XII.—*On the Foundations of the Kinetic Theory of Gases.* II.

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[*Erratum* in Part I., *anté*, p. 65. For 1676, read 1678, as the date of HOOKE'S Pamphlet.]

In the present communication I have applied the results of my first paper to the question of the transference of momentum, of energy, and of matter, in a gas or gaseous mixture; still, however, on the hypothesis of hard spherical particles, exerting no mutual forces except those of impact. The conclusions of §§ 23, 24 of that paper form the indispensable preliminary to the majority of the following investigations. For, except in extreme cases, in which the causes tending to disturb the “special” state are at least nearly as rapid and persistent in their action as is the process of recovery, we are entitled to assume, from the result of § 24, that in every part of a gas or gaseous mixture a local special state is maintained. And it is to be observed that this may be accompanied by a common translatory motion of the particles (or of each separate class of particles) in that region; a motion which, at each instant, may vary continuously in rate and direction from region to region; and which, in any one region, may vary continuously with time. This is a sort of generalisation of the special state, and all that follows is based on the assumption that such is the most general kind of motion which the parts of the system can have, at least in any of the questions here treated. Of course this translational speed is not the same for all particles in any small part of the system. It is merely an average, which is maintained in the same roughly approximate manner as is the

“special state,” and can like it be assumed to hold with sufficient accuracy to be made the basis of calculation. The mere fact that a “steady” state, say of diffusion, can be realized experimentally is a sufficient warrant for this assumption; and there seems to be no reason for supposing that the irregularities of distribution of the translatory velocity among the particles of a group should be more serious for the higher than for the lower speeds, or *vice versâ*. For each particle is sometimes a quick, sometimes a slow, moving one:—and exchanges these states many thousand times per second. All that is really required by considerations of this kind is allowed for by our way of looking at the mean free paths for different speeds.

I may take this opportunity of answering an objection which has been raised in correspondence by Professor NEWCOMB, and by Messrs WATSON and BURBURY, to a passage in § 3 of the First Part of this paper.* The words objected to are put in Italics:—

“But *the argument above shows*, further, that this density must be expressible in the form

$$f(x)f(y)f(z),$$

whatever rectangular axes be chosen, passing through the origin.”

The statement itself is not objected to, but it is alleged that it does not follow from the premises assumed.

This part of my paper was introduced when I revised it for press, some months after it was read; the date of revision, not of reading, being put at the head. It was written mainly for the purpose of stringing together what had been a set of detached fragments, and was in consequence not so fully detailed as they were. I made some general statements as to the complete verification of these preliminary propositions which was to be obtained from the more complex investigations to which they led; thus showing that I attached comparatively little weight to such introductory matters. If necessary, a detailed proof can be given on the lines of § 21 of the paper. The “argument” in question, however, may be given as below. It is really involved in the italicised words of the following passage of § 1:—“in place of the hopeless question of the behaviour of innumerable absolutely isolated individuals, the comparatively simple statistical question of *the average behaviour of the various groups of a community*.”

Suppose two ideal planes, parallel to $x=0$, to move with common speed, x , through the gas. The portion of gas between them will consist of two quite distinct classes of particles:—the greatly more numerous class being mere

* In the *Phil. Mag.*, for April 1887, the same objection is raised by Prof. BOLTZMANN; who has appended it to the English translation of his paper presently to be referred to. But he goes farther than the other objectors, and accuses me of reasoning in a circle.

fleeting occupants, the minority being (relatively) as it were permanent lodgers. These are those whose speed perpendicular to the planes is very nearly that of the planes themselves. The *individuals* of each class are perpetually changing, those of the majority with extraordinary rapidity compared with those of the minority; but each *class*, as such, forms a definite “*group* of the community.” The method of averages obviously applies to each of these classes separately; and it shows that the minority will behave, so far as y and z motions are concerned, as if they *alone* had been enclosed between two *material* planes, and as if their lines of centres at impact were always parallel to these. The instant that this ceases to be true of any one of them, that one ceases to belong to the group;—and another takes its place. Their behaviour under these circumstances (though not their number) must obviously be independent of the speed of the planes. Hence the law of distribution of components in the velocity space-diagram must be of the form

$$f(x) \cdot F(y, z);$$

and symmetry at once gives the result above.

[(*Inserted March 5th*, 1887.) Another objection, but of a diametrically opposite character, raised by Mr BURBURY* and supported by Professor BOLTZMANN,† is to the effect that in my first paper I have unduly multiplied the number of preliminary assumptions necessary for the proof of MAXWELL’S Theorem concerning the distribution of energy in a *mixture* of two gases. In *form*, perhaps, I may inadvertently have done so, but certainly not in *substance*.

The assumptions which (in addition to that made at the commencement of the paper (§ 5) for provision against simultaneous impacts of three or more particles, which was introduced expressly for the purpose of making the results applicable to real gases, not merely to imaginary hard spheres,) I found it necessary to make, are (§ 18) as follows; briefly stated.

(A) That the particles of the two systems are thoroughly mixed.

* The Foundations of the Kinetic Theory of Gases. *Phil. Mag.* 1886, I, p. 481.

† Über die zum theoretischen Beweise des Avogadro’schen Gesetzes erforderlichen Voraussetzungen. *Sitzb. der kais. Akad.* XCIV, 1886, Oct. 7. In this article Prof. BOLTZMANN states that I have nowhere expressly pointed out that my results are applicable only to the case of hard spheres. I might plead that the article he refers to is a brief *Abstract* only of my paper; but it contains the following statements, which are surely explicit enough as to the object I had in view:—

“This is specially the case with his [MAXWELL’S] investigation of the law of ultimate partition of energy in a mixture of smooth spherical particles of two different kinds.”

“It has since been extended by BOLTZMANN and others to cases in which the particles are no longer supposed to be hard smooth spheres.”

“Hence it is desirable that MAXWELL’S proof of his fundamental Theorem should be critically examined.” Then I proceed to examine it, *not* Professor BOLTZMANN’S extension of it. In my paper itself this limitation is most expressly insisted on.

(B) That the particles of each kind, separately, acquire and maintain the "special state."

(C) That there is free access for collision between each pair of particles, whether of the same or of different systems; and that the number of particles of one kind is not overwhelmingly greater than that of the other.

Of these, (A) and (B), though enunciated separately, are regarded as *consequences* of (C), which is thus my sole assumption for the proof of CLERK-MAXWELL'S Theorem. Professor BOLTZMANN states that the only necessary assumptions are:—that the particles of each kind be uniformly distributed in space, that they behave on the average alike in respect of all directions, and that (for any one particle?) the duration of an impact is short compared with the interval between two impacts. His words are as follows:—"Die einzigen Voraussetzungen sind, dass sowohl die Moleküle erster als auch die zweiter Gattung gleichförmig im ganzen Raume vertheilt sind, sich durchschnittlich nach allen Richtungen gleich verhalten und dass die Dauer eines Zusammenstosses kurz ist gegen die Zeit, welche zwischen zwei Zusammenstossen vergeht."

He farther states that neither system need have internal impacts; and that Mr BURBURY is correct in maintaining that a system of particles, which are so small that they practically do not collide with one another, will ultimately be thrown into the "special" state by the presence of a *single* particle with which they can collide.

Assuming the usual data as to the number of particles in a cubic inch of air, and the number of collisions per particle per second, it is easy to show (by the help of LAPLACE'S remarkable expression* for the value of $\Delta^n 0^m / n^m$ when m and n are very large numbers) that somewhere about 40,000 *years* must elapse before it would be so much as *even betting* that Mr BURBURY'S single particle (taken to have twice the diameter of a particle of air) had encountered, once at least, each of the 3.10^{20} very minute particles in a single cubic inch. He has not stated what is the average number of collisions necessary for each of the minute particles, before it can be knocked into its destined phase of the special state; but it must be at least considerable. Hence, even were the proposition true, æons would be required to bring about the result. As a result, it would be very interesting; but it would certainly be of no importance to the kinetic theory of gases in its practical applications.

I think it will be allowed that Professor BOLTZMANN'S assumptions, which (it is easy to see) practically beg the whole question, are themselves inadmissible

* *Théorie Analytique des Probabilités. Livre II, chap. ii, 4.* [In using this formula, we must make sure that the ratio m/n is sufficiently large to justify the approximation on which it is founded. It is found to be so in the present case. At my request Professor CAYLEY has kindly investigated the correct formula for the case in which m and n are of the *same* order of large quantities. His paper will be found in *Proc. R. S. E.*, April 4, 1887.]

except as consequences of the mutual impacts of the particles in each of the two systems separately. Professor BOLTZMANN himself, indirectly and without any justification (such as I have at least attempted to give), *assumes* almost all that he objects to as redundant in my assumptions, with a good deal more besides. But he says nothing as to the *relative* numbers of the two kinds of particles. Thus I need not, as yet, take up the question of the validity of Professor BOLTZMANN'S method of investigation (though, as hinted in § 31 of my first paper, I intend eventually to do so); and this for the simple reason that, in the present case, I cannot admit his premises.

Mr BURBURY assumes the non-colliding particles to be in the "special state," and proceeds to prove that the single additional particle will not disturb it. But, supposing for a moment this to be true, it does *not* prove that the solitary particle would (even after the lapse of ages) reduce any non-colliding system, with positions at any instant, speeds, and lines of motion, distributed absolutely at random (for here there cannot be so much as plausible grounds for the introduction of Professor BOLTZMANN'S assumptions) to the "special state." If it could do so, the perfect reversibility of the motions, practically limited in this case to the reversal of the motion *of the single particle alone*, shows that the single particle would (for untold ages) continue to throw a system of non-colliding particles further and further *out* of the "special" state; thus expressly contradicting the previous proposition. In this consequence of reversal we see the reason for postulating a very great number of particles of *each* kind. If Mr BURBURY'S sole particle possessed the extraordinary powers attributed to it, it would (except under circumstances of the most exact adjustment) not only be capable of producing, but *would* produce, absolute confusion among non-colliding particles already in the special state. Considering what is said above, I do not yet see any reason to doubt that the assumption of collisions among the particles of each kind, separately, is quite as essential to a valid proof of MAXWELL'S Theorem as is that of collisions between any two particles, one from each system. I have not yet seen any attempt to *prove* that two sets of particles, which have no internal collisions, will by their mutual collisions tend to the state assumed by Professor BOLTZMANN. Nor can I see any ground for dispensing with my farther assumption that the number of particles of one kind must not be overwhelmingly greater than that of the other. A small minority of one kind must (on any admissible assumption) have an average energy which will fluctuate, sometimes quickly sometimes very slowly, within very wide and constantly varying limits.

DE MORGAN* made an extremely important remark, which is thoroughly applicable to many investigations connected with the present question. It is to the effect that "no *primary* considerations connected with the subject of

* *Encyc. Metropolitana. Art. Theory of Probabilities.*

Probability can be, or ought to be, received if they depend upon the results of a complicated mathematical analysis." To this may be added the obvious remark, that the purely mathematical part of an investigation, however elegant and powerful it may be, is of no value whatever in physics unless it be based upon admissible assumptions. In many of the investigations, connected with the present subject, alike by British and by foreign authors, the above remark of DE MORGAN has certainly met with scant attention.]

In my first paper I spoke of the errors in the treatment of this subject which have been introduced by the taking of means before the expressions were ripe for such a process. In the present paper I have endeavoured throughout to keep this danger in view ; and I hope that the results now to be given will be found, even where they are most imperfect, at least more approximately accurate than those which have been obtained with the neglect of such precautions.

The nature of CLERK-MAXWELL'S earlier investigations on the Kinetic theory, in which this precaution is often neglected, still gives them a peculiar value ; as it is at once obvious, from the forms of some of his results, that he must have *thought them out* before endeavouring to obtain them, or even to express them, by analysis. One most notable example of this is to be seen in his *Lemma* (*Phil. Mag.* 1860, II. p. 23) to the effect that

$$\int_{-r}^r \pm U x^m dx = \frac{2}{m+2} \frac{d}{dx} (U r^{m+2});$$

where U and r are functions of x , not vanishing with x , and varying but slightly between the limits $-r$ and r of x ;—and where the signs in the integrand depend upon the character of m as an even or odd integer. This forms the starting point of his investigations in Diffusion and Conductivity. It is clear from the context why this curious proposition was introduced, but its accuracy, and even its exact meaning, seem doubtful.

In all the more important questions now to be treated, the mean free path of a particle plays a prominent part, and integrals involving the quantities e , or $e + e_1$ (as defined in §§ 9, 10, 28) occur throughout. We commence, therefore, with such a brief discussion of them as will serve to remove this merely numerical complication from the properly physical part of the reasoning.

X. On the Definite Integrals

$$\int_0^\infty \frac{\nu v^r}{e} \quad \text{and} \quad \int_0^\infty \frac{\nu v^r}{e_1 + z e_2}.$$

33. In the following investigations I employ, throughout, the definition of the mean free path for each speed as given in § 11. Thus all my results

necessarily differ, at least slightly, from those obtained by any other investigator.

By § 11 we see at once that

$$\begin{aligned}\int_0^\infty \frac{vv^r}{e} &= \frac{1}{n\pi s^2} \frac{\int_0^\infty \frac{\varepsilon^{-hv^2} v^{r+2} dv}{\int_0^v \varepsilon^{-hv_1^2} (v_1^2 + v_1^4/3v^2) dv_1 + \int_v^\infty \varepsilon^{-hv_1^2} (vv_1/3 + v_1^3/v) dv_1}}, \\ &= \frac{1}{n\pi s^2 \sqrt{h^r}} \frac{\int_0^\infty \frac{4x^{r+4} \varepsilon^{-x^2} dx}{x\varepsilon^{-x^2} + (2x^2 + 1) \int_0^x \varepsilon^{-x^2} dx}}, \\ &= \frac{C_r}{n\pi s^2 \sqrt{h^r}}, \text{ suppose.}\end{aligned}$$

The finding of C_r is of course a matter of quadratures, as in the *Appendix* to the First Part of this paper, where the values calculated are, in this notation, C_{-1} and C_0 ; and Mr CLARK has again kindly assisted me by computing the values of C_1 , C_3 , C_5 , which are those required when we are dealing with Viscosity and with Heat-Conduction in a single gas. The value of C_2 has also been found, with a view to the study of the general expression for C_r . These will be given in an *Appendix* to the present paper.

34. When we come to deal with Diffusion, except in the special case of equality of density in the gases, this numerical part of the work becomes extremely serious, even when the assumption of a “steady” state is permissible. As will be seen in § 28 of my first paper, we should have in general to deal with tables of double entry, for the expressions to be tabulated are of the form—

$$\begin{aligned}\int_0^\infty \frac{vv^r}{e_1 + ze_2} &= \frac{1}{n\pi s^2 \sqrt{h^r}} \frac{\int_0^\infty \frac{4x^{r+4} \varepsilon^{-x^2} dx}{x\varepsilon^{-x^2} + (2x^2 + 1) \int_0^x \varepsilon^{-x^2} dx + z \left(x_1 \varepsilon^{-x_1^2} + (2x_1^2 + 1) \int_0^{x_1} \varepsilon^{-x^2} dx \right)}}{=} \\ &= {}_1C_r = \frac{{}_1C_r}{n\pi s^2 \sqrt{h^r}}, \text{ suppose.}\end{aligned}$$

For the second gas the corresponding quantity will be written as ${}_2C_r$. Here

$$x_1 = x \sqrt{h_1/h},$$

and

$$z = \frac{n_1 h}{n h_1} \left(\frac{s + s_1}{2s} \right)^2;$$

so that they are numerical quantities, of which the first depends on the relative masses of particles of the two gases, while the second involves, in addition, not only their relative size but also their relative number. It is this last condition which introduces the real difficulty of the question, for we have to express the

value of the integral as a function of z before we can proceed with the further details of the solution, and then the equation for Diffusion ceases to resemble that of FOURIER for Heat-Conduction.

The difficulty, however, disappears entirely when we confine ourselves to the study of the "steady state" (and is likewise much diminished in the study of a variable state) in the special case when the mass of a particle is the same in each of the two gaseous systems, whether the diameters be equal or no. For, in that case, we have $h_1 = h$ and $x_1 = x$, so that the factor $1/(1+z)$ can be taken outside the integral sign. Thus, instead of ${}_1\mathfrak{C}_r$, we have only to calculate C_r of the previous section.

XI. *Pressure in a Mixture of Two Sets of Spheres.*

35. Suppose there be n_1 spheres of diameter s_1 and mass P_1 , and n_2 with s_2 , P_2 , per cubic unit. Let $s = (s_1 + s_2)/2$.

Then the average number of collisions of each P_1 with P_1 s is, per second,

$$2\sqrt{\frac{2\pi}{h_1}} n_1 s_1^2.$$

The impulse is, on the average (as in § 30),

$$-P_1 \sqrt{\frac{\pi}{2h}}.$$

Similarly, each P_1 encounters, in each second (§ 23), the average number

$$2n_2 \sqrt{\frac{\pi(h_1 + h_2)}{h_1 h_2}} \cdot s^2$$

of P_2 s, and the average impact is

$$-\frac{P_1 P_2}{P_1 + P_2} \sqrt{\frac{\pi(h_1 + h_2)}{h_1 h_2}}.$$

Thus the average sum of impacts on a P_1 is, per second,

$$\begin{aligned} & -2P_1 \sqrt{\frac{\pi}{h_1}} n_1 s_1^2, \text{ due to } P_1\text{s}; \text{ and} \\ & -2 \frac{P_1 P_2}{P_1 + P_2} \frac{h_1 + h_2}{h_1 h_2} \pi n_2 s^2, \text{ due to } P_2\text{s}. \end{aligned}$$

In the Virial expression $\frac{1}{2}\Sigma(Rr)$, {§ 30}, r must be taken as s_1 for the first of these portions, and as s for the second. Hence we have

$$\begin{aligned}\frac{1}{4}\Sigma(Rr) &= -\frac{\pi}{2} \left\{ \frac{P_1}{h_1} n_1^2 s_1^3 + 2 \frac{P_1 P_2 (h_1 + h_2)}{(P_1 + P_2) h_1 h_2} n_1 n_2 s^3 + \frac{P_2}{h_2} n_2^2 s_2^3 \right\}, \\ &= -\frac{\pi}{n} p \{ n_1^2 s_1^3 + 2 n_1 n_2 s^3 + n_2^2 s_2^3 \};\end{aligned}$$

for

$$\frac{P_1}{h_1} = \frac{P_2}{h_2} = \frac{P_1 + P_2}{h_1 + h_2} = \frac{1}{n} \left(\frac{n_1 P_1}{h_1} + \frac{n_2 P_2}{h_2} \right) = \frac{2p}{n},$$

where

$$n = n_1 + n_2.$$

In the special case $s_1 = s_2 = s$, this becomes, as in § 30,

$$\frac{1}{4}\Sigma(Rr) = -\pi p n s^3.$$

To obtain an idea as to how the "ultimate volume," spoken of in that section, is affected by the difference of size of the particles, suppose $n_1 = n_2$. The values of the above quantities are

$$-\frac{\pi n}{4} p \{ s_1^3 + 2s^3 + s_2^3 \} \text{ and } -\pi n p s^3;$$

so that (as we might have expected) disparity of size, with the same mean of diameters, *increases* the quantity in question.

Thus, if

$$s_1 : s : s_2 :: 1 : 2 : 3,$$

the ratio of the expressions above is 11 : 8. The utmost value it can have (when s_1/s_2 is infinite, or is evanescent) is 5 : 2.

XII. Viscosity.

36. Suppose the motion of the gas, *as a whole*, to be of the nature of a simple shear; such that, relatively to the particles in the plane of yz , those in the plane x have a common speed

$$V = Bx$$

parallel to y . V , even when x is (say) a few inches, is supposed small compared with the speed of mean square. We have to determine the amount of momentum parallel to y which passes, per second, across unit area of the plane of yz .

In the stratum between x and $x + \delta x$ there are, per second per unit surface, $n v \delta x$ collisions discharging particles with speed v to $v + dv$ (distributed uniformly in all directions) combined, of course, with the speed of translation of the stratum. The number of these particles which cross the plane of yz at angles θ to $\theta + d\theta$ with the axis of x is

$$\epsilon^{-ex \sec \theta} \sin \theta d\theta / 2.$$

[Strictly speaking, the exponent should have had an additional term of the order eBx^2/v ; but this is insensible compared with that retained until x is a very large multiple of the mean free path. See the remarks in § 39 below.] Each takes with it (besides its normal contribution, which need not be considered) the abnormal momentum

$$PBx,$$

relatively to yz and parallel to y .

Hence the whole momentum so transferred from x positive is

$$\frac{PBn}{2} \int_0^\infty \nu v \int_0^{\frac{\pi}{2}} \sin \theta d\theta \int_0^\infty e^{-ex \sec \theta} ex dx,$$

or

$$\frac{PBn}{2} \int_0^\infty \frac{\nu v}{e} \int_0^{\frac{\pi}{2}} \cos^2 \theta \sin \theta d\theta = \frac{PBn}{6} \int_0^\infty \frac{\nu v}{e}.$$

Doubling this, to get the full differential effect across the plane of yz , it becomes (§ 33)

$$\frac{PBnC_1}{3\pi ns^2 \sqrt{h}} = \frac{PBn \cdot 0.838}{3\pi ns^2 \sqrt{h}}.$$

The multiplier of B , *i.e.* of dV/dx , is the coefficient of Viscosity. Its numerical value, in terms of density and mean path, is

$$\frac{\rho\lambda}{\sqrt{h}} 0.412.$$

CLERK-MAXWELL, in 1860, gave the value

$$\frac{\rho l}{\sqrt{h}} 0.376,$$

which (because $l=707\lambda/677$, as in § 11) differs from this in the ratio 20 : 21. In this case the short cuts employed have obviously entailed little numerical error. Since $\rho\lambda$ is constant for any one gas, the Viscosity (as MAXWELL pointed out) is independent of the density.

37. Both expressions are proportional to the square-root of the absolute temperature. We may see at once that, on the hypothesis we have adopted, such must be the case. For, if we suppose the speed of every sphere to be suddenly increased m fold, the operations will go on precisely as before, only m times faster. But the absolute temperature will be increased as $m^2 : 1$. Similar anticipations may be made in the cases of Diffusion and of Thermal Conductivity.

MAXWELL was led by his experimental measures of Viscosity, which seemed to show* that it increases nearly in proportion to the first power of the absolute temperature, to discard the notion of hard spheres, and to introduce the hypothesis of particles repelling one another with force inversely as the fifth power of the distance. I have already stated that there are very grave objections to the introduction of *repulsion* into this subject, except of course in the form of elastic restitution. That the particles of a gas have *this* property is plain from their capability of vibrating, so that they must lose energy of translation by impact; and I intend, in the next instalment of this investigation, so far to modify the fundamental assumption hitherto made as to deduce the effects corresponding to a coefficient of restitution less than unity; and also to take account of molecular *attraction*, specially limited in its range to distances not much greater than the diameter of a sphere.

XIII. *Thermal Conductivity.*

38. We must content ourselves with the comparatively simple case of the steady flow of heat in one direction; say parallel to the axis of x . This will be assumed to be vertical, the temperature in the gas increasing upwards, so as to prevent convection currents. No attention need, otherwise, be paid to the effects of gravity.

Hence the following conditions must be satisfied:—

- (a) Each horizontal layer of the gas is in the special state, compounded with a definite translation *vertically*.
- (b) The pressure is constant throughout the gas.
- (c) There is, on the whole, no passage of gas across any horizontal plane.
- (d) Equal amounts of energy are, on the whole, transferred (in the same direction) across unit area of all such planes.

39. Let n be the number of particles per unit volume in the layer between x and $x+dx$; ν the fraction of them whose speed, relatively to the neighbours as a whole, lies between v and $v+dv$; α the speed of translation of the layer.

The *number* of particles which pass, per unit area per second, from x positive through the plane $x=0$, is the sum of those escaping, after collision, from all the layers for positive x , and not arrested on their way:—viz.,

$$\frac{1}{2} \int_0^\infty \int_0^{\frac{\pi}{2}} \int_0^a n \nu v \cos \theta e^{-\sec \theta \int_0^x \alpha dx} \sin \theta d\theta \frac{v \cos \theta - \alpha}{v \cos \theta} dx.$$

Here α , though in any ordinary case it need not be more than a very small fraction of an inch, is a quantity large compared with the mean free path of a

* Cf., however, STOKES, *Phil. Trans.*, 1886, vol. clxxvii. p. 786.

particle. Its value will be more exactly indicated when the reason for its introduction is pointed out.

The last factor of the integrand depends on the fact that the particles are emitted from *moving* layers:—involving the so-called DÖPPLER, properly the RÖMER, principle.

We neglect, however, as insensible the difference between the absorption due to *slowly* moving layers and that due to the same when stationary.

Because α , the range of x , is small we may write with sufficient approximation

$$n = n_0 + n_0'x, \text{ \&c., \&c.}$$

Introducing this notation, the expression above becomes

$$\frac{1}{2} \int_0^\infty \int_0^{\frac{\pi}{2}} \int_0^a n_0 \nu_0 v e_0 \left(1 + \left(\frac{n_0'}{n_0} + \frac{\nu_0'}{\nu_0} + \frac{e_0'}{e_0} \right) x + \dots \right) e^{-\sec \theta \int_0^x e dx} \sin \theta d\theta \frac{v \cos \theta - \alpha}{v \cos \theta} dx.$$

Now, to the degree of approximation adopted,

$$\int_0^x e dx = e_0 x + e_0' x^2/2.$$

The second term of this must always be very small in comparison with the first, even for an exceptionally long free path. But, if we were to make

$$x = 2e_0/e_0'$$

the second term would become *equal* to the first. Hence a , the upper limit of the x integration, must be made much smaller than this quantity. Thus we may write

$$e^{-\sec \theta \int_0^x e dx} = e^{-e_0 x \sec \theta} (1 - e_0' x^2 \sec \theta/2 + \dots).$$

We said, above, that

$$e_0 a = a \frac{1}{e_0}$$

is a large number, say of the order 10^2 . It appears then at once that terms in

$$e^{-e_0 a} = e^{-100} = 10^{-43} \text{ nearly}$$

may be neglected. Such terms occur at the upper limit in the integration with regard to x above, and what we have said shows, *first* why a had to be introduced, *second* why it disappears from the result.

Writing now only those factors of the above expression which are concerned in the integration with respect to x , we have

$$\int_0^a \left(1 + \left(\frac{n_0'}{n_0} + \frac{\nu_0'}{\nu_0} + \frac{e_0'}{e_0} \right) x + \dots \right) \left(1 - e_0' x^2 \sec \theta/2 + \dots \right) e^{-e_0 x \sec \theta} dx,$$

or

$$\frac{1}{e_0} \left(\cos \theta + \frac{1}{e_0} \left(\frac{n_0'}{n_0} + \frac{\nu_0'}{\nu_0} \right) \cos^2 \theta \right).$$

The terms in e_0' are found to have cancelled one another, a result which greatly simplifies the investigation.

Had we complicated matters by introducing $\alpha_0 + \alpha_0'x$ in place of α , the term in α_0' (which, if it exist at all, is at least very small) would have been divided on integration *twice* by e_0 , a quantity whose value is, on the average, of the order $5 \cdot 10^5$ (to an inch as unit of length).

The expression now becomes

$$\frac{1}{2} \int_0^\infty \int_0^{\frac{\pi}{2}} n\nu \left(1 + \left(\frac{n'}{n} + \frac{\nu'}{\nu} \right) \frac{\cos \theta}{e} \right) (v \cos \theta - \alpha) \sin \theta d\theta.$$

We have omitted the zero suffixes, as no longer required; and, as the plane $x=0$ is arbitrary, the expression is quite general.

Omitting the product of the two small terms, and integrating with respect to θ , we have

$$\frac{1}{2} \int_0^\infty n\nu \left(v/2 - \alpha + \left(\frac{n'}{n} + \frac{\nu'}{\nu} \right) v/3e \right).$$

The corresponding expression for the number of particles which pass through the plane from the negative side is, of course, to be obtained by simply changing the signs of the two last terms. Thus, by (c) of § 38, we have

$$\int_0^\infty n\nu \left(\alpha - \left(\frac{n'}{n} + \frac{\nu'}{\nu} \right) v/3e \right) = 0,$$

or

$$\alpha = \int_0^\infty \nu \left(\frac{n'}{n} + \frac{\nu'}{\nu} \right) v/3e \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

40. The *pressure* at the plane $x=0$, taken as the whole momentum (parallel to x) which crosses it per unit area per second, is to be found by introducing into our first integrand the additional factor

$$P(v \cos \theta - \alpha),$$

where P is the mass of a particle. There results

$$\frac{P}{2} \int_0^\infty n\nu \left(v^2/3 - v\alpha + \left(\frac{n'}{n} + \frac{\nu'}{\nu} \right) v^2/4e \right).$$

We must take the *sum* of this, and of the same with the signs of the two last terms changed; so that the pressure (which is constant throughout, by (b) of § 38) is

$$p = \frac{P}{3} \int_0^\infty n\nu v^2 = \frac{Pn}{2h} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

Thus n/h is constant throughout the gas.

[If a very small, thin, disc were placed in the gas, with its plane parallel to yz , and the steady state not thereby altered, the difference of pressures on its sides would be

$$nP \int_0^\infty v \left(2v\alpha - \left(\frac{n'}{n} + \frac{v'}{v} \right) v^{2/2e} \right)$$

or

$$p_{0.677} \frac{\lambda}{h} \left(\frac{8}{3\sqrt{\pi}} \left(\frac{5}{2} C_1 - C_3 \right) - \frac{5}{2} C_2 + C_4 \right).$$

For ordinary pressures, and a temperature gradient 10° C. per inch, this is of the order 10^{-7} atmosphere only.]

41. For the *energy* which passes per second per unit of area across $x=0$, we must introduce into the first integrand of § 39 the additional factor

$$\frac{P}{2} (v^2 - 2v\alpha \cos \theta);$$

and the result of operations similar to those for the number of particles is

$$E = -\frac{P}{6} \int_0^\infty n v^3 \left(\left(\frac{n'}{n} + \frac{v'}{v} \right) \left| e - 5\alpha/v \right| \right) . \quad . \quad . \quad . \quad (3.)$$

This expresses the excess of the energy passing from the negative to the positive side of $x=0$, over that passing from positive to negative; and, by (d) of § 38 must be constant.

42. To put (1) and (3) in a more convenient and more easily intelligible form, note that because

$$v = 4 \sqrt{\frac{h^3}{\pi}} e^{-h v^2} v^2 dv$$

we have

$$\frac{v'}{v} = \frac{3}{2} \frac{h'}{h} - h' v^2.$$

But, by (2),

$$\frac{n'}{n} = \frac{h'}{h}.$$

Thus, by (1),

$$\begin{aligned} \alpha &= \frac{h'}{h} \int_0^\infty v \left(\frac{5}{2} - h v^2 \right) \left| 3e \right|, \\ &= \frac{h'}{3\sqrt{h^3}} \frac{1}{n\pi s^2} \left(\frac{5}{2} C_1 - C_3 \right), \\ &= \frac{h'}{\sqrt{h^3}} \frac{P}{6p\pi s} \left(\frac{5}{2} C_1 - C_3 \right) . \quad . \quad . \quad . \quad . \quad (1') \end{aligned}$$

Similarly (3) becomes

$$E = \frac{h'}{\sqrt{h^3}} \frac{P}{6\pi s^2} \left(\frac{25}{4} C_1 - 5C_3 + C_5 \right) . \quad . \quad . \quad . \quad (3')$$

43. The only variable factor ($h'/h^{\frac{5}{2}}$) in these expressions for α , and for E , is the same in both. Hence, as E does not vary with x , $h'/h^{\frac{5}{2}}$ is constant, and so also is α . Thus since, if τ be absolute temperature, we have

$$h\tau = \text{constant};$$

we find at once,

$$\tau^{\frac{3}{2}} = A + Bx.$$

Thus the distribution of temperature, and therefore that of density, is determined when the terminal conditions are given. The formula just given agrees with the result first obtained by CLAUSIUS in an extremely elaborate investigation,* in which he showed that MAXWELL'S earliest theory of Heat-Conduction by gases is defective.

The general nature of the motion of the gas is now seen to be analogous to that of liquid mud when a scavenger tries to sweep it into a heap. The broom produces a translatory motion of the mud, which is counteracted by gravitation-sliding due to the surface gradient:—just as the displacement (by translation) of the whole gas, from hot to cold, is counteracted by the greater number of particles discharged (after collisions) from a colder and denser layer, than from an adjoining warmer and less dense layer.

44. The results of calculation of values of C , given in the *Appendix* enable us to put the expressions (1') and (3') into the more convenient forms

$$\alpha = \frac{h'}{\sqrt{h^5}} \frac{\rho\lambda}{p} 0.06 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1'')$$

$$E = \frac{h'}{\sqrt{h^5}} \rho\lambda 0.45 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3'')$$

where it is to be remarked that the product $\rho\lambda$ is independent of the temperature of the gas.

The Conductivity, k , is defined by the equation

$$k \frac{d\tau}{dx} = -E,$$

and thus its value is

$$k = \sqrt{\frac{\tau}{\tau_0^3}} \frac{\rho\lambda}{\sqrt{h_0^3}} 0.45,$$

where τ_0 , h_0 are simultaneous values of τ and h .

At 0°C . (*i.e.* $\tau = 274$) this is, for air, nearly 3.10^{-5} in thermal units on the pound-foot-minute-Centigrade system:—*i.e.* about $1/28,000$ of the conductivity of iron, or $1/3600$ of that of lead.† Of course, with our assumption

* *Pogg. Ann.*, cxv, 1862; *Phil. Mag.*, 1862, I.

† *Trans. R. S. E.*, 1878, p. 717.

of hard spherical particles, we have not reckoned the part of the conducted energy which, in real gases, is due to rotation or to vibration of individual particles.

XIV. *Diffusion.*

45. The complete treatment of this subject presents difficulties of a very formidable kind, several of which will be apparent even in the comparatively simple case which is treated below. We take the case of a uniform vertical tube, of unit area in section, connecting two vessels originally filled with different gases, or (better) mixtures of the same two gases in different proportions, both, however, maintained at the same temperature; and we confine ourselves to the investigation of the motion when it can be treated as approximately steady. We neglect the effect of gravity (the denser gas or mixture being the lower), and we suppose the speeds of the group-motions to be very small in comparison with the speed of mean square in either gas. [In some of the investigations which follow, there are (small) parts of the diffusion-tube in which one of the gases is in a hopeless minority as regards the other. Though one of the initial postulates (d of § 1) is violated, I have not thought it necessary to suppress the calculations which are liable to this objection; for it is obvious that the conditions, under which alone it could arise, are unattainable in practice.]

CLERK-MAXWELL'S Theorem (§ 15), taken in connection with our preliminary assumption, shows that at every part of the tube the number of spheres per cubic unit, and their average energy, are the same. Hence, if n_1, n_2 , be the numbers of the two kind of spheres, per cubic unit, at a section x of the tube

$$n_1 + n_2 = n = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

Also, if P_1, P_2 , be the masses of the spheres in the two systems respectively, h_1 and h_2 the measures (§ 3) of their mean square speeds, we have

$$P_1/h_1 = P_2/h_2 = (n_1 P_1/h_1 + n_2 P_2/h_2)/n = 2p/n, \quad . \quad . \quad . \quad (2.)$$

where p is the constant pressure.

Strictly speaking, the fact that there is a translational speed of each layer of particles must affect this expression, but only by terms of the first order of small quantities.

46. The number of particles of the P_1 kind which pass, on the whole, towards positive x through the section of the tube is (as in § 39)

$$n_1 \alpha_1 - n_1' \int_0^\infty v_1 v / 3 e_1;$$

where α_1 is the (common) translational speed of the P_1 s, and $1/e_1$ the mean

free path of a P_1 whose speed is v . We obtain this by remarking that, in the present problem, h_1 is regarded as constant, so that there is no term in v_1' .

Hence, if G_1 be the mass of the first gas on the negative side of the section, divided by the area of the section, we have

$$\frac{dG_1}{dt} = -P_1(n_1\alpha_1 - n_1'\alpha_1/3) \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

If G_2 be the corresponding mass of the second gas, we have (noting that, by (1), $n_1' + n_2' = 0$)

$$\frac{dG_2}{dt} = -P_2(n_2\alpha_2 + n_1'\alpha_1/3) \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

From the definitions of the quantities G_1 , G_2 , we have also

$$\left. \begin{aligned} \frac{dG_1}{dx} &= P_1 n_1, & \frac{d^2 G_1}{dx^2} &= P_1 n_1', \\ \frac{dG_2}{dx} &= P_2 n_2, & \frac{d^2 G_2}{dx^2} &= -P_2 n_1'. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (5.)$$

47. We have now to form the equations of motion for the layers of the two gases contained in the section of the tube between x and $x + \delta x$. The increase of momentum of the P_1 layer is due to the difference of pressures, behind and before, caused by P_1 s; minus the resistance due to that portion of the impacts of some of the P_1 s against P_2 s in the section itself, which depends upon the relative speeds of the two systems, each as a whole. This is a small quantity of the order the whole pressure on the surfaces of the particles multiplied by the ratio of the speed of translation to that of mean square. The remaining portion (relatively very great) of the impacts in the section is employed, as we have seen, in maintaining or restoring the "special state" in each gas, as well as the MAXWELL condition of partition of energy between the two gases. If R be the resistance in question, the equations of motion are

$$\left. \begin{aligned} \frac{\partial}{\partial t}(P_1 n_1 \alpha_1 \delta x) &= -\frac{1}{2} \frac{d}{dx} \left(\frac{P_1 n_1}{h_1} \right) \delta x - R \delta x, \\ \frac{\partial}{\partial t}(P_2 n_2 \alpha_2 \delta x) &= -\frac{1}{2} \frac{d}{dx} \left(\frac{P_2 n_2}{h_2} \right) \delta x + R \delta x, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (6.)$$

where ∂ represents *total* differentiation.

48. To calculate the value of R , note that, in consequence of the assumed smallness of α_1 , α_2 , relatively to the speeds of mean square of the particles, the number of collisions of a P_1 with a P_2 , and the circumstances of each, may be treated as practically the same as if α_1 and α_2 were each zero:—*except* in so far

that there will be, in the expression for the relative speed in the direction of the line of centres at impact, an additional term

$$(\alpha_1 - \alpha_2) \cos \psi,$$

where ψ is the inclination of the line of centres to the axis of x . Thus to the impulse, whose expression is of the form

$$-\frac{2PQ}{P+Q}(u-v),$$

as in § 19 of the First Part of the paper, there must be added the term we seek, viz.,

$$-\frac{2P_1P_2}{P_1+P_2}(\alpha_1 - \alpha_2) \cos \psi.$$

This must be resolved again parallel to x , for which we must multiply by $\cos \psi$. Also, as the line of centres may have with equal probability all directions, we must multiply further by $\sin \psi d\psi/2$, and integrate from 0 to π . The result will be the average transmission, per collision, per P_1 , of *translatory* momentum of the layer parallel to x . Taking account of the number of impacts of a P_1 on a P_2 , as in § 23, we obtain finally

$$R = \frac{4}{3} n_1 n_2 s^2 \sqrt{\frac{\pi(h_1+h_2)}{h_1 h_2}} \frac{P_1 P_2}{P_1 + P_2} (\alpha_1 - \alpha_2) \quad . \quad . \quad . \quad (7.)$$

where s is the semi-sum of the diameters of a P_1 and a P_2 .

49. To put this in a more convenient form, note that (2), in the notation of (5), gives us the relation

$$\frac{1}{h_1} \frac{dG_1}{dx} + \frac{1}{h_2} \frac{dG_2}{dx} = 2p,$$

whence

$$G_1/h_1 + G_2/h_2 = 2px. \quad . \quad . \quad . \quad . \quad . \quad (8.)$$

We have not added an arbitrary constant, for no origin has been specified for x . Nor have we added an arbitrary function of t , because (as will be seen at once from (3)) this could only be necessary in cases where the left-hand members of (6) are quantities comparable with the other terms in these equations. They are, however, of the order of

$$\frac{d^2 G_1}{dt^2}, \quad \frac{d^2 G_1}{dx dt} \alpha_1, \quad \&c.,$$

and cannot rise into importance except in the case of motions much more violent than those we are considering.

From (8) we obtain

$$\frac{dG_1}{dt} / h_1 + \frac{dG_2}{dt} / h_2 = 0, \quad . \quad . \quad . \quad . \quad . \quad (9.)$$

which signifies that equal *volumes* of the two gases pass, in the same time, in opposite directions through each section of the tube. This gives a general description of the nature of the cases to which our investigations apply.

But, by (3) and (4), we have for the value of

$$P_1 P_2 n_1 n_2 (\alpha_1 - \alpha_2)$$

the expression

$$-P_2 n_2 \left(\frac{dG_1}{dt} - \frac{1}{3} P_1 n_1' \mathfrak{C}_1 \right) + P_1 n_1 \left(\frac{dG_2}{dt} + \frac{1}{3} P_2 n_2' \mathfrak{C}_1 \right);$$

or, by (9), (2), and (5)

$$-2ph_2 \left(\frac{dG_1}{dt} - \frac{1}{3n} \frac{d^2 G_1}{dx^2} (n_{21} \mathfrak{C}_1 + n_{12} \mathfrak{C}_1) \right).$$

Substituting this for the corresponding factors of R in the first of equations (6), and neglecting the left-hand side, we have finally

$$0 = -\frac{1}{2h_1} \frac{d^2 G_1}{dx^2} + \frac{8}{3s^2} \sqrt{\frac{\pi(h_1 + h_2)}{h_1 h_2}} \frac{ph_2}{P_1 + P_2} \left\{ \frac{dG_1}{dt} - \frac{1}{3n} \frac{d^2 G_1}{dx^2} (n_{21} \mathfrak{C}_1 + n_{12} \mathfrak{C}_1) \right\}$$

or

$$\frac{dG_1}{dt} = \left(\frac{3}{16s^2} \frac{P_1 + P_2}{\sqrt{\pi(h_1 + h_2)h_1 h_2}} \cdot \frac{1}{p} + \frac{1}{3n} (n_{21} \mathfrak{C}_1 + n_{12} \mathfrak{C}_1) \right) \frac{d^2 G_1}{dx^2};$$

or, somewhat more elegantly,

$$\frac{dG_1}{dt} = \left(\frac{3}{8ns^2} \sqrt{\frac{h_1 + h_2}{\pi h_1 h_2}} + \frac{1}{3n} (n_{21} \mathfrak{C}_1 + n_{12} \mathfrak{C}_1) \right) \frac{d^2 G_1}{dx^2}. \quad (10.)$$

50. This equation resembles that of FOURIER for the linear motion of heat; but, as already stated in § 34, the quantities $\mathfrak{C}_1$ which occur in it render it in general intractable. The first part of what is usually called the *diffusion-coefficient* (the multiplier of $d^2 G_1/dx^2$ above) is constant; but the second, as is obvious from (5) and (8), is, except in the special case to which we proceed, a function of dG_1/dx ; *i.e.* of the percentage composition of the gaseous mixture.

51. In the special case of equality, both of mass and of diameter, between the particles of the two systems, the diffusion-coefficient becomes

$$D = \frac{3}{8ns^2} \sqrt{\frac{2}{\pi h}} + \frac{C_1}{3n\pi s^2 \sqrt{h}},$$

or

$$D = \left(\frac{3}{4} \sqrt{\frac{\pi}{2}} + \frac{C_1}{3} \right) \frac{\lambda}{0.677 \sqrt{h}} = \frac{\lambda}{\sqrt{h}} 1.8,$$

where λ is the mean free path in the system. Hence the diffusion-coefficient among equal particles is directly as the mean free path, and as the square root of the absolute temperature. FOURIER'S solutions of (10) are of course applicable in this special case.

If we now suppose that our arrangement is a tube of length l and section S , connecting two infinite vessels filled with the two gases respectively; and, farther, assume that the diffusion has become steady, the equation (10) becomes

$$\frac{dG_1}{dt} = D \frac{d^2 G_1}{dx^2},$$

where the left-hand member is constant. Also, it is clear that, since dG_1/dx must thus be a *linear* function of x , we have

$$\frac{dG_1}{dx} = Pn_1 = Pn \left(1 - \frac{x}{l}\right),$$

so that the mass of either gas which passes, per second, across any section of the tube is

$$SD\rho/l$$

where ρ is the common density of the two gases.

For comparison with the corresponding formulæ in the other cases treated below, we may now write our result as

$$l \frac{dG_1}{dt} = - \frac{P}{\pi s^2 \sqrt{h}} 1.22.$$

Also, to justify our assumption as to the order of the translatory speed, we find by (3)

$$\alpha_1 = \frac{1.38\lambda}{(l-x)\sqrt{h}}.$$

Hence, except where $l-x$ is of the order of one thousandth of an inch or less, this is very small compared with $h^{-\frac{1}{2}}$. And it may safely be taken as impossible that n_1 can (experimentally) be kept at 0 at the section $x=l$.

If the vessels be of finite size, and if we suppose the contents of each to be always thoroughly mixed, we can approximate to the law of mixture as follows. On looking back at the last result, we see that for ρ we must now substitute the *difference* of densities of the first gas at the ends of the connecting tube. Let g_1, g_2 be the quantities of the two gases which originally filled the vessels respectively; and neglect, in comparison with them, the quantity of either gas which would fill the tube. Then, obviously,

$$\frac{dG_1}{dt} = - \frac{SD\rho}{l} \left(\frac{G_1}{g_1} - \frac{g_1 - G_1}{g_2} \right),$$

whence

$$G_1 = \frac{g_1 g_2}{g_1 + g_2} \left\{ \frac{g_1}{g_2} + e^{-\frac{SD\rho}{l} \frac{g_1 + g_2}{g_1 g_2} t} \right\}.$$

This shows the steps by which the initial state $(g_1, 0)$ tends asymptotically to

the final state $\left(\frac{g_1}{g_1+g_2} g_1, \frac{g_2}{g_1+g_2} g_1\right)$, in which the gases are completely mixed. When the vessels are equal this takes the simple form

$$G_1 = \frac{g}{2} \left(1 + \epsilon^{-\frac{2SD\rho t}{g^l}}\right).$$

52. In the case just treated there is no transmission of energy, so that the fundamental hypotheses are fully admissible. In general, however, it is not so. The result of § 41, properly modified to apply to the present question, shows that the energy which, on the whole, passes positively across the section x is, per unit area per second,

$$\frac{5}{4} \left(\frac{P_1 n_1 \alpha_1}{h_1} + \frac{P_2 n_2 \alpha_2}{h_2} \right) - \frac{1}{6} n_1' (P_{11} \mathcal{C}_3 - P_{22} \mathcal{C}_3).$$

This, of course, in general differs from section to section, and thus a disturbance of temperature takes place. In such a case we can no longer assume that h_1 and h_2 are absolute constants; and thus terms in $\mathcal{C}_5$ would come in; just as a term in C_5 appeared in the expression for energy conducted (§ 42). Thus, in order that our investigation may be admissible, the process must be conducted at constant temperature. This, in general, presupposes conditions external to the apparatus.

53. Though it appears hopeless to attempt a general solution of equation (10), we can obtain from it (at least approximately) the conditions for a steady state of motion such as must, we presume, finally set in between two infinite vessels filled with different gases at the same temperature and pressure. For the left-hand member is then an (unknown) constant, a second constant is introduced by integrating once with respect to x ; and these, which determine the complete solution, are to be found at once by the terminal conditions

$$\frac{1}{P_1} \frac{dG_1}{dx} = n_1 = \begin{cases} n & \text{for } x=0, \\ 0 & \text{,, } = l. \end{cases} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11.)$$

And, by a slight but obvious modification of the latter part of § 51 above, we can easily extend the process to the case in which the vessels are of finite size:—always, however, on the assumption that their contents may be regarded as promptly assuming a state of uniform mixture. The consideration of § 52, however, shows that the whole of the contents must be *kept* at constant temperature, in order that this result may be strictly applicable.

54. Recurring to the special case of § 51, let us now suppose that, while the masses of the particles remain equal, their diameters are different in the two gases. Thus, suppose $s_1 > s_2$. Then it is clear that

$$s_1^2 - s^2, \quad \text{and} \quad s^2 - s_2^2,$$

are both positive. In this case, infinite terminal vessels being supposed, (10) gives for the steady state

$$A = \frac{P}{\pi n \sqrt{h}} \left\{ \frac{3}{4s^2} \sqrt{\frac{\pi}{2}} + \frac{C_1}{3} \left(\frac{n_2}{n_1 s_1^2 + n_2 s^2} + \frac{n_1}{n_1 s^2 + n_2 s_2^2} \right) \right\} \frac{dn_1}{dx}; \quad (12.)$$

whose integral, between limits as in (11) above, is

$$-Al = \frac{P}{\pi n \sqrt{h}} \left\{ \frac{3n}{4s^2} \sqrt{\frac{\pi}{2}} + \frac{C_1 n}{3} \left(\frac{1}{s^2 - s_2^2} - \frac{1}{s_1^2 - s^2} + \frac{2s_1^2}{(s_1^2 - s^2)^2} \log \frac{s_1}{s} + \frac{2s_2^2}{(s^2 - s_2^2)^2} \log \frac{s_2}{s} \right) \right\}.$$

Here A is the rate of passage of the first gas, in *mass* per second per unit area of the section of the tube.

If now we put

$$s_1 = s + \sigma, \quad s_2 = s - \sigma,$$

then, when σ is small compared with s , the multiplier of $C_1 n/3$ is

$$(1 + \sigma^2/3s^2)/s^2, \text{ nearly.}$$

When σ is nearly equal to s , *i.e.* one of the sets of particles exceedingly small compared with the other, it is nearly

$$1.283/s^2.$$

Thus it appears that a difference in size, the mean of the diameters being unchanged, favours diffusion.

Suppose, for instance,

$$s_1 : s : s_2 :: 3 : 2 : 1,$$

and we have

$$\begin{aligned} A &= -\frac{P}{\pi l s^2 \sqrt{h}} \left\{ \frac{3}{4} \sqrt{\frac{\pi}{2}} + \frac{2C_1}{3} \left(\frac{4}{15} + \frac{36}{25} \log \frac{3}{2} + \frac{4}{9} \log \frac{1}{2} \right) \right\}, \\ &= -\frac{P}{\pi l s^2 \sqrt{h}} \left\{ \frac{3}{4} \sqrt{\frac{\pi}{2}} + \frac{C_1}{3} 1.085 \right\} = -\frac{P}{\pi l s^2 \sqrt{h}} 1.24, \\ &= -\frac{\rho \lambda}{l \sqrt{h}} 1.83. \end{aligned}$$

Compare this with the result for equal particles (§ 51), remembering that λ now stands for the mean free path of a particle of either gas in a space filled with the other:—and we see that (so long at least as the masses are equal) diffusion depends mainly upon the mean of the diameters, being but little affected by even a considerable disparity in size between the particles of the two gases. Thus it appears that the viscosity and (if the experimental part of the inquiry could be properly carried out) conductivity give us much more definite information as to the relative sizes of particles of different gases than we can obtain from the results of diffusion.

Equation (12) shows how the *gradient* of density of either gas varies, in the stationary state, with its percentage in the mixture. For the multiplier of $\frac{dn_1}{dx}$ is obviously a maximum when

$$\frac{1}{s^2 + y s_1^2} + \frac{1}{s^2 + s_2^2/y},$$

in which $y = n_1/n_2$, is so. This condition gives

$$n_1/n_2 = y = s_2/s_1.$$

Hence the gradient is *least* steep at the section in which the proportion of the two gases is inversely as the ratio of the diameters of their particles; and it increases either way from this section to the ends of the tube, at each of which it has the same (greatest) amount. This consideration will be of use to the full understanding of the more complex case (below) in which the masses, as well as the diameters, of the particles differ in the two gases.

55. Let us now suppose the mass per particle to be different in the two gases. The last terms of the right-hand side of (10), viz.,

$$\frac{1}{3n} (n_{21} \mathfrak{C}_1 + n_{12} \mathfrak{C}_1) \frac{d^2 G_1}{dx^2},$$

may be written in the form

$$\frac{P_1}{3\pi n} \frac{dn_1}{dx} \left\{ \frac{(n-n_1)h_2}{\sqrt{h_1}} \int_0^\infty \frac{f(y)dy}{n_1 h_2 s_1^2 F(y) + (n-n_1)h_1 s^2 F\left(y \sqrt{\frac{h_2}{h_1}}\right)} + \frac{n_1 h_1}{\sqrt{h_2}} \int_0^\infty \frac{f(y)dy}{(n-n_1)h_1 s_2^2 F(y) + n_1 h_2 s^2 F\left(y \sqrt{\frac{h_1}{h_2}}\right)} \right\}$$

where the meanings of f and F are as in § 34.

If we confine ourselves to the steady state, we may integrate (10) directly with respect to x , since dG_1/dt is constant. In thus operating on the part just written, the integration with regard to x (with the limiting conditions as in (11)) can be carried out under the sign of integration with respect to y :—and then the y integration can be effected by quadratures.

The *form* of the x integral is the same in each of the terms. For

$$\int_n^0 \frac{(n-n_1)dn_1}{An_1 + B(n-n_1)} = \int_n^0 \frac{n_1 dn_1}{A(n-n_1) + Bn_1} = \frac{n}{A-B} \left\{ 1 + \frac{A}{A-B} \log \frac{B}{A} \right\}.$$

This expression is necessarily negative, as A and B are always positive. When A and B are nearly equal, so that $B = (1+e)A$, its value is

$$-\frac{n}{A} \left(\frac{1}{2} - \frac{e}{3} + \dots \right),$$

so that, even when A and B are equal, there is no infinite term.

It is easy to see, from the forms of $F(y)$, and of its first two differential coefficients, that the equation

$$h_2 s_1^2 F(y) = h_1 s_2^2 F\left(y \sqrt{\frac{h}{h_1}}\right)$$

can hold for, at most, *one* finite positive value of y .

56. As a particular, and very instructive case, let us suppose

$$P_1 : P_2 :: h_1 : h_2 :: 16 : 1,$$

the case of oxygen and hydrogen.

(a) First, assume the diameters to be equal. Then the integral of (10), with limits as in (11), taken on the supposition that the flow is constant, is

$$l \frac{dG_1}{dt} = -\frac{P_1}{\pi s^2 \sqrt{h_1}} \left\{ \frac{3}{8} \sqrt{17\pi} - \frac{1}{3} \int_0^\infty dy \left(\frac{f(y) - 16f\left(\frac{y}{4}\right)}{F(y) - 16F\left(\frac{y}{4}\right)} + \frac{F(y)f(y) - 16^2 F\left(\frac{y}{4}\right)f\left(\frac{y}{4}\right)}{\left(F(y) - 16F\left(\frac{y}{4}\right)\right)^2} \log \frac{16F\left(\frac{y}{4}\right)}{F(y)} \right) \right\}$$

As remarked above, the definite integral is essentially negative. For so is every expression of the form

$$\frac{a-b}{A-B} + \frac{Aa-Bb}{(A-B)^2} \log \frac{B}{A}$$

provided A , B , a , and b be all positive. When A and B are equal its value is

$$-\frac{1}{2A}(a+b).$$

I have made a rough attempt at evaluation of the integral, partly by calculation, partly by a graphic method. My result is, at best, an approximation, for the various instalments of the quadrature appear as the relatively small *differences* of two considerable quantities. Thus the three decimal places, to which, from want of leisure, I was obliged to confine myself, are not sufficient to give a very exact value. The graphical representations of my numbers were, however, so fairly smooth that there seems to be little risk of large error. The *full* curve in the sketch below shows (on a ten-fold scale) the values of the integrand (with their signs changed), as ordinates, to the values of y as abscissæ. The area is about -2.165 . Hence we have

$$l \frac{dG_1}{dt} = -\frac{P_1}{\pi s^2 \sqrt{h_1}} 3.463,$$

(b) Suppose next that the diameter of a P_1 is three times that of a P_2 , but the semi-sum of the diameters is s as before. The definite integral takes the form

$$\int_0^{\infty} dy \left\{ \frac{f(y)}{\frac{9}{4}F(y) - 16F\left(\frac{y}{4}\right)} - \frac{16f\left(\frac{y}{4}\right)}{F(y) - 4F\left(\frac{y}{4}\right)} + \frac{\frac{9}{4}F(y)f(y)}{\left(\frac{9}{4}F(y) - 16F\left(\frac{y}{4}\right)\right)^2} \log \frac{64F\left(\frac{y}{4}\right)}{9F(y)} - \frac{64F\left(\frac{y}{4}\right)f\left(\frac{y}{4}\right)}{\left(F(y) - 4F\left(\frac{y}{4}\right)\right)^2} \log \frac{4F\left(\frac{y}{4}\right)}{F(y)} \right\}$$

The corresponding curve is exhibited by the dashed line in the sketch, and its area is about -3.157 . Hence, in this case,

$$l \frac{dG_1}{dt} = - \frac{P_1}{\pi s^2 \sqrt{h_1}} 3.793.$$

(c) Still keeping the sum of the semidiameters the same, let the diameter of a P_2 be three times that of a P_1 . The integral is

$$\int_0^{\infty} dy \left\{ \frac{f(y)}{\frac{1}{4}F(y) - 16F\left(\frac{y}{4}\right)} - \frac{16f\left(\frac{y}{4}\right)}{F(y) - 36F\left(\frac{y}{4}\right)} + \frac{\frac{1}{4}F(y)f(y)}{\left(\frac{1}{4}F(y) - 16F\left(\frac{y}{4}\right)\right)^2} \log \frac{64F\left(\frac{y}{4}\right)}{F(y)} - \frac{576F\left(\frac{y}{4}\right)f\left(\frac{y}{4}\right)}{\left(F(y) - 36F\left(\frac{y}{4}\right)\right)^2} \log \frac{36F\left(\frac{y}{4}\right)}{F(y)} \right\}.$$

The curve is the dotted line in the cut, and its area is about -1.713 . Hence we have

$$l \frac{dG_1}{dt} = - \frac{P_1}{\pi s^2 \sqrt{h_1}} 3.312.$$

If we compare these values, obtained on such widely different assumptions as to the relative diameters of the particles, we see at once how exceedingly difficult would be the determination of diameters from observed results as to diffusion. (Compare § 54.)

But we see also how diffusion varies with the relative size of the particles, the sum of the diameters being constant. For the smaller, relatively, are the particles of smaller mass (those which have the greater mean-square speed) the more rapid is the diffusion.

And further, by comparison with the results of §§ 51, 54, we see how much more quickly a gas diffuses into another of different specific gravity than into another of the same specific gravity.

When the less massive particles are indefinitely small in comparison with the others, the diameter of these is s ; and for their rate of diffusion we have

$$l \frac{dG}{dt} = - \frac{P_1}{\pi s^2 \sqrt{h_1}} 4.26.$$

When it is the more massive particles which are evanescent in size, the numerical factor seems to be about 3.48. Hence it would appear that, even in the case of masses so different, there is a *minimum* value of the diffusion-coefficient, which is reached before the more massive particles are infinitesimal compared with the others.

[At one time I thought of expressing the results of this section in a form similar to that adopted in the expression for D in § 51. It is easy to see that the quantity corresponding to λ would now be what may be called the mean free path of a *single* particle of one gas in a space filled with another. Its value would be easily calculated by the introduction of h_1 for h in the factor ν of the integral

$$\int_0^\nu \frac{\nu}{e}$$

while keeping e in terms of h . This involves multiplication of each number in the fourth column of the *Appendix* to Part I. by the new factor $e^{-(h_1-h)x^2} h_1^{\frac{3}{2}}/h^{\frac{3}{2}}$. But, on reflection, I do not see that much would be gained by this.]

APPENDIX.

The notation is the same as in the Appendix to Part I.

x	xX_1/X_2	x^2X_1/X_2	x^3X_1/X_2	x^5X_1/X_2
0.1	·000049	·000005	·000001	·000000
·2	·000758	·000152	·000030	·000001
·3	·003594	·001078	·000323	·000029
·4	·010364	·004146	·001658	·000265
·5	·022505	·011252	·005626	·001407
·6	·040512	·024307	·014584	·005250
·7	·063623	·044536	·031175	·015276
·8	·089928	·071942	·057554	·036834
·9	·116712	·105041	·094537	·076575
1.0	·141040	·141040	·141040	·141040
1.1	·160292	·176321	·193953	·234683
1.2	·172656	·207187	·248624	·358019
1.3	·177229	·230398	·299517	·506184
1.4	·174174	·243844	·341382	·669108
1.5	·164430	·246645	·369968	·832427
1.6	·149568	·239309	·382894	·980209
1.7	·131393	·223368	·379726	1.097407
1.8	·111654	·200977	·361758	1.172098
1.9	·091960	·174724	·331976	1.198432
2.0	·073480	·146960	·293920	1.175680
2.1	·057015	·119731	·251435	1.108829
2.2	·043032	·094670	·208274	1.008046
2.3	·031579	·072632	·167054	·883714
2.4	·022584	·054202	·130085	·749288
2.5	·015750	·039375	·098438	·615234
2.6	·010686	·027784	·072238	·488332
2.7	·007074	·019099	·051567	·375926
2.8	·004536	·012701	·035563	·278812
2.9	·002871	·008326	·024145	·203063
3.0	·001710	·005130	·015390	·138510
3.1	·001071	·003320	·010294	·098925
3.2	·000629	·002014	·006445	·065997
3.3	·000361	·001192	·003935	·042852
3.4	·000211	·000689	·002344	·027098
3.5	·000111	·000389	·001361	·016671
3.6	·000066	·000240	·000865	·010004
3.7	·000037	·000136	·000505	·005839
3.8			·000229	·003307
3.9			·000118	·001798
4.0			·000062	·000985
	2.095244	2.954862	4.630593	14.624154

Thus the values of C_1 , C_2 , C_3 , and C_5 are respectively 0.838, 1.182, 1.852, and 5.849.