right]=\Delta(Q_1+Q_2).$$

In this equation we substitute in turn $Q=1$, $Q=m(u)$, and $Q=\frac{1}{2}m\{(u)^2+(v)^2+(w)^2\}$, thus obtaining the equations of density, momentum, and energy. Since all three of these quantities are conserved unchanged during the molecular encounters, we have in each case $\Delta(Q_1+Q_2)=0$. The first equation takes the form

$$(12·02)\qquad \frac{\partial\nu_0}{\partial t}+\frac{\partial\nu_0u_0}{\partial x}+\frac{\partial\nu_0v_0}{\partial y}+\frac{\partial\nu_0w_0}{\partial z}=0,$$

where we have made use of the notation of § 1. We will denote the operator

$$\frac{\partial}{\partial t}+u_0\frac{\partial}{\partial x}+v_0\frac{\partial}{\partial y}+w_0\frac{\partial}{\partial z}$$

by $\frac{D}{Dt}$, commonly known as the "mobile operator"; if q is any function of x, y z, t, $\frac{Dq}{Dt}$ denotes the rate of change, with respect to time, if the value of q at a point which moves with the mean velocity of the gas. Then the equation of continuity (12·02) may also be written in the form

$$(12·03)\qquad \frac{1}{\nu_0}\frac{D\nu_0}{Dt}+\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)=0.$$

The second equation, the equation of momentum, may be written as

$$(12·04)\quad \frac{\partial}{\partial t}(\rho_1u_1+\rho_2u_2)+\frac{\partial}{\partial x}\{\rho_1\overline{(u)_1^2}+\rho_2\overline{(u)_2^2}\}+\frac{\partial}{\partial y}\{\rho_1\overline{(u)_1(v_1)}+\rho_2\overline{(u)_2(v_2)}\}+\frac{\partial}{\partial z}\{\rho_1\overline{(u)_1(w)_1}+\rho_2\overline{(u)_2(w)_2}\}-(\nu_1X_1+\nu_2X_2)=0,$$

or (*cf.* § 1 and (11·01)) as

$$(12{\cdot}05)\quad \nu_0 X_0 = \frac{\partial}{\partial t}(\rho_0 u_0 + \rho'_0 u'_0) + \frac{\partial}{\partial x}\{\rho_0 u_0^2 + 2\rho'_0 u_0 u'_0 + p_{xx}\}$$
$$+ \frac{\partial}{\partial y}\{\rho_0 u_0 v_0 + \rho'_0 (u_0 v'_0 + u'_0 v_0) + p_{xy}\}$$
$$+ \frac{\partial}{\partial z}\{\rho_0 u_0 w_0 + \rho'_0 (u_0 w'_0 + u'_0 w_0) + p_{xz}\}$$
$$= \nu_0 \frac{\mathrm{D}}{\mathrm{D}t}\{m_0 u_0 + (m_1 - m_2) u'_0\} + \rho'_0 u_0 \left(\frac{\partial u'_0}{\partial x} + \frac{\partial v'_0}{\partial y} + \frac{\partial w'_0}{\partial z}\right)$$
$$+ \left(\frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{xy}}{\partial y} + \frac{\partial p_{xz}}{\partial z}\right) + \left(u'_0 \frac{\partial \rho'_0 u_0}{\partial x} + v'_0 \frac{\partial \rho'_0 u_0}{\partial y} + w'_0 \frac{\partial \rho'_0 u_0}{\partial z}\right).$$

In deducing the third equation, the equation of energy, it is convenient, first of all, to write out the following equations giving the appropriate special values of the various quantities which occur in (12·01):—

$$(12{\cdot}06)\quad \nu_1 \overline{Q_1} + \nu_2 \overline{Q_2} = \tfrac{1}{2}\nu_1 m_1 \left(c_0^2 + 2\frac{1}{\lambda_1}\Sigma u_0 u'_0 + \overline{C_1^2}\right) + \tfrac{1}{2}\nu_2 m_2 \left(c_0^2 - 2\frac{1}{\lambda_2}\Sigma u_0 u'_0 + \overline{C_2^2}\right)$$
$$= \tfrac{1}{2}\rho_0 c_0^2 + \rho'_0 \Sigma u_0 u'_0 + \tfrac{3}{2}\mathrm{R}\nu_0 \mathrm{T},$$

$$(12{\cdot}07)\quad \nu_1 \overline{(u)_1 Q_1} + \nu_2 \overline{(u)_2 Q_2} = u_0 (\tfrac{1}{2}\rho_0 c_0^2 + \rho'_0 \Sigma u_0 u'_0 + \tfrac{3}{2}\mathrm{R}\nu_0 \mathrm{T}) + \tfrac{1}{2}\rho'_0 u'_0 c_0^2$$
$$+ (u_0 p_{xx} + v_0 p_{xy} + w_0 p_{xz}) + (\tfrac{1}{2}\rho_1 \overline{\mathrm{U}_1 C_1^2} + \tfrac{1}{2}\rho_2 \overline{\mathrm{U}_2 C_2^2}),$$

$$(12{\cdot}08)\quad \frac{\nu_1}{m_1} X_1 \overline{\left(\frac{\partial Q_1}{\partial (u)_1}\right)} + \frac{\nu_2}{m_2} X_2 \overline{\left(\frac{\partial Q_2}{\partial (u)_2}\right)} = \nu_1 u_1 X_1 + \nu_2 u_2 X_2 = \nu_0 u_0 X_0 + \nu_0 u'_0 (X_1 - X_2).$$

On substitution of these values in (12·01), this becomes

$$(12{\cdot}09)\quad \nu_0 \frac{\mathrm{D}}{\mathrm{D}t}\{\tfrac{1}{2}m_0 c_0^2 + (m_1 - m_2)\Sigma u_0 u'_0 + \tfrac{3}{2}\mathrm{RT}\} + \tfrac{1}{2}\Sigma \frac{\partial}{\partial x}(\rho'_0 c_0^2 u'_0)$$
$$+ \Sigma \frac{\partial}{\partial x}(u_0 p_{xx} + v_0 p_{xy} + w_0 p_{xz}) + \Sigma \frac{\partial}{\partial x}(\tfrac{1}{2}\rho_1 \overline{\mathrm{U}_1 C_1^2} + \tfrac{1}{2}\rho_2 \overline{\mathrm{U}_2 C_2^2})$$
$$- \nu_0 \Sigma u'_0 (X_1 - X_2) - \nu_0 \Sigma u_0 X_0 = 0.$$

This equation can be simplified by eliminating $\nu_0 \Sigma u_0 X_0$; thus from (12·05) we deduce that

$$(12{\cdot}10)\quad \nu_0 \Sigma u_0 X_0 = \nu_0 \frac{\mathrm{D}}{\mathrm{D}t}(\tfrac{1}{2}m_0 c_0^2) + \nu_0 \Sigma u_0 \frac{\mathrm{D}}{\mathrm{D}t}(m_1 - m_2) u'_0 + \rho'_0 c_0^2 \left(\frac{\partial u'_0}{\partial x} + \frac{\partial v'_0}{\partial y} + \frac{\partial w'_0}{\partial z}\right)$$
$$\Sigma u_0 \left(\frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{xy}}{\partial y} + \frac{\partial p_{xz}}{\partial z}\right) + \tfrac{1}{2}\Sigma u'_0 \frac{\partial \rho'_0 c_0^2}{\partial x},$$

by means of which we may transform (12·09) into

$$(12{\cdot}11)\quad \tfrac{3}{2}\mathrm{R}\nu_0\frac{\mathrm{DT}}{\mathrm{D}t}+\nu_0(m_1-m_2)\,\Sigma u'_0\frac{\mathrm{D}u_0}{\mathrm{D}t}-\tfrac{1}{2}\rho'_0c_0^{\,2}\left(\frac{\partial u'_0}{\partial x}+\frac{\partial v'_0}{\partial y}+\frac{\partial w'_0}{\partial z}\right)-\nu_0\Sigma u'_0(\mathrm{X}_1-\mathrm{X}_2)$$

$$+\Sigma\left(p_{xx}\frac{\partial u_0}{\partial x}+p_{xy}\frac{\partial v_0}{\partial x}+p_{xz}\frac{\partial w_0}{\partial x}\right)+\Sigma\frac{\partial}{\partial x}\left(\tfrac{1}{2}\rho_1\overline{\mathrm{U}_1\mathrm{C}_1^{\,2}}+\tfrac{1}{2}\rho_2\overline{\mathrm{U}_2\mathrm{C}_2^{\,2}}\right)=0.$$

In this equation we substitute the values of p_{xx}, p_{xy}, p_{xz} from (11·04), (11·05), *et cetera.* Also we divide throughout by J, the mechanical equivalent of heat, and replace $\frac{3}{2}\frac{\mathrm{R}}{\mathrm{J}m_0}$ by C_v, the specific heat of the gas at constant volume.* After a little reduction we obtain the equation of energy in the following form :—

$$(12{\cdot}12)\quad \rho_0\mathrm{C}_v\frac{\mathrm{DT}}{\mathrm{D}t}+\tfrac{2}{3}\rho_0\mathrm{C}_v\mathrm{T}\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)=\frac{1}{\mathrm{J}}\Sigma\nu_0u'_0\left\{\left(\mathrm{X}_1-m_1\frac{\mathrm{D}u_0}{\mathrm{D}t}\right)-\left(\mathrm{X}_2-m_2\frac{\mathrm{D}u_0}{\mathrm{D}t}\right)\right\}$$

$$+\tfrac{1}{2}\frac{\nu_0}{\mathrm{J}}(m_1-m_2)\,c_0^{\,2}\left(\frac{\partial u'_0}{\partial x}+\frac{\partial v'_0}{\partial y}+\frac{\partial w'_0}{\partial z}\right)$$

$$+\frac{\kappa_{12}}{\mathrm{J}}\left\{2\Sigma\left(\frac{\partial u_0}{\partial x}\right)^2+\Sigma\left(\frac{\partial w_0}{\partial y}+\frac{\partial v_0}{\partial z}\right)^2-\tfrac{2}{3}\left(\Sigma\frac{\partial u_0}{\partial x}\right)^2\right\}$$

$$-\frac{1}{\mathrm{J}}\Sigma\frac{\partial}{\partial x}\left(\tfrac{1}{2}\rho_1\overline{\mathrm{U}_1\mathrm{C}_1^{\,2}}+\tfrac{1}{2}\rho_2\overline{\mathrm{U}_2\mathrm{C}_2^{\,2}}\right).$$

(*b*) *The Interpretation of the Equation of Energy.*

We will now consider the significance of the various terms in the equation of energy (12·12). The terms on the right depend on diffusion, viscosity, and thermal conduction (as will be made clearer later). If we neglect the small changes of energy produced by these means, as a first approximation (12·12) may be written

$$(12{\cdot}13)\qquad \frac{1}{\mathrm{T}}\frac{\mathrm{DT}}{\mathrm{D}t}+\tfrac{2}{3}\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)=0,$$

where we have omitted the right-hand side of (12·12), and divided the left hand by $\rho_0\mathrm{C}_v\mathrm{T}$.

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* The specific heat of a simple gas at constant volume is $\frac{3}{2}\frac{\mathrm{R}}{\mathrm{J}m}$, if m is the molecular mass (*cf.* JEANS' 'Dynamical Theory of Gases,' 2nd edit., § 261, (512)). Hence for a composite gas we have

$$\rho_0\mathrm{C}_v=\tfrac{3}{2}\rho_1\frac{\mathrm{R}}{\mathrm{J}m_1}+\tfrac{3}{2}\rho_2\frac{\mathrm{R}}{\mathrm{J}m_2}=\tfrac{3}{2}\frac{\mathrm{R}}{\mathrm{J}}\left(\frac{\rho_1}{m_1}+\frac{\rho_2}{m_2}\right)=\tfrac{3}{2}\nu_0\frac{\mathrm{R}}{\mathrm{J}},$$

and consequently

$$\mathrm{C}_v=\tfrac{3}{2}\frac{\mathrm{R}}{\mathrm{J}m_0},$$

By the equation of continuity (12·03), the last equation is equivalent to

$$(12{\cdot}14) \qquad \frac{1}{\mathrm{T}}\frac{\mathrm{DT}}{\mathrm{D}t}-\tfrac{2}{3}\frac{1}{\nu_0}\frac{\mathrm{D}\nu_0}{\mathrm{D}t}=0,$$

or to

$$(12{\cdot}15) \qquad \frac{\mathrm{D}}{\mathrm{D}t}(\mathrm{T}\nu_0^{-2/3})=0 \qquad \frac{\mathrm{D}}{\mathrm{D}t}(p_0\nu_0^{-5/3})=0.$$

Since we are neglecting diffusion, m_0 (or $\lambda_1 m_1+\lambda_2 m_2$) is invariable, and (12·15) expresses the adiabatic law of expansion of a monatomic gas as a given element is followed throughout its motion, viz.,

$$(12{\cdot}16) \qquad p_0 = k\rho_0^{5/3} \qquad \mathrm{T} = k'\rho_0^{2/3}.$$

Thus (12·12) may be regarded as giving the correction to this law owing to diffusion, viscosity, and conduction. The left-hand side represents the net rate of increase of energy of molecular agitation, being the increase corresponding to the rising temperature after allowing for the change of heat energy produced by adiabatic expansion or compression. The right-hand side indicates that this is due to the following causes:—

(α) We are considering the fluid contained in a volume element which moves with the mean motion of the fluid; but in addition to this motion there is one of inter-diffusion within the element, there being a stream of $\pm(\nu_0 u'_0,\ \nu_0 v'_0,\ \nu_0 w'_0)$ molecules per unit time per unit volume in opposite directions. The x-components of the effective forces on each of these molecules are $\mathrm{X}_1-m_1\dfrac{\mathrm{D}u_0}{\mathrm{D}t}$ and $\mathrm{X}_2-m_2\dfrac{\mathrm{D}u_0}{\mathrm{D}t}$ respectively, the second term depending on $\dfrac{\mathrm{D}u_0}{\mathrm{D}t}$ being present, since we are throughout concerned with the energy relative to the mean motion $(u_0,\ v_0,\ w_0)$. The work done on the fluid by these forces is expressed, in thermal units, by the first right-hand term of (12·12).

(β) Owing to the motion of diffusion there will be an increase in the number of molecules m_1 and an equal decrease in the number of molecules m_2, at the rate of $\left(\dfrac{\partial u'_0}{\partial x}+\dfrac{\partial v'_0}{\partial y}+\dfrac{\partial w'_0}{\partial z}\right)$ per unit time per unit volume. The mean energy of peculiar motion is the same for molecules m_1 and m_2, so that this change affects only the energy of mean motion, which is $\frac{1}{2}m_1c_0^2$ for a molecule m_1, and $\frac{1}{2}m_2c_0^2$ for a molecule m_2. The increase of energy due to this cause is represented by the second right-hand term of (12·12).

(γ) The third term gives the heat generated by the viscous forces acting in the gas, being, in fact, twice the "dissipation function" of the viscous motion.*

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* *Cf.* LAMB, 'Hydrodynamics,' p. 518.

(δ) The fourth term represents the increase of heat which ordinary physics regards as due to conduction, together with a term due to diffusion which has not, so far as I know, been hitherto recognised in either ordinary physics or the kinetic theory. These two terms are discussed in detail in the next section of this chapter.

(c) *Conduction of Heat and the Thermal Flux of Diffusion.*

If there is no mass motion the equation of energy takes the form

$$(12{\cdot}17) \qquad \rho_0 C_v \frac{\partial T}{\partial t} = \frac{1}{J}\Sigma \nu_0 u'_0 (X_1 - X_2) - \frac{1}{J}\Sigma \frac{\partial}{\partial x}\left(\tfrac{1}{2}\rho_1 \overline{U_1 C_1^2} + \tfrac{1}{2}\rho_2 \overline{U_2 C_2^2}\right),$$

and in the last term we will now substitute from (5·25), with the result

$$(12{\cdot}18) \qquad \rho_0 C_v \frac{\partial T}{\partial t} = \frac{1}{J}\Sigma \nu_0 u'_0 (X_1 - X_2)$$
$$+ \tfrac{1}{3}\Sigma \frac{\partial}{\partial x}\frac{RT}{J}\left\{A_0 \xi'_0 \sum_1^\infty r(\nu_1\alpha_r + \nu_2\alpha_{-r}) + B_0 \frac{\partial T}{\partial x}\sum_1^\infty(\nu_1\beta_r + \nu_2\beta_{-r})\right\}.$$

It is convenient to eliminate ξ'_0 by means of (3·15), and on so doing (12·18) becomes transformed into

$$(12{\cdot}19) \qquad \rho_0 C_v \frac{\partial T}{\partial t} = \frac{1}{J}\Sigma \nu_0 u'_0 (X_1 - X_2)$$
$$+ \Sigma \frac{\partial}{\partial x}\frac{RT}{J}\left[\frac{\sum_1^\infty r(\nu_1\alpha_r + \nu_2\alpha_{-r})}{\alpha'_0}u'_0 + \tfrac{1}{3}B_0 \frac{\partial T}{\partial x}\left\{\sum_1^\infty(\nu_1\beta_r + \nu_2\beta_{-r})\right.\right.$$
$$\left.\left. - \tfrac{1}{3}\frac{\beta'_0}{\alpha'_0}\sum_1^\infty r(\nu_1\alpha_r + \nu_2\alpha_{-r})\right\}\right].$$

If we suppose that no diffusion is taking place, so that (u'_0, v'_0, w'_0) are all zero, and compare (12·19) with FOURIER's equation of conduction of heat in a gas at rest, *i.e.*, with

$$(12{\cdot}20) \qquad \rho_0 C_v \frac{\partial T}{\partial t} = \Sigma \frac{\partial}{\partial x}\left(\vartheta \frac{\partial T}{\partial x}\right),$$

we obtain the following equation for the coefficient of thermal conduction ϑ :—

$$(12{\cdot}21) \qquad \vartheta = \tfrac{1}{3}B_0 \frac{RT}{J}\left\{\sum_1^\infty(\nu_1\beta_r + \nu_2\beta_{-r}) - \frac{\beta'_0}{\alpha'_0}\sum_1^\infty r(\nu_1\alpha_r + \nu_2\alpha_{-r})\right\}.$$

From (12·19) we perceive also that the motion of inter-diffusion is accompanied by a flow of heat, which is proportional to the velocity of diffusion, and also depends on the temperature and the molecular densities, but is independent of the other characteristics of the gas. We shall term this process the thermal flux of diffusion;

in the absence of thermal conduction and of external forces we shall have as the equation of energy

$$(12{\cdot}22) \qquad \rho_0 C_v \frac{\partial T}{\partial t} = \Sigma \frac{\partial}{\partial x} (\mathfrak{D} u'_0),$$

where $\mathfrak{D}$ is defined by the equation

$$(12{\cdot}23) \qquad \mathfrak{D} \equiv \frac{RT}{J} \frac{1}{\alpha'_0} \sum_{1}^{\infty} r (\nu_1 \alpha_r + \nu_2 \alpha_{-r}),$$

and is termed the specific energy of diffusion.

We now proceed to consider in detail the various coefficients of diffusion, conduction, viscosity, and specific energy of diffusion for which we have obtained general formulæ.

§ 13. THE COEFFICIENT OF DIFFUSION D_{12}.

(a) *The General Formula.*

The general formula for the coefficient of diffusion D_{12} is obtainable in terms of the molecular data by substitution in (10·05) of the value of α'_0 given by (5·35), thus

$$(13{\cdot}01) \qquad D_{12} = \tfrac{1}{9} A_0 RT \lambda_1 \lambda_2 \frac{\nabla' (\delta_{mn} a_{mn})}{\nabla (\delta_{mn} a_{mn})} \cdot$$

So far as § 9 (*b*) A_0 had remained quite arbitrary, only the product of A_0 into the coefficients α being definite. We there defined A_0 as having such a value as to make a_{00} equal to unity. We now substitute that value (*cf.* (9·022)), viz.,

$$(13{\cdot}02) \qquad A_0 = \frac{27 (m_1 + m_2)}{2\pi \lambda_1 \lambda_2 \nu_0 m_1 m_2 K'_{12}(0)}$$

in (13·01), with the result that

$$(13{\cdot}03) \qquad D_{12} = \frac{3 (m_1 + m_2) RT}{2\pi \nu_0 m_1 m_2 K'_{12}(0)} \frac{\nabla' (\delta_{mn} a_{mn})}{\nabla (\delta_{mn} a_{mn})},$$

where ∇' is the principal minor of ∇.

(b) *The Case of Maxwellian Molecules.*

In the case of Maxwellian molecules it is readily evident from (6·03) that all the elements of the first row and column of $\nabla (\delta_{mn} a_{mn})$, save the initial element a_{00}, are zero. Hence in this case ∇ is equal to $a_{00} \nabla'$, *i.e.*,

$$(13{\cdot}04) \qquad \frac{\nabla' (\delta_{mn} a_{mn})}{\nabla (\delta_{mn} a_{mn})} = \frac{1}{a_{00}} = 1,$$

in view of the convention in § 13 (a) as to the value of a_{00}. Hence, by (13·03), we have

$$D_{12} = \frac{3(m_1+m_2)RT}{2\pi\nu_0 m_1 m_2 K'_{12}(0)} \tag{13·05}$$

as the exact value of D_{12} when the molecules are Maxwellian. The same result follows readily also from (10·05), (6·03), and (6·04). It is the same, except as regards the notation, as the formula deduced by MAXWELL in his second great memoir on the dynamical theory of gases.*

(c) *A First Approximation to the Coefficient of Diffusion.*

Only in the case just considered does our general formula for D_{12} reduce to a simple finite form: usually we must, for practical purposes, be content to make approximations to the exact result. As in § 9, this may be effected by taking successive finite convergents to our infinite determinants, which is equivalent to neglecting all terms in the expansion of $f(\mathsf{U}, \mathsf{V}, \mathsf{W})$ after the first one, two or more at the beginning. Thus for a first approximation, taking only the central element of $\nabla(\delta_{mn}a_{mn})$, it is clear that ∇'/∇ is equal to $1/a_{00}$ or unity simply (*cf.* § 13a). Hence we have

$$D_{12} = \frac{3(m_1+m_2)RT}{2\pi\nu_0 m_1 m_2 K'_{12}(0)} \qquad \text{(1st approximation)}, \tag{13·06}$$

a result which also follows from (10·05) and (9·03). This, it will be noticed, is the same as (13·05), showing that what is in general only a first approximation to D_{12} is in the case of Maxwellian molecules a strictly accurate result.

The formula (13·06) is not new; it was first given by LANGEVIN,† and subsequently by myself‡ independently. In all these cases, and also in MAXWELL'S investigation the method used was an approximate one which involves the assumption that the peculiar velocities of the molecules of the two constituent gases are distributed about the *separate* mean velocities c_1, c_2 according to MAXWELL'S law for the steady state of a gas. The method of the present paper is based on an actual determination of the law of distribution. The assumed law just mentioned, if expressed in the manner adopted in § 3, would involve no α-coefficient beyond α_0 (neglecting squares or higher powers of the velocity of diffusion c'_0). This coincides with the true law only in the case of Maxwellian molecules (§ 6), so that only in that case is (13·06) exact: MAXWELL himself did not prove this rigorously, though he obtained the

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* MAXWELL, 'Phil. Trans.,' vol. 157 (1866); or 'Scientific Papers,' ii., p. 27.

† LANGEVIN, 'Ann. de Chimie et de Physique' (8), v., 245, 1905: *cf.* also ENSKOG, 'Phys. Zeit.,' xii. 533, 1911.

‡ 'Phil. Trans.,' A, vol. 211, p. 499 (35), 1911.

accurate expression. In the general case (13·06) is an approximation only, and the method used by MAXWELL and the other writers just named does not afford a ready means of estimating the error involved. The present investigation makes it clear that in extreme cases this is far from small.

(*d*) *A Second Approximation to the Coefficient of Diffusion.*

Passing now to a second approximation, by means of (10·05) and (9·15) we obtain the result

$$D_{12} = \frac{1}{1-\epsilon_0}\frac{3(m_1+m_2)RT}{2\pi\nu_0 m_1 m_2 K'_{12}(0)} \qquad \text{(2nd approximation).} \tag{13·07}$$

The correction to (13·06) consists of a factor $(1-\epsilon_0)^{-1}$, ϵ_0 being given by (9·14) and (9·09)–(9·13); since for Maxwellian molecules $k_1 = 1$, it follows from (9·14) that $\epsilon_0 = 0$ in their case. In order to estimate the importance of ϵ_0 in other cases we must consider some special typical molecular models, and determine the numerical values of ϵ_0 for such gases. The most important models are those for which $K'_{12}(0)$, k_t, etc., are given in § 9 (*f*).

In paragraph (*g*) of this section we shall consider in detail the range in the values of ϵ_0 calculated from these numbers, for various ratios of the molecular masses and diameters. Since ϵ_0 only affords a second approximation to D_{12}, however, and not the exact value, it is convenient first of all to examine certain particular cases of our formulæ (*cf.* §§ 7, 8) which throw some light on the accuracy of a second approximation in general.

(*e*) *The Coefficient of Diffusion when* $m_1 : m_2$ and σ_1/σ_2 *are Very Large.*

In the special case when the mass and size of a molecule of the first kind are so great, compared with that of a molecule of the second kind, that m_2/m_1 is negligible (*cf.* § 7), we obtain from (10·05), (7·20) and (13·03) the result

$$D_{12} = \frac{3RT}{2\pi\nu_0 m_2 K'_{12}(0)}\frac{D_0}{D} = \frac{D_0}{D}\frac{3}{16\nu_0(\sigma_1+\sigma_2)^2(h\pi m_2)^{1/2}}, \tag{13·08, 9}$$

where D is a determinant (occupying only a quadrant of the infinite plane) whose general element is given by (7·21), while D_0 is its principal minor. As usual, for Maxwellian molecules $D_0 = D$. We proceed to make successive numerical approximations to D_0/D in the case of molecules of other types.

For molecules which are rigid elastic spheres we have seen (9·32) that

$$k_t = \frac{(t+2)_t}{(t+\frac{3}{2})_t}, \tag{13·10}$$

so that by (7·21) the general element of D is

$$(13{\cdot}11) \qquad \delta_{rs}a_{rs} = \delta_{rs}\frac{(r+s+2)_{r+s}}{(r+\frac{3}{2})_r\,(s+\frac{3}{2})_s}, \qquad r \geqslant 0,\ s \geqslant 0.$$

The following are the numerical values of the elements as far as the fourth row and column, the exact values being given in the first expression, and the decimal values to three significant figures in the second :—

$$(13{\cdot}12)\quad D = \begin{vmatrix} 1 & \frac{1}{5} & -\frac{1}{5.7} & \frac{3}{5.7.9} \\ \frac{1}{5} & \frac{13}{5.5} & \frac{23}{5.5.7} & -\frac{33}{5.5.7.9} \\ -\frac{1}{5.7} & \frac{23}{5.5.7} & \frac{433}{5.5.7.7} & \frac{1077}{5.5.7.7.9} \\ \frac{3}{5.7.9} & -\frac{33}{5.5.7.9} & \frac{1077}{5.5.7.7.9} & \frac{26613}{5.5.7.7.9.9} \end{vmatrix} = \begin{vmatrix} 1{\cdot}000 & 0{\cdot}200 & -0{\cdot}029 & 0{\cdot}010 \\ 0{\cdot}200 & 0{\cdot}520 & 0{\cdot}131 & -0{\cdot}021 \\ -0{\cdot}029 & 0{\cdot}131 & 0{\cdot}353 & 0{\cdot}098 \\ 0{\cdot}010 & -0{\cdot}021 & 0{\cdot}098 & 0{\cdot}268 \end{vmatrix}$$

By neglecting the rows and columns of D after the first, second, third and fourth respectively we obtain the following four successive approximations to D_0/D :—

TABLE I.

Approximation.	D.	D_0/D.	
1st	$1{\cdot}000$	$1{\cdot}0000$	
2nd	$\frac{13}{25} = 0{\cdot}480$	$\frac{13}{12} = 1{\cdot}0833$	833
3rd	$\frac{4608}{25.25.49} = 0{\cdot}150$	$\frac{5100}{4608} = 1{\cdot}1068$	235
4th	$\frac{106168100}{5^6 7^4 9^2} = 0{\cdot}035$	$\frac{1185408^4}{1061681} = 1{\cdot}1165$	97

The successive approximations to D_0/D evidently converge with some rapidity to the value 1·12 or, more nearly, 1·13; the correction introduced by the second approximation covers two-thirds of the error of the first.

It is of importance and interest to notice that in this case an exact solution is obtainable by another method, less general than that of this memoir, but more effective in the particular case before us; this solution is due to LORENTZ, and may be expressed in our notation by[*]

(13·13)
$$D_{12} = \frac{2}{3\nu_0\pi(\sigma_1+\sigma_2)^2(h\pi m_2)^{1/2}}.$$

This is identical with our own solution (13·09) if

(13·14)
$$\frac{D_0}{D} = \frac{32}{9\pi} = 1{\cdot}1317,$$ [†]

and our approximations to D_0/D show how this numerical value is approached by the successive convergents to our infinite-determinantal solution.[‡] Incidentally, we may notice that (13·14) affords an expression for π of a kind which, so far as I am aware, is quite new.

If the molecules are n^{th} power centres of force (*cf.* § 9 (f)), our general formula (13·09) becomes (when m_2/m_1 is negligible)

(13·15)
$$D_{12} = \frac{D_0}{D}\,\frac{3\pi}{8\nu_0 I_1(n)(hm_1m_2K_{12})^{\frac{2}{n-1}}(h\pi m_2)^{1/2}\,\Gamma\left(3-\frac{2}{n-1}\right)},$$

and the general term of the determinant D is given by

(13·16)
$$\delta_{rs}a_{rs} = \delta_{rs}\frac{\Gamma\left(r+s+3-\frac{2}{n-1}\right)}{(r+\frac{3}{2})_r\,(s+\frac{3}{2})_s\,\Gamma\left(3-\frac{2}{n-1}\right)}.$$

With this we may compare the exact formula obtained by JEANS (*loc. cit.*), using the method of LORENTZ,

(13·17)
$$D_{12} = \frac{\frac{2}{3}\Gamma\left(2+\frac{2}{n-1}\right)}{\nu_0 I_1(n)(hm_1m_2K_{12})^{\frac{2}{n-1}}(h\pi m_2)^{1/2}}.$$

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[*] *Cf.* LORENTZ, 'Archives Néerlandaises,' 10, p. 336, 1905; 'Theory of Electrons,' p. 268. Also, for a more general theory along the same lines, *cf.* JEANS' 'Dynamical Theory of Gases' (2nd ed.), § 333 (654) or § 450 (890).

PIDDUCK, 'Proc. Lond. Math. Soc.' (2), 15, p. 112, 1915, has also deduced LORENTZ'S result as a special case of the general method of solution by integral equations.

[†] [I have now obtained a rigorous proof of this equation and of (13·18).—*February 22, 1917.*]

[‡] *Cf.* the footnote to page 171.

These are equivalent, so that

$$(13\cdot18)\quad \frac{D_0}{D} = \frac{16}{9\pi}\Gamma\left(2+\frac{2}{n-1}\right)\Gamma\left(3-\frac{2}{n-1}\right)$$

$$= \frac{16}{9\pi}\left(1+\frac{2}{n-1}\right)\frac{2}{n-1}\left(2-\frac{2}{n-1}\right)\left(1-\frac{2}{n-1}\right)\Gamma\left(\frac{2}{n-1}\right)\Gamma\left(1-\frac{2}{n-1}\right)$$

$$= \frac{16}{9}\left(1+\frac{2}{n-1}\right)\frac{2}{n-1}\left(2-\frac{2}{n-1}\right)\left(1-\frac{2}{n-1}\right)\frac{1}{\sin\frac{2\pi}{n-1}},$$

by a well-known formula in the theory of gamma functions. When $n = 5$ (the case of Maxwellian molecules), the last equation gives $D_0/D = 1$, as it should do. When $n = \infty$, corresponding to the case of rigid elastic spheres, $D_0/D = \frac{32}{9\pi}$, as before. It is of interest to consider one or two intermediate values of n in order to see with what rapidity our determinantal expression for D_0/D converges to the value given by (13·18); we shall not go beyond a third approximation.

The determinant D, as far as the third row and column, is as follows, where $\frac{1}{2}m$ has been written in place of $\frac{2}{n-1}$:—

$$(13\cdot19)\quad D = \begin{vmatrix} 1 & \frac{1-m}{5} & -\frac{1-m^2}{5.7} \\ \frac{1-m}{5} & \frac{13-4m+m^2}{5.5} & \frac{23-27m+5m^2-m^3}{5.5.7} \\ -\frac{1-m^2}{5.7} & \frac{23-27m+5m^2-m^3}{5.5.7} & \frac{433-216m+70m^2-8m^3+m^4}{5.5.7.7} \end{vmatrix}.$$

In the following table are given the first three approximations to D_0/D for a few typical values of n, together with the exact values calculated from (13·18):—

TABLE II.

n.	m.	D_0/D.			
		Approximations.			Exact value.
		1st.	2nd.	3rd.	
5	1	1·000	1·000	1·000	1·000
9	$\frac{1}{2}$	1·000	1·023	1·027	1·031
13	$\frac{1}{3}$	1·000	1·039	1·048	1·056
17	$\frac{1}{4}$	1·000	1·049	1·060	1·072
∞	0	1·000	1·083	1·107	1·132

This table well illustrates the general remarks on the convergence* of our formulæ which were made in § 9 (*a*).

(*f*) *The Coefficient of Self-Diffusion of a Gas.*

The next simplest case of a general character which we shall consider is that in which the two sets of molecules are alike in mass and dynamical properties; a special case of this is that of a simple gas, the two sets of molecules being identical—the corresponding coefficient of diffusion D_{12} will be written D_{11} and termed the coefficient of self-diffusion. From (10·05), and (8·9), the latter equation being the one appropriate to the case before us, we find that

$$(13{\cdot}20) \qquad D_{11} = \frac{3RT}{\pi\nu_0 m K'_{12}(0)} \frac{\nabla'_0}{\nabla_0},$$

where we may now omit the distinguishing suffixes 1, 2; ∇'_0 is the principal minor of ∇_0, whose general element is given by (8·10). We may note that the factor ∇'_0/∇_0 is independent of ν_1 and ν_2 (§ 8).

As far as the first two rows and columns, ∇_0 has the following form :—

$$(13{\cdot}21) \qquad \nabla_0 = \begin{vmatrix} 1 & \frac{1}{2}(k_1-1) \\ \frac{1}{2}(k_1-1) & \frac{1}{20}(11-10k_1+7k_2)+\frac{2}{25}k_{12}{}^0 \end{vmatrix}.$$

The first and second approximations to ∇'_0/∇_0 for a few typical molecular models are given in the subjoined table: the model chosen is the n^{th} power centre of force, which is equivalent to a rigid elastic sphere when $n = \infty$.

TABLE III.

∇_0/∇.	Maxwellian gas, $n = 5$.	$n = 9$.	$n = 17$.	Rigid elastic spheres, $n = \infty$.
1st approximation . . .	1·000	1·000	1·000	1·000
2nd approximation . . .	1·000	1·004	1·008	$\frac{209}{206} = 1{\cdot}015$

In calculating the approximations to ∇'_0/∇_0 for $n = 9$ and $n = 17$ we have adopted the values 0·420 and 0·390 respectively for $I_2(n)/I_1(n)$; it would be very troublesome

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* [*Added June 2, 1916.*—It is interesting to notice that in all the cases in Table II. the error of the third approximation to D_0/D is equal (to the order of accuracy of one unit in the last figure given) to the difference between the second and third approximations.

After each step in the approximation the ratio of successive increments seems to become progressively larger, and from Table I. it would be difficult to judge whether D_0/D converges to 1·12 or 1·13, if we did not know the correct value to be 1·1317.]

to calculate the exact values of these functions, but fortunately the present calculation does not require them to be known with any great accuracy. When $n = 5$ we have $I_2(5)/I_1(5) = 0{\cdot}501$, and when $n = \infty$ the value is $0{\cdot}333$ (*cf.* JEANS' treatise, 2nd ed., § 33), so that the assumed values when $n = 9$ and $n = 7$ cannot be materially in error.

The value of ∇'_0/∇_0 is in all the cases considered ($n = 5$ to $n = \infty$) very nearly equal to unity, the correction introduced by a second approximation being so small that further approximations are not likely to lead to any but a negligible increase in accuracy. Thus the exact value of ∇'_0/∇ in the case of rigid elastic spherical molecules, for instance, is not likely to differ from 1·017 (slightly greater than 1·015) by more than one part in a thousand.

The exact expression for D_{11} corresponding to molecules of the type just mentioned is consequently given by the following equation :—

$$D_{11} = 1{\cdot}017 \frac{3}{32\nu_0\sigma^2(2h\pi m)^{1/2}} \tag{13·22}$$

$$= \frac{0{\cdot}1520}{\nu(2\sigma)^2(hm)^{1/2}} \tag{13·23}$$

$$= 1{\cdot}200\frac{\kappa}{\rho}, \tag{13·24}$$

where in the last line we have made use of the formula for the coefficient of viscosity κ for a simple gas, which has already been given by the author ('Phil. Trans.,' A, vol. 216, § 11 (D), p. 337), viz.,

$$\kappa = 1{\cdot}016\frac{5}{64(2\pi)^{1/2}}\frac{1}{\nu\sigma^2(hm)^{1/2}}. \tag{13·25}$$

In my first paper on the kinetic theory ('Phil. Trans.,' A, vol. 211, p. 477, 1912) the formulæ (13·22)–(13·25) were given as above except for the omission of the factors 1·017 and 1·016 in the first and last, which resulted in 0·150 taking the place of 0·1520 in (13·23).

The expression (13·23) for D_{11} agrees almost exactly also with a result obtained by PIDDUCK* for the same quantity, by an entirely different method. Mr. PIDDUCK's work is based on HILBERT's transformation of BOLTZMANN's integral equation for the velocity-distribution function.† His formula for D_{11} (*loc. cit.*, p. 101, 41) is the same as (13·23) except that the numerical constant, there given only to three places of decimals, is 0·151.

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* PIDDUCK, 'Proc. Lond. Math. Soc.,' (2), 15, p. 89, 1915.

† HILBERT, 'Math. Ann.,' 72, p. 562, 1912; BOLTZMANN, 'Vorlesungen über Gastheorie,' I.

We may also compare (13·24) with the result obtained from the simple mean-free-path theory (first introduced by Maxwell*) with Jeans' correction† for the persistence of velocities, viz. (in our notation)

$$\mathrm{D}_{11} = 1{\cdot}34\,\frac{\kappa}{\rho}. \tag{13·26}$$

This is therefore about 10 per cent. larger than the exact value (13·24).

(*g*) *The Variation of* D_{12} *with the Relative Concentration of the Component Gases.*

In the course of the development of the kinetic theory perhaps no branch has been the subject of more dispute than that dealing with diffusion. The point of greatest difference was the effect on the rate of diffusion of the relative concentration of the diffusing gases. Meyer's elementary mean-free-path theory‡ led to a formula for D_{12} according to which the coefficient of diffusion should vary with the proportions of the mixture over the extreme range indicated by the equation

$$\frac{(\mathrm{D}_{12})_{\nu_1=0}}{(\mathrm{D}_{12})_{\nu_2=0}} = \frac{m_2}{m_1}. \tag{13·27}$$

Thus, when the molecular masses are very unequal, the range in the value of D_{12} should be very great. No such large variation is found to exist, however, according to the results of experiment.

Meyer's theory took no account of the tendency of a molecule to persist in motion along its original direction after collision: as Jeans§ has shown in connection with viscosity, however, "persistence of velocities" is a very important fact, the neglect of which leads to grave error in the mean-free-path theory. Kuenen‖ has shown that when taken account of in the theory of diffusion, it largely removes the discrepancy between the small observed variations of D_{12}, and the variations theoretically calculated by the method referred to.

An earlier modification of Meyer's theory by Gross¶ may also be mentioned. This predicts variations of amount similar to those observed, but generally of the wrong sign; its merits are not such as to demand more than this brief historical reference.

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[*] Maxwell, 'Scientific Papers,' i., p. 377, or 'Phil. Mag.,' 1860, January–July.

[†] Jeans' 'Dynamical Theory of Gases,' p. 273. The whole of the chapter on diffusion (ch. xii. in the second edition) is of great interest, and a general reference may be made to it for comparison both of theory and experiment with the results of this memoir.

[‡] Meyer, 'Kinetic Theory of Gases' (English edition), p. 255.

[§] Jeans' 'Dynamical Theory of Gases,' pp. 276, 292.

[‖] Kuenen, 'Supp. No. 8 to the Communications from the Leyden Physical Laboratory,' January, 1913. *Cf.* also Jeans' treatise, ch. xiii. (2nd ed.), p. 328.

[¶] Gross, 'Wied. Ann.,' 40, p. 424, 1890; the disagreement of Gross's theory with experiment has been indicated by Lonius, 'Ann. d. Phys.,' 29, p. 664, 1909.

In sharp distinction from MEYER'S theory, STEFAN* and MAXWELL† put forward a theory of diffusion which led to the result that D_{12} is entirely independent of the ratio $\nu_1 : \nu_2$, the formula involving only the sum $\nu_1+\nu_2$ or ν_0. STEFAN'S theory was based on the hypothesis of rigid elastic spherical molecules, and agrees with the corresponding form of our first approximation to D_{12} (13·06); the same result was subsequently obtained by LANGEVIN‡ and the present author§ on the most general molecular hypothesis, in the form (13·06). MAXWELL'S first formula related to the elastic sphere theory, and was greater than that of STEFAN by one-third, MAXWELL being considerably in error: his second formula related to Maxwellian molecules, and was identical with the exact formula for such molecules given in § 13 (*b*). All these results share the property that they are independent of $\nu_1 : \nu_2$, and as the present theory shows, all of them are in error in this respect, except MAXWELL'S second formula. They require to be multiplied by the correcting factor ∇'/∇ of (13·03): this factor is unity in the case of Maxwellian molecules, so that for a mixture of two sets of such molecules D_{12} is independent of their numerical proportions. This is one of the few properties of a gas which depends in its very nature (*i.e.*, not merely in absolute magnitude) on a particular molecular model: another such property will be noticed in § 14. The fact that the absence of variation is in disagreement with experimental results confirms the conclusion drawn from other sources of evidence that Maxwellian molecules are unsatisfactory representations of actual molecules.

The only other general case of independence of D_{12} or $\nu_1 : \nu_1$ is that in which the dynamical properties of the two sets of molecules are alike, as in the case of self-diffusion (§ 13 (*f*)). Hence we may speak of the coefficient of self-diffusion of a gas without specifying the ratio $\nu_1 : \nu_2$ in contemplation; in general, on the contrary, D_{12} is defined only when the value of $\nu_1 : \nu_2$ is assigned.

In the case when m_2/m_1 is negligible (§ 13 (*e*)) the mutual encounters of the light molecules are neglected, with the result that in this case also D_{12} depends only on ν_0. This, however, is perhaps hardly to be regarded as an additional exception to the general rule.

The error in the formulæ of STEFAN and the other authors mentioned arose from the neglect of the difference between the actual law of distribution of the peculiar velocities of the molecules and the assumed Maxwellian law. This is taken account of in the present paper, and leads to the correction factor ∇'/∇ in (13·03); we will now proceed to consider how this factor varies with the ratio $\nu_1 : \nu_2$ by studying the variation of the second approximation to it, *i.e.*, $(1-\epsilon_0)^{-1}$. From this we may readily

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* STEFAN, 'Wien. Sitzb.,' 63 (2), p. 63, 1871; 65, p. 323, 1872.

† MAXWELL, 'Scientific Papers,' i., p. 392; ii., p. 57 and p. 345. *Cf.* also BOLTZMANN, 'Wien. Sitzb.,' 66 (2), p. 324, 1872; 78, p. 733, 1878; 86, p. 63, 1882; 88, p. 835, 1883. Also 'Vorlesungen über Gastheorie,' i., p. 96.

‡ LANGEVIN, *loc. cit. ante.*

§ 'Phil. Trans.,' A, vol. 211, p. 449.

infer the character of the variation of ∇'/∇ itself, in view of our knowledge of the mode of convergence of the successive approximations as indicated in § 13 (*e*).

(*h*) *The Variation of* $(1-\epsilon_0)^{-1}$ *with* $\nu_1 : \nu_2$.

So far as regards our detailed discussion of ϵ_0, we shall confine ourselves to the case of rigid elastic spherical molecules; for Maxwellian molecules ϵ_0 is identically zero, while for n^{th} power centres of force $(5 < n < \infty)$ ϵ_0 is intermediate between 0 and the value appropriate to rigid elastic spheres (*cf.* Tables II., III., § 13), the character of its variations being similar in the two cases.

From § 9 (*c*) we have

(13·28)
$$\epsilon_0 = (k_1-1)^2 \frac{b_1\nu_1^2+2b_{12}\nu_1\nu_2+b_2\nu_2^2}{d_1\nu_1^2+2d_{12}\nu_1\nu_2+d_2\nu_2^2},$$

and in the case of rigid elastic spherical molecules (*cf.* § 9 (*c*) and § 9 (*f*)) we may write

(13·29)
$$(k_1-1)^2 \frac{b_{12}}{d_{12}} = \frac{6-\frac{56}{3}p}{\frac{80}{9}\frac{k}{p}+78-\frac{248}{3}p},$$

(13·30)
$$(k_1-1)^2 \frac{b_1}{d_1} = \frac{\mu_1^2}{30-\frac{100}{3}p-17\mu_1^2} \qquad (k_1-1)^2 \frac{b_2}{d_2} = \frac{\mu_2^2}{30-\frac{100}{3}p-17\mu_2^2},$$

where

(13·31)
$$p \equiv \mu_1\mu_2 \qquad k \equiv \left\{\frac{4\sigma_1\sigma_2}{(\sigma_1+\sigma_2)^2}\right\}^2,$$

so that

(13·32)
$$0 \leqslant p \leqslant \tfrac{1}{4} \qquad 0 \leqslant k \leqslant 1.$$

Since the suffix 1 refers to the heavier molecules, we have $\mu_1 \geqslant \mu_2$ and

(13·33)
$$\frac{b_1}{d_1} \geqslant \frac{b_2}{d_2}.$$

The condition that $\frac{b_{12}}{d_{12}}$ shall exceed $\frac{b_2}{d_2}$ is readily proved to be

(13·34)
$$\frac{\mu_2}{\mu_1} < f(p) \equiv \frac{81-342p+280p^2}{4k+81p-180p^2},$$

and it is found that, for the admissible values of p (*i.e.*, $0 \leqslant p \leqslant \frac{1}{4}$), $f(p)$ is positive and steadily diminishes as p increases; its least value is consequently $f(\frac{1}{4})$, which is equal to $13/(9+4k)$. Since k never exceeds unity, $f(p) \geqslant 1$, and hence $\mu_{21} \leqslant f(p)$, so that

(13·35)
$$\frac{b_{12}}{d_{12}} \geqslant \frac{b_2}{d_2}.$$

The sign of equality corresponds to the limiting case $k = 1$, $\mu_1 = \mu_2$, *i.e.*, to the case of self-diffusion, in which instance, therefore, $b_1/d_1 = b_2/d_2 = b_{12}/d_{12}$, ϵ_0 being independent of $\nu_1 : \nu_2$, as we have already seen (§ 13 (*f*)).

We cannot unconditionally make the further statement that $b_1/d_1 \geqslant b_{12}/d_{12}$, since the necessary condition for this, viz., $\mu_1/\mu_2 \geqslant f(p)$, is not always fulfilled; but it is easy to prove that

$$\frac{b_1}{d_1} \geqslant \frac{b_{12}}{d_{12}} \tag{13·36}$$

if

$$k \geqslant \tfrac{1}{4}\frac{\mu_2{}^3}{\mu_1}(1+80\mu_2-100\mu_1\mu_2). \tag{13·37}$$

When $\mu_1 = \mu_2 = \frac{1}{2}$, the last condition becomes $k \geqslant 1$, so that if $k = 1$ we have, as before, $b_1/d_1 = b_{12}/d_{12}$; if $\mu_1 = \mu_2 = \frac{1}{2}$ and $k < 1$, then $b_1/d_1 < b_{12}/d_{12}$. The condition (13·37) may be roughly expressed by saying that the more equal the molecular masses, the more equal, also, must be the molecular radii in order that b_1/d_1 shall exceed b_{12}/d_{12}; or, conversely, the more unequal the masses, the more unequal, also, may be the radii, consistently with the truth of (13·37).

Clearly, if (13·37) is satisfied, and

$$\frac{b_1}{d_1} \geqslant \frac{b_{12}}{d_{12}} \geqslant \frac{b_2}{d_2},$$

ϵ_0 steadily increases as the proportion of the heavier gas varies from 0 to 1, and consequently, also, D_{12} steadily increases (*cf.* (13·07)). If, however, (13·37) is not satisfied, ϵ_0 and D_{12} will first increase to a maximum and then diminish slightly, as the ratio $\nu_1 : \nu_0$ increases from 0 to 1.

As regards the actual value of ϵ_0, the range (corresponding to all possible ratios of molecular mass or radius) is from the minimum value of $(k_1-1)^2 c/f$, which is clearly zero (when $\mu_2 = 0$ and $\nu_1 = 0$, *i.e.*, when the heavier molecules are infinitesimal in number and the lighter molecules are infinitesimal in mass) to the maximum value of $(k_1-1)^2 b/e$, which is $\frac{1}{13}$ (when $\mu_2 = 0$ and $\nu_1 \neq 0$). The maximum value of $(k_1-1)^2 a/d$ is $\frac{3}{209}$, which lies between the above limits. The corresponding range of $(1-\epsilon_0)^{-1}$, the correction factor to the first approximation (13·06) to D_{12}, which is introduced on making a second approximation, is consequently from 1 to 1·083. Hence, in conjunction with § 13 (*e*), we may conclude that for rigid elastic spherical molecules the total possible range in the complete correction factor ∇'/∇ to the first approximation to D_{12} (*cf.* (13·01)) is from 1 to $\dfrac{32}{9\pi}$ or 1·132 (*cf.* (13·14)).

It would not be difficult to construct a table showing the values of $(1-\epsilon_0)^{-1}$ for various typical pairs of gases, but owing to the fact that there are three variables concerned (*i.e.*, m_1/m_2, σ_1/σ_2, and ν_1/ν_2) it would need to be somewhat complicated, and probably little more knowledge would be gained from it than may be deduced from the above discussion and from Table IV. of § 13 (*i*).

(*i*) *Variation of* D_{12} *with* $\nu_1 : \nu_2$. *Comparison with Experiment.*

In view of the conflicting theories regarding the relation between D_{12} and ν_1/ν_2, several series of experiments to test the question were made at Halle during the years 1904–1909, under the direction of Prof. E. DORN.* The gases used were helium—argon by SCHMIDT and LONIUS, oxygen—hydrogen by DEUTSCH and JACKMANN, carbon dioxide—hydrogen and oxygen—nitrogen by JACKMANN. In JACKMANN'S summary of the experiments it is pointed out that the observed variations in D_{12}, though far from negligible, are small compared with those predicted by MEYER'S theory, while GROSS'S theory (*cf.* § 13 (*g*)) is equally unsuccessful in that it predicts variations of the right order but in the wrong direction.

JEANS† compares these observations both with MEYER'S theory and with the corrected form of MEYER'S theory after allowing for the persistence of velocities (*cf.* § 13 (*g*). The following table is taken from § 446 of his treatise (2nd edition), and relates to the pair of gases, helium—argon:—

TABLE IV.—Variation of D_{12} for He-A.

ν_1/ν_2.	D_{12} observed (SCHMIDT and LONIUS).	D_{12} (calculated).	
		MEYER'S theory.	MEYER'S theory corrected (JEANS, KUENEN).
2·65	0·961	0·548	0·910
1·00	1·000	1·000	1·000
0·31	1·036	1·526	1·110

In this table the values of D_{12} have been multiplied by a factor in order to make the value corresponding to $\nu_1 = \nu_2$ equal to unity, for convenience of comparison. JEANS remarks, *à propos* of the above table, that the observed variations of D_{12} are insignificant compared with those predicted by MEYER'S theory, being small even compared with those predicted by the corrected theory, and that MAXWELL'S simpler formula (according to which D_{12} is independent of ν_1/ν_2) is after all the most accurate numerically. We shall see, however, that the present theory, with its correction ∇'/∇ to the usual first approximation (13·06) to D_{12}, gives results which are in much closer accordance with the observed phenomena.

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* SCHMIDT, 'Halle Dissertation' (1904), and 'Ann. d. Phys.,' 14, p. 801, 1904; DEUTSCH, 'Halle,' 1907; JACKMANN, 'Halle,' 1906; LONIUS, 'Halle,' 1909, and 'Ann. d. Phys.,' 29, p. 664, 1909, where the results of the whole series of experiments are summarised and discussed.

† JEANS' 'Dynamical Theory of Gases' (2nd ed.), § 446.

The following table contains the results of the HALLE experiments on D_{12}, as given in JACKMANN's summary. Additional columns give the values of (*a*) $\frac{1}{1-\epsilon_0}$, calculated from (13·28) on the hypothesis that the molecules are rigid elastic spheres* : (*b*) ∇'/∇—*cf.* (13·01)—estimated from the value of $\frac{1}{1-\epsilon_0}$ in accordance with § 9 (*a*) and § 13 (*e*) : and (*c*) of D_{12}, obtained by multiplying the values of ∇'/∇ by such a factor as to make the mean of the resulting values of D_{12} equal to the mean of the corresponding set of observed values. This is all that is here necessary, since we are concerned now only with the variations of D_{12}, and not with its absolute values.

TABLE V.—Variation of D_{12} with $\nu_1 : \nu_2$.

Gases. — Authority.	$\lambda_1 = \frac{\nu_1}{\nu_1+\nu_2}$.	$\frac{1}{1-\epsilon_0}$.	$\frac{\nabla'}{\nabla}$.	D_{12}.	
				Observed.	Calculated.
Argon-helium. — SCHMIDT† and LONIUS, $m_1/m_2 = 10$.	0·273	1·035	1·050	0·244	0·248
	0·315	1·040	1·056	0·250	0·250
	0·377†	1·044	1·063	0·250†	0·251
	0·500†	1·050	1·073	0·254†	0·254
	0·677	1·058	1·087	0·256	0·257
	0·763	1·062	1·094	0·263	0·259
Oxygen-hydrogen. — DEUTSCH† and JACKMANN, $m_1/m_2 = 16$.	0·25†	1·035	1·050	0·276†	0·276
	0·25			0·276	
	0·5†	1·050	1·073	0·280†	0·282
	0·5			0·273	
	0·75†	1·064	1·097	0·289†	0·289
Carbon dioxide-hydrogen. — DEUTSCH, $m_1/m_2 = 22$.	0·25	1·029	1·040	0·214	0·212
	0·5	1·059	1·089	0·218	0·222
	0·75	1·070	1·108	0·228	0·226
Nitrogen-hydrogen. — JACKMANN, $m_1/m_2 = 14$.	0·235	1·030	1·042	0·268	0·263
	0·5	1·050	1·073	0·266	0·271
Oxygen-nitrogen. — JACKMANN, $m_1 m_2 = 8/7$.	0·467	1·012	1·013	0·0733	0·0731
	0·5	1·013	1·014	0·0730	0·0732

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* The values of the molecular radii used in the calculation of ϵ_0 were taken from the table on p. 476 of my first paper ('Phil. Trans.,' A, vol. 211, 1912) ; *cf.* the column there headed "elastic sphere theory."

We may conclude from the above table that the calculated values of D_{12} are in very satisfactory agreement with the observed data, the differences between the two being not greater than the experimental errors would render probable, if we may judge of these errors from the internal accordance of the observed results. It should also be remembered that the molecular model chosen for calculation is not the best representation of an actual gas molecule, though it is sufficiently good for the purpose, especially in view of its simplicity for numerical work.

(*j*) *The Absolute Magnitude of* D_{12}.

We next consider the absolute magnitude of the coefficient of diffusion. A comparison of a theoretical expression for D_{12} with the corresponding observed value involves not only the accuracy of the theory and experiment, but also the suitability of the molecular model adopted as the basis of the theory. If we choose the rigid elastic sphere as model (and for many purposes this very simple model is fairly satisfactory) we may deduce from the observed value of D_{12} for a specified gas-mixture the corresponding value of $\sigma_1+\sigma_2$ (*cf.* (13·01) and (9·31)). By doing this for three pairs of gases A–B, B–C, C–A we can obviously determine from the resulting values of $\sigma_a+\sigma_b$, $\sigma_b+\sigma_c$, $\sigma_c+\sigma_a$ the individual molecular radii σ_a, σ_b, σ_c.* By taking different sets of pairs we may obtain more than one determination of each molecular radius, and the mutual accordance of these affords some sort of check on the theory —mainly, I think, relating to the suitability of the molecular model. But we cannot in this way test whether the theoretical formula is in error by a factor which is nearly or quite constant, since this would merely alter the deduced values of the radii in a common ratio.

[*Revised June 2, 1916.*—By another method, as follows, we can to some extent check the absolute magnitude of the theoretical results. Having determined values of σ in the above manner, we can use σ_1 (the radius for a particular gas) to calculate D_{11} by the formula which expresses D_{12} in the case of dissimilar molecules, putting $m_2 = m_1$, $\sigma_2 = \sigma_1$. In this way, practically by interpolation, we obtain a virtually experimental value of D_{11} (which cannot be measured directly). But the theoretical expression for D_{11} can also be written in the form $D'_{11} \equiv k\frac{\kappa_1}{\rho_1}$, κ_1 and ρ_1 being respectively the viscosity and density of the gas, while k is a numerical constant. If the correct theoretical expression for κ_1 is used here, the theoretical value of k should agree with the experimentally measured value $D_{11}\rho_1/\kappa_1$. The former depends, of course, on the molecular hypothesis adopted, varying from 1·120 for rigid elastic spheres to 1·504 for Maxwellian molecules. The following table gives several experimental values of k (taken from JEANS' treatise†), which all lie between the

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* This method is due to Lord KELVIN, 'Baltimore Lectures,' p. 295.

† *Cf.* JEANS' 'Dynamical Theory of Gases,' 2nd ed., §§ 447, 448. The value of k deduced from the corrected MEYER'S theory is 1·34 as against the value $k = 1·20$ given by the present theory (13·24). The formula for κ there used is that given in my second memoir.

values here theoretically deduced. The values of n, calculated from the variation of viscosity with temperature, on the hypothesis that the molecules are the n^{th} power centres of force, are given alongside. The formula of interpolation used to obtain D_{11} from D_{12} is based on the theory of rigid elastic spherical molecules, and this, together with the rather early date of the diffusion constants used (they were determined by LOSCHMIDT), may prevent us from expecting a very close agreement with theory. I have not calculated the theoretical values of k for values of n between 5 and ∞, since they depend on certain integrals which must be evaluated by quadratures; but it would be interesting to have these quantities determined.]

	n.	$\frac{D_{11}\rho_1}{\kappa_1}$.
Theory	∞	1·200
Hydrogen	12	1·36
Carbon-monoxide	9·3	1·34
Oxygen	7·9	1·43
Carbon-dioxide	5·2	1·50
Theory	5·0	1·504

Perhaps the most satisfactory comparison between theory and experiment is provided by calculating σ_1 both from the coefficient of diffusion, as above, and also in some other way as, *e.g.*, from the coefficient of viscosity κ_1. Assuming that the experimental data and the molecular representation underlying the theory are satisfactory, the accordance of the two values of σ affords a complete check on the theory of D_{12} and κ *jointly*. Such a comparison was made in my first memoir ('Phil. Trans.,' A, vol. 211, p. 480), using the approximate formulæ for D_{12} and κ there given; the confirmation of the theory thus provided was perhaps as good as the accuracy of the data might allow one to expect. The table in that paper requires revision, because of the corrections to my original formulæ which have been deduced in the present and my second memoir. Until more modern and accurate data for the coefficient of diffusion are available, however (and of such there is need), this revision is hardly worth while in view of the smallness of the corrections mentioned.

In connection with this matter, finally, it may be pointed out that in tables giving values of D_{12} intended for accurate theoretical purposes it is necessary to specify the ratio *by volumes* of the diffusing gases, since the theoretical expression for D_{12}, in general, involves this ratio $(\nu_1 : \nu_2)$. This practice has not usually been adopted hitherto.

(k) *The Variation of* D_{12} *with Pressure and Temperature.*

Since the theoretical expression for D_{12}, on whatever molecular hypothesis, contains at least one quantity (molecular diameter or force constant) which is not directly measurable, two or more values of D_{12}, corresponding to different temperatures or pressures, are necessary in order to obtain evidence from diffusion as to the best molecular model. It is, therefore, of some importance to consider the variation of D_{12} with pressure (or density) and temperature.

The first approximation to D_{12} (13·06) varies as $T^{\frac{n+3}{2(n-1)}+1}$ in the case of molecules which are n^{th} power centres of force, the case $n = \infty$, $T^{3/2}$, corresponding to rigid elastic spheres (*cf.* 'Phil. Trans.,' A, vol. 211, p. 479). It may readily be seen that the correction factor ∇'/∇ in (13·01) is independent of h or T for these particular molecular models (*cf.* 'Phil. Trans.,' A, vol. 216, § 9 (B), p. 321).

Another molecular model, considered in my two previous memoirs, is the rigid elastic sphere surrounded by a field of attractive force (the SUTHERLAND molecule). The first approximation to D_{12} in this varies as $T^{3/2}/(1+S'/T)$, where S' is known as SUTHERLAND'S constant of diffusion.* It may be proved without difficulty, as in the case of the coefficient of viscosity for a simple gas (*cf.* my second memoir, §§ 9–11) that the correction ∇'/∇ is usually intermediate between unity and the value corresponding to rigid elastic spheres without attraction. The correction factor in the case of SUTHERLAND'S molecules also depends upon the temperature, but the variation is so very slight as to be negligible.

As regards variation with density, the first approximation to D_{12} varies inversely as the total density of the gas mixture, and is independent of the relative proportions of the two gases. The correction factor ∇'/∇ in (13·01) has been seen to vary with the relative proportions (ν_1/ν_2), but if $\nu_1 : \nu_2$ is fixed, the factor may readily be shown not to vary with the total density $\nu_1+\nu_2$.

§ 14. THE COEFFICIENT OF THERMAL DIFFUSION.

(*a*) *The General Formula for* D_T.

The coefficient of thermal diffusion D_T was defined in § 10 (*a*) by the equation

$$(14·01) \qquad u'_0 = -D_T \frac{1}{T}\frac{\partial T}{\partial x} = -D_T \frac{\partial \log T}{\partial x},$$

and was found to be given by (*cf.* (10·10), (5·36))

$$(14·02) \qquad D_T = -\tfrac{1}{9}B_0\beta'_0 T = \tfrac{1}{9}\lambda_1\lambda_2 B_0 T \frac{\nabla'_0(\delta_{mn}b_{mn})}{\nabla(\delta_{mn}b_{mn})}.$$

In the case of Maxwellian molecules it was found that β'_0 vanishes (*cf.* (6·05)), so that for a gas composed of such molecules D_T is zero, and the phenomenon of thermal diffusion is non-existent. This, together with the absence of variation of D_{12} with ν_1/ν_2 (*cf.* § 13 (*g*)), is one of the few properties of a gas which depends essentially on

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* *Cf.* SUTHERLAND, 'Phil. Mag.' (5), 38, p. 1, 1894, and my first memoir, p. 479.

the particular characteristics of the molecules. We shall see later that the phenomenon is also differential, *i.e.*, it occurs only when the masses or diameters of the molecules are not the same for the two kinds. Thus when they are alike in mass and dynamical properties β'_0 (and consequently also D_T) is exactly zero (*cf.* (8·13)); this is true whatever the nature of the molecules.

(*b*) *The First Approximation to* D_T.

The first approximation to D_T is obtained by substituting the value of β'_0 given, to this degree of accuracy, by (9·20), viz. (*cf.* (9·17), (9·09)–(9·13)),

$$D_T = \frac{3(m_1+m_2)RT}{2\pi\nu_0 m_1 m_2 K'_{12}(0)} \frac{\epsilon_1(k_1-1)}{\Delta_1\nu_0}. \tag{14·03}$$

We shall not go beyond a first approximation in the general case, but (as in § 13 (*e*) with regard to D_{12}) we shall briefly examine the order of magnitude of the corrections introduced by further approximations, by a consideration of the special case when m_2/m_1 and σ_2/σ_1 are very small (§ 7).

(*c*) *The Value of* D_T *when* m_1/m_2 *and* σ_1/σ_2 *are very large.*

In this instance the value of β'_0 is given by (7·22), and

$$D_T = \frac{3\lambda_2 RT}{2\pi\nu_0 m_2 K'_{12}(0)} \frac{D'_1}{D'}. \tag{14·04}$$

When the molecules are rigid elastic spheres of radii σ_1, σ_2, this assumes the form

$$D_T = \frac{3\lambda_2}{16\nu_0(\sigma_1+\sigma_2)^2(h\pi m_2)^{1/2}} \frac{D'_1}{D'}, \tag{14·05}$$

or (*cf.* (7·26)) the same expression except that D_1/D replaces D'_1/D'. In each case the suffix 1 to D or D′ denotes the second minor of the corresponding determinant.

We have already given the value of D as far as the fourth row and column (§ 13 (*e*)). From this we find that the first three approximations to D_1/D are, with their successive differences equal to

$$\begin{array}{rl} \frac{5}{12} = 0·417 & \\ & 77 \\ \frac{2280}{4608} = 0·494 & \\ & 30 \\ \frac{556416}{1061681} = 0·524. & \end{array}$$

These indicate the magnitude of D_1/D sufficiently for our purpose, though for an accuracy of (say) 1 per cent. it might perhaps be necessary to carry the calculation two or three steps further. If we take the limit of these approximations as 0·58, we have (*cf.* (13·13))

$$(14{\cdot}06) \qquad D_T = 0{\cdot}58 \frac{3\lambda_2}{16\nu_0(\sigma_1+\sigma_2)^2(h\pi m_2)^{1/2}} = 0{\cdot}51\lambda_2 D_{12}.$$

In this case, therefore, D_T is comparable with D_{12}, though it may be remarked that if λ_2 is too nearly equal to unity, our assumption (§ 7) that the effect of collisions among the lighter molecules is negligible may require revision. It may, indeed, be readily seen from the general expression for D_T that this always vanishes if either λ_1 or λ_2 becomes zero.

We may briefly examine the case also of n^{th} power centres of force by means of (13·19). Considering only a first approximation, the following results are obtained for various values of n:—

First Approximations to D'_1/D'.

$n = 5$	$(m = 1)$	$D'_1/D' = 0$, exactly.
$n = 7$	$(m = \frac{2}{3})$	0·156, approximately.
$n = 9$	$(m = \frac{1}{2})$	0·227 ,,
$n = 13$	$(m = \frac{1}{3})$	0·294 ,,
$n = 17$	$(m = \frac{1}{4})$	0·326 ,,
$n = 33$	$(m = \frac{1}{8})$	0·372 ,,
$n = \infty$	$(m = 0)$	0·417 ,,

The general formula for the first approximation to D'_1/D' is readily seen to be

$$\frac{5}{2}\,\frac{1-m}{6-m} = \frac{5}{12}\,\frac{n-5}{n-\frac{5}{3}} \quad \left(m = \frac{4}{n-1}\right).$$

The last table shows that a very slight excess of n over its value for Maxwellian molecules ($n = 5$) suffices to raise D_T to a considerable proportion of its magnitude corresponding to $n = \infty$ (rigid elastic spheres). The phenomenon of thermal diffusion clearly disappears only under conditions which must be fulfilled with great nicety.

As an instance of the correction introduced by a second approximation in the case of a finite value of n, it may be noticed that the result of a second approximation for $n = 9$ is 0·246.

(d) *The Approximate Value of* D_T *when* $\sigma_1 = \sigma_2$ *and* m_1/m_2 *is very large.*

The case considered in the last sub-section is realised physically in a metal or gas, among the molecules of which are found free electrons. Another case of physical importance is that in which the molecules are similar except in mass, m_1/m_2 being large; the diameters of ordinary molecules do not differ greatly, while their masses may be widely different. Thus the diameters of the oxygen and hydrogen molecules are approximately $1{\cdot}78 \,.\, 10^{-8}$ and $1{\cdot}33 \,.\, 10^{-8}$ respectively, the ratio of their masses being 16. If in our first approximation to D_T given by (14·03) we insert the values of $K'_{12}(0)$, k_1, &c., appropriate to rigid elastic spherical molecules, and write $\sigma_1 = \sigma_2$, $\mu_1 = 1$, $\mu_2 = 0$, the result is

$$D_T = \frac{15\lambda_1\lambda_2}{4\,(9+\lambda_2)}\,\frac{3}{16\nu_0\,(\sigma_1+\sigma_2)^2}\left(\frac{m_1+m_2}{hm_1m_2}\right)^{1/2}, \text{ approximately.}$$

The corresponding value of ϵ_0 (9·15) is $3\lambda_1/(39+\lambda_2)$, so that

$$D_{12} = \frac{39+\lambda_2}{4\,(9+\lambda_2)}\,\frac{3}{16\nu_0\,(\sigma_1+\sigma_2)^2}\left(\frac{m_1+m_2}{hm_1m_2}\right)^{1/2}, \text{ approximately,}$$

and

$$D_T = \frac{15\lambda_1\lambda_2}{39+\lambda_2}\,D_{12}, \text{ approximately.} \tag{14·07}$$

Thus when $\lambda_1 = \lambda_2 = \frac{1}{2}$, D_T/D_{12} becomes 0·095, which is nearly equal to the maximum value for this particular gas. When λ_1 or λ_2 vanishes, so also does D_T, another instance of the general theorem on which remark has already been made.

(e) *General Remarks and Numerical Values.*

It is now evident, from the special cases treated in the preceding sub-sections, that the importance of the phenomenon of thermal diffusion, as compared with ordinary diffusion, is greater or less according as the difference between the molecular masses and diameters is large or small. If the mass and diameter of the one set of molecules are very large compared with those for the other set, D_T rises to about $\frac{1}{2}D_{12}$; if there is a large inequality in mass, but no difference in size, D_T is about $\frac{1}{10}D_{12}$ at most*; if mass and diameter are both the same for the different molecules, $D_T = 0$, which is also its limiting value when λ_1 or λ_2 tends to zero, and its invariable value when the molecules are Maxwellian.

The following are a few values of D_T/D_{12} corresponding to typical pairs of actual

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[*] See Note E (p. 197) for the case of nearly equal masses and very unequal sizes.

gases, and are obtained by comparing the approximations to D_T and D_{12} contained in (13·07) and (14·03); calling their ratio k_T, we have

$$\begin{aligned} k_T &= \frac{\epsilon_1(1-\epsilon_0)}{\nu_0\Delta_1} \\ &= \frac{2(k_1-1)[15(\lambda_1\mu_2+\lambda_2\mu_1)(\mu_1-\mu_2)-4\mu_1\mu_2k_{12}{}^0(\lambda_1-\lambda_2)+(\lambda_1\mu_{12}k_{11}{}^0-\lambda_2\mu_{21}k_{22}{}^0)]}{d+e\dfrac{\nu_1}{\nu_2}+f\dfrac{\nu_2}{\nu_1}} \\ &= \frac{\frac{2}{3}\mu_1\mu_2(\lambda_1-\lambda_2)+6(\lambda_2\mu_1{}^2-\lambda_1\mu_2{}^2)+(\lambda_2\mu_1A_1-\lambda_1\mu_2A_2)}{A_1A_2+(6-\frac{20}{3}\mu_1\mu_2)(A_1+A_2)-\frac{18}{5}(\mu_1{}^2A_1+\mu_2{}^2A_2)+\frac{72}{5}-\frac{688}{15}\mu_1\mu_2}, \end{aligned}$$

where

$$A_1 = \tfrac{4}{3}\frac{\nu_1}{\nu_2\mu_2}\left(\frac{2\sigma_1}{\sigma_1+\sigma_2}\right)^2, \qquad A_2 = \tfrac{4}{3}\frac{\nu_2}{\nu_1\mu_1}\left(\frac{2\sigma_2}{\sigma_1+\sigma_2}\right)^2.$$

The values of σ used in calculating the results in the following table are taken from the table on p. 476 of my first memoir.

TABLE VI.—Comparison of D_T, D_p, D_{12}.

Ratio of the two gaseous components.	Argon-helium.			Oxygen-hydrogen.			Oxygen-nitrogen.		
	$\frac{m_1}{m_2} = 9\cdot8$, $\frac{\sigma_1}{\sigma_2} = 1\cdot69$, $k_T = \frac{20\cdot4\lambda_1+4\cdot8\lambda_2}{32\cdot6+58\cdot6\frac{\nu_1}{\nu_2}+4\cdot4\frac{\nu_2}{\nu_1}}$.			$\frac{m_1}{m_2} = 16$, $\frac{\sigma_1}{\sigma_2} = 1\cdot34$, $k_T = \frac{28\cdot0\lambda_1+5\cdot2\lambda_2}{45\cdot5+78\cdot3\frac{\nu_1}{\nu_2}+5\cdot8\frac{\nu_2}{\nu_1}}$.			$\frac{m_1}{m_2} = \frac{16}{14}$, $\frac{\sigma_1}{\sigma_2} = 0\cdot97$, $k_T = \frac{0\cdot33\lambda_1+0\cdot41\lambda_2}{22\cdot2+9\cdot3\frac{\nu_1}{\nu_2}+8\cdot7\frac{\nu_2}{\nu_1}}$.		
	$k_T = \frac{D_T}{D_{12}}$.	$k_p = \frac{D_p}{D_{12}}$.	$\frac{D_p}{D_T}$.	$k_T = \frac{D_T}{D_{12}}$.	$k_p = \frac{D_p}{D_{12}}$.	$\frac{D_p}{D_T}$.	$k_T = \frac{D_T}{D_{12}}$.	$k_p = \frac{D_p}{D_{12}}$.	$\frac{D_p}{D_T}$.
$\lambda_1 = \frac{1}{4}$, $\frac{\nu_1}{\nu_2} = \frac{1}{3}$	0·133	0·513	3·9	0·122	0·592	4·8	0·008	0·026	3·2
$\lambda_1 = \frac{1}{2}$, $\frac{\nu_1}{\nu_2} = \frac{1}{1}$	0·132	0·408	3·1	0·128	0·441	3·4	0·010	0·033	3·3
$\lambda_1 = \frac{3}{4}$, $\frac{\nu_1}{\nu_2} = \frac{3}{1}$	0·079	0·166	2·1	0·079	0·230	2·9	0·007	0·024	3·4

We may remark, finally, on the direction of thermal diffusion: since D_T has been found to be a positive quantity (14·01) shows that the heavier gas tends to diffuse towards regions of lower temperature, while the lighter gas tends to diffuse towards those of higher temperature.*

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* *Cf.*, however, Note E, p. 197.

§ 15. The Coefficient of Pressure Diffusion.

In § 10 we saw that, among other causes, a pressure gradient is an agent in producing diffusion, according to the law (*cf.* (10·08)),

$$(15{\cdot}01) \qquad u'_0 = \mathrm{D}_p \frac{1}{p_0}\frac{\partial p_0}{\partial x} = \mathrm{D}_p \frac{\partial \log p_0}{\partial x},$$

where (*cf.* (10·09)),

$$(15{\cdot}02) \qquad \mathrm{D}_p = \frac{m'_0}{m_0}\mathrm{D}_{12} = \frac{\lambda_1\lambda_2(m_1-m_2)}{\lambda_1 m_1+\lambda_2 m_2}\mathrm{D}_{12} = k_p \mathrm{D}_{12},$$

if

$$(15{\cdot}03) \qquad k_p \equiv \frac{\lambda_1\lambda_2(m_1-m_2)}{\lambda_1 m_1+\lambda_2 m_2}.$$

The phenomenon depends essentially on the difference of mass of the molecules, and we may note also that, like thermal diffusion, it tends to zero with λ_1 or λ_2. If m_1/m_2 is very large, k_p clearly has the value λ_2, except when λ_2 is very nearly equal to 1.

It is interesting to compare the degree of diffusion produced by equal gradients of $\log p_0$ and $\log \mathrm{T}$. This is equivalent to comparing k_p and k_T. When m_1/m_2 is very large, $k_p/k_\mathrm{T} = 1/0{\cdot}51$ or approximately 2, if σ_1/σ_2 is also large (*cf.* (14·06)), or $(39+\lambda_2)/15\lambda_1$ if $\sigma_1 = \sigma_2$ (*cf.* (14·07)), save when λ_1 is small. The factor k_p, unlike k_T, is not dependent on the relative size of the molecules.

In Table VI. are given the values of k_p corresponding to the three typical pairs of gases considered in § 14 (*c*). It appears that D_p is of thrice or four times the magnitude of D_T for such gases.

§ 16. The Steady State Without Diffusion.

We will now briefly consider the steady state, without diffusion, of a gas subject to the influence of (*a*) external forces or (*b*) boundary conditions which maintain a constant non-uniform distribution of temperature. If we write zero in place of u'_0 in (10·11), and divide by D_{12}, we have

$$(16{\cdot}01) \qquad \frac{\partial \lambda'_0}{\partial x} - 2h\left(\mathrm{X}'_0 + \frac{1}{\nu_0}\frac{\partial p_0}{\partial x}\right) + k_\mathrm{T}\frac{\partial \log \mathrm{T}}{\partial x} = 0$$

as the equation of state. It is more convenient to express the middle term as in the following equations (substituting for $\frac{1}{\nu_0}\frac{\partial p_0}{\partial x}$ from 2·04—$\frac{\partial u_0}{\partial t}$ being zero, since the state of the gas is steady—and expressing the result in terms of X_1 and X_2 instead of X_0 and X'_0):—

$$\frac{\partial \lambda_1}{\partial x} = 2h\lambda_1\lambda_2(X_1 - X_2) - k_T \frac{\partial \log T}{\partial x}, \tag{16·02}$$

$$\frac{\partial \lambda_2}{\partial x} = 2h\lambda_1\lambda_2(X_2 - X_1) + k_T \frac{\partial \log T}{\partial x}. \tag{16·03}$$

Since

$$\frac{\partial}{\partial x}\left(\frac{\nu_1}{\nu_2}\right) = \frac{\partial}{\partial x}\left(\frac{\lambda_1}{\lambda_2}\right) = \frac{1}{\lambda_2}\frac{\partial \lambda_1}{\partial x} - \frac{\lambda_1}{\lambda_2^2}\frac{\partial \lambda_2}{\partial x} = \frac{\lambda_1+\lambda_2}{\lambda_2^2}\frac{\partial \lambda_1}{\partial x} = \frac{1}{\lambda_2^2}\frac{\partial \lambda_1}{\partial x}, \tag{16·04}$$

we may re-write (16·02) or (16·03) in the form

$$\frac{\partial}{\partial x}\left(\frac{\nu_1}{\nu_2}\right) = 2h\frac{\nu_1}{\nu_2}(X_1 - X_2) - \frac{1}{\lambda_2^2}k_T\frac{\partial \log T}{\partial x}, \tag{16·05}$$

or

$$\frac{\partial \log(\nu_1/\nu_2)}{\partial x} = 2h(X_1 - X_2) - \frac{k_T}{\lambda_1\lambda_2}\frac{\partial \log T}{\partial x}. \tag{16·06}$$

If the temperature and external forces are uniform, from (16·06) and the two similar y and z equations we may deduce the integral

$$\frac{\nu_1}{\nu_2} = \left(\frac{\nu_1}{\nu_2}\right)_0 e^{2h\{(X_1-X_2)x + (Y_1-Y_2)y + (Z_1-Z_2)z\}}, \tag{16·07}$$

which is a well-known result directly deducible from the statistical theory of distribution of density in a gas.* If the external forces are gravitational, the z axis being vertically upwards,

$$X = Y = 0, \qquad Z_1 = -m_1 g, \qquad Z_2 = -m_2 g,$$

and, if g be regarded as constant, we have

$$\frac{\nu_1}{\nu_2} = \left(\frac{\nu_1}{\nu_2}\right)_0 e^{-2hgz(m_1-m_2)}.$$

The heavier gas, naturally, is relatively denser in the lower strata, the amount of the effect being greater the greater the inequality of mass and the smaller the temperature. In the case of the atmosphere, since the molecular masses of oxygen and nitrogen are nearly equal, the magnitude of this imperfection of diffusion is but small. It is found that the change in the value of ν_1/ν_2 would amount only to about $\frac{1}{5}$ per cent. per kilometre.†

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* *Cf.* JEANS' 'Dynamical Theory of Gases' (2nd. ed.), p. 91 (234, 235).

† *Cf.* JEANS' treatise, § 369.

The variation of relative density in the atmosphere due to the temperature gradient (which is about 7° C. per kilometre) is still smaller, and in the opposite direction. Thus, taking $\nu_1 : \nu_2$ for oxygen and nitrogen as 1 : 3 roughly, and T as 280° C. approximately, the equation giving the variation of $\nu_1 : \nu_2$ near the earth's surface (independently of the effect of the difference in mass) is

$$\frac{\partial}{\partial x}\left(\frac{\nu_1}{\nu_2}\right) = -\frac{1}{\lambda_2{}^2} k_{\mathrm{T}} \frac{1}{\mathrm{T}} \frac{\partial \mathrm{T}}{\partial x}.$$

By Table VI., $k_{\mathrm{T}} = 0{\cdot}008$, $\lambda_2 = \frac{3}{4}$, while if we adopt one kilometre as the unit of length, writing $\mathrm{T} = 280$ and $\frac{\partial \mathrm{T}}{\partial x}$ as -7, the change in $\frac{\nu_1}{\nu_2}$ per unit length is found to be

$$\frac{16}{9} \,.\, 0{\cdot}008 \,.\, \frac{1}{280} \,.\, 7 = 0{\cdot}00035,$$

or $\frac{1}{30}$ per cent. per kilometre. This variation is of one-sixth the magnitude of the gravity variation, which it tends to neutralise, since the heavier gas tends to rise owing to the temperature gradient. These changes are masked, however, by the effects of convection currents ; it has been found that the proportions of nitrogen and oxygen in our atmosphere are the same for all altitudes up to 10 kilometres, and, indeed, above this height, right into the isothermal layer or stratosphere.

As another instance of the phenomenon of a concentration gradient due to temperature, we may consider the case of a mixture of equal parts (by volume) of oxygen and hydrogen, or argon and helium, placed between two plates which are maintained at freezing and boiling points respectively. Neglecting the small variation in ν_1/ν_2, as far as the integration with respect to x is concerned, in the equation

$$\frac{\partial}{\partial x}\left(\frac{\nu_1}{\nu_2}\right) = -\frac{1}{\lambda_2{}^2} k_{\mathrm{T}} \frac{\partial \log \mathrm{T}}{\partial x},$$

we may conclude that, independently of the distance between the plates,* the change in the value of ν_1/ν_2 is

$$-4 \,.\, 0{\cdot}130 \,.\, \log_e \tfrac{373}{273} = 0{\cdot}161,$$

where we have taken $k_{\mathrm{T}} = 0{\cdot}130$ (*cf.* Table VI.), which is approximately the case either for Ar-He or O-H. Thus near the hot plate there will be approximately 48 per cent. of the heavier gas to 52 per cent. of the lighter, and *vice versâ* near the cool plate. This remarkable result is independent of the pressure of the gas, assuming this to be uniform between the two plates, as will be the case in the

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* To the order of accuracy according to which k_{T} may be regarded as constant.

absence of external forces; the density, on the other hand, will vary inversely as the temperature.

These numbers are based on the hypothesis that the molecules are rigid elastic spheres; for n^{th} power centres of force the effect would be somewhat less, vanishing altogether if $n = 5$. It seems very desirable that the theory should be experimentally tested; the effect predicted is of easily measurable amount, and could be further magnified by taking a greater temperature range. The magnitude of the concentration gradient is so large as to seem improbable, and it is possible that some circumstance has been overlooked which would modify the theory, but I have been unable to detect any such flaw. It is difficult to say how long a time it would take to reach the steady state, or what influence the constant flow of heat through the gas, from the hot plate to the cold, would have upon the phenomenon. (See Note D, p. 196.)

§ 17. The Coefficient of Viscosity.

The general expression for the coefficient of viscosity is (*cf.* (11·06))

$$\kappa_{12} = \frac{2}{225}\frac{\mathrm{C}_0}{2h}\sum_0^\infty(\nu_1\gamma_r+\nu_2\gamma_{-r}). \tag{17·01}$$

We shall not trouble here to go beyond a first approximation to this expression, even this being somewhat complicated. Referring to (9·27), we obtain the following result as our first approximation:—

$$\kappa_{12} = \frac{5\mathrm{RT}}{\pi\mathrm{K}'_{12}(0)}\frac{c_1\nu_1^{\,2}+2c_{12}\nu_1\nu_2+c_2\nu_2^{\,2}}{k^0{}_{11}c_1\nu_1^{\,2}+2k^0{}_{12}c'_{12}\nu_1\nu_2+k^0{}_{22}c_2\nu_2^{\,2}}. \tag{17·02}$$

The values of c_1, c_2, c_{12}, c'_{12} are defined by (9·28)–(9·30). The equation (17·02) is identical, except as regards notation, with that given in my first memoir on the kinetic theory (*loc. cit.*, p. 451). When $\nu_2 = 0$, the formula reduces to

$$\frac{5\mathrm{RT}}{\pi\mathrm{K}'_{12}(0)}\frac{1}{k_{11}{}^0} = \frac{5\mathrm{RT}}{\pi\mathrm{K}_{11}{}^2(0)}, \tag{17·03}$$

which is the first approximation to the coefficient of viscosity of a simple gas composed entirely of molecules of the first kind. Some idea of the accuracy of (17·02) as a first approximation may be gained from the fact that for a simple gas the error (*i.e.*, of (17·03)) amounts to only 1·6 per cent. for rigid elastic spherical molecules, and less for n^{th} power centres of force (*cf.* my second memoir, *loc. cit.*, § 11), the first approximation being too small. How the error varies with $\nu_1 : \nu_2$ cannot be stated without carrying the calculation further, but it is probable that it is always of the same order of magnitude, 1 or 2 per cent. A second approximation to κ_{12} would replace the last factor of (17·02) by the quotient of one homogeneous quartic polynomial in ν_1, ν_2 by another, reducing, when $\nu_2 = 0$, to the second approximation to κ_1, the coefficient of viscosity of a simple gas. The present importance of such a second approximation to κ_{12} does not seem to render the complicated calculation worth while. In my first memoir (*loc. cit.*, pp. 469–472) a comparison of (17·02) with experimental data is given, which suggests that the formula satisfactorily represents the behaviour of actual gases in respect of the variation of κ_{12} with ν_1/ν_2.*

When the molecules are rigid elastic spheres, (17·02) has the special form

$$\kappa_{12} = \frac{5}{32}\left\{\frac{\mathrm{RT}}{2\pi}\frac{m_1 m_2}{m_1+m_2}\right\}^{1/2} \frac{(1+\frac{3}{5}\mu_{12})\,\nu_1^2+\frac{4}{5}\left\{1+\frac{3}{2\mu_1\mu_2}\frac{\sigma_1^2+\sigma_2^2}{(\sigma_1+\sigma_2)^2}\right\}\nu_1\nu_2+(1+\frac{3}{5}\mu_{21})\,\nu_2^2}{(1+\frac{3}{5}\mu_{12})\,\sigma_1^2\nu_1^2+\left\{\frac{1}{2}(\sigma_1+\sigma_2)^2+\frac{6}{5\mu_1\mu_2}\frac{\sigma_1^2\sigma_2^2}{(\sigma_1+\sigma_2)^2}\right\}\nu_1\nu_2+(1+\frac{3}{5}\mu_{21})\,\sigma_2^2\nu_2^2},$$

where we have quoted from § 9 (*f*). The special forms appropriate to molecules of other particular types may likewise easily be written down.

§ 18. THE COEFFICIENT OF THERMAL CONDUCTION.

In § 12 the following expression for the coefficient of thermal conduction ϑ was found (*cf.* (12·21)):—

$$(18{\cdot}01)\qquad \vartheta = \tfrac{1}{9}\mathrm{B}_0\frac{\mathrm{RT}}{\mathrm{J}}\left\{\sum_1^\infty(\nu_1\beta_r+\nu_2\beta_{-r})-\frac{\beta'_0}{\alpha'_0}\sum_1^\infty r\,(\nu_1\alpha_r+\nu_2\alpha_{-r})\right\}.$$

Owing to the complexity of even a first approximation, we shall not go further than this in the present paper; in making the approximation, we use the results of § 9, which lead to the equation

$$(18{\cdot}02)\qquad \vartheta = \frac{25\,(\lambda_1 m_1+\lambda_2 m_2)\,(m_1+m_2)\,\mathrm{C}_v\mathrm{RT}}{2\pi m_1 m_2 \mathrm{K}'_{12}(0)\,(a_1\nu_1^2+2a_{12}\nu_1\nu_2+a_2\nu_2^2)} \left[\left(\frac{\mu_2}{k_{11}^0}\,a_1\nu_1^2+2a'_{12}\nu_1\nu_2+\frac{\mu_1}{k_{22}^0}\,a_2\nu_2^2\right)-\frac{2}{25}\frac{(k_1-1)^2\,\nu_1\nu_2\epsilon_1^2}{d_1\nu_1^2+2d_{12}\nu_1\nu_2+d_2\nu_2^2}\right].$$

If we put $\nu_1 = 0$ in this expression it becomes

$$(18{\cdot}03)\qquad \vartheta = \frac{25\mathrm{RTC}_v}{2\pi k_{11}^0\mathrm{K}'_{12}(0)} = \tfrac{5}{2}\kappa_1\mathrm{C}_v,$$

by (17·03); this agrees with the first approximation to ϑ for a simple gas which was given in my two previous memoirs (*loc. cit.*, p. 462, p. 337, respectively). The

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* In particular, the theory there given indicates that the viscosity of a gas mixture may rise to a maximum (for a certain value of ν_1/ν_2) which exceeds the viscosity of either component separately. This had already been proved by MAXWELL for the particular type of gas dealt with in his second paper. KUENEN has recently shown that the ordinary elastic-sphere theory leads to a similar result, when allowance is made for the persistence of velocities after collision ('Amsterdam Acad. Proc.,' 16, p. 1162, 1914).

expression in (18·02) for a composite gas does not, however, agree with the corresponding first approximation in my original memoir ('Phil. Trans.,' A, vol. 211, p. 452, *cf.* 40 and 41). This is because it was there assumed (§ 2) that thermal conduction was independent of diffusion, whereas we have seen that a temperature gradient is inseparable from either diffusion or a concentration gradient; this invalidates the equations (24) of that paper. The second term within the square bracket of (18·02) especially arises from the terms in the velocity-distribution function which represent the diffusion effect, although the first term is also affected. Evidently even the first approximation to ϑ involves the quotient of a homogeneous quartic in ν_1, ν_2 by the product of two homogeneous quadratics, a complexity which makes it hardly worth while to compare the result with the scanty experimental data at present available. A brief discussion of my earlier formula, which may be expected to differ only slightly from (18·02) in numerical magnitude, is given in § 18 of my first memoir.

§ 19. The Specific Energy of Diffusion.

In § 12 (*c*) we saw that in a gas which is at rest and at a uniform temperature, so that no conduction of heat is taking place, there may yet be a continual rise in temperature if diffusion is going on. The gas being at rest as a whole, no gain of thermal energy accrues through the medium of internal friction, and the thermal flux of diffusion may proceed also in the absence of external forces, *i.e.*, solely as a result of variations of concentration. However the diffusion is produced, in the latter or any of the other ways described in § 10, the equation of energy will contain a term equivalent to that on the right of the following equation:—

(19·01)
$$\rho_0 \mathrm{C}_v \frac{\partial \mathrm{T}}{\partial t} = \Sigma \frac{\partial}{\partial x}(\mathfrak{D} u'_0).$$

This is identical with (12·22), and assumes that only the thermal flux of diffusion is operating to increase the heat energy of the gas.

By (12·23) we have the following expression for $\mathfrak{D}$, which we have termed the specific energy of diffusion:—

(19·02)
$$\begin{aligned}\mathfrak{D} &= \frac{\mathrm{RT}}{\mathrm{J}}\frac{1}{\alpha'_0}\sum_1^\infty r(\nu_1\alpha_r+\nu_2\alpha_{-r})\\ &= -\frac{\mathrm{RT}}{\mathrm{J}}\frac{\mathrm{B}_0\beta'_0}{\mathrm{A}_0\mathrm{R}\alpha'_0}\frac{\nu_0}{\lambda_1\lambda_2}\\ &= -\frac{\nu_0}{\lambda_1\lambda_2}\frac{\mathrm{RT}}{\mathrm{J}}\frac{\mathrm{D_T}}{\mathrm{D}_{12}},\end{aligned}$$

by (9·20) and (10·05), (10·10). Since C_v, the specific heat at constant volume for the composite gas, is given by

(19·03)
$$\mathrm{C}_v = \tfrac{3}{2}\frac{\mathrm{R}}{\mathrm{J}m_0},$$

we have, writing k_T for D_T/D_{12}, as in § 14,

$$\mathfrak{D} = -\tfrac{2}{3}\frac{\nu_0 m_0 C_v T}{\lambda_1\lambda_2}\, k_T \tag{19·04}$$

$$= -\tfrac{2}{3}\frac{k_T}{\lambda_1\lambda_2}\,\rho_0 C_v T.$$

Thus we may write (19·01) in the form

$$\rho_0 C_v \frac{\partial T}{\partial t} = -\Sigma\frac{\partial}{\partial x}\left\{\tfrac{2}{3}\frac{k_T}{\lambda_1\lambda_2}\,\rho_0 C_v T u'_0\right\}. \tag{19·05}$$

We may notice that there is an interesting analogy between this equation and the ordinary equation of continuity

$$\frac{\partial\rho_0}{\partial t} = -\Sigma\frac{\partial}{\partial x}(\rho_0 u_0), \tag{19·06}$$

which refers the rate of concentration of matter in a volume element to the differential rate of transfer of matter across its extent. In the case of diffusion, the opposing inter-diffusing streams carry equal numbers of molecules in opposite directions, but while the energy of molecular agitation is the same for either group of molecules, the kinetic energy of diffusion is different, owing to the *different* masses with the *same* velocity of diffusion $\pm(u'_0, v'_0, w'_0)$. It is, I imagine, to this cause that the thermal flux of diffusion is due, though the suggestion is only tentative and does not affect the accuracy of (19·05) one way or the other. It is clear, however, that if the velocity of diffusion is such as to cause a concentration of the more massive molecules in any region, at the expense of the lighter molecules (since the total number ν_0 is not affected by diffusion), the temperature of the region will rise, k_T being positive (§ 14); this readily follows from a comparison of (19·05) and (19·06). From our discussion of the magnitude of k_T in § 14, it appears that the specific energy of diffusion is greater the greater the difference in mass and size between the molecules, as we should expect.

§ 20. Appendix on the Inequality of Temperature between the Component Gases.

[*Added June 2, 1916.*]

Up to the end of § 3 the equations of this paper take account of the possibility of a difference of temperature (as defined in § 1 (*c*)) between the component gases. After that point it is virtually assumed that T'_0 is zero. We will now briefly consider what modification must be made in order to cover the general case.

It is clear from (3·151) that the component gases have different temperatures only when the ratio of the two gases, by volume, is changing with time. Consequently in all steady states the temperatures are the same, although the gas may be non-uniform in temperature, velocity, or composition; in this case §§ 4–19 give a complete account of the first-order phenomena of the gas.

When the relative proportions of the component gas are varying, so that the temperatures are unequal, the determination of the coefficients α, β, γ in §§ 4–9 is unaffected, but we must examine how far the physical equations of the succeeding sections remain valid. It is immediately evident that all the phenomena grouped under the general term "diffusion" (*cf.* § 10 and §§ 13–16) are uninfluenced by the presence or absence of the temperature difference, because the former depend solely on the terms in $f/(f)_0$ which are of odd degree in U, V, W (*cf.* § 3 (*a*)), while the terms relating to T'_0 or $\frac{\partial \lambda'_0}{\partial t}$ are of even degree.

Further, it is readily manifest that the equations of viscosity are likewise unmodified. The mean hydrostatic pressures of the component gases p_1, p_2 are indeed altered, but their sum p_0 remains constant with the value defined in terms of ν_0 and T_0 by (1·18). Since the series $J(C^2)$ of § 3 (*a*) is symmetrical in U, V, W, the partial pressures $(p_{xx})_1$, $(p_{yy})_1$, $(p_{zz})_1$ are all affected equally with p_1, and similarly for the corresponding pressures for the second component gas. The differences $p_{xx}-p_0$, $p_{yy}-p_0$, $p_{zz}-p_0$ are therefore independent of T'_0, and it is clear from (3·03), (3·04) that this is true also of p_{yz}, p_{zx}, p_{xy}. Hence the equations of viscous stress given in § 11 are applicable both to steady and unsteady states of the gas.

Finally, it may be seen on inspection that the equation of energy, deduced in § 12, is true independently of the existence of a temperature difference between the component gases. The equations (12·06), (12·07), on which the equation of energy is based, remain true in all cases, if T is taken to be T_0. Also the presence of the even power series $J(C^2)$ in the expression for $f(U, V, W)$ does not affect the value of $\overline{UC^2}$, so that the expressions of § 12 (*c*) for the coefficient of thermal conduction and the specific energy of diffusion are universally true.

It remains only to form an estimate of the magnitude of T'_0 by determining approximately the coefficients δ_r in $J(C^2)$. For this purpose it is simplest to make use of equation (2·23), viz.,

$$(20·01) \qquad \frac{(2h_0m_1)^s}{1\,.\,3\,.\,5\,\ldots\,(2s+1)}\,\Delta C_1^{2s} = \nu_0\frac{\partial \lambda'_0}{\partial t} = -\frac{(2h_0m_2)^s}{1\,.\,3\,.\,5\,\ldots\,(2s+1)}\,\Delta C_2^{2s}.$$

Then it may readily be proved, after the manner of §§ 6, 7 of my second paper (*loc. cit.*), and as a consequence of the expressions (3·03), (3·04) for $f(U, V, W)$, that

$$(20·02) \quad \frac{(2h_0m_1)^s}{1\,.\,3\,.\,5\,\ldots\,(2s+1)}\,\Delta C_1^{2s} = 32D_0\frac{\partial \lambda'_0}{\partial t}\sum_{r=0}^{\infty}\left[\{d_{1111}(r,s)+d_{1212}(r,s)\}\,\delta_r+d_{2112}(r,s)\,\delta_{-r}\right],$$

$$(20·03) \quad \frac{(2h_0m_2)^s}{1\,.\,3\,.\,5\,\ldots\,(2s+1)}\,\Delta C_2^{2s} = 32D_0\frac{\partial \lambda'_0}{\partial t}\sum_{r=0}^{\infty}\left[d_{1221}(r,s)\,\delta_r+\{d_{2222}(r,s)+d_{2121}(r,s)\}\,\delta_{-r}\right],$$

where

$$(20{\cdot}04) \qquad d_{1111}(r,\ s) = \mathrm{N}_{r-1,\,s-1}\nu_1^2 \iint e^{-(x^2+y^2)}\, x^2y^2 \sum_{k=0}^{r,\,s} \phi_{11}{}^{k}(y)\, \mathrm{B}^{k}{}_{1111}(r,\ s)\, dx\, dy,$$

$$(20{\cdot}05) \qquad d_{1212}(r,\ s) = \mathrm{N}_{r-1,\,s-1}\nu_1\nu_2 \iint e^{-(x^2+y^2)}\, x^2y^2 \sum_{k=0}^{r,\,s} \phi_{12}{}^{k}(y)\, \mathrm{B}^{k}{}_{1212}(r,\ s)\, dx\, dy,$$

$$(20{\cdot}06) \qquad d_{2112}(r,\ s) = \mathrm{N}_{r-1,\,s-1}\nu_1\nu_2 \iint e^{-(x^2+y^2)}\, x^2y^2 \sum_{k=0}^{r,\,s} (-1)^k \phi_{12}{}^{k}(y)\, \mathrm{B}^{k}{}_{2112}(r,\ s)\, dx\, dy.$$

There are similar equations in which the suffixes 1, 2 are interchanged, which need not be written down.

From a comparison of (20·01) with (20·02), (20·03) we obtain the following equations for δ_r, δ_{-r} :—

$$(20{\cdot}07) \qquad 32\mathrm{D}_0 \frac{1}{\nu_0} \sum_{0}^{\infty} [\{d_{1111}(r,\ s) + d_{1212}(r,\ s)\}\, \delta_r + d_{2112}(r,\ s)\, \delta_{-r}] = 1,$$

$$(20{\cdot}08) \qquad 32\mathrm{D}_0 \frac{1}{\nu_0} \sum_{0}^{\infty} [d_{1221}(r,\ s)\, \delta_r + \{d_{2222}(r,\ s) + d_{2121}(r,\ s)\}\, \delta_{-r}] = -1.$$

In these equations s ranges from 1 to ∞ (that the zero value is excluded may be readily seen from § 2 (*c*), (*e*)). Similarly r effectively ranges over the same values, since it is clear from (20·04)–(20·06) that $d(0,\ s) = 0$ in all cases.* Hence the equations (20·07), (20·08) do not enable us to determine δ_0 and δ_{-0}, which are given by (3·101), (3·102) in terms of the remaining δ's. Indeed, to obtain T'_0 in terms of $\frac{\partial\lambda'_0}{\partial t}$, by means of (3·151), we need only to calculate $\sum_{1}^{\infty} r\delta_r$ or $\sum_{1}^{\infty} r\delta_{-r}$ (*cf.* (3·122)). Symmetrical determinantal expressions for these can be deduced as in § 5, if desired, but we shall be content here to determine δ'_0 to a first approximation only.

The two central terms of the two central equations of type (20·07), (20·08) are

$$(20{\cdot}09) \qquad 32\mathrm{D}_0 \frac{1}{\nu_0} [\{d_{1111}(1,\ 1) + d_{1212}(1,\ 1)\}\, \delta_1 + d_{2112}(1,\ 1)\, \delta_{-1}] = 1,$$

$$(20{\cdot}10) \qquad 32\mathrm{D}_0 \frac{1}{\nu_0} d_{1221}(1,\ 1)\, \delta_1 + \{\partial_{2222}(1,\ 1) + d_{2121}(1,\ 1)\}\, \delta_{-1}] = -1,$$

and it may readily be seen that

$$(20{\cdot}11) \qquad d_{1111}(1,\ 1) = \frac{\pi}{144}\, \nu_1{}^2 \mathrm{K}'_{11}(0),$$

$$(20{\cdot}12) \qquad d_{2222}(1,\ 1) = \frac{\pi}{144}\, \nu_2{}^2 \mathrm{K}'_{22}(0),$$

$$(20{\cdot}13) \quad d_{1212}(1,\ 1) = -d_{1221}(1,\ 1) = d_{2121}(1,\ 1) = -d_{2112}(1,\ 1) = \frac{\pi}{36}\, \mu_1\mu_2\nu_1\nu_2 \mathrm{K}'_{12}(0).$$

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* When r or s is zero, $k = 0$, and $\phi^k(y) = 0$. *Cf.* (4·17).

Hence, if we assign to D_0 (which has so far been arbitrary) the value given by

$$D_0 = \frac{9\nu_0}{8\pi\mu_1\mu_2\nu_1\nu_2 K'_{12}(0)}, \tag{20·14}$$

we may write the equations (20·09), (20·10) as follows:—

$$\left(1+\frac{\lambda_{12}k_1^{\,0}}{4\mu_1\mu_2}\right)\delta_1-\delta_{-1} = 1, \tag{20·15}$$

$$-\delta_1+\left(1+\frac{\lambda_{21}k_2^{\,0}}{4\mu_1\mu_2}\right)\delta_{-1} = -1. \tag{20·16}$$

We have here introduced the notation

$$k_1^{\,0} \equiv \frac{K'_{11}(0)}{K'_{12}(0)}, \qquad k_2^{\,0} \equiv \frac{K'_{22}(0)}{K'_{12}(0)}. \tag{20·17}$$

From (3·122) we deduce the following equation for δ'_0:—

$$\delta'_0 = -2\lambda_1\lambda_2 \sum_1^\infty r(\delta_r-\delta_{-r}). \tag{20·18}$$

The first approximation to this is found, from (20·15), (20·16), to be given by

$$\delta'_0 = -2\lambda_1\lambda_2 \frac{\lambda_{12}k_1^{\,0}+\lambda_{21}k_2^{\,0}}{\lambda_{12}k_1^{\,0}+\lambda_{21}k_2^{\,0}+\dfrac{k_1^{\,0}k_2^{\,0}}{4\mu_1\mu_2}}. \tag{20·19}$$

Hence, by (3·151) and (20·14) we have

$$\begin{aligned} T'_0 &\doteq \tfrac{1}{3}D_0 T_0 \delta'_0 \frac{\partial\lambda'_0}{\partial t} \\ &= -\frac{3T_0}{4\pi\nu_0\mu_1\mu_2 K'_{12}(0)}\left\{1+\frac{k_1^{\,0}k_2^{\,0}}{4\mu_1\mu_2(\lambda_{12}k_1^{\,0}+\lambda_{21}k_2^{\,0})}\right\}^{-1}\frac{\partial\lambda'_0}{\partial t} \\ &= -\tfrac{1}{3}D_{12}^{\,0}\frac{m_1+m_2}{2R}\left\{1+\frac{k_1^{\,0}k_2^{\,0}}{4\mu_1\mu_2(\lambda_{12}k_1^{\,0}+\lambda_{21}k_2^{\,0})}\right\}^{-1}\frac{\partial\lambda'_0}{\partial t} \\ &\equiv -I_\lambda\frac{\partial\lambda'_0}{\partial t}, \end{aligned} \tag{20·20}$$

where $D_{12}^{\,0}$ is the first approximation to the coefficient of diffusion (*cf.* (13·08)), while I_λ is a new quantity, defined by the last equation, which we may term the anisothermal diffusion constant.

We may easily gain some idea of the order of magnitude of I_λ if we consider two gases of similar dynamical properties, *i.e.*, such that $m_1 = m_2$, and $k_1^{\,0} = k_2^{\,0} = 1$. The last factor in I_λ is nearly equal to unity, so that we shall neglect it in our approximate calculations. In this case, therefore,

$$I_\lambda = -\tfrac{1}{3}\frac{D_{11}{}^0}{R/m}.$$

For oxygen the value of $D_{11}{}^0$ is approximately 0·19 (*cf.* JEANS' treatise, p. 335), while $R/m = 260 . 10^4$ (*loc. cit.*, p. 131). Hence $I_\lambda = 0{\cdot}24 . 10^{-7}$ approximately. Thus if the density-ratio of the two gases is changing by 1 per cent. per second, the difference of temperature, if they are equally mixed (*i.e.*, $\lambda_1 = \lambda_2 = \frac{1}{2}$), is approximately one thousand-millionth of a degree centigrade.* The hotter gas is the one which is diminishing in relative concentration. In fact, we may perhaps regard the slightly excess speed of the molecules of this gas as the cause of its relative expansion and consequent rarefaction. It is clear from these figures, however, that the phenomenon is likely to be of very minute dimensions in ordinary cases.

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* Thus $T'_0 = \lambda_1\lambda_2(T_1 - T_2) = \frac{1}{4}(T_1 - T_2) = -0{\cdot}24 . 10^{-7}\frac{\delta\lambda_0}{\delta t} = -0{\cdot}24 . 10^{-9}$, so that $T_1 - T_2 = -10^{-9}$ approximately.

Note A. (To p. 118, line 3.)

[Since this paper was communicated to the Royal Society, this part of the theory has been experimentally tested and confirmed, at least qualitatively. An account of the preliminary qualitative experiments, made by Dr. F. W. DOOTSON, will be found in the 'Philosophical Magazine,' xxxiii, p. 248.—*Note added February 22, 1917.*]

Note B. (To p. 118, middle.)

[Recently I have succeeded in proving the identity of π and $\sin \pi x$ with the determinants referred to, using elementary algebraical methods. The construction of a formal justification of the analytical methods used in the present paper is also being proceeded with, and I hope to be able later to deal with the questions of convergence raised here, and to bring the present theory into satisfactory relation with that based on BOLTZMANN'S equation.—*Note added February 22, 1917.*]

Note C. (To p. 129, line 2.)

[In a later paper it will be shown that considerations of convergence require a re-grouping of the terms in these expansions, so that they become series of polynomials in C^2. The expansions are really used in this form in the present paper, the re-grouping of the terms being effected by means of the difference-transformations described in § 5 (*d*).—*Note added February 22, 1917.*]

Note D. (To p. 189, line 12.)

[Since the above was written the indicated result has been qualitatively confirmed in the case of three pairs of gases. The time taken to attain the steady state was only a few hours in the experiments referred to; they are described in a Note by Dr. F. W. DOOTSON and the author in the 'Philosophical Magazine,' xxxiii, p. 248.—*Note added February 22, 1917.*]

Note E. (To pp. 158, 184, 185.)

[In a note recently communicated to the 'Philosophical Magazine,' I have considered thermal diffusion in the case of two molecules nearly or quite equal in mass, and very unequal in size. If the difference of mass is sufficiently small, the *larger* molecules will tend towards the cooler regions.—*April 30, 1917.*]

Note F. (To p. 115.)

[In his 'Inaugural Dissertation,' Upsala, 1917 (received just before the final revision of the proofs of this paper), D. Enskog gives a mathematical theory of simple and composite monatomic gases, based upon Boltzmann's integral equation for the velocity-distribution function. The method of solution is, however, different from that of his 1912 paper. The numerical and other results, including those relating to thermal diffusion, are in agreement with those of this paper, though not always identical in form. While perhaps less developed from the physical standpoint, Dr. Enskog's work is mathematically much the more complete. His elegant and accurate proofs will materially lighten the task of proving my own work to be in conformity with Boltzmann's equation.—*April 30, 1917.*]