IV. *On the Dynamical Theory of Gases.* *By* J. Clerk Maxwell, *F.R.S. L. & E*

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Theories of the constitution of bodies suppose them either to be continuous and homogeneous, or to be composed of a finite number of distinct particles or molecules.

In certain applications of mathematics to physical questions, it is convenient to suppose bodies homogeneous in order to make the quantity of matter in each differential element a function of the coordinates, but I am not aware that any theory of this kind has been proposed to account for the different properties of bodies. Indeed the properties of a body supposed to be a uniform *plenum* may be affirmed dogmatically, but cannot be explained mathematically.

Molecular theories suppose that all bodies, even when they appear to our senses homogeneous, consist of a multitude of particles, or small parts the mechanical relations of which constitute the properties of the bodies. Those theories which suppose that the molecules are at rest relative to the body may be called statical theories, and those which suppose the molecules to be in motion, even while the body is apparently at rest, may be called dynamical theories.

If we adopt a statical theory, and suppose the molecules of a body kept at rest in their positions of equilibrium by the action of forces in the directions of the lines joining their centres, we may determine the mechanical properties of a body so constructed, if distorted so that the displacement of each molecule is a function of its coordinates when in equilibrium. It appears from the mathematical theory of bodies of this kind, that the forces called into play by a small change of form must always bear a fixed proportion to those excited by a small change of volume.

Now we know that in fluids the elasticity of form is evanescent, while that of volume is considerable. Hence such theories will not apply to fluids. In solid bodies the elasticity of form appears in many cases to be smaller in proportion to that of volume than the theory gives*, so that we are forced to give up the theory of molecules whose displacements are functions of their coordinates when at rest, even in the case of solid bodies.

The theory of moving molecules, on the other hand, is not open to these objections. The mathematical difficulties in applying the theory are considerable, and till they are surmounted we cannot fully decide on the applicability of the theory. We are able, however, to explain a great variety of phenomena by the dynamical theory which have not been hitherto explained otherwise.

The dynamical theory supposes that the molecules of solid bodies oscillate about their

* [In glass, according to Dr. Everett's second series of experiments (1866), the ratio of the elasticity of form to that of volume is greater than that given by the theory. In brass and steel it is less.—March 7, 1867.]

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positions of equilibrium, but do not travel from one position to another in the body. In fluids the molecules are supposed to be constantly moving into new relative positions, so that the same molecule may travel from one part of the fluid to any other part. In liquids the molecules are supposed to be always under the action of the forces due to neighbouring molecules throughout their course, but in gases the greater part of the path of each molecule is supposed to be sensibly rectilinear and beyond the sphere of sensible action of the neighbouring molecules.

I propose in this paper to apply this theory to the explanation of various properties of gases, and to show that, besides accounting for the relations of pressure, density, and temperature in a single gas, it affords a mechanical explanation of the known chemical relation between the density of a gas and its equivalent weight, commonly called the Law of Equivalent Volumes. It also explains the diffusion of one gas through another, the internal friction of a gas, and the conduction of heat through gases.

The opinion that the observed properties of visible bodies apparently at rest are due to the action of invisible molecules in rapid motion is to be found in LUCRETIUS. In the exposition which he gives of the theories of DEMOCRITUS as modified by EPICURUS, he describes the invisible atoms as all moving downwards with equal velocities, which, at quite uncertain times and places, suffer an imperceptible change, just enough to allow of occasional collisions taking place between the atoms. These atoms he supposes to set small bodies in motion by an action of which we may form some conception by looking at the motes in a sunbeam. The language of LUCRETIUS must of course be interpreted according to the physical ideas of his age, but we need not wonder that it suggested to LE SAGE the fundamental conception of his theory of gases, as well as his doctrine of ultramundane corpuscles.

Professor CLAUSIUS, to whom we owe the most extensive developments of the dynamical theory of gases, has given* a list of authors who have adopted or given countenance to any theory of invisible particles in motion. Of these, DANIEL BERNOULLI, in the tenth section of his 'Hydrodynamics,' distinctly explains the pressure of air by the impact of its particles on the sides of the vessel containing it.

CLAUSIUS also mentions a book entitled "Deux Traités de Physique Mécanique, publiés par PIERRE PREVOST, comme simple Éditeur du premier et comme Auteur du second," Genève et Paris, 1818. The first memoir is by G. LE SAGE, who explains gravity by the impact of "ultramundane corpuscles" on bodies. These corpuscles also set in motion the particles of light and various æthereal media, which in their turn act on the molecules of gases and keep up their motions. His theory of impact is faulty, but his explanation of the expansive force of gases is essentially the same as in the dynamical theory as it now stands. The second memoir, by PREVOST, contains new applications of the principles of LE SAGE to gases and to light. A more extensive application of the theory of moving molecules was made by HERAPATH†. His theory of the collisions of

* POGGENDORFF'S 'Annalen,' Jan. 1862. Translated by G. C. FOSTER, B.A., Phil. Mag. June 1862.

† Mathematical Physics, &c., by JOHN HERAPATH, Esq. 2 vols. London: Whittaker & Co., and Herapath's Railway Journal Office, 1847.

perfectly hard bodies, such as he supposes the molecules to be, is faulty, inasmuch as it makes the result of impact depend on the absolute motion of the bodies, so that by experiments on such hard bodies (if we could get them) we might determine the absolute direction and velocity of the motion of the earth*. This author, however, has applied his theory to the numerical results of experiment in many cases, and his speculations are always ingenious, and often throw much real light on the questions treated. In particular, the theory of temperature and pressure in gases and the theory of diffusion are clearly pointed out.

Dr. JOULE† has also explained the pressure of gases by the impact of their molecules, and has calculated the velocity which they must have in order to produce the pressure observed in particular gases.

It is to Professor CLAUSIUS, of Zurich, that we owe the most complete dynamical theory of gases. His other researches on the general dynamical theory of heat are well known, and his memoirs "On the kind of Motion which we call Heat," are a complete exposition of the molecular theory adopted in this paper. After reading his investigation‡ of the distance described by each molecule between successive collisions, I published some propositions§ on the motions and collisions of perfectly elastic spheres, and deduced several properties of gases, especially the law of equivalent volumes, and the nature of gaseous friction. I also gave a theory of diffusion of gases, which I now know to be erroneous, and there were several errors in my theory of the conduction of heat in gases which M. CLAUSIUS has pointed out in an elaborate memoir on that subject‖.

M. O. E. MEYER¶ has also investigated the theory of internal friction on the hypothesis of hard elastic molecules.

In the present paper I propose to consider the molecules of a gas, not as elastic spheres of definite radius, but as small bodies or groups of smaller molecules repelling one another with a force whose direction always passes very nearly through the centres of gravity of the molecules, and whose magnitude is represented very nearly by some function of the distance of the centres of gravity. I have made this modification of the theory in consequence of the results of my experiments on the viscosity of air at different temperatures, and I have deduced from these experiments that the repulsion is inversely as the *fifth* power of the distance.

If we suppose an imaginary plane drawn through a vessel containing a great number of such molecules in motion, then a great many molecules will cross the plane in either direction. The excess of the mass of those which traverse the plane in the positive

* Mathematical Physics, &c., p. 134.

† Some Remarks on Heat and the Constitution of Elastic Fluids, Oct. 3, 1848.

‡ Phil. Mag. Feb. 1859.

§ Illustrations of the Dynamical Theory of Gases, Phil. Mag. 1860, January and July.

‖ POGGENDORFF, Jan. 1862; Phil. Mag. June 1862.

¶ Ueber die innere Reibung der Gase (POGGENDORFF, vol. CXXV. 1865).

direction over that of those which traverse it in the negative direction, gives a measure of the flow of gas through the plane in the positive direction.

If the plane be made to move with such a velocity that there is no excess of flow of molecules in one direction through it, then the velocity of the plane is the mean velocity of the gas resolved normal to the plane.

There will still be molecules moving in both directions through the plane, and carrying with them a certain amount of momentum into the portion of gas which lies on the other side of the plane.

The quantity of momentum thus communicated to the gas on the other side of the plane during a unit of time is a measure of the force exerted on this gas by the rest. This force is called the pressure of the gas.

If the velocities of the molecules moving in different directions were independent of one another, then the pressure at any point of the gas need not be the same in all directions, and the pressure between two portions of gas separated by a plane need not be perpendicular to that plane. Hence, to account for the observed equality of pressure in all directions, we must suppose some cause equalizing the motion in all directions. This we find in the deflection of the path of one particle by another when they come near one another. Since, however, this equalization of motion is not instantaneous, the pressures in all directions are perfectly equalized only in the case of a gas at rest, but when the gas is in a state of motion, the want of perfect equality in the pressures gives rise to the phenomena of viscosity or internal friction. The phenomena of viscosity in all bodies may be described, independently of hypothesis, as follows:—

A distortion or strain of some kind, which we may call S, is produced in the body by displacement. A state of stress or elastic force which we may call F is thus excited. The relation between the stress and the strain may be written $F=ES$, where E is the coefficient of elasticity for that particular kind of strain. In a solid body free from viscosity, F will remain $=ES$, and

$$\frac{dF}{dt}=E\frac{dS}{dt}.$$

If, however, the body is viscous, F will not remain constant, but will tend to disappear at a rate depending on the value of F, and on the nature of the body. If we suppose this rate proportional to F, the equation may be written

$$\frac{dF}{dt}=E\frac{dS}{dt}-\frac{F}{T},$$

which will indicate the actual phenomena in an empirical manner. For if S be constant,

$$F=ESe^{-\frac{t}{T}},$$

showing that F gradually disappears, so that if the body is left to itself it gradually loses any internal stress, and the pressures are finally distributed as in a fluid at rest.

If $\frac{dS}{dt}$ is constant, that is, if there is a steady motion of the body which continually

increases the displacement,

$$F = ET\frac{dS}{dt} + Ce^{-\frac{t}{T}},$$

showing that F tends to a constant value depending on the rate of displacement. The quantity ET, by which the rate of displacement must be multiplied to get the force, may be called the coefficient of viscosity. It is the product of a coefficient of elasticity, E, and a time T, which may be called the "time of relaxation" of the elastic force. In mobile fluids T is a very small fraction of a second, and E is not easily determined experimentally. In viscous solids T may be several hours or days, and then E is easily measured. It is possible that in some bodies T may be a function of F, and this would account for the gradual untwisting of wires after being twisted beyond the limit of perfect elasticity. For if T diminishes as F increases, the parts of the wire furthest from the axis will yield more rapidly than the parts near the axis during the twisting process, and when the twisting force is removed, the wire will at first untwist till there is equilibrium between the stresses in the inner and outer portions. These stresses will then undergo a gradual relaxation; but since the actual value of the stress is greater in the outer layers, it will have a more rapid rate of relaxation, so that the wire will go on gradually untwisting for some hours or days, owing to the stress on the interior portions maintaining itself longer than that of the outer parts. This phenomenon was observed by WEBER in silk fibres, by KOHLRAUSCH in glass fibres, and by myself in steel wires.

In the case of a collection of moving molecules such as we suppose a gas to be, there is also a resistance to change of form, constituting what may be called the linear elasticity, or "rigidity" of the gas, but this resistance gives way and diminishes at a rate depending on the amount of the force and on the nature of the gas.

Suppose the molecules to be confined in a rectangular vessel with perfectly elastic sides, and that they have no action on one another, so that they never strike one another, or cause each other to deviate from their rectilinear paths. Then it can easily be shown that the pressures on the sides of the vessel due to the impacts of the molecules are perfectly independent of each other, so that the mass of moving molecules will behave, not like a fluid, but like an elastic solid. Now suppose the pressures at first equal in the three directions perpendicular to the sides, and let the dimensions a, b, c of the vessel be altered by small quantities, δa, δb, δc.

Then if the original pressure in the direction of a was p, it will become

$$p\left(1 - 3\frac{\delta a}{a} - \frac{\delta b}{b} - \frac{\delta c}{c}\right);$$

or if there is no change of volume,

$$\frac{\delta p}{p} = -2\frac{\delta a}{a},$$

showing that in this case there is a "longitudinal" elasticity of form of which the coefficient is $2p$. The coefficient of "Rigidity" is therefore $=p$.

This rigidity, however, cannot be directly observed, because the molecules continually deflect each other from their rectilinear courses, and so equalize the pressure in all directions. The rate at which this equalization takes place is great, but not infinite; and therefore there remains a certain inequality of pressure which constitutes the phenomenon of viscosity.

I have found by experiment that the coefficient of viscosity in a given gas is independent of the density, and proportional to the absolute temperature, so that if ET be the viscosity, $\mathrm{ET} \propto \frac{p}{\varrho}$.

But $\mathrm{E}=p$, therefore T, the time of relaxation, varies inversely as the density and is independent of the temperature. Hence the number of collisions producing a given deflection which take place in unit of time is independent of the temperature, that is, of the velocity of the molecules, and is proportional to the number of molecules in unit of volume. If we suppose the molecules hard elastic bodies, the number of collisions of a given kind will be proportional to the velocity, but if we suppose them centres of force, the angle of deflection will be smaller when the velocity is greater; and if the force is inversely as the fifth power of the distance, the number of deflections of a given kind will be independent of the velocity. Hence I have adopted this law in making my calculations.

The effect of the mutual action of the molecules is not only to equalize the pressure in all directions, but, when molecules of different kinds are present, to communicate motion from the one kind to the other. I formerly showed that the final result in the case of hard elastic bodies is to cause the average *vis viva* of a molecule to be the same for all the different kinds of molecules. Now the pressure due to each molecule is proportional to its *vis viva*, hence the whole pressure due to a given number of molecules in a given volume will be the same whatever the mass of the molecules, provided the molecules of different kinds are permitted freely to communicate motion to each other.

When the flow of *vis viva* from the one kind of molecules to the other is zero, the temperature is said to be the same. Hence equal volumes of different gases at equal pressures and temperatures contain equal numbers of molecules.

This result of the dynamical theory affords the explanation of the "law of equivalent volumes" in gases.

We shall see that this result is true in the case of molecules acting as centres of force. A law of the same general character is probably to be found connecting the temperatures of liquid and solid bodies with the energy possessed by their molecules, although our ignorance of the nature of the connexions between the molecules renders it difficult to enunciate the precise form of the law.

The molecules of a gas in this theory are those portions of it which move about as a single body. These molecules may be mere points, or pure centres of force endowed with inertia, or the capacity of performing work while losing velocity. They may be systems of several such centres of force, bound together by their mutual actions, and in

this case the different centres may either be separated, so as to form a group of points, or they may be actually coincident, so as to form one point.

Finally, if necessary, we may suppose them to be small solid bodies of a determinate form; but in this case we must assume a new set of forces binding the parts of these small bodies together, and so introduce a molecular theory of the second order. The doctrines that all matter is extended, and that no two portions of matter can coincide in the same place, being deductions from our experiments with bodies sensible to us, have no application to the theory of molecules.

The actual energy of a moving body consists of two parts, one due to the motion of its centre of gravity, and the other due to the motions of its parts relative to the centre of gravity. If the body is of invariable form, the motions of its parts relative to the centre of gravity consist entirely of rotation, but if the parts of the body are not rigidly connected, their motions may consist of oscillations of various kinds, as well as rotation of the whole body.

The mutual interference of the molecules in their courses will cause their energy of motion to be distributed in a certain ratio between that due to the motion of the centre of gravity and that due to the rotation, or other internal motion. If the molecules are pure centres of force, there can be no energy of rotation, and the whole energy is reduced to that of translation; but in all other cases the whole energy of the molecule may be represented by $\frac{1}{2}Mv^2\beta$, where β is the ratio of the total energy to the energy of translation. The ratio β will be different for every molecule, and will be different for the same molecule after every encounter with another molecule, but it will have an average value depending on the nature of the molecules, as has been shown by CLAUSIUS. The value of β can be determined if we know either of the specific heats of the gas, or the ratio between them.

The method of investigation which I shall adopt in the following paper, is to determine the mean values of the following functions of the velocity of all the molecules of a given kind within an element of volume:—

(α) the mean velocity resolved parallel to each of the coordinate axes;

(β) the mean values of functions of two dimensions of these component velocities;

(γ) the mean values of functions of three dimensions of these velocities.

The rate of translation of the gas, whether by itself, or by diffusion through another gas, is given by (α), the pressure of the gas on any plane, whether normal or tangential to the plane, is given by (β), and the rate of conduction of heat through the gas is given by (γ).

I propose to determine the variations of these quantities, due, 1st, to the encounters of the molecules with others of the same system or of a different system; 2nd, to the action of external forces such as gravity; and 3rd, to the passage of molecules through the boundary of the element of volume.

I shall then apply these calculations to the determination of the statical cases of the final distribution of two gases under the action of gravity, the equilibrium of tempe-

rature between two gases, and the distribution of temperature in a vertical column. These results are independent of the law of force between the molecules. I shall also consider the dynamical cases of diffusion, viscosity, and conduction of heat, which involve the law of force between the molecules.

On the Mutual Action of Two Molecules.

Let the masses of these molecules be M_1, M_2, and let their velocities resolved in three directions at right angles to each other be ξ_1, η_1, ζ_1 and ξ_2, η_2, ζ_2. The components of the velocity of the centre of gravity of the two molecules will be

$$\frac{\xi_1 M_1 + \xi_2 M_2}{M_1 + M_2}, \quad \frac{\eta_1 M_1 + \eta_2 M_2}{M_1 + M_2}, \quad \frac{\zeta_1 M_1 + \zeta_2 M_2}{M_1 + M_2}.$$

The motion of the centre of gravity will not be altered by the mutual action of the molecules, of whatever nature that action may be. We may therefore take the centre of gravity as the origin of a system of coordinates moving parallel to itself with uniform velocity, and consider the alteration of the motion of each particle with reference to this point as origin.

If we regard the molecules as simple centres of force, then each molecule will describe a plane curve about this centre of gravity, and the two curves will be similar to each other and symmetrical with respect to the line of apses. If the molecules move with sufficient velocity to carry them out of the sphere of their mutual action, their orbits will each have a pair of asymptotes inclined at an angle $\frac{\pi}{2} - \theta$ to the line of apses. The asymptotes of the orbit of M_1 will be at a distance b_1 from the centre of gravity, and those of M_2 at a distance b_2, where

$$M_1 b_1 = M_2 b_2.$$

The distance between two parallel asymptotes, one in each orbit, will be

$$b = b_1 + b_2.$$

If, while the two molecules are still beyond each other's action, we draw a straight line through M_1 in the direction of the relative velocity of M_1 to M_2, and draw from M_2 a perpendicular to this line, the length of this perpendicular will be b, and the plane including b and the direction of relative motion will be the plane of the orbits about the centre of gravity.

When, after their mutual action and deflection, the molecules have again reached a distance such that there is no sensible action between them, each will be moving with the same velocity relative to the centre of gravity that it had before the mutual action, but the direction of this relative velocity will be turned through an angle 2θ in the plane of the orbit.

The angle θ is a function of the relative velocity of the molecules and of b, the form of the function depending on the nature of the action between the molecules.

If we suppose the molecules to be bodies, or systems of bodies, capable of rotation,

internal vibration, or any form of energy other than simple motion of translation, these results will be modified. The value of θ and the final velocities of the molecules will depend on the amount of internal energy in each molecule before the encounter, and on the particular form of that energy at every instant during the mutual action. We have no means of determining such intricate actions in the present state of our knowledge of molecules, so that we must content ourselves with the assumption that the value of θ is, on an average, the same as for pure centres of force, and that the final velocities differ from the initial velocities only by quantities which may in each collision be neglected, although in a great many encounters the energy of translation and the internal energy of the molecules arrive, by repeated small exchanges, at a final ratio, which we shall suppose to be that of 1 to $\beta-1$.

We may now determine the final velocity of M_1 after it has passed beyond the sphere of mutual action between itself and M_2.

Let V be the velocity of M_1 relative to M_2, then the components of V are

$$\xi_1-\xi_2, \quad \eta_1-\eta_2, \quad \zeta_1-\zeta_2.$$

The plane of the orbit is that containing V and b. Let this plane be inclined φ to a plane containing V and parallel to the axis of x; then, since the direction of V is turned round an angle 2θ in the plane of the orbit, while its magnitude remains the same, we may find the value of ξ_1 after the encounter. Calling it ξ_1',

$$\xi_1'=\xi_1+\frac{M_2}{M_1+M_2}\{(\xi_2-\xi_1)2\sin^2\theta+\sqrt{(\eta_2-\eta_1)^2+(\zeta_2-\zeta_1)^2}\sin 2\theta\cos\varphi\}. \quad . \quad . \quad (1)$$

There will be similar expressions for the components of the final velocity of M_1 in the other coordinate directions.

If we know the initial positions and velocities of M_1 and M_2 we can determine V, the velocity of M_1 relative to M_2; b the shortest distance between M_1 and M_2 if they had continued to move with uniform velocity in straight lines; and φ the angle which determines the plane in which V and b lie. From V and b we can determine θ, if we know the law of force, so that the problem is solved in the case of two molecules.

When we pass from this case to that of two systems of moving molecules, we shall suppose that the time during which a molecule is beyond the action of other molecules is so great compared with the time during which it is deflected by that action, that we may neglect both the time and the distance described by the molecules during the encounter, as compared with the time and the distance described while the molecules are free from disturbing force. We may also neglect those cases in which three or more molecules are within each other's spheres of action at the same instant.

On the Mutual Action of Two Systems of Moving Molecules.

Let the number of molecules of the first kind in unit of volume be N_1, the mass of each being M_1. The velocities of these molecules will in general be different both in magnitude and direction. Let us select those molecules the components of whose velocities

lie between

$$\xi_1 \text{ and } \xi_1+d\xi_1, \quad \eta_1 \text{ and } \eta_1+d\eta_1, \quad \zeta_1 \text{ and } \zeta_1+d\zeta_1,$$

and let the number of these molecules be $d\mathrm{N}_1$. The velocities of these molecules will be very nearly equal and parallel.

On account of the mutual actions of the molecules, the number of molecules which at a given instant have velocities within given limits will be definite, so that

$$d\mathrm{N}_1=f_1(\xi_1\eta_1\zeta)d\xi_1 d\eta_1 d\zeta_1 \quad \ldots \ldots \ldots \ldots \quad (2)$$

We shall consider the form of this function afterwards.

Let the number of molecules of the second kind in unit of volume be N_2, and let $d\mathrm{N}_2$ of these have velocities between ξ_2 and $\xi_2+d\xi_2$, η_2 and $d\eta_2+\eta_2$, ζ_2 and $\zeta_2+d\zeta_2$, where

$$d\mathrm{N}_2=f_2(\xi_2\eta_2\zeta_2)d\xi_2 d\eta_2 d\zeta_2.$$

The velocity of any of the $d\mathrm{N}_1$ molecules of the first system relative to the $d\mathrm{N}_2$ molecules of the second system is V, and each molecule M_1 will in the time δt describe a relative path $\mathrm{V}\delta t$ among the molecules of the second system. Conceive a space bounded by the following surfaces. Let two cylindrical surfaces have the common axis $\mathrm{V}\delta t$ and radii b and $b+db$. Let two planes be drawn through the extremities of the line $\mathrm{V}\delta t$ perpendicular to it. Finally, let two planes be drawn through $\mathrm{V}\delta t$ making angles φ and $\varphi+d\varphi$ with a plane through V parallel to the axis of x. Then the volume included between the four planes and the two cylindric surfaces will be $\mathrm{V}bdbd\varphi\delta t$.

If this volume includes one of the molecules M_2, then during the time δt there will be an encounter between M_1 and M_2, in which b is between b and $b+db$, and φ between φ and $\varphi+d\varphi$.

Since there are $d\mathrm{N}_1$ molecules similar to M_1 and $d\mathrm{N}_2$ similar to M_2 in unit of volume, the whole number of encounters of the given kind between the two systems will be

$$\mathrm{V}bdbd\varphi\delta t d\mathrm{N}_1 d\mathrm{N}_2.$$

Now let Q be any property of the molecule M_1, such as its velocity in a given direction, the square or cube of that velocity or any other property of the molecule which is altered in a known manner by an encounter of the given kind, so that Q becomes Q′ after the encounter, then during the time δt a certain number of the molecules of the first kind have Q changed to Q′, while the remainder retain the original value of Q, so that

$$\delta\mathrm{Q}d\mathrm{N}_1=(\mathrm{Q}'-\mathrm{Q})\mathrm{V}bdbd\varphi\delta t d\mathrm{N}_1 d\mathrm{N}_2,$$

or

$$\frac{\delta\mathrm{Q}d\mathrm{N}_1}{\delta t}=(\mathrm{Q}'-\mathrm{Q})\mathrm{V}bdbd\varphi d\mathrm{N}_1 d\mathrm{N}_2. \quad \ldots \ldots \ldots \quad (3)$$

Here $\frac{\delta\mathrm{Q}d\mathrm{N}_1}{\delta t}$ refers to the alteration in the sum of the values of Q for the $d\mathrm{N}_1$ molecules, due to their encounters of the given kind with the $d\mathrm{N}_2$ molecules of the second sort. In order to determine the value of $\frac{\delta\mathrm{QN}_1}{\delta t}$, the rate of alteration of Q among all the molecules of the first kind, we must perform the following integrations:—

1st, with respect to φ from $\varphi=0$ to $\varphi=2\pi$.

2nd, with respect to b from $b=0$ to $b=\infty$. These operations will give the results of the encounters of every kind between the dN_1 and dN_2 molecules.

3rd, with respect to dN_2, or $f_2(\xi_2\eta_2\zeta_2)d\xi_2 d\eta_2 d\zeta_2$.

4th, with respect to dN_1, or $f_1(\xi_1\eta_1\zeta_1)d\xi_1 d\eta_1 d\zeta_1$.

These operations require in general a knowledge of the forms of f_1 and f_2.

1st. *Integration with respect to* φ.

Since the action between the molecules is the same in whatever plane it takes place, we shall first determine the value of $\int_0^{2\pi}(Q'-Q)d\varphi$ in several cases, making Q some function of ξ, η, and ζ.

(α) Let $Q=\xi_1$ and $Q'=\xi'_1$, then

$$\int_0^{2\pi}(\xi'_1-\xi_1)d\varphi=\frac{M_2}{M_1+M_2}(\xi_2-\xi_1)4\pi\sin^2\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(β) Let $Q=\xi_1^2$ and $Q'=\xi_1'^2$,

$$\int_0^{2\pi}(\xi_1'^2-\xi_1^2)d\varphi=\frac{M_2}{(M_1+M_2)^2}\Big\{(\xi_2-\xi_1)(M_1\xi_1+M_2\xi_2)8\pi\sin^2\theta+M_2\big((\eta_2-\eta_1)^2+(\zeta_2-\zeta_1)^2-2(\xi_2-\xi_1)^2\big)\pi\sin^2 2\theta\Big\}. \quad (5)$$

By transformation of coordinates we may derive from this

$$\int_0^{2\pi}(\xi'_1\eta'_1-\xi_1\eta_1)d\varphi=\frac{M_2}{(M_1+M_2)^2}\Big\{\big(M_2\xi_2\eta_2-M_1\xi_1\eta_1+\tfrac{1}{2}(M_1-M_2)(\xi_1\eta_2+\xi_2\eta_1)\big)8\pi\sin^2\theta-3M_2(\xi_2-\xi_1)(\eta_2-\eta_1)\Big\}, \quad (6)$$

with similar expressions for the other quadratic functions of ξ, η, ζ.

(γ) Let $Q=\xi_1(\xi_1^2+\eta_1^2+\zeta_1^2)$, and $Q'=\xi'_1(\xi_1'^2+\eta_1'^2+\zeta_1'^2)$; then putting $\xi_1^2+\eta_1^2+\zeta_1^2=V_1^2$, $\xi_1\xi_2+\eta_1\eta_2+\zeta_1\zeta_2=U$, $\xi_2^2+\eta_2^2+\zeta_2^2=V_2^2$, and $(\xi_2-\xi_1)^2+(\eta_2-\eta_1)^2+(\zeta_2-\zeta_1)^2=V^2$, we find

$$\left.\begin{aligned}\int_0^{2\pi}(\xi'_1V_1'^2-\xi_1V_1^2)d\varphi=&\frac{M_2}{M_1+M_2}4\pi\sin^2\theta\{(\xi_2-\xi_1)V_1^2+2\xi_1(U-V_1^2\}\\&+\left(\frac{M_2}{M_1+M_2}\right)^2(8\pi\sin^2\theta-3\pi\sin^2 2\theta)2(\xi_2-\xi_1)(U-V_1^2)\\&+\left(\frac{M_2}{M_1+M_2}\right)^2(8\pi\sin^2\theta+2\pi\sin^2 2\theta)\xi_1V^2\\&+\left(\frac{M_2}{M_1+M_2}\right)^3(8\pi\sin^2\theta-2\pi\sin^2 2\theta)2(\xi_2-\xi_1)V^2.\end{aligned}\right\} \quad . \quad . \quad (7)$$

These are the principal functions of ξ, η, ζ whose changes we shall have to consider; we shall indicate them by the symbols α, β, or γ, according as the function of the velocity is of one, two, or three dimensions.

2nd. *Integration with respect to* b.

We have next to multiply these expressions by bdb, and to integrate with respect to b from $b=0$ to $b=\infty$. We must bear in mind that θ is a function of b and V, and can only be determined when the law of force is known. In the expressions which we have

to deal with, θ occurs under two forms only, namely, $\sin^2\theta$ and $\sin^2 2\theta$. If, therefore, we can find the values of

$$B_1=\int_0^\infty 4\pi b db \sin^2\theta, \text{ and } B_2=\int_0^\infty \pi b db \sin^2 2\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

we can integrate all the expressions with respect to b.

B_1 and B_2 will be functions of V only, the form of which we can determine only in particular cases, after we have found θ as a function of b and V.

Determination of θ for certain laws of Force.

Let us assume that the force between the molecules M_1 and M_2 is repulsive and varies inversely as the nth power of the distance between them, the value of the moving force at distance unity being K, then we find by the equation of central orbits,

$$\frac{\pi}{2}-\theta=\int_0^{x'}\frac{dx}{\sqrt{1-x^2-\frac{2}{n-1}\left(\frac{x}{\alpha}\right)^{n-1}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $x=\frac{b}{r}$, or the ratio of b to the distance of the molecules at a given time: x is therefore a numerical quantity; α is also a numerical quantity and is given by the equation

$$\alpha=b\left(\frac{V^2M_1M_2}{K(M_1+M_2)}\right)^{\frac{1}{n-1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The limits of integration are $x=0$ and $x=x'$, where x' is the least positive root of the equation

$$1-x^2-\frac{2}{n-1}\left(\frac{x}{\alpha}\right)^{n-1}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

It is evident that θ is a function of α and n, and when n is known θ may be expressed as a function of α only.

Also

$$bdb=\left(\frac{K(M_1+M_2)}{V^2M_1M_2}\right)^{\frac{2}{n-1}}\alpha d\alpha\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

so that if we put

$$A_1=\int_0^\infty 4\pi\alpha d\alpha \sin^2\theta, \quad A_2=\int_0^\infty \pi\alpha d\alpha \sin^2 2\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

A_1 and A_2 will be definite numerical quantities which may be ascertained when n is given, and B_1 and B_2 may be found by multiplying A_1 and A_2 by $\left(\frac{K(M_1+M_2)}{M_1M_2}\right)^{\frac{2}{n-1}}V^{\frac{-4}{n-1}}$.

Before integrating further we have to multiply by V, so that the form in which V will enter into the expressions which have to be integrated with respect to dN_1 and dN_2 will be

$$V^{\frac{n-5}{n-1}}.$$

It will be shown that we have reason from experiments on the viscosity of gases to believe that $n=5$. In this case V will disappear from the expressions of the form (3), and they will be capable of immediate integration with respect to dN_1 and dN_2.

If we assume $n=5$ and put $\alpha^4=2\cot^2 2\phi$ and $x=\sqrt{1-\tan^2\phi}\cos\psi$,

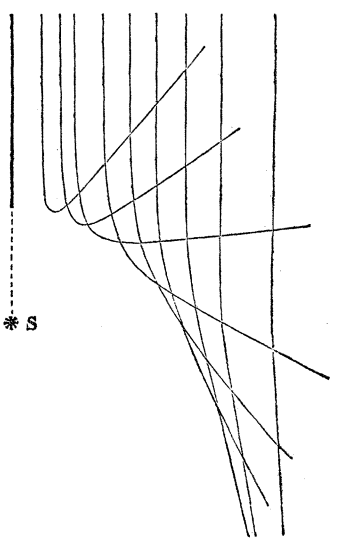
$$\left.\begin{aligned}\frac{\pi}{2}-\theta&=\sqrt{\cos 2\phi}\int_0^{\frac{\pi}{2}}\frac{d\psi}{\sqrt{1-\sin^2\phi\sin^2\psi}}\\&=\sqrt{\cos 2\phi}\,\mathrm{F}_{\sin\phi},\end{aligned}\right\}\quad\ldots\ldots\ldots\quad(14)$$

where $\mathrm{F}_{\sin\phi}$ is the complete elliptic function of the first kind and is given in LEGENDRE'S Tables. I have computed the following Table of the distance of the asymptotes, the distance of the apse, the value of θ, and of the quantities whose summation leads to A_1 and A_2.

ϕ.	b.	Distance of apse.	θ.	$\frac{\sin^2\theta}{\sin^2 2\phi}$.	$\frac{\sin^2 2\theta}{\sin^2 2\phi}$.
° ′			° ′		
0 0	infinite	infinite	0 0	0	0
5 0	2381	2391	0 31	·00270	·01079
10 0	1658	1684	1 53	·01464	·03689
15 0	1316	1366	4 47	·02781	·11048
20 0	1092	1172	8 45	·05601	·21885
25 0	916	1036	14 15	·10325	·38799
30 0	760	931	21 42	·18228	·62942
35 0	603	845	31 59	·31772	·71433
40 0	420	772	47 20	·55749	1·02427
41 0	374	758	51 32	·62515	·96763
42 0	324	745	56 26	·70197	·85838
43 0	264	732	62 22	·78872	·67868
44 0	187	719	70 18	·88745	·40338
44 30	132	713	76 1	·94190	·21999
45 0	0	707	90 0	1·00000	·00000

$$\mathrm{A}_1=\int 4\pi\alpha d\alpha\sin^2\theta=2\cdot6595.\quad\ldots\ldots\ldots\quad(15)$$

$$\mathrm{A}_2=\int\pi\alpha d\alpha\sin^2 2\theta=1\cdot3682.\quad\ldots\ldots\ldots\quad(16)$$



The paths described by molecules about a centre of force S, repelling inversely as the fifth power of the distance, are given in the figure.

The molecules are supposed to be originally moving with equal velocities in parallel paths, and the way in which their deflections depend on the distance of the path from S is shown by the different curves in the figure.

3rd. *Integration with respect to* dN_1.

We have now to integrate expressions involving various functions of ξ, η, ζ, and V with respect to all the molecules of the second sort. We may write the expression to

be integrated

$$\iiint QV^{\frac{n-5}{n-1}} f_2(\xi_2\eta_2\zeta_2)d\xi_2 d\eta_2 d\zeta_2,$$

where Q is some function of ξ, η, ζ, &c., already determined, and f_2 is the function which indicates the distribution of velocity among the molecules of the second kind.

In the case in which $n=5$, V disappears, and we may write the result of integration

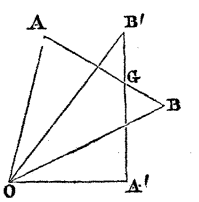
$$\overline{Q}N_2,$$

where $\overline{Q}$ is the mean value of Q for all the molecules of the second kind, and N_2 is the number of those molecules.

If, however, n is not equal to 5, so that V does not disappear, we should require to know the form of the function f_2 before we could proceed further with the integration.

The only case in which I have determined the form of this function is that of one or more kinds of molecules which have by their continual encounters brought about a distribution of velocity such that the number of molecules whose velocity lies within given limits remains constant. In the Philosophical Magazine for January 1860, I have given an investigation of this case, founded on the assumption that the probability of a molecule having a velocity resolved parallel to x lying between given limits is not in any way affected by the knowledge that the molecule has a given velocity resolved parallel to y. As this assumption may appear precarious, I shall now determine the form of the function in a different manner.

On the Final Distribution of Velocity among the Molecules of Two Systems acting on one another according to any Law of Force.



From a given point O let lines be drawn representing in direction and magnitude the velocities of every molecule of either kind in unit of volume. The extremities of these lines will be distributed over space in such a way that if an element of volume dV be taken anywhere, the number of such lines which will terminate within dV will be $f(r)dV$, where r is the distance of dV from O.

Let $OA=a$ be the velocity of a molecule of the first kind, and $OB=b$ that of a molecule of the second kind before they encounter one another, then BA will be the velocity of A relative to B; and if we divide AB in G inversely as the masses of the molecules, and join OG, OG will be the velocity of the centre of gravity of the two molecules.

Now let $OA'=a'$ and $OB'=b'$ be the velocities of the two molecules after the encounter, $GA=GA'$ and $GB=GB'$, and $A'GB'$ is a straight line not necessarily in the plane of OAB. Also $AGA'=2\theta$ is the angle through which the relative velocity is turned in the encounter in question. The relative motion of the molecules is completely defined if we know BA the relative velocity before the encounter, 2θ the angle through which BA is turned during the encounter, and ϕ the angle which defines the direction of the plane in which BA and B′A′ lie. All encounters in which the magnitude and direction of BA, and also θ and ϕ, lie within certain almost contiguous limits,

we shall class as encounters of the given kind. The number of such encounters in unit of time will be

$$n_1 n_2 \mathrm{F} de, \quad \ldots \ldots \ldots \ldots \quad (17)$$

where n_1 and n_2 are the numbers of molecules of each kind under consideration, and F is a function of the relative velocity and of the angle θ, and de depends on the limits of variation within which we class encounters as of the same kind.

Now let A describe the boundary of an element of volume $d\mathrm{V}$ while AB and A′B′ move parallel to themselves, then B, A′, and B′ will also describe equal and similar elements of volume.

The number of molecules of the first kind, the lines representing the velocities of which terminate in the element $d\mathrm{V}$ at A, will be

$$n_1 = f_1(a) d\mathrm{V}. \quad \ldots \ldots \ldots \ldots \quad (18)$$

The number of molecules of the second kind which have velocities corresponding to OB will be

$$n_2 = f_2(b) d\mathrm{V}; \quad \ldots \ldots \ldots \ldots \quad (19)$$

and the number of encounters of the given kind between these two sets of molecules will be

$$f_1(a) f_2(b) d\mathrm{V}^2 \mathrm{F} de. \quad \ldots \ldots \ldots \ldots \quad (20)$$

The lines representing the velocities of these molecules after encounters of the given kind will terminate within elements of volume at A′ and B′, each equal to $d\mathrm{V}$.

In like manner we should find for the number of encounters between molecules whose original velocities corresponded to elements equal to $d\mathrm{V}$ described about A′ and B′, and whose subsequent velocities correspond to elements equal to $d\mathrm{V}$ described about A and B,

$$f_1(a') f_2(b') d\mathrm{V}^2 \mathrm{F}' de, \quad \ldots \ldots \ldots \ldots \quad (21)$$

where F′ is the same function of B′A′ and A′GA that F is of BA and AGA′. F is therefore equal to F′.

When the number of pairs of molecules which change their velocities from OA, OB to OA′ OB′ is equal to the number which change from OA′, OB′ to OA, OB, then the final distribution of velocity will be obtained, which will not be altered by subsequent exchanges. This will be the case when

$$f_1(a) f_2(b) = f_1(a') f_2(b'). \quad \ldots \ldots \ldots \ldots \quad (22)$$

Now the only relation between a, b and a', b' is

$$\mathrm{M}_1 a^2 + \mathrm{M}_2 b^2 = \mathrm{M}_1 a'^2 + \mathrm{M}_2 b'^2, \quad \ldots \ldots \ldots \quad (23)$$

whence we obtain

$$f_1(a) = \mathrm{C}_1 e^{-\frac{a^2}{\alpha^2}}, \quad f_2(b) = \mathrm{C}_2 e^{-\frac{b^2}{\beta^2}}, \quad \ldots \ldots \ldots \quad (24)$$

where

$$\mathrm{M}_1 \alpha^2 = \mathrm{M}_2 \beta^2. \quad \ldots \ldots \ldots \ldots \quad (25)$$

By integrating $\iiint \mathrm{C}_1 e^{-\frac{\xi^2+\eta^2+\zeta^2}{\alpha^2}} d\xi\, d\eta\, d\zeta$, and equating the result to N_1, we obtain the value of C_1. If, therefore, the distribution of velocities among N_1 molecules is such that

the number of molecules whose component velocities are between ξ and $\xi+d\zeta$, η and $\eta+d\eta$, and ζ and $\zeta+d\zeta$ is

$$dN_1=\frac{N_1}{\alpha^3\pi^{\frac{3}{2}}}e^{-\frac{\xi^2+\eta^2+\zeta^2}{\alpha^2}}d\xi\,d\eta\,d\zeta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

then this distribution of velocities will not be altered by the exchange of velocities among the molecules by their mutual action.

This is therefore a possible form of the final distribution of velocities. It is also the only form; for if there were any other, the exchange between velocities represented by OA and OA′ would not be equal. Suppose that the number of molecules having velocity OA′ increases at the expense of OA. Then since the total number of molecules corresponding to OA′ remains constant, OA′ must communicate as many to OA″, and so on till they return to OA.

Hence if OA, OA′, OA″, &c. be a series of velocities, there will be a tendency of each molecule to assume the velocities OA, OA′, OA″, &c. in order, returning to OA. Now it is impossible to assign a reason why the successive velocities of a molecule should be arranged in this cycle, rather than in the reverse order. If, therefore, the direct exchange between OA and OA′ is not equal, the equality cannot be preserved by exchange in a cycle. Hence the direct exchange between OA and OA′ is equal, and the distribution we have determined is the only one possible.

This final distribution of velocity is attained only when the molecules have had a great number of encounters, but the great rapidity with which the encounters succeed each other is such that in all motions and changes of the gaseous system except the most violent, the form of the distribution of velocity is only slightly changed.

When the gas moves in mass, the velocities now determined are compounded with the motion of translation of the gas.

When the differential elements of the gas are changing their figure, being compressed or extended along certain axes, the values of the mean square of the velocity will be different in different directions. It is probable that the form of the function will then be

$$f_1(\xi\eta\zeta)=\frac{N_1}{\alpha\beta\gamma\pi^{\frac{3}{2}}}e^{-\left(\frac{\xi^2}{\alpha^2}+\frac{\eta^2}{\beta^2}+\frac{\zeta^2}{\gamma^2}\right)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where α, β, γ are slightly different. I have not, however, attempted to investigate the exact distribution of velocities in this case, as the theory of motion of gases does not require it.

When one gas is diffusing through another, or when heat is being conducted through a gas, the distribution of velocities will be different in the positive and negative directions, instead of being symmetrical, as in the case we have considered. The want of symmetry, however, may be treated as very small in most actual cases.

The principal conclusions which we may draw from this investigation are as follows. Calling α the modulus of velocity,

1st. The mean velocity is $\qquad \bar{v}=\frac{2}{\sqrt{\pi}}\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$

2nd. The mean square of the velocity is $\overline{v^2}=\frac{3}{2}\alpha^2$. . . . . (29)

3rd. The mean value of ξ^2 is $\overline{\xi^2}=\frac{1}{2}\alpha^2$. . . . . (30)

4th. The mean value of ξ^4 is $\overline{\xi^4}=\frac{3}{4}\alpha^4$. . . . . (31)

5th. The mean value of $\xi^2\eta^2$ is $\overline{\xi^2\eta^2}=\frac{1}{4}\alpha^4$. . . . . (32)

6th. When there are two systems of molecules

$$M_1\alpha^2=M_2\beta^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

whence

$$M_1v_1^2=M_2v_2^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

or the mean *vis viva* of a molecule will be the same in each system. This is a very important result in the theory of gases, and it is independent of the nature of the action between the molecules, as are all the other results relating to the final distribution of velocities. We shall find that it leads to the law of gases known as that of Equivalent Volumes.

Variation of Functions of the Velocity due to encounters between the Molecules.

We may now proceed to write down the values of $\frac{\delta\overline{Q}}{\delta t}$ in the different cases. We shall indicate the mean value of any quantity for all the molecules of one kind by placing a bar over the symbol which represents that quantity for any particular molecule, but in expressions where all such quantities are to be taken at their mean values, we shall, for convenience, omit the bar. We shall use the symbols δ_1 and δ_2 to indicate the effect produced by molecules of the first kind and second kind respectively, and δ_3 to indicate the effect of external forces. We shall also confine ourselves to the case in which $n=5$, since it is not only free from mathematical difficulty, but is the only case which is consistent with the laws of viscosity of gases.

In this case V disappears, and we have for the effect of the second system or the first,

$$\frac{\delta Q}{\delta t}=N_2\left(\frac{K(M_1+M_2)}{M_1M_2}\right)^{\frac{1}{2}}A\int_0^{2\pi}(Q'-Q)d\phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where the functions of ξ, η, ζ in $\int(Q'-Q)d\phi$ must be put equal to their mean values for all the molecules, and A_1 or A_2 must be put for A according as $\sin^2\theta$ or $\sin^2 2\theta$ occurs in the expressions in equations (4), (5), (6), (7). We thus obtain

$$(\alpha)\quad \frac{\delta_2\xi_1}{\delta t}=\left(\frac{K}{M_1M_2(M_1+M_2)}\right)^{\frac{1}{2}}N_2M_2A_1(\xi_2-\xi_1); \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$(\beta)\quad \left.\begin{aligned}\frac{\delta_2\xi_1^2}{\delta t}=&\left(\frac{K}{M_1M_2(M_1+M_2)}\right)^{\frac{1}{2}}\frac{N_2M_2}{M_1+M_2}\\ &\{2A_1(\xi_2-\xi_1)(M_1\xi_1+M_2\xi_2)+A_2M_2(\overline{\eta_2-\eta_1}^2+\overline{\zeta_2-\zeta_1}^2-2\overline{\xi_2-\xi_1}^2)\};\end{aligned}\right\} \quad . \quad . \quad (37)$$

$$\left.\begin{aligned}\frac{\delta_2\xi_1\eta_1}{\delta t}=&\left(\frac{K}{M_1M_2(M_1+M_2)}\right)^{\frac{1}{2}}\frac{N_2M_2}{M_1+M_2}\\ &\left\{A_1\left(2M_2\xi_2\eta_2-2M_1\xi_1\eta_1+(M_1-M_2)(\xi_1\eta_2+\xi_2\eta_1)\right)-3A_2M_2(\xi_2-\xi_1)(\eta_2-\eta_1)\right\};\end{aligned}\right\}(38)$$

$$(\gamma)\quad \frac{\delta_2\xi_1 V_1}{\delta t}=\left(\frac{K}{M_1M_2(M_1+M_2)}\right)^{\frac{1}{2}}N_2M_2\Big\{A_1\big(\overline{\xi_2-\xi_1}V_1^2+2\xi_1(U-V_1^2)\big)$$
$$+\frac{M_2}{M_1+M_2}(2A_1-3A_2)2(\xi_2-\xi_1)(U-V_1^2)$$
$$+\frac{M_2}{M_1+M_2}(2A_1+2A_2)\xi_1V^2$$
$$+\left(\frac{M_2}{M_1+M_2}\right)^2(2A_1-2A_2)2(\xi_2-\xi_1)V^2\Big\}; \qquad (39)$$

using the symbol δ_2 to indicate variations arising from the action of molecules of the second system.

These are the values of the rate of variation of the mean values of ξ_1, ξ_1^2 ξ_1 η_1, and ξ_1 V_1^2, for the molecules of the first kind due to their encounters with molecules of the second kind. In all of them we must multiply up all functions of ξ, η, ζ, and take the mean values of the products so found. As this has to be done for all such functions, I have omitted the bar over each function in these expressions.

To find the rate of variation due to the encounters among the particles of the same system, we have only to alter the suffix $_{(2)}$ into $_{(1)}$ throughout, and to change K, the coefficient of the force between M_1 and M_2 into K_1, that of the force between two molecules of the first system. We thus find

$$(\alpha)\quad \frac{\delta_1\overline{\xi_1}}{\delta t}=0; \qquad (40)$$

$$(\beta)\quad \frac{{}_1\overline{\xi_1^2}}{dt}=\left(\frac{K_1}{2M_1^3}\right)^{\frac{1}{2}}M_1N_1A_2\{\overline{\eta_1^2}+\overline{\zeta_1^2}-2\overline{\xi_1^2}-(\overline{\eta_1}.\overline{\eta_1}+\overline{\zeta_1}.\overline{\zeta_1}-2\overline{\xi_1}\,\overline{\xi_1})\}; \qquad (41)$$

$$\frac{\delta_1\overline{\xi_1\eta_1}}{\delta t}=\left(\frac{K_1}{2M_1^3}\right)^{\frac{1}{2}}M_1N_1A_2 3\{\overline{\xi_1}.\overline{\eta_1}-\overline{\xi_1\eta_1}\}; \qquad (42)$$

$$(\gamma)\quad \frac{\delta_1\overline{\xi_1V_1^2}}{\delta t}=\left(\frac{K_1}{2M_1^3}\right)^{\frac{1}{2}}M_1N_1A_2 3(\overline{\xi_1}.\overline{V_1^2}-\overline{\xi_1V_1^2}). \qquad (43)$$

These quantities must be added to those in equations (36) to (39) in order to get the rate of variation in the molecules of the first kind due to their encounters with molecules of both systems. When there is only one kind of molecules, the latter equations give the rates of variation at once.

On the Action of External Forces on a System of Moving Molecules.

We shall suppose the external force to be like the force of gravity, producing equal acceleration on all the molecules. Let the components of the force in the three coordinate directions be X, Y, Z. Then we have by dynamics for the variations of ξ, ξ^2, and ξV^2 due to this cause,

$$(\alpha)\quad \frac{\delta_3\xi}{\delta t}=X; \qquad (44)$$

$$(\beta)\quad \frac{\delta_3 . \xi^2}{\delta t} = 2\xi X; \quad \ldots \quad (45)$$

$$\frac{\delta_3 . \xi\eta}{\delta t} = \eta X + \xi Y; \quad \ldots \quad (46)$$

$$(\gamma)\quad \frac{\delta_3 . \xi V^2}{\delta t} = 2\xi(\xi X + \eta Y + \zeta Z) + X V^2; \quad \ldots \quad (47)$$

where δ_3 refers to variations due to the action of external forces.

On the Total rate of change of the different functions of the velocity of the molecules of the first system arising from their encounters with molecules of both systems and from the action of external forces.

To find the total rate of change arising from these causes, we must add

$$\frac{\delta_1 Q}{\delta t}, \frac{\delta_2 Q}{\delta t}, \text{ and } \frac{\delta_3 Q}{\delta t},$$

the quantities already found. We shall find it, however, most convenient in the remainder of this investigation to introduce a change in the notation, and to substitute for

$$\xi, \eta, \text{ and } \zeta, \quad u+\xi, \quad v+\eta, \text{ and } w+\zeta, \quad \ldots \quad (48)$$

where u, v, and w are so chosen that they are the mean values of the components of the velocity of all molecules of the same system in the immediate neighbourhood of a given point. We shall also write

$$M_1 N_1 = \varrho_1, \; M_2 N_2 = \varrho_2, \quad \ldots \quad (49)$$

where ϱ_1 and ϱ_2 are the densities of the two systems of molecules, that is, the mass in unit of volume. We shall also write

$$\left(\frac{K_1}{2M_1^3}\right)^{\frac{1}{2}} = k_1, \; \left(\frac{K}{M_1 M_2 (M_1 + M_2)}\right)^{\frac{1}{2}} = k, \text{ and } \left(\frac{K_2}{2M_2^3}\right)^{\frac{1}{2}} = k_2; \quad \ldots \quad (50)$$

ϱ_1, ϱ_2, k_1, k_2, and k are quantities the absolute values of which can be deduced from experiment. We have not as yet experimental data for determining M, N, or K.

We thus find for the rate of change of the various functions of the velocity,

$$(\alpha)\quad \frac{\delta u_1}{\delta t} = k A_1 \varrho_2 (u_2 - u_1) + X; \quad \ldots \quad (51)$$

$$\left.\begin{aligned}(\beta)\quad \frac{\delta . \xi_1^2}{\delta t} &= k_1 A_2 \varrho_1 \{\eta_1^2 + \zeta_1^2 - 2\xi_1^2\} \\ &+ k\varrho_2 \frac{M_2}{M_1 + M_2}\left\{2A_1 (u_2 - u_1)^2 + A_2\left(\overline{v_2 - v_1}^2 + \overline{w_2 - w_1}^2 - 2\overline{u_2 - u_1}^2\right)\right\} \\ &+ \frac{k\varrho_2}{M_1 + M_2}\left\{2A_1 (M_2 \xi_2^2 - M_1 \xi_1^2) + A_2 M_2 (\eta_1^2 + \zeta_1^2 - 2\xi_1^2 + \eta_2^2 + \zeta_2^2 - 2\xi_2^2)\right\};\end{aligned}\right\} . \quad (52)$$

also

$$\left.\begin{aligned}\frac{\delta . \xi\eta}{\delta t} &= -3k_1 A_2 \varrho_1 \xi_1 \eta_1 + k\varrho_2 \frac{M_2}{M_1 + M_2}(2A_1 - 3A_2)(u_2 - u_1)(v_2 - v_1) \\ &+ \frac{k\varrho_2}{M_1 + M_2}\left\{2A_1 (M_2 \xi_2 \eta_2 - M_1 \xi_1 \eta_1) - 3A_2 M_2 (\xi_1 \eta_1 + \xi_2 \eta_2)\right\}.\end{aligned}\right\} . \quad (53)$$

(γ) As the expressions for the variation of functions of three dimensions in mixed media are complicated, and as we shall not have occasion to use them, I shall give the case of a single medium,

$$\frac{\delta}{\delta t}(\xi_1^3+\xi_1\eta_1^2+\xi_1\zeta_1^2)=-3k_1\rho_1 A_2(\xi_1^3+\xi_1\eta_1^2+\xi_1\zeta_1^2)+X(3\xi_1^2+\eta_1^2+\zeta_1^2)+2Y\xi_1\eta_1+2Z\xi_1\zeta_1. \quad (54)$$

Theory of a Medium composed of Moving Molecules.

We shall suppose the position of every moving molecule referred to three rectangular axes, and that the component velocities of any one of them, resolved in the directions of x, y, z, are

$$u+\xi, \quad v+\eta, \quad w+\zeta,$$

where u, v, w are the components of the mean velocity of all the molecules which are at a given instant in a given element of volume, and ξ, η, ζ are the components of the relative velocity of one of these molecules with respect to the mean velocity.

The quantities u, v, w may be treated as functions of x, y, z, and t, in which case differentiation will be expressed by the symbol d. The quantities ξ, η, ζ, being different for every molecule, must be regarded as functions of t for each molecule. Their variation with respect to t will be indicated by the symbol δ.

The mean values of ξ^2 and other functions of ξ, η, ζ for all the molecules in the element of volume may, however, be treated as functions of x, y, z, and t.

If we consider an element of volume which always moves with the velocities u, v, w, we shall find that it does not always consist of the same molecules, because molecules are continually passing through its boundary. We cannot therefore treat it as a mass moving with the velocity u, v, w, as is done in hydrodynamics, but we must consider separately the motion of each molecule. When we have occasion to consider the variation of the properties of this element during its motion as a function of the time we shall use the symbol ∂.

We shall call the velocities u, v, w the velocities of translation of the medium, and ξ, η, ζ the velocities of agitation of the molecules.

Let the number of molecules in the element $dx\,dy\,dz$ be N $dx\,dy\,dz$, then we may call N the number of molecules in unit of volume. If M is the mass of each molecule, and ρ the density of the element, then

$$MN=\rho. \quad (55)$$

Transference of Quantities across a Plane Area.

We must next consider the molecules which pass through a given plane of unit area in unit of time, and determine the quantity of matter, of momentum, of heat, &c. which is transferred from the negative to the positive side of this plane in unit of time.

We shall first divide the N molecules in unit of volume into classes according to the value of ξ, η, and ζ for each, and we shall suppose that the number of molecules in unit of volume whose velocity in the direction of x lies between ξ and $\xi+d\xi$, η and $\eta+d\eta$, ζ and $\zeta+d\zeta$ is dN, dN will then be a function of the component velocities, the sum of

which being taken for all the molecules will give N the total number of molecules. The most probable form of this function for a medium in its state of equilibrium is

$$dN=\frac{N}{\alpha^3\pi^{\frac{3}{2}}}e^{-\frac{\xi^2+\eta^2+\zeta^2}{\alpha^2}}d\xi\,d\eta\,d\zeta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

In the present investigation we do not require to know the form of this function.

Now let us consider a plane of unit area perpendicular to x moving with a velocity of which the part resolved parallel to x is u'. The velocity of the plane relative to the molecules we have been considering is $u'-(u+\xi)$, and since there are dN of these molecules in unit of volume it will overtake

$$\big(u'-(u+\xi)\big)dN$$

such molecules in unit of time, and the number of such molecules passing from the negative to the positive side of the plane, will be

$$(u+\xi-u')dN.$$

Now let Q be any property belonging to the molecule, such as its mass, momentum, *vis viva*, &c., which it carries with it across the plane, Q being supposed a function of ξ or of ξ, η, and ζ, or to vary in any way from one molecule to another, provided it be the same for the selected molecules whose number is dN, then the quantity of Q transferred across the plane in the positive direction in unit of time is

$$\int(u-u'+\xi)QdN,$$

or

$$(u-u')\int QdN+\int\xi QdN. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

If we put $\overline{Q}N$ for $\int QdN$, and $\overline{\xi Q}N$ for $\int\xi QdN$, then we may call $\overline{Q}$ the mean value of Q, and ξQ the mean value of $\overline{\xi Q}$, for all the particles in the element of volume, and we may write the expression for the quantity of Q which crosses the plane in unit of time

$$(u-u')\overline{Q}N+\overline{\xi Q}N. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

(α) *Transference of Matter across a Plane—Velocity of the Fluid.*

To determine the quantity of matter which crosses the plane, make Q equal to M the mass of each molecule; then, since M is the same for all molecules of the same kind, $\overline{M}=M$; and since the mean value of ξ is zero, the expression is reduced to

$$(u-u')MN=(u-u')\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

If $u=u'$, or if the plane moves with velocity u, the whole excess of matter transferred across the plane is zero; the velocity of the fluid may therefore be defined as the velocity whose components are u, v, w.

(β) *Transference of Momentum across a Plane—System of Pressures at any point of the Fluid.*

The momentum of any one molecule in the direction of x is $M(u+\xi)$. Substituting this for Q, we get for the quantity of momentum transferred across the plane in the

positive direction

$$(u-u')u\varrho+\overline{\xi^2}\varrho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

If the plane moves with the velocity u, this expression is reduced to $\overline{\xi^2}\varrho$, where $\overline{\xi^2}$ represents the mean value of ξ^2.

This is the whole momentum in the direction of x of the molecules projected from the negative to the positive side of the plane in unit of time. The mechanical action between the parts of the medium on opposite sides of the plane consists partly of the momentum thus transferred, and partly of the direct attractions or repulsions between molecules on opposite sides of the plane. The latter part of the action must be very small in gases, so that we may consider the pressure between the parts of the medium on opposite sides of the plane as entirely due to the constant bombardment kept up between them. There will also be a transference of momentum in the directions of y and z across the same plane,

$$(u-u')v\varrho+\overline{\xi\eta}\varrho, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

and

$$(u-u')w\varrho+\overline{\xi\zeta}\varrho, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

where $\overline{\xi\eta}$ and $\overline{\xi\zeta}$ represent the mean values of these products.

If the plane moves with the mean velocity u of the fluid, the total force exerted on the medium on the positive side by the projection of molecules into it from the negative side will be

a normal pressure	$\overline{\xi^2}\varrho$	in the direction of x,
a tangential pressure	$\overline{\xi\eta}\varrho$	in the direction of y,
and a tangential pressure	$\overline{\xi\zeta}\varrho$	in the direction of z.

If X, Y, Z are the components of the pressure on unit of area of a plane whose direction cosines are l, m, n,

$$\left.\begin{aligned} X&=l\overline{\xi^2}\varrho+m\overline{\xi\eta}\varrho+n\overline{\xi\zeta}\varrho,\\ Y&=l\overline{\xi\eta}\varrho+m\overline{\eta^2}\varrho+n\overline{\eta\zeta}\varrho,\\ Z&=l\overline{\xi\zeta}\varrho+m\overline{\eta\zeta}\varrho+n\overline{\zeta^2}\varrho. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

When a gas is not in a state of violent motion the pressures in all directions are nearly equal, in which case, if we put

$$\overline{\xi^2}\varrho+\overline{\eta^2}\varrho+\overline{\zeta^2}\varrho=3p, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

the quantity p will represent the mean pressure at a given point, and $\overline{\xi^2}\varrho$, $\overline{\eta^2}\varrho$, and $\overline{\zeta^2}\varrho$ will differ from p only by small quantities; $\overline{\eta\zeta}\varrho$, $\overline{\zeta\xi}\varrho$, and $\overline{\xi\eta}\varrho$ will then be also small quantities with respect to p.

Energy in the Medium—Actual Heat.

The actual energy of any molecule depends partly on the velocity of its centre of gravity, and partly on its rotation or other internal motion with respect to the centre of gravity. It may be written

$$\tfrac{1}{2}M\{(u+\xi)^2+(v+\eta)^2+(w+\zeta)^2\}+\tfrac{1}{2}EM, \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

where $\frac{1}{2}$EM is the internal part of the energy of the molecule, the form of which is at present unknown. Summing for all the molecules in unit of volume, the energy is

$$\tfrac{1}{2}(u^2+v^2+w^2)\varrho+\tfrac{1}{2}(\xi^2+\eta^2+\zeta^2)\varrho+\tfrac{1}{2}\overline{\mathrm{E}}\varrho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

The first term gives the energy due to the motion of translation of the medium in mass, the second that due to the agitation of the centres of gravity of the molecules, and the third that due to the internal motion of the parts of each molecule.

If we assume with CLAUSIUS that the ratio of the mean energy of internal motion to that of agitation tends continually towards a definite value $(\beta-1)$, we may conclude that, except in very violent disturbances, this ratio is always preserved, so that

$$\overline{\mathrm{E}}=(\beta-1)(\xi^2+\eta^2+\zeta^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

The total energy of the invisible agitation in unit of volume will then be

$$\tfrac{1}{2}\beta(\xi^2+\eta^2+\zeta^2)\varrho, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

or

$$\tfrac{3}{2}\beta p. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

This energy being in the form of invisible agitation, may be called the total heat in the unit of volume of the medium.

(γ) *Transference of Energy across a Plane—Conduction of Heat.*

Putting

$$\mathrm{Q}=\tfrac{1}{2}\beta(\xi^2+\eta^2+\zeta^2)\mathrm{M}, \quad \text{and } u=u', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

we find for the quantity of heat carried over the unit of area by conduction in unit of time

$$\tfrac{1}{2}\beta(\overline{\xi^3}+\overline{\xi\eta^2}+\overline{\xi\zeta^2})\varrho, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

where ξ^3, &c. indicate the mean values of ξ^3, &c. They are always small quantities.

On the Rate of Variation of Q *in an Element of Volume,* Q *being any property of the Molecules in that Element.*

Let Q be the value of the quantity for any particular molecule, and $\overline{\mathrm{Q}}$ the mean value of Q for all the molecules of the same kind within the element.

The quantity $\overline{\mathrm{Q}}$ may vary from two causes. The molecules within the element may by their mutual action or by the action of external forces produce an alteration of $\overline{\mathrm{Q}}$, or molecules may pass into the element and out of it, and so cause an increase or diminution of the value of $\overline{\mathrm{Q}}$ within it. If we employ the symbol δ to denote the variation of Q due to actions of the first kind on the individual molecules, and the symbol ∂ to denote the actual variation of Q in an element moving with the mean velocity of the system of molecules under consideration, then by the ordinary investigation of the increase or diminution of matter in an element of volume as contained in treatises on Hydrodynamics,

$$\left.\begin{aligned}\frac{\partial\overline{\mathrm{Q}}\mathrm{N}}{\partial t}=\frac{\delta\overline{\mathrm{Q}}}{\delta t}\mathrm{N}-\frac{d}{dx}\left\{(u-u')\overline{\mathrm{Q}}\mathrm{N}+\overline{\xi\mathrm{Q}}\mathrm{N}\right\}\\ -\frac{d}{dy}\left\{(v-v')\overline{\mathrm{Q}}\mathrm{N}+\overline{\eta\mathrm{Q}}\mathrm{N}\right\}-\frac{d}{dz}\left\{(w-w')\overline{\mathrm{Q}}\mathrm{N}+\overline{\zeta\mathrm{Q}}\mathrm{N}\right\},\end{aligned}\right\} \quad . \quad . \quad . \quad (72)$$

where the last three terms are derived from equation (59) and two similar equations, and denote the quantity of Q which flows out of an element of volume, that element moving with the velocities u', v', w'. If we perform the differentiations and then make $u'=u$, $v'=v$, and $w'=w$, then the variation will be that in an element which moves with the actual mean velocity of the system of molecules, and the equation becomes

$$\frac{\partial\overline{\mathrm{QN}}}{\partial t}+\overline{\mathrm{Q}}\mathrm{N}\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)+\frac{d}{dx}(\overline{\xi\mathrm{Q}}\mathrm{N})+\frac{d}{dy}(\overline{\eta\mathrm{Q}}\mathrm{N})+\frac{d}{dz}(\overline{\zeta\mathrm{Q}}\mathrm{N})=\frac{\delta\mathrm{Q}}{\delta t}\mathrm{N}. \quad . \quad . \quad (73)$$

Equation of Continuity.

Put Q=M the mass of a molecule; M is unalterable, and we have, putting $\mathrm{MN}=\varrho$,

$$\frac{\partial\varrho}{\partial t}+\varrho\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (74)$$

which is the ordinary equation of continuity in hydrodynamics, the element being supposed to move with the velocity of the fluid. Combining this equation with that from which it was obtained, we find

$$\mathrm{N}\frac{\partial\overline{\mathrm{Q}}}{\partial t}+\frac{d}{dx}(\overline{\xi\mathrm{Q}}\mathrm{N})+\frac{d}{dy}(\overline{\eta\mathrm{Q}}\mathrm{N})+\frac{d}{dz}(\overline{\zeta\mathrm{Q}}\mathrm{N})=\mathrm{N}\frac{\delta\mathrm{Q}}{\delta t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (75)$$

a more convenient form of the general equation.

Equations of Motion (α).

To obtain the Equation of Motion in the direction of x, put $\mathrm{Q}=\mathrm{M}_1(u_1+\xi_1)$, the momentum of a molecule in the direction of x.

We obtain the value of $\frac{\delta\mathrm{Q}}{\delta t}$ from equation (51), and the equation may be written

$$\varrho_1\frac{\partial u_1}{\partial t}+\frac{d}{dx}(\varrho_1\overline{\xi_1^2})+\frac{d}{dy}(\varrho_1\overline{\xi_1\eta_1})+\frac{d}{dz}(\varrho_1\overline{\xi_1\zeta_1})=k\mathrm{A}_1\varrho_1\varrho_2(u_2-u_1)+\mathrm{X}\varrho_1. \quad . \quad . \quad . \quad (76)$$

In this equation the first term denotes the efficient force per unit of volume, the second the variation of normal pressure, the third and fourth the variations of tangential pressure, the fifth the resistance due to the molecules of a different system, and the sixth the external force acting on the system.

The investigation of the values of the second, third, and fourth terms must be deferred till we consider the variations of the second degree.

Condition of Equilibrium of a Mixture of Gases.

In a state of equilibrium u_1 and u_2 vanish, $\varrho_1\overline{\xi_1^2}$ becomes p_1, and the tangential pressures vanish, so that the equation becomes

$$\frac{dp_1}{dx}=\mathrm{X}\varrho_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (77)$$

which is the equation of equilibrium in ordinary hydrostatics.

This equation, being true of the system of molecules forming the first medium inde-

pendently of the presence of the molecules of the second system, shows that if several kinds of molecules are mixed together, placed in a vessel and acted on by gravity, the final distribution of the molecules of each kind will be the same as if none of the other kinds had been present. This is the same mode of distribution as that which DALTON considered to exist in a mixed atmosphere in equilibrium, the law of diminution of density of each constituent gas being the same as if no other gases were present.

This result, however, can only take place after the gases have been left for a considerable time perfectly undisturbed. If currents arise so as to mix the strata, the composition of the gas will be made more uniform throughout.

The result at which we have arrived as to the final distribution of gases, when left to themselves, is independent of the law of force between the molecules.

Diffusion of Gases.

If the motion of the gases is slow, we may still neglect the tangential pressures. The equation then becomes for the first system of molecules

$$\varrho_1 \frac{\partial u_1}{\partial t} + \frac{dp_1}{dx} = k\mathrm{A}_1\varrho_1\varrho_2(u_2 - u_1) + \mathrm{X}\varrho_1, \quad \ldots \ldots \ldots \quad (78)$$

and for the second,

$$\varrho_2 \frac{\partial u_2}{\partial t} + \frac{dp_2}{dx} = k\mathrm{A}_1\varrho_1\varrho_2(u_1 - u_2) + \mathrm{X}\varrho_2. \quad \ldots \ldots \ldots \quad (79)$$

In all cases of quiet diffusion we may neglect the first term of each equation. If we then put $p_1 + p_2 = p$, and $\varrho_1 + \varrho_2 = \varrho$, we find by adding,

$$\frac{dp}{dx} = \mathrm{X}\varrho. \quad \ldots \ldots \ldots \ldots \ldots \quad (80)$$

If we also put $p_1u_1 + p_2u_2 = pu$, then the volumes transferred in opposite directions across a plane moving with velocity u will be equal, so that

$$p_1(u_1 - u) = p_2(u - u_2) = \frac{p_1p_2}{p\varrho_1\varrho_2 k\mathrm{A}_1} \cdot \left(\mathrm{X}\varrho_1 \frac{dp_1}{dx}\right). \quad \ldots \ldots \ldots \quad (81)$$

Here $p_1(u_1 - u)$ is the volume of the first gas transferred in unit of time across unit of area of the plane reduced to pressure unity, and at the actual temperature; and $p_2(u - u_2)$ is the equal volume of the second gas transferred across the same area in the opposite direction.

The external force X has very little effect on the quiet diffusion of gases in vessels of moderate size. We may therefore leave it out in our definition of the coefficient of diffusion of two gases.

When two gases not acted on by gravity are placed in different parts of a vessel at equal pressures and temperatures, there will be mechanical equilibrium from the first, and u will always be zero. This will also be approximately true of heavy gases, provided the denser gas is placed below the lighter. Mr. GRAHAM has described in his paper on the Mobility of Gases*, experiments which were made under these conditions. A vertical

* Philosophical Transactions, 1863.

tube had its lower tenth part filled with a heavy gas, and the remaining nine-tenths with a lighter gas. After the lapse of a known time the upper tenth part of the tube was shut off, and the gas in it analyzed, so as to determine the quantity of the heavier gas which had ascended into the upper tenth of the tube during the given time.

In this case we have $u=0$, ... (82)

$$p_1 u_1 = -\frac{p_1 p_2}{\varrho_1 \varrho_2 k \mathrm{A}_1} \frac{1}{p} \frac{dp_1}{dx}, \quad \ldots \ldots \quad (83)$$

and by the equation of continuity,

$$\frac{dp_1}{dt} + \frac{d}{dx}(p_1 u_1) = 0, \quad \ldots \ldots \quad (84)$$

whence

$$\frac{dp_1}{dt} = \frac{p_1 p_2}{\varrho_1 \varrho_2 k \mathrm{A}_1} \frac{1}{p} \frac{d^2 p_1}{dx^2}; \quad \ldots \ldots \quad (85)$$

or if we put $\mathrm{D} = \frac{p_1 p_2}{\varrho_1 \varrho_2 k \mathrm{A}_1} \frac{1}{p}$,

$$\frac{dp_1}{dt} = \mathrm{D} \frac{d^2 p_1}{dx^2}. \quad \ldots \ldots \quad (86)$$

The solution of this equation is

$$p_1 = \mathrm{C}_1 + \mathrm{C}_2 e^{-n^2 \mathrm{D} t} \cos(nx + \alpha) + \&c. \quad \ldots \ldots \quad (87)$$

If the length of the tube is a, and if it is closed at both ends,

$$p_1 = \mathrm{C}_1 + \mathrm{C}_2 e^{-\frac{\pi^2 \mathrm{D}}{a^2} t} \cos \frac{\pi x}{a} + \mathrm{C}_3 e^{-4 \frac{\pi^2 \mathrm{D}}{a^2} t} \cos 2 \frac{\pi x}{a} + \&c., \quad \ldots \ldots \quad (88)$$

where C_1, C_2, C_3 are to be determined by the condition that when $t=0$, $p_1=p$, from $x=0$ to $x=\frac{1}{10}a$, and $p_1=0$ from $x=\frac{1}{10}a$ to $x=a$. The general expression for the case in which the first gas originally extends from $x=0$ to $x=b$, and in which after a time t the gas from $x=0$ to $x=c$ is collected, is

$$\frac{p_1}{p} = \frac{b}{a} + \frac{2a}{\pi^2 c} \left\{ e^{-\frac{\pi^2 \mathrm{D}}{a^2} t} \sin \frac{\pi b}{a} \sin \frac{\pi c}{a} + \frac{1}{2^2} e^{-4 \frac{\pi^2 \mathrm{D}}{a^2} t} \sin \frac{2\pi b}{a} \sin \frac{2\pi c}{a} + \&c. \right\}, \quad \ldots \quad (89)$$

where $\frac{p_1}{p}$ is the proportion of the first gas to the whole in the portion from $x=0$ to $x=c$.

In Mr. GRAHAM's experiments, in which one-tenth of the tube was filled with the first gas, and the proportion of the first gas in the tenth of the tube at the other end ascertained after a time t, this proportion will be

$$\frac{p_1}{p} = \frac{1}{10} - \frac{20}{\pi^2} \left\{ e^{-\frac{\pi^2 \mathrm{D}}{a^2} t} \sin^2 \frac{\pi}{10} - e^{-2^2 \frac{\pi^2 \mathrm{D}}{a^2} t} \sin^2 2 \frac{\pi}{10} + e^{-3^2 \frac{\pi^2 \mathrm{D}}{a^2} t} \sin^2 3 \frac{\pi}{10} - \&c. \right\}. \quad \ldots \quad (90)$$

We find for a series of values of $\frac{p_1}{p}$ taken at equal intervals of time T, where

$$\mathrm{T} = \frac{\log_e 10}{10 \pi^2} \frac{a^2}{\mathrm{D}}.$$

Time.	$\frac{p_1}{p}$.
0	0
T	·01193
2 T	·02305
3 T	·03376
4 T	·04366
5 T	·05267
6 T	·06072
8 T	·07321
10 T	·08227
12 T	·08845
∞	·10000

Mr. GRAHAM'S experiments on carbonic acid and air, when compared with this Table, give T=500 seconds nearly for a tube 0·57 metre long. Now

$$D=\frac{\log_e 10}{10\pi^2}\frac{a^2}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

whence

$$D=\cdot 0235$$

for carbonic acid and air, in inch-grain-second measure.

Definition of the Coefficient of Diffusion.

D is the volume of gas reduced to unit of pressure which passes in unit of time through unit of area when the total pressure is uniform and equal to p, and the pressure of either gas increases or diminishes by unity in unit of distance. D may be called the coefficient of diffusion. It varies directly as the square of the absolute temperature, and inversely as the total pressure p.

The dimensions of D are evidently L^2T^{-1}, where L and T are the standards of length and time.

In considering this experiment of the interdiffusion of carbonic acid and air, we have assumed that air is a simple gas. Now it is well known that the constituents of air can be separated by mechanical means, such as passing them through a porous diaphragm, as in Mr. GRAHAM'S experiments on Atmolysis. The discussion of the interdiffusion of three or more gases leads to a much more complicated equation than that which we have found for two gases, and it is not easy to deduce the coefficients of interdiffusion of the separate gases. It is therefore to be desired that experiments should be made on the interdiffusion of every pair of the more important pure gases which do not act chemically on each other, the temperature and pressure of the mixture being noted at the time of experiment.

Mr. GRAHAM has also published in BRANDE'S Journal for 1829, pt. 2, p. 74, the results

of experiments on the diffusion of various gases out of a vessel through a tube into air. The coefficients of diffusion deduced from these experiments are—

Air and Hydrogen	·026216
Air and Marsh-gas	·010240
Air and Ammonia	·00962
Air and Olefiant gas.	·00771
Air and Carbonic acid	·00682
Air and Sulphurous acid . . .	·00582
Air and Chlorine	·00486

The value for carbonic acid is only one third of that deduced from the experiment with the vertical column. The inequality of composition of the mixed gas in different parts of the vessel is, however, neglected; and the diameter of the tube at the middle part, where it was bent, was probably less than that given.

Those experiments on diffusion which lasted ten hours, all give smaller values of D than those which lasted four hours, and this would also result from the mixture of the gases in the vessel being imperfect.

Interdiffusion through a small hole.

When two vessels containing different gases are connected by a small hole, the mixture of gases in each vessel will be nearly uniform except near the hole; and the inequality of the pressure of each gas will extend to a distance from the hole depending on the diameter of the hole, and nearly proportional to that diameter.

Hence in the equation

$$\varrho_1 \frac{\partial u_1}{dt} + \frac{dp_1}{dx} = k\mathrm{A}\varrho_1\varrho_2(u_2 - u_1) + \mathrm{X}\varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (92)$$

the term $\frac{dp_1}{dx}$ will vary inversely as the diameter of the hole, while u_1 and u_2 will not vary considerably with the diameter.

Hence when the hole is very small the right-hand side of the equation may be neglected, and the flow of either gas through the hole will be independent of the flow of the other gas, as the term $k\mathrm{A}\varrho_1\varrho_2(u_2 - u_1)$ becomes comparatively insignificant.

One gas therefore will escape through a very fine hole into another nearly as fast as into a vacuum; and if the pressures are equal on both sides, the volumes diffused will be as the square roots of the specific gravities inversely, which is the law of diffusion of gases established by GRAHAM*.

Variation of the invisible agitation (β).

By putting for Q in equation (75)

$$\mathrm{Q} = \frac{\mathrm{M}}{2}\left((u_1 + \xi_1)^2 + (v_1 + \eta_1)^2 + (w_1 + \zeta_1)^2 + (\beta - 1)(\xi_1^2 + \eta_1^2 + \zeta_1^2)\right), \quad . \quad . \quad (93)$$

* Trans. Royal Society of Edinburgh, vol. xii. p. 222.

and eliminating by means of equations (76) and (52), we find

$$\left.\begin{aligned}
&\tfrac{1}{2}\varrho_1\frac{\partial}{\partial t}\beta_1(\xi_1^2+\eta_1^2+\zeta_1^2)+\varrho_1\xi_1^2\frac{du_1}{dx}+\varrho_1\eta_1^2\frac{dv_1}{dy}+\varrho_1\zeta_1^2\frac{dw_1}{dz}\\
&\quad+\varrho_1\eta_1\zeta_1\left(\frac{dv_1}{dz}+\frac{dw_1}{dy}\right)+\varrho_1\zeta_1\xi_1\left(\frac{dw_1}{dx}+\frac{du_1}{dz}\right)+\varrho_1\xi_1\eta_1\left(\frac{du_1}{dy}+\frac{dv_1}{dx}\right)\\
&\quad+\beta_1\left\{\frac{d}{dx}(\varrho_1\xi_1^3+\varrho_1\xi_1\eta_1^2+\varrho_1\xi_1\zeta_1^2)+\frac{d}{dy}(\varrho_1\eta_1\xi_1^2+\varrho_1\eta_1^3+\varrho_1\eta_1\zeta_1^2)+\frac{d}{dz}(\varrho_1\zeta_1\xi_1^2+\varrho_1\zeta_1\eta_1^2+\varrho_1\zeta_1^3)\right\}\\
&\quad=\frac{k\varrho_1\varrho_2 A_1}{M_1+M_2}\left\{M_2[(u_2-u_1)^2+(v_2-v_1)^2+(w_2-w_1)^2]+M_2(\xi_2^2+\eta_2^2+\zeta_2^2)-M_1(\xi_1^2+\eta_1^2+\zeta_1^2)\right\}.
\end{aligned}\right\}\quad(94)$$

In this equation the first term represents the variation of invisible agitation or heat; the second, third, and fourth represent the cooling by expansion; the fifth, sixth, and seventh the heating effect of fluid friction or viscosity; and the last the loss of heat by conduction. The quantities on the other side of the equation represent the thermal effects of diffusion, and the communication of heat from one gas to the other.

The equation may be simplified in various cases, which we shall take in order.

1st. *Equilibrium of Temperature between two Gases.—Law of Equivalent Volumes.*

We shall suppose that there is no motion of translation, and no transfer of heat by conduction through either gas. The equation (94) is then reduced to the following form,

$$\tfrac{1}{2}\varrho_1\frac{\partial}{\partial t}\beta_1(\xi_1^2+\eta_1^2+\zeta_1^2)=\frac{k\varrho_1\varrho_2 A_1}{M_1+M_2}\left\{M_2(\xi_2^2+\eta_2^2+\zeta_2^2)-M_1(\xi_1^2+\eta_1^2+\zeta_1^2)\right\}.\quad(95)$$

If we put

$$\frac{M_1}{M_1+M_2}(\xi_1^2+\eta_1^2+\zeta_1^2)=Q_1,\quad\text{and}\quad\frac{M_2}{M_1+M_2}(\xi_2^2+\eta_2^2+\zeta_2^2)=Q_2,\quad(96)$$

we find

$$\frac{\partial}{\partial t}(Q_2-Q_1)=-\frac{2kA_1}{M_1+M_2}(M_2\varrho_2\beta_1+M_1\varrho_1\beta_2)(Q_2-Q_1),\quad(97)$$

or

$$Q_2-Q_1=Ce^{-nt},\quad\text{where } n=\frac{2kA_1}{M_1+M_2}(M_2\varrho_2\beta_2+M_1\varrho_1\beta_1)\frac{1}{\beta_1\beta_2}.\quad(98)$$

If, therefore, the gases are in contact and undisturbed, Q_1 and Q_2 will rapidly become equal. Now the state into which two bodies come by exchange of invisible agitation is called equilibrium of heat or equality of temperature. Hence when two gases are at the same temperature,

$$Q_1=Q_2,\quad(99)$$

or

$$1=\frac{Q_1}{Q_2}=\frac{M_1(\xi_1^2+\eta_1^2+\zeta_1^2)}{M_2(\xi_2^2+\eta_2^2+\zeta_2^2)}$$

$$=\frac{M_1\dfrac{p_1}{\varrho_1}}{M_2\dfrac{p_2}{\varrho_2}}.$$

Hence if the pressures as well as the temperatures be the same in two gases,

$$\frac{M_1}{\varrho_1}=\frac{M_2}{\varrho_2}, \quad \ldots \ldots \ldots \ldots \quad (100)$$

or the masses of the individual molecules are proportional to the density of the gas.

This result, by which the relative masses of the molecules can be deduced from the relative densities of the gases, was first arrived at by GAY-LUSSAC from chemical considerations. It is here shown to be a necessary result of the Dynamical Theory of Gases; and it is so, whatever theory we adopt as to the nature of the action between the individual molecules, as may be seen by equation (34), which is deduced from perfectly general assumptions as to the nature of the law of force.

We may therefore henceforth put $\frac{s_1}{s_2}$ for $\frac{M_1}{M_2}$, where s_1, s_2 are the specific gravities of the gases referred to a standard gas.

If we use θ to denote the temperature reckoned from absolute zero of a gas thermometer, M_0 the mass of a molecule of hydrogen, V_0^2 its mean square of velocity at temperature unity, s the specific gravity of any other gas referred to hydrogen, then the mass of a molecule of the other gas is

$$M=M_0 s. \quad \ldots \ldots \ldots \ldots \quad (101)$$

Its mean square of velocity,

$$V^2=\frac{1}{s}V_0^2\theta. \quad \ldots \ldots \ldots \ldots \quad (102)$$

Pressure of the gas,

$$p=\tfrac{1}{3}\frac{\varrho}{s}\theta V_0^2. \quad \ldots \ldots \ldots \ldots \quad (103)$$

We may next determine the amount of cooling by expansion.

Cooling by Expansion.

Let the expansion be equal in all directions, then

$$\frac{du}{dx}=\frac{dv}{dy}=\frac{dw}{dz}=-\frac{1}{3\varrho}\frac{\partial\varrho}{\partial t}, \quad \ldots \ldots \ldots \ldots \quad (104)$$

and $\frac{du}{dy}$ and all terms of unsymmetrical form will be zero.

If the mass of gas is of the same temperature throughout there will be no conduction of heat, and the equation (94) will become

$$\tfrac{1}{2}\varrho\beta\frac{\partial\overline{V}^2}{t}-\tfrac{1}{3}\overline{V}^2\frac{\partial\varrho}{\partial t}=0, \quad \ldots \ldots \ldots \ldots \quad (105)$$

or

$$2\frac{\partial\varrho}{\varrho}=3\beta\frac{\partial\overline{V}^2}{\overline{V}}=3\beta\frac{\partial\theta}{\theta}, \quad \ldots \ldots \ldots \ldots \quad (106)$$

or

$$\frac{\partial\theta}{\theta}=\frac{2}{3\beta}\frac{\partial\varrho}{\varrho}, \quad \ldots \ldots \ldots \ldots \quad (107)$$

which gives the relation between the density and the temperature in a gas expanding

without exchange of heat with other bodies. We also find

$$\frac{\partial p}{p}=\frac{\partial \varrho}{\varrho}+\frac{\partial \theta}{\theta}$$
$$=\frac{2+3\beta}{3\beta}\frac{\partial \varrho}{\rho}, \quad \ldots \ldots \ldots \ldots \quad (108)$$

which gives the relation between the pressure and the density.

Specific Heat of Unit of Mass at Constant Volume.

The total energy of agitation of unit of mass is $\beta V^2=E$, or

$$E=\frac{3\beta}{2}\frac{p}{\varrho}. \quad \ldots \ldots \ldots \ldots \quad (109)$$

If, now, additional energy in the form of heat be communicated to it without changing its density,

$$\partial E=\frac{3\beta}{2}\frac{\partial p}{\varrho}=\frac{3\beta}{2}\frac{p}{\varrho}\frac{\partial \theta}{\theta}. \quad \ldots \ldots \ldots \quad (110)$$

Hence the specific heat of unit of mass of constant volume is in dynamical measure

$$\frac{\partial E}{\partial \theta}=\frac{3\beta}{2}\frac{p}{\varrho\theta}. \quad \ldots \ldots \ldots \ldots \quad (111)$$

Specific Heat of Unit of Mass at Constant Pressure.

By the addition of the heat ∂E the temperature was raised $\partial\theta$ and the pressure ∂p. Now, let the gas expand without communication of heat till the pressure sinks to its former value, and let the final temperature be $\theta+\partial'\theta$. The temperature will thus sink by a quantity $\partial\theta-\partial'\theta$, such that

$$\frac{\partial\theta-\partial'}{\theta}=\frac{2}{2+3\beta}\frac{\partial p}{p}=\frac{2}{2+3\beta}\frac{\partial\theta}{\theta},$$

whence

$$\frac{\partial'\theta}{\theta}=\frac{3\beta}{2+3\beta}\frac{\partial\theta}{\theta}; \quad \ldots \ldots \ldots \ldots \quad (112)$$

and the specific heat of unit of mass at constant pressure is

$$\frac{\partial E}{\partial'\theta}=\frac{2+3\beta}{2}\frac{p}{\varrho\theta}. \quad \ldots \ldots \ldots \ldots \quad (113)$$

The ratio of the specific heat at constant pressure to that of constant volume is known in several cases from experiment. We shall denote this ratio by

$$\gamma=\frac{2+3\beta}{3\beta}, \quad \ldots \ldots \ldots \ldots \quad (114)$$

whence

$$\beta=\tfrac{2}{3}\frac{1}{\gamma-1}. \quad \ldots \ldots \ldots \ldots \quad (115)$$

The specific heat of unit of volume in ordinary measure is at constant volume

$$\frac{1}{\gamma-1}\frac{p}{J\theta}, \quad \ldots \ldots \ldots \ldots \quad (116)$$

and at constant pressure

$$\frac{\gamma}{\gamma-1}\frac{p}{J\theta}, \quad \ldots \ldots \ldots \ldots \quad (117)$$

where J is the mechanical equivalent of unit of heat.

From these expressions Dr. RANKINE* has calculated the specific heat of air, and has found the result to agree with the value afterwards determined experimentally by M. REGNAULT†.

Thermal Effects of Diffusion.

If two gases are diffusing into one another, then, omitting the terms relating to heat generated by friction and to conduction of heat, the equation (94) gives

$$\left.\begin{aligned}&\tfrac{1}{2}\varrho_1\frac{\partial}{\partial t}\beta_1(\xi_1^2+\eta_1^2+\zeta_1^2)+\tfrac{1}{2}\varrho_2\frac{\partial}{\partial t}\beta_2(\xi_2^2+\eta_2^2+\zeta_2^2)+p_1\left(\frac{du_1}{dx}+\frac{dv_1}{dy}+\frac{dw_1}{dz}\right)+p_2\left(\frac{du_2}{dx}+\frac{dv_2}{dy}+\frac{dw_2}{dz}\right)\\&\quad=k\varrho_1\varrho_2A_1\{(u_1-u_2)^2+(v_1-v_2)^2+(w_1-w_2)^2\}.\end{aligned}\right\} \quad 118)$$

By comparison with equations (78), (79), the right-hand side of this equation becomes

$$\begin{aligned}&X(\varrho_1u_1+\varrho_2u_2)+Y(\varrho_1v_1+\varrho_2v_2)+Z(\varrho_1w_1+\varrho_2w_2)\\&\quad-\left(\frac{dp_1}{dx}u_1+\frac{dp_1}{dy}v_1+\frac{dp_1}{dz}w_1\right)-\left(\frac{dp_2}{dx}u_2+\frac{dp_2}{dy}v_2+\frac{dp_2}{dz}w_2\right)\\&\quad-\tfrac{1}{2}\varrho_1\frac{\partial}{\partial t}(u_1^2+v_1^2+w_1^2)-\tfrac{1}{2}\varrho_2\frac{\partial}{\partial t}(u_2^2+v_2^2+w_2^2).\end{aligned}$$

The equation (118) may now be written

$$\left.\begin{aligned}&\tfrac{1}{2}\varrho_1\frac{\partial}{\partial t}\left(u_1^2+v_1^2+w_1^2+\beta_1(\xi_1^2+\eta_1^2+\zeta_1^2)\right)+\tfrac{1}{2}\varrho_2\frac{\partial}{\partial t}\left(u_2^2+v_2^2+w_2^2+\beta_2(\xi_2^2+\eta_2^2+\zeta_2^2)\right)\\&\quad=X(\varrho_1u_1+\varrho_2u_2)+Y(\varrho_1v_1+\varrho_2v_2)+Z(\varrho_1w_1+\varrho_2w_2)-\left(\frac{d.pu}{dx}+\frac{d.pv}{dy}+\frac{d.pw}{dz}\right).\end{aligned}\right\} \quad (119)$$

The whole increase of energy is therefore that due to the action of the external forces *minus* the cooling due to the expansion of the mixed gases. If the diffusion takes place without alteration of the volume of the mixture, the heat due to the mutual action of the gases in diffusion will be exactly neutralized by the cooling of each gas as it expands in passing from places where it is dense to places where it is rare.

Determination of the Inequality of Pressure in different directions due to the Motion of the Medium.

Let us put

$$\varrho_1\xi_1^2=p_1+q_1 \text{ and } \varrho_2\xi_2^2=p_2+q_2. \quad \ldots \ldots \ldots \quad (120)$$

Then by equation (52),

$$\left.\begin{aligned}\frac{\delta q_1}{\delta t}=&-3k_1A_2\varrho_1q_1-\frac{k}{M_1+M_2}(2M_1A_1+3M_2A_2)\varrho_2q_1-k(3A_2-2A_1)\frac{M_1}{M_1+M_2}\varrho_1q_2\\&-k\varrho_1\varrho_2\frac{M_2}{M_1+M_2}A_2-\frac{2}{3}A_1)(\overline{2u_1-u_2}^2-\overline{v_1-v_2}^2-\overline{w_1-w_2}^2),\end{aligned}\right\} \quad (121)$$

* Transactions of the Royal Society of Edinburgh, vol. xx. (1850).

† Comptes Rendus, 1853.

the last term depending on diffusion; and if we omit in equation (75) terms of three dimensions in ξ, η, ζ, which relate to conduction of heat, and neglect quantities of the form $\xi\eta\varrho$ and $\varrho\xi^2-p$, when not multiplied by the large coefficients k, k_1, and k_2, we get

$$\frac{\partial q}{\partial t}+2p\frac{du}{dx}-\frac{2}{3}p\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)=\frac{\delta q}{\delta t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (122)$$

If the motion is not subject to any very rapid changes, as in all cases except that of the propagation of sound, we may neglect $\frac{\partial q}{\partial t}$. In a single system of molecules

$$\frac{}{\delta t}=-3k\mathrm{A}_2\varrho q, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (123)$$

whence

$$q=-\frac{2p}{3k\mathrm{A}_2\varrho}\left\{\frac{du}{dx}-\frac{1}{3}\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (124)$$

If we make

$$\frac{1}{3}\frac{1}{k\mathrm{A}_2}\frac{p}{\varrho}=\mu, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (125)$$

μ will be the coefficient of viscosity, and we shall have by equation (120),

$$\left.\begin{aligned}\varrho\xi^2&=p-2\mu\left\{\frac{du}{dx}-\frac{1}{3}\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)\right\},\\ \varrho\eta^2&=p-2\mu\left\{\frac{dv}{dy}-\frac{1}{3}\left(\frac{du}{dx}+\frac{dv}{d}+\frac{dw}{dz}\right)\right\},\\ \varrho\zeta^2&=p-2\mu\left\{\frac{dw}{dz}-\frac{1}{3}\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)\right\};\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (126)$$

and by transformation of coordinates we obtain

$$\left.\begin{aligned}\varrho\eta\zeta&=-\mu\left(\frac{dv}{dz}+\frac{dw}{dy}\right),\\ \varrho\zeta\xi&=-\mu\left(\frac{dw}{dx}+\frac{du}{dz}\right),\\ \varrho\xi\eta&=-\mu\left(\frac{du}{dy}+\frac{dv}{dx}\right).\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (127)$$

These are the values of the normal and tangential stresses in a simple gas when the variation of motion is not very rapid, and when μ, the coefficient of viscosity, is so small that its square may be neglected.

Equations of Motion corrected for Viscosity.

Substituting these values in the equation of motion (76), we find

$$\varrho\frac{\partial u}{\partial t}+\frac{dp}{dx}-\mu\left\{\frac{d^2u}{dx^2}+\frac{d^2u}{dy^2}+\frac{d^2u}{dz^2}\right\}-\frac{1}{3}\mu\frac{d}{dx}\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)=\mathrm{X}\varrho, \quad . \quad . \quad . \quad . \quad (128)$$

with two other equations which may be written down from symmetry. The form of these equations is identical with that of those deduced by POISSON* from the theory of

* Journal de l'École Polytechnique, 1829, tom. xiii. cah. xx. p. 139.

elasticity, by supposing the strain to be continually relaxed at a rate proportional to its amount. The ratio of the third and fourth terms agrees with that given by Professor STOKES*.

If we suppose the inequality of pressure which we have denoted by q to exist in the medium at any instant, and not to be maintained by the motion of the medium, we find, from equation (123),

$$q_1 = \mathrm{C}e^{-3k\mathrm{A}_2\varrho t} \quad \ldots \quad (129)$$

$$= \mathrm{C}e^{-\frac{t}{\mathrm{T}}} \text{ if } \mathrm{T} = \frac{1}{3k\mathrm{A}_2\varrho} = \frac{\mu}{p}; \quad \ldots \quad (130)$$

the stress q is therefore relaxed at a rate proportional to itself, so that

$$\frac{\delta q}{q} = \frac{\delta t}{\mathrm{T}}. \quad \ldots \quad (131)$$

We may call T the modulus of the time of relaxation.

If we next make $k=0$, so that the stress q does not become relaxed, the medium will be an elastic solid, and the equation

$$\frac{\partial(\varrho\xi^2 - p)}{\partial t} + 2p\frac{du}{dx} - \tfrac{2}{3}p\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right) = 0 \quad \ldots \quad (132)$$

may be written

$$\frac{\partial}{\partial t}\left\{(p_{xx} - p) + 2p\frac{d\alpha}{dx} - \tfrac{2}{3}p\left(\frac{d\alpha}{dx} + \frac{d\beta}{dy} + \frac{d\gamma}{dz}\right)\right\} = 0, \quad \ldots \quad (133)$$

where α, β, γ are the displacements of an element of the medium, and p_{xx} is the normal pressure in the direction of x. If we suppose the initial value of this quantity zero, and p_{xx} originally equal to p, then, after a small displacement,

$$p_{xx} = p - p\left(\frac{d\alpha}{dx} + \frac{d\beta}{dy} + \frac{d\gamma}{dz}\right) - 2p\frac{d\alpha}{dx}; \quad \ldots \quad (134)$$

and by transformation of coordinates the tangential pressure

$$p_{xy} = -p\left(\frac{d\alpha}{dy} + \frac{d\beta}{dx}\right). \quad \ldots \quad (135)$$

The medium has now the mechanical properties of an elastic solid, the rigidity of which is p, while the cubical elasticity is $\frac{5}{3}p$†.

The same result and the same ratio of the elasticities would be obtained if we supposed the molecules to be at rest, and to act on one another with forces depending on the distance, as in the statical molecular theory of elasticity. The coincidence of the properties of a medium in which the molecules are held in equilibrium by attractions and repulsions, and those of a medium in which the molecules move in straight lines without acting on each other at all, deserves notice from those who speculate on theories of physics.

The fluidity of our medium is therefore due to the mutual action of the molecules, causing them to be deflected from their paths.

* "On the Friction of Fluids in Motion and the Equilibrium and Motion of Elastic Solids," Cambridge Phil. Trans. vol. viii. (1845), p. 297, equation (12).

† Ibid. p. 311, equation (29).

$$\left.\begin{array}{l}\text{The coefficient of instantaneous rigidity of a gas is therefore } p.\\ \text{The modulus of the time of relaxation is T.}\\ \text{The coefficient of viscosity is } \mu = p\mathrm{T}.\end{array}\right\} \quad . \quad . \quad . \quad (136)$$

Now p varies as the density and temperature conjointly, while T varies inversely as the density.

Hence μ varies as the absolute temperature, and is independent of the density.

This result is confirmed by the experiments of Mr. GRAHAM on the Transpiration of Gases*, and by my own experiments on the Viscosity or Internal Friction of Air and other Gases†.

The result, that the viscosity is independent of the density, follows from the Dynamical Theory of Gases, whatever be the law of force between the molecules. It was deduced by myself‡ from the hypothesis of hard elastic molecules, and M. O. E. MEYER§ has given a more complete investigation on the same hypothesis.

The experimental result, that the viscosity is proportional to the absolute temperature, requires us to abandon this hypothesis, which would make it vary as the square root of the absolute temperature, and to adopt the hypothesis of a repulsive force inversely as the fifth power of the distance between the molecules, which is the only law of force which gives the observed result.

Using the foot, the grain, and the second as units, my experiments give for the temperature of 62° FAHRENHEIT, and in dry air,

$$\mu = 0{\cdot}0936.$$

If the pressure is 30 inches of mercury, we find, using the same units,

$$p = 477360000.$$

Since $p\mathrm{T} = \mu$, we find that the modulus of the time of relaxation of rigidity in air of this pressure and temperature is

$$\frac{1}{5099100000} \text{ of a second.}$$

This time is exceedingly small, even when compared with the period of vibration of the most acute audible sounds; so that even in the theory of sound we may consider the motion as steady during this very short time, and use the equations we have already found, as has been done by Professor STOKES ||.

Viscosity of a Mixture of Gases.

In a complete mixture of gases, in which there is no diffusion going on, the velocity at any point is the same for all the gases.

* Philosophical Transactions, 1846 and 1849.

† Proceedings of the Royal Society, February 8, 1866; Philosophical Transactions, 1866, p. 249.

‡ Philosophical Magazine, January 1860. § POGGENDORFF'S 'Annalen,' 1865.

|| "On the effect of the Internal Friction of Fluids on the motion of Pendulums," Cambridge Transactions, vol. ix. (1850), art. 79.

Putting

$$\frac{2}{3}\left(2\frac{du}{dx}-\frac{dv}{dy}-\frac{dw}{dz}\right)=\mathrm{U}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (137)$$

equation (122) becomes

$$p_1\mathrm{U}=-3k_1\mathrm{A}_2\varrho_1 q_1-\frac{k}{\mathrm{M}_1+\mathrm{M}_2}(2\mathrm{M}_1\mathrm{A}_1+3\mathrm{M}_2\mathrm{A}_2)\varrho_2 q_1-k(3\mathrm{A}_2-2\mathrm{A}_1)\frac{\mathrm{M}_2}{\mathrm{M}_1+\mathrm{M}_2}\varrho_1 q_2. \quad . \quad (138)$$

Similarly,

$$p_2\mathrm{U}=-3k_2\mathrm{A}_2\varrho_2 q_2-\frac{k}{\mathrm{M}_1+\mathrm{M}_2}(2\mathrm{M}_2\mathrm{A}_1+3\mathrm{M}_1\mathrm{A}_2)\varrho_1 q_2-k(3\mathrm{A}_2-2\mathrm{A}_1)\frac{\mathrm{M}_1}{\mathrm{M}_1+\mathrm{M}_2}\varrho_2 q_1. \quad . \quad (139)$$

Since $p=p_1+p_2$ and $q=q_1+q_2$, where p and q refer to the mixture, we shall have

$$\mu\mathrm{U}=-q=-(q_1+q_2),$$

where μ is the coefficient of viscosity of the mixture.

If we put s_1 and s_2 for the specific gravities of the two gases, referred to a standard gas, in which the values of p and ϱ at temperature θ_0 are p_0 and ϱ_0,

$$\mu=\frac{p_0\theta}{\varrho_0\theta_0}\cdot\frac{\mathrm{E}p_1^2+\mathrm{F}p_1p_2+\mathrm{G}p_2^2}{3\mathrm{A}_2k_1s_1\mathrm{E}p_1^2+\mathrm{H}p_1p_2+3\mathrm{A}_2k_2s_2\mathrm{G}p_2^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (140)$$

where μ is the coefficient of viscosity of the mixture, and

$$\left.\begin{aligned}
\mathrm{E}&=\frac{ks_1}{s_1+s_2}(2s_2\mathrm{A}_1+3s_1\mathrm{A}_2),\\
\mathrm{F}&=3\mathrm{A}_2(k_1s_1+k_2s_2)-(3\mathrm{A}_2-2\mathrm{A}_1)k\frac{2s_1s_2}{s_1+s_2},\\
\mathrm{G}&=\frac{ks_2}{s_1+s_2}(2s_1\mathrm{A}_1+3s_2\mathrm{A}_2),\\
\mathrm{H}&=3\mathrm{A}_2s_1s_2\{3k_1k_2\mathrm{A}_2+2k^2\mathrm{A}_1\}.
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (141)$$

This expression is reduced to μ_1 when $p_2=0$, and to μ_2 when $p_1=0$. For other values of p_1 and p_2 we require to know the value of k, the coefficient of mutual interference of the molecules of the two gases. This might be deduced from the observed values of μ for mixtures, but a better method is by making experiments on the interdiffusion of the two gases. The experiments of GRAHAM on the transpiration of gases, combined with my experiments on the viscosity of air, give as values of k_1 for air, hydrogen, and carbonic acid,

Air	$k_1=\ \ 4{\cdot}81\times10^{10}$,
Hydrogen . . .	$k_1=142{\cdot}8\ \times10^{10}$,
Carbonic acid . .	$k_1=\ \ 3{\cdot}9\ \ \times10^{10}$.

The experiments of GRAHAM in 1863, referred to at page 73, on the interdiffusion of air and carbonic acid, give the coefficient of mutual interference of these gases,

Air and carbonic acid . $k=5{\cdot}2\times10^{10}$;

and by taking this as the absolute value of k, and assuming that the ratios of the coefficients of interdiffusion given at page 76 are correct, we find

Air and hydrogen . . $k=29{\cdot}8\times10^{10}$.

These numbers are to be regarded as doubtful, as we have supposed air to be a simple gas in our calculations, and we do not know the value of k between oxygen and nitrogen. It is also doubtful whether our method of calculation applies to experiments such as the earlier observations of Mr. GRAHAM.

I have also examined the transpiration-times determined by GRAHAM for mixtures of hydrogen and carbonic acid, and hydrogen and air, assuming a value of k roughly, to satisfy the experimental results about the middle of the scale. It will be seen that the calculated numbers for hydrogen and carbonic acid exhibit the peculiarity observed in the experiments, that a small addition of hydrogen *increases* the transpiration-time of carbonic acid, and that in both series the times of mixtures depend more on the slower than on the quicker gas.

The assumed values of k in these calculations were—

For hydrogen and carbonic acid $k=12{\cdot}5\times10^{10}$,
For hydrogen and air . . . . $k=18{\cdot}8\times10^{10}$;

and the results of observation and calculation are, for the times of transpiration of mixtures of—

Hydrogen and Carbonic acid.		Observed.	Calculated.	Hydrogen and Air.		Observed.	Calculated.
100	0	·4321	·4375	100	0	·4434	·4375
97·5	2·5	·4714	·4750	95	5	·5282	·5300
95	5	·5157	·5089	90	10	·5880	·6028
90	10	·5722	·5678	75	25	·7488	·7438
75	25	·6786	·6822	50	50	·8179	·8488
50	50	·7339	·7652	25	75	·8790	·8946
25	75	·7535	·7468	10	90	·8880	·8983
10	90	·7521	·7361	5	95	·8960	·8996
0	100	·7470	·7272	0	100	·9000	·9010

The numbers given are the ratios of the transpiration-times of mixtures to that of oxygen as determined by Mr. GRAHAM, compared with those given by the equation (140) deduced from our theory.

Conduction of Heat in a Single Medium (γ).

The rate of conduction depends on the value of the quantity

$$\tfrac{1}{2}\beta\varrho(\overline{\xi^3}+\overline{\xi\eta^2}+\overline{\xi\zeta^2}),$$

where $\overline{\xi^3}$, $\overline{\xi\eta^2}$, and $\overline{\xi\zeta^2}$ denote the mean values of those functions of ξ, η, ζ for all the molecules in a given element of volume.

As the expressions for the variations of this quantity are somewhat complicated in a mixture of media, and as the experimental investigation of the conduction of heat in gases is attended with great difficulty, I shall confine myself here to the discussion of a single medium.

Putting

$$Q=M(u+\xi)\{u^2+v^2+w^2+2u\zeta+2v\eta+2w\zeta+\beta(\xi^2+\eta^2+\zeta^2)\}, \quad . \quad . \quad . \quad (142)$$

and neglecting terms of the forms $\xi\eta$ and ξ^3 and $\xi\eta^2$ when not multiplied by the large coefficient k_1, we find by equations (75), (77), and (54),

$$\left.\begin{aligned}\varrho\frac{\partial}{\partial t}\beta(\xi^3+\xi\eta^2+\xi\zeta^2)+\beta\frac{d}{dx}\cdot\varrho(\xi^4+\xi^2\eta^2+\xi^2\zeta^2)-\beta(\xi^2+\eta^2+\zeta^2)\frac{dp}{dx}-2\beta\xi^2\frac{dp}{dx}\\ =-3k_1\varrho^2A_2\beta\{\xi^3+\xi\eta^2+\xi\zeta^2\}.\end{aligned}\right\} \quad . \quad . \quad (143)$$

The first term of this equation may be neglected, as the rate of conduction will rapidly establish itself. The second term contains quantities of four dimensions in ξ, η, ζ, whose values will depend on the distribution of velocity among the molecules. If the distribution of velocity is that which we have proved to exist when the system has no external force acting on it and has arrived at its final state, we shall have by equations (29), (31), (32),

$$\overline{\xi^4}=\overline{3\xi^2}\,.\,\overline{\xi^2}=3\frac{p^2}{\varrho^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (144)$$

$$\overline{\xi^2\eta^2}=\overline{\xi^2}\,.\,\overline{\eta^2}=\frac{p^2}{\varrho^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (145)$$

$$\overline{\xi^2\zeta^2}=\overline{\xi^2}\,.\,\overline{\zeta^2}=\frac{p^2}{\varrho^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (146)$$

and the equation of conduction may be written

$$5\beta\frac{p^2}{\varrho\theta}\frac{d\theta}{dx}=-3k_1\varrho^2A_2\beta\{\xi^3+\xi\eta^2+\xi\zeta^2\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (147)$$

[Addition made December 17, 1866.]

[*Final Equilibrium of Temperature.*]

[The left-hand side of equation (147), as sent to the Royal Society, contained a term $2(\beta-1)\frac{p}{\varrho}\frac{dp}{dx}$, the result of which was to indicate that a column of air, when left to itself, would assume a temperature varying with the height, and greater above than below. The mistake arose from an error* in equation (143). Equation (147), as now corrected, shows that the flow of heat depends on the variation of temperature only, and not on the direction of the variation of pressure. A vertical column would therefore, when in thermal equilibrium, have the same temperature throughout.

When I first attempted this investigation I overlooked the fact that $\overline{\xi^4}$ is not the same as $\overline{\xi^2}\,.\,\overline{\xi^2}$, and so obtained as a result that the temperature diminishes as the height increases at a greater rate than it does by expansion when air is carried up in mass. This leads at once to a condition of instability, which is inconsistent with the second law of thermodynamics. I wrote to Professor Sir W. THOMSON about this result, and the difficulty I had met with, but presently discovered *one* of my mistakes, and arrived at the conclusion that the temperature would increase with the height. This does not lead to mecha-

* The last term on the left-hand side was not multiplied by β.

nical instability, or to any self-acting currents of air, and I was in some degree satisfied with it. But it is equally inconsistent with the second law of thermodynamics. In fact, if the temperature of any substance, when in thermic equilibrium, is a function of the height, that of any other substance must be the same function of the height. For if not, let equal columns of the two substances be enclosed in cylinders impermeable to heat, and put in thermal communication at the bottom. If, when in thermal equilibrium, the tops of the two columns are at different temperatures, an engine might be worked by taking heat from the hotter and giving it up to the cooler, and the refuse heat would circulate round the system till it was all converted into mechanical energy, which is in contradiction to the second law of thermodynamics.

The result as now given is, that temperature in gases, when in thermal equilibrium, is independent of height, and it follows from what has been said that temperature is independent of height in all other substances.

If we accept this law of temperature as the actual one, and examine our assumptions, we shall find that unless $\overline{\xi^4}=3\overline{\xi^2}\,.\,\overline{\xi^2}$, we should have obtained a different result. Now this equation is derived from the law of distribution of velocities to which we were led by independent considerations. We may therefore regard this law of temperature, if true, as in some measure a confirmation of the law of distribution of velocities.]

Coefficient of Conductivity.

If C is the coefficient of conductivity of the gas for heat, then the quantity of heat which passes through unit of area in unit of time measured as mechanical energy, is

$$C\frac{d\theta}{dx}=\frac{5}{6}\,\frac{\beta}{k_1A_2}\,\frac{p^2}{\varrho^2\theta}\,\frac{d\theta}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (148)$$

by equation (147).

Substituting for β its value in terms of γ by equation (115), and for k_1 its value in terms of μ by equation (125), and calling p_0, ϱ_0, and θ_0 the simultaneous pressure, density, and temperature of the standard gas, and s the specific gravity of the gas in question, we find

$$C=\frac{5}{3(\gamma-1)}\,\frac{p_0}{\varrho_0\theta_0}\,\frac{\mu}{s}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (149)$$

For air we have $\gamma=1{\cdot}409$, and at the temperature of melting ice, or $274^\circ{\cdot}6$ C. above absolute zero, $\sqrt{\frac{p}{\varrho}}=918{\cdot}6$ feet per second, and at $16^\circ{\cdot}6$ C., $\mu=0{\cdot}0936$ in foot-grain-second measure. Hence for air at $16^\circ{\cdot}6$ C the conductivity for heat is

$$C=1172. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (150)$$

That is to say, a horizontal stratum of air one foot thick, of which the upper surface is kept at 17° C., and the lower at 16° C., would in one second transmit through every square foot of horizontal surface a quantity of heat the mechanical energy of which is equal to that of 2344 grains moving at the rate of one foot per second.

Principal FORBES* has deduced from his experiments on the conduction of heat in bars, that a plate of wrought iron one foot thick, with its opposite surfaces kept 1° C. different in temperature, would, when the mean temperature is 25° C., transmit in one minute through every square foot of surface as much heat as would raise one cubic foot of water 0°·0127 C.

Now the dynamical equivalent in foot-grain-second measure of the heat required to raise a cubic foot of water 1° C. is $1{\cdot}9157 \times 10^{10}$.

It appears from this that iron at 25° C. conducts heat 3525 times better than air at 16°·6 C.

M. CLAUSIUS, from a different form of the theory, and from a different value of μ, found that lead should conduct heat 1400 times better than air. Now iron is twice as good a conductor of heat as lead, so that this estimate is not far different from that of M. CLAUSIUS in actual value.

In reducing the value of the conductivity from one kind of measure to another, we must remember that its dimensions are MLT^{-3}, when expressed in absolute dynamical measure.

Since all the quantities which enter into the expression for C are constant except μ, the conductivity is subject to the same laws as the viscosity, that is, it is independent of the pressure, and varies directly as the absolute temperature. The conductivity of iron diminishes as the temperature increases.

Also, since γ is nearly the same for air, oxygen, hydrogen, and carbonic oxide, the conductivity of these gases will vary as the ratio of the viscosity to the specific gravity. Oxygen, nitrogen, carbonic oxide, and air will have equal conductivity, while that of hydrogen will be about seven times as great.

The value of γ for carbonic acid is 1·27, its specific gravity is $\frac{11}{8}$ of oxygen, and its viscosity $\frac{8}{11}$ of that of oxygen. The conductivity of carbonic acid for heat is therefore about $\frac{7}{9}$ of that of oxygen or of air.

* "Experimental Inquiry into the Laws of the Conduction of Heat in Bars," Edinburgh Transactions, 1861–62.