

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

AUGUST 1902.

XVIII. *On the Weights of Atoms* *.
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§ 23. **H**ITHERTO in all our views we have seen nothing of absolute dimensions in molecular structure, and have been satisfied to consider the distance between neighbouring molecules in gases, or liquids, or crystals, or non-crystalline solids to be very small in comparison with the shortest wave-length of light with which we have been concerned. Even in respect to dispersion, that is to say, difference of propagational velocity for different wave-lengths, it has not been necessary for us to accept Cauchy's doctrine that the spheres of molecular action are comparable with the wave-length. We have seen that dispersion can be, and probably in fact is, truly explained by the periods of our waves of light being not infinitely great in comparison with some of the periods of molecular vibration; and, with this view, the dimensions of molecular structure might, so far as dispersion is concerned, be as small as we please to imagine them, in comparison with wave-lengths of light. Nevertheless it is exceedingly interesting and important for intelligent study of molecular structures and the dynamics of light, to have some well-founded understanding in respect to probable distances between centres of neighbouring molecules in all kinds of ponderable matter, while for the present at all

* This is Lecture XVII. of my Baltimore Lectures, as now extended and prepared for press. For convenience of reference the sectional numbers have been retained as in the volume of Lectures.

† Communicated by the Author.

events we regard ether as utterly continuous and structureless. It may be found in some future time that ether too has a molecular structure, perhaps much finer than any structure of ponderable matter; but at present we neither see nor imagine any reason for believing ether to be other than continuous and homogeneous through infinitely small contiguous portions of space void of other matter than ether.

§ 24. The first suggestion, so far as we now know, for estimating the dimensions of molecular structure in ordinary matter was given in 1805 by Thomas Young*, as derived from his own and Laplace's substantially identical theories of capillary attraction. In this purely dynamical theory he found that the range of the attractive force of cohesion is equal to $3T/K$; where T denotes the now well-known Young's tension of the free surface of a liquid, and K denotes a multiple integral which appears in Laplace's formulas and is commonly now referred to as Laplace's K , as to the meaning of which there has been much controversy in the columns of 'Nature' and elsewhere. Lord Rayleigh in his article of 1890, "On the Theory of Surface Forces†," gives the following very interesting statement in respect to Young's estimate of molecular dimensions:—

§ 25. "One of the most remarkable features of Young's treatise is his estimate of the range a of the attractive force on the basis of the relation $T = \frac{1}{3}aK$. Never once have I seen it alluded to; and it is, I believe, generally supposed that the first attempt of the kind is not more than twenty years old. Estimating K at 23000 atmospheres, and T at 3 grains per inch, Young finds that 'the extent of the cohesive force must be limited to about the 250 millionth of an inch [10^{-8} cm.]'; and he continues, 'nor is it very probable that any error in the suppositions adopted can possibly have so far invalidated this result as to have made it very many times greater or less than the truth' Young continues:—"Within similar limits of uncertainty, we may obtain something like a conjectural estimate of the mutual distance of the particles of vapours, and even of the actual magnitude of the elementary atoms of liquids, as supposed to be nearly in contact with each other; for if the distance at which the force of cohesion begins is constant at the same temperature, and if the particles of

* "On the Cohesion of Fluids," Phil. Trans. 1805; Collected Works, vol. i. p. 461.

† Phil. Mag. vol. xxx. 1890, p. 474

“‘steam are condensed when they approach within this
 “‘distance, it follows that at 60° of Fahrenheit the distance
 “‘of the particles of pure aqueous vapour is about the 250
 “‘millionth of an inch; and since the density of this vapour
 “‘is about one sixty thousandth of that of water, the distance
 “‘of the particles must be about forty times as great;
 “‘consequently the mutual distance of the particles of water
 “‘must be about the ten thousand millionth of an inch *
 “‘[$\cdot 025 \times 10^{-8}$ cm.]. It is true that the result of this calcu-
 “‘lation will differ considerably according to the temperature
 “‘of the substances compared. . . . This discordance does not
 “‘however wholly invalidate the general tenour of the con-
 “‘clusion . . . and on the whole it appears tolerably safe to
 “‘conclude that, whatever errors may have affected the
 “‘determination, the diameter or distance of the particles of
 “‘water is between the two thousand and the ten thousand
 “‘millionth of an inch’ [between $\cdot 125 \times 10^{-8}$ and $\cdot 025 \times 10^{-8}$
 “‘of a cm.]. This passage, in spite of its great interest, has
 “‘been so completely overlooked that I have ventured briefly
 “‘to quote it, although the question of the size of atoms lies
 “‘outside the scope of the present paper.”

§ 26. The next suggestion, so far as I know, for estimating the dimensions of molecular structure in ordinary matter, is to be found in an extract from a letter of my own to Joule on the contact electricity of metals, published in the ‘Proceedings’ of the Manchester Literary and Philosophical Society †, Jan. 21, 1862, which contains the following passage:—“Zinc and copper connected by a metallic arc
 “‘attract one another from any distance. So do platinum
 “‘plates coated with oxygen and hydrogen respectively.
 “‘I can now tell the amount of the force, and calculate how
 “‘great a proportion of chemical affinity is used up electrically,
 “‘before two such discs come within 1/1000 of an inch of
 “‘one another, or any less distance down to a limit within
 “‘which molecular heterogeneousness becomes sensible. This
 “‘of course will give a definite limit for the sizes of atoms, or
 “‘rather, as I do not believe in atoms, for the dimensions of
 “‘molecular structures.” The theory thus presented is somewhat more fully developed in a communication to ‘Nature’

* Young here, curiously insensible to the kinetic theory of gases, supposes the molecules of vapour of water at 60° Fahr. to be within touch (or direct mutual action) of one another; and thus arrives at a much finer-grainedness for liquid water than he would have found if he had given long enough free paths to molecules of the vapour to account for its approximate fulfilment of Boyle’s law.

† Reproduced as Art. 22 of my ‘Electrostatics and Magnetism.’

in March 1870, on "The Size of Atoms"*, and in a Friday evening lecture † to the Royal Institution on the same subject on February 3, 1883; but to illustrate it, information was wanted regarding the heat of combination of copper and zinc. Experiments by Professor Roberts-Austen and by Dr. A. Galt, made within the last four years, have supplied this want; and in a postscript of February 1898 to a Friday evening lecture on "Contact Electricity," which I gave at the Royal Institution on May 21, 1897, I was able to say "We cannot avoid seeing molecular structures beginning to be perceptible at distances of the hundred-millionth of a centimetre, and we may consider it as highly probable that the distance from any point in a molecule of copper or zinc to the nearest corresponding point of a neighbouring molecule is less than one one-hundred-millionth, and greater than one one-thousand-millionth of a centimetre"; and also to confirm amply the following definite statement which I had given in my 'Nature' article (1870) already referred to:—"Plates of zinc and copper of a three-hundred-millionth of a centimetre thick, placed close together alternately, form a near approximation to a chemical combination, if indeed such thin plates could be made without splitting atoms."

§ 27. In that same article thermodynamic considerations in stretching a fluid film against surface tension led to the following result:—"The conclusion is unavoidable, that a water-film falls off greatly in its contractile force before it is reduced to a thickness of a two hundred-millionth of a centimetre. It is scarcely possible, upon any conceivable molecular theory, that there can be any considerable falling off in the contractile force as long as there are several molecules in the thickness. It is therefore probable that there are not several molecules in a thickness of a two-hundred-millionth of a centimetre of water." More detailed consideration of the work done in stretching a water-film led me in my Royal Institution Lecture of 1883 to substitute one one-hundred-millionth of a centimetre for one two-hundred-millionth in this statement. On the other hand a consideration of the large black spots which we now all know in a soap-bubble or soap-film before it bursts, and which were described in a most interesting manner by Newton ‡, gave

* Republished as Appendix (F) in Thomson and Tait's 'Natural Philosophy, part ii. second edition.

† Republished in 'Popular Lectures and Addresses,' vol. i.

‡ Newton's 'Optics,' pp. 187, 191, Edition 1721, Second Book, Part i.: quoted in my Royal Institution Lecture, 'Pop. Lectures and Addresses,' vol. i. p. 175.

absolute demonstration that the film retains its tensile strength in the black spot "where the thickness is clearly much less than $1/60000$ of a centimetre, this being the thickness of "the dusky white" with which the black spot is bordered. And further in 1883 Reinold and Rücker's* admirable application of optical and electrical methods of measurement proved that the thickness of the black film in Plateau's "liquide glycérique" and in ordinary soap solution is between one eight-hundred-thousandth of a centimetre and one millionth of a centimetre. Thus it was certain that the soap-film has full tensile strength at a thickness of about a millionth of a centimetre, and that between one millionth and one one-hundred-millionth the tensile strength falls off enormously.

§ 28. Extremely interesting in connection with this is the investigation, carried on independently by Röntgen† and Rayleigh‡, and published by each in 1890, of the quantity of oil spreading over water per unit area required to produce a sensible disturbance of its capillary tension. Both experimenters expressed results in terms of thickness of the film, calculated as if oil were infinitely homogeneous and therefore structureless, but with very distinct reference to the certainty that their films were molecular structures not approximately homogeneous. Rayleigh found that olive oil, spreading out rapidly all round on a previously cleaned surface of water from a little store carried by a short length of platinum wire, produced a perceptible effect on little floating fragments of camphor at places where the thickness of the oil was 10.6×10^{-8} cm., and no perceptible effect where the thickness was 8.1×10^{-8} cm. It will be highly interesting to find, if possible, other tests (optical or dynamical or electrical or chemical) for the presence of a film of oil over water, or of films of various liquids over solids such as glass or metals, demonstrating by definite effects smaller and smaller thicknesses. Röntgen, using ether instead of camphor, found analogous evidence of layers 5.6×10^{-8} cm. thick. It will be very interesting for example to make a thorough investigation of the electric conductance of a clean rod of white glass of highest insulating quality surrounded by an atmosphere containing measured quantities of vapour of water. When the glass is at any temperature above the dew-point of

* "On the Limiting Thickness of Liquid Films," Roy. Soc. Proc. April 19, 1883; Phil. Trans. 1883, part ii. p. 645.

† Wied. *Ann.* vol. xli. 1890, p. 321.

‡ Proc. Roy. Soc. vol. xlvii. 1890, p. 364

the vapour, it presents, so far as we know, no optical appearance to demonstrate the pressure of condensed vapour of water upon it: but enormous differences of electric conductance, according to the density of the vapour surrounding it, prove the presence of water upon the surface of the glass, or among the interstices between its molecules, of which electric conductance is the only evidence. Rayleigh has himself expressed this view in a recent article, "Investigations on Capillarity," in the *Philosophical Magazine**. From the estimates of the sizes of molecules of argon, hydrogen, oxygen, carbonic oxide, carbonic acid, ethylene (C_2H_4), and other gases, which we shall have to consider (§ 47 below), we may judge that in all probability if we had eyes microscopic enough to see atoms and molecules, we should see in those thin films of Rayleigh and Röntgen merely molecules of oil lying at greater and less distances from one another, but at no part of the film one molecule of oil lying above another or resting on others.

§ 29. A very important and interesting method of estimating the size of atoms, founded on the kinetic theory of gases, was first, so far as I know, thought of by Loschmidt† in Austria and Johnstone Stoney in Ireland. Substantially the same method occurred to myself later and was described in 'Nature,' March 1870, in an article‡ on the "Size of Atoms" already referred to, § 26 above, from which the quotations in §§ 29, 30 are taken.

"The kinetic theory of gases suggested a hundred years ago by Daniel Bernoulli has, during the last quarter of a century, been worked out by Herapath, Joule, Clausius, and Maxwell to so great perfection that we now find in it satisfactory explanations of all non-chemical" and non-electrical "properties of gases. However difficult it may be to even imagine what kind of thing the molecule is, we may regard it as an established truth of science that a gas consists of moving molecules disturbed from rectilinear paths and constant velocities by collisions or mutual influences, so rare that the mean length of nearly rectilinear portions of the path of each molecule is many times greater than the average distance from the centre of each molecule to the centre of the molecule nearest it at any time. If, for a moment, we suppose the molecules to be hard elastic

* *Phil. Mag.* Oct. 1899, p. 337.

† *Sitzungsberichte* of the Vienna Academy, Oct. 12, 1865, p. 395.

‡ Reprinted as Appendix (F) in Thomson and Tait's 'Natural Philosophy,' part. ii. p. 499.

“globes all of one size, influencing one another only through actual contact, we have for each molecule simply a zigzag path composed of rectilinear portions, with abrupt changes of direction But we cannot believe that the individual molecules of gases in general, or even of any one gas, are hard elastic globes. Any two of the moving particles or molecules must act upon one another somehow, so that when they pass very near one another they shall produce considerable deflexion of the path and change in the velocity of each. This mutual action (called force) is different at different distances, and must vary, according to variations of the distance, so as to fulfil some definite law. If the particles were hard elastic globes acting upon one another only by contact, the law of force would be . . . zero force when the distance from centre to centre exceeds the sum of the radii, and infinite repulsion for any distance less than the sum of the radii. This hypothesis, with its ‘hard and fast’ demarcation between no force and infinite force, seems to require mitigation.” Boscovich’s theory supplies clearly the needed mitigation.

§ 30. To fix the ideas we shall still suppose the force absolutely zero when the distance between centres exceeds a definite limit, λ ; but when the distance is less than λ , we shall suppose the force to begin either attractive or repulsive, and to come gradually to a repulsion of very great magnitude, with diminution of distance towards zero. Particles thus defined I call Boscovich atoms. We thus call $\frac{1}{2}\lambda$ the radius of the atom, and λ its diameter. We shall say that two atoms are in collision when the distance between their centres is less than λ . Thus “two molecules in collision will exercise a mutual repulsion in virtue of which the distance between their centres, after being diminished to a minimum, will begin to increase as the molecules leave one another. This minimum distance would be equal to the sum of the radii, if the molecules were infinitely hard elastic spheres; but in reality we must suppose it to be very different in different collisions.”

§ 31. The essential quality of a gas is that the straight line of uniform motion of each molecule between collisions, called the free path, is long in comparison with distances between centres during collision. In an ideal perfect gas the free path would be infinitely long in comparison with distances between centres during collision, but infinitely short in comparison with any length directly perceptible to our senses; a condition which requires the number of molecules in any

perceptible volume to be exceedingly great. We shall see that in gases which at ordinary pressures and temperatures approximate most closely, in respect to compressibility, expansion by heat, and specific heats, to the ideal perfect gas, as, for example, hydrogen, oxygen, nitrogen, carbon-monoxide, the free path is probably not more than about one hundred times the distance between centres during collisions, and is little short of 10^{-5} cm. in absolute magnitude. Although these moderate proportions suffice for the well-known exceedingly close agreement with the ideal gaseous laws presented by those real gases, we shall see that large deviations from the gaseous laws are presented with condensations sufficient to reduce the free paths to two or three times the diameter of the molecule, or to annul the free paths altogether.

§ 32. It is by experimental determinations of diffusivity that the kinetic theory of gases affords its best means for estimating the sizes of atoms or molecules and the number of molecules in a cubic centimetre of gas at any stated density. Let us therefore now consider carefully the kinetic theory of these actions, and with them also, the properties of thermal conductivity and viscosity closely related to them, as first discovered and splendidly developed by Clausius and Clerk Maxwell.

§ 33. According to their beautiful theory, we have three kinds of diffusion; diffusion of molecules, diffusion of energy, and diffusion of momentum. Even in solids, such as gold and lead, Roberts-Austen has discovered molecular diffusion of gold into lead and lead into gold between two pieces of the metals when pressed together. But the rate of diffusion shown by this admirable discovery is so excessively slow that for most purposes, scientific and practical, we may disregard wandering of any molecule in any ordinary solid to places beyond direct influence of its immediate neighbours. In an elastic solid we have diffusion of momentum by wave motion, and diffusion of energy constituting the conduction of heat through it. These diffusions are effected solely by the communication of energy from molecule to molecule and are practically not helped at all by the diffusion of molecules. In liquids also, although there is thorough molecular diffusivity, it is excessively slow in comparison with the two other diffusivities, so slow that the conduction of heat and the diffusion of momentum according to viscosity are not practically helped by molecular diffusion. Thus, for example, the

thermal diffusivity * of water ($\cdot 002$, according to J. T. Bottomley's first investigation, or about $\cdot 0015$ † according to later experimenters) is several hundred times, and the diffusivity for momentum is from one to two thousand times, the diffusivity of water for common salt, and other salts such as sulphates, chlorides, bromides, and iodides.

§ 34. We may regard the two motional diffusivities of a liquid as being each almost entirely due to communication of motion from one molecule to another. This is because every molecule is always under the influence of its neighbours and has no free path. When a liquid is rarefied, either gradually as in Andrews' experiments showing the continuity of the liquid and gaseous states, or suddenly as in evaporation, the molecules become less crowded and each molecule gains more and more of freedom. When the density is so small that the straight free paths are great in comparison with the diameters of molecules, the two motional diffusivities are certainly due, one of them to carriage of energy, and the other to carriage of momentum, chiefly by the free rectilinear motion of the molecules between collisions. Interchange of energy or of momentum between two molecules during collision will undoubtedly to some degree modify the results of mere transport; and we might expect on this account the motional diffusivities to be approximately equal to, but each somewhat greater than, the molecular diffusivity. If this view were correct, it would follow that, in a homogeneous gas when the free paths are long in comparison with the diameters of molecules, the viscosity is equal to the molecular diffusivity multiplied by the density, and the thermal conductivity is equal to the molecular diffusivity multiplied by the thermal capacity per unit bulk, pressure constant: and that whatever deviation from exactness of these equalities there may be, would be in the direction of the motional diffusivities being somewhat greater than the molecular diffusivity. But alas, we shall see, § 45 below, that hitherto experiment does not confirm these conclusions: on the contrary the laminar diffusivities (or diffusivities of momentum) of the only four gases of which molecular diffusivities have been determined by experiment, instead of being greater than, or at least equal to, the density multiplied by the molecular diffusivity, are each somewhat less than three-fourths of the amount thus calculated.

* 'Math. and Phys. Papers,' vol. iii. p. 226. For explanation regarding diffusivity and viscosity see same volume, pp. 428-435.

† See a paper by Milner and Chattock, *Phil. Mag.* vol. xlviii. 1899.

§ 35. I see no explanation of this deviation from what seems thoroughly correct theory. Accurate experimental determinations of viscosities, whether of gases or liquids, are easy by Graham's transpirational method. On the other hand even roughly approximate experimental determinations of thermal diffusivities are exceedingly difficult, and I believe none, on correct experimental principles, have really been made *; certainly none unvitiated by currents of the gas experimented upon, or accurate enough to give any good test of the theoretical relation between thermal and material diffusivities, expressed by the following equation, derived from the preceding verbal statement regarding the three diffusivities of a gas,

$$\theta = K\rho \frac{\mu}{\rho} = K\mu = kc\mu.$$

where θ denotes the thermal conductivity, μ the viscosity, ρ the density, $K\rho$ the thermal capacity per unit bulk pressure constant, K the thermal capacity per unit mass pressure constant, c the thermal capacity per unit mass volume constant, and k the ratio of the thermal capacity pressure constant to the thermal capacity volume constant. It is interesting to remark how nearly theoretical investigators † have come to the relation $\theta = kc\mu$; Clausius gave $\theta = \frac{5}{4}c\mu$; O. E. Meyer, $\theta = 1.6027c\mu$, and Maxwell, $\theta = \frac{5}{3}c\mu$. Maxwell's in fact is $\theta = kc\mu$ for the case of a monatomic gas.

§ 36. To understand exactly what is meant by molecular diffusivity consider a homogeneous gas between two infinite parallel planes, GGG and RRR , distance a apart, and let it be initially given in equilibrium; that is to say, with equal numbers of molecules and equal total kinetic energies in equal volumes, and with integral of component momentum in any and every direction, null. Let N be the number of molecules per unit volume. Let every one of the molecules be marked either green or red, and whenever a red molecule strikes the plane GGG , let its marking be altered to green, and, whenever a green molecule strikes RRR , let its marking be altered to red. These markings are not to alter in the slightest

* So far as I know, all attempts hitherto made to determine the thermal conductivities of gases have been founded on observations of rate of communication of heat between a thermometer-bulb, or a stretched metallic wire constituting an electric resistance thermometer, and the walls of the vessel enclosing it and the gas experimented upon. See Wiedemann's *Annalen* (1888), vol. xxxiv. p. 623, and 1891, vol. xlv. p. 177. For other references, see O. E. Meyer, § 107.

† See the last ten lines of O. E. Meyer's book.

degree the mass or shape or elastic quality of the molecules, and they do not disturb the equilibrium of the gas or alter the motion of any one of its particles; they are merely to give us a means of tracing ideally the history of any one molecule, or set of molecules, moving about and colliding with other molecules according to the kinetic nature of a gas.

§ 37. Whatever may have been the initial distribution of the greens and reds, it is clear that ultimately there must be a regular transition from all greens at the plane GGG and all reds at the plane RRR , according to the law

$$g = N \frac{x}{a}; \quad r = N \frac{a-x}{a} \quad . \quad . \quad . \quad (1),$$

where g and r denote respectively the number of green molecules and of red molecules per unit volume at distance x from the plane RRR . In this condition of statistical equilibrium, the total number of molecules crossing any intermediate parallel plane from the direction GGG towards RRR will be equal to the number crossing from RRR towards GGG in the same time; but a larger number of green molecules will cross towards RRR than towards GGG , and, by an equal difference, a larger number of red molecules will cross towards GGG than towards RRR . If we denote this difference per unit area per unit time by QN , we have for what I call the material diffusivity (called by Maxwell, "co-efficient of diffusion"),

$$D = Qa \quad . \quad . \quad . \quad . \quad . \quad (2).$$

We may regard this equation as the definition of diffusivity. Remark that Q is of dimensions LT^{-1} , because it is a number per unit of area per unit of time (which is of dimensions $L^{-2}T^{-1}$) divided by N , a number per unit of bulk (dimensions L^{-3}). Hence the dimensions of a diffusivity are L^2T^{-1} ; and practically we reckon it in square centimetres per second.

§ 38. Hitherto we have supposed the G and the R particles to be of exactly the same quality in every respect, and the diffusivity which we have denoted by D is the inter-diffusivity of the molecules of a homogeneous gas. But we may suppose G and R to be molecules of different qualities; and assemblages of G molecules and of R molecules to be two different gases. Everything described above will apply to the inter-diffusions of these two gases; except that the two differences which are equal when the red and green molecules are of the same quality are now not equal or, at all events, must

not without proof be assumed to be equal. Let us therefore denote by $Q_g N$ the excess of the number of G molecules crossing any intermediate plane towards RRR over the number crossing towards GGG , and by $Q_r N$ the excess of the number of R molecules crossing towards GGG above that crossing towards RRR . We have now two different diffusivities of which the mean values through the whole range between the bounding planes are given by the equations

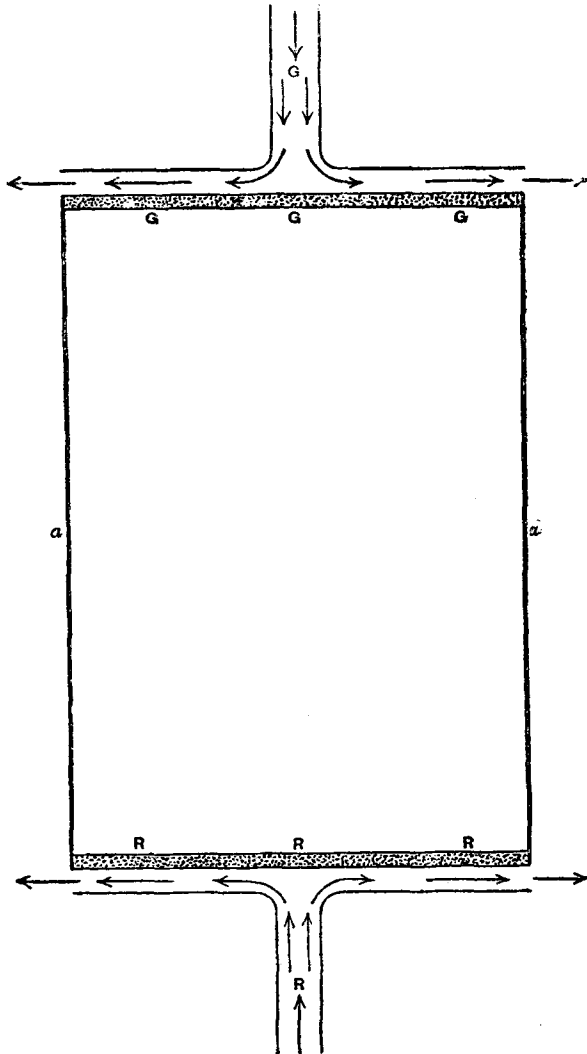
$$D_g = Q_g a ; D_r = Q_r a ;$$

one of them, D_g , the diffusivity of the green molecules, and the other, D_r , the diffusivity of the red molecules through the heterogeneous mixture in the circumstances explained in § 37. We must not now assume the gradients of density of the two gases to be uniform as expressed by (1) of § 37, because the homogeneousness on which these equations depend no longer exists.

§ 39. To explain all this practically*, let in the diagram the planes GGG , and RRR , be exceedingly thin plates of dry porous material such as the fine unglazed earthenware of Graham's experiments. Instead of our green and red marked molecules of the same kind, let us have two gases, which we shall call G and R , supplied in abundance at the middles of the two ends of a non-porous tube of glass or metal, and guided to flow away radially in contact with the end-plates as indicated in the diagram. If the two axial supply-streams of the two pure gases are sufficiently abundant, the spaces GGG , RRR , close to the inner sides of the porous end-plates will be occupied by the gases G and R , somewhat nearly pure. They could not be rigorously pure even if the velocities of the scouring gases on the outer sides of the porous end-plates were comparable with the molecular velocities in the gases, and if the porous plates were so thin as to have only two or three

* For a practical experiment it might be necessary to allow for the difference of the proportions of the G gas on the two sides of the RRR plate and of the R gas on the two sides of the GGG plate. This would be exceedingly difficult, though not impossible, in practice. The difficulty is analogous to that of allowing for the electric resistances of the connexions at the ends of a stout bar of metal of which it is desired to measure the electric resistance. But the simple and accurate "potential method" by which the difficulty is easily and thoroughly overcome in the electric case is not available here. I do not, however, put forward the arrangement described in the text as an eligible plan for measuring the inter-diffusivity of two gases. Even if there were no other difficulty, the quantities of the two pure gases required to realize it would be impracticably great.

molecules of solid matter in their thickness. The gases in contact with the near faces of the porous plates would however, probably be somewhat approximately pure in practice



with a practically realisable thinness of the porous plates, if a , the distance between the two plates, is not less than five or six centimetres and the scouring velocities moderately, but not impracticably, great. According to the notation of § 37,

Q_g is the quantity of the G gas entering across GGG and leaving across RRR per sec. of time per sq. cm. of area; Q_r is the quantity of the R gas entering across RRR and leaving across GGG per sec. of time per sq. cm. of area; the unit quantity of either gas being that which occupies a cubic centimetre in its entry tube. The equations

$$D_g = Q_g \frac{a}{(1-g-r)}, \quad D_r = Q_r \frac{a}{(1-g-r)},$$

where g and r are the proportions of the G gas at R and of the R gas at G , define the average diffusivities of the two gases in the circumstances in which they exist in the different parts of the length a between the end-plates. This statement is cautiously worded to avoid assuming either equal values of the diffusivities of the two gases or equality of the diffusivity of either gas throughout the space between the end-plates. So far as I know difference of diffusivity of the two gases has not been hitherto suggested by any writer on the subject. What is really given by Loschmidt's experiments, § 43 below, is the arithmetic mean of the two diffusivities D_g and D_r .

§ 40. In 1877 O. E. Meyer expressed the opinion on theoretical grounds, which seem to me perfectly valid, that the inter-diffusivity of two gases varies according to the proportions of the two gases in the mixture. In the 1899 edition of his 'Kinetic Theory of Gases'* he recalls attention to this view and quotes results of various experimenters, Loschmidt, Obermayer, Waitz, seeming to support it, but, as he says, not quite conclusively. On the other hand, Maxwell's theory (§ 41 below) gives inter-diffusivity as independent of the proportions of the two gases; and only a single expression for diffusivity, which seems to imply that the two diffusivities are equal according to his theory. The subject is of extreme difficulty and of extreme interest, theoretical and practical; and thorough experimental investigation is greatly to be desired.

§ 41. In 1873 Maxwell† gave, as a result of a theoretical investigation, the following formula which expresses the inter-diffusivity (D_{12}) of two gases independently of the proportion of the two gases in any part of the mixture: each gas being supposed to consist of spherical Boscovich atoms mutually acting according to the law, force zero for all distances exceeding the sum of the radii (denoted by s_{12}) and infinite repulsion when the distance between their centres is infinitely

* Baynes' translation, p. 264.

† "On Loschmidt's Experiments on Diffusion in relation to the Kinetic Theory of Gases," *Nature*, Aug. 1873; *Scientific Papers*, vol. ii. pp. 343-350.

little less than this distance :

$$D_{12} = \frac{1}{2\sqrt{6\pi N}} \sqrt{\left(\frac{1}{w_1} + \frac{1}{w_2}\right) \frac{1}{s_{12}^2}} \cdot \cdot \cdot \quad (1),$$

where w_1, w_2 are the masses of the molecules in the two gases in terms of that of hydrogen called unity ; V is the square root of the mean of the squares of the velocities of the molecules in hydrogen at 0°C. ; and N is the number of molecules in a cubic centimetre of a gas (the same for all gases according to Avogadro's law) at 0°C. and standard atmospheric pressure. I find the following simpler formula more convenient

$$D_{12} = \frac{1}{2\sqrt{6\pi N s_{12}^2}} \sqrt{(V_1^2 + V_2^2)} \cdot \cdot \cdot \quad (2),$$

where V_1^2, V_2^2 are the mean squares of the molecular velocities of the two gases at 0°C. , being the values of $3 p/\rho$ for the two gases, or three times the squares of their Newtonian velocities of sound, at that temperature. For brevity, we shall call mean molecular velocity the square root of the mean of the squares of the velocities of the molecules. The same formula is, of course, applicable to the molecular diffusivity of a single gas by taking $V_1 = V_2 = V$ its mean molecular velocity, and $s_{12} = s$ the diameter of its molecules ; so that we have

$$D = \frac{1}{2\sqrt{3\pi N s^2}} \sqrt{V^2} \cdot \cdot \cdot \cdot \cdot \quad (3).$$

§ 42. It is impossible by any direct experiment to find the molecular diffusivity of a single gas as we have no means of marking its particles in the manner explained in § 37 above ; but Maxwell's theory gives us, in a most interesting manner, the means of calculating the diffusivity of each of three separate gases from three experiments determining the inter-diffusivities of their pairs. From the inter-diffusivity of each pair determined by experiment we find, by (2) § 41, a value of $s_{12} \sqrt{(2\sqrt{3\pi N})}$ for each pair, and we have $s_{12} = \frac{1}{2}(s_1 + s_2)^*$, whence

$$s_1 = s_{12} + s_{13} - s_{23} ; s_2 = s_{12} + s_{23} - s_{13} ; s_3 = s_{13} + s_{23} - s_{12} \cdot \quad (1).$$

Calculating thus the three values of $s \sqrt{(2\sqrt{3\pi N})}$, and using them in (3) § 41, we find the molecular diffusivities of the three separate gases.

§ 43. In two communications † to the Academy of Science

* This agrees with Maxwell's equation (4), but shows his equation (6) to be incorrect.

† "Experimental-Untersuchungen über die Diffusion von Gasen ohne poröse Scheidewände," *Sitz. d. k. Akad. d. Wissensch.*, March 10 and May 12, 1870.

of Vienna in 1870, Loschmidt describes experimental determinations of the inter-diffusivities of ten pairs of gases made, by a well-devised method, with great care to secure accuracy. In each case the inter-diffusivity determined by the experiment would be, at all events, somewhat approximately the mean of the two diffusivities, § 39 above, if these are unequal. The results reduced to 0° C. and standard atmospheric pressure, and multiplied by 2·78 to reduce from Loschmidt's square metres per hour to the now usual square centimetres per second, are as follows :—

TABLE OF INTER-DIFFUSIVITIES *D*.

Pairs of Gases.	<i>D</i> in sq. cms. per sec.
H ₂ , O ₂	·7214
H ₂ , CO	·6422
H ₂ , CO ₂	·5558
O ₂ , CO	·1802
O ₂ , CO ₂	·1409
CO, CO ₂	·1406
CO ₂ , Air	·1423
CO ₂ , NO	·0984
CO ₂ , CH ₄	·1587
SO ₂ , H ₂	·4809

In the first six of these, each of the four gases H₂, O₂, CO, CO₂ occurs three times and we have four sets of three inter-diffusivities giving in all three determinations of the diffusivity of each gas as follows :—

Gases.	Pairs of gases. <i>D</i> ₁ .		Pairs of gases. <i>D</i> ₂ .	
	(12, 13, 23).....	1·31	(12, 13, 23).....	·193
H ₂ (1) O ₂ (2) CO (3) CO ₂ (4)	(12, 14, 24).....	1·44	(12, 14, 24).....	·190
	(13, 14, 34).....	1·22	(23, 24, 34).....	·182
	Mean 1·32		Mean ·188	
	<i>D</i> ₃ .		<i>D</i> ₄ .	
	(12, 13, 23).....	·168	(12, 14, 24).....	·107
	(13, 14, 34).....	·175	(13, 14, 34).....	·112
	(23, 24, 34).....	·172	(23, 24, 34).....	·110
	Mean ·172		Mean ·110	

Considering the great difficulty of the experimental investigation, we may regard the agreements of the three results for each separate gas as, on the whole, very satisfactory, both in respect to the accuracy of Loschmidt's experiments and the correctness of Maxwell's theory. It certainly is a very remarkable achievement of theory and experiment to have found in the four means of the sets of three determinations, what must certainly be somewhat close approximations to the absolute values for the four gases, hydrogen, oxygen, carbon-monoxide, and carbon-dioxide, of something seemingly so much outside the range of experimental observation as the inter-diffusivity of the molecules of a separate gas.

§ 44. Maxwell, in his theoretical writings of different dates, gave two very distinct views of the inner dynamics of viscosity in a single gas, both interesting, and each, no doubt, valid. In one*, viscous action is shown as a subsidence from an "instantaneous rigidity of a gas." In the other †, viscosity is shown as a diffusion of momentum: and in p. 347 of his article quoted in § 41 above he gives as from "the theory," but without demonstration, a formula (5), which, taken in conjunction with (1), makes

$$\frac{\mu}{\rho} = D \quad . \quad . \quad . \quad . \quad . \quad . \quad (1);$$

ρ denoting the density, μ the viscosity, and D the molecular diffusivity, of any single gas. On the other hand, in his 1866 paper he had given formulas making ‡

$$\frac{\mu}{\rho} = .648D \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

§ 45. Viewing viscosity as explained by diffusion of momentum we may, it has always seemed to me (§ 34 above), regard (1) as approximately true for any gas, monatomic, diatomic, or polyatomic, provided only that the mean free

* Trans. Roy. Soc., May 1866; Scientific Papers, vol. ii. p. 70.

† "Molecules," a lecture delivered before the Brit. Assoc. at Bradford, Scientific Papers, vol. ii. p. 378. See also O. E. Meyer's 'Kinetic Theory of Gases,' (Baynes' trans. 1899), §§ 74-76.

‡ The formula for viscosity (Sci. Papers, vol. ii. p. 68) taken with the formula for molecular diffusivity of a single gas, derived from the formula of inter-diffusivity of two gases of equal densities, gives $\frac{\mu}{\rho D} = \frac{A_1}{3A_2}$, which is equal to .648 according to the values of A_1 and A_2 shown in p. 42 of vol. ii. Sci. Papers.

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path is large in comparison with the sum of the durations of the collisions. Unfortunately for this view, however, comparisons of Loschmidt's excellent experimental determinations of diffusivity with undoubtedly accurate determinations of viscosity from Graham's original experiments on transpiration, and more recent experiments of Obermeyer and other accurate observers, show large deviations from (1) and are much more nearly in agreement with (2). Thus taking $\cdot0000900$, $\cdot001430$, $\cdot001234$, $\cdot001974$ as the standard densities of the four gases, hydrogen, oxygen, carbon-monoxide, and carbon-dioxide, and multiplying these respectively by the diffusivities from Loschmidt's experiments and Maxwell's theory, we have the following comparison with Obermeyer's viscosities at 0°C. and standard pressure, which shows the discrepancy from experiment and seeming theory referred to in § 34.

Col. 1.	Col. 2.	Col. 3.	Col. 4.
Gas.	Viscosity calculated by Maxwell's theory from Loschmidt's diffusivities $\mu = \rho D$.	Viscosities according to Obermeyer.	Ratio of values in Col. 3 to those in Col. 2.
H ₂	$\cdot000119$	$\cdot0000822$	$\cdot691$
O ₂	$\cdot000269$	$\cdot0001873$	$\cdot695$
CO	$\cdot000212$	$\cdot0001630$	$\cdot769$
CO ₂	$\cdot000218$	$\cdot0001414$	$\cdot649$

§ 46. Leaving this discrepancy unexplained, and eliminating D between (1) of § 44 and (3) of § 41, we find as Maxwell's latest expression of the theoretical relation between number of molecules per cubic centimetre, diameter of the molecules, molecular velocity, density, and viscosity of a single gas,

$$Ns^2 = \frac{1}{2\sqrt{3}\pi} \frac{V\rho}{\mu} = \cdot1629 \frac{V\rho}{\mu} \quad . \quad . \quad . \quad (1).$$

The number of grammes and the number of molecules in a cubic centimetre being respectively ρ and N , ρ/N is the mass of one molecule in grammes; and therefore, denoting this by m , we have

$$m = 2\sqrt{3}\pi \frac{\mu}{V} s^2 = 6\cdot140 \frac{\mu}{V} s^2 \quad . \quad . \quad . \quad (2).$$

In these formulas, as originally investigated by Maxwell for the case of an ideal gas composed of hard spherical atoms, s is definitely the diameter of the atom, and is the same at all temperatures and densities of the gas. When we apply the formulas to diatomic or polyatomic gases, or to a monatomic gas consisting of spherical atoms whose spheres of action may overlap more or less in collision according to the severity of the impact, s may be defined as the diameter which an ideal hard spherical atom, equal in mass to the actual molecule, must have to give the same viscosity as the real gas, at any particular temperature. This being the rigorous definition of s , we may call it the proper mean shortest distance of inertial centres of the molecules in collision to give the true viscosity; a name or expression which helps us to understand the thing defined.

§ 47. For the ideal gas of hard spherical atoms, remembering that V is independent of the density and varies as t^3 (t denoting absolute temperature), § 46 (2) proves that the viscosity is independent of the density and varies approximately as $t^{\frac{1}{2}}$. Rayleigh's experimental determinations of the viscosity of argon at different temperatures show that for this monatomic gas the viscosity varies as $t^{.815}$; hence § 46 (2) shows that s^2 varies as $t^{-.315}$, and therefore s varies as $t^{-.16}$. Experimental determinations by Obermayer* of viscosities and their rates of variation with temperature for carbonic acid, ethylene, ethylene-chloride, and nitrous oxide, show that for these the viscosity is somewhat nearly in simple proportion to the absolute temperature: hence for them s^2 varies nearly as $t^{-.5}$. His determinations for the five molecularly simpler gases, air, hydrogen, carbonic oxide, nitrogen, and oxygen show that the increases of μ , and therefore of s^{-2} , with temperature are, as might be expected, considerably smaller than for the more complex of the gases on which he experimented. Taking his viscosities at 0° Cent., for carbonic acid and for the four other simple gases named above, and Rayleigh's for argon, with the known densities of all the six gases at 0° C. and standard atmospheric pressure, we have the following table (p. 196) of the values concerned in § 46 (1).

§ 48. The meaning of " s ," the diameter, as defined in § 46, is simpler for the monatomic gas, argon, than for any of the others; and happily we know for argon the density,

* Obermayer, Wien. Akad. 1876, Mar. 16th, vol. 73, p. 433.

not only in the gaseous state ($\cdot 001781$) but also in the liquid state ($1\cdot 212$)*. The latter of these is 681 times the former. Now, all things considered, it seems probable that the crowd of atoms in the liquid may be slightly less dense than an assemblage of globes of diameter s just touching one another in cubic order; but, to make no hypothesis in the first place, let qs be the distance from centre to centre of a cubic arrangement of the molecules 681 times denser than the gas at 0° C. and standard atmospheric pressure; q will be greater than unity if the liquid is less dense, or less than unity if the liquid is denser, than the cubic arrangement with molecules,

Col. 1.	Col. 2.	Col. 3.	Col. 4.	Col. 5.	Col. 6.	Col. 7.	Col. 8.	Col. 9.
Gas.	ρ in terms of grammes per cubic centi- metre.	μ in terms of dynes per square centimetre.	V in terms of centi- metres per second.	Ns^2 in terms of (centi- metre) $^{-1}$.	Hence taking $N=10^{20}$ (§ 50) we have s at 0° Cent. in terms of centimetres.	Taking $N=10^{20}$, m in terms of grammes.	Mean free paths ac- cording to Maxwell's formula † $l = \frac{1}{\sqrt{2} \cdot \pi N s^2}$ in terms of centimetres.	Ratio of volume oc- cupied by molecules to whole volume $N \frac{\pi}{6} s^3$.
CO ₂	$\cdot 001974$	$\cdot 0001414$	39200	89500	$2\cdot 99 \cdot 10^{-8}$	$19\cdot 74 \cdot 10^{-24}$	$2\cdot 52 \cdot 10^{-6}$	$1\cdot 340 \cdot 10^{-3}$
H ₂	$\cdot 0000900$	$\cdot 0000822$	184200	32900	1 \cdot 81 "	0 \cdot 90 "	6 \cdot 84 "	311 "
CO	$\cdot 001234$	$\cdot 0001630$	49600	61300	2 \cdot 48 "	12 \cdot 34 "	3 \cdot 62 "	799 "
N ₂	$\cdot 001257$	$\cdot 0001635$	49000	61600	2 \cdot 48 "	12 \cdot 57 "	3 \cdot 64 "	799 "
O ₂	$\cdot 00143$	$\cdot 0001873$	46100	57500	2 \cdot 40 "	14 \cdot 3 "	3 \cdot 91 "	724 "
Argon	$\cdot 001781$	$\cdot 0002083$	41400	57700	2 \cdot 40 "	17 \cdot 81 "	3 \cdot 89 "	724 "

regarded as spherical of diameter s , just touching. We have

$$681N = 1/(qs)^3 \quad . \quad . \quad . \quad (3),$$

and for argon we have by § 46 (1),

$$Ns^2 = 57700 \quad . \quad . \quad . \quad (4).$$

Eliminating s between these equations we find

$$N = 681^2 \cdot 57700^3 q^6 = 8\cdot 9 \cdot 10^{19} \cdot q^6 \quad . \quad . \quad (5).$$

If the atoms of argon were ideal hard globes, acting on one another with no force except at contact, we should almost certainly have $q \geq 1$ (because with closer packing than that of

* See Ramsay and Travers, Proc. R. S., Nov. 1900, p. 331.

† Maxwell's Collected Papers, vol. ii. p. 348, eqn. (7). The formula as printed in this paper contains a very embarrassing mistake, $\sqrt{2}\pi$ for $\sqrt{2} \cdot \pi$.

cubic order it seems not possible that the assemblage could have sufficient relative mobility of its parts to give it fluidity) and therefore N would be $\geq 8 \cdot 9 \cdot 10^{19}$.

§ 49. For carbonic acid, hydrogen, nitrogen, and oxygen, we have experimental determinations of their densities in the solid or liquid state; and dealing with them as we have dealt with argon, irrespectively of their not being monatomic gases, we find results for the five gases as shown in the following table :

Col. 1.	Col. 2.	Col. 3.	Col. 4.	Col. 5.	
Gas.	Solid or liquid density.	Ratio of solid or liquid density to standard gaseous density.	Number of molecules per cubic centimetre of gas at standard density.	Values of q (§ 48) according to $q^{-6} = \cdot 89$ for argon (liquid compared with gas at 0° and atmospheric pressure).	
			N		
CO ₂	Solid.....	1·58	800	$45\cdot 9 \cdot 10^{19} \cdot q^6$	·776
H ₂	liquid at 17° absolute...	·090	1000	3·56	1·188
N ₂	{ liquid	1·047	833	16·2	·923
	{ solid	1·400	1114	29·0	·837
O ₂	liquid at its freezing pt.	1·27	888	15·0	·935
Argon	{ liquid	1·212	681	8·9	1·020
	{ solid at 86° absolute ...	1·396*	784	12·8	·960

In this table, q denotes the ratio to s of the distance from centre to centre of nearest molecules in an ideal cubic assemblage of the same density as the solid or liquid, as indicated in cols. 3 and 2.

§ 50. According to Avogadro's doctrine, the number of molecules per cubic centimetre is the same for all "perfect" gases at the same temperature and pressure; and even carbonic acid is nearly enough a "perfect gas" for our present considerations. Hence the actual values of q^6 are inversely proportional to the numbers by which they are multiplied in col. 3 of the preceding table. Now, as said in § 48, all things considered, it seems probable that for argon, liquid at density 1·212, q may be somewhat greater, but not much greater, than unity. If it were exactly unity, N would be $8 \cdot 9 \cdot 10^{19}$; and I have chosen $q = (\cdot 89)^{-\frac{1}{6}}$ or 1·020, to make N the round number 10^{20} . Col. 6, in the table of § 47

* From information communicated by Prof. W. Ramsay, July 23, 1901.

above, is calculated with this value of N ; but it is not improbable that the true value of N may be considerably greater than 10^{20} *.

§ 51. As compared with the value for argon, monatomic, the smaller values of q for the diatomic gases, nitrogen and oxygen, and the still smaller values for carbonic acid, triatomic, are quite as might be expected without any special consideration of law of force at different distances between atoms. It seems that the diatomic molecules of nitrogen and oxygen and still more so the triatomic molecule of carbonic acid, are effectively larger when moving freely in the gaseous condition, than when closely packed in liquid or solid assemblage. But the largeness of q for the diatomic hydrogen is not so easily explained: and is a most interesting subject for molecular speculation, though it or any other truth in nature is to be explained by a proper law of force according to the Boscovichian doctrine which we all now accept (many of us without knowing that we do so) as the fundamental hypothesis of physics and chemistry. I hope to return to this question as to hydrogen in a crystallographic appendix.

I am deeply indebted to Professor Dewar for information regarding the density of liquid hydrogen, and the densities of other gases, liquefied or frozen, which he has given me at various times within the last three years.

[To be continued.]

* Maxwell, judging from "molecular volumes" of chemical elements estimated by Lorentz, Meyer and Kopp, unguided by what we now know of the densities of liquid oxygen and liquid hydrogen and of the liquid of the then undiscovered gas argon, estimated $N = 19 \cdot 10^{20}$ (Maxwell's Collected Papers, vol. ii. p. 350) which is rather less than one-fifth of my estimate 10^{26} . On the same page of his paper is given a table of estimated diameters of molecules which are about 3·2 or 3·3 times larger than my estimates in col. 6 of the table in § 47. In a previous part of his paper (p. 348) Maxwell gives estimates of free paths for the same gases, from which by his formula (7), corrected as in col. 8 of my table in § 47, I find values of N ranging from $6\cdot05 \cdot 10^{19}$ to $6\cdot96 \cdot 10^{18}$ or about one-third of $19 \cdot 10^{20}$. His uncorrected formula $\sqrt{2\pi}$ (instead of $\sqrt{2 \cdot \pi}$) gives values of N which are $\sqrt{\pi}$ times, or 1·77 times as great, which are still far short of his final estimate. The discrepancy is therefore not accounted for by the error in the formula as printed, and I see no explanation of it. The free paths as given by Maxwell are about 1·3 or 1·4 times as large as mine.