

XIII. CONTRIBUTIONS TO THE THEORY OF TRANSPIRATION, DIFFUSION AND THERMAL CONDUCTION IN RARIFIED GASES.

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I.

The phenomena of viscosity and of thermal transpiration in rarified gases, which had aroused general interest thirty years ago and which partly had inspired Maxwell¹⁾ for his famous paper „On Stresses in Rarified Gases“, have been entirely neglected since that time, although there remained enough to be done; only recently some important researches on this subject have been published by Mr. Knudsen²⁾, advancing our knowledge to the range of lowest pressures, hitherto not investigated so exactly. Without entering in a discussion of the experimental part of these researches, I should like to offer here some theoretical remarks, as the theoretical treatment of the problem in Mr. Knudsen's papers, although rather elaborate, seems to me to lack clearness and rigour. The method employed by him is the method used by Maxwell in his first researches, by Clausius, O. E. Meyer and many others; it is based on the assumption of molecules acting like elastic spheres, on the notion of the mean length of free path and on the assumption that Maxwell's law of distribution of velocities can be applied in its ordinary form.

It is well known, however³⁾, that all such calculations, as far

as viscosity, thermal conductivity and diffusion are concerned, are defective. Maxwell and Boltzmann have shown that the law of distribution of velocities is modified when these phenomena occur and that the neglect of this factor, as involved in such calculations, implies errors of the same order of magnitude as the final results. No one has succeeded hitherto in carrying out such calculations, on the elastic sphere hypothesis, in a tolerably correct manner¹⁾; in the present state of knowledge, the best we can do is to follow Maxwell's method explained in his later papers (especially the one referred to above) where, availing himself of the celebrated inverse fifth-power hypothesis, he is able (in a comparatively easy manner) to take account of the altered form of the law of distribution. Experimental evidence shows that the molecules of a gas are something intermediate between what is assumed in both theories, but Maxwell's assumption has the advantage that a theory can be built on its foundation which is free from inherent contradiction.

I do not desire to go so far as to deny any value to calculations based on the old defective method, provided they are considered only as heuristic means for deriving empirical formulae; and provided one does not expect to find quantitative agreement between calculation and experimental results. The objections to some of Mr. Knudsen's calculations, in his second paper, relative to thermal transpiration, are of a more serious character, since the reasoning is based there on a foundation which is the very point of failure of the old method.

The author imagines a gas contained in a tube whose temperature varies in the direction from one end to the other in linear progression. He evaluates the quantity of tangential momentum communicated to the wall by the molecular impacts, assuming as usually equal probability of molecular motion in every direction; he finds it to be different from zero, as the molecules coming from the hotter parts carry with them greater momentum; whence the conclusion is drawn that the gas must exercise a tangential pressure on the wall, or it must have an inverse tangential motion to

¹⁾ Except for diffusion, where exact general formulae have been given by Langevin: C. R. 140, 35, 1905; Ann. chim. phys. 5, 245, 1905. An interesting, although insufficient, attempt at settling the difficulty has been made by Jeans: Phil. Mag. 8, 670, 1904.

²⁾ Maxwell, Scientific Papers II, p. 681; Phil. Trans. 170, 231, 1879.

³⁾ Knudsen, Ann. d. Phys. 28, 75, 1909; 31, 205, 633, 1910.

⁴⁾ Boltzmann, Wien. Sitzgsber., 81, 117, 1880; 84, 40, 1230, 1881.

begin with. Now, an analogous calculation would show the momentum carried through any cross section of the gas to be different from zero (to be proportional to

$$Nm\lambda\Omega\frac{d\Omega}{dl},$$

in Mr. Knudsen's notation), which in the same way would prove the existence of a gradient of pressure along the axis of the tube, quite independent of its radius and of the density of the gas. Here we perceive the fallacy of the method. This is the point which is emphasized in Kirchhoff's *Lectures on Heat* p. 210 and in Boltzmann's *Gastheorie* I, pp. 93—97: if for a gas with linear slope of temperature the change in the law of distribution of velocities is neglected, either the pressure comes out unequal or the gas cannot be at rest. By following Maxwell's (loc. cit.) and Boltzmann's method (*Gastheorie* I, p. 185) one can indeed show easily that the ordinary form of the law of distribution of velocities is changed in this case and becomes

$$(1) f(\xi, \eta, \zeta) d\xi d\eta d\zeta = Ae^{-N(\xi^2 + \eta^2 + \zeta^2)} [1 + a\xi + b\xi(\xi^2 + \eta^2 + \zeta^2)] d\xi d\eta d\zeta$$

where the coefficient a can be chosen so as to make the motion in the direction of X disappear, while the coefficient b is connected with the gradient of temperature and accordingly with the conduction of heat. Hence the normal pressure or momentum carried through any plane:

$$p = m \int \xi^2 f d\xi d\eta d\zeta = m \int \eta^2 f d\xi d\eta d\zeta = m \int \zeta^2 f d\xi d\eta d\zeta$$

is found to be equal everywhere and identical with the constant gas pressure.

According to Maxwell, stresses in the interior of a gas exist only in the case when the gradient of temperature is not constant; in the case above considered there must also exist a tangential current along the surface of the wall of the tube, but it is caused only by the fact that such a wall acts like an incompletely reflecting mirror. As Maxwell puts it, the fraction $(1-f)$ of the incident molecules is reflected with unchanged velocity (reversed normal component only), while the fraction f is absorbed by the

wall and emitted again in accordance with the normal law of distribution. Thus the partial restoration of the ordinary law of distribution, instead of (1), at the surface is the real cause of the tangential current along the wall.

Knudsen appears not to have been acquainted with Maxwell's and Reynolds' researches when he published his first two papers; his hypothesis, however, as to the nature of the wall is quite analogous to that of Maxwell, except that he puts a priori $f=1$, which seems to be nearly true, but is perhaps an unnecessary limitation of generality. For the rest, the result obtained by him, concerning the gradient of pressure produced in a capillary tube by thermal surface currents, happens to be of the right order of magnitude; nevertheless, as has been said, we cannot consider the demonstration satisfactory. Hitherto only Maxwell's formula (77), loc. cit., connecting the effects of slipping and of thermal transpiration, can be accepted as established in a satisfactory manner; even this formula probably is not quite exact, as it rests on simplifying suppositions as to the behaviour of the gaseous surface layer. It certainly does not hold for high rarefactions, where other laws apply which will be explained later.

I may be allowed to insert here some remarks relating to a necessary consequence of these phenomena, viz. the increase of heat transferring power of gases, as produced by the molecular surface currents. The question arises whether any observable effects may possibly result from that source. In order to get an approximate idea of the order of magnitude of this effect, let us consider a gas contained between two infinite parallel plates whose distance be l and whose temperature varies in linear progression with y . Then if the axis X is normal to the plates, the surface effects are defined according to Maxwell's formula (68) by the equation:

$$(2) \quad v - G \frac{\partial v}{\partial x} = \frac{2}{3} \frac{\mu}{\rho \theta} \frac{\partial \theta}{\partial y} - \frac{2}{3} G \frac{\mu}{\rho \theta} \frac{\partial^2 \theta}{\partial y \partial x}$$

where v is the velocity of the gas in the direction of Y , μ denotes the coefficient of viscosity and G the coefficient of slipping:

$$(3) \quad G = \frac{\mu}{2} \sqrt{\frac{2\pi}{p\theta}} (2 - f).$$

For the interior of the gas we have the approximate hydrodynamical equation:

$$(4) \quad \frac{\partial p}{\partial y} = \mu \frac{\partial^2 v}{\partial x^2}$$

and the condition of thermal equilibrium is:

$$(5) \quad \kappa \left(\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} \right) + v \rho s \frac{\partial \theta}{\partial y} = 0$$

where κ denotes the conductivity, s the specific heat. Equation (4) and the surface conditions (2) for both plates are fulfilled if we take

$$(6) \quad v = \varepsilon + \frac{\partial p}{\partial y} \frac{x^2 - lx - lG}{2\mu}$$

where ε denotes the right hand member of equation (2).

If the space occupied by the gas is closed, the quantity passing through a cross section

$$\int_0^l v dx$$

must be zero, whence:

$$(7) \quad \frac{\partial p}{\partial y} = \frac{12\varepsilon\mu}{l^2 + 6lG}$$

In order to obtain an approximate solution of (5), let us suppose the dimensions of the space in the direction of the axis Y to be large in comparison with the X dimensions, so that the temperature can be taken as:

$$\theta = \alpha y + \varphi(x),$$

where α is constant and φ will be found by means of (5). We thus get:

$$(8) \quad \theta = \alpha y + \frac{A}{2} \frac{x^4 - 2lx^3 + l^2x^2}{l^2 + 6lG}$$

if we denote by A the quantity $\rho s \varepsilon \alpha / \kappa$. Now the total quantity of heat carried by the molecular convective currents is

$$\rho s \int_0^l v \theta dx,$$

whereas the quantity transmitted by conduction is

$$l \kappa \frac{\partial \theta}{\partial y}.$$

The evaluation of the integral shows that the molecular currents increase the heat transmission by a fraction amounting to

$$(9) \quad \frac{1}{1120} \left(\frac{l}{\theta} \frac{\partial \theta}{\partial y} \right)^2 \left(\frac{l}{l + 6G} \right)^2.$$

We see this effect is also present at high pressures and in wide vessels, whereas the other stress effects as a rule are vanishing except at low pressures and in capillary tubes; its amount however must be very small under ordinary circumstances and to demonstrate experimentally its existence will not be an easy task.

As mentioned before, Maxwell's calculation cannot be applied in the case of great rarefaction, when the mean free path is comparable with the diameter of the tube, since it involves the supposition that the state of the gas does not change appreciably in such lengths. In this case the degree of approximation to which we have gone in accounting for the behaviour of the surface layer of the gas is not sufficient; our calculations would require profound modifications which we will not endeavour to effect. Mr. Knudsen's calculations of course are far from applying exactly to this case; they necessitate the introduction of rough approximations and of empirical assumptions.

II.

Things are getting again plain and intelligible when the rarefaction is so great that the bore of the tube can be considered small compared with the mean free path; in this case the influence of the mutual encounters of the molecules can be altogether neglected in comparison with the impacts on the walls of the tube, and a simple law of distribution prevails. The state of the gas in this case is analogous to radiation in a closed vessel. This case which for the first time has been treated theoretically by Osborne Reynolds, has been investigated in detail by Mr. Knudsen and has been called by him „Molekularströmung“, as contrasted with the „innere Reibungsströmung“, going on at higher pressures. It will be analysed more fully in what follows, by use of a simpler and more exact analysis which will lead to similar but somewhat modified results.

Let us consider the case of ordinary transpiration through a tube of any form of cross section, at uniform temperature; let us

first admit with Knudsen that $f = 1$, or that the walls act as completely diffuse reflectors. Then a surface element dS' of the wall of the tube will emit a quantity of incident molecules equal to $\nu dS'$, as if they were entering through an aperture dS' from an outer space filled with gas in a state of rest and thermal equilibrium.

Thus, as Knudsen rightly observes, the quantity

$$\frac{\nu}{\pi} \cos(nr) dS' d\omega$$

will be emitted in the solid angle $d\omega$, in strict analogy with Lambert's Cosine-Law. The number of impacts ν is connected with the number n of molecules in unit volume of the fictitious gas by the known relation:

$$(10) \quad \nu = \int_0^\infty \xi d\xi \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f d\eta d\zeta = \frac{nc}{\sqrt{6\pi}}$$

where f is Maxwell's probability function

$$f = n \left(\frac{h}{\pi} \right)^{3/2} e^{-h^2(\xi^2 + \eta^2 + \zeta^2)}$$

and c is the square root of the mean square of velocities.

If the density of the gas is increasing (towards the right hand side) along the axis of the tube, which henceforth will be supposed to be the X axis, then the quantity ν will be variable and we shall obtain the number of molecules passing from the right to the left, through an element dS , by forming the integral

$$(11) \quad I = \frac{1}{\pi} dS \int \frac{\nu(x') \cos(n'r) \cos(nr)}{r^2} dS'$$

where r is the radius vector between the elements dS and dS' , x' its component along the axis, (nr) and $(n'r)$ the angles between the radius vector and the normals to these elements.

Now we have evidently

$$\frac{\cos(n'r)}{r^2} dS' = d\omega$$

where $d\omega$ is the solid angle under which dS' is seen from the point dS . This can be put equal to $\sin \varphi d\varphi d\varepsilon$, if φ is the angle

designed before by (nr) and ε the angle between two planes laid through the normal to dS , a fixed one and a variable one, containing r . Thus we have, expanding $\nu(x')$:

$$(12) \quad I = \frac{dS}{\pi} \int_0^{\pi/2} \int_0^{2\pi} \sin \varphi \cos \varphi \left[\nu(x) + x' \frac{\partial \nu}{\partial x} + \frac{x'^2}{2} \frac{\partial^2 \nu}{\partial x^2} + \dots \right] d\varphi d\varepsilon = \\ = dS \left[\nu(x) + \frac{1}{\pi} \int_0^{\pi/2} \int_0^{2\pi} \sin \varphi \cos \varphi d\varphi d\varepsilon \cdot x' \frac{\partial \nu}{\partial x} + \dots \right].$$

This expression may be used, first, to find the condition which obtains for a steady state. In this case the number of molecules impinging on an element of the wall must be equal to the number of emitted molecules. Therefore, if we identify dS with an element of surface of the wall, we must have

$$I = \nu(x) dS$$

for any value of x , which evidently will be fulfilled if ν is a linear function of x , as the integral referring to $\frac{\partial \nu}{\partial x}$, containing equal positive and negative values of x' , must vanish. Thus we see that the density and the pressure in the stationary state must be linear functions of x .

By means of formula (12) let us calculate now the number of molecules which are passing through an element of the cross-section, from right to left. Then φ is the angle between r and X and we have $x' = R \cos \varphi$ if R is the projection of r on the plane of the cross section; thus (12) reduces to

$$(13) \quad I = dS \left[\nu(x) + \frac{1}{\pi} \frac{\partial \nu}{\partial x} \int_0^{\pi/2} \int_0^{2\pi} R \cos^2 \varphi d\varphi d\varepsilon \right]$$

where the integration of $\cos^2 \varphi d\varphi$ can be effected. A corresponding quantity with negative sign for $\frac{\partial \nu}{\partial x}$ is to be taken for the molecules crossing from left to right and the resultant flux of molecules passing from right to left will be:

$$q = \frac{1}{2} dS \frac{\partial \nu}{\partial x} \int_0^{2\pi} R d\varepsilon.$$

The mass of gas passing through the whole cross section is by use of (10)

$$(14) \quad Q = \frac{m}{2} \frac{\partial v}{\partial x} \int \int dS \int R d\epsilon = \\ = \frac{c}{2\sqrt{6}\pi} \frac{\partial q}{\partial x} A = \frac{1}{2\sqrt{2}\pi} \sqrt{\frac{p_0}{p_0}} \frac{p_2 - p_1}{L} A$$

where A is an abbreviation for the triple integral and p_1, p_2 denote the pressures at the ends of the tube.

In order to evaluate A , let us first suppose a tube with circular bore, of radius a . Then A (which is the mean distance between the

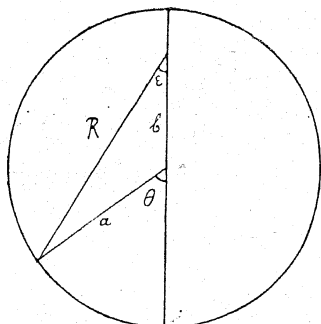


Fig. 1.

point dS and the periphery, multiplied by 2π) is easily transformed [see fig. (1)] into

$$A = a \int \int dS \int_0^{2\pi} \frac{a + b \cos \theta}{\sqrt{a^2 + b^2 + 2ab \cos \theta}} d\theta.$$

We see that, contrarily to Knudsen's opinion, the molecular current has different intensities in different points of the cross section. The greatest value

$$q = a\pi \frac{\partial v}{\partial x}$$

corresponds to the middle (for $b = 0$), the smallest value

$$q = 2a \frac{\partial v}{\partial x}$$

to the surface of the wall (for $b = a$). The integral could be reduced to elliptic integrals, but if we only wish to know the whole flux Q , we better transform it by considering that $R d\epsilon$ (in the general case of any form of cross section) can be put

$$R d\epsilon = ds \cos(nR)$$

where ds is an element of the periphery. Now we may divide the cross section into triangular sectors, corresponding to infinitesimal increments of the angle (nR) which may be called α for brevity. Their area will be $dS = \frac{1}{2} R^2 d\alpha$, if R now denotes the whole length of the chord belonging to the angle α . Thus we get

$$(15) \quad A = \frac{1}{2} \int ds \int_{-\pi/2}^{+\pi/2} R^2 \cos \alpha d\alpha.$$

By applying this expression to the circle we get

$$(16) \quad A = a\pi \int_{-\pi/2}^{+\pi/2} 4a^2 \cos^3 \alpha d\alpha = \frac{16a^3\pi}{3}$$

and the whole mass streaming through a circular tube is:

$$(17) \quad Q = \frac{4\sqrt{2}\pi}{3} a^3 \sqrt{\frac{p_0}{p_0}} \frac{p_2 - p_1}{L}.$$

In the general case, when the surface element of the wall dS' is partially reflecting, partially absorbing and radiating, it will emit only $f\nu dS'$ molecules in the manner above described; the rest, $(1-f)\nu dS'$, are molecules that have been reflected at the point dS' and in reality are coming from a greater distance. The fraction f of them have been radiated from the point of intersection of the wall with the reflected direction of the ray r , the rest originates at still greater distance. By combining them with the corresponding molecules which approach the element dS from the other side, we easily see that molecules having undergone one reflection contribute to the flux Q three times as much as those molecules that have undergone no reflection; indeed the distance (in x) of the corresponding points of emission is three times as great. Molecules which

were twice reflected act five times as intensively. Adding them all we get, if we denote by Q_0 the amount calculated before (17)

$$Q = f[1 + 3(1-f) + 5(1-f)^2 + \dots] Q_0.$$

The value of this expression is found by putting $1-f=\delta$:

$$Q = \frac{1+\delta}{1-\delta} Q_0 = \frac{2-f}{f} Q_0$$

and we have finally:

$$(18) \quad Q = \frac{2-f}{f} \frac{4\sqrt{2\pi}}{3} a^3 \sqrt{\frac{p_0}{p_0}} \frac{p_2 - p_1}{L}.$$

It is satisfactory to learn that Knudsen's formula, found by him to be in good agreement with experiments, is identical with (17), but both his methods of demonstrating it (loc. cit., pp. 105—114) seem to me rather misleading¹⁾.

The difference in the general result (14) and (15) and Knudsen's formula p. 108 appears when we calculate Q for tubes of other forms of cross section. For a rectangle with sides α, β we get:

$$(19) \quad A = 2 \left[\alpha^2 \beta \log \left(\frac{\beta}{\alpha} + \sqrt{1 + \left(\frac{\beta}{\alpha} \right)^2} \right) + \alpha \beta^2 \log \left(\frac{\alpha}{\beta} + \sqrt{1 + \left(\frac{\alpha}{\beta} \right)^2} \right) - \frac{(\alpha^2 + \beta^2)^{3/2}}{3} + \frac{\alpha^3 + \beta^3}{3} \right]$$

which for a quadratic cross section takes the simpler form:

$$(20) \quad A = 4\alpha^3 \left[\log(1 + \sqrt{2}) + \frac{1 - \sqrt{2}}{3} \right] = 2.973 \alpha^3$$

whereas according to Knudsen we should have

$$Q = \frac{\alpha^3}{3} \sqrt{\frac{8}{\pi}} \sqrt{\frac{p_0}{p_0}} \frac{p_2 - p_1}{L}$$

which corresponds to a value $A = \frac{8}{3} \alpha^3$.

¹⁾ Thus for instance the momentum parallel to X carried through unit surface of the plane XZ by a gas which is streaming with velocity v in the direction X , is not the quantity B calculated p. 106, but: $\frac{1}{2} n m v \Omega$. On the other hand, the stream velocity v is not the same in all points of the cross section and Maxwell's law is true for the emitted molecules, but not for the incident ones.

Knudsen's result, implying inverse proportionality of Q to the circumference for a given area of cross section, appears *a priori* improbable since in this case Q could be indefinitely diminished by cutting narrow radial gaps in infinite number in the walls of the tube.

It is worth noticing that the velocities of the molecules in a given element of volume are not distributed according to Maxwell's law. The probability of velocities ξ, η, ζ at the point x, y, z is defined by the value of the density function $\nu(x')$, where x' is the distance (along the axis X) of the point of intersection between the direction $-\xi, -\eta, -\zeta$ and the wall of the tube. We have:

$$\frac{y' - y}{\eta} = \frac{z' - z}{\zeta} = \frac{x'}{\xi}$$

and in the case of a circular tube: $y'^2 + z'^2 = a^2$, wherefrom we find x' ; thus the probability of ξ, η, ζ is proportional to:

$$(21) \quad e^{-N(\xi^2 + \eta^2 + \zeta^2)} \left[\nu(x) - \left(\frac{\partial \nu}{\partial x} \right) \frac{\xi \eta y + \xi \zeta z}{\eta^2 + \zeta^2} + \right. \\ \left. + \sqrt{(a^2 - y^2 - z^2)} \frac{\xi^2}{\eta^2 + \zeta^2} + \left[\frac{\xi \eta y + \xi \zeta z}{\eta^2 + \zeta^2} \right]^2 \right]$$

where $\left(\frac{\partial \nu}{\partial x} \right)$ is constant. We satisfy ourselves easily that this fulfills the well-known Maxwell-Boltzmann condition for a stationary state:

$$(22) \quad \xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} = \int \int (ff' - f_1 f'_1) g b db d\epsilon$$

when we neglect the integral accounting for the influence of the mutual encounters, as we are entitled to do in our case.

The law expressed by (14) can easily be generalized for a vessel of any form, provided its dimensions are small in comparison with the mean free path. In this case, the only distinctive quality of different kinds of molecules being their mass, the method of dynamical similarity can be applied which easily shows that the volume passing through the vessel, for given values of the pressure at both ends, must be inversely proportional to the square root of the molecular weight of the gas and directly proportional to the square

root of the temperature. The process is thus quite analogous to that of effusion through a small hole, as has been demonstrated long ago by Graham's and Osborne Reynolds' experiments on diffusion of gases through porous materials which proved the validity of that density relation for porous bodies of sufficiently fine texture.

Besides, as mutual encounters are neglected, every constituent in a mixture of gases must move quite independently of the others; this gives rise to the phenomenon of „atmolysis“ (Graham, Christiansen). Thus we see that the phenomena of interdiffusion of gases are completely changed when the conditions of the present case are fulfilled. At higher pressures the process of mutual diffusion of gases must also be modified in the neighbourhood of the walls of the vessel, namely by the friction against the wall, and there must exist a surface effect, analogous to the discontinuity of temperature in conduction of heat, but its theory is much more complicated and its experimental demonstration, like all experiments on diffusion, will offer greater difficulties.

Let us consider now the case when the temperature of the walls of the tube is varying with x . By the same reasoning as before, we again get the formula:

$$Q = \frac{m}{2} \frac{\partial \nu}{\partial x} A.$$

If the tube is closed at both ends, or if in any way the passage of the gas is prevented, we have $Q = 0$ and $\nu = \text{const.}$, which implies according to (10) that the pressure increases towards the hotter end, in proportion of the square root of the temperature. This relation is characteristic of thermal transpiration at low pressures in narrow channels, while in the other extreme case, when the diameter of the channel is large compared with the free path, Maxwell's formula (77) or a relation of similar form must be applied. The same result has been deduced in a different way by Knudsen on pp. 222—223, and has been verified to some degree of approximation by his experiments; on a larger scale it has been confirmed by O. Reynolds' researches on thermal transpiration through Meerscham-plates etc., in 1879. In such porous materials, of course, the channels cannot be considered to be cylindrical tubes; but if the analogy of the behaviour of a rarified gas with the phe-

nomenon of radiation is considered, the above result can easily be generalized so as to apply to a vessel of any form. In a closed vessel of any shape, radiation is known to be in thermal equilibrium when the density of incident (or emitted) radiation is everywhere the same. In our case the quantity of incident radiation corresponds to the number of incident molecules per unit time and unit surface, emitted radiation to the emitted molecules which, if the walls allow no passage, are both identical with ν . The condition of stationary state requires therefore everywhere $\nu = \text{const.}$ which, with the aid of (10), proves the above proposition. This will hold not only on the assumption that $f = 1$, but also for any reflective or absorptive power of the surface.

III.

The apparent decrease of thermal conductivity of gases when rarified is due, as I have shown in a series of papers¹⁾, to a surface phenomenon, analogous to the slipping of gases discovered by Kundt and Warburg. The kinetic theory of gases shows besides²⁾ that, at very low pressures, when the mean free path is much greater than the dimensions of the vessel in which conduction is going on, another law must come into action, the transmitted heat being proportional then to the gas pressure and independent of the thickness of the layer of gas. Some experimental evidence in support of this law has been given by Mr. Brush; recently much ampler material is available, owing to a careful investigation published by Messrs. Soddy and Berry³⁾.

The form of the law being established, the question arises as to the value of the factor of proportionality or, as the last-named authors put it: of the quantity of heat, Q , reduced to unit of hot surface, one degree of difference of temperature, and 0.01 mm of mercury pressure.

¹⁾ Ann. d. Phys. 64, 101, 1898; Wien. Sitzgsber. 107, 304, 1898; 108, 5, 1899; Phil. Mag. 46, 199, 1898. [Vol. I, pp. 83, 113, 139 and 199. Ed.] See also Gehreke, Ann. d. Phys. 2, 102, 1900.

²⁾ Wien. Sitzgsber. 107, 323, 1898. [Vol. I, p. 113. Ed.]

³⁾ Brush, Phil. Mag. 45, 31, 1898. Soddy and Berry, Proc. Roy. Soc. 83 A, 254, 1910.

By a roughly approximative reasoning (assuming that the molecules can be divided in three classes, moving parallel to the axes) I had found that the flux of conducted heat (for 1° and 1 cm^2) ought to be of the order of magnitude: $\frac{1}{3} \rho s c$ where ρ is the density, s the specific heat at constant volume, c the mean velocity. This expression corresponds to the case when every molecule, by its impact on the solid wall, assumes the *vis viva* corresponding to the temperature of the latter, but it is to be multiplied by

$$\frac{1-\beta}{1+\beta}$$

if only a partial equalisation of temperature is taking place, according to the formula:

$$\vartheta - \theta_0 = \beta(\theta_m - \theta_0)$$

where θ_0 , θ_m , ϑ denote the temperature of the wall, of the impinging, and of the emitted molecules. Messrs. Soddy and Berry use the same formula with a slight difference of notation, putting

$$Q = \frac{nHG}{6N}$$

where n is the number of molecules per cm^3 at 0.01 mm pressure, N the number contained in one gram, H the molecular heat at constant volume, G the mean velocity. Their experiments enabled them to determine the ratio of the observed transport of heat K to the calculated value Q for eleven gases, and from these numbers, ranging between 1.09 and 0.25 , they intend to draw conclusions relating to the factor β . Now these results appeared to be of a somewhat unexpected character, since only values inferior to unity were supposed to be admissible. But as soon as exact numbers are in question, such a rough estimate as that referred to above is evidently insufficient and an exact calculation becomes necessary.

Consider a gas contained between two parallel horizontal plates, the upper one at temperature θ_2 , the lower one at temperature θ_1 (one degree lower). It is convenient then, instead of making the above supposition with respect to β , to follow Maxwell's assumption as to the reflected and emitted molecules. The total number of molecules n in unit volume will be composed of four parts:

n_1	molecules moving upwards	with mean velocity	c_1
n'_1	" " " downwards	" " "	c_1
n_2	" " " upwards	" " "	c_2
n'_2	" " " downwards	" " "	c_2

where c_1 and c_2 are the velocities corresponding to the temperatures θ_1 and θ_2 . These four kinds make together

$$(23) \quad n = n_1 + n_2 + n'_1 + n'_2;$$

they do not undergo mutual influence, except at the impacts on the plates; each will move with velocities distributed according to Maxwell's law.

The number of impinging molecules is given by (10); but here we denote by n the number of molecules moving in one direction only, and therefore we must take

$$(24) \quad v = \frac{2nc}{\sqrt{6\pi}}.$$

Now considering the process at the lower plate, we see that the molecules n_1 are made up of the "reflected" fraction $(1-f)$ of the incident molecules n'_1 and of the fraction f of the whole number of molecules which are impinging on the lower plate; whence:

$$(25) \quad n_1 c_1 = (1-f) n'_1 c_1 + f(n'_1 c_1 + n'_2 c_2)$$

and similarly

$$(26) \quad n_2 c_2 = (1-f) n'_2 c_2$$

By adding these two relations we get a solution expressing the fact that no one-sided current takes place:

$$(27) \quad n_1 c_1 + n_2 c_2 = n'_1 c_1 + n'_2 c_2.$$

This equation and (26) and a similar one for the molecules moving in reverse direction take the following form:

$$\begin{aligned} (n_1 - n'_1) c_1 &= (n'_2 - n_2) c_2 \\ n_2 &= (1-f) n'_2 \\ n'_1 &= (1-f) n_1 \end{aligned}$$

whence it follows that:

$$(28) \quad \begin{cases} n'_2 c_2 = n_1 c_1 \\ n'_1 c_1 = n_2 c_2 = (1-f)n_1 c_1. \end{cases}$$

The quantity of heat lost by the lower plate is:

$$Q = \frac{2ms}{\sqrt{6\pi}} [\theta_2 (n'_2 c_2 - n_2 c_2) + \theta_1 (n'_1 c_1 - n_1 c_1)] = \frac{2ms}{\sqrt{6\pi}} (\theta_2 - \theta_1) f n_1 c_1.$$

Now relations (23) and (28) give

$$n_1 = \frac{n}{2-f} \frac{c_2}{c_1 + c_2}$$

so that we have:

$$(29) \quad Q = \frac{2fmns}{\sqrt{6\pi}(2-f)} \frac{c_1 c_2}{c_1 + c_2} (\theta_2 - \theta_1).$$

If we put

$$c = \frac{2c_1 c_2}{c_1 + c_2},$$

and $f = 1 - \beta$, we finally get:

$$(30) \quad Q = \frac{Qcs}{\sqrt{6\pi}} \frac{1-\beta}{1+\beta} (\theta_2 - \theta_1).$$

This is the exact value for conduction of heat in a highly rarified gas; we see it is greater than the value calculated before.

The numbers given by Messrs Soddy and Berry for $\frac{K}{Q}$ ought to be multiplied with the factor $\sqrt{\frac{4}{3}\pi} = 0.7236$, which gives the series¹⁾

	A	Ne	N ₂	O ₂	CO	N ₂ O	C ₂ H ₂	CO ₂	CH ₄	He	H ₂
$\frac{K}{Q}$	0.79	0.75	0.68	0.62	0.59	0.56	0.52	0.52	0.49	0.37	0.18

We therefore see that the coefficient β cannot be neglected; in other words, the interchange of energy on impact is always imperfect. The order of gases: A, Ne, N₂, O₂, CO, N₂O, C₂H₂, CO₂,

CH₄, He, H₂, seems to suggest the following rule: the interchange of energy is worse for smaller molecular weights; it is more defective for polyatomic and diatomic molecules than for monatomic ones. The first part of this rule is easily intelligible; a simple mechanical reasoning shows¹⁾ that the interchange of energy between colliding spheres is the more imperfect the greater the difference of their masses, and here the wall was composed of the heavy Pt molecules. The second part is also in accordance with other phenomena of conduction of heat, showing that intramolecular energy is comparatively less disposed to equalisation by single impacts than energy of progressive motion.

¹⁾ Wien. Sitzgsber. 107, 324, 1898. [Vol. I, p. 113. *Ed.*].

¹⁾ [Inserted here from a reimpression of a part of the present paper, cf. *Phil. Mag.* for January 1911, pp. 11-14. *Ed.*].