The Kinetic Theory of a Gas Constituted of Spherically Symmetrical Molecules

S. Chapman

Phil. Trans. R. Soc. Lond. A 1912 **211**, 433-483
doi: 10.1098/rsta.1912.0012

XII. *The Kinetic Theory of a Gas Constituted of Spherically Symmetrical Molecules.*

By S. Chapman, *M.Sc., Trinity College, Cambridge; Chief Assistant, Royal Observatory, Greenwich.*

Communicated by Sir Joseph Larmor, *Sec. R.S.*

Received May 29,—Read June 29,—Received after Revision and Alteration as indicated in the text, with the addition of Part III., pp. 460–483, November 9, 1911.

Contents.

Introduction.

The principal kinetic theories of a gas proceed either on the hypothesis that the molecules are rigid elastic spheres, or that they are point centres of forces which vary inversely as the fifth power of the distance. Maxwell has worked out the consequences of the latter hypothesis in his well-known theory,[*] which is unrivalled in its high degree of accuracy and (after some improvements by Boltzmann[†]) in its perfection of mathematical form. All the quantities not taken account of in the theory (such as the time occupied by molecular encounters, and the effect of collisions in which more than two molecules take part) are properly negligible under ordinary conditions. The theory has the disadvantage, however, that the underlying hypothesis is highly artificial (being chosen chiefly on account of mathematical simplifications connected with it, rather than from any physical reasons), and does not represent the real facts at all adequately.

---

[*] 'Phil. Trans.,' 1867; 'Scientific Papers,' vol. ii., p. 23. For convenience we shall refer to a gas of the type there contemplated as a Maxwellian gas. Of course, its molecules possess no internal energy.

[†] 'Vorlesungen über Gastheorie,' vol. i.

The other hypothesis referred to seems to be much more in agreement with fact, but its consequences have been worked out less accurately. The method which has almost always been used is the one originally devised by CLAUSIUS and MAXWELL; MAXWELL abandoned it later, however, as it had "led him at times into grave error." In spite of its apparent simplicity, numerical errors of large amount may undoubtedly creep in in a very subtle way. Hence the theory of a gas whose molecules are elastic spheres remains in a rather unsatisfactory state. As a "descriptive" theory (to use MEYER'S apt term) it has, however, served a useful purpose; the general laws of gaseous phenomena have been developed by its aid in an elementary way, which has conduced to a wider diffusion of knowledge of the kinetic theory than would have been possible if the sole line of development had been by the more mathematical and accurate methods used by MAXWELL and BOLTZMANN.

In this paper I have applied the latter methods, with an extension of the analysis, to the elastic-sphere theory among others. In fact, I have obtained expressions for the viscosity, diffusivity, and conductivity of a gas without assuming any properties of the molecules save that they are spherically symmetrical. Many known laws are thus proved more generally than in any former theories, but the formulæ so obtained cannot in all cases be put into a really useful form without a knowledge of the nature of the molecules. The supplementary calculations required to complete the general formulæ of Part I. of this paper are carried out in Part II. for three special cases, viz., rigid elastic spherical molecules, molecules which are centres of repulsive or attractive force varying inversely as the n^{th} power of the distance, and rigid elastic spherical molecules surrounded by fields of attractive force. In Part III. the general formulæ are completed in these cases and discussed in their relations to the results of former theories and of experiment.

PART I.—GENERAL THEORY.

1. *Statement of the Problem.*

We shall deal with a gas composed of two kinds of molecules, which are all supposed to be spherically symmetrical; m, m', ν, ν' will denote their masses and the number of each kind per unit volume respectively. Similarly the velocity components of typical molecules of the two kinds will be denoted by (u, v, w), (u', v', w'). Let Q be any function of the velocity components of a single molecule (*e.g.*, momentum, energy). At any point (x, y, z) let $\overline{Q}$ be the mean value of Q, so that

$$\overline{Q} = \iiint Q f(u, v, w)\, du\, dv\, dw,$$

where $f(u, v, w)$ is the function which expresses the law of distribution of the velocities among the molecules m.* Thus the aggregate value of ΣQ for the $\nu\, dx\, dy\, dz$ molecules m in a volume element $dx\, dy\, dz$ at the point considered is given by

$$\Sigma Q = \nu \bar{Q}\, dx\, dy\, dz.$$

Let (u_0, v_0, w_0), (u_0', v_0', w_0') be the mean values of (u, v, w), (u', v', w'). Except in considering diffusion, we shall suppose that the mean velocities of each system of molecules is the same, so that $u_0 = u_0'$, $v_0 = v_0'$, $w_0 = w_0'$. We shall write $U = u - u_0$, $U' = u' - u_0'$, and so on, so that $\bar{U} = \bar{V} = \bar{W} = 0$, $\overline{U'} = \overline{V'} = \overline{W'} = 0$.

The general equation of transfer of Q, independent of the action of external forces is†

$$(1) \quad \nu \frac{D\bar{Q}}{Dt} = \sum_{x, y, z} \left[-\frac{\partial}{\partial x}(\nu \overline{UQ}) + \frac{\partial \bar{Q}}{\partial u_0} \left\{ \nu \frac{Du_0}{Dt} + \frac{\partial}{\partial x}(\nu \overline{U^2}) + \frac{\partial}{\partial y}(\nu \overline{UV}) + \frac{\partial}{\partial z}(\nu \overline{UW}) \right\} \right] + \Delta Q;$$

here $\frac{D}{Dt}$ denotes the "mobile operator" $\left(\frac{d}{dt} + u_0 \frac{\partial}{\partial x} + v_0 \frac{\partial}{\partial y} + w_0 \frac{\partial}{\partial z}\right)$ of the hydrodynamical equations. The only term of the above equation which needs explanation is ΔQ, which denotes the rate of change of $\bar{Q}$ due to the molecular encounters; thus the increase in ΣQ which is produced in the element $dx\, dy\, dz$ by collisions‡ in time dt is $dx\, dy\, dz\, dt\, \Delta Q$. The calculation of ΔQ is the immediate object of our investigation.

The motion of the mass centre G of two colliding molecules remains unaltered by the encounter, and this point may be taken as the origin of a system of uniformly moving axes, relative to which each molecule will describe an orbit in a plane through G; the two orbits will be similar to each other and symmetrical with respect to the line of apses. If the molecules move with sufficient velocity to carry them beyond the range of each other's action, the orbits will each have a pair of asymptotes; the asymptotes of the paths while entering on collision are parallel and separated by a distance p (say), and the effect of the collision is to turn the direction

---

* Thus the number of molecules m in a volume element $dx\, dy\, dz$ which possess velocities whose three components lie between u and $u + du$, v and $v + dv$, w and $w + dw$, is

$$\nu f(u, v, w)\, du\, dv\, dw\, dx\, dy\, dz;$$

this property *defines* $f(u, v, w)$. Evidently

$$\iiint f(u, v, w)\, du\, dv\, dw = 1;$$

$f(u, v, w)$ is, of course, also a function of x, y, z and t in general. A similar function $f'(u', v', w')$ exists for the molecules m'.

† See JEANS' "Dynamical Theory of Gases" (Camb. Univ. Press, 1904), pp. 276–279; or BOLTZMANN'S 'Vorlesungen über Gastheorie,' vol. i., § 20.

‡ The terms collision and encounter are used indifferently to signify any mutual action of the molecules which affects their velocities.

of the relative velocity V_0 (say) through an angle 2χ in the plane of the orbits (where $\frac{1}{2}\pi-\chi$ is the angle between an asymptote and the line of apses), the molecules travelling away from one another along the second pair of asymptotes with the relative velocity unchanged. The angle χ is a function of p and V_0 which depends upon the nature of the molecular forces.

The velocity components (u_{12}, v_{12}, w_{12}) of a molecule m after collision with a molecule m' can therefore be written down,* from merely geometrical considerations, in terms of the original components (u, v, w), (u', v', w'), m, m', χ, and ϵ, the latter being the angle between the plane of the orbits (which contains V_0 and p) and a plane containing V_0 and parallel with the axis of x. Thus

$$(2) \qquad u_{12} = u+\frac{m'}{m+m'}\left[2\,(u'-u)\sin^2\chi-\sqrt{\{V_0^2-(u'-u)^2\}}\sin 2\chi\cos(\epsilon-w_1)\right],$$

$$(3) \qquad v_{12} = v+\frac{m'}{m+m'}\left[2\,(v'-v)\sin^2\chi-\sqrt{\{V^2-(v'-v)^2\}}\sin 2\chi\cos(\epsilon-w_2)\right],$$

$$(4) \qquad w_{12} = w+\frac{m'}{m+m'}\left[2\,(w'-w)\sin^2\chi-\sqrt{\{V^2-(w'-w)^2\}}\sin 2\chi\cos(\epsilon-w_3)\right].$$

The angle w_1 is introduced only for symmetry, as it is zero; w_2 and w_3 are given by

$$(5) \qquad (u'-u)\,(v'-v)+\sqrt{\{[V_0^2-(u'-u)^2]\,[V_0^2-(v'-v)^2]\}}\cos w_2 = 0,$$

and a similar equation in which $w'-w$ replaces $v'-v$. Of course,

$$(6) \qquad V_0^2 = (u'-u)^2+(v'-v)^2+(w'-w)^2.$$

This notation having been explained, we return to the consideration of ΔQ; we divide this into two parts $\Delta_{11}Q$ and $\Delta_{12}Q$, the former representing the part due to collisions of the molecules m among themselves, the latter that due to collisions with the molecules m'. Thus

$$(7) \qquad \Delta Q = \Delta_{11}Q+\Delta_{12}Q.$$

Then it is not difficult to prove† that

$$(8) \quad \Delta_{12}Q=\iiint_{-\infty}^{+\infty}\iiint_{-\infty}^{+\infty}\int_0^{\infty}\int_0^{2\pi}\nu\nu'(\delta_{12}Q)f(u,v,w)f'(u',v',w')\,du\,dv\,dw\,du'\,dv'\,dw'\,V_0\,p\,dp\,d\epsilon,$$

where $\delta_{12}Q = Q_{12}-Q$ in which Q_{12} is the same function of (u_{12}, v_{12}, w_{12}) as is Q of (u, v, w); thus $\delta_{12}Q$ denotes the change in the value of Q for a molecule m, produced by a collision with a molecule m'.

---

* See JEANS' "Dynamical Theory of Gases," pp. 284–288; BOLTZMANN'S 'Vorlesungen über Gastheorie,' vol. i., § 21.

† See the original papers by MAXWELL, or the treatises by BOLTZMANN and JEANS, already quoted.

The value of $\Delta_{11}Q$ may be obtained from $\Delta_{12}Q$ by making $m' = m$, $\nu' = \nu$, &c., throughout.

The problem before us consists in the evaluation of the integral on the right-hand side of the last equation, with certain special forms of Q. Before proceeding with this we shall first write down the forms assumed by the equation of transfer (1) in these cases.

2. *Special Forms of the Equation of Transfer.*

The equation (1) is more convenient for use in the equivalent form

$$\nu\left[\frac{D\overline{Q}}{Dt}-\frac{\partial Q}{\partial u_0}\cdot\frac{Du_0}{Dt}-\frac{\partial\overline{Q}}{\partial v_0}\cdot\frac{Dv_0}{Dt}-\frac{\partial\overline{Q}}{\partial w_0}\cdot\frac{Dw_0}{Dt}\right]$$

$$=\sum_{x,y,z}\left[-\frac{\partial}{\partial x}(\nu\overline{UQ})+\frac{\partial\overline{Q}}{\partial u_0}\left\{\frac{\partial}{\partial x}(\nu\overline{U^2})+\frac{\partial}{\partial y}(\nu\overline{UV})+\frac{\partial}{\partial z}(\nu\overline{UW})\right\}\right]+\Delta Q.$$

In dealing with the problem of heat conduction we shall have to put $Q = u(u^2+v^2+w^2)$ and $Q = u^2+v^2+w^2$; but in this case it will be sufficient to consider the case of a gas at rest, so that $u_0 = v_0 = w_0 = 0$, and the left-hand side of the above equation becomes simply $\nu\frac{D\overline{Q}}{Dt}$. On the right-hand side, in finding $\frac{\partial\overline{Q}}{\partial u_0}$, $\frac{\partial\overline{Q}}{\partial v_0}$, $\frac{\partial\overline{Q}}{\partial w_0}$, we must, of course, not put $u_0 = v_0 = w_0 = 0$ till the differentiation has been performed. Thus, when $Q = u^2+v^2+w^2$ we have $\overline{Q} = u_0{}^2+v_0{}^2+w_0{}^2+\overline{U^2+V^2+W^2}$, so that $\frac{\partial\overline{Q}}{\partial u_0} = \frac{\partial\overline{Q}}{\partial v_0} = \frac{\partial\overline{Q}}{\partial w_0} = 0$, and the equation of transfer becomes*

$$(9)\qquad 3\nu\frac{Dq}{Dt} = -\sum_{x,y,z}\frac{\partial}{\partial x}\left[\nu\,\overline{U(U^2+V^2+W^2)}_0\right]+\Delta_{12}(u^2+v^2+w^2),$$

where we have written q for $\frac{1}{3}\overline{U^2+V^2+W^2}$; $\Delta_{11}(u^2+v^2+w^2)$ vanishes because the energy of the molecules, being wholly translational, is unaltered by the encounters of the molecules m among themselves.

In writing out these equations of transfer, it is customary and sufficient to neglect the mean values of odd functions of U, V, W in comparison with the mean values of even functions, and also to neglect the *differences* between the mean values of *corresponding* even functions (such as U^2, V^2, W^2) in comparison with these mean values themselves; thus we may write $\overline{U^2} = \overline{V^2} = \overline{W^2} = q$, and neglect $\overline{UV}$, $\overline{VW}$, $\overline{WU}$ in comparison with q. Similarly we may neglect $\overline{UV(U^2+V^2+W^2)}$ in comparison with $\overline{U^2(U^2+V^2+W^2)}$, and the latter we may calculate as if MAXWELL'S law of

---

* The suffix 0 on the right-hand side is to indicate that we are considering a gas at rest. Similarly in equation (10).

distribution of velocity held exactly. This is because we shall only be considering slight disturbances from the uniform steady state.

Thus from MAXWELL'S law of distribution* we find that $q = (2hm)^{-1}$, $\overline{\mathrm{U}^2(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)} = 5q^2$. Putting $\mathrm{Q} = u(u^2+v^2+w^2)$, and taking $u_0 = v_0 = w_0 = 0$, we find that $\dfrac{\partial\overline{\mathrm{Q}}}{\partial u_0} = 5q$, $\dfrac{\partial\overline{\mathrm{Q}}}{\partial v_0} = \dfrac{\partial\overline{\mathrm{Q}}}{\partial w_0} = 0$, so that the equation of transfer takes the form

$$\nu\frac{\mathrm{D}}{\mathrm{D}t}\overline{\mathrm{U}(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)_0} = -5\nu q\frac{\partial q}{\partial x} + \Delta u(u^2+v^2+w^2)_0,$$

or (since, as we shall see later, on p. 447, the left-hand side of this equation is of a lower order than the terms on the right)

$$(10) \qquad 5\nu q\frac{\partial q}{\partial x} = \Delta u(u^2+v^2+w^2)_0.$$

We next put $\mathrm{Q} = u^2$ and $\mathrm{Q} = uv$ in order to consider the phenomenon of viscosity; in this case, of course, we must take into account the mass velocity of the gas. The substitution of these values of Q in the general equation is quite straightforward,† so that we set down the results at once:—

$$(11) \qquad -\tfrac{2}{3}\nu q\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)+2\nu q\frac{\partial u_0}{\partial x} = \Delta u^2,$$

$$(12) \qquad \nu q\left(\frac{\partial v_0}{\partial x}+\frac{\partial w_0}{\partial y}\right) = \Delta uv.$$

We now turn to the calculation of Δu^2 and $\Delta u(u^2+v^2+w^2)_0$; the value of Δuv will not be calculated directly, but obtained from Δu^2 by transformation of co-ordinates, and the value of $\Delta_{12}(u^2+v^2+w^2)_0$ will ultimately be eliminated from our equations, and so need not be calculated.

First of all we shall calculate the values of $\delta_{12}\mathrm{Q}$ from equations (2)–(5) for substitution in (8). Since, however, several terms of $\delta_{12}\mathrm{Q}$ disappear on integration with respect to ϵ, it will be most convenient if we immediately calculate $\int_0^{2\pi}\delta_{12}\mathrm{Q}\,d\epsilon$.

3. *Values of* $\int_0^{2\pi}\delta_{12}\mathrm{Q}\,d\epsilon$.

In calculating $\delta_{12}\mathrm{Q}$ we shall find it convenient, partly for immediate brevity, but much more for the sake of a subsequent transformation of the variables of integration in (8), to write

$$(13) \qquad (m+m')(\mathrm{U}'-\mathrm{U}) = \mathrm{X}, \quad (m+m')(\mathrm{V}'-\mathrm{V}) = \mathrm{Y}, \quad (m+m')(\mathrm{W}'-\mathrm{W}) = \mathrm{Z},$$

$$(14) \qquad m\mathrm{U}+m'\mathrm{U}' = \mathrm{X}_1, \quad m\mathrm{V}+m'\mathrm{V}' = \mathrm{Y}_1, \quad m\mathrm{W}+m'\mathrm{W}' = \mathrm{Z}_1.$$

---

* In which $f(u, v, w) = \left(\dfrac{hm}{\pi}\right)^{3/2} e^{-hm\Sigma \mathrm{V}^2}$.

† See JEANS' treatise, §§ 336, 338.

Thus

$$\mathrm{X}^2+\mathrm{Y}^2+\mathrm{Z}^2 = (m+m')^2\mathrm{V}_0{}^2,$$

and

$$(15) \qquad (m+m')(m\Sigma\mathrm{U}^2+m'\Sigma\mathrm{U}'^2) = \mathrm{V}_1{}^2+mm'\mathrm{V}_0{}^2,$$

writing $\mathrm{V}_1{}^2 = \mathrm{X}_1{}^2+\mathrm{Y}_1{}^2+\mathrm{Z}_1{}^2$. Also, we have

$$(16) \qquad (m+m')\,\mathrm{U} = \mathrm{X}_1-k'\mathrm{X}, \quad (m+m')\,\mathrm{V} = \mathrm{Y}_1-k'\mathrm{Y}, \quad (m+m')\,\mathrm{W} = \mathrm{Z}_1-k'\mathrm{Z},$$

$$(17) \qquad (m+m')\,\mathrm{U}' = \mathrm{X}_1+k\mathrm{X}, \quad (m+m')\,\mathrm{V}' = \mathrm{Y}_1+k\mathrm{Y}, \quad (m+m')\,\mathrm{W}' = \mathrm{Z}_1+k\mathrm{Z},$$

where $k = \dfrac{m}{m+m'}$, $\quad k' = \dfrac{m'}{m+m'}$.

Since the mass velocities of the two systems of molecules are the same, we have

$$(m+m')(u'-u) = (m+m')(\mathrm{U}'-\mathrm{U}) = \mathrm{X},$$

and two similar equations.

Considering $\mathrm{Q} = u^2$, it is easily seen that

$$\int_0^{2\pi}\delta_{12}u^2\,d\epsilon = \int_0^{2\pi}(u_{12}{}^2-u^2)\,d\epsilon$$
$$= \frac{m'}{(m+m')^2}\left[(u'-u)(mu+m'u')\,8\pi\sin^2\chi+m'\left\{\mathrm{V}_0{}^2-3\,(u'-u)^2\right\}\pi\sin^2 2\chi\right],$$

where we have expressed the result in terms of $\sin^2\chi$ and $\sin^2 2\chi$; on making the above transformations we obtain

$$(18) \quad \int_0^{2\pi}\delta_{12}u^2\,d\epsilon = \frac{m'}{(m+m')^3}\{\mathrm{X}_1\mathrm{X}+(m+m')u_0\mathrm{X}\}\,4\pi\sin^2\chi+\frac{m'^2}{(m+m')^2}(\mathrm{Y}^2+\mathrm{Z}^2-2\mathrm{X}^2)\pi\sin^2 2\chi.$$

We next consider $\delta_{12}\,u\,(u^2+v^2+w^2)_0$; we write $u_{12} = u+a-a'\cos(\epsilon-w_1)$, where $a = 2k'(u'-u)\sin^2\chi$, $a' = k'\sqrt{\mathrm{V}_0{}^2-(u'-u)^2}\sin 2\chi$, and similarly for v_{12} and w_{12}. Since

$$u_{12}{}^2+v_{12}{}^2+w_{12}{}^2 = \Sigma\,(u+a)^2-2\Sigma\,(u+a)\,a'\cos(\epsilon-w_1)+\Sigma a'^2\cos^2(\epsilon-w_1),$$

we have

$$\frac{1}{2\pi}\int_0^{2\pi}u_{12}\,(u_{12}{}^2+v_{12}{}^2+w_{12}{}^2)\,d\epsilon = (u+a)\,\Sigma\,(u+a)^2+\tfrac{1}{2}(u+a)\,\Sigma a'^2+a'\Sigma\,(u+a)\,a'\cos w_1.$$

It is easy to show that

$$a'\Sigma\,(u+a)\,a'\cos w_1 = \frac{m'^2}{(m+m')^4}\{u\,(\mathrm{Y}^2+\mathrm{Z}^2)-v\mathrm{XY}-w\mathrm{XZ}\}\sin^2 2\chi,$$

and from the last three equations it readily follows that

$$(19) \quad \int_0^{2\pi}\delta_{12}\,u\,(u^2+v^2+w^2)_0\,d\epsilon = \frac{m'}{(m+m')^4}(2\mathrm{X}_1\Sigma\mathrm{X}\mathrm{X}_1+\mathrm{X}\mathrm{V}_1{}^2+m'^2\mathrm{X}\mathrm{V}_0{}^2)\,4\pi\sin^2\chi$$
$$-\frac{2m'^2}{(m+m')^5}(3\mathrm{X}\Sigma\mathrm{X}\mathrm{X}_1-\mathrm{X}_1\Sigma\mathrm{X}^2)\,\pi\sin^2 2\chi.$$

Integration with Respect to p.

The integrand of equation (8) contains p explicitly in the term p, and implicitly in χ (which is a function of p and V_0); the latter occurs only in the form $\sin^2\chi$ and $\sin^2 2\chi$. Hence to integrate with respect to p we need only know the values of the two integrals*

$$4\pi V_0 \int_0^{2\pi} \sin^2\chi \, . \, p\, dp, \qquad \pi V_0 \int_0^{2\pi} \sin^2 2\chi \, . \, p\, dp,$$

which are functions of V_0 only. It is sufficient, at present, to denote them by the symbols $\Omega'(V_0)$ and $\Omega''(V_0)$, leaving their further consideration till later. As the functional relation between χ, V_0, and p, and consequently also the values of the above integrals, depends on the law of molecular interaction, which will differ according as the collision in question takes place between two molecules m, two molecules m', or one of each kind, we distinguish between the three cases by adding the suffixes 11, 22, 12 respectively to $\Omega'(V_0)$ and $\Omega''(V_0)$.

Thus

$$(20) \qquad \Delta_{12}u^2 = \frac{\nu\nu' m'}{(m+m')^3} \iiiint\!\!\iint [2\{XX_1 + (m+m')u_0X\}\,\Omega'_{12}(V_0)$$
$$+ k'(Y^2+Z^2-2X^2)\,\Omega''_{12}(V_0)]\, f(u,v,w)\, f'(u',v',w')\, du\, dv\, dw\, du'\, dv'\, dw'.$$

$$(21) \qquad \Delta_{12}\, u\,(u^2+v^2+w^2)_0 = \frac{\nu\nu' m'}{(m+m')^4} \iiiint\!\!\iint [(2X_1\Sigma XX_1 + XV_1^2 + m'^2XV_0^2)\,\Omega'_{12}(V_0)$$
$$-2k'(3X\Sigma XX_1 - X_1\Sigma X^2)\,\Omega''_{12}(V_0)]\, f(u,v,w)\, f'(u',v',w')\, du\, dv\, dw\, du'\, dv'\, dw'.$$

In the case of a Maxwellian gas† the expressions $\Omega(V_0)$ are independent of V_0, so that the integrals just written can be evaluated in terms of mean values of functions of U, V, W without any knowledge of the functions $f(u, v, w)$, $f'(u', v', w')$. In general, however, this is not possible; we require some knowledge of these functions, which express the law of distribution of velocity, in order to make further progress.

4. *The Law of Distribution of Velocity.*

It is well known that in a gas which has had time to attain a uniform state the functions f, f' have the respective forms

$$\left(\frac{hm}{\pi}\right)^{3/2} e^{-hm\Sigma U^2}, \qquad \left(\frac{hm'}{\pi}\right)^{3/2} e^{-hm'\Sigma U'^2}$$

---

* The factors $4\pi V_0$ and πV_0 are added merely for convenience.

† Also in the case of a gas whose molecules are point centres of force which *attract* one another according to the fifth-power law. This case, among others, is considered in Part II., and probably is nearer to actual fact than MAXWELL'S case.—*Note added October*, 1911.

which we shall denote by f_0, f'_0. When there are slight inequalities of temperature and mass motion in the gas, we shall suppose that

$$f = f_0\{1+\mathrm{F}(\mathrm{U}, \mathrm{V}, \mathrm{W})\}, \qquad f' = f'_0\{1+\mathrm{F}'(\mathrm{U}', \mathrm{V}', \mathrm{W}')\},$$

where F and F′ are expansible in the form of power series (without the constant terms) in the variables (U, V, W) and (U′, V′, W′) respectively. The coefficients will be small quantities which are functions of the velocity and temperature, and their derivatives, at the point considered. Thus F and F′ represent the small disturbances from the normal law of distribution, caused by the slight lack of uniformity in the gas. MAXWELL and BOLTZMANN* considered that the terms of the first three degrees are sufficient for the adequate representation of the disturbed state, and I shall follow them in this assumption. Thus we write

$$(22) \quad \mathrm{F}(\mathrm{U}, \mathrm{V}, \mathrm{W}) = (2hm)^{1/2}(a_1\mathrm{U}+a_2\mathrm{V}+a_3\mathrm{W})+2hm\left(\tfrac{1}{2}\Sigma a_{11}\mathrm{U}^2+2\Sigma a_{12}\mathrm{UV}\right)$$
$$+(2hm)^{3/2}\left(\tfrac{1}{6}\Sigma a_{111}\mathrm{U}^3+\tfrac{1}{2}\Sigma a_{122}\mathrm{UV}^2+a_{123}\mathrm{UVW}\right)$$

where the factors $(2hm)^{1/2}$, $(2hm)$, $(2hm)^{3/2}$ are added merely for convenience in the integration. We shall have a similar equation for F′, in which m, a_1, a_2, ... are replaced by m', a'_1, a'_2, ... Since, by definition,

$$\iiint f(u, v, w)\,du\,dv\,dw = 1, \qquad \iiint f'(u', v', w')\,du'\,dv'\,dw' = 1,$$

we have

$$1+a_{11}+a_{22}+a_{33} = 1, \qquad 1+a'_{11}+a'_{22}+a'_{33} = 1,$$

or

$$(23) \qquad a_{11}+a_{22}+a_{33} = 0, \qquad a'_{11}+a'_{22}+a'_{33} = 0.$$

---

* By MAXWELL in his memoir "On Stresses in Rarefied Gases," 'Phil. Trans.,' 1879, or 'Scientific Papers,' vol. ii., p. 681; by BOLTZMANN in his 'Vorlesungen über Gastheorie,' vol. i., p. 185. In each case the assumption was made in connection with a Maxwellian gas, but there are good grounds for believing that it is equally valid in general. As neither MAXWELL nor BOLTZMANN considered it necessary to give any justification for their procedure, I deliberately followed the same course, more especially as the attempt to make the step perfectly rigorous would have necessitated the introduction of much mathematical analysis which would be out of place here.

I should also mention that ENSKOG ('Phys. Zeitschrift,' xii., 58, January, 1911) has made an attempt to determine directly the form of the function F (u, v, w), applying methods of integration, similar in many ways to those used in this paper to evaluate ΔQ, to an equation arrived at by BOLTZMANN ('Vorlesungen,' vol. i., p. 114). From the expression for F (u, v, w) thus obtained ENSKOG deduces values of the coefficients of viscosity and thermal conduction for a simple gas.

I am indebted to Prof. LARMOR for the reference to ENSKOG'S work, of which I was unaware till after this paper had been communicated to the Royal Society.—*Note added October*, 1911. Some of these statements are modified by the last note on p. 483.

Similarly, since $\overline{\mathrm{U}} = \overline{\mathrm{V}} = \overline{\mathrm{W}} = 0$, $\overline{\mathrm{U}'} = \overline{\mathrm{V}'} = \overline{\mathrm{W}'} = 0$ by definition, we have

$$(24) \qquad 2a_1 + a_{111} + a_{122} + a_{133} = 0, \qquad 2a'_1 + a'_{111} + a'_{122} + a'_{133} = 0,$$

and four similar equations.*

We require the mean values of the following functions of U, V, W :—

$$\overline{\mathrm{U}^2} = (2hm)^{-1}(1+a_{11}), \quad \overline{\mathrm{UV}} = (2hm)^{-1}a_{12}, \quad \overline{\mathrm{U}^3} = (2hm)^{-3/2}a_{111}, \quad \overline{\mathrm{UV}^2} = (2hm)^{-3/2}a_{122},$$

$$\overline{\mathrm{U}(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)} = (2hm)^{-3/2}(a_{111}+a_{122}+a_{133}) = -2(2hm)^{-3/2}a_1\,;$$

similarly for the second system of molecules.

As usual, θ being the absolute temperature, we have $(2h)^{-1} = \mathrm{R}\theta$. The various components of partial pressure due to the first gas, p_{xx}, p_{xy}, &c., are given by

$$p_{xx} = \rho\overline{\mathrm{U}^2} = \frac{\nu}{2h}(1+a_{11}), \qquad p_{xy} = \rho\overline{\mathrm{UV}} = \frac{\nu}{2h}a_{12}$$

since $\rho = \nu m$; the mean hydrostatic pressure p is given by

$$p = \tfrac{1}{3}(p_{xx}+p_{yy}+p_{zz}) = \frac{\nu}{6h}(3+a_{11}+a_{22}+a_{33}) = \frac{\nu}{2h} = \mathrm{R}\nu\theta\,;$$

similarly for the second set of molecules.

In substituting ff' in the equations (20), (21), we shall write

$$ff' = f_0 f'_0(1+\mathrm{F}+\mathrm{F}') = \left(\frac{h^2mm'}{\pi^2}\right)^{3/2} e^{-\frac{h}{m+m'}(\mathrm{V}_1{}^2+mm'\mathrm{V}_0{}^2)}(1+\mathrm{F}+\mathrm{F}')$$

(by equation 15) since FF′, being the product of two first order small quantities, is negligible.

---

* It should be noted that the above expression for F is of the lowest degree consistent with the satisfaction of the requirements. The function F must provide for small changes in the mean values of even functions of U, V, W, and also of odd functions, both these changes being of the same order. The terms of the second degree do this for the even functions, a_{11}, a_{22}, a_{33} being of the first order; it might at first sight be thought that the terms of the first degree would provide for the odd functions of U, V, W, but this is not so on account of the conditions $\overline{\mathrm{U}} = \overline{\mathrm{V}} = \overline{\mathrm{W}} = 0$. Hence the terms of the third degree must be present, and their coefficients must be of the same order as a_1, a_{11}, &c.—*Note added October*, 1911. See the note on p. 483.

5. *Reduction of the Integrals.*

The evaluation of the expressions (20) and (21) is facilitated by changing the variables (U, V, W), (U′, V′, W′) to (X, Y, Z), (X_1, Y_1, Z_1) in accordance with equations (16) and (17). The Jacobian of transformation is easily found to be $(m+m')^{-6}$, and the limits remain as before, viz., $-\infty$ and $+\infty$. The two integrals are now of the form

$$A\iiint\iiint e^{-a\Sigma X^2-b\Sigma X_1^2}\,\Omega(V_0)\,\psi(X, Y, Z, X_1, Y_1, Z_1)\,(1+F+F')\,dX\,dY\,dZ\,dX_1\,dY_1\,dZ_1$$

where ψ is an integral polynomial in the given variables; F and F′ are also polynomials in these variables. Evidently only those terms in the product of ψ and (1+F+F′) which are of even degree in each of the six variables separately will give any result upon integration. It is easy, though tedious, to pick out these terms; evidently if ψ is of odd degree in the six variables combined, only those terms of F and F′ whose a-coefficients have an odd number of suffixes will need to be considered; similarly, if ψ is of even degree, we need only consider terms in F which have a_{11}, a_{12}, ... for coefficients. Having picked out these terms we are left with a number of integrals of the form

$$\iiint\iiint e^{-a\Sigma X^2-b\Sigma X_1^2}\,\Omega(V_0)\,X^{2l}Y^{2m}Z^{2n}X_1^{2l'}Y_1^{2m'}Z_1^{2n'}\,dX\,dY\,dZ\,dX_1\,dY_1\,dZ_1.$$

The integration with respect to X_1, Y_1, Z_1 can be carried out immediately—most conveniently by changing to polar co-ordinates. We do the same also in the case of the variables X, Y, Z changing to the variables V_0, θ, ϕ. The integration with respect to the latter two variables is simple, and there remains an integral of the form

$$\iiint e^{-\alpha V_0^2}\,\Omega(V_0)\,V_0^{2n}\,dV_0,$$

where $\alpha = \dfrac{hmm'}{m+m'}$, $\frac{1}{2}hm$, or $\frac{1}{2}hm'$ according as $\Omega(V_0)$ or Δ has the suffix 12, 11, or 22 respectively.

We shall consider this more particularly later; at present it is sufficient to denote it by a symbol. As we shall only need to consider the three cases $n = 2$, $n = 3$, $n = 4$, it is, perhaps, most convenient to denote it by P, R, S respectively, instead of adopting a more general notation. To distinguish between the different cases arising from the various functions $\Omega(V_0)$ occurring in the integrand, we add the same dashes and suffixes to P, R, S. Thus we have integrals P'_{12}, P'_{11}, P''_{11}, and so on, corresponding to the cases when in the above integral $n = 2$ and $\Omega(V_0)$ has the special forms Ω'_{12}, Ω'_{11}, Ω''_{11}, and so on: similarly for R and S.

Though the execution of the processes indicated is rather lengthy, it is quite simple and straightforward, so that, without entering into the details of the calculation, we shall quote the results forthwith. After simplification by means of the equations (23) and (24), we obtain the formulæ

$$(25)\quad \Delta_{12}u^2 = -4\pi^{-1/2}\nu\nu'\frac{mm'^2}{(m+m')^3}\left(\frac{hmm'}{m+m'}\right)^{3/2}\left[\tfrac{2}{3}\left(\frac{2}{h}\right)^{1/2}mm'u_0\left(\frac{a_1}{m^{3/2}}-\frac{a'_1}{m'^{3/2}}\right)\left(\mathrm{P}'_{12}-\tfrac{2}{5}\frac{hmm'}{m+m'}\mathrm{R}'_{12}\right)\right.$$
$$\left. +\tfrac{2}{3}(a_{11}-a'_{11})\,\mathrm{P}'_{12}+\tfrac{2}{5}\frac{hmm'^2}{m+m'}\left(\frac{a_{11}}{m}+\frac{a'_{11}}{m'}\right)\mathrm{R}''_{12}\right].$$

$$(26)\quad \Delta_{12}u(u^2+v^2+w^2)_0 = 4\pi^{-1/2}\nu\nu'\frac{mm'^2}{(m+m')^4}\left(\frac{hmm'}{m+m'}\right)^{3/2}\left(\frac{2}{h}\right)^{1/2}\left[\tfrac{8}{15}\frac{hmm'^2}{m+m'}\left(\frac{a_1}{m^{1/2}}+\frac{a'_1}{m'^{1/2}}\right)\mathrm{R}''_{12}\right.$$
$$\left. -\left\{\tfrac{5}{6}\,mm'\left(1-k_1+\frac{m'}{m}\overline{k_1-k_2}\right)\left(\frac{a_1}{m^{3/2}}-\frac{a'_1}{m'^{3/2}}\right)-(m^{1/2}a_1-m'^{1/2}a'_1)\right\}\mathrm{P}'_{12}\right]$$

where for convenience we have written k_1 and k_2 for the quantities given by

$$(27)\qquad k_1 = \tfrac{2}{5}\frac{hmm'}{m+m'}\frac{\mathrm{R}'_{12}}{\mathrm{P}'_{12}},\qquad k_2 = \left(\tfrac{2}{5}\frac{hmm'}{m+m'}\right)^2\frac{\mathrm{S}'_{12}}{\mathrm{P}'_{12}}.$$

By putting $m = m'$, $\nu = \nu'$, $a = a'$ in the above equations we get also the following :—

$$(28)\qquad \Delta_{11}u^2 = -4\pi\nu^2\left(\frac{hm}{2\pi}\right)^{3/2}\frac{hm}{20}\,a_{11}\mathrm{R}''_{11}.$$

$$(29)\qquad \Delta_{11}u\,(u^2+v^2+w^2)_0 = 4\pi\nu^2\left(\frac{hm}{2\pi}\right)^{3/2}\tfrac{1}{30}\,a_1\,(2hm)^{1/2}\,\mathrm{R}''_{11}.$$

By transformation of co-ordinates we obtain the following equations from (25) and (28) :—

$$(30)\quad \Delta_{12}uv$$
$$= -4\pi^{-1/2}\nu\nu'\frac{mm'^2}{(m+m')^3}\left(\frac{hmm'}{m+m'}\right)^{3/2}\left[\tfrac{2}{3}(m+m')(a_{12}-a'_{12})\mathrm{P}'_{12}+\tfrac{2}{5}\frac{hmm'^2}{m+m'}\left(\frac{a_{12}}{m}+\frac{a'_{12}}{m'}\right)\mathrm{R}''_{12}\right.$$
$$\left. +\tfrac{1}{3}\,(2h)^{1/2}\,mm'\left\{v_0\left(\frac{a_1}{m^{3/2}}-\frac{a'_1}{m'^{3/2}}\right)+u_0\left(\frac{a_2}{m^{3/2}}-\frac{a'_2}{m'^{3/2}}\right)\right\}\left\{\mathrm{P}'_{12}-\tfrac{2}{5}\frac{hmm'}{m+m'}\mathrm{R}'_{12}\right\}\right].$$

$$(31)^*\qquad \Delta_{11}uv = -4\pi\nu^2\left(\frac{hm}{2\pi}\right)^{3/2}\frac{hm}{20}\,a_{12}\mathrm{R}''_{11}.$$

---

* All the formulæ (25)–(31) were in the present form before the paper was revised, with the exception of (26). Their calculation was given almost in full, and was performed by essentially the same methods as those explained above. The work was made rather more lengthy than necessary by the use of an unsymmetrical transformation of the integrals in place of that given in equations (13)–(17), to which I was led while endeavouring to simplify the calculation of $\Delta_{12}u(u^2+v^2+w^2)_0$. The calculation of $\Delta u(u^2+v^2+w^2)$ was also complicated by the fact that the gas was not assumed to be at rest; but on revision, despite these simplifications, I decided to omit the routine calculations altogether.

Equation (26) was not given in the paper as originally written because it is connected with the conductivity of mixed gases, and I was then unaware of any experiments on the subject which would make so tedious a calculation worth the while. I have since found such experimental data, and have therefore worked out the formula (26), the results of which (as will be seen in Part III.) show very satisfactory agreement with the observations.—*Note added October*, 1911.

6. *Calculation of* $\Delta_{12}u$.

Finally we turn to consider $\Delta_{12}u$, the calculation of which is rather different from that of the foregoing quantities because u_0 and u'_0, v_0 and v'_0, w_0 and w'_0 are now different. We require $\Delta_{12}u$ in order to determine the coefficient of diffusion.

It is evident from equation (2) that

$$\int_0^{2\pi} \delta_{12}u \, d\epsilon = 4\pi \frac{m'}{m+m'}(u'-u),$$

so that

$$\Delta_{12}u = \nu\nu' \frac{m'}{m+m'} \iiint\iiint \Omega'_{12}(\mathrm{V}_0)(u'-u) f(u, v, w) f'(u', v', w') \, du \, dv \, dw \, du' \, dv' \, dw'.$$

In the present case we may neglect the small deviation from MAXWELL'S law of distribution of velocities, and thus avoid making any assumption as to the form of F. This is so because in this case (unlike all the preceding cases considered) the unit term of $(1+\mathrm{F}+\mathrm{F}')$ in the expression for ff' leads to a term in the final result, so that the terms which would result from the inclusion of F and F′, being multiplied by the small coefficients a and a', are negligible to our order of accuracy. The term arising from the unit in $(1+\mathrm{F}+\mathrm{F}')$ is itself a multiple of u'_0-u_0, which we assume to be so small that its squares and higher powers are negligible; u'_0-u_0 being thus a small quantity of the first order, the terms arising from F and F′ are of the second and higher orders of small quantities.

Thus we now have

$$ff' = \left(\frac{h^2mm'}{\pi^2}\right)^{3/2} e^{-h[m\Sigma(u-u_0)^2+m'\Sigma(u'-u'_0)^2]}$$

$$= \left(\frac{h^2mm'}{\pi^2}\right)^{3/2} e^{-h[(m+m')\Sigma u^2+2\Sigma(mu_0+m'\overline{u'_0+x})u-m'\Sigma(u'_0+x)^2-m\Sigma u_0^2]}$$

where we have written (x, y, z) for $(u-u', v-v', w-w')$, so that $\mathrm{V}_0^2 = x^2+y^2+z^2$. Changing the variables in the above integral to (x, y, z) in place of u', v', w', and recalling that

$$\int_{-\infty}^{\infty} e^{-at^2+bt} \, dt = \left(\frac{\pi}{a}\right)^{1/2} e^{b^2/4a},$$

on integration with respect to u, v, w we obtain

$$\Delta_{12}u = -\nu\nu' \frac{m'}{m+m'} \left\{\frac{hmm'}{\pi(m+m')}\right\}^{3/2} \iiint \Omega'_{12}(\mathrm{V}_0) \, x e^{-\frac{hmm'}{m+m'}(\mathrm{V}_0^2-2\rho\mathrm{V}_0\cos\lambda+\rho^2)} \, dx \, dy \, dz$$

where we have written $(\mathrm{V}_0^2-2\rho\mathrm{V}_0\cos\lambda+\rho^2)$ for $\Sigma(x+u'_0-u_0)^2$; thus

$$\rho^2 = (u'_0-u_0)^2+(v'_0-v_0)^2+(w'_0-w_0)^2, \quad \rho\mathrm{V}_0\cos\lambda = x(u'_0-u_0)+y(v'_0-v_0)+z(w'_0-w_0).$$

Since, as has already been mentioned, ρ^2 is a small quantity of the second order the term $e^{-\frac{hmm'}{m+m'}\rho^2}$ may be neglected, since it is equal to unity to our order of approximation. Transforming the variables x, y, z in the last integral to polar co-ordinates, we have

$$\Delta_{12}u = -\nu\nu'\frac{m'}{m+m'}\left\{\frac{hmm'}{\pi(m+m')}\right\}^{3/2}\iiint \mathrm{V}_0{}^3\Omega'_{12}(\mathrm{V}_0)\,e^{-\frac{hmm'}{m+m'}\mathrm{V}_0{}^2}$$
$$\left\{\sum_0^\infty \frac{1}{n!}\left(\frac{hmm'}{m+m'}2\rho\mathrm{V}_0\cos\lambda\right)^n\right\}d\mathrm{V}_0\sin\theta\cos\theta\,d\theta\,d\phi$$

by putting $x = \mathrm{V}_0\cos\theta$, &c. It must be remembered that λ is a function of θ and ϕ, since

$$\cos\lambda = \frac{u_0-u'_0}{\rho}\cos\theta+\frac{v_0-v'_0}{\rho}\sin\theta\cos\phi+\frac{w_0-w'_0}{\rho}\sin\theta\sin\phi.$$

All the terms of the exponential series occurring in the integrand of the last integral are negligible (on account of the factors ρ^2, ρ^3, and so on) except the unit term and the term of the first degree. The unit term leads to a null result on integration with respect to θ and ϕ. The first degree term alone contributes to the final result, which (in our previous notation) is easily seen to be

$$(32)\qquad \Delta_{12}u = \tfrac{8}{3}\pi^{-1/2}\nu\nu'\frac{m'}{m+m'}\left(\frac{hmm'}{m+m'}\right)^{5/2}(u'_0-u_0)\,\mathrm{P}'_{12}.$$

If we put $m = m'$, $u_0 = u'_0$, $\nu = \nu'$ we find that $\Delta_{11}u = 0$, as is otherwise evident, since the momentum of a system of molecules is unaltered by their mutual encounters.

Having now calculated all the values of $\Delta\mathrm{Q}$ which we require, we proceed to substitute them in the various special forms of the equation of transfer, in order to obtain expressions for the coefficients of viscosity, diffusion, and conduction in simple and mixed gases.

7. *The Coefficient of Viscosity of a Simple Gas.*

First considering a gas composed of molecules of one kind only, we substitute for Δu^2 (which in this case equals $\Delta_{11}u^2$) and Δuv from equations (27) and (30) in the special equations of transfer (11) and (12) respectively. We get

$$4\pi\nu^2\left(\frac{hm}{2\pi}\right)^{3/2}\frac{hm}{20}a_{11}\mathrm{R}''_{11} = \tfrac{2}{3}\nu q\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)-2\nu q\frac{\partial u_0}{\partial x},$$

$$4\pi\nu^2\left(\frac{hm}{2\pi}\right)^{3/2}\frac{hm}{20}a_{11}\mathrm{R}''_{11} = -\nu q\left(\frac{\partial v_0}{\partial x}+\frac{\partial u_0}{\partial y}\right).$$

Remembering that $a_{11} = \dfrac{2h}{\nu}(p_{xx}-p)$, $a_{12} = \dfrac{2h}{\nu}p_{xy}$ (see p. 442), and comparing these equations with those of a viscous fluid whose coefficient of viscosity is μ, viz.,

$$p_{xx}-p = \mu\left[\tfrac{2}{3}\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)-2\,\frac{\partial u_0}{\partial x}\right]$$

$$p_{xy} = -\mu\left(\frac{\partial v_0}{\partial x}+\frac{\partial u_0}{\partial y}\right)$$

we obtain the following expression for μ :—

$$(33) \qquad \mu = \frac{5q}{2h^2m}\left(\frac{2\pi}{hm}\right)^{3/2}\frac{1}{\pi\mathrm{R}''_{11}} = \frac{5}{4h^3m^2}\left(\frac{2\pi}{hm}\right)^{3/2}\frac{1}{\pi\mathrm{R}''_{11}}.$$

8. *The Coefficient of Thermal Conductivity of a Simple Gas.*

We next substitute for $\Delta u\,(u^2+v^2+w^2)_0$ in equation (10), and so obtain

$$5\nu q\,\frac{\partial q}{\partial x} = +4\pi\nu^2\left(\frac{hm}{2\pi}\right)^{3/2}\tfrac{1}{30}\,a_1\,(2hm)^{1/2}\,\mathrm{R}''_{11}$$

$$= -4\pi\nu^2\left(\frac{hm}{2\pi}\right)^{3/2}\tfrac{1}{60}\,(2hm)^2\,\mathrm{R}''_{11}\,\overline{\mathrm{U}\,(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)}$$

on substituting for a_1 from the equation on p. 442. This equation is simplified if we recall the value of μ from equation (32). Thus*

$$\frac{\partial q}{\partial x} = -\frac{2\rho}{15\mu}\,\overline{\mathrm{U}\,(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)}.$$

If we now substitute for $\overline{\mathrm{U}\,(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)}$ in the equation (9), we get

$$3\rho\,\frac{\mathrm{D}q}{\mathrm{D}t} = +\sum_{x,y,z}\frac{\partial}{\partial x}\left(\tfrac{15}{2}\mu\,\frac{\partial q}{\partial x}\right).$$

If we compare this with the equation of conduction of heat in a gas at rest, whose thermal conductivity is ϑ—viz., with

$$\mathrm{C}_v\rho\,\frac{\mathrm{D}\theta}{\mathrm{D}t} = \sum_{x,y,z}\frac{\partial}{\partial x}\left(\vartheta\,\frac{\partial\theta}{\partial x}\right)$$

(where C_v is the specific heat at constant volume)—and remember that q is directly proportional to the absolute temperature θ, we find that

$$(34) \qquad \vartheta = \tfrac{5}{2}\mu\mathrm{C}_v.$$

---

* We can now see why the term $\nu\,\frac{\mathrm{D}}{\mathrm{D}t}\,\overline{\mathrm{U}\,(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)}$ on the left-hand side of the equation preceding equation (10) is negligible. The ratio of its coefficient ν to the coefficient of $\overline{\mathrm{U}\,(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)}$ on the right hand (viz., in $\Delta u\,(u^2+v^2+w^2)_0$) is now seen to be μ/p, which is an exceedingly small quantity in all gases under normal conditions.

9. *The Coefficient of Diffusion.*

The general equation of transfer (1) is true for any system of molecules in a gas, whether in the presence of other systems of molecules or not, provided that no diffusion is taking place (this restriction arises in the elimination of the external forces,* where it is assumed that $\Delta u = 0$, which is true, of course, only when the restriction just mentioned is satisfied). The form of the equation of transfer which is applicable to the more general case now under consideration, where diffusion is taking place, is†

$$\nu \frac{d\overline{\mathrm{Q}}}{dt} = \sum_{x, y, z} \left[-\nu u_0 \frac{\partial \overline{\mathrm{Q}}}{\partial x} - \frac{\partial}{\partial x}(\nu \overline{\mathrm{UQ}}) + \frac{\nu}{m} \mathrm{X} \frac{\partial \overline{\mathrm{Q}}}{\partial u_0} \right] + \Delta \mathrm{Q},$$

where X is the component of external force. If we put $\mathrm{Q} = u$, and suppose that there are no external forces, and that the motion has assumed a steady state, the equation becomes

$$\frac{\partial p}{\partial x} = m \Delta_{12} u,$$

where we have neglected products of u_0, v_0, w_0 as being small quantities of the second order; similarly we have neglected such terms as $\overline{\mathrm{UV}}$, and have given $\nu m \overline{\mathrm{UQ}}$ its proper value p.

The equation just obtained applies to the first system of molecules, p being the partial pressure due to this system; there is a similar equation

$$\frac{\partial p'}{\partial x} = m' \Delta_{21} u$$

for the second system. Since the temperature is supposed to remain constant, we have

$$\frac{\partial p}{\partial x} = \frac{\partial}{\partial x}\left(\frac{\nu}{2h}\right) = \frac{1}{2h} \frac{\partial \nu}{\partial x}, \qquad \frac{\partial p'}{\partial x} = \frac{1}{2h} \frac{\partial \nu'}{\partial x}.$$

Now, from equation (31), it follows by symmetry that

$$m' \Delta_{21} u = -m \Delta_{12} u,$$

so that

$$\frac{\partial \nu}{\partial x} = -\frac{\partial \nu'}{\partial x} = \tfrac{8}{3} \nu \nu' \frac{mm'}{m+m'} \left(\frac{hmm'}{m+m'}\right)^{5/2} \pi^{-1/2} 2h (u'_0 - u_0) \mathrm{P}'_{12}.$$

The total flow of molecules of the first kind per unit area per unit time is clearly νu_0, and also (by the definition of the coefficient of diffusion D_{12}) is equal to $-\mathrm{D}_{12} \frac{\partial \nu}{\partial x}$.

---

* See JEANS' treatise, p. 279.

† *Ibid.*, p. 278

Hence

$$\nu u_0 = -\mathrm{D}_{12}\frac{\partial \nu}{\partial x}, \qquad \nu' u'_0 = -\mathrm{D}_{12}\frac{\partial \nu'}{\partial x} = \mathrm{D}_{12}\frac{\partial \nu}{\partial x},$$

by which the preceding equation may be reduced to

$$\frac{\partial \nu}{\partial x} = +\tfrac{8}{3}\frac{mm'}{m+m'}\left(\frac{hmm'}{m+m'}\right)^{5/2}\pi^{-1/2}2h(\nu+\nu')\,\mathrm{P}_{12}\mathrm{D}_{12}\frac{\partial \nu}{\partial x}.$$

This gives us* as the expression for D_{12}

$$\mathrm{D}_{12} = \tfrac{3}{16}\pi^{1/2}\left(\frac{m+m'}{hmm'}\right)^{7/2}\frac{1}{(\nu+\nu')\,\mathrm{P}'_{12}}. \tag{35}$$

By putting $m = m'$, $\nu = \nu'$, we get the following expression for the coefficient of diffusion D_{11} of a gas into itself:—

$$\mathrm{D}_{11} = \frac{3}{\nu}\left(\frac{\pi}{2}\right)^{1/2}(hm)^{-7/2}\frac{1}{\mathrm{P}'_{11}}. \tag{36}$$

10. *The Coefficient of Viscosity of a Compound Gas.*

As in dealing with the case of diffusion, we must now use an equation of transfer for each system of molecules. Writing

$$2\frac{\partial u_0}{\partial x} - \tfrac{2}{3}\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right) = \mathrm{E}, \qquad \frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} = \mathrm{F},$$

where (since the various systems of molecules are not supposed to be diffusing through one another, so that $u_0 = u'_0$, &c.) E and F are the same for both systems of molecules, by equations (11) and (12) we have

$$\Delta u^2 = \nu q\mathrm{E}, \qquad \Delta u'^2 = \nu' q'\mathrm{E},$$
$$\Delta uv = \nu q\mathrm{F}, \qquad \Delta u'v' = \nu' q'\mathrm{F}.$$

In the expressions already obtained for $\Delta_{12}u^2$, $\Delta_{12}uv$ (viz., (25) and (29)) there occur terms containing the coefficients a_1, a'_1. As we have already seen in discussing the conduction of heat, these coefficients depend upon the existence of variations of temperatures in the gas. We shall here suppose that the gas is at a uniform temperature throughout, so that the said terms will disappear.

---

* Since this paper was written I have found that the expression (35) had already been obtained by LANGEVIN ('Ann. de Chimie et de Physique,' (8), v., 245, 1905), who applied it to the motion of electrons in an electric field. The present proof is shorter than LANGEVIN'S. ENSKOG ('Phys. Zeitschrift,' xii., 533, July, 1911) has also published a simplified proof on lines not unlike those of the above proof. I am indebted to Prof. LARMOR for the reference to ENSKOG'S paper (which appeared while this paper was in the hands of the Royal Society), where I found the further reference to LANGEVIN'S theory.—*Note added October*, 1911.

Thus we have

$$\Delta_{12}u^2 = -4\pi^{-1/2}\nu\nu'\frac{mm'^2}{(m+m')^3}\left(\frac{hmm'}{m+m'}\right)^{3/2}\left[\left\{\tfrac{2}{3}\mathrm{P}'_{12}+\tfrac{2}{5}\frac{hm'^2}{m+m'}\mathrm{R}''_{12}\right\}\alpha_{11}\right.$$
$$\left.-\left\{\tfrac{2}{3}\mathrm{P}'_{12}-\tfrac{2}{5}\frac{hmm'}{m+m'}\mathrm{R}''_{12}\right\}\alpha'_{11}\right].$$

If we write

$$k = \left(\tfrac{2}{5}\frac{hmm'}{m+m'}\mathrm{R}''_{12}\right)\Big/\tfrac{2}{3}\mathrm{P}'_{12}, \tag{37}$$

and substitute for P'_{12} in terms of the coefficient of diffusion D_{12}, the equation for $\Delta_{12}u^2$ is simplified to

$$\Delta_{12}u^2 = -\tfrac{1}{2}\frac{\nu\nu'}{\nu+\nu'}\frac{m'}{h^2mm'(m+m')}\frac{1}{\mathrm{D}_{12}}\left\{\left(1+k\frac{m'}{m}\right)\alpha_{11}-(1-k)\,\alpha'_{11}\right\}.$$

Again, by means of the expression obtained for μ, the equation (27) for $\Delta_{11}u^2$ reduces to

$$\Delta_{11}u^2 = -\frac{\nu^2\alpha_{11}}{4h^2m\mu}.$$

We get similar equations for $\Delta_{11}u'^2$ and $\Delta_{12}u'^2$, writing μ' for the coefficient of viscosity of a gas composed only of the second kind of molecules. Hence, remembering that $\Delta\mathrm{Q} = \Delta_{11}\mathrm{Q}+\Delta_{12}\mathrm{Q}$, we have

$$\mathrm{E} = \mathrm{A}\alpha_{11}+\mathrm{B}\alpha'_{11}, \qquad \mathrm{E} = \mathrm{C}\alpha_{11}+\mathrm{D}\alpha'_{11},$$

where

$$\mathrm{A} = -\frac{\nu'}{\nu+\nu'}\frac{1}{h(m+m')}\frac{1}{\mathrm{D}_{12}}\left(1+k\frac{m'}{m}\right)-\frac{\nu}{2h\mu},$$

$$\mathrm{B} = \frac{\nu'}{\nu+\nu'}\frac{1}{h(m+m')}\frac{1}{\mathrm{D}_{12}}(1-k),$$

$$\mathrm{C} = \frac{\nu'}{\nu+\nu'}\frac{1}{h(m+m')}\frac{1}{\mathrm{D}_{12}}(1-k),$$

$$\mathrm{D} = -\frac{\nu'}{\nu+\nu'}\frac{1}{h(m+m')}\frac{1}{\mathrm{D}_{12}}\left(1+k\frac{m}{m'}\right)-\frac{\nu'}{2h\mu'}.$$

We next substitute for α_{11} and α'_{11} their values $\frac{2h}{\nu}p_{xx}$, $\frac{2h}{\nu'}p'_{xx}$ respectively in the above equations, and solve so as to obtain $p_{xx}+p'_{xx}$ (the total normal pressure parallel to Ox) in terms of E. After a little reduction we find that

$$p_{xx}+p'_{xx} = -\frac{\mathrm{A}'+\mathrm{B}'+\mathrm{C}'+\mathrm{D}'}{\mathrm{A}'\mathrm{D}'-\mathrm{B}'\mathrm{C}'}\mathrm{E},$$

where

$$\mathrm{A}' = \frac{\nu'}{\nu}\mathrm{G}\left(1+k\frac{w'}{w}\right)+\frac{1}{\mu}, \qquad \mathrm{B}' = \mathrm{G}(1-k) = \mathrm{C}', \qquad \mathrm{D}' = \frac{\nu}{\nu'}\mathrm{G}\left(1+k\frac{w}{w'}\right)+\frac{1}{\mu'}.$$

In these last expressions w and w' are the specific gravities of the two component gases referred to a standard gas whose density at the pressure and temperature of the compound gas here considered is ρ_0; and G is given by

$$\text{(38)} \qquad \mathrm{G} = \frac{2}{w+w'}\,\frac{1}{\rho_0}\,\frac{1}{\mathrm{D}_{12}}.$$

Since the partial pressures of the component gases are directly proportional to ν, ν' $\left(\text{for } p = \frac{\nu}{2h},\ p' = \frac{\nu'}{2h}\right)$, we may write

$$p_{xx}+p'_{xx} = -\frac{\left(1+k\,\frac{w}{w'}\right)p^2+\left\{2\left(1-k\right)+\frac{1}{\mathrm{G}}\left(\frac{1}{\mu}+\frac{1}{\mu'}\right)\right\}pp'+\left(1+k\,\frac{w'}{w}\right)p'^2}{\frac{1}{\mu}\left(1+k\,\frac{w}{w'}\right)p^2+\left\{\frac{(w+w')^2}{ww'}\,k\mathrm{G}+\frac{1}{\mathrm{G}\mu\mu'}\right\}pp'+\frac{1}{\mu'}\left(1+k\,\frac{w'}{w}\right)p'^2}.$$

Similarly we may show that $p_{xy}+p'_{xy}$ is the same multiple of F. Hence, recalling the denotation of E and F, and comparing the said equations with the equations of pressure in a medium whose coefficient of viscosity is μ_{12}, as in § 7, we obtain the following equation:—

$$\text{(39)} \qquad \mu_{12} = \frac{\left(1+k\,\frac{w}{w'}\right)p^2+\left\{2\left(1-k\right)+\frac{1}{\mathrm{G}}\left(\frac{1}{\mu}+\frac{1}{\mu'}\right)\right\}pp'+\left(1+k\,\frac{w'}{w}\right)p'^2}{\frac{1}{\mu}\left(1+k\,\frac{w}{w'}\right)p^2+\left\{\frac{(w+w')^2}{ww'}\,k\mathrm{G}+\frac{1}{\mathrm{G}\mu\mu'}\right\}pp'+\frac{1}{\mu'}\left(1+k\,\frac{w'}{w}\right)p'^2}.$$

11. *The Coefficient of Thermal Conductivity of a Compound Gas.**

From equations (26) and (29) we see that $\Delta u\,(u^2+v^2+w^2)_0$ and $\Delta u'\,(u'^2+v'^2+w'^2)_0$ can be expressed as in the following equations:—

$$\Delta u\,(u^2+v^2+w^2)_0 = -2\nu\left\{\mathrm{A}\,(2hm)^{-3/2}\,\alpha_1+\mathrm{B}\,(2hm')^{-3/2}\,\alpha'_1\right\},$$

$$\Delta u'\,(u'^2+v'^2+w'^2)_0 = -2\nu'\left\{\mathrm{C}\,(2hm)^{-3/2}\,\alpha_1+\mathrm{D}\,(2hm')^{-3/2}\,\alpha'_1\right\},$$

where A, B, C, D are written for convenience in place of some rather long expressions which can easily be written down from the equations cited.

Remembering the values of α_1 and α'_1 as found in § 4, and substituting from equation (10) for $\Delta u\,(u^2+v^2+w^2)_0$, the last equations may be written

$$5\nu q\,\frac{\partial q}{\partial x} = \nu\left(\mathrm{A}\,\overline{\mathrm{U}\,(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)_0}+\mathrm{B}\,\overline{\mathrm{U}'\,(\mathrm{U}'^2+\mathrm{V}'^2+\mathrm{W}'^2)_0}\right),$$

$$5\nu' q'\,\frac{\partial q'}{\partial x} = \nu'\left(\mathrm{C}\,\overline{\mathrm{U}\,(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)_0}+\mathrm{D}\,\overline{\mathrm{U}'\,(\mathrm{U}'^2+\mathrm{V}'^2+\mathrm{W}'^2)_0}\right).$$

---

* *Added October*, 1911.—See the footnote to p. 444.

Since $q = 1/2hm$, so that $mq = m'q'$, on solving for $\overline{U(U^2+V^2+W^2)_0}$ we obtain

$$(AD-BC)\,\overline{U(U^2+V^2+W^2)_0} = 5\left(\frac{q}{m}D-\frac{q'}{m'}B\right)\frac{\partial mq}{\partial x},$$

$$(AD-BC)\,\overline{U'(U'^2+V'^2+W'^2)_0} = 5\left(\frac{q'}{m'}A-\frac{q}{m}C\right)\frac{\partial mq}{\partial x}.$$

If we multiply equation (9) by m, and add the corresponding equation for the second system of molecules, we get

$$3(\nu+\nu')\frac{Dmq}{Dt} = -\sum_{x,y,z}\frac{\partial}{\partial x}\left\{\nu m\,\overline{U(U^2+V^2+W^2)_0}+\nu'm'\,\overline{U'(U'^2+V'^2+W'^2)_0}\right\}$$

since the sum of the remaining terms

$$m\Delta_{12}(u^2+v^2+w^2)_0+m'\Delta_{12}(u'^2+v'^2+w'^2)_0$$

vanishes. This follows from the principle of conservation of energy, for the last expression represents twice the rate of change of the combined energy of the two systems of molecules due to their mutual collisions, which is evidently zero.

We substitute the values already obtained for $\overline{U(U^2+V^2+W^2)_0}$ and $\overline{U'(U'^2+V'^2+W'^2)_0}$ in the last equation, and compare the resulting equation with the equation of conduction of heat in a medium at rest. As in the case of a simple gas (§ 8) we obtain the following expression for the thermal conductivity ϑ_{12}:—

$$\vartheta_{12} = -\tfrac{5}{3}\left[\frac{\nu}{m}D+\frac{\nu'}{m'}A-\nu\frac{m}{m'^2}B-\nu'\frac{m'}{m^2}C\right]\frac{R\rho\theta(C_v)_{12}}{\nu+\nu'}\cdot\frac{1}{AD-BC}.$$

In this equation we must substitute the proper values for A, B, C, D. I shall not enter into the details of the calculation, which is rather long and complicated, but will simply quote the result in the simplest form. It must first be mentioned that $(C_v)_{12}$, the specific heat of the compound gas at constant volume, is connected with the same constants for the component gases, viz., C_v and C'_v, by the following relation:—

(39A) $$(C_v)_{12} = \frac{pwC_v+p'w'C'_v}{pw+p'w'}$$

using the notation of § 10.

The formula finally obtained is

(40) $$\vartheta_{12} = \tfrac{5}{2}\,\frac{pwC_v+p'w'C'_v}{p+p'}\;\frac{Ep^2+Fpp'+Gp'^2}{E\frac{w}{\mu}p^2+F_1pp'+G\frac{w'}{\mu'}p'^2}$$

where E, F, F_1, G are given by the following equations, in which the quantities k, k_1, k_2 have the values assigned to them in equations (27) and (37):—

$$(41)\quad \left\{\begin{aligned} \mathrm{E} &= \tfrac{8}{9}k-\tfrac{5}{6}(1-k_1)-\tfrac{5}{6}(k_1-k_2)\frac{w}{w'}+\frac{w'}{w},\\ \mathrm{G} &= \tfrac{8}{9}k-\tfrac{5}{6}(1-k_1)-\tfrac{5}{6}(k_1-k_2)\frac{w'}{w}+\frac{w}{w'},\\ \mathrm{F} &= \tfrac{2}{9}\frac{(w+w')^2}{ww'}\rho_0\mathrm{D}_{12}\left(\frac{w}{\mu}+\frac{w'}{\mu'}\right)-\left\{\tfrac{16}{9}k+\tfrac{5}{6}\frac{(w-w')^2}{ww'}(1-k_1)-\tfrac{1}{3}(1+5k_2)\right\},\\ \mathrm{F}_1 &= \frac{3ww'}{(w+w')^2}\frac{1}{\rho_0\mathrm{D}_{12}}\left\{\tfrac{2}{9}k(1+5k_2)\frac{(w+w')^2}{ww'}-\tfrac{5}{4}(k_1-k_2)\left(\frac{w'}{w}-\frac{w}{w'}\right)^2\right\}+\tfrac{2}{9}\frac{(w+w')^2}{\mu\mu'}\rho_0\mathrm{D}_{12}. \end{aligned}\right.$$

This completes the first part of the paper. We proceed now to the evaluation of the quantities P'_{12}, R'_{12}, k, k_1, and k_2 in some special cases.

PART II.—ON CERTAIN SPECIAL FORMS OF MOLECULAR INTERACTION.

12. The general expressions which we have obtained in §§ 7–11 contain four integrals, P'_{12}, R'_{12}, R''_{12}, S'_{12}, given by the equations

$$(42)\quad \left\{\begin{aligned} \mathrm{P}'_{12} &= \int_0^\infty \mathrm{V}_0^4\Omega'_{12}(\mathrm{V}_0)\,e^{-\frac{hmm'}{m+m'}\mathrm{V}_0^2}\,d\mathrm{V}_0, &\qquad \mathrm{R}''_{12} &= \int_0^\infty \mathrm{V}_0^6\Omega''_{12}(\mathrm{V}_0)\,e^{-\frac{hmm'}{m+m'}\mathrm{V}_0^2}\,d\mathrm{V}_0,\\ \mathrm{R}'_{12} &= \int_0^\infty \mathrm{V}_0^6\Omega'_{12}(\mathrm{V}_0)\,e^{-\frac{hmm'}{m+m'}\mathrm{V}_0^2}\,d\mathrm{V}_0, &\qquad \mathrm{S}'_{12} &= \int_0^\infty \mathrm{V}_0^8\Omega'_{12}(\mathrm{V}_0)\,e^{-\frac{hmm'}{m+m'}\mathrm{V}_0^2}\,d\mathrm{V}_0. \end{aligned}\right.$$

The remaining integrals, P'_{11} and R''_{11} can be obtained at once from P'_{12} and R''_{12} by changing m to m', and Ω_{12} to Ω_{11}.

We recall the values of $\Omega'_{12}(\mathrm{V}_0)$ and $\Omega''_{12}(\mathrm{V}_0)$ from the latter part of § 3. They are

$$(43)\qquad \Omega'_{12}(\mathrm{V}_0) = 4\pi\mathrm{V}_0\int_0^\infty \sin^2\chi\,.\,p\,dp,\qquad \Omega''_{12}(\mathrm{V}_0) = \pi\mathrm{V}_0\int_0^\infty \sin^2 2\chi\,.\,p\,dp$$

where 2χ is the angle through which the direction of the relative velocity V_0 is turned by the mutual action of the two molecules m and m', while p is the distance between the asymptotes of their orbits relative to their mass centre (§ 1).

As the above expressions cannot, however, be integrated except in certain special cases (which fortunately include the most interesting cases) we consider these in order.

13. *Rigid Elastic Spheres.*

The simplest case is that of molecules which are rigid and perfectly elastic spheres, of radii σ and σ'. Clearly if p exceeds $\sigma+\sigma'$ the spheres will not affect one another's motion, so that $\chi = 0$. When p is less than $\sigma+\sigma'$, it is evident that

$$\sin\chi = \frac{p}{\sigma+\sigma'}.$$

Hence

$$\Omega'_{12}(\mathrm{V}_0) = 4\pi\mathrm{V}_0\int_0^{\sigma+\sigma'}\frac{p^2}{(\sigma+\sigma')^2}p\,dp = \pi\mathrm{V}_0(\sigma+\sigma')^2,$$

and

$$\Omega''_{12}(\mathrm{V}_0) = \pi\mathrm{V}_0\int_0^{\sigma+\sigma'}(\sigma+\sigma')^2\sin^2 2\chi\sin\chi\cos\chi\,d\chi = \tfrac{1}{3}\pi\mathrm{V}_0(\sigma+\sigma')^2.$$

Consequently we find that

$$(44)\qquad \mathrm{P}'_{12} = \pi(\sigma+\sigma')^2\int_0^\infty \mathrm{V}_0^{\,5}\,e^{-\frac{hmm'}{m+m'}\mathrm{V}_0^2}\,d\mathrm{V}_0 = \pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^3,$$

$$\mathrm{R}'_{12} = \pi(\sigma+\sigma')^2\int_0^\infty \mathrm{V}_0^{\,7}\,e^{-\frac{hmm'}{m+m'}\mathrm{V}_0^2}\,d\mathrm{V}_0 = 3\pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^4,$$

$$\mathrm{R}''_{12} = \pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^4,$$

$$\mathrm{S}'_{12} = 12\pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^5.$$

From these we obtain the equations

$$(45)\qquad \mathrm{P}'_{11} = 32\pi\sigma^2\left(\frac{1}{hm}\right)^3,\qquad \mathrm{R}''_{11} = 64\pi\sigma^2\left(\frac{1}{hm}\right)^4,$$

$$(46)\qquad k = \tfrac{3}{5},\qquad k_1 = \tfrac{6}{5},\qquad k_2 = \tfrac{48}{25},$$

so that in this case the constants k, k_1, k_2 (defined by equations (27) and (37)) are numerical constants; in general, they are functions of the temperature (*i.e.*, of h).

14. *Molecules which are Point Centres of Force.*

We next consider the hypothesis that the molecules are geometrical points endowed with inertia and repelling or attracting one another with forces which are functions only of the distance between their centres.

Let $\phi_{12}(r)$ be the mutual potential energy of two molecules m, m' at distance r, and let us write $\phi'_{12}(r)$ in place of $\dfrac{m+m'}{mm'}\phi_{12}(r)$. The first two integrals of the equations of motion of the second molecule in terms of co-ordinates r, θ with the first molecule as origin are as usual

$$r^2\dot{\theta} = \mathrm{A},\qquad \tfrac{1}{2}(\dot{r}^2+r^2\dot{\theta}^2) = \phi'_{12}+\mathrm{B}$$

where A and B are constants. Eliminating the time from these equations we get

$$\tfrac{1}{2}\left\{\left(\frac{\partial r}{\partial\theta}\right)^2+r^2\right\}\frac{\mathrm{A}^2}{r^4} = \phi'_{12}(r)+\mathrm{B}\qquad\text{or}\qquad\left(\frac{\partial r}{\partial\theta}\right)^2 = \frac{2r^4}{\mathrm{A}^2}\{\phi'_{12}(r)+\mathrm{B}\}-r^2.$$

Taking the direction of one asymptote for initial line this has the integral

$$\theta = \int_\infty^r \left[\frac{2\mathrm{B}}{\mathrm{A}^2} r^4 - r^2 + \frac{2r^4}{\mathrm{A}^2} \phi'_{12}(r)\right]^{-1/2} dr.$$

Since V_0 is the relative velocity before collision, and p is the perpendicular from the origin on to the asymptote, we have

$$\mathrm{A} = p\mathrm{V}_0, \qquad \mathrm{B} = \tfrac{1}{2}\mathrm{V}_0^2 - \phi'_{12}(\infty),$$

so that

$$\theta = \int_\infty^r \left[\frac{r^4}{p^2} - r^2 + \frac{2r^4}{p^2\mathrm{V}_0^2}\{\phi'_{12}(r) - \phi'_{12}(\infty)\}\right]^{-1/2} dr.$$

The apse is given by the vanishing of the expression in square brackets. If r_0 is the positive root, we have

$$\chi = \int_\infty^{r_0} \left[\frac{r^4}{p^2} - r^2 + \frac{2r^4}{p^2\mathrm{V}_0^2}\{\phi'_{12}(r) - \phi'_{12}(\infty)\}\right]^{-1/2} dr$$

since χ is the angle between the asymptote and the apsidal radius vector.

For some purposes it is more convenient to transform the variable of the last integral to η, where $\eta = p/r$. We thus get

$$\chi = \int_0^{\eta_0} \left[1 - \eta^2 + \frac{2}{\mathrm{V}_0^2}\left\{\phi'_{12}\left(\frac{p}{\eta}\right) - \phi'_{12}(\infty)\right\}\right]^{-1/2} d\eta,$$

η_0 being the least positive root of the expression in square brackets.

No further progress can be made without knowledge of the form of ϕ'_{12} or ϕ_{12}. The simplest and most natural form to consider is that corresponding to the case in which the molecules attract or repel one another with a force varying inversely as the n_{12}th power of the distance. In this case

$$\phi_{12}(r) = \int_\infty^r \frac{\mathrm{K}_{12}}{r^{n_{12}}} mm'\, dr = -mm' \frac{\mathrm{K}_{12}}{(n_{12}-1)\, r^{n_{12}-1}},$$

$$\phi'_{12}(r) = -(m+m')\frac{\mathrm{K}_{12}}{(n-1)\, r^{n-1}}, \qquad \phi'_{12}(\infty) = 0,$$

where K is a constant depending on the nature of the molecules.

Hence

$$\chi = \int_0^{\eta_0}\left[1 - \eta^2 - \frac{2\mathrm{K}_{12}(m+m')}{(n-1)\mathrm{V}_0^2 p^{n-1}}\eta^{n-1}\right]^{-1/2} d\eta = \int_0^{\eta_0}\left[1 - \eta^2 - \left(\frac{\eta}{\alpha}\right)^{n-1}\right]^{-1/2} d\eta$$

where*

$$\alpha = p\left\{\frac{n_{12}-1}{2\mathrm{K}_{12}(m+m')}\right\}^{\frac{1}{n_{12}-1}} \mathrm{V}_0^{\frac{2}{n_{12}-1}}.$$

Thus χ is now a function of α only.

---

* When the forces are attractive the sign of α^{n-1} is reversed. In the text the case considered is that of repulsion.

We now transform the variable in the integrals Ω', Ω'' from p to α so that

$$p\,dp = \mathrm{K}'_{12}\mathrm{V}_0^{-\frac{4}{n_{12}-1}}\,\alpha\,d\alpha$$

where

$$\mathrm{K}'_{12} = \left\{\frac{2\mathrm{K}_{12}(m+m')}{n_{12}-1}\right\}^{\frac{2}{n_{12}-1}}. \tag{47}$$

Thus we have

$$\Omega'_{12}(\mathrm{V}_0) = \mathrm{K}'_{12}\mathrm{V}_0^{1-\frac{4}{n_{12}-1}}\int_0^\infty 4\pi\sin^2\chi\,.\,\alpha\,d\alpha,$$

$$\Omega''_{12}(\mathrm{V}_0) = \mathrm{K}'_{12}\mathrm{V}_0^{1-\frac{4}{n_{12}-1}}\int_0^\infty \pi\sin^2 2\chi\,.\,\alpha\,d\alpha.$$

The definite integrals in the last two expressions are pure numbers depending on n_{12} alone.* We shall denote them by $\lambda'(n_{12})$ and $\lambda''(n_{12})$ respectively. We thus have†

$$\Omega'_{12}(\mathrm{V}_0) = \mathrm{K}'_{12}\lambda'(n_{12})\,\mathrm{V}_0^{1-\frac{4}{n_{12}-1}},$$

$$\Omega''_{12}(\mathrm{V}_0) = \mathrm{K}'_{12}\lambda''(n_{12})\,\mathrm{V}_0^{1-\frac{4}{n_{12}-1}},$$

so that, as in the case of molecules which are elastic spheres, Ω'' is merely a constant multiple of Ω' If we substitute the last expressions in the integrals for P, R, S (see equations (42)) and remember that

$$\int_0^\infty \mathrm{V}_0^{k+1}e^{-\frac{hmm'}{m+m'}\mathrm{V}_0^2}\,d\mathrm{V}_0 = \tfrac{1}{2}\left(\frac{m+m'}{hmm'}\right)^{\frac{1}{2}k+1}\Gamma\left(\tfrac{1}{2}k+1\right),$$

we find that

$$\left\{\begin{aligned}
&\mathrm{P}'_{12} = \tfrac{1}{2}\mathrm{K}'_{12}\lambda'(n_{12})\left(\frac{m+m'}{hmm'}\right)^{3-\frac{2}{n_{12}-1}}\Gamma\left(3-\frac{2}{n_{12}-1}\right),\\
&\mathrm{P}'_{11} = \tfrac{1}{2}\mathrm{K}'_{11}\lambda'(n_{11})\left(\frac{2}{hm}\right)^{3-\frac{2}{n_{11}-1}}\Gamma\left(3-\frac{2}{n_{11}-1}\right),\quad \mathrm{R}''_{11} = \tfrac{1}{2}\mathrm{K}'_{11}\lambda''(n_{11})\left(\frac{2}{hm}\right)^{4-\frac{2}{n_{11}-1}}\Gamma\left(4-\frac{2}{n_{11}-1}\right)\\
&k = \tfrac{3}{5}\frac{\lambda''(n_{12})}{\lambda'(n_{12})}\left(3-\frac{2}{n_{12}-1}\right),\quad k_1 = \tfrac{2}{5}\left(3-\frac{2}{n_{12}-1}\right),\quad k_2 = \tfrac{4}{25}\left(3-\frac{2}{n_{12}-1}\right)\left(4-\frac{2}{n_{12}-1}\right)
\end{aligned}\right. \tag{48}$$

where

$$\mathrm{K}'_{11} = \left(\frac{4\mathrm{K}_{11}}{n_{11}-1}\right)^{\frac{2}{n_{11}-1}},$$

---

* And on whether the molecules repel or attract, there being one value for each case, corresponding to each value of n.

† These formulæ are true whether the forces are repulsive or attractive. The only difference occurs in the value of the numerical constants λ' and λ''.

K_{11} being the constant of attraction or repulsion between two molecules m in the same way as K_{12} is the constant for two unlike molecules.

Thus k, k_1, k_2 are in this case, as in the preceding case of § 13, numerical constants. The calculation of λ' and λ'' for various values of n from the definite integrals already indicated would afford an interesting theoretical investigation, but as actual molecules do not conform very closely to our hypothesis, the practical importance of the matter would hardly justify the labour. MAXWELL calculated their values, however, by quadrature, in the special case $n = 5$ (the forces being repulsive), and found that*

$$\lambda'(5) = 2{\cdot}6595, \qquad \lambda''(5) = 1{\cdot}3682. \tag{49}$$

15. *Rigid Elastic Spheres which Attract One Another.*

It is an undoubted fact that molecules attract one another at small distances (as is manifest from the force of cohesion, to take but a single example). By considering the effect of such forces in bringing about collisions between molecules (regarded as rigid elastic spheres) which would otherwise pass by one another, SUTHERLAND† had great success in explaining the variation of viscosity with temperature. His treatment of the problem, while very suggestive, and forming an important contribution to the kinetic theory, laid no claim to rigour.

In applying the present methods to the study of the same problem, we shall use the notation σ, σ', ϕ_{12}, ϕ'_{12} of §§ 13 and 14; $\phi_{12}(r)$ will now represent the mutual potential due to the forces of cohesion. As before, we consider the path of the centre of the second molecule relative to that of the first. When the apsidal distance exceeds $\sigma+\sigma'$, no collision takes place, and the deflection 2χ is given by the same equation as in § 14, viz., by

$$\chi = \int_0^{\eta_0}\left[1-\eta^2+\frac{2}{V_0^{\,2}}\left\{\phi'_{12}\left(\frac{p}{\eta}\right)-\phi'_{12}(\infty)\right\}\right]^{-1/2} d\eta. \tag{50}$$

When, however, the apsidal distance is less than $\sigma+\sigma'$ a collision will take place, and the deflection 2χ is twice the angle between the asymptote of the relative path and the radius vector from the centre of the first molecule to that of the second when the two are in contact (*i.e.*, for $r = \sigma+\sigma'$).

The differential equation of the relative path is

$$\frac{1}{r^2}\left(\frac{dr}{d\theta}\right)^2 = \frac{2r^2}{p^2V_0^{\,2}}\{\tfrac{1}{2}V_0^{\,2}+\phi'_{12}(r)-\phi'_{12}(\infty)\}-1.$$

The condition for a collision is evidently

$$p^2 < \frac{2(\sigma+\sigma')^2}{V_0^{\,2}}\{\tfrac{1}{2}V_0^{\,2}+\phi'_{12}(\sigma+\sigma')-\phi'_{12}(\infty)\}.$$

---

* 'Scientific Papers,' vol. ii., p. 42. $\lambda'(5)$ and $\lambda''(5)$ are, of course, the same as MAXWELL'S A_1 and A_2.

† 'Phil. Mag.,' 1893, (5), xxxvi., p. 507

Since the forces are attractive, $\frac{d\phi'_{12}}{dr}$ is negative, so that

(51) $$\phi'_{12}(\sigma+\sigma')-\phi'_{12}(\infty) = -\int_r^\infty \frac{d\phi'_{12}}{dr}\,dr$$

is positive; we shall denote it by $\frac{1}{2}b^2$ for convenience. If we write p_{V} for

$$\frac{\sigma+\sigma'}{\mathrm{V}_0}(b^2+\mathrm{V}_0{}^2)^{1/2},$$

the condition for a collision becomes

$$p < p_{\mathrm{V}_0}.$$

Next, by elementary geometry, the angle χ, between the radii vectores $r = \sigma+\sigma'$ and $r = \infty$, is given by

$$\tan\chi = r\frac{d\theta}{dr},$$

so that for $p < p_{\mathrm{V}_0}$ we have

$$\sin^2\chi = \left\{\frac{1}{r^2}\left(\frac{dr}{d\theta}\right)^2+1\right\}^{-1} = \frac{p^2\mathrm{V}_0{}^2}{(\sigma+\sigma')^2(b^2+\mathrm{V}_0{}^2)} = \frac{p^2}{p_{\mathrm{V}_0}{}^2},$$

$$\sin^2 2\chi = 4\,\frac{p^2}{p_{\mathrm{V}_0}{}^2}\left(1-\frac{p^2}{p_{\mathrm{V}_0}{}^2}\right).$$

Consequently we have

$$\Omega'_{12}(\mathrm{V}_0) = 4\pi\mathrm{V}_0\int_0^\infty \sin^2\chi\,.\,p\,dp = 4\pi\mathrm{V}_0\int_0^{p_{\mathrm{V}_0}}\frac{p^2}{p_{\mathrm{V}_0}{}^2}p\,dp+4\pi\mathrm{V}_0\int_{p_{\mathrm{V}_0}}^\infty \sin^2\chi\,.\,p\,dp,$$

where in the latter integral χ is given by equation (50). We denote the latter integral by $f'_{12}(\mathrm{V}_0)$, the form of the function depending on the law of attraction between the molecules.

Thus

$$\Omega'_{12}(\mathrm{V}_0) = \pi\mathrm{V}_0\frac{(\sigma+\sigma')^2(b^2+\mathrm{V}_0{}^2)}{\mathrm{V}_0{}^2}+4\pi\mathrm{V}_0 f'_{12}(\mathrm{V}_0).$$

Similarly we have

$$\Omega''_{12}(\mathrm{V}_0) = \tfrac{1}{3}\pi\mathrm{V}_0\frac{(\sigma+\sigma')^2(b^2+\mathrm{V}_0{}^2)}{\mathrm{V}_0{}^2}+\pi\mathrm{V}_0 f''_{12}(\mathrm{V}_0),$$

where

$$f''_{12}(\mathrm{V}_0) = \int_{p_{\mathrm{V}_0}}^\infty \sin^2 2\chi\,.\,p\,dp.$$

Substituting these values in the integrals P, R, S, we find that

$$\mathrm{P}'_{12} = \pi(\sigma+\sigma')^2\left\{\int_0^\infty \mathrm{V}_0{}^5 e^{-\frac{hmm'}{m+m'}\mathrm{V}_0{}^2}\,d\mathrm{V}_0+b^2\int_0^\infty \mathrm{V}_0{}^3 e^{-\frac{hmm'}{m+m'}\mathrm{V}_0{}^2}\,d\mathrm{V}_0\right\}+\int_0^\infty f'_{12}(\mathrm{V}_0)\,\mathrm{V}_0{}^5 e^{-\frac{hmm'}{m+m'}\mathrm{V}_0{}^2}\,d\mathrm{V}_0,$$

$$= \pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^3\left\{1+\tfrac{1}{2}b^2\frac{hmm'}{m+m'}\right\}+\boldsymbol{\mathsf{P}}'_{12},$$

where $\boldsymbol{\mathsf{P}}'_{12}$ denotes the last integral on the preceding line.

With a similar notation for $\mathbf{R}'_{12}$, &c., we find that

$$\mathrm{R}'_{12} = 3\pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^4\left\{1+\tfrac{1}{3}b^2\frac{hmm'}{m+m'}\right\}+\mathbf{R}'_{12},$$

$$\mathrm{S}'_{12} = 12\pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^5\left\{1+\tfrac{1}{4}b^2\frac{hmm'}{m+m'}\right\}+\mathbf{S}'_{12}.$$

The terms $\mathbf{P}'_{12}$, &c., represent the effect of the attractive forces in deflecting the molecules without inducing collisions; they are functions of the temperature in general, and can be expanded in ascending powers of $\frac{hmm'}{m+m'}$, *i.e.*, in descending powers of θ. It may be shown that in each case they are of the form

$$(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^s\left\{\mathrm{A}\left(\frac{hmm'}{m+m'}\right)^2+\mathrm{B}\left(\frac{hmm'}{m+m'}\right)^3+\ldots\right\},$$

where $s = 3$, 4, or 5, according as we are considering P, R, or S.

Hence the preceding formulæ may be written

$$\mathrm{P}'_{12} = \pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^3\left(1+\frac{\mathrm{C}_{12}}{\theta}+\frac{\mathrm{A}}{\theta^2}+\ldots\right),$$

$$\mathrm{R}'_{12} = 3\pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^3\left(1+\tfrac{3}{2}\frac{\mathrm{C}_{12}}{\theta}+\frac{\mathrm{A}_1}{\theta^2}+\ldots\right),$$

and so on, where we have put $\mathrm{C}_{12} = \frac{1}{4}\frac{b^2}{\mathrm{R}}\frac{mm'}{m+m'}$.*

SUTHERLAND, in his formula for the coefficient of viscosity, neglected all the terms of lower order in θ than C_{12}/θ, and the success of the formula in representing the variations of viscosity with temperature (in the case of gases, though not in the case of vapours) seems to show that this procedure is legitimate under ordinary conditions in gases. This is equivalent to the neglect of the effect of the attractive forces in deflecting molecules without producing collisions.

If we agree to neglect these terms our formulæ become

$$(52)\quad\left\{\begin{aligned}
&\mathrm{P}'_{12} = \pi(\sigma+\sigma')^2\left(\frac{m+m'}{hmm'}\right)^3\left(1+\frac{\mathrm{C}_{12}}{\theta}\right),\\
&\mathrm{P}'_{11} = 4\pi\sigma^2\left(\frac{2}{hm}\right)^3\left(1+\tfrac{3}{2}\frac{\mathrm{C}_{11}}{\theta}\right),\qquad \mathrm{R}''_{11} = 4\pi\sigma^2\left(\frac{2}{hm}\right)^4\left(1+\frac{\mathrm{C}_{11}}{\theta}\right),\\
&k = \tfrac{3}{5}\,\frac{1+\frac{2}{3}\frac{\mathrm{C}_{12}}{\theta}}{1+\frac{\mathrm{C}_{12}}{\theta}},\qquad k_1 = \tfrac{6}{5}\,\frac{1+\frac{2}{3}\frac{\mathrm{C}_{12}}{\theta}}{1+\frac{\mathrm{C}_{12}}{\theta}},\qquad k_2 = \tfrac{48}{25}\,\frac{1+\frac{1}{2}\frac{\mathrm{C}_{12}}{\theta}}{1+\frac{\mathrm{C}_{12}}{\theta}},
\end{aligned}\right.$$

---

* R denotes the universal gas-constant of the formula $pv = (\mathrm{R}/m)\,\theta$

where we have written

$$C_{11} = \tfrac{1}{12}\frac{b^2 m}{R}.$$

In this case, therefore, the constants k are no longer independent of the temperature. It must not be forgotten that these last equations do not apply to vapours.

PART III.—DISCUSSION OF THE THEORETICAL RESULTS, AND COMPARISON WITH EXPERIMENTAL DATA.*

16. The principal formulæ arrived at in the first part of this work are (33)–(41); they are quite general and involve no hypothesis as to the mode of interaction between molecules (it being always understood that these are spherically symmetrical). Although these formulæ indicate certain general laws, which require no knowledge of the nature of the encounters, for the most part the equations can be reduced to a useful form only when the quantities symbolically denoted by P'_{11}, P'_{12}, R'_{11}, k, k_1, and k_2 are properly evaluated. This can be done only in certain special cases; and in Part II. these calculations have been performed for three kinds of molecules, viz., rigid elastic spheres, point centres of force repelling or attracting one another according to the inverse n^{th} power law, and rigid elastic spheres surrounded by fields of attractive force. The results of these calculations are given in equations (44)–(46), (48), and (52) respectively.

When the formulæ are thus completed, by comparison with experimental data we may find which of these three representations of the molecules best explains the facts, though, as all of them are somewhat artificial and ideal, it is not necessary that any one should excel the others in all respects. We shall find, however, that the third hypothesis (that the molecules are rigid elastic attracting spheres) is, on the whole, much the best of the three. It is, indeed, remarkable that so simple a mechanism can explain so much.

As it might be considered that the choice of formula allowed by the general nature of our theory may possibly conceal errors due to some weakness in the foundations of the analysis, I shall first consider the cases wherein this latitude of choice is least, beginning with the case where there is none at all. I refer to equation (34), viz.,

$$\vartheta = \tfrac{5}{2}\mu C_v,$$

which is a perfectly definite relation between three measurable quantities. I shall

---

* Part III. has been entirely rewritten in October–November, 1911; much new matter, not in the original Part III., has been added, this consisting chiefly (at Prof. LARMOR'S suggestion) of further comparisons of the theory with experiment. Wherever possible I have used recent data, and I have in particular made great use of the results obtained by the pupils of Prof. DORN, of Halle, from a well-directed series of experiments on viscosity, diffusion, and conduction. I am indebted to Prof. DORN for the loan of many reprints and dissertations relating to these experiments.

next discuss the formulæ for the conductivity and viscosity of mixed gases, as these only entail reference to the special law of interaction in the case of the numerical constants k, k_1, and k_2 (whose values are, moreover, approximately known, as they do not differ very much with the special nature of the molecules). Lastly, I shall consider diffusion and the viscosity of a simple gas, as the corresponding formulæ involve the most intimate molecular data, which can be measured only in very indirect ways.

Any defect in analytical approximation involved in the theory is probably quite negligible under ordinary conditions of pressure and temperature; the assumption made in § 4 concerning the law of distribution of velocities is the only place where error might arise, and both on theoretical and experimental grounds this appears to be inappreciable.* Therefore, where no definite molecular hypothesis is involved, the agreement with experimental data should be perfect within the limits of experimental error. These conditions apply to equation (34) just quoted, and to a less extent to the formulæ for conductivity and viscosity in mixed gases, where only slight weight attaches to the special law of force which must in their cases be assumed.

Very different considerations apply to the formulæ for diffusion and viscosity. These have great weight in indicating the best representation of the molecules by the manner in which they vary with the temperature, but if we use them to determine the molecular diameter which is involved in the expressions for D_{12} and μ, we are treading on hazardous ground. Any discrepancy between the molecular diameter obtained from μ and that obtained from D_{12} must be ascribed rather to the artificial nature of the molecules postulated by the theory than to any defect in the theory itself. From what modern electrical theories teach us, it appears extremely unlikely that any definite molecular diameter exists at all, even in the case of monatomic gases. Hence, while the formulæ D_{12} and μ afford valuable independent means of determining the approximate dimensions of molecules, their interpretation must not be strained too far; the agreement between the two sets of values may not necessarily lie within the limits of experimental error.

While the present theory is strictly concerned only with monatomic gases, it is largely applicable to polyatomic gases; for, as the molecules are in rapid motion, they must exert their actions equally in all directions during any short space of time, and will therefore behave very much as though they were spherically symmetrical. All general laws which hold good for monatomic gases may be expected to hold also for polyatomic gases; and the results of experiment bear out this conclusion. Numerical agreement is not to be looked for, however, as the variable action of the polyatomic molecule will affect the numerical constants of the theory in taking the mean, just as would be the case if we had supposed all the molecules to be moving with the same speed, instead of different speeds varying widely about a mean value. In addition,

---

* See the note on p. 483.

as the present theory does not deal in any way with internal molecular energy, it will not apply to the conduction of heat in polyatomic gases.

17. *The Coefficient of Thermal Conduction.*

Our expression for this quantity in terms of the coefficient of viscosity and the specific heat at constant volume is

$$\vartheta = \tfrac{5}{2}\mu C_v,$$

which assumes that the molecules are spherically symmetrical, but is otherwise perfectly general. All previous writers on the kinetic theory have agreed on the conclusion that

$$\vartheta = f\mu C_v,$$

where f is a numerical factor; but here agreement ends. MAXWELL,[*] dealing with molecules which are point centres of force repelling one another according to the inverse fifth-power law, found as a result of his theory that $f = \frac{5}{2}$; this is, of course, a very special case of the present theorem. Other writers, such as CLAUSIUS, STEFAN, and O. E. MEYER, have found values for f varying from 0·5 upwards, many of these calculations, however, being confessedly rough attempts, while MAXWELL'S theory attained a very high degree of accuracy.

MAXWELL'S hypothesis is known not to be borne out by experimental facts (such as the variation of viscosity with temperature), and the theory of conduction which has hitherto found most acceptance is MEYER'S, which assumes that the molecules are rigid elastic spheres. MEYER'S work was a valuable attempt at an exact treatment of the problem, but the method adopted (that used by CLAUSIUS and MAXWELL in their early researches, but afterwards abandoned by MAXWELL as being misleading) did not really allow of great accuracy. The expression for f which was arrived at involved a definite integral, which was calculated (using mechanical quadratures) by CONRAU and NEUGEBAUER.[†] JEANS[‡] improved the proof of MEYER'S theorem, but his corrections did not affect the final result. The law obtained was

$$\vartheta = 1{\cdot}6027\mu C_v;$$

it has generally been considered that the difference between this value of f, and MAXWELL'S value $\frac{5}{2}$, arose from the different nature of the molecules considered. This view is in sharp contradiction to the theorem we have proved. Hence, since actual molecules do not conform to MAXWELL'S hypothesis, whatever

---

[*] 'Scientific Papers,' vol. ii., p. 74. By a numerical slip he gave the value of f as $\frac{5}{3}$. The error was pointed out by BOLTZMANN and POINCARÉ.

[†] MEYER'S 'Kinetic Theory of Gases' (English edition, 1899), Chapter IX.

[‡] JEANS' "Dynamical Theory of Gases," Chapter XIII.

experimental evidence we can adduce in favour of the value $f = \frac{5}{2}$ will confirm that theorem.

As both theories treat of monatomic gases, we must seek for evidence with regard to them. When this paper was written the only monatomic gas, of which I was aware, for which ϑ is known was mercury vapour, referred to by MEYER.* While a number of polyatomic gases obeyed his law fairly closely, this monatomic gas alone formed a striking exception. KOCH† has determined μ for mercury vapour at 273° C. and 380° C., and also at the much lower temperature 203° C.; SCHLEIERMACHER‡ has determined ϑ at 203° C.; these data, together with the theoretically calculated value of C_v, lead to 3·15 as the value of f. MEYER raises some weighty objections against the accuracy of the data, viz., (i) that KOCH'S three values of μ show an unlikely amount of variation with the temperature; (ii) that the condensation of saturated mercury in the capillary tube probably affected the determination of μ; and (iii) that it is uncertain whether the vapour is completely monatomic at 203° C. While the resulting value of f is certainly unreliable, it is hard to conceive of the experimental errors being so great as to explain the difference between 1·6027 and 3·15. So far as it goes, it tends rather to the support of the present theory.

Quite recently, however, I have found that SCHWARZE had disproved MEYER'S theory nine years ago, by showing that $f = 2·5$ for the true monatomic gases argon and helium.§ As these determinations are important in this connection, a few details of them will be given. SCHLEIERMACHER'S method, now generally accepted as the best, was used to determine ϑ, heat being conducted by the gas from a heated platinum wire. The gases were very carefully prepared and purified,‖ and in the reduction of the observations (which were made at two temperatures) due corrections were applied for the heat lost by conduction along the wire and for the temperature drop at the walls. The following values of ϑ_0 were obtained:—

Argon 0·00003894, Helium 0·0003386, Air 0·00005690,

the last named being determined as a check on the apparatus, and agreeing well with

---

* 'Kinetic Theory,' p. 295.

† 'WIED. Ann.,' 1889, xxxvi., p. 346.

‡ *Ibid.*, 1883, xix., p. 857.

§ W. SCHWARZE, 'Inaugural Dissertation,' Halle, 1902; 'Ann. d. Physik,' 11, p. 303, 1903; 'Phys. Zeitschrift,' 4, p. 229, 1903.

MEHLISS ('Halle Diss.,' 1902) made an earlier determination of ϑ for argon by the STEFAN-WINKELMANN method, and found $f = 2·44$; this result was in such striking disagreement with MEYER'S theory that SCHWARZE investigated the matter very thoroughly, both for argon and for helium, by the more accurate method due to SCHLEIERMACHER. The result was quite unexpected, and neither observer seemed inclined to regard it as a confirmation of MAXWELL'S hypothesis, but rather as being due to a numerical defect in MEYER'S theory—which view is nearer the truth, according to the present theory.

‖ The helium contained $\frac{1}{2}$ per cent. impurity (probably of neon); the same material was used by SCHULTZE ('Ann. d. Phys.,' 6, p. 303, 1901) to determine the value of μ used above.

WINKELMANN'S* value 0·0000568 and MÜLLER'S† value 0·000056. MEHLISS‡ obtained 0·000038 for argon.

SCHULTZE§ determined the following values of μ_0 for argon and helium, using the same materials as SCHWARZE:—

Argon 0·0002104, Helium 0·0001891.

Using the following values of C_v:—

Argon¶ 0·0740, Helium‖ 0·7142,

SCHWARZE thus finds these values of f:—

Argon **2·501**, Helium **2·507**.

I proceed to discuss briefly the case of polyatomic gases. It is immediately obvious that the present theory does not apply here, for C_v in actual fact differs widely from its value for the monatomic gas contemplated in the foregoing calculations (this is not to say that f is *not* equal to $\frac{5}{2}$ for any polyatomic gas, but merely that our theory leaves the question perfectly open). The same remark applies to any theory which supposes the molecules to be devoid of internal energy—in particular to MEYER'S theory. But the latter has derived all its support from polyatomic gases. MEYER'S views on this point underwent some changes. In 1877** he seems reluctantly to have accepted the theory (strongly upheld by STEFAN and BOLTZMANN) that the internal and translational molecular energies travelled at different rates (the latter most rapidly), so that the conductivity would be less for a gas whose molecules possess much atomic energy than for a similar gas with little atomic energy.

In 1899,†† however, he held that the conductivity is the same for both kinds of energy, and supported this view by an unsound argument based on the law of equipartition. This enabled him to assert that f is equal to 1·6027 for all gases, and so obtain all possible support from the data for polyatomic gases. More modern data would give much less support to the theory, as we shall see. But such disproof is unnecessary, for SCHWARZE'S experiments conclusively show (i) that MEYER'S value

---

* 'WIED. Ann.,' 48, p. 180, 1893.

† *Ibid.*, 60, p. 82, 1897.

‡ 'Halle Diss.,' 1902.

§ 'Halle Diss.,' 1901; 'Ann. d. Phys.,' 5, p. 140, 1901, and 6, p. 302, 1901.

‖ Calculated from the formula $\frac{3}{2}R/Jm$; $m = 0·1439$ for the helium used, and J was taken as 427. This leads to the above value of f, given in 'Ann. d. Phys.,' 11, p. 303, 1903. In 'Phys. Zeitschrift,' 8, p. 229, 1903, J was taken as 424, which made $f = 2·490$.

¶ C_v for argon is calculated from C_p (determined as 0·1233 by DITTENBERGER, 'Halle Diss.,' 1897) and γ (determined as 1·667 by NIEMEYER, *cf.* 'Smithsonian Physical Tables,' 1910, p. 232). Thus $C_p/\gamma = 0·0002104$.

** 'Kinetic Theory of Gases,' 1st edition, 1877.

†† *Ibid*, 2nd edition, English translation, 1899, pp. 291–296.

of f is theoretically unsound, and (ii) that the internal energy does not travel at the same rate as the translational energy. Hence the agreement of Meyer's theory with experiment must be accidental.

Boltzmann, who opposed Meyer's view, developed a theory of conduction* on the basis of Maxwell's hypothesis, taking into account the internal energy. He obtained the following relation between f and γ, the ratio of the specific heats,

$$f = \tfrac{15}{4}(\gamma - 1).$$

This reduces to Maxwell's law when $\gamma = \frac{5}{3}$, but the formula, as we shall see, is not borne out by the experimental data.

I have not attempted to work out a theory of conduction in polyatomic gases, and shall be content with pointing out how (in a general way, and with some marked exceptions, which may, however, be due to faulty data) f tends to be larger or smaller (while always less than $\frac{5}{2}$) according as a gas has less or more internal energy. The table below gives the values of ϑ_0 for all the gases for which determinations are available, together with γ, C_v, μ, and the values of f calculated from them, and also f as calculated from Boltzmann's formula. The gases are arranged in increasing order of γ, *i.e.*, in diminishing order of β, the ratio of internal energy to total energy.

Gas.	γ.†	C_v.‡	$\mu_0 \times 10^7$.	$\vartheta_0 \times 10^7$.	f (observed).	f (Boltzmann).
Ethane	1·219[1]	0·302[4]	843	495[7]	1·94	0·82
Ethylene	1·248	0·274	944	395[8]	1·53	0·93
Carbon dioxide . . .	1·300	0·1477	1388	307[8]	1·50	1·12
Nitrous oxide	1·304	0·1483	1381	350[8]	1·71	1·14
Methane.	1·316[2]	0·451[5]	104	746[7]	1·59	1·19
Ammonia	1·317[3]	0·397[6]	960	458[8]	1·20	1·19
Nitric oxide	1·394	0·1665	1680	451[9]	1·61	1·48
Oxygen	1·402	0·1563	1900	578[11]	1·95	1·51
Air	1·405	0·1695	1721	569[10]	1·95	1·52
Nitrogen	1·405	0·1738	1670	569[11]	1·96	1·52
Hydrogen	1·402	2·427	854	387.1[11]	1·87	1·51
Carbon monoxide . .	1·409	0·1730	1628	499[8]	1·77	1·53

---

* 'Pogg. Ann.,' 157, 1876, pp. 457–469. The theory is partly empirical, being an adaptation of Maxwell's formula in which $f = \frac{5}{2}$. Boltzmann states (p. 468) that the numerical coefficients would have to be altered if any other molecular hypothesis were adopted. Our theorem shows that this is not true, at any rate when $\gamma = \frac{5}{3}$.

† These values of γ are taken from Jeans' "Dynamical Theory of Gases" (pp. 220, 221), except where the contrary is indicated.

[1] Landolt and Börnstein's tables; observed by Müller.

[2] 'Smithsonian Physical Tables,' 1910; observed by Müller.

[3] *Ibid.*; by Wüllner.

‡ These values of C_v are taken from Jeans' treatise (p. 218), except where the contrary is indicated. They are due to Wiedemann and Wüllner.

[4] Calculated from γ.

[5], [6] Calculated from C_p and γ, as given in the Smithsonian tables.

[7] ZIEGLER, 'Halle Diss.,' 1904. STEFAN ('Wiener Sitz.,' 72, II., p. 69, 1875) had found $\vartheta_0 \times 10^7 = 780$ for methane, and WINKELMANN ('POGG. Ann.,' 156, p. 497, 1875) obtained the value 647. There are no previous determinations for ethane.

[8] Determined by WINKELMANN, as given in the Smithsonian tables.

[9] WINKELMANN (MEYER, p. 295).

[10] SCHWARZE, *loc. cit.*; WINKELMANN'S and MÜLLER'S determinations have already been mentioned. There are also experiments by TODD ('Roy. Soc. Proc.,' A, 1909, 83, p. 19) and ECKERLEIN ('Ann. d. Phys.,' 3, p. 120, 1900), the latter being at low temperatures (for air, hydrogen, and carbon dioxide).

[11] GÜNTHER, 'Halle Diss.,' 1906. Also see MEYER'S treatise for earlier determinations.

The authorities for the above values of μ_0 will be given later, when we come to discuss the coefficient of viscosity. The table shows that the results agree neither with MEYER'S nor BOLTZMANN'S theory. The values of f for methane and ammonia stand out from the others, which show a tendency to increase with γ; as all the values of f are less than $\frac{5}{2}$ it would appear that the view of STEFAN and BOLTZMANN is correct, that the atomic energy travels slower than the translational energy.

In conclusion it may be remarked that the formula $\vartheta = f\mu C_v$ shows that ϑ will behave (as the temperature or pressure varies) in a way which can be predicted from the behaviour of μ and C_v separately, if the equation is correct. Experiments have confirmed this, and we shall therefore leave the discussion of these laws till we come to the simpler case of μ itself.

18. *The Coefficient of Conduction for a Mixed Gas.*

The expression we have obtained for this quantity enables us to determine it in terms of the coefficients of viscosity of the two pure gases forming the mixture, and of their coefficient of diffusion, provided that we know the law of interaction between the molecules. The latter is involved in the constants k, k_1, and k_2, but these do not vary very much with the law of force. In Part II. of this paper we have determined their values in some special cases as follows:—

Rigid elastic spheres (46)—

$$k = \tfrac{3}{5}, \qquad k_1 = \tfrac{6}{5}, \qquad k_2 = \tfrac{48}{25},$$

MAXWELL'S repelling molecules (48 and 49)—

$$k = 0{\cdot}771, \qquad k_1 = 1, \qquad k_2 = \tfrac{7}{5},$$

Attracting rigid spheres (52)—

$$k = \tfrac{3}{5}\,\frac{1+\frac{2}{3}C_{12}/\theta}{1+C_{12}/\theta}, \qquad k_1 = \tfrac{6}{5}\,\frac{1+\frac{2}{3}C_{12}/\theta}{1+C_{12}/\theta}, \qquad k_2 = \tfrac{48}{25}\,\frac{1+\frac{1}{2}C_{12}/\theta}{1+C_{12}/\theta},$$

where (as we shall see in § 21) the constant C_{12} must be determined by experiments on the variation of the coefficient of diffusion (of the gases concerned) with temperature.

The formula for the coefficient of conduction in a mixed gas (equations 40 and 41) seems very complicated, but the calculations from it in any particular case are quite simple. Fortunately we have experimental data for testing the law. WACHSMUTH,* at Halle, has recently determined the conductivity of mixtures of argon and helium in various proportions; the gases being monatomic, our formulæ are properly applicable. WACHSMUTH himself undertook the research, at Prof. DORN'S suggestion, in order to determine f in the formula $\vartheta = f\mu C_v$, taking the value of μ from TÄNZLER'S experiments (which will be discussed in the next section) on the viscosity of mixtures of argon and helium. He found that f so determined for the mixture was greater than $\frac{5}{2}$, approaching a maximum (about 4) when there was 60 per cent. of helium in the gas, and falling to $\frac{5}{2}$, as SCHWARZE showed, when either gas was eliminated. This fact is interesting, but, in the absence of any explanatory theory, does not lead to anything further.

WACHSMUTH also found that the observations could be represented to within 2 per cent. or 3 per cent. by the formula

$$\vartheta_{12} = \frac{\vartheta}{1+\mathrm{A}p'/p} + \frac{\vartheta'}{1+\mathrm{B}p/p'}$$

(modelled on a similar formula for the viscosity of gases which we shall consider presently). As there were only four observations and two empirical constants the fact is not very remarkable; when $p = 0$ of course $\vartheta_{12} = \vartheta'$, and when $p' = 0$ we have $\vartheta_{12} = \vartheta$. A much better agreement was obtained by allowing the empirical constants A and B (obtained by the method of least squares) to be imaginary. In this case the expression reduces to the quotient of a cubic by a quartic homogeneous expression in the variables p, p'; as WACHSMUTH remarks, the relation is good as an interpolation formula, but that is all.

We proceed to determine the value of ϑ_{12} from our formula. Taking oxygen as the standard gas (for which $\rho_0 = 0{\cdot}001429$ at 0° C. and normal pressure) we have w (for argon) equal to 1·224, and $w' = 0{\cdot}125$. The values of μ_0 (*i.e.*, μ at 0° C.) determined by SCHULTZE (*loc. cit.* on p. 463), viz., 0·0002104 and 0·0001891 respectively, will be used; also the previously given values of C_v. The coefficient of diffusion D_{12} for argon and helium has been determined by SCHMIDT and LONIUS (references given in § 21); reduced to 0° C. and normal pressure, in C.G.S. units it is 0·650.† We now have all the necessary data for the calculation of ϑ_{12} in the case of rigid spherical molecules and of Maxwellian molecules. For the case of attracting spherical molecules we need also the coefficient C_{12}; this has not been determined, to

---

[*] 'Halle Diss.,' 1907; 'Phys. Zeitschrift,' 7, p. 235, 1908. The method was that due to SCHLEIERMACHER, and the apparatus was that previously used by SCHWARZE and GÜNTHER, already quoted.

[†] As explained in § 21, this value is uncertain to within 2 per cent. or 3 per cent.

my knowledge, but the value 100 (intermediate between the values of C_{11} for argon and helium) is near enough for our purpose, as the constant does not have much weight in the formula.

From the equations (41) it is an easy matter to calculate the constants E, F, G, E_1, F_1, G_1; we find the following values* for the three special kinds of molecules considered :—

Rigid spheres—

$$E = 6{\cdot}66, \qquad F = 20{\cdot}73, \qquad G = 10{\cdot}60,$$
$$E_1 = 3{\cdot}93 \times 10^4, \qquad F_1 = 3{\cdot}76 \times 10^4, \qquad G_1 = 0{\cdot}704 \times 10^4.$$

Maxwellian molecules—

$$E = 4{\cdot}10, \qquad F = 17{\cdot}56, \qquad G = 10{\cdot}65,$$
$$E_1 = 2{\cdot}42 \times 10^4, \qquad F_1 = 2{\cdot}65 \times 10^4, \qquad 0{\cdot}706 \times 10^4.$$

Attracting spheres—

$$E = 5{\cdot}38, \qquad F = 19{\cdot}0, \qquad G = 10{\cdot}56,$$
$$E_1 = 3{\cdot}17 \times 10^4, \qquad F_1 = 3{\cdot}13 \times 10^4, \qquad G_1 = 0{\cdot}700 \times 10^4.$$

We have written E_1 and G_1 in place of Ew/μ and Gw'/μ' respectively. Our formula thus becomes

$$\vartheta_{12} = \tfrac{5}{2}(C_v)_{12}\frac{Ep^2+Fpp'+Gp'^2}{E_1p^2+F_1pp'+G_1p'^2},$$

where $(C_v)_{12}$ is given by equation (39A). The following table gives the values of p and p' and the observed values of ϑ_{12},† from WACHSMUTH's paper, together with ϑ_{12} calculated according to the above three hypotheses :—

THERMAL Conductivity of Mixtures of Argon and Helium.

p (argon).	p' (helium).	$(C_v)_{12}$.	$\vartheta_0 \times 10^7$ (observed).	$\vartheta_0 \times 10^7$ (calculated).		
				Rigid spheres.	Attracting spheres.	Maxwellian molecules.
1·000	0·0000	0·0740	389	389	389	389
0·730	0·270	0·0984	741	675	723	797
0·546	0·454	0·1257	1077	957	1054	1230
0·153	0·847	0·3094	2320	2208	2370	2550
0·0539	0·946	0·4952	2939	2750	2850	2900
0·0000	1·000	0·7142	3386	3386	3386	3386

---

* These and nearly all the other calculations in Part III. have been performed with a slide rule, which is accurate enough for the purpose.

† ϑ_{12} was determined at two temperatures; we are, of course, using the value reduced to 0° C., as given by WACHSMUTH.

Considering the nature of the calculation, the agreement is extremely good in all three cases (of course the values of ϑ for the pure gases are taken from the formula 34). The hypothesis that the molecules are rigid elastic spheres surrounded by fields of attractive force gives notably the best results, however, the agreement being within 3 per cent. in every case—which is little, if any, more than is introduced by uncertainty of the data.

The above are the only available data for monatomic gases, so far as I know. Wassilewja* has determined the conductivity of mixtures of hydrogen and oxygen, and, of course, we have the conductivity of air; but as these are mixtures of polyatomic gases our formula does not apply to them, so that they will not be discussed here.

In conclusion, it is hardly necessary to remark that our formula for the conductivity of a mixed gas reduces to that for a pure gas on putting p or p' equal to zero. Since (as we shall see) D_{12}, the coefficient of diffusion, varies inversely as the total pressure, $\rho_0 D_{12}$ is independent of the pressure, as also are all the other quantities entering into E, F, G, F_1; hence the coefficient of conduction of a mixture, like that of a pure gas, is independent of the total pressure. This has been experimentally verified in the case of air.†

19. *The Coefficient of Viscosity of Mixed Gases.*

The viscosity of mixed gases has been much studied, both theoretically and experimentally. It is especially interesting on account of the curious fact, first noticed by Graham ('Phil. Trans.,' 1846), that the addition of a moderate amount of light gas (hydrogen, in the case mentioned) to a much more viscous and heavy gas (carbon dioxide) may actually *increase* the viscosity of the latter. The same phenomenon was commented on by Maxwell in a Bakerian Lecture (1866), the gases receiving particular mention being air and hydrogen.

The principal formulæ which have been deduced for the viscosity of a mixture are due to Maxwell,‡ Puluj,§ Sutherland,|| and Thiesen.¶ Of these only the first is based on an adequate proof, but as it is a particular case of my own formula (got by putting $k = A_2/A_1 = 0{\cdot}771$) it does not need separate discussion. Puluj's formula is based on an ingenious adaptation of the earlier theories of viscosity of a pure gas, and although, like those theories, it is only approximate, and in some ways not

---

* 'Phys. Zeitschrift,' 5, 1904, p. 737.

† Meyer, 'Kinetic Theory,' Chapter IX.; Todd, 'Roy. Soc. Proc.,' A, 83, p. 19, 1909.

‡ 'Scientific Papers,' vol. ii., p. 72.

§ 'Carl's Repertorium,' xv., p. 590; 'Wien. Sitzungsber.,' 1879, lxxix., Abth. 2, pp. 97, 745; see also Meyer, 'Kinetic Theory,' p. 200.

|| 'Phil. Mag.,' 1895, xl., p. 421.

¶ 'Verh. d. Deutsch. Phys. Ges.,' 4, p. 238, 1902.

satisfactory,* it nevertheless forms a useful interpolation formula. The expression is

$$\frac{(mp+m'p')^{1/2}}{(p\mu^{-3/2}m^{3/4}+p'\mu'^{-3/2}m'^{3/4})^{2/3}} \qquad \text{(Puluj).}$$

SUTHERLAND, by an argument which though not rigorous is very interesting and suggestive, arrives at the formula

$$\frac{\mu}{1+\mathrm{A}p'/p}+\frac{\mu'}{1+\mathrm{B}p/p'} \qquad \text{(Sutherland, Thiesen),}$$

which THIESEN also obtained by a different method of proof. While, however, THIESEN left the formula as an empirical one, SUTHERLAND strove to find expressions for A and B in terms of molecular constants. He found such expressions, but did so half empirically by a study of GRAHAM'S data. In the case of the gases which he considered, a very fair agreement was obtained.

My own formula (39) can be written

$$(53) \qquad \frac{\mathrm{E}p^2+\mathrm{F}pp'+\mathrm{G}p'^2}{\mu^{-1}\mathrm{E}p^2+\mathrm{F}_1pp'+\mu'^{-1}\mathrm{G}p'^2}$$

where E, F, G, F_1 are given by equation (39) in terms of μ, μ', D_{12} (the coefficient of diffusion), and a constant k which depends on the particular law of action between the molecules; k is unknown, but may be expected to lie near or between the values already found for it in special cases (0·60 for elastic spheres, 0·771 for Maxwellian molecules).

Of the above formulæ, that by PULUJ is the only one which is perfectly explicit. THIESEN'S expression is completely empirical, and is useful only as an interpolation formula. PULUJ'S relation shares the virtues and defects of the theory on which it is founded, and therefore prescribes a law of variation with temperature inconsistent with the facts for most gases. THIESEN'S law, on the other hand, does not give any information concerning variation with temperature, and the constants A and B must be empirically determined for each case.

The formula (34) or (53), as we shall see later, completely expresses the relation between μ_{12} and the temperature, but, being quite general, it specifies a different law for each molecular hypothesis; and while, conversely, the determination of k and the law of temperature variation from experimental data may lead to further knowledge as to the best molecular hypothesis, this very generality gives the formula a semi-empirical character.

On theoretical grounds it is desirable that the success of equation (34) as an interpolation formula should be tested. Excellent experimental material exists for the purpose. SCHMITT† has lately given a *resumé* of an extensive series of experi-

---

* Thus it tacitly implies that the viscosity varies as the square root of the absolute temperature (since the theories on which it is based lead to this law).

† 'Ann. d. Phys.,' 30, p. 393, 1909. Full references to the original sources of the data are there given. SCHMITT was apparently unaware of SUTHERLAND'S formula, but, of course, it is the same as THIESEN'S, if treated empirically.

ments on viscosity carried on at Halle, and has compared the results with the formulæ of Puluj and Thiesen. The former agrees remarkably well with the observations, the residuals seldom exceeding 3 per cent. Thiesen's formula agrees even better still, the residuals rarely exceeding 1 per cent. This is not unnatural, as the constants A and B were found by the method of least squares to three or four significant figures. I have taken two of the longest tables given by Schmitt, and have roughly found the value of k (by trial and error) which makes the formula (34) or (53) agree most closely with the observations. The results are given in the following tables* :—

Viscosity of Mixtures of Argon and Helium at 15° C.

p (argon).	p' (helium).	$\mu_{12} \cdot 10^7$ (observed).	$\mu_{12} \cdot 10^7$ (calculated) $k = 0 \cdot 692$.
1·0000	0·0000	2220	2220
0·9507	0·0493	2231	2230
0·9093	0·0907	2243	2240
0·8571	0·1429	2253	2249
0·8074	0·1926	2266	2259
0·7705	0·2295	2264	2266
0·6846	0·3154	2266	2283
0·6119	0·3881	2303	2294
0·5337	0·4663	2299	2297
0·2915	0·7085	2280	2292
0·1921	0·8079	2226	2246
0·0000	1·0000	1966	1966

Viscosity of Mixtures of Oxygen and Hydrogen at 15° C.

p (oxygen).	p' (hydrogen).	$\mu_{12} \cdot 10^7$ (observed).	$\mu_{12} \cdot 10^7$ (calculated) $k = 0 \cdot 65$.
0·0000	1·0000	878	878
0·0521	0·9479	1092	1076
0·0878	0·9122	1191	1191
0·1561	0·8439	1359	1370
0·3333	0·6667	1674	1672
0·5678	0·4322	1877	1876
0·8126	0·1874	1992	1975
0·9555	0·0445	2014	2007
1·0000	0·0000	2014	2014

---

* In the first table the experimental constants used were as follows: $\mu \times 10^{-7} = 2220$, $\mu' \times 10^7 = 1966$, $w = 1 \cdot 224$, $w' = 0 \cdot 125$ (relative to oxygen), ρ_0 (at 15° C.) $= 0 \cdot 001353$, D_{12} (at 15° C. and in C.G.S. units) $= 0 \cdot 705$ (from Schmidt's experiments, *cf.* p. 478). The values of E, F, G, F_1 were 7·897, 6·897, 1·069, and $2 \cdot 776 \times 10^4$ respectively.

In the second table the values of $\mu \times 10^7$ were 2014 and 878, $w = 1$, $w' = 0 \cdot 0629$, $\rho_0 = 0 \cdot 001353$, D_{12} (from Jackmann's experiments, *cf.* p. 478) $= 0 \cdot 760$, at 15° C. and in C.G.S. units. The values of E, F, G, F_1 were 11·34, 9·676, 1·049, and $5 \cdot 205 \times 10^4$ respectively.

The sum of the residuals between columns 3 and 4 is 77 in the first case, 54 in the second*; more accurate determinations of k would probably reduce these figures, but the agreement is already within the limits of experimental error. It will be seen that the values of k which have been found, viz., 0·69 for argon and helium and 0·65 for oxygen and hydrogen, are intermediate between the values corresponding to the elastic-sphere theory and MAXWELL'S hypothesis, a result which confirms our theory. It is impossible to tell what special molecular structure these numbers indicate until the integrals of Part II. of this paper are worked out for other cases; it may be that a very slight modification of one of the hypotheses there considered would explain the figures.

The above tables, and others which might be given, show that our formula agrees well with observation, with a value of k accordant with the theory; its success is therefore more significant than that of THIESEN'S formula, with its two empirical constants. It may be noticed that THIESEN'S expression can also be put into the form (53), with the speciality, however, that a relation exists between the three independent constants of (53) reducing them to two. Nevertheless, this agreement in functional form is sufficient to explain the success of THIESEN'S expression as an interpolation formula over the limited range (0, 1) of p and p'. It may be concluded that, *as far as the latter purpose goes*, PULUJ'S formula, though not theoretically well founded, is the best (when the values of μ and μ' at the temperature considered are assigned), because it is very simple in form, quite definite, and sufficiently accurate for most purposes; while THIESEN'S formula requires the knowledge of two empirical constants, and my own formula is not so well suited for numerical calculation.†

The study of the variation of the viscosity of mixed gases with the temperature is best deferred till the analogous question has been discussed for simple gases; the subject will therefore be briefly discussed in § 22.

20. *The Coefficient of Viscosity of a Simple Gas.*

The formulæ which have already been discussed do not contain any reference to the internal structure of the molecule, so far as this could be avoided, but are

---

* The corresponding figures for THIESEN'S formula are 55 and 51, and for PULUJ'S formula 126 and 187. *Cf.* K. SCHMITT, 'Ann. d. Phys.,' 30, p. 393, 1909; pp. 408, 406.

† The form of the expression (53) is well suited to explain the phenomenon mentioned at the beginning of this section. It shows that μ_{12} is really a weighted mean between μ, μ' and F/F_1, the weight depending on the ratios $E : F : G$ and varying with p and p'. For mixtures of CO_2 and H we have $F/F_1 > \mu > \mu'$; also as $E : G$, or $1 + kw/w' : 1 + kw'/w$ is large, on account of the largeness of w/w', μ' is given very little weight in the mean except when p is very small. Therefore, for moderate values of the ratio p/p', the value of μ_{12} lies between F/F_1 and μ, and may exceed the latter considerably.

The same thing may be noted to a small extent in the above argon-helium table. From the figures already given, we have $F/F_1 = 2482 \times 10^{-7}$, which is greater than 2220×10^{-7}, the viscosity of argon at the temperature considered.

expressed as relations between directly measurable quantities. This enabled us to verify that our conclusions were borne out by the results of experiment. The equations might have been written otherwise, however, so that the formulæ should express ϑ, ϑ_{12}, μ_{12} in terms of unknown molecular data, which might then be found from the experimental values of ϑ and μ_{12}; there would still be some check on the theory by the comparison of the values of the molecular constants found from different formulæ. The reference to these constants was avoided by substitution of μ and D_{12} into the formulæ, which were thus rendered much simpler; no such simplification can be made in the expressions for μ and D_{12}, and as these involve the molecular data in the least complicated form, they are much the most suitable for the purpose of determining the diameter of molecules.

Our expression (33) for the viscosity of a simple gas is

$$\mu = \frac{5}{4h^3m^2}\left(\frac{2\pi}{hm}\right)^{3/2}\frac{1}{\pi R''_{11}};$$

R''_{11} is a function of the temperature only, so also is h (since $2h = 1/R\theta$); and m, the mass of a molecule, is a constant for any gas. Hence we have obtained a perfectly general proof (for the case of a monatomic gas) that the coefficient of viscosity is independent of the pressure and density of a gas, and depends only on the temperature. This remarkable law was first discovered by MAXWELL.

If we substitute the values of R''_{11}, which we have already found in special cases (see equations 45, 52, and 48), we get the following special laws:—

$$(54) \qquad \mu = \frac{5m}{64\sqrt{\pi}}\cdot\frac{1}{\sqrt{(2hm)}}\cdot\frac{1}{\sigma^2} = \frac{5m}{64\sigma^2\sqrt{\pi}}\left(\frac{R}{m}\theta\right)^{1/2} \qquad \text{(elastic spheres)},$$

$$(55) \qquad \mu = \frac{5m}{64\sigma^2\sqrt{\pi}}\left(\frac{R}{m}\theta\right)^{1/2}\frac{1}{1+\dfrac{C_{11}}{\theta}} \qquad \text{(attracting spheres)},$$

$$(56) \qquad \mu = A\theta^{\frac{n+3}{2(n-1)}} \qquad \text{(centres of force} \propto 1/r^n\text{)},$$

where in the last equation we have

$$A = \frac{5\sqrt{\pi}}{2^{3-4/(n-1)}}\frac{m}{\lambda''(n)\,\Gamma\left(4-\dfrac{2}{n-1}\right)}\left(\frac{n-1}{4K_{11}m}\right)^{\frac{2}{n-1}}\left(\frac{R}{m}\right)^{\frac{1}{2}+\frac{2}{n-1}}$$

(the force between two molecules at distance r being $K_{11}m^2/r^n$), and $\lambda''(n)$ is a number depending only on n, having two values for each one of n, according as the force is attractive or repulsive.

The first equation shows that if the molecules are simple elastic spheres the viscosity varies as the square root of the absolute temperature (this law is due to MAXWELL); the second shows that when the spheres also attract one another the viscosity varies as $\theta^{1/2}(1+C/\theta)^{-1}$, as was first discovered by SUTHERLAND[*]; while the last equation shows that, if the molecules attract or repel one another according to the inverse n^{th} power law, then μ is proportional to the $(n+3)/2(n-1)^{\text{th}}$ power of θ. It is interesting to notice that Lord RAYLEIGH[†] predicted this law of variation from a consideration of dimensions alone; the present formula is complete, with an exact analytical expression for the numerical constant. If we write μ_0 for the viscosity at 0° C., the three laws just indicated may be written

$$\frac{\mu}{\mu_0}=\left(\frac{\theta}{\theta_0}\right)^{1/2}, \qquad \frac{\mu}{\mu_0}=\left(\frac{\theta}{\theta_0}\right)^{1/2}\frac{1+C/\theta_0}{1+C/\theta}, \qquad \frac{\mu}{\mu_0}=\left(\frac{\theta}{\theta_0}\right)^{\frac{n+3}{2(n-1)}}.$$

When the molecules repel one another according to the inverse fifth power of the distance, the last equation becomes

$$\mu/\mu_0=\theta/\theta_0,$$

which was obtained by MAXWELL.

Experiment shows that the second formula (generally known as SUTHERLAND'S formula) agrees far better with the actual facts than the others. MAXWELL'S two hypothetical laws, $\mu\propto\theta^{1/2}$ and $\mu\propto\theta$, are obeyed (even approximately) by very few gases. The law $\mu\propto\theta^s$ (where $s=(n+3)/2(n-1)$) represents the variation much better in most cases, but even this applies only over a small range of temperature, after which a new value of n is required. On the other hand, SUTHERLAND'S formula applies universally so far as it has been tested.[‡] It will be sufficient to mention the cases of helium and hydrogen. SCHMITT[§] gives tables showing that the law agrees with the observations of these gases from −60° C. to 185° C.; below −60° C. the agreement ceases to be good. Thus this evidence tends to confirm the hypothesis that the molecules behave for our purpose like attracting spheres.

The value of C has been shown in Part II. (pp. 457–460) to be a multiple of the mutual potential of two molecules in contact with one another. This was shown by SUTHERLAND in his original paper, but as his mathematics was intentionally only approximate, his numerical constant is not correct.[‖] The correction may be of importance when the theory of the constant C is further developed.[¶] It must be remembered always that $1+C/\theta$ is only the beginning of an infinite series of powers

---

[*] 'Phil. Mag.,' 1893 (5), xxxvi., p. 507.

[†] "On the Viscosity of Argon as affected by Temperature," 'Scientific Papers,' vol. iv., p. 452, and p. 481.

[‡] We are referring to gases under normal conditions; when the critical point is approached, the law ceases to be valid.

[§] 'Ann. d. Phys.,' 30, 1909, p. 399, where references to the original sources will be found, as well as data for other gases.

[‖] This does not affect his discussion (*loc. cit.*) of the law of attraction between molecules, as he was there concerned only with the relative values of C for different gases.

[¶] It is interesting to notice that RANKINE ('Phil. Mag.,' January, 1911, p. 45, and 'Roy. Soc. Proc.,' 84 p. 190) has found that for several gases C is proportional to the critical temperature.

of $1/\theta$, and that later terms become important in the case of vapours, though for ordinary gases these, the first two, terms appear to be enough.

As we have seen, the above laws of variation with temperature given by our theory have been announced before. The difference between our formulæ and the earlier ones chiefly consists (as regards viscosity) in the numerical constants. We have already seen, in the case of the coefficient of conduction, to what grave errors ($f = 1{\cdot}60$ instead of $2{\cdot}50$) the older elastic-sphere theory may lead. The expression given by MEYER for the viscosity differs considerably from the present one; JEANS* made an undoubted improvement in the older theory by allowing for the persistence of velocities after molecular collisions. The fact that this important consideration had been previously overlooked illustrates the imperfections of that theory. As it is, the correction for persistence of velocities is itself of uncertain amount†; however, by its means the discordance between the formula of the older theory, and that given by the present theory for the case of elastic spherical molecules, is reduced almost to 10 per cent.‡

From equations (54) and (55) we proceed to determine what evidence the various hypotheses lead to, as regards the size of molecules. Those formulæ are strictly true only for monatomic gases, but can be applied to polyatomic gases with much more safety than could the formulæ for the conductivity of gases, where the internal energy (which here plays little or no part) was very important. The formula (56) could also be used to determine the relative force constants of the molecules when assumed to be point-centres of force, but as this is of less interest we shall not trouble to do so.

The said equations contain R/m, which can be determined from data as to the density of a gas at a given temperature and pressure. A table of values of R/m for several gases is given by JEANS (p. 113, *loc. cit.*). To determine σ, the radius of the molecule, we also require to know m, or, since $\rho = \nu m$, we require to know ν, which is AVOGADRO's constant. JEANS used the value 4×10^{19}, the best one then available; but recent researches§ agree in indicating $2{\cdot}77 \times 10^{19}$ as the correct values, which we shall therefore use here. In the following table are given the values of μ_0, C, and $\sigma \times 10^8$ for some gases, the latter being calculated according to the two hypotheses considered. It will be noticed that the radii of the molecules on the hypothesis that they attract one another is less than that when no such forces exist; of course, in the

---

* "Dynamical Theory of Gases," p. 238, p. 250.

† *Ibid.*, p. 250, line 13, where it is assumed for the sake of simplicity that the excess of momentum above that appropriate to the point of collision goes in equal proportions to each molecule.

‡ In our notation, JEANS' formula (581) may be written

$$\frac{\cdot 88}{\sqrt{\pi}} \frac{m}{4\pi\sigma^2}\left(\frac{\mathrm{R}}{m}\theta\right)^{1/2}$$

which is $\cdot 896$ times our own expression.

§ SUTHERLAND ('Phil. Mag.,' 1909, February, p. 320) quotes RUTHERFORD as the authority for this figure, and mentions that it is in good agreement with PLANCK'S value $2 \cdot 80 \times 10^{19}$.

latter case the apparent size includes part of the extension of the field of force of the molecule. In selecting the values of μ_0 and C I have preferred to use the mean of recent determinations (where these exist) rather than to go back to GRAHAM'S or OBERMAYER'S experiments.

Gas.	$\mu_0 \times 10^7$.	C.	$\sigma \times 10^8$.	
			Elastic-sphere theory.	Attracting-sphere theory.
Air	1721[1]	111·5	1·830	1·542
Hydrogen	854[2]	75·6	1·332	1·180
Oxygen	1900[3]	130·3	1·781	1·469
Nitrogen	1672[4]	111·7	1·842	1·553
Nitrous oxide . . .	1381[5]	167	2·267	1·787
Nitric oxide . . .	1680[5]	195	1·869	1·429
Carbon dioxide . .	1388[6]	249	2·259	1·636
Carbon monoxide . .	1628[7]	156	1·868	1·490
Chlorine	1280[5]	199	2·654	2·019
Ethylene	990[5]	249	2·389	1·730
Helium	1885[8]	75·3	1·065	0·943
Argon	2107[9]	162	1·790	1·508
Neon	2981[10]	56	1·266	1·154
Krypton	2334[10]	142	1·622	1·317
Xenon	2107[10]	252	2·408	1·738

---

[1] Authorities: The value of μ_0 is a mean of 1714 ('LANDOLT and BÖRNSTEIN'S Tables'), 1713 (HOGG, 'Proc. Amer. Acad.,' 40, 18, p. 611, 1905), 1733 (BREITENBACH, 'Ann. d. Phys.,' 5, 1901, p. 166), 1730 (SCHULTZE, 'Ann. d. Phys.,' 5, 1901, p. 140), 1736 (TÄNZLER, 'Verh. Deutsch. Phys. Gesell.,' 8, p. 221, 1906), and 1702 (GRINDLEY and GIBSON, 'Roy. Soc. Proc.,' A, 80, p. 114); the value of C is a mean of 119·4 (BREITENBACH), 113 (SUTHERLAND, 'Phil. Mag.,' February, 1909, p. 320), 111·3 (RAYLEIGH, 'Scientific Papers,' vol. iv., p. 452, p. 481), and 102·5 (GRINDLEY and GIBSON).

[2] μ_0 is the mean of 864 ('LANDOLT'S Tables'), 857·4 (BREITENBACH, *loc. cit.*), 841 (MARKOWSKI, 'Ann. d. Phys.,' 14, p. 742, 1904); C is the mean of 71·7 (BREITENBACH), 72·2 (RAYLEIGH, *loc. cit.*), 83 (MARKOWSKI, *loc. cit.*), 79 and 72 (SUTHERLAND, 'Phil. Mag.' (5), 36, p. 507, 1893, and February, 1909, p. 320).

[3] The mean of 1873 (LANDOLT) and 1926 (MARKOWSKI, *loc. cit.*); C from 128·2 (RAYLEIGH, 'Roy. Soc. Proc.,' 62, 1897; 66, 1900; 67, 1900), 138 (MARKOWSKI), 127 and 128 (SUTHERLAND, *loc. cit.*).

[4] GRAHAM and OBERMAYER (*cf.* MEYER'S 'Kinetic Theory') 1660, 1670, and MARKOWSKI, 1675; C from 115, 113 (MARKOWSKI), 109, 110 (SUTHERLAND, *loc. cit.*).

[5] μ_0 from JEANS' treatise, p. 251 (due to OBERMAYER); C from SUTHERLAND, *loc. cit.*

[6] BREITENBACH'S value of μ_0, and his and SUTHERLAND'S values of C (239, 258); both as previously cited.

[7] μ_0 from 'LANDOLT'S Tables'; C from SUTHERLAND, 'Phil. Mag.,' February, 1909, calculated from 'LANDOLT'S Tables.'

[8] μ_0 from 1891 (SCHULTZE, *loc. cit.*), 1887 (SCHIERLOH, 'Halle Diss.,' 1908, cited by SCHMITT, 'Ann. d. Phys.,' 30, 1909, p. 393), 1879 (RANKINE, 'Phil. Mag.,' January, 1911, p. 45); and C from 80·3 (SCHULTZE), 72·2 (RAYLEIGH), 78·2 (SCHIERLOH), 70 (RANKINE), 76 (SUTHERLAND, *loc. cit.*).

[9] μ_0 from 2104 (SCHULTZE, *loc. cit.*), 2114 (SCHIERLOH, *loc. cit.*), 2102 (RANKINE, *loc. cit.*); C from 169·9 174·6, 142 (by the preceding three authorities), and 160 (SUTHERLAND, *loc. cit.*).

[10] RANKINE (*loc. cit.*).

As we shall see, independent values of the radii of molecules may be obtained from the coefficient of diffusion, which we proceed to consider.

21. *The Coefficient of Diffusion.*

As the coefficient of diffusion of a gas into itself can be expressed much more simply than that of one gas into another, we will discuss it first, though it cannot be measured experimentally.

The expression obtained in Part I. was

$$D_{11} = \frac{3}{\nu}\left(\frac{\pi}{2}\right)^{1/2}(hm)^{-7/2}\frac{1}{P'_{11}}.$$

Since ν is proportional to the pressure, it follows that D_{11} varies inversely as the pressure, the other factors being functions of the temperature alone. If we substitute for P'_{11} from equations (45), (48), and (52), and eliminate the molecular constants by means of the expressions found in the preceding section for the corresponding values of μ, we get the following results:—

$$D_{11} = \tfrac{6}{5}\frac{\mu}{\rho} \qquad \text{(rigid elastic spheres)},$$

$$D_{11} = \tfrac{6}{5}\frac{\lambda''(n)}{\lambda'(n)}\left(3-\frac{2}{n-1}\right)\frac{\mu}{\rho} \qquad \text{(centres of force } Km^2r^{-n}\text{)},$$

$$D_{11} = \tfrac{6}{5}\frac{1+\tfrac{2}{3}\dfrac{C}{\theta}}{1+\dfrac{C}{\theta}}\frac{\mu}{\rho} \qquad \text{(attracting spheres)},$$

where in the last case C is the constant in SUTHERLAND's law of viscosity. All these formulæ agree in showing that D_{11} is a numerical multiple of μ/ρ, the factor generally being a function of the temperature, though with the first two hypotheses above, the factor is a constant. When, in the case of the second hypothesis, we take $n = 5$ (as MAXWELL did, the force being repulsive), the formula becomes

$$D_{11} = 1{\cdot}543\frac{\mu}{\rho} \qquad \text{(MAXWELL's fifth-power law)},$$

using the values already given for A_1 and A_2. The extension to general values of n is interesting, if only for the unobvious character of the factor $\left(3-\dfrac{2}{n-1}\right)$.

The best value of the numerical factor hitherto obtained, on the hypothesis that the molecules are elastic spheres, is due to JEANS (see his treatise, p. 273). After allowing for persistence of velocities, he deduces that 1·34 is its approximate value; this is in very fair agreement with $\frac{6}{5}$, the result of the present theory.

The expression obtained in Part I. for the coefficient of diffusion between two gases is

$$\tfrac{3}{16}\pi^{1/2}\left(\frac{m+m'}{hmm'}\right)^{7/2}\frac{1}{(\nu+\nu')\,\mathrm{P}'_{12}}.$$

Since

$$\frac{1}{\nu+\nu'}=\frac{\mathrm{R}\theta}{p+p'}=\frac{\mathrm{R}\theta}{p_t},$$

where p_t is the total pressure, and since ν and ν' do not occur elsewhere in the expression, it follows that, according to the present theory, the coefficient of diffusion is independent of the relative proportions of the gases in the mixture. On this point STEFAN and MAXWELL were at issue with MEYER,* whose theory predicted a large change in the coefficient of diffusion as the proportions of the gases were varied. Several experiments† have recently been made at Halle to test the rival theories. The pairs of gases taken were O–H, O–N, H–N, A–He, CO_2–H. The ratio of the components was varied from 1 : 3 to 3 : 1 (roughly), and the results showed systematic differences in the values of D_{12} which reached 8 per cent. in extreme cases. Though part of this variation may be due to experimental errors, it is undoubtedly the case that appreciable variations of D_{12} exist, or, at any rate, variations in the values of D_{12} as derived from the accepted theory of the experiments. This theory is of rather an elaborate nature, and takes no account of the boundary conditions; any attempt at a revision of the theory of diffusion should include an examination of the theory of the experiments by which the diffusion is measured; and it is by no means impossible that faults in the accepted theory of the experiment may account for the small variations of 5 per cent. or so in the determinations of D_{12}. At the same time it must be remembered that the value of D_{12} here arrived at theoretically is based on the assumption that the square of the velocity of diffusion, together with small deviations from MAXWELL'S law of distribution, are negligible. If these had been taken account of (and it is easy to do so) part or the whole of the outstanding discrepancy would probably be explained. As the variations are so small, however, I have not troubled to carry out these calculations.

The experiments emphatically disprove MEYER'S theory, which predicts changes of 20 per cent. or more in D_{12}, and there can be no doubt that the general principles of the theory as laid down by STEFAN and MAXWELL are much nearer the truth than those advocated by MEYER. A modification of MEYER'S theory by GROSS,‡ which reduced the amount of the variations predicted by MEYER, has also been shown to be incorrect, since the actual variations of D_{12}, though similar in amount to the theoretical values deduced by GROSS, are in the opposite direction.

---

* See his 'Kinetic Theory,' Chapter VIII.

† R. SCHMIDT, 'Halle Diss.,' 1904, and 'Ann. d. Phys.,' 14, 1904, p. 801; R. DEUTSCH, 'Halle Diss.,' 1907; JACKMANN, 'Halle Diss.,' 1906; and LONIUS, 'Halle Diss.,' 1909. All these results are summarized by LONIUS, 'Ann. d. Phys.,' 29, 1909, p. 664.

‡ G. GROSS, 'WIED. Ann.,' 40, p. 424, 1890

The special forms of the coefficient of diffusion, corresponding to the three molecular hypotheses considered in Part II., are as follows :—

$$D_{12} = \tfrac{3}{16}\sqrt{\frac{2}{\pi}}\,\frac{1}{(\sigma+\sigma')^2}\left(\frac{1}{w}+\frac{1}{w'}\right)^{1/2}\left(\frac{p_0}{\rho_0}\right)^{1/2}\frac{1}{\nu_0}\,\frac{p_0}{p}\left(\frac{\theta}{\theta_0}\right)^{3/2} \qquad \begin{pmatrix}\text{rigid elastic}\\ \text{spheres}\end{pmatrix},$$

$$D_{12} = \frac{3\pi^{1/2}}{8}\,\frac{1}{K'_{12}\lambda'(n)\,\Gamma\left(3-\dfrac{2}{n-1}\right)}\left\{\left(\frac{1}{w}+\frac{1}{w'}\right)\frac{2p_0}{\rho_0}\,\frac{\theta}{\theta_0}\right\}^{\frac{n+3}{2(n-1)}}\frac{p_0}{p}\cdot\frac{\theta}{\theta_0}\cdot\frac{1}{\nu_0} \qquad \begin{pmatrix}\text{centres}\\ \text{of force}\end{pmatrix},$$

$$D_{12} = \tfrac{3}{16}\sqrt{\frac{2}{\pi}}\,\frac{1}{(\sigma+\sigma')^2}\left(\frac{1}{w}+\frac{1}{w'}\right)^{1/2}\left(\frac{p_0}{\rho_0}\right)^{1/2}\frac{1}{\nu_0}\,\frac{p_0}{p}\left(\frac{\theta}{\theta_0}\right)^{3/2}\frac{1}{1+C_{12}/\theta} \qquad \begin{pmatrix}\text{attracting}\\ \text{spheres}\end{pmatrix},$$

where after substitution from equations (45), (48), and (52) we have put the formulæ into a more convenient form as above; w and w' are, as before, the specific gravities relative to a standard gas whose density at pressure p_0 and temperature θ_0 is ρ_0; ν_0 is AVOGADRO'S constant, at the same pressure and temperature. It may be noticed that MAXWELL,* by applying the methods of his fifth-power-law theory to the case of a gas whose molecules were elastic spheres, obtained an expression $\frac{4}{3}$ times as great as (but in other respects identical with) the first of the equations just given; as he did not give any details, it is impossible to say how his error arose—probably by a numerical slip.

The following equations simply express the law of variation of D_{12} with temperature, as shown by the above three equations :—

$$D_{12}/(D_{12})_0 = (\theta/\theta_0)^{3/2} \qquad \text{(rigid elastic spheres)},$$

$$D_{12}/(D_{12})_0 = (\theta/\theta_0)^{\frac{n+3}{2(n-1)}+1} \qquad \text{(point-centres of force)},$$

$$D_{12}/(D_{12})_0 = (\theta/\theta_0)^{3/2}\,\{1+C_{12}/\theta_0\}/\{1+C_{12}/\theta\} \qquad \text{(attracting spheres)}.$$

So far as I am aware, the variation of the coefficient of diffusion with the temperature has never been properly examined experimentally; the values of D_{12} are generally found only at one temperature, or two at most, and this is insufficient to decide between the second and third of the laws just given. From the analogous behaviour of viscosity, as affected by temperature, however, the third law is probably most nearly true, and the values of C_{12} have been worked out by SUTHERLAND on this hypothesis.† In view of the importance of the constant C_{12}, it is desirable that further experiments be made on the variation of the coefficient of diffusion with temperature.

---

* 'Nature,' vol. viii.; 'Scientific Papers,' vol. ii., p. 343.

† The present theory shows that C_{12}, the temperature constant for diffusion, is a different multiple of the mutual potential of two molecules in contact from that in the case of C_{11}, the temperature constant for viscosity. This fact was not indicated in SUTHERLAND'S investigation; see 'Phil. Mag.' (5), 38, p. 1, 1894.

As in the case of the coefficient of viscosity, we proceed to give the values of the molecular radii (according to the two theories of elastic spherical molecules, with and without attraction) calculated from the coefficient of diffusion. From the latter we get $\sigma+\sigma'$, the sum of the radii of molecules of each kind considered. By taking three pairs of the same three gases, like O–H, N–H, H–N, we can derive the actual values of σ in each case, which may then be compared with the values obtained from the coefficient of viscosity. I have thought it preferable, however, to compare the values of $\sigma+\sigma'$ obtained from diffusion with the sums $\sigma+\sigma'$ of the values obtained from viscosity (on the corresponding molecular hypothesis). The values of the coefficient of diffusion (which are in C.G.S. units, and for the temperature 0° C.) are taken from the Smithsonian tables (1910 edition); they are uncertain (partly for reasons already discussed, partly for other reasons) to within about 5 per cent.; different authorities give values differing by from 5 per cent. to 10 per cent.; I have taken the mean, where two values are given in the table cited. The constants C_{12} are taken from a table given by SUTHERLAND*; as they depend only on two values of D_{12}, and as C occurs in such a form as to be largely affected by experimental errors, these values are not well determined, though they are probably the best available. In several cases I have not been able to find the value of C.

Gases undergoing diffusion.	Coefficient of diffusion.	Temperature coefficient, C_{12}.	$(\sigma+\sigma')\times 10^8$.			
			Elastic-sphere theory.		Attracting-sphere theory.	
			From diffusion.	From viscosity.	From diffusion.	From viscosity.
Air–hydrogen	0·661	74·5	2·99	3·16	2·65	2·62
Air–oxygen	0·1775	—	3·42	3·61	—	—
Carbon dioxide–air	0·138	250	3·73	4·09	2·70	3·18
Carbon dioxide–carbon monoxide	0·136	—	3·79	4·13	—	—
Carbon dioxide–nitrous oxide	0·0983	380	4·19	4·53	2·71	3·42
Carbon dioxide–oxygen	0·1802	187	3·23	4·04	2·49	3·10
Carbon monoxide–ethylene	0·101	—	4·61	4·26	—	—
Carbon monoxide–hydrogen	0·642	70	3·03	3·20	2·70	2·57
Carbon monoxide–oxygen	0·183	113	3·38	3·63	2·84	2·96
Hydrogen–carbon dioxide	0·538	115	3·29	3·59	2·76	2·72
Hydrogen–ethylene	0·486	—	3·48	3·72	—	—
Hydrogen–nitrous oxide	0·535	—	3·30	3·60	—	—
Hydrogen–oxygen	0·679	100	2·94	3·11	2·52	2·55
Nitrogen–oxygen	0·174	117	3·47	3·62	2·87	3·02
Argon–helium†	0·650	—	2·53	2·85	—	—

Considering the possibility of occasional exceptionally large errors due to the

---

* 'Phil. Mag.,' 1895, 40, p. 421; 1894, 38, p. 1.

† R. SCHMIDT, 'Ann. d. Phys.,' 14, 1904, p. 801.

number of experimental data entering into each of the above determinations of molecular radii, the agreement shown is very good. It is notably better on the hypothesis that the molecules attract one another than on the ordinary elastic sphere theory (the large discrepancy in the case of CO_2–N_2O is probably due to the value of C_{12}, which is larger than the value of C_{11} for either gas, and this is somewhat improbable). In the case of the latter theory the value of $\sigma+\sigma'$ determined directly from diffusion is in almost every case less than that obtained from separate observations of viscosity; there is a slight tendency for the same thing to show itself with the values deduced from the other theory. This is probably to be attributed to the artificial nature of our hypotheses; the effective distance of reversal of motion between two different molecules may not really be half the sum of the effective distances for two pairs of like molecules, though the rigid sphere hypotheses assume this. The third hypothesis we have considered does not do so; but a comparison of diffusion and viscosity on this hypothesis would only give us the relation between the force constants between the molecules of one kind and different molecules, while the interesting question is the one we have just tested, viz., how nearly alike will a molecule behave towards another of the same kind, and towards one of a different kind.

The following table* may be of interest, showing how the values of σ obtained from VAN DER WAALS' law agree with those obtained from viscosity (on the attracting sphere theory):—

Gas.	$\sigma \times 10^8$ (VAN DER WAALS' theory).	$\sigma \times 10^8$ (attracting sphere theory).
Hydrogen	1·15	1·18
Nitrogen	1·76	1·55
Air	1·64	1·54
Carbon dioxide	1·70	1·49
Helium	1·16	0·94
Argon	1·43	1·51
Krypton	1·56	1·32
Xenon	1·71	1·74

22. *The Variation of the Viscosity of Mixed Gases with Temperature.*

This question was deferred till after the similar questions regarding the viscosity of simple gases, and diffusion, had been discussed. The formula we obtained for μ_{12}

---

* The values of σ for the first four gases are calculated from values of b (in VAN DER WAALS' equation) given by JEANS ('Dynamical Theory of Gases,' p. 141) from the experiments of VAN DER WAALS and ROSE INNES; but the value of ν has been taken as $2\cdot77\times10^{19}$ instead of $4\cdot0\times10^{19}$, as used by JEANS. The values of b for the last four gases are taken from a paper by RUDORF, 'Phil. Mag.,' June, 1909, p. 795.

was

$$\frac{\left(1+k\dfrac{w}{w'}\right)p^2+\left\{2\left(1-k\right)+\mathrm{G}\left(\dfrac{1}{\mu}+\dfrac{1}{\mu'}\right)\right\}pp'+\left(1+k\dfrac{w'}{w}\right)p'^2}{\dfrac{1}{\mu}\left(1+k\dfrac{w}{w'}\right)p^2+\left\{\dfrac{(w+w')^2}{ww'}k\mathrm{G}+\dfrac{1}{\mathrm{G}\mu\mu'}\right\}pp'+\dfrac{1}{\mu'}\left(1+k\dfrac{w'}{w}\right)p'^2},$$

where

$$\mathrm{G}=\frac{2}{w+w'}\frac{1}{\rho_0\mathrm{D}_{12}}.$$

We have already seen that, on the elastic sphere hypothesis, and the point centre of force ($\mathrm{K}_{12}mm'r^{-n}$) hypothesis,

$$\mathrm{D}_{12}\propto\theta^{s+1},\qquad\mu\propto\theta^s,\qquad\mu'\propto\theta^s,$$

where $s=\frac{1}{2}$ in the former case, and varies with n in the latter case. Hence

$$\rho_0\mathrm{D}_{12}\propto\theta^s,$$

so that G, $1/\mu$, and $1/\mu'$ all vary with the temperature in the same way (we are supposing that the value of n is the same for both kinds of molecules). Moreover, we have seen in Part II. that k is independent of the temperature in these hypotheses. Hence the numerator of the above fraction is independent of θ, while the denominator varies as θ^{-s}. In other words, the coefficient of viscosity of the mixed gas behaves in exactly the same way as that of the component gases, as the temperature varies.

The case is rather different on the attracting sphere hypothesis; remembering the expressions already found for k and μ and D_{12} it may easily be seen that

$$\mu_{12}=\mathrm{A}\theta^{3/2}\frac{\mathrm{B}+\mathrm{C}\theta}{\mathrm{D}+\mathrm{E}\theta+\mathrm{F}\theta^2}$$

where for any given mixture A, B, C, D, E, F are independent of the temperature. Over a limited range of θ it is possible to find a constant K such that

$$\frac{\mathrm{B}+\mathrm{C}\theta}{\mathrm{D}+\mathrm{E}\theta+\mathrm{F}\theta^2}-\frac{\mathrm{A}'}{\mathrm{K}+\theta}$$

is extremely small, so that we may write

$$\mu_{12}=\frac{\mathrm{A}_1\theta^{1/2}}{1+\mathrm{K}/\theta}$$

showing that according to the attracting-sphere theory SUTHERLAND'S formula holds for mixtures as well as for simple gases—indeed, the formula has been more often tested for air than for any simple gas. SCHMITT[*] and others have shown that experimental results fully bear out this conclusion.[†]

[*] 'Ann. d. Phys.,' 30, p. 393, 1909; TÄNZLER ('Verh. Deutsch. Phys. Ges.,' 8, 12, p. 122, 1906).

[†] THIESEN ('Verh. Deutsch. Phys. Ges.,' 8, 12, p. 236, 1906) states that SUTHERLAND'S formula and his own law (see § 18 of this paper) are incompatible, although TÄNZLER'S experiments demonstrate the contrary.

Note added February 15, 1912.

Later investigation shows that the neglect of the terms of higher degree than the third, in the expression for the function F (p. 441), is not easily justifiable by rigorous analysis. The omitted terms have been considered by ENSKOG ('Phys. Zeitschrift,' xii., 58, 1911); his work suffices to show that the formulæ in this paper are correct except as regards a factor which in general is a function of the temperature (only), and in particular cases is a numerical constant. The latter cases include the case of elastic spherical molecules (as pointed out by ENSKOG), and also of point centres of force varying inversely as the n^{th} power of the distance. Thus Lord RAYLEIGH'S theorem (p. 474) can be rigorously established.

I have endeavoured to form a numerical estimate of the correction factors to be applied to the formulæ, but the analytical difficulties involved have thus far proved unsurmountable. The expressions obtained do not converge rapidly, and the calculations are very laborious; but the problem is now perfectly definite, and improved analysis may remove the difficulties.

The present theory must therefore be regarded as approximate only. In conjunction with ENSKOG'S work, however, it provides rigorous proofs of the relations connecting viscosity and conductivity with the pressure and molecular diameter and mass, and in special cases also with temperature; the relations themselves are well known in the case of simple gases, but not in that of compound gases. The numerical constants are not rigorously determined, and are subject to correction; but the agreement with experiment seems to show that the approximation is a good one.

Lastly, it should be remarked that the theory of diffusion is unaffected by the terms omitted, so that the above statements do not apply to it.