

EXTRAIT DU BULLETIN DE L'ACADÉMIE DES SCIENCES DE CRACOVIE
CLASSE DES SCIENCES MATHÉMATIQUES ET NATURELLES. SÉRIE A: SCIENCES MATHÉMATIQUES
JUILLET 1910

Contributions to the theory of transpiration, diffusion and thermal conduction in rarefied gases

by

M. Smoluchowski



CRACOVIE
IMPRIMERIE DE L'UNIVERSITÉ
1910

L'ACADÉMIE DES SCIENCES DE CRACOVIE A ÉTÉ FONDÉE EN 1873 PAR
S. M. L'EMPEREUR FRANÇOIS JOSEPH I.

PROTECTEUR DE L'ACADÉMIE:

S. A. I. L'ARCHIDUC FRANÇOIS FERDINAND D'AUTRICHE-ESTE,

VICE-PROTECTEUR: *Vacat.*

PRÉSIDENT: S. E. M. LE COMTE STANISLAS TARNOWSKI.

SECRÉTAIRE GÉNÉRAL: M. BOLESLAS ULANOWSKI.

EXTRAIT DES STATUTS DE L'ACADÉMIE:

(§ 2). L'Académie est placée sous l'auguste patronage de Sa Majesté Impériale Royale Apostolique. Le Protecteur et le Vice-Protecteur sont nommés par S. M. l'Empereur.

(§ 4). L'Académie est divisée en trois classes:

a) Classe de Philologie,

b) Classe d'Histoire et de Philosophie,

c) Classe des Sciences Mathématiques et Naturelles.

(§ 12). La langue officielle de l'Académie est la langue polonaise.

Depuis 1885, l'Académie publie le «Bulletin International» qui paraît tous les mois, sauf en août et septembre. Le Bulletin publié par les Classes de Philologie, d'Histoire et de Philosophie réunies, est consacré aux travaux de ces Classes. Le Bulletin publié par la Classe des Sciences Mathématiques et Naturelles paraît en deux séries. La première est consacrée aux travaux sur les Mathématiques, l'Astronomie, la Physique, la Chimie, la Minéralogie, la Géologie etc. La seconde série contient les travaux se rapportant aux Sciences Biologiques.

Publié par l'Académie
sous la direction de M. **Ladislav Natanson**,
Secrétaire de la Classe des Sciences Mathématiques et Naturelles.

24 sierpnia 1910.

Nakładem Akademii Umiejętności.

Kraków, 1910. — Drukarnia Uniwersytetu Jagiellońskiego pod zarządkiem Józefa Filipowskiego.

Biblioteka Wydziału Fizyki



Contributions to the theory of transpiration, diffusion and thermal conduction in rarefied gases

by

M. Smoluchowski



Przyczynek do kinetycznej teoryi transpiracyi, dyfuzyi i przewodnictwa cieplnego w gazach rozrzedzonych. — Contributions to the theory of transpiration, diffusion and thermal conduction in rarefied gases.

Mémoire

de M. **MARYAN SMOLUCHOWSKI** m. c.,
présenté dans la séance du 4 Juillet 1910.

I.

The phenomena of viscosity and of thermal transpiration in rarefied gases, which had aroused general interest thirty years ago and which partly had inspired Maxwell¹⁾ for his famous paper «On Stresses in Rarefied 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 old method used by Maxwell in his first researches, by Clausius, O. E. Meyer and many others; it is based on the supposition 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.

Now it is well known³⁾ that all such calculations — as far as viscosity, thermal conductivity and diffusion are concerned — are

¹⁾ Maxwell, Scientific Papers II p. 681; Phil. Trans. 170, 231, 1879.

²⁾ Knudsen, Ann. d. Phys. 28, 75, 1909; 31, 205, 633, 1910.

³⁾ Boltzmann, Wien. Sitzgsber. 81, 117, 1880; 84, 40, 1230, 1881.

defective. Maxwell and Boltzmann have shown that the law of distribution of velocities is modified when the above phenomena are going on, and that the neglect of this factor — as involved in these 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 that is free from inherent contradiction.

I would 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 any quantitative agreement between calculation and experimental results. But 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 there is based 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 any 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.

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

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

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 this method. It is the same point which is emphasized in Kirchhoff's *Lectures on Heat* p. 210 and in Boltzmann's *Gastheorie* I p. 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 easily show indeed that the ordinary form of the law of distribution of velocities is changed in this case and becomes

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

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. Here the normal pressure or momentum carried through any plane:

$$p = m \int_{-\infty}^{+\infty} \xi^2 f d\xi d\eta d\zeta = m \int \eta^2 f d\xi d\eta d\zeta = m \int \zeta^2 f d\xi d\eta d\zeta$$

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, but his hypothesis 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 near the truth, 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 and even this probably is not quite exact, as it rests on simplifying suppositions as to the behaviour of the gaseous surface layer. Certainly it does not hold for high rarefactions, where other laws set in which will be explained later on.

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) (loc. cit.) by the equation:

$$(2) \dots \quad v - G \frac{\partial v}{\partial x} = \frac{3}{4} \frac{\mu}{\rho \theta} \frac{\partial \theta}{\partial y} - \frac{3}{2} G \frac{\mu}{\rho \theta} \frac{\partial^2 \theta}{\partial y \partial x}$$

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

$$(3) \dots \quad G = \frac{\mu}{2} \sqrt{\frac{2\pi}{p\theta}} (f - 1)$$

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

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

and the condition of thermal equilibrium is:

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

where κ denotes the conductivity, s the specific heat.

Equation (4) and the surface conditions (2) for both plates are fulfilled if we take

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

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

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

$$\int_0^l v dx$$

must be zero, whence:

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

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). Thus we get:

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

if we denote by A the quantity $\rho s \varepsilon \alpha' / \kappa$.

Now the total quantity of heat carried by the molecular convective currents will be

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

whereas the quantity transmitted by conduction is

$$lx \frac{\partial \theta}{\partial y}.$$

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

$$(9) \dots \frac{3}{1120} \left(\frac{l}{\theta} \frac{\partial \theta}{\partial y} \right)^2 \left(\frac{l}{l+6G} \right)^2.$$

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 and 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 will prevail. The state of the gas in this case is analogous to the radiation in a closed vessel. This case which for the first time has been treated theoretically by 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 wholly as 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 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 of molecules in unit volume n of the fictitious gas by the known relation:

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

where f is Maxwell's probability function

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

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 get the number of molecules passing from the right to the left, through an element dS , by forming the integral

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

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 this 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 $\nu(x')$:

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

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 this 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 belonging 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 .

Now by means of formula (12) let us calculate 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 $x' = R \operatorname{ctg}\varphi$, if R is the projection of r on the plane of the cross section, and thus (12) reduces to

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

where the integration of $\cos^2\varphi d\varphi$ (between the limits 0 and $\frac{\pi}{2}$) can be effected. A corresponding quantity with negative sign of $\frac{\partial\nu}{\partial x}$ 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)

$$(14) \dots Q = \frac{m}{2} \frac{\partial v}{\partial x} \int \int dS \int R d\varepsilon = \frac{c}{2\sqrt{6\pi}} \frac{\partial q}{\partial x} A = \\ = \frac{1}{2\sqrt{2\pi}} \sqrt{\frac{q_0}{p_0}} \frac{p_2 - p_1}{L} A$$

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

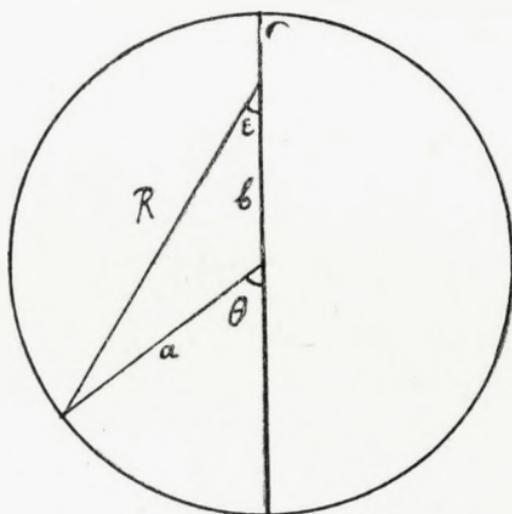


Fig. 1.

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, contrary to Knudsen's opinion, the molecular current has different intensity 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 $Rd\varepsilon$ (in the general case of any form of cross section) can be put

$$Rd\varepsilon = ds \cos(nR)$$

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 denotes now the whole length of the chord belonging to the angle α . Thus we get

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

By applying this expression to the circle we get

$$(16) \dots \quad A = a\pi \int_0^{2\pi} 4a^2 \sin^3\left(\frac{\theta}{2}\right) d\left(\frac{\theta}{2}\right) = \frac{16a^3\pi}{3}$$

and the whole mass streaming through a circular tube will be:

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

In the general case, when the surface element of the wall dS' is partially reflecting, partially absorbing and radiating, it will emit only $f v dS'$ molecules in the manner above described; the rest, $(1 - f)v dS'$, 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 originate 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 $1-f = \delta$:

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

and we have finally:

$$(18) \dots \quad Q = \frac{2-f}{f} \frac{4\sqrt{2}\pi}{3} a^3 \sqrt{\frac{\rho_0}{p_0}} \frac{p_2 - p_1}{L}$$

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

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

which for a quadratic cross section takes the simpler form:

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

whereas according to Knudsen we should have

$$Q = \frac{\alpha^3}{3} \sqrt{\frac{8}{\pi}} \sqrt{\frac{\rho_0}{p_0}} \frac{p_2 - p_1}{L}$$

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: $\frac{1}{4} n m v \Omega$. On the other hand, the stream 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 improbable a priori as 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 certain 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 will be proportional to:

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

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 of the gas:

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

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 molecular weight of the gas and dir-

ectly 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 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 applying exactly the same reasoning as before, we again get the formula:

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

Now, if the tube is closed at both ends, or if in any way the passage of the gas is prevented, we must have $Q=0$ and $v=\text{const.}$, which implies according to (10) that the pressure will increase towards the hotter end, in proportion to 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 Reynolds' researches on thermal transpiration through Meerscham-plates etc., in 1879.

In such porous materials of course the channels cannot be con

sidered as cylindrical tubes; but if the analogy of a rarefied gas with the phenomenon 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 $\nu = \text{const.}$ everywhere, 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 rarefied 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 and recently much ampler material is available, owing to a careful investigation by Messrs. Soddy and Berry³⁾.

The form of this 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.

See also Gehrcke, Ann. d. Phys. **2**, 102, 1900.

²⁾ Wien. Sitzgsber. **107**, 328, 1898.

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: $\frac{1}{6} \rho s c$ 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 ought to be made.

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 whole number of molecules in unit volume n will now be composed of four parts:

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

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

they do not undergo any mutual influence, except at the impacts on the plates, and 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

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

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:

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

and similarly

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

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

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

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 follows:

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

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:

$$(29) \dots \quad Q = \frac{2f m n s}{\sqrt{6\pi} (2 - f)} \frac{c_1 c_2}{c_1 + c_2}$$

If we put

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

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

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

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

All the numbers given by Messrs Soddy and Berry for $\frac{K^*}{Q}$ ought to be multiplied by the factor $\frac{1}{4}\sqrt{\pi} = 0.7236$. They will range between 0.79 for argon and 0.18 for hydrogen, which shows that the coefficient β is never to 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 and it is worse for polyatomic and diatomic molecules than for monatomic ones. The first part of this rule is easily intelligible; a simple mechanical reasoning shows¹⁾

¹⁾ Wien. Sitzgsber. 107, 324, 1898.

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.

BULLETIN INTERNATIONAL

DE L'ACADÉMIE DES SCIENCES DE CRACOVIE CLASSE DES SCIENCES MATHÉMATIQUES ET NATURELLES.

SÉRIE A: SCIENCES MATHÉMATIQUES.

DERNIERS MÉMOIRES PARUS.

(Les titres des Mémoires sont donnés en abrégé).

S. Motylewski. Über Methoxyphenylkumarone	Nov. 1909
S. Kreutz. Über Alstonit	Nov. 1909
Z. Rozen. Die alten Laven im Gebiete von Krakau	Nov. 1909
L. Natanson. Note on the Theory of Dispersion in gaseous bodies	Déc. 1909
L. Natanson. On the Theory of Extinction in gaseous bodies. . .	Déc. 1909
W. Świętosławski. Thermochem. Untersuch. organ. Verbindungen	Déc. 1909
L. Marchlewski, J. Robel. Azofarbstoffe d. Hämopyrrols etc. . .	Janv. 1910
W. Sierpiński. Valeur asymptotique d'une certaine somme . . .	Janv. 1910
J. de Kowalski. Abweichungen vom Stokes'schen Gesetze . . .	Janv. 1910
J. de Kowalski. Absorption und Phosphoreszenz	Janv. 1910
J. Salpeter. Bestimmung d. Ionenkonstanten d. Ra-A	Janv. 1910
W. Kuźniar. Tektonik des Fylsches nördlich v. d. Tatra . . .	Févr. 1910
W. Arnold. Neue Farbenreaktion von Eiweisskörpern	Févr. 1910
W. Arnold. Die Organpeptide	Févr. 1910
G. Smoleński. Genese d. nord-podolischen Steilrandes	Mars 1910
C. Zakrzewski. Dispersion d. Metalle im sichtb. Spektrum I. . .	Mars 1910
A. Korczyński. Addition von HCl an subst. Aniline	Mars 1910
H. Merczyng. Elektrisches Spektrum (sehr kurze Wellen) . . .	Avril 1910
C. Zakrzewski. Dispersion d. Metalle im sichtb. Spektrum. II. .	Avril 1910
S. Opolski. Über Benzolsulfonitrilanilidester	Avril 1910
M. Smoluchowski. Conductibilité calorifique des corps pulvérisés .	Mai 1910
J. Buraczewski, T. Nowosielski. Oxydat-produkte d. Br-Strychnine	Mai 1910
H. Malarski, L. Marchlewski. Studien in der Chlorophyllgruppe	Juin 1910
M. Limanowski. Les Dinarides des environs d'Adelsberg	Juin 1910
L. Bruner, M. Królikowski. Photochem. Umlagerung d. Maleinsäure	Juin 1910
S. Tolloczko. Auflösung verschiedener Flächen d. Gipses	Juin 1910
S. Tolloczko, J. Tokarski. Wachstums- und Auflösungsgeschwin- digkeiten der Kristalle; Reversibilität d. Vorgänge	Juin 1910
T. Koźniewski. Alkaloide d. Wurzeln v. Sanguinaria Canadensis .	Juin 1910
W. Łoziński. Endmoränen d. Bug-Tieflandes	Juin 1910
L. Natanson. Double Refraction in electric or magnetic field . .	Juin 1910
St. Loria, C. Zakrzewski. Die optischen Konstanten einiger das Kerr-Phänomen aufweisenden Substanzen	Juin 1910
K. Jabłczyński, St. Jabłoński. Réactions dans les systèmes hété- rogènes. Influence de l'alcool	Juin 1910

Avis.

Les livraisons du «Bulletin International» se vendent séparément. — Adresser les demandes à la Librairie «Spółka Wydawnicza Polska», Rynek Gł., Cracovie (Autriche).
