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### LII. The viscosity of gases and molecular force

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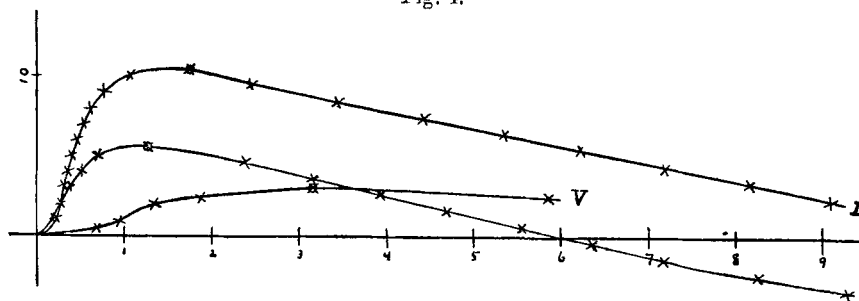
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likewise depends upon the ratio between the diameter and length.

5th. That there are two maxima: one produced by increasing the current, another by decreasing the current from that point which produced the first maximum.

6th. They confirm Prof. A. M. Mayer's observations, that the first contact gives more expansion than the second and following contacts, and, further, even these seem to disagree slightly among themselves, the expansion falling off with subsequent contacts.

Fig. 4.



In fig. 4 I have plotted the expansion-curves of three of the bars which show the greatest differences.

Mr. Bidwell's curves are similar in form to those produced by bars I. and II., while M. Alfonse Berget's curve, as would be expected, agrees more closely in form with that of bar V.

The experiments were carried on in the physical laboratory of Clark University, under the direction of Prof. A. G. Webster, to whom acknowledgment should be made for frequent suggestions.

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### LII. *The Viscosity of Gases and Molecular Force.*

By WILLIAM SUTHERLAND\*.

IT is now well known that a full acceptance of the kinetic theory of gases was suddenly accelerated by the experimental verification of Maxwell's theoretical discovery of the paradoxical independence of the coefficient of viscosity of a gas on pressure. Contrary to the general sentiment of physicists, the premisses of the kinetic theory were found to lead to the conclusion that a vibrating pendulum would be just as much hindered by gaseous friction in an environment under one twentieth of an atmo pressure as under twenty atmo, and experiment soon afterwards showed the coefficient of viscosity

\* Communicated by the Author.

of gases to be actually constant down to pressures as low as one thousandth of an atmo. Naturally this confirmation gave a great stimulus to the development of the kinetic theory; and as the same equation which asserted that the viscosity of a gas is independent of its pressure also asserted it to be proportional to the square root of the absolute temperature, the experimental examination of the relation between viscosity and temperature was taken up with enthusiasm. When the first experimental difficulties had been overcome, it was proved quite clearly that with the natural gases the variation of viscosity with temperature is more rapid than was asserted by theory; instead of the relation  $\eta \propto T^{\frac{1}{2}}$  it was found that  $\eta \propto T^n$ , where  $n$  ranges from its lowest value of about .7 for hydrogen to about 1.0 for the less perfect gases.

Maxwell, by some inaccurate experiments, was led to believe that for the perfect natural gases  $\eta \propto T$ , and recast the kinetic theory in a special form to bring it into harmony with this supposed fact of nature. In the original form of the kinetic theory the molecules are supposed to collide with one another as small actual spherical bodies do, only with a coefficient of restitution unity, to which actual bodies approximate but never attain. Maxwell now supposed the molecules to behave as centres of repulsive force, and deduced that if  $\eta \propto T$  the centres of force must repel one another with a force inversely as the fifth power of the distance between them. But as more accurate experiments proved that  $\eta$  does not vary as  $T$ , the hypothesis of repulsion inversely as the fifth power had to be abandoned. It is to be remembered that Maxwell probably worked out the details of this hypothesis more for the sake of illustrating the mathematical methods to be applied to centres of force than for the actual results obtained.

The only other hypothesis which has hitherto been advanced to account for the discrepancy between theory and experiment is that of O. E. Meyer, who pointed out that if the molecules, instead of being regarded as of constant size, were supposed to shrink with increase of temperature, then the experimental results would be explained. But the great objection to this explanation was that it made the size of the molecules vary far too much with temperature: for instance, if  $\sigma$  is the sectional area of the sphere by which the hydrogen molecule may be supposed to be replaced,  $\eta \propto T^{\frac{1}{2}}/\sigma$ , that is  $T^{\frac{7}{2}} \propto T^{\frac{5}{2}}/\sigma$ , or the sectional area varies inversely as the fifth root of the absolute temperature. No independent confirmation of such great variability of molecular size has been given, and has been tacitly regarded as hardly possible.

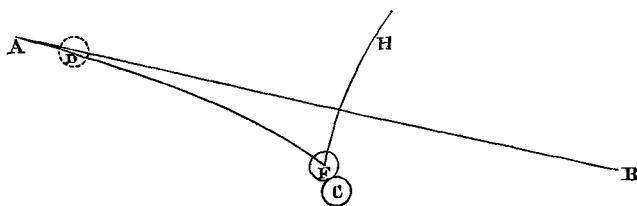
The object of the present paper is to show that the whole of the discrepancy between theory and experiment disappears if in the theory account is taken of molecular force. According to the usual presentation of the kinetic theory, the molecules are supposed to be spheres colliding with coefficient of restitution unity, molecular force is neglected because at the average distance apart of the molecules in a gas it is very small. Now molecular attraction has been proved to exist, and, though negligible at the average distance apart of molecules in a gas, it is not negligible when two molecules are passing quite close to one another, it can cause two molecules to collide which in its absence might have passed one another without collision; and the lower the velocities of the molecules, the more effective does molecular force become in bringing about collisions which would be avoided in its absence: thus molecular force cannot be neglected in investigating the relation between viscosity and molecular velocity or temperature.

Molecular force alone without collisions will not carry us far in the explanation of viscosity of gases as known to us in nature, because in all experiments on the viscosity of gases there is a solid body which either communicates to the gas motion parallel to its surface or destroys such motion, so that the molecules of the gas must collide with the molecules of the solid; for if the molecules of gas and solid act on one another only as centres of force, then each molecule of gas when it comes out of the range of the molecular force of the solid must have the same kinetic energy as when it went in, so that without collision between molecules of gas and solid there can be no communication of motion to the gas. If, then, molecules of gas and solid collide, molecules of gas must collide amongst themselves.

Of course, if this difficulty about communicating motion to a number of centres of force is ignored, then, as Maxwell does, we can proceed to trace viscosity in the gas as due to the fact that when two centres pass close to one another they deflect each other's path through an angle depending on the relative velocity and nearness of approach: thus the centres which leave the surface of a moving solid with their thermal velocities of agitation compounded with the velocity  $v$  of the solid, have the resultant velocities deflected in so haphazard a manner that at a certain distance from the solid they are uniformly distributed in all directions, and thus the energy of the velocity  $v$  is converted into heat, and there is viscous action between the successive layers of gas. And this holds whether the force be attractive or repulsive; hence we see

that in the case of molecules which do collide amongst themselves a portion of the viscosity will be due to molecular attraction on account of mutual deflection of paths experienced by those pairs of molecules which pass close to one another without actual collision.

It is thus apparent that a full mathematical theory of the viscosity of a medium composed of colliding molecules which attract one another would be a complicated affair, but to anyone familiar with the available knowledge of the size of molecules and the strength of molecular attraction, the following considerations lend themselves to simplify the problem of the viscosity of actual gases:—First, that where the average relative velocity is so low and the molecular force is so strong that it happens in a large number of cases that a pair of molecules describe closed paths relative to their centre of mass, then there must be a still larger number of cases of pairs of molecules which deflect each other's path through a large angle. In other words, deflection of paths, on account of molecular attraction and irrespective of collisions, may become an appreciable factor in viscosity in the case of vapours below their critical temperatures. Second, that where a closed path is of rare occurrence, that is, in the case of gases above the critical temperature and at no great pressure, the effect of deflection due to molecular attraction is negligible in comparison with that due to collision as a factor in the production of viscosity, except in so far as molecular attraction causes collisions to occur which would not happen in its absence. This effect of molecular force is illustrated by the figure, where AB represents the relative



path of the two spheres C and D when no molecular force is supposed to act between them, C being considered to be at rest: according to the figure no collision can occur in the absence of molecular attraction; but if molecular attraction acts a collision can occur as in the position CF, and the relative path is changed into the two curved branches AF and FH, AB being the asymptote to the branch AF, if in respect to molecular force A is practically at an infinite distance from C. It is evident that this effect of molecular

force in increasing the number of collisions is fundamental; and we will proceed to determine the number of collisions that occur amongst the molecules of a gas when molecular force is in operation, in comparison with the number when there is no molecular force. Let  $b$  be the perpendicular distance from the centre of molecule C to AB the asymptote to the relative path of the molecule D, both molecules being supposed to be spheres of radius  $a$ ; let  $V$  be the relative velocity of D when it is so far from C as to be moving almost along the asymptote, then with the usual notation for orbits under central forces  $h = bV$ , where  $h$  is twice the area described in unit time by the vector CD denoted by  $r$ , and  $1/r$  being denoted by  $u$ .

Let  $m^2F(u)$  be the molecular attraction, and  $m^2f(u)$  be the mutual potential energy of two molecules of mass  $m$  at distance  $r$  apart, then the usual differential equation of the orbit is

$$\frac{d^2u}{d\theta^2} + u - \frac{mF(u)}{h^2u^2} = 0,$$

with its first integral the equation of energy,

$$\frac{1}{2}h^2 \left\{ \left( \frac{du}{d\theta} \right)^2 + u^2 \right\} = \frac{1}{2}v^2 = mf(u) + \frac{1}{2}V^2,$$

$v$  being the velocity at any reciprocal-distance  $u$ .

Now when this orbit is such that there is no collision, we can determine the nearest distance to which the molecules approach one another (an apsidal distance) by the condition  $du/d\theta = 0$ ; denote the reciprocal of this distance by  $w$ , it is then given by

$$\frac{1}{2}h^2w^2 = mf(w) + \frac{1}{2}V^2,$$

or

$$mf(w) - \frac{1}{2}b^2V^2w^2 + \frac{1}{2}V^2 = 0.$$

Now there will be a collision if  $1/w$  is less than  $2a$ , that is, if  $w$  is greater than  $1/2a$ ; hence the greatest value of  $b$  for which a collision is possible is given by

$$\left. \begin{aligned} mf(1/2a) - \frac{1}{2}b^2V^2/(2a)^2 + \frac{1}{2}V^2 &= 0 \\ \text{or } b^2 &= (2a)^2 \left( 1 + \frac{2mf(1/2a)}{V^2} \right) \end{aligned} \right\}, \quad \dots \quad (1)$$

and there is a collision for every value of  $b$  from 0 up to that given by the last equation. Testing this assertion by applying it to the case when there is no molecular force, we put  $mf(1/2a) = 0$ , and find that there is a collision for all values of  $b$  from 0 up to  $2a$ , which is correct. Hence, molecular force

causes the spheres to behave as regards collisions as if they were larger spheres devoid of force, the diameter-squared  $(2a)^2$  being enlarged in the proportion  $1 + 2mf(1/2a)/V^2 : 1$ .

Hence, in the theory of viscosity as worked out for forceless molecules, we need only increase the square of the molecular sphere-diameter in this proportion to take account of molecular force. As the expression diminishes with increasing  $V^2$ , that is with increasing temperature, we see at once why the apparent result of increasing temperature was to make the molecules shrink: increase of temperature does not make the real molecules shrink (at least to the extent imagined), but produces shrinkage of the imaginary enlarged forceless spheres which could exhibit the same viscosity as the real molecules.

So far we have considered only a typical case of two molecules: to obtain the effect of molecular force in the average case we should have to calculate, in accordance with Maxwell's law of the distribution of velocities amongst the molecules, the number of pairs that have relative velocities between  $V$  and  $V + dV$  and sum for all values of  $V$ . This process can easily be carried out when necessary, but it will be quite accurate enough for our purpose to assume that the pair of molecules we have studied is an average pair, that is, a pair which has the square of the relative velocity equal to the average value of the square of the relative velocities for all the molecules; this is proportional to the mean squared velocity, and according to Maxwell's law of velocities is equal to twice it, in the usual notation  $\bar{V}^2 = 2\bar{v}^2$ .

Now if there are  $n$  spheres of radius  $a$  moving about in unit volume with Maxwell's distribution of velocities of which the average is  $\bar{v}$ , then the average number of collisions per second per sphere is  $2^{\frac{1}{2}}n\pi a^2\bar{v}$  when the spheres are forceless; when the spheres attract one another it becomes

$$2^{\frac{1}{2}}n\pi a^2\bar{v}\left(1 + \frac{2mf(1/2a)}{V^2}\right).$$

This number is fundamental in the kinetic theory of matter, though more spoken of under another form, namely the mean free path of a sphere; accordingly we can state the highly convenient result that all the investigations of the founders and developers of the kinetic theory on the properties of gases which depend on the mean free path or mean number of collisions of forceless molecules can be applied to attracting molecules by simply replacing  $a^2$  by  $a^2 \left(1 + 2mf(1/2a)/V^2\right)$ . The chief properties depending on number of collisions are

viscosity, thermal conduction, diffusion, and characteristic equation.

The coefficient of viscosity for forceless spheres with the Maxwell distribution of velocities is given by Tait (Trans. Roy. Soc. Edin. vols. xxxiii. and xxxv.) as

$$\eta = \cdot 882 \times \cdot 838 \frac{m}{3\pi(2a)^2} \left( \frac{2\bar{v}^2}{3} \right)^{\frac{1}{2}} = \cdot 064 \frac{m(\bar{v}^2)^{\frac{1}{2}}}{(2a)^2} :$$

hence when we take account of molecular force, the coefficient of viscosity is

$$\eta = \frac{\cdot 064 m (\bar{v}^2)^{\frac{1}{2}}}{(2a)^2 \left( 1 + \frac{2mf(1/2a)}{V^2} \right)} ;$$

but  $m\bar{v}^2$  is proportional to absolute temperature ; let  $m\bar{v}^2 = cT$ , and therefore  $mV^2 = 2cT$ , then

$$\eta = \frac{\cdot 064 c^{\frac{1}{2}} m^{\frac{1}{2}} T^{\frac{1}{2}}}{(2a)^2 \left( 1 + \frac{m^2 f(1/2a)}{cT} \right)} . . . . . (2)$$

Now for a given substance  $\cdot 064 c^{\frac{1}{2}} m^{\frac{1}{2}}$ ,  $2a$ , and  $m^2 f(1/2a)/c$  remain constant ; denote  $m^2 f(1/2a)/c$  by  $C$  ; and then

$$\eta \propto \frac{T^{\frac{1}{2}}}{1 + \frac{C}{T}} . . . . . (3)$$

is the law of variation of viscosity with temperature in the case of gases at temperatures not below the critical, and at pressures for which the departure from Boyle's law is not great.

There is some fine experimental material for testing the above theoretical law, for Holman (Phil. Mag. 5th ser. vol. xxi.), in the light of results already obtained by O. E. Meyer, Puluj, Obermayer, and E. Wiedemann, made special measurements of great exactness of the variation of the viscosity of air and carbonic dioxide at temperatures from 0° C. to 124° and from 0° to 225°. Barus for air and hydrogen pushed the temperature range up to 1400° C. (Amer. Journ. Sc. 3rd ser. vol. cxxxv.).

If  $\eta_0$  is the value of  $\eta$  at 0° C., then, from our equation (3),

$$\frac{\eta}{\eta_0} = \left( \frac{T}{273} \right)^{\frac{1}{2}} \frac{1 + C/273}{1 + C/T} ; . . . . . (4)$$



so that from each of Holman's values of  $\eta/\eta_0$  we can calculate a value of C, which is now given.

Temp. C. ....	14°	43°	67·8°	88·8°	99·2°	124·4°
$\eta/\eta_0$ .....	1·0377	1·1180	1·1850	1·2411	1·2698	1·3306
C .....	88	104	111	114	118	116

There appears to be a tendency for the values of C to increase with the temperature-interval; but it is of no importance, because the smaller temperature-intervals are too small to give a reliable measure of C. Giving each of the values of C a weight in proportion to the temperature-interval from which it is derived, we get the mean value of C as 113. With this value of C in the theoretical equation, the following values of  $\eta/\eta_0$  have been calculated for comparison with Holman's experimental results :—

Temp. C. ....	14°	43°	67·8°	88·8°	99·2°	124·4°
Exper. ....	1·038	1·118	1·185	1·241	1·270	1·331
Calcul. ....	1·040	1·120	1·186	1·241	1·267	1·329

The agreement is within the limits of experimental error.

Barus's results for air are now given with the values of C derived from them :—

Temp. C....	442°	565°	569°	592°	982°	995°	1210°	1216°
$\eta/\eta_0$ .....	1·991	2·083	2·149	2·117	2·711	2·693	3·214	3·147
C.....	118	84	101	83	99	93	118	107

The range in the values of C is about the same as in Holman's experiments, but the mean value is less, namely 100, but in this mean the values at certain temperatures get undue weight; and seeing that the measurement of temperature is the most difficult part of the experiment, it would be fairer to take for instance the mean of 84 and 101 at 565° and 569° as 92 at 567°, and in this way to get the values 118, 92, 83, 96, 118, and 107, of which the mean is 102. But to compare theory with experiment we will retain the value 113 already found from Holman's results.

Temp. C....	442°	565°	569°	592°	982°	995°	1210°	1216°
Exper. ...	1·991	2·083	2·149	2·117	2·711	2·693	3·214	3·147
Calcul. ....	1·976	2·183	2·190	2·225	2·781	2·799	3·179	3·185

It is evident, from a comparison of the experimental numbers among themselves, that the agreement between theory and experiment is within the limit of experimental error in these difficult experiments, and the theoretical law is

proved to hold over the great range of temperature up to 1216° C. Barus found that his results for air could be well represented by the empirical form  $\eta/\eta_0 = (T/273)^{\frac{1}{2}}$ , and, further, that the results for hydrogen could be equally well represented by the same form: hence for hydrogen the value of C in our theoretical equation would from his experiments have the same value as for air, namely 113; and the theoretical law applies to hydrogen as well as to air up to high temperatures.

Holman's experiments on carbonic dioxide furnish a still better test of the theory. Here are his values of  $\eta/\eta_0$  at the given temperatures with the values of C calculated therefrom:—

Temp. C. ....	18°	41°	59°	79.5°	100.2°	119.4°
$\eta/\eta_0$ exper. ....	1.068	1.146	1.213	1.285	1.351	1.415
C. ....	315	265	286	292	277	274
$\eta/\eta_0$ calcul. ....	1.066	1.148	1.211	1.280	1.351	1.414
Temp. C. ....	142°	158°	181°	224°		
$\eta/\eta_0$ exper. ....	1.484	1.537	1.619	1.747		
C. ....	266	270	284	279		
$\eta/\eta_0$ calcul. ....	1.490	1.541	1.614	1.746		

Giving each value of C a weight proportional to the temperature-interval from which it is found, we get the mean value  $C=277$ , with which the calculated values of  $\eta/\eta_0$  in the last table were obtained. The agreement between the experimental and calculated numbers is again within the limits of experimental error.

The law of the connexion of viscosity and temperature being thus established, we can now examine some important consequences of the theoretical formula (2),

$$\eta = \frac{.064c^{\frac{1}{2}}m^{\frac{1}{2}}T^{\frac{1}{2}}}{(2a)^2 \left(1 + \frac{m^2 f(1/2a)}{cT}\right)}.$$

The value of C, that is of  $m^2 f(1/2a)/c$ , is proportional to the potential energy  $m^2 f(1/2a)$  of two molecules in contact, and it is therefore desirable to obtain values of C for as many substances as possible; and as C is a function of  $2a$  it will be advantageous to use the values of C to calculate relative values of  $2a$  for different substances by means of the above formula, so that we may be in possession of relative values of the diameters of molecules and of the mutual potential energy of two molecules whose centres are at the distance apart of a diameter. The equation of the kinetic theory of forceless molecules,  $\eta \propto m^{\frac{1}{2}} T^{\frac{1}{2}} / (2a)^2$ , was applied by

Naumann and L. Meyer (*Lieb. Ann. Suppl. Bd. v. p. 253*, and *Phil. Mag.* 1867, xxxiv. p. 551) to the calculation of the relative sizes of molecules, and with considerable success; but when the same method was applied to vapours of liquids, certain discrepancies arose which have caused this method of inquiry as to molecular size to come to a standstill. We can now see that the reason for these discrepancies lies in the fact that the form of relation for the viscosity of vapours is different from that for gases, and also in the fact that with gases also inaccuracies are introduced by ignoring molecular force in the factor  $1 + C/T$  by which it expresses itself.

The published data from which values of  $C$  for other substances can be obtained are those of Obermayer (*Sitz. Akad. Wien*, lxxiii.) on the variation of viscosity with temperature; the following values are calculated from his results.

Values of  $C$ .

$N_2$ .	$O_2$ .	$CO$ .	$C_2H_4$ .	$N_2O$ .
84	127	100	272	260

The mean value of  $C$  for hydrogen from Obermayer's experiments with different capillary tubes comes out 79, ranging from 88 to 69, which is much smaller than the value given by Barus's experiments, namely 113, the same value as for air; but it is to be remembered that the viscosity of hydrogen is a difficult physical constant to measure on account of the large effect of impurities, and moreover in Barus's experiments at very high temperatures the hydrogen began to pass through the walls of the platinum capillary tube, and it is possible that a slight similar action at lower temperatures might interfere with the apparent variation of viscosity with temperature. As Barus's experiments were carried out with a different object from that of getting the best value of a constant for pure hydrogen, it is probable that Obermayer's value, though derived from a temperature-interval of only  $40^\circ$ , is more nearly the value for pure hydrogen. For nitrogen the value 84, obtained from Obermayer's experiments, is too different from the value 113 for air to be quite satisfactory; so that I think it is better to derive the value for nitrogen from those for air and oxygen, thus  $C_{4/5} + 127/5 = 113$ , whence  $C = 109$ .

In the case of  $C_2H_4$  and  $N_2O$ , the values of the viscosity found by Obermayer at  $-21^\circ$  have been excluded in the calculation of  $C$  as coming from a region too near the vaporous.

To get relative values of  $(2a)^2$  for the substances for which we know  $C$  and  $\eta_0$ , we may write our relation (2) thus

$$(2a)^2 = \frac{0.64 (273 \text{ cm})^{\frac{1}{2}}}{\eta_0 (1 + C/273)} = \frac{km^{\frac{1}{2}}}{\eta_0 (1 + C/273)},$$

where  $k$  is the same for all bodies. As we do not know the actual masses  $m$ , but only the molecular mass  $M$  compared to that of the hydrogen atom, we will take

$$M^{\frac{1}{2}} / \{10^2 \eta_0 (1 + C/273)\}$$

as giving relative values of the square of molecular diameters. Subjoined are the data and the results calculated from them; the values of  $\eta_0$  are those given by Obermayer, and the numbers given as  $(2a)^2$  (relative) are the values of

$$M^{\frac{1}{2}} / \{10^2 \eta_0 (1 + C/273)\}.$$

	H <sub>2</sub> .	N <sub>2</sub> .	O <sub>2</sub> .	CO.	CO <sub>2</sub> .	N <sub>2</sub> O.	C <sub>2</sub> H <sub>4</sub> .
$10^6 \eta_0$ .....	86	166	187	162	138	135	92
$M$ .....	2	28	32	28	44	44	28
$C$ .....	79	109	127	100	277	260	272
$(2a)^2$ (relative) .....	127	228	206	239	239	261	288
$(2a)^3$ (relative) .....	1440	3440	2963	3698	3686	4230	4884

Now in the characteristic equations given in my paper on the "Laws of Molecular Force" (Phil. Mag. March 1893), there is a limiting volume in the liquid state denoted by  $\beta$  and values of  $\beta$  are given for a gramme of each of the above substances except CO, so that multiplying them by the molecular masses (weights) we get numbers giving other relative values of the volumes of the molecules which should stand in a constant ratio to those already tabulated as  $(2a)^3$  (relative). The following are the values of  $M\beta$  and the ratio of  $(2a)^3$  (relative) to  $M\beta$  :—

	H <sub>2</sub> .	N <sub>2</sub> .	O <sub>2</sub> .	CO <sub>2</sub> .	N <sub>2</sub> O.	C <sub>2</sub> H <sub>4</sub> .
$M\beta$ .....	8.6	22.7	19.3	30.3	29.0	42.8
$(2a)^3$ (relative) / $M\beta$	167	153	153	121	137	114

The value of the ratio is larger for the elements than for the compounds; but considering that  $M\beta$  ranges from 8.6 to 42.8, the ratio approaches near enough to constancy to show that the theory is right in its essentials, while it is possible that departure of shape of molecules from the assumed spherical form will have to be taken account of

before perfect constancy can be attained in the ratio just considered.

But fortunately we can test our theory in a more complete manner in another direction, namely, in that of the values of  $C$  which are proportional to the potential energy of two molecules in contact. Now, if the law of molecular force is that discussed by me in various papers, namely, that of the inverse fourth power, or, if the force between two molecules of mass  $m$  at distance  $r$  apart is  $3Am^2/r^4$ , where  $A$  is a constant characteristic of each substance, then  $m^2f(1/r)$  becomes  $Am^2/r^3$ , and  $C$  or  $m^2f(1/2a)/c$  becomes  $Am^2/(2a)^3c$ , so that  $(2a)^3 C$  is proportional to  $Am^2$ .

In the characteristic equations alluded to (Phil. Mag. March 1893) there is a term representing the virial of the attractions of the molecules, which by definition is  $\frac{1}{2} \cdot \frac{1}{2} \sum \sum 3Am^2/r^3$ , where the summations are extended to all the molecules in unit mass, and this is shown to be proportional to  $3A\pi\rho$  where  $\rho$  is the density; when this is written in the form  $l\rho$ ,  $l$  is called the virial constant and is proportional to  $3A$ , and as values of  $M^2l$  have been tabulated for a large number of substances ("Laws of Molecular Force," Phil. Mag. March 1893), we can use them for relative values of  $Am^2$ . If, then, the law of molecular force is that of the inverse fourth power, the ratio of the values of  $(2a)^3 C$ , from this paper, to the values of  $M^2l$ , from that paper, must be constant. As  $M\beta$  has been seen to be approximately proportional to  $(2a)^3$ , and there are means of getting its value for substances for which  $(2a)^3$  cannot at present be found, we will use  $M\beta$  in place of  $(2a)^3$ , and study the relation of  $M\beta C$  to  $M^2l$ . The following table contains the values of  $M\beta C$ ,  $M^2l$ , and the ratio  $M\beta C/M^2l$ :—

	H <sub>2</sub> .	N <sub>2</sub> .	O <sub>2</sub> .	CO <sub>2</sub> .	N <sub>2</sub> O.	C <sub>2</sub> H <sub>4</sub> .
$M\beta C/10$ .....	67·9	247	245	839	755	1167
$M^2l$ .....	·22	1·23	1·16	7·1	8·8	6·5
$M\beta C/10^2 M^2l$ ...	31	20	21	12	8·6	18

The values of the ratio as they stand do not look promising, but in the paper on the "Laws of Molecular Force" it is shown that while in the elements  $l$  retains its value from the gaseous to the liquid state, in most compounds it attains in the liquid a value one half of the limiting value in the gas, and CO<sub>2</sub> and N<sub>2</sub>O conform to this, while in the case of ethylene, which is peculiar,  $l$  falls in the liquid to 4·15/5·79 of its value in the gas, that is to 0·7166  $l$ . If, then, we use the values of  $M^2l$  which hold in the above substances as liquids,

we get the following values of the above ratios:—

31                      20                      21                      24                      17                      25

Excepting in the case of hydrogen, where through experimental difficulties the value of  $C$  is uncertain, the values of the ratio now show a satisfactory approach to constancy if all the difficulties of the comparison are allowed for, and they furnish satisfactory confirmation of the truth of the inverse fourth power law of force. In view of the importance of this confirmation, it will be well to extend it to as many substances as possible, and although we have exhausted the direct experimental determinations of  $C$ , there is an indirect method of obtaining some more by means of the results already established.

For  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{C}_2\text{H}_4$ ,  $(2a)^3(\text{relative})/M\beta$  has the values 121, 137, and 114, of which the mean is 124; and assuming this to be the value for all compounds, we can obtain from the values of  $\beta$  and  $M$  the values of  $(2a)^3(\text{relative})$ , then those of  $(2a)^2(\text{relative})$  which stands for

$$M^{\frac{1}{2}}/\{10^3\eta_0(1+C/273)\},$$

so that with values of  $\eta_0$  it is possible to calculate those of  $C$ . The following are the data for the gases  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{SO}_2$ , the values of  $\eta_0$  being those given by Obermayer from Graham's transpiration experiments.

	$\text{CH}_4$ .	$\text{NH}_3$ .	$\text{SO}_2$ .
$\beta$ .....	1.59	1.22	.55
$M$ .....	16	17	64
$M\beta$ .....	25.4	20.7	35.2
$(2a)^2(\text{relative})$ .....	215	188	267
$10^3\eta_0$ ..	104	96	122
$C$ .....	215	352	397

As before, we can compare  $M\beta C$  and  $M^2l$ :

	$\text{CH}_4$ .	$\text{NH}_3$ .	$\text{SO}_2$ .
$M\beta C/10$ .....	547	729	1399
$M^2l$ .....	2.2	8.5	15
$M\beta C/10^3M^2l$ .....	25	8.6	9.3

As before, we must double the value of the ratio for the compounds  $\text{NH}_3$  and  $\text{SO}_2$ , but not for  $\text{CH}_4$ , because I have shown its characteristic equation to be of the same form as

that for the elements which have an unchanging virial constant; thus we get the numbers

25

17

19

in agreement with the previous series of ratios. The fact that here  $\text{CH}_4$  behaves as an element gas is noteworthy.

Exact values of  $\beta$  are at present lacking for other gases, but sufficiently exact ones for the present comparison can be got by reducing the volume of a gramme of the gas when liquefied at its boiling-point under one atmo in the ratio  $\cdot 64$ , and thus we get:—

	$\text{Cl}_2$	$\text{HCl}$	$\text{H}_2\text{S}$	$\text{C}_2\text{N}_2$
$\beta$ .....	$\cdot 48$	$\cdot 75$	$\cdot 70$	$\cdot 73$
$M$ .....	70.8	36.4	34.0	52.0
$M\beta$ .....	33.6	27.1	23.9	38.2
$(2a)^2(\text{relative})$ .....	259	224	206	282
$10^6\eta_0$ .....	129	138	115	95
$C$ .....	410	256	395	461

With these values we get:—

	$\text{Cl}_2$	$\text{HCl}$	$\text{H}_2\text{S}$	$\text{C}_2\text{N}_2$
$M\beta C/10$ .....	1377	695	944	1762
$M^2l$ .....	5.8	7.9	10.5	17.7
$M\beta C/10^2 M^2l$ .....	24.0	8.8	9.0	10.0

Here, again, the ratio for the element chlorine is about what it ought to be, while for the compounds it is about half of what it is for elements; doubling its value for compounds we get the values 24, 17, 20, which again harmonize with the previous values, the complete series being

31 20 21 24 17 25 25 17 19 24 17 18 20: Mean 21.

Thus of the available data there is not one at variance with the theory, while the distinction between the elements with methane on the one hand and compounds on the other, which was drawn in the study of characteristic equations, is borne out here. In the paper on the "Laws of Molecular Force" it was suggested that the difference in characteristic equations between compounds and elements is due to molecular pairing in compounds, all the molecules being in pairs in the liquid state, but in the gaseous state only a certain portion of them depending on the volume occupied. Now in considering viscosity we seem to have taken no account of such a phenomenon as that of pairing, but we have found that the

mutual potential energy of two compound molecules in contact in the gaseous state is affected in the same way as the virial (or potential energy) of all the molecules when brought close to one another in the liquid state. With our present knowledge the simplest explanation of this fact is got by supposing that in a compound gas each collision of two molecules is of the nature of a brief pairing with formation of a temporary bimolecule, rearrangement of atomic energy, and alteration of constant of mutual energy, all in a reversible manner when the molecules can get out of one another's influence, as in a gas, but not reversible in the limited free range of a molecule in a liquid. Thus, as in the theory of viscosity we have been dealing only with the mutual potential energy of two molecules in contact, the possibility of pairing in this manner has not been excluded. In connexion with a more complete testing of the theory of this paper, it may be pointed out that approximate values of  $C$  have been given on theoretical grounds for  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , and  $\text{C}_2\text{N}_2$ , the experimental determination of which would supply a further check on the sufficiency of the theory.

Although it is not proposed to deal fully in this paper with the viscosity of vapours, still, as the cause of a difference in the cases of gases and vapours has been pointed out, it may be as well to indicate what is the degree of importance of that cause, namely the deflexion of molecular paths produced by molecular attraction without the occurrence of actual collisions. The best way to do this will be to calculate the part of the viscosity of vapours due to collisions, and compare it with the total viscosity found by experiment. Determinations of viscosity have been made for the following substances:—Ethyl chloride by Obermayer, with the capillary-tube method (*Sitzb. Akad. Wien*, lxxiii.); ethyl oxide, ethyl alcohol, steam, benzene, acetone, chloroform, and carbon disulphide, by Puluj, with the vibration method (*ibid.* lxxviii.); and a number of esters by O. Schumann by the vibration method (*Wied. Ann.* xxiii.). A still greater number of esters had been previously examined by L. Meyer and O. Schumann with the capillary-tube method (*Wied. Ann.* xiii.), with results which brought out the viscosities much larger than they were afterwards found by Schumann with the vibration method; and as the reason for the discrepancy has not been demonstrated (though we can see on theoretical grounds that it is probably due to the use of pressures too near that of saturation), we will not use these doubtful data.

The viscosity of any substance as a gas at any temperature



is given by the formulæ

$$(2a)^2(\text{relative}) = \frac{M^{\frac{1}{2}}}{10^2 \eta_0 (1 + C/273)},$$

$$\eta/\eta_0 = (T/273)^{\frac{1}{2}} \frac{1 + \frac{C}{273}}{1 + \frac{C}{T}},$$

and we have seen that for compounds

$$(2a)^3(\text{relative}) = 124 M\beta \quad \text{and} \quad M\beta C 10^{-2} = 21 M^2 l/2;$$

so that with values of  $\beta$  and  $M^2 l$  we can calculate the viscosities of substances as gases. Values of  $M^2 l$  are tabulated (Phil. Mag. March 1893), and the method of calculating them from chemical composition is also given, and values of  $\beta$ , the limiting volume of a gramme of the above substances, are calculable from existing data by means of the characteristic equation for liquids given in the same paper, or by a much simplified unpublished equation which gives the same values to the degree of accuracy required for the present purpose. Here are the values of  $M$ ,  $M\beta$ , and  $M^2 l$  for the above substances:—

	$C_2H_5Cl.$	$(C_2H_5)_2O.$	$C_2H_5OH.$	$H_2O.$	$C_6H_6.$	$(CH_3)_2CO.$
$M$ .....	64.4	74	46	18	78	58
$M\beta$ .....	55.5	82.1	46 (near)	16 (near)	75.5	56 (near)
$M^2 l$ .....	27.4	40.2	17.6	6.8	43.8	31.1

	$CHCl_3.$	$CS_2.$	Methyl formate.	Propyl acetate.	Methyl isobutyrate.	Ethyl propionate.
$M$ .....	119.2	76	60	102	102	102
$M\beta$ .....	72	50	46	97	97	97
$M^2 l$ .....	36.9	26.9	22.9	58.5	58.5	58.5

With these the following values of the viscosity at  $0^\circ C.$ , due to collisions only, have been calculated, and will be denoted by  $H_0$  to distinguish them from  $\eta_0$ , the total viscosity of the vapour.

	$C_2H_5Cl.$	$(C_2H_5)_2O.$	$C_2H_5OH.$	$H_2O.$	$C_6H_6.$	$(CH_3)_2CO.$
$H_0...$	76.6	63.5	92	102	61.7	65.6
	$CHCl_3.$	$CS_2.$	Methyl formate.	Propyl acetate.	Methyl isobutyrate.	Ethyl propionate.
$H_0 \dots$	85.5	84.3	83.4	58.1	58.1	58.1

With these values the part of the viscosity due to collisions

only (to be denoted by  $H$ ) at any temperature can be calculated by the formula (4) above, where the symbol  $H$  is represented by  $\eta$ .

In the following table  $t$  denotes temperature C. and  $\eta$  is the viscosity of the vapour found by experiment at that temperature, while  $H$  is the part of the viscosity calculated as due to collisions, and then the difference between the two expressed as percentage of the calculated numbers is denoted by  $\text{diff. } \%$ .

$(C_2H_5)_2O$ .							
$t$ .....	7.2	10	15.5	18.9	25.8	31.4	36.5
$\eta$ .....	71.2	71.6	73.2	73.5	75.5	77.1	79.3
H .....	65.5	66.2	67.7	68.6	70.3	71.9	73.3
Diff. %/o.	9	8	8	7	7	7	8
$C_2H_5Cl$ .							
$t$ .....	16.4	53.5	157	$C_6H_6$ , 17	$(CH_3)_2CO$ , 17	$CHCl_3$ , 17	
$\eta$ .....	94.1	105.8	144.0	76	78	103	
H .....	81.7	93.8	126.7	66.2	71	92	
Diff. %/o.....	15	13	14	15	10	12	
Methyl formate.							
$t$ .....	$CS_2$ 17	$H_2O$ 17	$C_2H_5OH$ , 17	20	100		
$\eta$ .....	99	97	88.5	92.3	135.2		
H .....	90	109	98.2	90.8	119.0		
Diff. %/o.....	10	-11	-10	2	13		
Propyl acetate.			Methyl isobutyrate.				
$t$ .....	15	77.8	100	24	65.5	100	
$\eta$ .....	74.3	95.4	109.6	75.4	99.9	112.2	
H .....	62.0	77.8	83.6	64.3	74.5	83.6	
Diff. %/o.....	20	23	31	17	34	34	

The comparison, except in the case of water and alcohol, establishes the theoretical provision that the viscosity of a vapour is greater than that due to the collisions of its molecules, and water and alcohol have been proved to be exceptional as regards molecular force, both as vapours and liquids, so that we have no right to expect them to be otherwise than exceptional here; indeed, we see here another opening towards the elucidation of the exceptional nature of these substances.

Excepting the esters, we can say that at ordinary temperatures the part of viscosity due to deflexion of paths by molecular attraction without collision is between 8 and 16 per

cent. of that due to collisions; with rising temperature and diminishing pressure, that is with nearer approach to the gaseous state, this difference ought to diminish towards 0 as a limit; in the case of the esters the reverse of this appears to hold, but the experiments are perhaps at fault. For the complete elucidation of this part of the subject further experiments are required, in which the various values of the viscosity of a substance are followed from the one limit when it is a gas to other limits when it is a saturated vapour. The theoretical investigation of this part of the subject would not be difficult, though it might be tedious, and not very interesting unless hand in hand with experiment.

The other main properties of a gas besides viscosity which depend on the molecular free path or number of collisions are the coefficient of diffusion into other gases, the thermal conductivity and the characteristic equation, in all of which molecular attraction plays as fundamental a part as in viscosity, and in the theory of which molecular attraction can be taken account of on the same simple principle as has been applied to viscosity, namely, imagine the molecular spheres to have their sections increased in the proportion  $(1 + C/T):1$ , and then proceed with the theory of them as if they were forceless.

The difficulties that confront us in diffusion and conductivity arise entirely from the fact that the theory of these phenomena, even for forceless molecules, is incomplete; in the case of diffusion chiefly on account of mathematical difficulties, and in that of conductivity because it is not known what provision there is for the transmission of other forms of molecular kinetic energy besides that of translatory motion. However, this much may be said in general terms, that experiment has shown that if theory and experiment were brought into harmony for viscosity they would be in as good harmony for diffusion and conductivity as could be expected in the confessedly incomplete state of theory. In the case of diffusion the question is still further complicated by the fact that we have to deal with the attractions of unlike molecules, a subject which will yet become of great importance, but too large to open in this paper, so it must suffice to repeat that, assuming the attractions of unlike molecules to be of about the same strength as those of like, then the experiments of Loschmidt and Obermayer show that when the temperature-variation of viscosity is correctly explained by theory the temperature-variation of diffusion must also be correctly accounted for. A complete theoretical discussion of diffusion would come in more naturally in connexion with a general

investigation of the properties of mixed gases (viscosity, conductivity, and characteristic equation), where the attraction of unlike molecules would be an essential element in the question. The experimental investigation of the properties of mixed gases could also be extended with advantage.

With regard to conduction, the kinetic theory of forceless, smooth, spherical molecules leads to the result that in a first approximation the thermal conductivity  $k = \cdot 826 \eta m \bar{v}_0^2 / m T_0$ , where  $m \bar{v}_0^2 / 2$  is the mean kinetic energy of a molecule of mass  $m$  at temperature  $T_0$ . But if in order to come nearer to what must be the conditions of conduction in natural gases, we assume that the natural molecules transmit the whole of their molecular kinetic energy in the same proportion as they would transmit their translatory kinetic energy if they were smooth spheres, then  $k = \cdot 826 \eta c$ , where  $c$  is the specific heat of the gas at constant pressure. According to this formula the effect of molecular force on conductivity is found by putting for  $\eta$  the value obtained when molecular force is allowed for. The temperature-variation of the conductivity of only three gases has been thoroughly investigated, namely of air, hydrogen, and  $\text{CO}_2$ . The temperature-variation of  $c$  for air and hydrogen is so small that within ordinary temperature-ranges it can be neglected, but for  $\text{CO}_2$   $c_{100}/c_0$  according to E. Wiedemann is 1.11, and according to Regnault 1.147. For these three gases the theoretical ratio of the conductivities at  $100^\circ \text{C}$ . and  $0^\circ \text{C}$ . is calculable according to the relation

$$\frac{k_{100}}{k_0} = \frac{c_{100}}{c_0} \frac{\eta_{100}}{\eta_0} = \frac{c_{100}}{c_0} \left( \frac{373}{273} \right)^{\frac{1}{2}} \frac{1 + C/273}{1 + C/373},$$

using for each the appropriate value of  $C$  already found, namely 113 for air, 79 for hydrogen, and 277 for  $\text{CO}_2$ , with which we get :—

Authority.	Date.	Air.	Hydrogen.	$\text{CO}_2$ .
Theory .....	1893	1.268	1.243	1.50 or 1.55
Winkelman .....	1876	1.277	1.277	1.50
Graetz .....	1881	1.185	1.160	1.22
Winkelman .....	1883	1.208	1.208	1.38
Winkelman .....	1886	1.206	1.206	1.366
Schleiermacher .....	1888	1.289	1.275	1.548
Eichborn .....	1890	1.199	1.199	1.367
Winkelman .....	1891	1.190	1.175	1.401

It will be noticed that the theoretical numbers agree best with Winkelman's determinations of 1876 and with Schleiermacher's ; but Winkelman, returning with great devotion to these difficult measurements, obtains persistently smaller

results, and if the experimental difficulties were not so great, we should be led to the conclusion that the theory is inadequate; but the variation of the individual numbers from which these means are derived is so great that we cannot yet accept so definite a conclusion.

Schleiermacher's results are obtained by a special and apparently very appropriate method, namely that of measuring the heat conducted through a gaseous envelope from a wire heated by an electric current, and yet his values of  $k_{100}/k_0$  range from 1.256 to 1.318 for air, from 1.200 to 1.315 for hydrogen, and from 1.485 to 1.584 for  $\text{CO}_2$ , and the separate measurements of other experimenters vary in the same manner. Under the circumstances of the case all that we can say is that when molecular force is taken account of in the theory of the conductivity of gases, the theoretical variation of conductivity with temperature is brought within the range of present experimental determinations in a manner which is not possible when molecular force is ignored. The direction in which further experimental work is desirable is that of testing for other compound gases where  $c$  is largely variable with temperature, whether  $k \propto cT^{\frac{1}{2}}/(1 + C/T)$ .

The whole theory of the conduction of heat in gases awaits development; it has been touched on here in only one aspect, namely that of its dependence on molecular force.

The last property of a gas which we shall take as being affected by molecular force in a manner hitherto ignored is its characteristic equation. I have shown (Phil. Mag., March 1893) that the equation of Van der Waals applies only to the element gases and methane and not to compounds; but if it only applied to a single substance it would still be of great interest in relation to the kinetic theory. In the theoretical deduction which Van der Waals gave of his characteristic equation  $(p + a/v^2)(v - b) = RT$  the number of encounters of a molecule was shown to have the important effect of introducing the constant  $b$  into the equation,  $b$  being (when molecular force is ignored as affecting the number of collisions) equal to four times the volumes of all the sphere-molecules in volume  $v$ ; but when the influence of molecular force on the number of collisions is allowed for, then  $b$  can no longer be regarded as a constant equal to four times the volumes of the molecules, and the theoretical form of the characteristic equation of gases is rather profoundly affected.

In tracing this effect of molecular force it will be most convenient to reproduce the essentials of Tait's method of presenting the establishment of the characteristic equation for forceless molecules (Trans. Roy. Soc. Edinb. xxxiii. and

xxxv.) and introduce the necessary modifications for attracting molecules.

The starting-point is Clausius's equation of the Virial,

$$\frac{3}{2}pv = \Sigma \frac{1}{2}mv^2 - \frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma Rr,$$

where  $R$  is the force acting between two molecules at distance  $r$  apart. Now the forces  $R$  consist of two sets, first the continuously acting attractions to be denoted by  $R_a$ , and second, the discontinuous repulsions that act during the collision of two molecules to be denoted by  $R_b$ , thus

$$\Sigma \Sigma Rr = \Sigma \Sigma R_a r - \Sigma \Sigma R_b r.$$

Of the actual values of  $R_b$  we know nothing, but if  $\nu$  is the number of encounters of a molecule in a second and  $\mu$  is the average momentum communicated to a molecule in an encounter, then we can treat the virial of the unknown impulsive forces as equivalent to that of an average continuous force of repulsion  $\mu\nu$  acting at points  $2a$  apart (the distance of two centres at collision), so that  $\Sigma \Sigma R_b r$  becomes  $\Sigma 2a\mu\nu$ . The value of  $\mu$  for forceless spheres is  $m(\pi\bar{v}^2/3)^{\frac{1}{2}}$ .

When molecular attraction acts, the molecules at the instant of collision have on the average a relative velocity greater than that which rules amongst molecules that are remote from one another's influence; calling it  $V_e$ , then

$$\frac{1}{2}mV_e^2 = \frac{1}{2}mV^2 + m^2f(1/2a) - m^2f(1/D),$$

where  $D$  is the distance apart of molecules remote from one another's influence, so that  $m^2f(1/D)$  can be neglected, and then

$$V_e = \{V^2 + 2mf(1/2a)\}^{\frac{1}{2}} = V\{1 + 2mf(1/2a)/V^2\}^{\frac{1}{2}}.$$

Thus, then, for attracting molecules the value of  $\mu$  is got by supposing the velocities of forceless molecules increased in the ratio  $\{1 + mf(1/2a)/\bar{v}^2\}^{\frac{1}{2}}$ . The value of  $\nu$  for  $N$  forceless molecules in volume  $B$  when the diameter of a molecule is so small that it can be neglected in comparison to the mean free path is  $2\frac{N}{B}\pi(2a)^2(4\bar{v}^2/3\pi)^{\frac{1}{2}}$ . But when the diameter  $2a$  cannot be so neglected this must be increased in the ratio  $1:1 - \frac{2}{3}\frac{N}{B}\pi(2a)^3$ , so that

$$\nu = 2\frac{N}{B}\pi(2a)^2(4\bar{v}^2/3\pi)^{\frac{1}{2}}/\{1 - \frac{2}{3}\frac{N}{B}\pi(2a)^3\};$$

hence for forceless molecules,

$$\frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma R_b r = \Sigma \frac{\pi N m (2a)^3 \bar{v}^2 / 3B}{1 - 2N\pi(2a)^3 / 3B} = m \frac{\bar{v}^2 N}{2B} \frac{b}{1 - b/B},$$

where  $b$  is four times the volume of the  $N$  spheres ; with the usual notation of  $v$  for  $B$  the volume, the last expression becomes

$$\frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma R_b r = N \frac{m \bar{v}^2}{2} \frac{b}{v - b}.$$

We have now to take up the evaluation of  $\nu$  for attracting molecules. In the first place, if we neglect molecular diameter compared to free path and also neglect curvature of path and acceleration of velocity due to molecular force, then the number of encounters per second of each of  $N$  molecules in volume  $B$  is obtained, according to our principle, from that given for forceless molecules by increasing  $(2a)^2$  to  $(2a)^2(1 + mf(1/2a)/\bar{v}^2)$ . But it may not appear legitimate to neglect curvature of path and acceleration of velocity due to molecular force, even although they tend to neutralize one another, so we will prove them to be practically negligible in determining the average time taken by a molecule starting with relative velocity  $V$  from distance  $D$  to reach distance  $2a$  from the centre of attraction. Neglecting  $m^2 f(1/D)$ ,  $v^2 = V^2 + 2mf(1/r)$  gives the velocity  $v$  at distance  $r$ ; but

$$v^2 = \left(\frac{ds}{dt}\right)^2 = \left(\frac{dr}{dt}\right)^2 + r^2 \left(\frac{d\theta}{dt}\right)^2,$$

and with the usual notation for orbital motion,

$$r^2 \frac{d\theta}{dt} = h = Vb,$$

$b$  being the perpendicular from the centre of attraction on the asymptote to the orbit ; hence

$$\frac{dr}{dt} = \left( V^2 + 2mf(1/r) - \frac{V^2 b^2}{r^2} \right)^{\frac{1}{2}};$$

$$t = \int_{2a}^D \frac{dr}{V \left( 1 + \frac{2mf(1/r)}{V^2} - \frac{b^2}{r^2} \right)^{\frac{1}{2}}}.$$

Now in the case of molecules collisions occur for all values of  $b$  from 0 up to  $2a(1 + 2mf(1/2a)/V^2)^{\frac{1}{2}}$ , to be denoted by  $b'$ ; hence the average value of  $t$  under these conditions is

$$\bar{t} = \frac{1}{\pi b'^{\frac{1}{2}}} \int_0^{b'} 2\pi b \, db \int_{2a}^D \frac{dr}{V \left( 1 + \frac{2mf(1/r)}{V^2} - \frac{b^2}{r^2} \right)^{\frac{1}{2}}}.$$

Integrating first with respect to  $h$ , we get

$$\begin{aligned}\bar{t} &= \frac{2}{b^{1/2}V} \int_{2a}^D r^2 dr \left[ \{1 + 2mf(1/r)/V^2\}^{\frac{1}{2}} - \{1 + 2mf(1/r)/V^2 - b^{1/2}/r^2\}^{\frac{1}{2}} \right] \\ &= \frac{2}{b^{1/2}V} \int_{2a}^D \frac{r^2 dr \, b^{1/2}/r^2}{\{1 + 2mf(1/r)/V^2\}^{\frac{1}{2}} + \{1 + 2mf(1/r)/V^2 - b^{1/2}/r^2\}^{\frac{1}{2}}} \\ &= \frac{D-2a}{V} + 2 \frac{2a}{V} \int_{2a}^D \frac{dr}{2a} \left[ \frac{1}{\{1 + 2mf(1/r)/V^2\}^{\frac{1}{2}} + \{1 + 2mf(1/r)/V^2 - b^{1/2}/r^2\}^{\frac{1}{2}}} - \frac{1}{2} \right].\end{aligned}$$

We could proceed no farther without a knowledge of the law of force, but if it is that of the inverse fourth power,

$$f(1/r) = A/r^3.$$

Even with this substitution the handling of the last integral in a general way would occupy too much space, and for present purposes we shall be better served by a consideration of its values in particular typical cases, say those of hydrogen, oxygen, or nitrogen at particular temperatures:  $2mf(1/r)/V^2$  takes the form  $(2a)^3 C/r^3 T$ , and  $b^{1/2} = (2a)^2(1 + C/T)$ . For hydrogen  $C=79$ , and taking  $T$  as 173, 273, 373, 473, and  $\infty$ , we get by approximation the following numerical values of the last integral, assuming  $1/D=0$  :—

T . . . . .	173°	273°	373°	473°	$\infty$
Integral . . .	·1647	·1652	·1658	·1664	·1666

I do not guarantee the fourth figure of these values to be accurate, but the main result is clear enough, namely, that for hydrogen as a gas the integral is almost independent of  $V^2$  or temperature; and as the integral has for nitrogen ( $C=109$ ) the above values at temperatures 239°, 377°, 515°, 653°, and  $\infty$ , and for oxygen at 278°, 439°, 600°, 760°, and  $\infty$ , we can say that for the element gases the value of the integral is  $1/6$ , and thus

$$\bar{t} = \frac{D-2a}{V} + \frac{2a}{3V},$$

which, of course, is the result also for forceless molecules, as it is exactly true when  $V=\infty$ , in which case finite force becomes negligible. Accordingly it has been shown that the effect which curvature of path and acceleration due to molecular force have on the time between two encounters or on the number of encounters may be neglected, and the number  $\nu$  for attracting molecules is

$$2 \frac{N}{B} \pi (2a)^2 \left( 1 + \frac{mf(1/2a)}{v^2} \right) (4v^2/3\pi)^{\frac{1}{2}} \left\{ 1 - \frac{2}{3} \frac{N}{B} \pi (2a)^3 \right\},$$



and

$$\mu = m(\pi \bar{v}^2/3)^{\frac{1}{2}}(1 + mf(1/2a)/\bar{v}^2)^{\frac{1}{2}};$$

hence

$$\begin{aligned} \frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma R_a r &= \frac{1}{4} \Sigma 2a\mu v = \Sigma \frac{N\pi(2a)^3 \{1 + mf(1/2a)/\bar{v}^2\}^{\frac{1}{2}}/3B}{1 - \frac{2}{3} \frac{N}{B} \pi(2a)^3} \cdot m\bar{v}^2 \\ &= \left(1 + \frac{mf(1/2a)}{\bar{v}^2}\right)^{\frac{1}{2}} \frac{N}{B} \frac{m\bar{v}^2}{2} \frac{b}{1-b/B}, \end{aligned}$$

showing that for attracting molecules the virial of the collisional forces is  $(1 + mf(1/2a)/\bar{v}^2)^{\frac{1}{2}}$  times its value when the effect of molecular force on the number of collisions is neglected. The form of the characteristic equation is soon obtained in both cases, for the virial of the molecular attractions  $\frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma R_a r$  reduces to the form  $3a/2B$  or  $3a/2v$ ; hence when the effect of molecular force on collisions is neglected,

$$\frac{3}{2}pv = N \frac{m\bar{v}^2}{2} + N \frac{m\bar{v}^2}{2} \frac{b}{v-b} - \frac{3}{2} \frac{a}{v};$$

$$\begin{aligned} \therefore \quad \left. \begin{aligned} \left(p + \frac{a}{v^2}\right)v &= N \frac{m\bar{v}^2}{3} \left(1 + \frac{b}{v-b}\right) = RT \frac{v}{v-b} \\ \text{or} \quad \left(p + \frac{a}{v^2}\right)(v-b) &= RT; \end{aligned} \right\} \quad (A) \end{aligned}$$

this form depending on the fact that the coefficient of  $b/(v-b)$  is unity. When the effect of molecular force on the number of collisions is allowed for, the coefficient of  $b/(v-b)$  becomes  $\{1 + mf(1/2a)/\bar{v}^2\}^{\frac{1}{2}}$  or  $(1 + C/T)^{\frac{1}{2}}$ , and thus the characteristic equation is

$$pv = RT \left\{ 1 + (1 + C/T)^{\frac{1}{2}} \cdot \frac{b}{v-b} \right\} - \frac{a}{v}. \quad (B)$$

Now of the two forms (A) and (B), it has been shown (Phil. Mag., March 1893) that (A) represents fairly well the facts of Amagat's experiments down to the critical volume, so that (B) cannot do so, seeing that it implies at low volumes or high pressures a considerable variation of  $\partial p/\partial T$  with  $T$ , which does not occur at volumes above the critical.

How are we to explain that the more accurate equation represents the experimental facts worse than the less accurate? Simply in this way, that we have no right to expect to get the virial of the collisional forces of actual molecules by treating them as smooth spheres. There are certain properties of

molecules that can be explained by representing the molecules as smooth spheres, but there are others which cannot be so explained, the best known of the latter being the specific heat. It is well to see how far a simplifying hypothesis such as that of smooth spherical molecules can lead us ; but it is also well to recognize when the hypothesis has got to the end of its tether. Van der Waals's theoretical equation agrees closely with experiment for the element gases only through an accidental compensation in the effects of two neglected causes, namely, the effect of molecular force on the number of collisions of molecules and the effect of a difference between the forces called into play in the collision of molecules and of smooth spheres. It must also be remembered that the empirical equation given for compound gases in my paper on the "Laws of Molecular Force" is quite different in form from that for elements, and that a theoretical explanation of it must involve considerations beyond the range of the spherical molecule. Indeed it appears to me that a combined and collated study of specific heat, characteristic equation, and thermal conductivity of gases might now be expected to yield some of that knowledge of the internal dynamics of molecules which is absolutely necessary for the advancement of the kinetic theory in the most interesting directions.

Melbourne, June 1893.

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LIII. *On the Passage of Electric Wave-trains through Layers of Electrolyte.* By G. UDNY YULE\*.

*Introduction.*

THE attempt to compare the resistances of electrolytes with rapidly alternating currents, by utilizing for that purpose electric radiation, was first made by Prof. J. J. Thomson in 1888†. The method he used was as follows :—Between a circular oscillator and a resonator was placed a large shallow dish, into which an electrolyte was poured, forming an absorbent layer which greatly weakened the resonator-sparks and finally extinguished them. So long as the layer be thin, the thickness of liquid necessary to *just* extinguish the sparks is inversely proportional to its conductivity. In this way the conductivities of several different solutions were compared, and the ratios found were approximately those of the conduc-

\* Communicated by the Author. A preliminary note was published, Proc. Roy. Soc. liv. p. 96, May 1893.

† Proc. Roy. Soc. xlv. p. 269 (1889).