

and therefore the ratio of $\delta'Q$ to δQ , or of the two specific heats at constant pressure and constant volume respectively, becomes

$$\frac{\sigma + 3 \frac{dX}{dT} + 2}{\sigma + 3 \frac{dX}{dT}}$$

$\frac{dX}{dT}$ is unknown in all respects except that it must be positive; also we know that σ must be integral and not less than 3; if we denote $3 \frac{dX}{dT}$ by e we have for the ratio

$$\frac{\sigma + 2 + e}{\sigma + e}$$

or

$$1 + \frac{2}{\sigma + e}$$

which, with the necessary limitations of σ and e , cannot be greater than $1\frac{1}{2}$ or $1\cdot6$, and in this limiting case the gas must be monatomic.

If, therefore, any value above $1\cdot6$ of the ratio for mercury vapour be insisted upon, the theory must be abandoned so far as present investigations are concerned. If, however, the difference between $1\cdot6$ and any higher value given by the observations be regarded as within reasonable limits of experimental error, this value for mercury vapour, a gas which on chemical grounds is regarded as monatomic, may be viewed as confirming the theory, at least *pro tanto*.

If two spherical atoms were united by a rigid rod to form a molecule, such a molecule would have five degrees of freedom and the specific heat ratio would in this case be $1\frac{1}{2}$, for e would then be zero. This value has a plausible approximation to the observed value $1\cdot408$ of the ratio in a great number of two-atom gases, such as hydrogen, nitrogen, oxygen, and others, but all observations agree so completely in the ratio $1\cdot408$, or from $1\cdot405$ to $1\cdot408$, that it hardly seems reasonable to regard the difference, $0\cdot008$ as within the limits of experimental error, unless, indeed, we had grounds for suspecting a tendency to excess in all the methods employed for the determination of the ratio. But there are other difficulties more formidable still, arising from the spectroscopic properties of heated gases. The light emitted by such gases, so long as they are of no great density, never presents a continuous spectrum, but a spectrum consisting of bright lines with intervening dark spaces. Thus the spectrum of hydrogen gives thirty-two bright lines, that of mercury vapour six lines, that of nitrogen eighteen, and so on. So long as light is regarded as an energy intercommunicable with heat, and light of definite refrangibility is referred to vibrations of given period, we must regard these discontinuous spectra as connected with, and arising from, vibrations of determinate periods in the molecule of the heated gas. And if a gas such as hydrogen or nitrogen be constituted, as we are supposing, of an indefinite repetition of similar molecules, it must follow that such molecules must be capable, at any rate when not too closely packed together, of as many independent vibrations as there are bright lines in the spectrum; that is to say, in addition to the three degrees of freedom arising from motion of translation in solid space, each molecule must possess as many additional degrees of freedom or possible relative motion of its parts as are indicated by the number of spectrum lines. The degrees of freedom corresponding to motion of translation cannot well contribute anything to these luminous vibrations owing to their assumed irregularity and independence of any law; but it is otherwise with the internal or relative degrees of freedom of each molecule, for, unless the gas be very dense, we may easily conceive a sufficient interval of time between one encounter and the next of any molecule with another for very many vibrations, each according to its own law, to take place in the relative positions of different parts of the molecule. At each encounter the whole molecule would be roughly shaken, and when the encounters increased in frequency the vibrations would become irregular and the spectrum would degenerate into a general diffused light of no definite refrangibility, just as music degenerates into ordinary noise. And this is exactly what occurs in the spectra of dense gases.

To bring the theory, therefore, into agreement with observed phenomena, we require very many more degrees of freedom in each molecule than could possibly be assigned to it in accordance with the observed value of the ratios of the specific heats,—mercury vapour, for example, admitting with difficulty the minimum number of three such degrees, as we have just now seen, while its spectrum would require at least nine. And the difficulty increases as we pass to hydrogen and other gases.

We might perhaps conceive, with the view of possibly explaining this difficulty, that there were in all gases a number of composite molecules with many degrees of freedom mixed up with the other molecules with three or five such degrees, but in so small a proportion to these molecules that their presence produces no appreciable effect upon the specific heats; or, since we have no experimental determination of the specific heats of gases at light-giving temperature,

we might, at least until such experimental determination has been arrived at, conceive that our atoms may change their constitution under increased temperature, and become themselves capable of vibration. There is nothing in the conception of an atom as we are considering it which is really inconsistent with such a hypothesis.

Certain observed phenomena accompanying dissociation and combination give rise to other difficulties in the way of the acceptance of the kinetic theory in addition to those arising from the equal distribution of mean kinetic energy just now discussed. For when nitrogen and hydrogen, for example, are mixed in proportion to form ammonia it is observed (1) that at ordinary temperatures they do not exhibit the slightest tendency to combine directly with each other, while, on the other hand, (2) ammonia at ordinary temperatures does not exhibit the slightest tendency to decompose into nitrogen or hydrogen. But ammonia when subjected to certain very high temperatures becomes partially decomposed—that is, becomes a mixture of so many parts of ammonia and of so many other parts of nitrogen and hydrogen in the proportions to form ammonia; and if the temperature be high enough the decomposition may be complete. But, in accordance with the kinetic theory, the conditions, whatever they may be, which at high temperature cause the ammonia to decompose, must sometimes occur to individual molecules at ordinary temperature, because temperature, as we understand it, merely indicates a certain quantity of kinetic energy, and therefore in a gas, however cold, there will be always some molecules in a state for dissociation; and this dissociation having taken place can by (1) never be compensated by recombination; therefore dissociation should be going on in ammonia at all temperatures, and this result is contrary to the observed phenomena (2). It might possibly be conceived, as a way of meeting this last-mentioned difficulty, that the dissociation attendant upon high temperature—that is, upon an average large molecular velocity of translation—requires that there should be a fairly rapid repetition of encounters among molecules moving with dissociation velocity to ensure the production of dissociation, and that in the case of a gas at low temperature, or small average velocity, the chance of two molecules encountering one another at high velocities is small, and the chance of any molecule meeting with any rapid succession of such encounters is practically insensible, and therefore that the dissociation spoken of really never takes place.

As above stated, we conceive that in any gas at ordinary pressure and temperature the intermolecular forces are very small in the aggregate—that is, in Clausius's language, have a very small virial,—by which is understood, not that the forces themselves, where acting, are small, but that, considering the whole aggregate of molecules at any instant, there are very few pairs near enough to each other to exert any appreciable force on each other. Or, if we could watch any individual molecule for any time, we should find that during by far the greater portion of the time it was sensibly free from any action by surrounding molecules. The distance traversed by the type molecule between the instant when it passes out of the sphere of action of one molecule and the instant when it passes into the sphere of action of the next—that is, from one encounter to another—is called its *free path*.

We may find the chance that a molecule starting from any point with velocity ω in a uniform gas shall have free path between x and $x + dx$ from that point.

If a^2 be the chance for such a molecule of free path at least unity, then a^2 is the chance of a free path at least 2. Hence the chance of free path at least x must be of the form a^x .

Following the method employed by O. E. Meyer,¹ let us write this in the form

$$l = -\frac{x}{\log a}$$

where therefore

$$l = -\frac{x + dx}{\log a}$$

then the chance of free path $x + dx$ is

$$e^{-\frac{x+dx}{l}}$$

The chance that such a molecule shall have its first encounter between x and $x + dx$ is the difference of these two expressions; that is,

$$e^{-\frac{x}{l}} \frac{dx}{l}$$

This is the chance of a free path between x and $x + dx$.

The mean free path for such a molecule must then be

$$\int_0^\infty e^{-\frac{x}{l}} \frac{x}{l} dx \div \int_0^\infty e^{-\frac{x}{l}} \frac{1}{l} dx = l$$

This is the meaning of the constant l in $e^{-\frac{x}{l}}$. But if we denote by B the number of encounters which a molecule moving through space with velocity ω experiences on the average per unit of time,

$$B = \frac{\omega}{l}; \text{ or } \frac{1}{l} = \frac{B}{\omega}$$

Hence the chance for such a molecule of free path between x and $x + dx$ is

$$\frac{B}{\omega} e^{-\frac{Bx}{\omega}}$$

with the above definition of B .

The chance of a molecule whose velocity is ω having free path x is of course the same as the chance of its free path having the duration $\frac{x}{\omega}$. If $t = \frac{x}{\omega}$, the chance of duration between t and $t + dt$ is thus

$$\frac{B}{\omega} e^{-Bt} \omega dt; \text{ or } B e^{-Bt} dt$$

Meyer determines the value of B , if the molecules be spheres, in the form

$$B = N\pi s^2 \Omega \left\{ 1 + \frac{1}{1.3} \frac{1}{\omega^2 h} - \frac{1}{1.2} \cdot \frac{1}{3.5} \frac{1}{\omega^4 h^2} + (-)^{n-1} \frac{1}{n} \frac{1}{2n-1} \cdot \frac{1}{2n+1} (\omega^2 h)^n \dots \right\},$$

where $\Omega = \frac{2}{\sqrt{\pi} h}$, and s is the sum of the radii of two molecules.

It will be observed that the series converges very rapidly if $\omega^2 h$ is less than unity, the successive coefficients being

$$\frac{1}{3}, -\frac{1}{30}, +\frac{1}{210}, -\frac{1}{1512}, +\frac{1}{11880} \&c.$$

Having found B for the number of encounters experienced per unit of time by a molecule having velocity ω , we have for the average number of encounters experienced by any molecule per unit of time, which we denote by C ,

$$C = \frac{4}{\sqrt{\pi}} \frac{1}{h^{\frac{3}{2}}} \int_0^\infty e^{-h\omega^2} \omega^3 B d\omega$$

From which Meyer deduces

$$C = 2 \frac{\sqrt{2\pi}}{h} \cdot N s^2 = \Omega \sqrt{2} \cdot N \pi s^2$$

Hence the mean value of the free path for all molecules, irrespective of velocity, is $L = \frac{\Omega}{C} = \frac{1}{\pi \sqrt{2} N s^2}$

Thus the kinetic theory of gases presents to us the conception of apparently perfect rest, as the result of motion irregular in detail but permanent and stable on the average. Whatever difficulty may be felt at first sight in the acceptance of this theory in the case of a medium at rest is greatly enhanced when we pass to the contemplation of a disturbed medium like a mass of gas through which a wave of sound is passing. In our ordinary investigations of such a disturbance the gas is treated as a continuous body, subjected to small relative motions of its parts, accompanied by corresponding variations of internal pressure. When a disturbance or a local condensation or rarefaction is set up in any portion of this gas we calculate the resulting effects by the well-known equations of sound motion. But on this kinetic theory the medium is supposed to consist of a number of discrete masses—elastic spheres or the like—which preserve the physical properties of the medium merely by the recurrence of their mutual collisions, such collisions obeying no law in individual cases, but preserving a certain average uniformity in the motion of the whole aggregate; and we need some further investigation to assure ourselves of the applicability of the ordinary treatment of wave motion to such a medium.

Now we observe that the physical properties of our medium, so far as the relation between pressure, density, and temperature is concerned, merely require that the temperature be measured by the mean total kinetic energy of translation, and that the mean kinetic energy of translation parallel to any fixed line be equal to one-third of the mean total energy of translation. If the molecules constituting any portion of this medium were animated by a common velocity or acceleration, the physical properties of this portion would be similarly determined by the velocities and kinetic energies relative to the common motion. When the distribution of such relative velocities is stable or permanent, the average relative kinetic energy in any fixed direction is one-third of the average relative total kinetic energy, such property constituting normal distribution.

Suppose that in any portion of a medium, consisting of equal elastic spheres, this distribution has been disturbed—that is, $\sum mv^2$, $\sum mv^2$, and $\sum mv^2$ are unequal. If V were the relative velocity of any pair of spheres after such disturbance and before they collide, and θ the angle between V and the common normal at the point of impact, then the normal and tangential relative velocities

before impact are $V \cos \theta$ and $V \sin \theta$, and after impact they become $-V \cos \theta$ and $V \sin \theta$ respectively. The relative velocity after impact, resolved in the direction of relative velocity before impact, is therefore

$$-V \cos^2 \theta + V \sin^2 \theta, \text{ or } -V \cos 2\theta;$$

and the chance of θ being between θ and $\theta + d\theta$ is

$$\frac{\sin 2\theta d\theta}{\sin 2\theta}$$

Therefore the average square relative velocity resolved in the original direction becomes after impact

$$\bar{V}^2 \int_0^\pi \cos^2 2\theta \sin 2\theta d\theta, \text{ or } \frac{\bar{V}^2}{3}$$

The relative velocity after impact in the plane of V , and the normal perpendicular to the direction of V before impact is

$$V \sin \theta \cos \theta + V \sin \theta \cos \theta, \text{ or } V \sin 2\theta$$

And, if a fixed line be taken in the plane perpendicular to V , the average value of the square of the relative velocity after impact, resolved parallel to this line, is

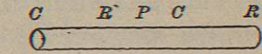
$$\frac{\bar{V}^2}{2\pi} \int_0^{2\pi} \int_0^\pi \sin^2 2\theta \cos^2 \phi d\theta d\phi, \text{ or } \frac{\bar{V}^2}{3} \text{ as before.}$$

Hence we conclude that, in whatever manner the distribution is disturbed in any portion of the medium at any instant, it will, for all those pairs of spheres which within any given interval encounter each other, have assumed the normal distribution after that interval.

If τ denote the average time between two collisions for any given sphere, the chance that this sphere shall continue for any time t free from collisions is, as we have seen, $e^{-\frac{t}{\tau}}$.

If, therefore, D be the number of spheres within any region whose total relative velocity is between w and $w + dw$, but so distributed that the mean square of their relative velocities along any fixed line is not $\frac{w^2}{3}$, then after a time t considerably greater than τ , say ten times τ , the number of the D spheres which have escaped collision will be utterly inconsiderable, and the distribution will have become normal throughout the region.

Suppose, for instance, that a sound wave is passing along a tube filled with air.



the air in the tube is, at any instant, in a state of alternate compression and rarefaction, as at C, B, C, R above.

If the note sounded be (say) 500 vibrations per second, the length of the wave CR is about $\frac{1}{1000}$ feet, and the time taken by the wave in traversing that distance is about $\frac{1}{1000}$ th of a second.

The air in any section of the tube near P has alternately a small positive momentum and an equal small negative momentum; the reversal taking place in every $\frac{1}{1000}$ th of a second; also the same cause which produces the average momentum in either case disturbs the distribution of energy among the x, y , and z directions, i.e., it is always producing an excess or defect in mv^2 above or below that of mv^2 and mv^2 . By what has been proved above, this abnormal distribution of energy becomes inappreciable, owing to molecular collisions in a time considerably less than $\frac{1}{1000}$ th of a second—in fact, in about $\frac{1}{1000000}$ th of a second, when the value of T for atmospheric air is considered. It is therefore legitimate, in calculating the velocity of sound in air (at least on the elastic sphere hypothesis), to regard the distribution as always normal in any section of the tube, the air in that section or in any elementary portion of it possessing, as a whole, any given velocity or acceleration, estimated as if we were dealing with a continuous mass.

DIFFUSION OF GASES.

If any further light is to be thrown on the physical nature of a molecule from investigations, experimental or analytical, concerning gases, it will most probably be by means of experiments on the diffusion of gases, or else on the internal friction or viscosity of gases, and the comparison of these results with those obtained analytically by the methods of the kinetic theory. Such investigations have been undertaken experimentally by Graham, Loschmidt, Maxwell, O. E. Meyer, and others. An account of them will be found in O. E. Meyer's work above referred to. The same problems have also been discussed analytically by Maxwell,¹ and by Stefan, O. E. Meyer, and Boltzmann in the treatises referred to below. We proceed to give a short account of Meyer's results.

¹ Phil. Mag., July 1860, and Feb. and March 1868.

¹ Kinetische Theorie der Gase, Breslau, 1877.

The term "diffusion" has sometimes been applied to the process by which a gas passes through a porous diaphragm. This, however, is now generally denominated *transpiration*. It has also been applied to the expansion of a gas into vacuum, as on the removal of a diaphragm separating the gas from an exhausted receiver. This is now generally denominated *free expansion*. We shall understand, as is now usual, by the term diffusion the process by which, when two or more gases are mixed throughout any space in different proportions at different points, but so that if all molecules were of the same gas the whole would be in equilibrium, the different gases pass through each other and tend to equalize the proportions at all points in the space.

Suppose, for instance, a tube containing a mixture of two gases, *A* and *B*, at constant temperature and constant pressure of the combined gases throughout the tube and subject to no forces, but the density of gas *A* increasing and that of *B* diminishing from one end of the tube to the other. Let the axis of the tube be taken for the axis of *x*. If N_a be the number of molecules of gas *A*, and N_b the number of molecules of gas *B* in unit volume, we have, owing to the constant pressure and temperature at all points of the tube, $N_a + N_b = N$, a constant. But at a given instant N_a and N_b at any point are severally functions of *x*. It will be found that under these circumstances more molecules of gas *A* pass through any section of the tube, which may be in the plane of *yz*, in one direction, say from left to right, than in the opposite direction. On the other hand, more molecules of gas *B* pass from right to left than from left to right. And this will go on till the mixture becomes uniform throughout the tube.

The investigation of the rate at which the unequal distribution tends to equalize itself in this simple case—that is, the excess of the number of molecules of gas *A* which cross a section of the tube from left to right over the number crossing in the same time from right to left—is the problem of diffusion. We give the results obtained by O. E. Meyer as follows:—if the molecules of the two gases had the same mass and dimensions (to put an ideal case), then the excess of molecules of either gas passing through the section in one direction—

that is, the stream velocity—would be $\frac{1}{3} \frac{dN_a}{dx} \bar{\omega}_a$, where l denotes the mean free path for a molecule having velocity ω , and $\bar{\omega}_a$ is the average value of that function for all molecules of the gas.

When we come to deal with two gases, the molecules of one not being of the same size and dimensions with those of the other, we shall find that, in the absence of any common velocity of the two gases at the plane of *yz*, more, or fewer, molecules of gas *A* would cross the plane per unit of time from left to right than of gas *B* from right to left, because, assuming constant pressure and temperature of the mixture at every point in the tube, the number of molecules of the two gases combined must be the same at every point—that is, $N_a + N_b = N$, where N is constant. Hence

$$\frac{dN_a}{dx} = -\frac{dN_b}{dx}$$

Now the excess of molecules of gas *A* coming from left to right per unit of time is $\frac{1}{3} \frac{dN_a}{dx} \bar{\omega}_a$, and similarly the excess of molecules of gas *B* crossing from right to left per unit of time is $\frac{1}{3} \frac{dN_b}{dx} \bar{\omega}_b$, if we now distinguish by suffixes *a* and *b* quantities relating to the two gases respectively. Here l_a and l_b are mean free paths for velocity ω of the two kinds of molecules through the mixed gases, and $\bar{\omega}_a$ is not generally equal to $\bar{\omega}_b$. Hence the total number of molecules crossing the plane from left to right exceeds the number coming from right to left by $\frac{1}{3} \frac{dN}{dx} (\bar{\omega}_a - \bar{\omega}_b)$.

Meyer here assumes that the combined gases have a common velocity $-\frac{1}{3} \frac{dN}{dx} (\bar{\omega}_a - \bar{\omega}_b)$, and that such common velocity will not affect the relative motion of the molecules. On that hypothesis the rate of diffusion can be calculated as follows. The proportion of the stream of the combined gases which consists of molecules of gas *A* is

$$\frac{N_a}{N_a + N_b} \frac{1}{3} \frac{dN_a}{dx} (\bar{\omega}_a - \bar{\omega}_b)$$

Hence, the total surplus number of molecules of gas *A* passing through dx area of the plane per unit of time is

$$\begin{aligned} &= \frac{1}{3} \frac{dN_a}{dx} \left\{ \frac{N_a}{N_a + N_b} (\bar{\omega}_a - \bar{\omega}_b) + \bar{\omega}_a \right\} \\ &= \frac{1}{3} \frac{dN_a}{dx} \{ N_b \bar{\omega}_a + N_a \bar{\omega}_b \}, \end{aligned}$$

or

$$\frac{1}{3N} \frac{dN_a}{dx} \{ N_b \bar{\omega}_a + N_a \bar{\omega}_b \}.$$

The expression

$$\frac{1}{3N} \{ N_b \bar{\omega}_a + N_a \bar{\omega}_b \}$$

is defined to be the "coefficient of diffusion" of gas *A* into gas *B*. It is evidently the same as that of gas *B* into gas *A*.

The Relation of the Coefficient of Diffusion to Density.—It can be shown that $l\omega$, the mean free path for a molecule having velocity ω , is for any single gas inversely proportional to the density, and for any mixture of gases inversely proportional to λ , the aggregate volume occupied by matter in unit space. Hence, in the expression $\frac{1}{3} \bar{\omega} \frac{dN}{dx}$, $\bar{\omega}$ is inversely proportional to the density, or to λ , as the case may be.

Now the rate of diffusion on this theory depends upon $\frac{1}{3} \frac{dN}{dx} \bar{\omega}$.

Hence, given the absolute increase of density of a gas per unit of length, that is, given $\frac{dN}{dx}$, the rate of diffusion ought to vary inversely as the density of the combined gases. On the other hand,

given the proportional increase of the density, or $\frac{1}{N} \frac{dN}{dx}$, the rate of diffusion ought to be independent of the density, because in that case $\frac{dN}{dx}$ varies directly, and $\bar{\omega}$ inversely, as N . The analytical result,

that at given temperatures, and given the absolute value of $\frac{dN}{dx}$, the rate of diffusion is inversely proportional to the density of the gases agrees with the experimental results obtained by Loschmidt for carbonic acid gas and air, carbonic acid gas and hydrogen, hydrogen and oxygen.¹

Relation of the Coefficient of Diffusion to Temperature.—The coefficient of diffusion varies directly as the square root of the absolute temperature, for

$$\bar{\omega} \propto \sqrt{T},$$

and

$$B = 2N_s^2 \frac{\sqrt{\pi}}{\sqrt{h}} \left\{ e^{-h\omega^2} + \frac{2h\omega^2 + 1}{\omega\sqrt{h}} \int_0^{\omega\sqrt{h}} d\mu e^{-\mu^2} \right\};$$

or, if $\omega\sqrt{h} = y$,

$$B = 2N_s^2 \frac{\sqrt{\pi}}{\sqrt{h}} \left\{ e^{-y^2} + \frac{2y^2 + 1}{y} \int_0^y e^{-\mu^2} d\mu \right\}$$

Hence

$$\frac{1}{B} = \frac{\sqrt{h}}{\sqrt{\pi} N_s^2} \psi(y),$$

where ψ denotes a certain function, and

$$\left(\frac{\omega^2}{B} \right) \propto h^{\frac{3}{2}} \int_0^{\omega\sqrt{h}} d\omega e^{-h\omega^2} \omega^4$$

$$\propto h \int_0^{\infty} dy e^{-y^2} \frac{y^4}{y^3} \frac{1}{B} \propto \frac{1}{\sqrt{h}} \int_0^{\infty} dy e^{-y^2} y^2 \psi(y) \propto \frac{1}{\sqrt{h}}.$$

This analytical result also agrees fairly with Loschmidt's experiments above referred to.

FRICION OR VISCOSITY OF GASES.

Suppose two layers of gas separated by an imaginary plane, similar in all respects except that the molecules of one have a small common momentum in a certain direction parallel to the plane. We may take the imaginary plane for that of *yz*, and the average direction of motion of the molecules on one side of the plane, e.g., the left-hand side, for the axis of *y*, the molecules on the right-hand side of the plane having no average momentum. Then the molecules crossing from the left to the right side carry with them an average momentum in the direction *y*, and so tend to impress the right-hand stratum of gas with that momentum. On the other hand, the molecules of the right-hand stratum crossing the plane into the left-hand one have, relatively to the molecules in the latter, an average momentum in the opposite direction, and therefore tend to diminish the average momentum of the left-hand stratum.

¹ *Sitzungsberichte*, 1870, Bd. li. S. 380.

² See Meyer's *Kin. Theorie*, p. 295.

Hence, if we attempt to cause one stratum of gas to pass over another in parallel planes, we experience a resistance due to the interchange of molecules between the portions of gas separated by the plane. This is in some respects analogous to sliding friction between solid bodies, and is called by German writers the "friction" (*Reibung*), by Maxwell and others the "viscosity," of the gas. Meyer¹ investigates this effect of friction in a manner somewhat similar to that employed in case of diffusion, and obtains for the coefficient of viscosity $\frac{1}{3} mN\omega l$.

Relation of the Coefficient of Viscosity to Density and Temperature.—The viscosity of a gas is independent of the density, being, according to O. E. Meyer, $\frac{mN}{3} \omega l$. Now, for any one gas, $l\omega$ is, as

we have seen, inversely proportional to the density, and therefore ωl is inversely proportional to the density. On the other hand, N is directly proportional to the density. Hence the viscosity is independent of the density. This agrees with the result obtained by Maxwell from the kinetic theory in 1860, and with the results of experiments by Maxwell² and O. E. Meyer.³ Also, experiments by O. E. Meyer and Springmühl⁴ on the *transpiration* of gases show that the times in which two different gases under similar circumstances flow through a tube maintain the same constant ratio to one another. As in the case of the coefficient of diffusion, ωl is inversely proportional to the square root of the absolute temperature. As both the coefficient of diffusion and that of viscosity depend on the same function ωl , it should be possible from experiments on viscosity to determine the rate of diffusion. Experiments with this object have been conducted by Stefan⁵ with very satisfactory results, his calculated values for the coefficient of diffusion agreeing very closely with those determined by Loschmidt's direct experiment.⁶

We have given the above results for the coefficients of diffusion and viscosity from O. E. Meyer's work, because his method has met with very general acceptance. It has been shown, however, by Boltzmann,⁷ that the method is incomplete. Meyer's results can only be obtained on the assumption that the molecules of a gas undergoing diffusion or internal friction, which have any given velocity, u , are moving with that velocity in all directions indifferently. We may calculate the number of molecules having velocity u that pass through a given plane during a short time dt , starting from encounters at any given distance from the plane. If we assume that the molecules, issuing from such encounters with velocity u , move indifferently in all directions, we obtain Meyer's result. This assumption is true only of a gas at rest—that is, having no velocity of translation—so that our result so obtained would express, in case of diffusion, the rate at which two gases begin to diffuse, if given at any instant both at rest—that is, with no stream velocity—but mixed in unequal proportions in different parts of space. In any actual case of diffusion, either of the two diffusing gases acquires a small velocity of translation. If we take this velocity into account in calculating the number of molecules of the gas passing through a plane, according to Meyer's method, we shall find that it introduces two new terms, one of which, when the motion becomes steady, is equal and opposite to the result obtained by Meyer. This is proved by Boltzmann in the case of viscosity in the treatise above referred to. The same proof is easily applied in the case of diffusion.

Stefan's Method.—Stefan⁸ regards the two diffusing gases as having small velocities of translation, or stream velocities, u_1 and u_2 , in opposite directions, so that the molecules of one gas, of mass m_1 , have an average momentum $m_1 u_1$ in direction from left to right, and those of the other gas, of mass m_2 , an average momentum $m_2 u_2$ from right to left. By virtue of encounters between the two sets of molecules, each gas is always imparting to the other a portion of its own average momentum, and receiving from the other a corresponding momentum in the opposite direction. The momentum so transferred or interchanged is what Stefan calls the *resistance* which one gas offers to the other's diffusion. In this investigation Stefan assumes that all classes of molecules of one gas, whatever their molecular velocity in space, have the same average velocity in the direction of diffusion—that is, the same stream velocity—so that the motion of the molecules of a diffusing gas would be exactly represented by considering the molecules of a gas at rest—that is, with only its molecular velocity—at the same

¹ See pp. 311-325 of the work above referred to.

² *Proceedings of the Royal Society*, 8th February 1860.

³ *Poggendorff's Annalen*, 1871, cxliii. 14.

⁴ *Pogg. Ann.*, 1873, cxlviii. 1 and 526.

⁵ *Sitzungsber. d. k. k. Akad.*, 1872, lxx. 323.

⁶ For a full account of these and other experiments on diffusion and viscosity, see O. E. Meyer, *Kinetische Theorie d. Gase*, under the heads "Reibung" and "Diffusion."

⁷ "Zur Gas-Reibung," in the *Sitzungsber. d. k. k. Akad.*, 1881.

⁸ Memoir "On the Dynamical Theory of Diffusion" (*Sitzungsber. d. k. k. Akad.*, lxx).

temperature and pressure, and then giving to each molecule the additional common velocity u in the direction of diffusion. Boltzmann, however, shows that, in order correctly to represent the motion of the diffusing gas, we must impart to molecules having different molecular velocities independent of direction different common velocities in the direction of diffusion. And it will be found that the resistance of the gases is sensibly modified by this property.⁹

The complete solution of the problem,—that is, the determination of u as a function of v , on the hypothesis that the molecules are elastic spheres,—is difficult.

If we assume molecules to be centres of force varying inversely as the n th power of the distance, so that the force at distance r is $\frac{\mu}{r^n}$, where μ is constant, we obtain the following result. We assume the molecules of gas *A* whose absolute velocities are between v and $v + dv$ to have an average stream velocity u in direction of the tube, where u is a function of v . Then, if the terminal condition at the ends of the tube be maintained constant, we obtain an equation of the form

$$\frac{p}{N} \frac{dN}{dx} = \frac{4n-8}{8n-8} C \cdot \frac{m_1 m_2}{m_1 + m_2} \frac{\pi N_a N_b}{\text{unit volume}}$$

multiplied by the average value for all molecules of gas *A* of

$u \sqrt{v^{n-1}}$, where V is the relative velocity of two molecules, one taken from each gas, and C is a constant, and m_1, m_2 the masses of the molecules of gas *A* and gas *B* respectively.

By making n infinite we obtain the result for elastic spheres: in that case $\sqrt{v^{n-1}} = V$, and the problem is to find the average value of uV .

Since p varies as the absolute temperature, and the average value of V varies as the square root of the absolute temperature, we may infer that the average value of u —that is, the stream velocity—will vary approximately as the square root of the temperature, as it appears to do from experimental evidence. If, on the other hand, $n=5$, V disappears, and $\frac{4n-8}{8n-8} = 1$. In this case the analytical determination of u presents no difficulty; but in the result the stream velocity varies as the absolute temperature, which accords less satisfactorily with experiments.

ON MOLECULAR DIMENSIONS.

Many attempts have been made in recent years to form an estimate or conjecture, more or less accurate, of the numerical value of the dimensions of a molecule and the absolute force between molecules.¹⁰

In accordance with the view of the subject considered in this article, we are here concerned with such speculations only in so far as they are founded upon the kinetic theory of gases, or supported by it. The phenomena of diffusion and viscosity especially have afforded grounds for estimates of molecular dimensions.

It is first necessary to define what is meant by the dimensions of a molecule. Regarded as an elastic sphere, it has dimensions with the conception of which we are familiar. It is not, of course, seriously contended by any physicists that the molecules of a gas are actually hard elastic spheres, exerting no force on each other at any distance greater than that of actual contact, and then an infinite force. It is necessary to conceive the forces as finite, although they may diminish so rapidly with the distance as that the motions of molecules in the aggregate differ little from what they would be if the molecules were ideal elastic spheres. Nevertheless, they must be finite forces; and, that being the case, it is difficult, if not impossible, to frame a definition of the boundary of a molecule, except as a certain surface at which the forces acting between the molecule in question and other molecules attain a certain value.

If, for instance, we were to regard a molecule as a centre of force,

⁹ For Boltzmann's own treatment of the subject we cannot, within the limits of this article, do more than refer the reader to the memoir above mentioned, "Zur Gas-Reibung," and another as yet unfinished memoir "On Diffusion," in the *Sitzungsber. d. k. k. Akad.*, 1882.

¹⁰ An account of these will be found in O. E. Meyer's *Kin. Theorie d. Gase*, in Professor Tait's *Recent Advances in Physical Science*, lect. xii., and in the following memoirs:—*Phil. Mag.*, July 1879, "On the Size of Molecules," by N. D. C. Hodges; *Phil. Mag.*, March 1880, "On the Mean Free Path of Molecules," by the same author. See also, lecture delivered by Sir W. Thomson at the Royal Institution, 2d Feb. 1883.