ward : and above all, the principle of selection should be other than that of competitive examination. The man with the peculiar talents and proved industry which are wanted for the post must be carefully sought for, and the place must be made for him, rather than the man manufactured for the place. The managing body must be allowed perfect liberty either to found a new Fellowship for the particular man, or to refuse to fill up a vacant appointment. All our Research Fellows will be, according to the German system, in extraordinary posts. From this it will follow that direct endowment of this kind, though the ultimate aim of our efforts, and by far the principal part of our scheme, is not the manner in which a beginning should be made. This form of endowment, so far as can at present be foreseen, must be comparatively exceptional, and therefore, when the right man is found, his position should be made one of handsome emolument, and it ought to be rendered impossible that he should be negligently passed over.

The other ways in which research should be endowed may be regarded in the ultimate scheme as chiefly subsidiary to this, but in the order of time they must come first. The funds of the Colleges which are not wanted for teaching purposes, may at once be utilised for our object in an infinite number of indirect ways. They ought to be regarded as an abundant reservoir, from which may be continually drawn generous encouragement and ready help for those who happen to be carrying on some special investigation in any branch of Science. The Colleges should take the place which was occupied in England some century ago by those noble and wealthy patrons to whom Science, Art, and Literature all owe so much. They should give in no grudging spirit, for they may be assured that an apparent waste in one direction will be amply compensated by the unlooked-for returns which they will reap in another. By throwing open their libraries, by building museums and laboratories, by supplying instruments or needful materials, by paying for laborious calculations or expensive publications, as well as by subsidising any particular investigation, they would breed up, so far as any artificial means can, that race of men from whom the selection must afterwards be made for their new Fellowships. To those who have had unfortunate experience of the management of college business, and of the sort of matters which come before a college meeting, such a reform as has been sketched out will doubtless appear as a visionary ideal ; yet it might be realised with very little trouble if the richest Colleges would transfer some of the attention which they now bestow upon ecclesiastical and educational interests, to the cause of original research, and when realised, the result would be more nearly akin than the present, to that which the original statutes contemplated.

To answer the two other questions proposed need not take long, for an implicit reply to them has already been given. Fortunately, modern Science has taken such definite shape, and is pursued in such full publicity, that each branch has even now, at its head, certain acknowledged leaders, to whose judgments and recommendations in their special subjects, all deference is due. Until the Universities and the Colleges become sufficiently penetrated with the new scientific

spirit, it will be natural that they should endow research under the guidance of the scientific societies, and of course it will be always necessary that they should be fully conscious of their responsibilities to the public for the appointments they confer upon the candidates, however selected. The analogy of the Smithsonian Institution will here again come in, for its assistance is never given in any case unless after a favourable report from a Commission of scientific men, who are experts in the particular matter submitted to them.

With regard to the objection that the plan will inevitably tend to the foundation of a new store of sinecures, it is not incumbent to say more than that scientific posts, where the duty itself is of absorbing pleasure, are the least likely to degenerate in the way suggested, and that the insinuation comes with an ill grace from those who are the present recipients of benefactions which they do so little to deserve.   C.

ON LOSCHMIDT'S EXPERIMENTS ON DIFFUSION IN RELATION TO THE KINETIC THEORY OF GASES

THE kinetic theory asserts that a gas consists of separate molecules, each moving with a velocity amounting, in the case of hydrogen, to 1,800 metres per second. This velocity, however, by no means determines the rate at which a group of molecules set at liberty in one part of a vessel full of the gas will make their way into other parts. In spite of the great velocity of the molecules, the direction of their course is so often altered and reversed by collision with other molecules, that the process of diffusion is comparatively a slow one.

The first experiments from which a rough estimate of the rate of diffusion of one gas through another can be deduced are those of Graham.[*] Professor Loschmidt, of Vienna, has recently[†] made a series of most valuable and accurate experiments on the interdiffusion of gases in a vertical tube, from which he has deduced the coefficient of diffusion of ten pairs of gases. These results I consider to be the most valuable hitherto obtained as data for the construction of a molecular theory of gases.

There are two other kinds of diffusion capable of experimental investigation, and from which the same data may be derived, but in both cases the experimental methods are exposed to much greater risk of error than in the case of diffusion. The first of these is the diffusion of momentum, or the lateral communication of sensible motion from one stratum of a gas to another. This is the explanation, on the kinetic theory, of the viscosity or internal friction of gases. The investigation of the viscosity of gases requires experiments of great delicacy, and involving very considerable corrections before the true coefficient of viscosity is obtained. Thus the numbers obtained by myself in 1865 are nearly double of those calculated by Prof. Stokes from the experiments of Baily on pendulums, but not much more than half those deduced by O. E. Meyer from his own experiments. The other kind of diffusion is that of the energy of agitation of the molecules. This is called the conduction of heat. The experimental investigation

[*] *Brande's Journal* for 1829, pt. ii., p. 74, "On the Mobility of Gases," Phil. Trans., 1863.
[†] Sitzb. d. k. Akad. d. Wissench, 10 März. 1870.

of this subject is confessedly so difficult, that it is only recently that Prof. Stefan of Vienna,* by means of a very ingenious method, has obtained the first experimental determination of the conductivity of air. This result is, as he says, in striking agreement with the kinetic theory of gases.

The experiments on the interdiffusion of gases, as conducted by Prof. Loschmidt and his pupils, appear to be far more independent of disturbing causes than any experiments on viscosity or conductivity. The interdiffusing gases are left to themselves in a vertical cylindrical vessel, the heavier gas being underneath. No disturbing effect due to currents seems to exist, and the results of different experiments with the same pair of gases appear to be very consistent with each other.

They prove conclusively that the co-efficient of diffusion varies inversely as the pressure, a result in accordance with the kinetic theory, whatever hypothesis we adopt as to the nature of the mutual action of the molecules during their encounters.

They also show that the co-efficient of diffusion increases as the temperature rises, but the range of temperature in the experiments appears to be too small to enable us to decide whether it varies as T^2, as it should be according to the theory of a force inversely as the fifth power of the distance adopted in my paper in the Phil. Trans. 1866, or as $T^{\frac{3}{2}}$ as it should do according to the theory of elastic spherical molecules, which was the hypothesis originally developed by Clausius, by myself in the Phil. Mag. 1860, and by O. E. Meyer.

In comparing the co-efficients of diffusion of different pairs of gases, Prof. Loschmidt has made use of a formula according to which the co-efficient of diffusion should vary inversely as the geometric mean of the atomic weights of the two gases. I am unable to see any ground for this hypothesis in the kinetic theory, which in fact leads to a different result, involving the diameters of the molecules, as well as their masses. The numerical results obtained by Prof Loschmidt do not agree with his formula in a manner corresponding to the accuracy of his experiments. They agree in a very remarkable manner with the formula derived from the kinetic theory.

I have recently been revising the theory of gases founded on that of the collisions of elastic spheres, using, however, the methods of my paper on the dynamical theory of gases (Phil. Trans. 1866) rather than those of my first paper in the Phil. Mag., 1860, which are more difficult of application, and which led me into great confusion, especially in treating of the diffusion of gases.

The co-efficient of interdiffusion of two gases, according to this theory, is—

$$D_{12} = \frac{1}{2\sqrt{6\pi}} \; \frac{V}{N} \; \sqrt{\frac{1}{w_1} + \frac{1}{w_2}} \; \frac{1}{s^2_{12}} \quad (1)$$

where w_1 and w_2 are the molecular weights of the two gases, that of hydrogen being unity.

s_{12} is the distance between the centres of the molecules at collision in centimetres.

V is the "velocity of mean square" of a molecule of hydrogen at 0° C.

$$V = \sqrt{\frac{3p}{\rho}} = 185,900 \text{ centimetres per second.}$$

* Sitzb. d. k. Akad., Feb. 22, 1872.

N is the number of molecules in a cubic centimetre at 0° C. and 76 cm. B. (the same for all gases).

D_{12} is the co-efficient of interdiffusion of the two gases in $\dfrac{(\text{centimetre})^2}{\text{second}}$ measure.

We may simplify this expression by writing—

$$a^2 = \frac{1}{2\sqrt{6\pi}} \frac{V}{N}, \; \sigma_{12}{}^2 = \frac{1}{D_{12}} \sqrt{\frac{1}{w_1} + \frac{1}{w_2}} \quad (2)$$

Here a is a quantity the same for all gases, but involving the unknown number N.

σ is a quantity which may be deduced from the corresponding experiment of M. Loschmidt. We have thus—

$$s_{12} = a\,\sigma_{12} \quad (3)$$

or the distance between the centres of the molecules at collision is proportional to the quantity σ, which may be deduced from experiment.

If d_1 and d_2 are the diameters of the two molecules.

$$s_{12} = \tfrac{1}{2}(d_1 + d_2).$$
Hence if $d = a\,\delta \ldots \sigma_{12} = \tfrac{1}{2}(\delta_1 + \delta_2).$ (4)

Now M. Loschmidt has determined D for the six pairs of gases which can be formed from Hydrogen, Oxygen, Carbonic Oxide, and Carbonic Acid. The six values of σ deduced from these experiments ought not to be independent, since they may be deduced from the four values of δ belonging to the two gases. Accordingly we find, by assuming

TABLE I.

$\delta\,(\text{H}) = 1\cdot739$
$\delta\,(\text{O}) = 2\cdot283$
$\delta\,(\text{CO}) = 2\cdot461$
$\delta\,(\text{CO}_2) = 2\cdot775$

σ_{12}	Calculated $\tfrac{1}{2}(\delta_1 + \delta_2)$	Observed $\sqrt{\dfrac{1}{D}} \sqrt{\dfrac{1}{w_1} + \dfrac{1}{w_2}}$
For H and O	2·011	1·992
For H and CO	2·100	2·116
For H and CO$_2$	2·257	2·260
For O and CO	2·372	2·375
For O and CO$_2$	2·529	2·545
For CO and CO$_2$	2·618	2·599

NOTE.—These numbers must be multiplied by 0·6 to reduce them to (centimetre-second) measure from the (metre-hour) measure employed by Loschmidt.

The agreement of these numbers furnishes, I think, evidence of considerable strength in favour of this form of the kinetic theory, and if it should be confirmed by the comparison of results obtained from a greater number of pairs of gases it will be greatly strengthened.

Evidence, however, of a higher order may be furnished by a comparison between the results of experiments of entirely different kinds, as for instance, the coefficients of diffusion and those of viscosity. If μ denotes the coefficient of viscosity, and ρ the density of a gas at 0° C. and 760 mm. B, the theory gives—

$$\frac{\mu}{\rho} = a^2 \sqrt{\frac{2}{w}} \; \frac{1}{d^3} \quad (5)$$

so that the following relation exists between the viscosities of two gases and their coefficient of interdiffusion—

$$D_{12} = \frac{1}{2}\left(\frac{\mu_1}{\rho_1} + \frac{\mu_2}{\rho_2}\right) \quad (6)$$

Calculating from the data of Table I., the viscosities of the gases, and comparing them with those found by O. E. Meyer and by myself, and reducing all to centimetre, gramme, second measure, and to 0° C.—

TABLE II.
Coefficient of Viscosity

Gas.	Loschmidt.	O. E. Meyer.	Maxwell.
H	0·000116	0·000134	0·000097
O	0·000270	0·000306	
CO	0·000217	0·000266	
CO_2	0·000214	0·000231	0·000161

The numbers given by Meyer are greater than those derived from Loschmidt. Mine, on the other hand, are much smaller. I think, however, that of the three, Loschmidt's are to be preferred as an estimate of the absolute value of the quantities, while those of Meyer, derived from Graham's experiments, may possibly give the ratios of the viscosities of different gases more correctly. Loschmidt has also given the coefficients of interdiffusion of four other pairs of gases, but as each of these contains a gas not contained in any other pair, I have made no use of them.

In the form of the theory as developed by Clausius, an important part is played by a quantity called the *mean length of the uninterrupted path of a molecule*, or, more concisely, the *mean path*. Its value, according to my calculations, is

$$l = \frac{1}{\sqrt{2}\,\pi\,s^2 N} = \frac{\sqrt{12}}{\sqrt{\pi}}\frac{1}{V}\frac{1}{\delta^2}\,* \qquad (7)$$

Its value in tenth-metres (1 metre $\times 10^{-10}$) is

TABLE III.

For Hydrogen . . 965   Tenth-metres at 0° C. and 760 B
For Oxygen . . 500
For Carbonic Oxide 482
For Carbonic Acid 430

(The wave-length of the hydrogen ray F is 4,861 tenth-metres, or about ten times the mean path of a molecule of carbonic oxide.)

We may now proceed for a few steps on more hazardous ground, and inquire into the actual size of the molecules. Prof. Loschmidt himself, in his paper "Zur Grösse der Luftmolecüle" (Acad. Vienna, Oct. 12, 1865), was the first to make this attempt. Independently of him and of each other, Mr. G. J. Stoney (Phil. Mag. Aug. 1868), and Sir W. Thomson (NATURE, March 31, 1870), have made similar calculations. We shall follow the track of Prof. Loschmidt.

The volume of a spherical molecule is $\frac{\pi}{6} s^3$, where s is its diameter. Hence if N is the number of molecules in unit of volume, the space actually filled by the molecules is $\frac{\pi}{6} Ns^3$.

This, then, would be the volume to which a cubic centimetre of the gas would be reduced if it could be so compressed as to leave no room whatever between the molecules. This, of course, is impossible; but we may, for the sake of clearness, call the quantity—

* The difference between this value and that given by M. Clausius in his paper of 1858, arises from his assuming that all the molecules have equal velocities, while I suppose the velocities to be distributed according to the "law of errors."

$$\epsilon = \frac{\pi}{6} Ns^3 \qquad (8)$$

the ideal coefficient of condensation. The actual coefficient of condensation, when the gas is reduced to the liquid or even the solid form, and exposed to the greatest degree of cold and pressure, is of course greater than ϵ.

Multiplying equations 7 and 8, we find—

$$s = 6\sqrt{2}\,\epsilon\, l \qquad (9)$$

where s is the diameter of a molecule, ϵ the coefficient of condensation, and l the mean path of a molecule.

Of these quantities, we know l approximately already, but with respect to ϵ we only know its superior limit. It is only by ascertaining whether calculations of this kind, made with respect to different substances, lead to consistent results, that we can obtain any confidence in our estimates of ϵ.

M. Lorenz Meyer * has compared the "molecular volumes" of different substances, as estimated by Kopp from measurements of the density of these substances and their compounds, with the values of s^3 as deduced from experiments on the viscosity of gases, and has shown that there is a considerable degree of correspondence between the two sets of numbers.

The "molecular volume" of a substance here spoken of is the volume in cubic centimetres of as much of the substance in the liquid state as contains as many molecules as one gramme of hydrogen. Hence if ρ_0 denote the density of hydrogen, and $\mathfrak{v}$ the molecular volume of a substance, the actual coefficient of condensation is—

$$\epsilon' = \rho_0\, \mathfrak{v} \qquad (10)$$

These "molecular volumes" of liquids are estimated at the boiling-points of the liquids, a very arbitrary condition, for this depends on the pressure, and there is no reason in the nature of things for fixing on 760 mm. B. as a standard pressure merely because it roughly represents the ordinary pressure of our atmosphere. What would be better, if it were not impossible to obtain it, would be the volume at − 273° C. and ∞B.

But the volume relations of potassium with its oxide and its hydrated oxide as described by Faraday seem to indicate that we have a good deal yet to learn about the volumes of atoms.

If, however, for our immediate purpose, we assume the smallest molecular volume of oxygen given by Kopp as derived from a comparison of the volume of tin with that of its oxide and put

$$\mathfrak{v}(O = 16) = 2\cdot7$$

we find for the diameters of the molecules—

TABLE IV.

Hydrogen . . . . 5·8 tenth-metres.
Oxygen . . . . . 7·6
Carbonic Oxide . . 8·3
Carbonic Acid . . 9·3

The mass of a molecule of hydrogen on this assumption is

$$4\cdot6 \times 10^{-24}\ \text{gramme.}$$

The number of molecules in a cubic centimetre of any gas at 0° C. and 760 mm. B. is

$$N = 19 \times 10^{18}.$$

Hence the side of a cube which, on an average, would contain one molecule would be

$$N^{-\frac{1}{3}} = 37 \text{ tenth-metres.}$$

J. CLERK-MAXWELL

* Annalen d. Chemie u Pharmacie V. Supp. bd. 2, Heft (1867).