

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

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

where  $F_{\sin \phi}$  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  $\theta$ , and of the quantities whose summation leads to  $A_1$  and  $A_2$ .

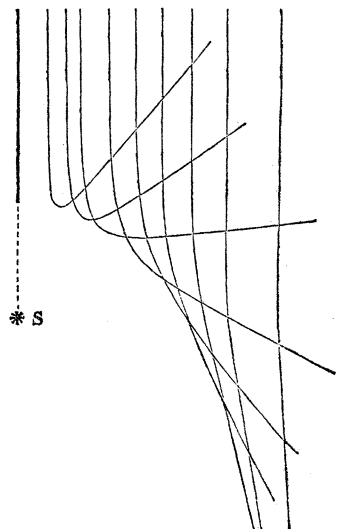
$\phi.$	$b.$	Distance of apse.	$\theta.$	$\frac{\sin^2 \theta}{\sin^2 2\phi}$	$\frac{\sin^2 2\theta}{\sin^2 2\phi}$
$\overset{\circ}{0} \overset{\prime}{0}$	infinite	infinite	$\overset{\circ}{0} \overset{\prime}{0}$	0	0
5 0	2381	2391	0 31	·00270	·01079
10 0	1658	1684	1 53	·01464	·03689
15 0	1316	1366	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

$$A_1 = \int 4\pi\alpha da \sin^2 \theta = 2\cdot6595. \dots \dots \dots (15)$$

$$A_2 = \int \pi\alpha da \sin^2 2\theta = 1\cdot3682. \dots \dots \dots (16)$$

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  $\xi, \eta, \zeta$ , 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  $\xi, \eta, \zeta$ , &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

$$\overline{Q}N_2,$$

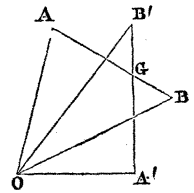
where  $\overline{Q}$  is the mean value of Q for all the molecules of the second kind, and  $N_2$  is the number of those molecules.

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,  $2\theta$  the angle through which BA is turned during the encounter, and  $\phi$  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  $\theta$  and  $\phi$ , 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

$$n_1 n_2 F de, \dots \dots \dots (17)$$

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  $\theta$ , 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  $dV$  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  $dV$  at  $A$ , will be

$$n_1 = f_1(a) dV. \dots \dots \dots (18)$$

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

$$n_2 = f_2(b) dV; \dots \dots \dots (19)$$

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

$$f_1(a) f_2(b) dV^2 F de. \dots \dots \dots (20)$$

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  $dV$ .

In like manner we should find for the number of encounters between molecules whose original velocities corresponded to elements equal to  $dV$  described about  $A'$  and  $B'$ , and whose subsequent velocities correspond to elements equal to  $dV$  described about  $A$  and  $B$ ,

$$f_1(a') f_2(b') dV^2 F' de, \dots \dots \dots (21)$$

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

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

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

$$M_1 a^2 + M_2 b^2 = M_1 a'^2 + M_2 b'^2, \dots \dots \dots (23)$$

whence we obtain

$$f_1(a) = C_1 e^{-\frac{a^2}{\alpha^2}}, \quad f_2(b) = C_2 e^{-\frac{b^2}{\beta^2}}, \dots \dots \dots (24)$$

where

$$M_1 \alpha^2 = M_2 \beta^2. \dots \dots \dots (25)$$

By integrating  $\iiint C_1 e^{-\frac{\xi^2 + \eta^2 + \zeta^2}{\alpha^2}} d\xi d\eta d\zeta$ , 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  $\xi$  and  $\xi + d\xi$ ,  $\eta$  and  $\eta + d\eta$ , and  $\zeta$  and  $\zeta + d\zeta$  is

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

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

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

where  $\alpha, \beta, \gamma$  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  $\alpha$  the modulus of velocity,

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

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

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

4th. The mean value of  $\xi^4$  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  
 $M_1 \alpha^2 = M_2 \beta^2$ , . . . . . (33)

whence

$M_1 v_1^2 = M_2 v_2^2$ , . . . . . (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  $\delta_1$  and  $\delta_2$  to indicate the effect produced by molecules of the first kind and second kind respectively, and  $\delta_3$  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,

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

where the functions of  $\xi, \eta, \zeta$  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

$$(\alpha) \quad \frac{\delta_2 \xi_1}{\delta t} = \left( \frac{K}{M_1 M_2 (M_1 + M_2)} \right)^{\frac{1}{2}} N_2 M_2 A_1 (\xi_2 - \xi_1); \quad \dots \dots \dots (36)$$

$$(\beta) \quad \left. \begin{aligned} \frac{\delta_2 \xi_1^2}{\delta t} &= \left( \frac{K}{M_1 M_2 (M_1 + M_2)} \right)^{\frac{1}{2}} \frac{N_2 M_2}{M_1 + M_2} \\ &\quad \{ 2A_1 (\xi_2 - \xi_1) (M_1 \xi_1 + M_2 \xi_2) + A_2 M_2 (\overline{\eta_2 - \eta_1}^2 + \overline{\zeta_2 - \zeta_1}^2 - 2\overline{\xi_2 - \xi_1}^2) \}; \end{aligned} \right\} \dots \dots (37)$$

$$\left. \begin{aligned} \frac{\delta_2 \xi_1 \eta_1}{\delta t} &= \left( \frac{K}{M_1 M_2 (M_1 + M_2)} \right)^{\frac{1}{2}} \frac{N_2 M_2}{M_1 + M_2} \\ &\quad \{ A_1 (2M_2 \xi_2 \eta_2 - 2M_1 \xi_1 \eta_1 + (M_1 - M_2) (\xi_1 \eta_2 + \xi_2 \eta_1)) - 3A_2 M_2 (\xi_2 - \xi_1) (\eta_2 - \eta_1) \}; \end{aligned} \right\} (38)$$

$$(\gamma) \quad \frac{\delta_2 \xi_1 V_1}{\delta t} = \left( \frac{K}{M_1 M_2 (M_1 + M_2)} \right)^{\frac{1}{2}} N_2 M_2 \left\{ \begin{aligned} & A_1 (\bar{\xi}_2 - \bar{\xi}_1 V_1^2 + 2 \bar{\xi}_1 (U - V_1^2)) \\ & + \frac{M_2}{M_1 + M_2} (2A_1 - 3A_2) 2(\bar{\xi}_2 - \bar{\xi}_1)(U - V_1^2) \\ & + \frac{M_2}{M_1 + M_2} (2A_1 + 2A_2) \bar{\xi}_1 V^2 \\ & + \left( \frac{M_2}{M_1 + M_2} \right)^2 (2A_1 - 2A_2) 2(\bar{\xi}_2 - \bar{\xi}_1) V^2 \end{aligned} \right\}; \quad (39)$$

using the symbol  $\delta_2$  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  $\xi_1, \xi_1^2, \xi_1 \eta_1$ , and  $\xi_1 V_1^2$ , 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  $\xi, \eta, \zeta$ , 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

$$(\alpha) \quad \frac{\delta_1 \bar{\xi}_1}{\delta t} = 0; \quad \dots \dots \dots (40)$$

$$(\beta) \quad \frac{\delta_1 \bar{\xi}_1^2}{\delta t} = \left( \frac{K_1}{2M_1^3} \right)^{\frac{1}{2}} M_1 N_1 A_2 \{ \bar{\eta}_1^2 + \bar{\zeta}_1^2 - 2\bar{\xi}_1^2 - (\bar{\eta}_1 \cdot \bar{\eta}_1 + \bar{\zeta}_1 \cdot \bar{\zeta}_1 - 2\bar{\xi}_1 \bar{\xi}_1) \}; \quad (41)$$

$$\frac{\delta_1 \bar{\xi}_1 \bar{\eta}_1}{\delta t} = \left( \frac{K_1}{2M_1^3} \right)^{\frac{1}{2}} M_1 N_1 A_2 3 \{ \bar{\xi}_1 \cdot \bar{\eta}_1 - \bar{\xi}_1 \bar{\eta}_1 \}; \quad \dots \dots \dots (42)$$

$$(\gamma) \quad \frac{\delta_1 \bar{\xi}_1 V_1^2}{\delta t} = \left( \frac{K_1}{2M_1^3} \right)^{\frac{1}{2}} M_1 N_1 A_2 3 (\bar{\xi}_1 \cdot \bar{V}_1^2 - \bar{\xi}_1 \bar{V}_1^2). \quad \dots \dots \dots (43)$$

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  $\xi, \xi^2$ , and  $\xi V^2$  due to this cause,

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

$$(\beta) \frac{\delta_3 \cdot \xi^2}{\delta t} = 2\xi X; \dots \dots \dots (45)$$

$$\frac{\delta_3 \cdot \xi \eta}{\delta t} = \eta X + \xi Y; \dots \dots \dots (46)$$

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

where  $\delta_3$  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

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

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

$$M_1 N_1 = \rho_1, \quad M_2 N_2 = \rho_2, \quad \dots \dots \dots (49)$$

where  $\rho_1$  and  $\rho_2$  are the densities of the two systems of molecules, that is, the mass in unit of volume. We shall also write

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

$\rho_1, \rho_2, k_1, k_2,$  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,

$$(\alpha) \frac{\delta u_1}{\delta t} = k A_1 \rho_2 (u_2 - u_1) + X; \dots \dots \dots (51)$$

$$(\beta) \left. \begin{aligned} \frac{\delta \cdot \xi_1^2}{\delta t} &= k_1 A_2 \rho_1 \{ \eta_1^2 + \zeta_1^2 - 2\xi_1^2 \} \\ &+ k \rho_2 \frac{M_2}{M_1 + M_2} \left\{ 2A_1 (u_2 - u_1)^2 + A_2 (\overline{v_2 - v_1}^2 + \overline{w_2 - w_1}^2 - 2\overline{u_2 - u_1}^2) \right\} \\ &+ \frac{k \rho_2}{M_1 + M_2} \left\{ 2A_1 (M_2 \xi_2^2 - M_1 \xi_1^2) + A_2 M_2 (\eta_1^2 + \zeta_1^2 - 2\xi_1^2 + \eta_2^2 + \zeta_2^2 - 2\xi_2^2) \right\}; \end{aligned} \right\} \dots (52)$$

also

$$\left. \begin{aligned} \frac{\delta \cdot \xi \eta}{\delta t} &= -3k_1 A_2 \rho_1 \xi_1 \eta_1 + k \rho_2 \frac{M_2}{M_1 + M_2} (2A_1 - 3A_2) (u_2 - u_1) (v_2 - v_1) \\ &+ \frac{k \rho_2}{M_1 + M_2} \left\{ 2A_1 (M_2 \xi_2 \eta_2 - M_1 \xi_1 \eta_1) - 3A_2 M_2 (\xi_1 \eta_1 + \xi_2 \eta_2) \right\}. \end{aligned} \right\} \dots (53)$$

( $\gamma$ ) 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,

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

*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  $\xi, \eta, \zeta$  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  $\xi, \eta, \zeta$ , 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  $\delta$ .

The mean values of  $\xi^2$  and other functions of  $\xi, \eta, \zeta$  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  $\partial$ .

We shall call the velocities  $u, v, w$  the velocities of translation of the medium, and  $\xi, \eta, \zeta$  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  $\rho$  the density of the element, then

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

*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  $\xi, \eta$ , and  $\zeta$  for each, and we shall suppose that the number of molecules in unit of volume whose velocity in the direction of  $x$  lies between  $\xi$  and  $\xi + d\xi, \eta$  and  $\eta + d\eta, \zeta$  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

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

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  $w'$ . The velocity of the plane relative to the molecules we have been considering is  $w' - (u + \xi)$ , and since there are  $dN$  of these molecules in unit of volume it will overtake

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

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

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

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  $\xi$  or of  $\xi, \eta$ , and  $\zeta$ , 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

$$\int (u - w' + \xi) Q dN,$$

or

$$(u - w') \int Q dN + \int \xi Q dN. \quad \dots \dots \dots (57)$$

If we put  $\bar{Q}N$  for  $\int Q dN$ , and  $\bar{\xi}Q$  for  $\int \xi Q dN$ , then we may call  $\bar{Q}$  the mean value of  $Q$ , and  $\bar{\xi}Q$  the mean value of  $\xi Q$ , 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

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

( $\alpha$ ) *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,  $\bar{M} = M$ ; and since the mean value of  $\xi$  is zero, the expression is reduced to

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

If  $u = w'$ , 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  $u, v, w$ .

( $\beta$ ) *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

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

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  $\xi^2$ .

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,

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

and

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

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  $l, m, n$ ,

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

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

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

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;  $\overline{\eta\zeta}\varrho, \overline{\xi\zeta}\varrho$ , 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

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

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

$$\frac{1}{2}(u^2 + v^2 + w^2)\rho + \frac{1}{2}(\xi^2 + \eta^2 + \zeta^2)\rho + \frac{1}{2}\bar{E}\rho. \quad \dots \dots \dots (66)$$

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

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

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

$$\frac{1}{2}\beta(\xi^2 + \eta^2 + \zeta^2)\rho, \quad \dots \dots \dots (68)$$

or

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

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

( $\gamma$ ) *Transference of Energy across a Plane—Conduction of Heat.*

Putting

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

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

$$\frac{1}{2}\beta(\bar{\xi}^3 + \bar{\xi}\bar{\eta}^2 + \bar{\xi}\bar{\zeta}^2)\rho, \quad \dots \dots \dots (71)$$

where  $\bar{\xi}^3$ , &c. indicate the mean values of  $\xi^3$ , &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  $\bar{Q}$  the mean value of  $Q$  for all the molecules of the same kind within the element.

The quantity  $\bar{Q}$  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  $\bar{Q}$ , or molecules may pass into the element and out of it, and so cause an increase or diminution of the value of  $\bar{Q}$  within it. If we employ the symbol  $\delta$  to denote the variation of  $Q$  due to actions of the first kind on the individual molecules, and the symbol  $\partial$  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,

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

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  $u'=u, v'=v, w'=w$ , 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

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

*Equation of Continuity.*

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

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

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

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

a more convenient form of the general equation.

*Equations of Motion ( $\alpha$ ).*

To obtain the Equation of Motion in the direction of  $x$ , put  $Q=M_1(u_1 + \xi_1)$ , the momentum of a molecule in the direction of  $x$ .

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

$$\rho_1 \frac{\partial u_1}{\partial t} + \frac{d}{dx}(\rho_1 \bar{\xi}_1^2) + \frac{d}{dy}(\rho_1 \bar{\xi}_1 \bar{\eta}_1) + \frac{d}{dz}(\rho_1 \bar{\xi}_1 \bar{\zeta}_1) = k A_1 \rho_1 \rho_2 (u_2 - u_1) + X \rho_1. \quad (76)$$

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,  $\rho_1 \bar{\xi}_1^2$  becomes  $p_1$ , and the tangential pressures vanish, so that the equation becomes

$$\frac{dp_1}{dx} = X \rho_1, \quad (77)$$

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

$$\rho_1 \frac{\partial u_1}{\partial t} + \frac{dp_1}{dx} = kA_1 \rho_1 \rho_2 (u_2 - u_1) + X_{\rho_1}, \dots \dots \dots (78)$$

and for the second,

$$\rho_2 \frac{\partial u_2}{\partial t} + \frac{dp_2}{dx} = kA_1 \rho_1 \rho_2 (u_1 - u_2) + X_{\rho_2} \dots \dots \dots (79)$$

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  $\rho_1 + \rho_2 = \rho$ , we find by adding,

$$\frac{dp}{dx} = X_{\rho} \dots \dots \dots (80)$$

If we also put  $p_1 u_1 + p_2 u_2 = pu$ , then the volumes transferred in opposite directions across a plane moving with velocity  $u$  will be equal, so that

$$p_1(u_1 - u) = p_2(u - u_2) = \frac{p_1 p_2}{p \rho_1 \rho_2 k A_1} \cdot \left( X_{\rho_1} \frac{dp_1}{dx} \right) \dots \dots \dots (81)$$

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)

$$p_1 u_1 = - \frac{p_1 p_2}{g_1 g_2 k A_1 p} \frac{1}{p} \frac{dp_1}{dx}, \dots \dots \dots (83)$$

and by the equation of continuity,

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

whence

$$\frac{dp_1}{dt} = \frac{p_1 p_2}{g_1 g_2 k A_1 p} \frac{1}{p} \frac{d^2 p_1}{dx^2}; \dots \dots \dots (85)$$

or if we put  $D = \frac{p_1 p_2}{g_1 g_2 k A_1 p} \frac{1}{p}$ ,

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

The solution of this equation is

$$p_1 = C_1 + C_2 e^{-n^2 D t} \cos (nx + \alpha) + \&c. \dots \dots \dots (87)$$

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

$$p_1 = C_1 + C_2 e^{-\frac{\pi^2 D}{a^2} t} \cos \frac{\pi x}{a} + C_3 e^{-4 \frac{\pi^2 D}{a^2} t} \cos 2 \frac{\pi x}{a} + \&c., \dots \dots \dots (88)$$

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

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

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

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

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

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

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
$\infty$	·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

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

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

$$g_1 \frac{\partial u_1}{\partial t} + \frac{dp_1}{dx} = kA g_1 g_2 (u_2 - u_1) + Xg \quad . . . . . (92)$$

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  $kA g_1 g_2 (u_2 - u_1)$  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 ( $\beta$ ).*

By putting for Q in equation (75)

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

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



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

$$\begin{aligned}
 & \frac{1}{2} \rho_1 \frac{\partial}{\partial t} \beta_1 (\xi_1^2 + \eta_1^2 + \zeta_1^2) + \rho_1 \xi_1^2 \frac{du_1}{dx} + \rho_1 \eta_1^2 \frac{dv_1}{dy} + \rho_1 \zeta_1^2 \frac{dw_1}{dz} \\
 & + \rho_1 \eta_1 \zeta_1 \left( \frac{dv_1}{dz} + \frac{dw_1}{dy} \right) + \rho_1 \zeta_1 \xi_1 \left( \frac{dw_1}{dx} + \frac{du_1}{dz} \right) + \rho_1 \xi_1 \eta_1 \left( \frac{du_1}{dy} + \frac{dv_1}{dx} \right) \\
 & + \beta_1 \left\{ \frac{d}{dx} (\rho_1 \xi_1^3 + \rho_1 \xi_1 \eta_1^2 + \rho_1 \xi_1 \zeta_1^2) + \frac{d}{dy} (\rho_1 \eta_1 \xi_1^2 + \rho_1 \eta_1^3 + \rho_1 \eta_1 \zeta_1^2) + \frac{d}{dz} (\rho_1 \zeta_1 \xi_1^2 + \rho_1 \zeta_1 \eta_1^2 + \rho_1 \zeta_1^3) \right\} \\
 & = \frac{k \rho_1 \rho_2 A_1}{M_1 + M_2} \left\{ M_2 [(u_2 - u_1)^2 + (v_2 - v_1)^2 + (w_2 - w_1)^2] + M_2 (\xi_2^2 + \eta_2^2 + \zeta_2^2) - M_1 (\xi_1^2 + \eta_1^2 + \zeta_1^2) \right\}.
 \end{aligned} \tag{94}$$

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,

$$\frac{1}{2} \rho_1 \frac{\partial}{\partial t} \beta_1 (\xi_1^2 + \eta_1^2 + \zeta_1^2) = \frac{k \rho_1 \rho_2 A_1}{M_1 + M_2} \left\{ M_2 (\xi_2^2 + \eta_2^2 + \zeta_2^2) - M_1 (\xi_1^2 + \eta_1^2 + \zeta_1^2) \right\}. \tag{95}$$

If we put

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

we find

$$\frac{\partial}{\partial t} (Q_2 - Q_1) = - \frac{2kA_1}{M_1 + M_2} (M_2 \rho_2 \beta_1 + M_1 \rho_1 \beta_2) (Q_2 - Q_1), \tag{97}$$

or

$$Q_2 - Q_1 = C e^{-nt}, \quad \text{where} \quad n = \frac{2kA_1}{M_1 + M_2} (M_2 \rho_2 \beta_2 + M_1 \rho_1 \beta_1) \frac{1}{\beta_1 \beta_2}. \tag{98}$$

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,

$$Q_1 = Q_2, \tag{99}$$

or

$$\begin{aligned}
 1 &= \frac{Q_1}{Q_2} = \frac{M_1 (\xi_1^2 + \eta_1^2 + \zeta_1^2)}{M_2 (\xi_2^2 + \eta_2^2 + \zeta_2^2)} \\
 &= \frac{M_1 p_1}{M_2 p_2} \frac{\rho_2}{\rho_1}
 \end{aligned}$$

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

$$\frac{M_1}{\rho_1} = \frac{M_2}{\rho_2}, \dots \dots \dots (100)$$

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  $\theta$  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

$$M = M_0 s. \dots \dots \dots (101)$$

Its mean square of velocity,

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

Pressure of the gas,

$$p = \frac{1}{3} \frac{\rho}{s} \theta V_0^2. \dots \dots \dots (103)$$

We may next determine the amount of cooling by expansion.

*Cooling by Expansion.*

Let the expansion be equal in all directions, then

$$\frac{du}{dx} = \frac{dv}{dy} = \frac{dw}{dz} = -\frac{1}{3\theta} \frac{\partial \rho}{\partial t}, \dots \dots \dots (104)$$

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

$$\frac{1}{2} \rho \beta \frac{\partial \bar{V}^2}{\partial t} - \frac{1}{3} \bar{V}^2 \frac{\partial \rho}{\partial t} = 0, \dots \dots \dots (105)$$

or

$$2 \frac{\partial \rho}{\partial t} = 3 \beta \frac{\partial \bar{V}^2}{\partial t} = 3 \beta \frac{\partial \theta}{\partial t}, \dots \dots \dots (106)$$

or

$$\frac{\partial \theta}{\partial t} = \frac{2}{3\beta} \frac{\partial \rho}{\partial t}, \dots \dots \dots (107)$$

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

without exchange of heat with other bodies. We also find

$$\begin{aligned} \frac{\partial p}{p} &= \frac{\partial \rho}{\rho} + \frac{\partial \theta}{\theta} \\ &= \frac{2+3\beta}{3\beta} \frac{\partial \rho}{\rho}, \end{aligned} \quad \dots \dots \dots (108)$$

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

$$E = \frac{3\beta}{2} \frac{p}{\rho} \dots \dots \dots (109)$$

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

$$\partial E = \frac{3\beta}{2} \frac{\partial p}{\rho} = \frac{3\beta}{2} \frac{p}{\rho} \frac{\partial \theta}{\theta} \dots \dots \dots (110)$$

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

$$\frac{\partial E}{\partial \theta} = \frac{3\beta}{2} \frac{p}{\rho \theta} \dots \dots \dots (111)$$

*Specific Heat of Unit of Mass at Constant Pressure.*

By the addition of the heat  $\partial E$  the temperature was raised  $\partial \theta$  and the pressure  $\partial p$ . 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

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

whence

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

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

$$\frac{\partial E}{\partial' \theta} = \frac{2+3\beta}{2} \frac{p}{\rho \theta} \dots \dots \dots (113)$$

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

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

whence

$$\beta = \frac{2}{3} \frac{1}{\gamma-1} \dots \dots \dots (115)$$

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

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

and at constant pressure

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

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

$$\left. \begin{aligned} & \frac{1}{2}\rho_1 \frac{\partial}{\partial t} \beta_1 (\xi_1^2 + \eta_1^2 + \zeta_1^2) + \frac{1}{2}\rho_2 \frac{\partial}{\partial t} \beta_2 (\xi_2^2 + \eta_2^2 + \zeta_2^2) + p_1 \left( \frac{du_1}{dx} + \frac{dv_1}{dy} + \frac{dw_1}{dz} \right) + p_2 \left( \frac{du_2}{dx} + \frac{dv_2}{dy} + \frac{dw_2}{dz} \right) \\ & = k\rho_1\rho_2 A_1 \{ (u_1 - u_2)^2 + (v_1 - v_2)^2 + (w_1 - w_2)^2 \}. \end{aligned} \right\} (118)$$

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

$$\begin{aligned} & X(\rho_1 u_1 + \rho_2 u_2) + Y(\rho_1 v_1 + \rho_2 v_2) + Z(\rho_1 w_1 + \rho_2 w_2) \\ & - \left( \frac{dp_1}{dx} u_1 + \frac{dp_1}{dy} v_1 + \frac{dp_1}{dz} w_1 \right) - \left( \frac{dp_2}{dx} u_2 + \frac{dp_2}{dy} v_2 + \frac{dp_2}{dz} w_2 \right) \\ & - \frac{1}{2}\rho_1 \frac{\partial}{\partial t} (u_1^2 + v_1^2 + w_1^2) - \frac{1}{2}\rho_2 \frac{\partial}{\partial t} (u_2^2 + v_2^2 + w_2^2). \end{aligned}$$

The equation (118) may now be written

$$\left. \begin{aligned} & \frac{1}{2}\rho_1 \frac{\partial}{\partial t} (u_1^2 + v_1^2 + w_1^2 + \beta_1 (\xi_1^2 + \eta_1^2 + \zeta_1^2)) + \frac{1}{2}\rho_2 \frac{\partial}{\partial t} (u_2^2 + v_2^2 + w_2^2 + \beta_2 (\xi_2^2 + \eta_2^2 + \zeta_2^2)) \\ & = X(\rho_1 u_1 + \rho_2 u_2) + Y(\rho_1 v_1 + \rho_2 v_2) + Z(\rho_1 w_1 + \rho_2 w_2) - \left( \frac{d.pu}{dx} + \frac{d.pv}{dy} + \frac{d.pw}{dz} \right). \end{aligned} \right\} \dots (119)$$

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

$$\rho_1 \xi_1^2 = p_1 + q_1 \quad \text{and} \quad \rho_2 \xi_2^2 = p_2 + q_2. \dots \dots \dots (120)$$

Then by equation (52),

$$\left. \begin{aligned} \frac{\delta q_1}{\delta t} = & -3k_1 A_2 \rho_1 q_1 - \frac{k}{M_1 + M_2} (2M_1 A_1 + 3M_2 A_2) \rho_2 q_1 - k(3A_2 - 2A_1) \frac{M_1}{M_1 + M_2} \rho_1 q_2 \\ & - k\rho_1 \rho_2 \frac{M_2}{M_1 + M_2} A_2 - \frac{2}{3} A_1 (2u_1 - u_2 - v_1 - v_2 - w_1 - w_2), \end{aligned} \right\} \dots (121)$$

\* 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  $\xi, \eta, \zeta$ , which relate to conduction of heat, and neglect quantities of the form  $\xi\eta\zeta$  and  $\xi^2 - p$ , when not multiplied by the large coefficients  $k, k_1$ , and  $k_2$ , we get

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

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

$$\frac{\partial q}{\partial t} = -3kA_2 \xi q, \dots \dots \dots (123)$$

whence

$$q = -\frac{2p}{3kA_2 \xi} \left\{ \frac{du}{dx} - \frac{1}{3} \left( \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right) \right\} \dots \dots \dots (124)$$

If we make

$$\frac{1}{3} \frac{1}{kA_2 \xi} p = \mu, \dots \dots \dots (125)$$

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

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

and by transformation of coordinates we obtain

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

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  $\mu$ , 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

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

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),

$$q_1 = Ce^{-3kA_2gt} \dots \dots \dots (129)$$

$$= Ce^{-\frac{t}{T}} \text{ if } T = \frac{1}{3kA_2g} = \frac{\mu}{p}; \dots \dots \dots (130)$$

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

$$\frac{\delta q}{q} = \frac{\delta t}{T} \dots \dots \dots (131)$$

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

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

may be written

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

where  $\alpha, \beta, \gamma$  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,

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

and by transformation of coordinates the tangential pressure

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

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).

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

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

Hence  $\mu$  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,

$$\mu = 0.0936.$$

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

$$p = 477360000.$$

Since  $pT = \mu$ , 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

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

equation (122) becomes

$$p_1 U = -3k_1 A_2 \varrho_1 q_1 - \frac{k}{M_1 + M_2} (2M_1 A_1 + 3M_2 A_2) \varrho_2 q_1 - k(3A_2 - 2A_1) \frac{M_2}{M_1 + M_2} \varrho_1 q_2. \dots (138)$$

Similarly,

$$p_2 U = -3k_2 A_2 \varrho_2 q_2 - \frac{k}{M_1 + M_2} (2M_2 A_1 + 3M_1 A_2) \varrho_1 q_2 - k(3A_2 - 2A_1) \frac{M_1}{M_1 + M_2} \varrho_2 q_1. \dots (139)$$

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

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

where  $\mu$  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  $q$  at temperature  $\theta_0$  are  $p_0$  and  $q_0$ ,

$$\mu = \frac{p_0 \theta}{\varrho_0 \theta_0} \cdot \frac{E p_1^2 + F p_1 p_2 + G p_2^2}{3A_2 k_1 s_1 E p_1^2 + H p_1 p_2 + 3A_2 k_2 s_2 G p_2^2}, \dots \dots \dots (140)$$

where  $\mu$  is the coefficient of viscosity of the mixture, and

$$\left. \begin{aligned} E &= \frac{k s_1}{s_1 + s_2} (2s_2 A_1 + 3s_1 A_2), \\ F &= 3A_2 (k_1 s_1 + k_2 s_2) - (3A_2 - 2A_1) k \frac{2s_1 s_2}{s_1 + s_2}, \\ G &= \frac{k s_2}{s_1 + s_2} (2s_1 A_1 + 3s_2 A_2), \\ H &= 3A_2 s_1 s_2 \{ 3k_1 k_2 A_2 + 2k^2 A_1 \}. \end{aligned} \right\} \dots \dots \dots (141)$$

This expression is reduced to  $\mu_1$  when  $p_2 = 0$ , and to  $\mu_2$  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  $\mu$  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,

$$\begin{aligned} \text{Air} & \dots \dots \dots k_1 = 4.81 \times 10^{10}, \\ \text{Hydrogen} & \dots \dots \dots k_1 = 142.8 \times 10^{10}, \\ \text{Carbonic acid} & \dots \dots \dots k_1 = 3.9 \times 10^{10}. \end{aligned}$$

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,

$$\text{Air and carbonic acid} \quad k = 5.2 \times 10^{10};$$

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

$$\text{Air and hydrogen} \quad k = 29.8 \times 10^{10}.$$



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  $k=12.5 \times 10^{10}$ ,

For hydrogen and air . . . .  $k=18.8 \times 10^{10}$ ;

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	·5232	·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 ( $\gamma$ ).*

The rate of conduction depends on the value of the quantity

$$\frac{1}{2}\beta g(\xi^3 + \xi\eta^2 + \xi\zeta^2),$$

where  $\xi^3$ ,  $\xi\eta^2$ , and  $\xi\zeta^2$  denote the mean values of those functions of  $\xi$ ,  $\eta$ ,  $\zeta$  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

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

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

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

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  $\xi$ ,  $\eta$ ,  $\zeta$ , 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),

$$\overline{\xi^4} = 3\overline{\xi^2} \cdot \overline{\xi^2} = 3\frac{p^2}{\rho^2}, \dots (144)$$

$$\overline{\xi^2\eta^2} = \overline{\xi^2} \cdot \overline{\eta^2} = \frac{p^2}{\rho^2}, \dots (145)$$

$$\overline{\xi^2\zeta^2} = \overline{\xi^2} \cdot \overline{\zeta^2} = \frac{p^2}{\rho^2}; \dots (146)$$

and the equation of conduction may be written

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

[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  $2(\beta-1) \frac{p}{\rho} \frac{dp}{dx}$ , 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  $\overline{\xi^2} \cdot \overline{\xi^2}$ , 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  $\beta$ .

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  $\bar{\xi}^2 = 3\bar{\xi}^2 \cdot \bar{\xi}^2$ , 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

$$C \frac{d\theta}{dx} = \frac{5}{6} \frac{\beta}{k_1 A_2} \frac{p^2}{g^{2\theta}} \frac{d\theta}{dx} \dots \dots \dots (148)$$

by equation (147).

Substituting for  $\beta$  its value in terms of  $\gamma$  by equation (115), and for  $k_1$  its value in terms of  $\mu$  by equation (125), and calling  $p_0$ ,  $g_0$ , and  $\theta_0$  the simultaneous pressure, density, and temperature of the standard gas, and  $s$  the specific gravity of the gas in question, we find

$$C = \frac{5}{3(\gamma-1)} \frac{p_0}{g_0 \theta_0} \frac{\mu}{s} \dots \dots \dots (149)$$

For air we have  $\gamma=1.409$ , and at the temperature of melting ice, or  $274^\circ.6$  C. above absolute zero,  $\sqrt{\frac{p}{g}}=918.6$  feet per second, and at  $16^\circ.6$  C.,  $\mu=0.0936$  in foot-grain-second measure. Hence for air at  $16^\circ.6$  C the conductivity for heat is

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

That is to say, a horizontal stratum of air one foot thick, of which the upper surface is kept at  $17^\circ$  C., and the lower at  $16^\circ$  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  $1^{\circ}$  C. different in temperature, would, when the mean temperature is  $25^{\circ}$  C., transmit in one minute through every square foot of surface as much heat as would raise one cubic foot of water  $0^{\circ}\cdot0127$  C.

Now the dynamical equivalent in foot-grain-second measure of the heat required to raise a cubic foot of water  $1^{\circ}$  C. is  $1\cdot9157 \times 10^{10}$ .

It appears from this that iron at  $25^{\circ}$  C. conducts heat 3525 times better than air at  $16^{\circ}\cdot6$  C.

M. CLAUSIUS, from a different form of the theory, and from a different value of  $\mu$ , 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  $\mu$ , 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  $\gamma$  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  $\gamma$  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.