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Physics. — “*The coefficient of diffusion for gases according to O. E. MEYER.*” By Prof. J. P. KUENEN.

(Communicated in the meeting of January 25, 1913).

Among the various methods of deriving an expression for the coefficient of diffusion from the kinetic theory on the assumption that the molecules behave like elastic spheres there is one — that of O. E. MEYER.¹⁾ — which leads to a result differing largely from the others and from observation, although the fundamental assumptions are essentially the same.

The deduction of MEYER's formula is shortly as follows²⁾: a plane of unit area is considered at right angles to the gradient of concentration and therefore to the diffusion stream, and the numbers of molecules of each kind are calculated which cross the plane per second. It is assumed that the molecules have on the average had their last collision at a distance l (mean free path) from the point where they cross the plane and that their number in each direction is proportional to their density at the point where the last collision has taken place. The numbers in question of both kinds of molecules are found to be

$$a_1 = -\frac{1}{3} u_1 l_1 \frac{dn_1}{dx} \quad \text{and} \quad a_2 = -\frac{1}{3} u_2 l_2 \frac{dn_2}{dx},$$

where u is the mean molecular velocity, n the number of molecules in unit volume and x the direction of the diffusion stream; obviously $\frac{dn_1}{dx} = -\frac{dn_2}{dx}$, for l_1 and l_2 , the mean free paths of the two kinds of molecules in the mixture, we have

$$l_1 = 1 : \left\{ \sqrt{2} n_1 \pi s_1^2 + n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \right\}$$

and

$$l_2 = 1 : \left\{ \sqrt{2} n_2 \pi s_2^2 + n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \right\};$$

where s is the diameter of the molecule and $\sigma = \frac{1}{2}(s_1 + s_2)$.

Owing to this double stream of molecules a total number $a_1 + a_2$ pass through the plane: this would in general represent a motion of the gas. As the gas considered as a whole is supposed to be at rest, the stream $a_1 + a_2$ will produce a pressure gradient by which a stream of the gas as a whole of the same amount in the opposite

¹⁾ O. E. MEYER, Die kin. Theorie der Gase p. 252 seq. 1899.

²⁾ e. g. L. BOLTZMANN, Kin. Theorie. I. p. 89 seq. 1896.

direction is generated. When this stream is superposed on the first, the numbers of molecules become $a_1 - \frac{n_1}{n}(a_1 + a_2)$ and $a_2 - \frac{n_2}{n}(a_1 + a_2)$ and the coefficient of diffusion D

$$D = \frac{1}{3n} (n_2 u_1 l_1 + n_1 u_2 l_2).$$

According to this formula, D would vary strongly with the composition of the mixture, when m_1 and m_2 differ much. In order to show this we put successively $n_1 = 0$ and $n_2 = 0$ and find for the limiting values of D :

$$D(n_1 = 0) = \frac{1}{3} \frac{u_1}{n\pi\sigma^2} \sqrt{\frac{m_2}{m_1 + m_2}}$$

$$D(n_2 = 0) = \frac{1}{3} \frac{u_2}{n\pi\sigma^2} \sqrt{\frac{m_1}{m_1 + m_2}}$$

Using the relation $u_1^2 m_1 = u_2^2 m_2 = \frac{4}{\pi h}$, where h is the constant in MAXWELL'S law of distribution, we can also write

$$D(n_1 = 0) = \frac{2}{3\pi n\sigma^2} \frac{1}{\sqrt{\pi h}} \sqrt{\frac{m_2}{m_1} \frac{1}{m_1 + m_2}}$$

$$D(n_2 = 0) = \frac{2}{3\pi n\sigma^2} \frac{1}{\sqrt{\pi h}} \sqrt{\frac{m_1}{m_2} \frac{1}{m_1 + m_2}}$$

The two values of D are to each other as $m_2 : m_1$ e. g. for carbon dioxide and hydrogen as 2 : 44.

The experimental evidence¹⁾ is in favour of a coefficient which varies with n_1 and n_2 , but only to a very small extent, so that a variation as given by MEYER'S formula is out of the question.

The coefficient of diffusion according to STEFAN²⁾ is:

$$D = \frac{3}{16n\sigma^2} \frac{1}{\sqrt{\pi h}} \sqrt{\frac{m_1 + m_2}{m_1 m_2}},$$

therefore independent of the composition of the mixture, which agrees approximately with experiment. The same expression follows from MAXWELL'S second theory when applied to elastic molecules; this was proved by LANGEVIN³⁾. The only simplifying supposition which

¹⁾ Compare A. LONIUS, Ann. d. Ph. (4) 29 p. 664. 1909

²⁾ J. STEFAN, Wien. Sitz.ber. 65 p. 323. 1872

³⁾ P. LANGEVIN, Ann. chim. phys. (8) 5 p. 245. 1905. MAXWELL himself had used the same method (Nature 8. p. 298. 1873): his result given without proof differs by the factor $\frac{4}{3}$ from that of LANGEVIN.

he had to make in order to carry out the required integrations was, that in ordinary slow diffusion MAXWELL'S law of distribution may be taken as fulfilled. The want of rigour which this implies may perhaps account for the small difference between the formula and observation mentioned.

The question arises, what causes the great difference between MEYER'S result and the others. GROSS¹⁾ criticised the superposition of the gas current on the diffusion current: he tried to improve the theory by leaving out the former and by taking $\frac{1}{2}(a_1 + a_2)$ as the real diffusion stream; but this is certainly illegitimate, as the definition of D presupposes the gas to be at rest or the plane through which the diffusion stream is calculated to move with the gas.

LANGEVIN²⁾ pointed out, that the dynamical action between the two kinds of molecules is lost sight of altogether in MEYER'S method, but he failed to indicate, how to modify or supplement it in order to take this action into account. Neither does BOLTZMANN explain the striking contradiction between the two methods.

It is possible to remove this contradiction for the greater part by making use of the notion of *persistence* of molecular velocity which JEANS³⁾ introduces into the kinetic theory and which also plays an important part in the theory of the Brownian movement. This quantity depends on the principle that, when a molecule collides with other molecules, it will after a collision on the average have retained a component of velocity in the original direction. JEANS has calculated what fraction of the original velocity this component is on the average: he calls this fraction the *persistence* ϑ and finds

$$\vartheta = \frac{1}{4} + \frac{1}{4\sqrt{2}} \log(1 + \sqrt{2}) = 0.406.$$

JEANS shows that the usual calculations in the kinetic theory of the various transport-phenomena of which diffusion is an example have to be corrected for this persistence. For the sake of simplicity it is assumed that a molecule describes the same distance l between successive collisions. Owing to persistence a molecule will on the average after describing a path l travel on in the same direction over distances successively of $l\vartheta, l\vartheta^2$ etc., therefore altogether describe a distance $l/(1-\vartheta)$ before its motion in the given direction is exhausted and similarly a molecule which reaches a plane from a distance l will not on the average have had a component 0 in the given

1) G. GROSS. Wied. Ann. 40 p, 424 1890.

2) l.c.

3) J. H. JEANS. The dynamical theory of gases p. 236 sqq. 1904.

direction at that distance before it collided there, but at a distance $l/(1-\vartheta)$. We can also say, that the molecules which have had a collision at a distance $l/(1-\vartheta)$ succeed on the average in getting to the plane before their velocity in the given direction is reduced to 0. In the calculation of the numbers that cross the plane it was assumed that the velocities were evenly distributed in all directions at a distance l : as it now appears that this condition does not hold for a distance l but for the distance $l/(1-\vartheta)$, the correct result is obtained by replacing l by $l/(1-\vartheta)$ in the final formula.

In this manner JEANS corrects MEYER's formula¹⁾, but it is clear that by this means no improvement is effected, as D is multiplied by a constant factor and the anomalous dependence on n_1 and n_2 remains. An important point has however been overlooked by JEANS viz. that the persistence obtains a different value when one deals with a mixture of two kinds of molecules of different mass.

When the calculation of ϑ is carried out for a molecule m_1 amongst molecules m_2 , one finds

$$\vartheta = \frac{m_1 + m_2 \left\{ -\frac{1}{2} + \frac{1}{2\sqrt{2}} \log(1 + \sqrt{2}) \right\}}{m_1 + m_2} = \frac{m_1 - 0.188 m_2}{m_1 + m_2}.$$

For $m_1 = m_2$ this expression reduces to the one given by JEANS.

As a molecule m_1 collides not only with molecules m_2 but also with molecules of its own kind, the correct expression for the persistence is obtained by multiplying the average number of collisions of the latter kind by 0.406 and that of the former by the above fraction. In this manner the factor $1/(1-\vartheta)$ becomes

$$f_1 = 1: \left\{ 1 - n_1 \pi s_1^2 \sqrt{2} l_1 \times 0.406 - n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} l_1 \frac{m_1 - 0.188 m_2}{m_1 + m_2} \right\}$$

for the molecules m_1 and

$$f_2 = 1: \left\{ 1 - n_2 \pi s_2^2 \sqrt{2} l_2 \times 0.406 - n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} l_2 \frac{m_2 - 0.188 m_1}{m_1 + m_2} \right\}.$$

for the molecules m_2 .

Repeating MEYER's argument we find for D

$$D = \frac{1}{3n} (n_2 u_1 l_1 f_1 + n_1 u_2 l_2 f_2).$$

If we now put $n_i = 0$, we obtain

¹⁾ JEANS l.c. p. 273. Comp. M. v. SMOLUCHOWSKI, Bull. de l'Ac. d. Sc. de Cracovie 1906, p. 202.

$$D(n_1 = 0) = \frac{u_1}{3n\pi\sigma^2} \sqrt{\frac{m_2}{m_1 + m_2}} \frac{1}{1 - \frac{m_1 - 0.188m_2}{m_1 + m_2}}$$

$$= \frac{u_1}{3n\pi\sigma^2} \sqrt{\frac{m_1 + m_2}{m_1}} \times \frac{1}{1.188} = \frac{2}{3\pi n\sigma^2} \frac{1}{1.188} \frac{1}{\sqrt{\pi h}} \sqrt{\frac{m_1 + m_2}{m_1 m_2}}$$

The symmetry of this expression shows that exactly the same value holds for $n_2 = 0$. The form of D also agrees with STEFAN'S expression: the coefficients are in the relation of 1 : 1.05; therefore, considering the approximate character of the deduction, there is practically complete agreement.

For intermediate compositions the difference between the two expressions for D becomes material only when m_1 and m_2 are very different. This is probably due to the method of calculation which compels us to work with averages from the beginning. Moreover JEANS'S method of calculating the persistence is not rigorous: it might perhaps be found possible by applying more rigorous methods to reduce the remaining difference between MEYER'S corrected formula and the other one. As a matter of fact the object of this paper was not so much to deduce a correct formula, considering that the near accuracy of LANGEVIN'S method cannot well be doubted, as to remove the strong contradiction between the two results.

In conclusion it may be added, that the method which is indicated in this paper can immediately be used to deduce rational formulae for the viscosity and the conduction of heat for gas mixtures.

Mathematics. — "On bilinear null-systems." Communicated by Prof. JAN DE VRIES.

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§ 1. In a *bilinear* null-system any point admits one *null-plane*, any plane one *null-point*. The lines incident with a point and its null-plane are called *null-rays*. If these lines form a linear complex, we have the generally known null-system, which is a special case of the correlation of two collocal spaces (null-system of MOBIUS). The null-rays of any other null-system (1,1) fill the entire space of rays; with R. STURM we denote by γ the number indicating how many times any line is null-ray.

In the first we suppose $\gamma = 1$ and we examine the null-systems which may be called *trilinear* and which can be represented by (1,1,1).