

Citation:

Kuener, J.P., The diffusion-coefficient of gases and the viscosity of gas-mixtures, in:
KNAW, Proceedings, 17 III, 1914-1915, Amsterdam, 1915, pp. 1068-1073

Physics. -- "*The diffusion-coefficient of gases and the viscosity of gas-mixtures.*" By Prof. J. P. KUENEN. (Communications from the Physical Laboratory at Leiden. Suppl. 38).

In two previous communications¹⁾ on the same subject it was shown to what cause the difference between the results of the two current theories of gas-diffusion is to be ascribed. Whereas MAXWELL'S theory (STEFAN, LANGEVIN, CHAPMAN²⁾) leads to the result, that the coefficient of diffusion is independent of the proportion in which two gases are mixed, O. E. MEYER'S theory which uses the method of the molecular free path gives a coefficient which changes with the composition of the mixture. For two gases whose molecules have masses m_1 and m_2 , the coefficient of diffusion lies between two limiting values which are to each other in the proportion $m_1 : m_2$. The coefficient of diffusion for carbon-dioxide ($M_1 = 44$) with a trace of hydrogen ($M_2 = 2$) would be 22 times larger than that of hydrogen with a trace of carbon-dioxide; between those limiting values D would diminish regularly with the composition.

The cause of this difference between the two results is due to the circumstance, that in O. E. MEYER'S theory no account is taken of the "persistence" of molecular motion which was introduced into the kinetic theory by JEANS³⁾. The persistence consists in that a molecule, when colliding with another, retains on the average a component of velocity in the direction of its motion before the collision, so that after a collision all directions are not, as used to be generally assumed, equally probable. The manner in which JEANS corrects O. E. MEYER'S formula for the persistence is incorrect, however, and does not lead to a better result, because he takes for the persistence the value derived by him for a single gas, whereas the persistence in a mixture should have been introduced. In the previous papers cited above it was shown, that by doing the latter, the formula is modified in such a way, that the strong contradiction with the result of the other theory disappears.

Qualitatively the matter may be put as follows. Let us first consider carbon-dioxide with a trace of hydrogen; the theory shows that in this mixture D is determined by the mobility and by the free path of the hydrogen-molecules which are both relatively large,

¹⁾ J. P. KUENEN. These Proc. 15. p. 1152. 1913. 16. p. 1162. 1914. Comm. Leiden, Suppl. 28, 36.

²⁾ S. CHAPMAN, Phil. Trans. 211 A p. 433. 1912; this article which was not mentioned in the previous papers may be specially referred to on this occasion.

³⁾ J. H. JEANS Dyn. Theory of gases. 1904, p. 236. seq.

viz. the former inversely proportional to $\sqrt{m_2}$ and the latter proportional to $\sqrt{m_1}$, so that D is proportional to $\sqrt{\frac{m_1}{m_2}}$. Similarly for a trace of carbon-dioxide in hydrogen D is proportional to $\sqrt{\frac{m_2}{m_1}}$, so that the ratio of the two coefficients is as $m_1 : m_2 = 44 : 2$. When the persistence is taken into account the ratio becomes quite different: the persistence is much smaller for the light hydrogen-molecules than for the heavy carbon-dioxide molecules, the consequence being, that the diffusion-coefficient is much less increased by the correction in the former than in the latter case. With the value given for the persistence in the papers mentioned the compensation was even complete, so that D for $n_1 = 0$, became equal to D for $n_2 = 0$, whereas for intermediate mixtures D obtained other values.

Quite recently Miss A. SNETHLAGE, student of physics at Amsterdam, who is engaged on an investigation of various applications of the persistence-theory, has drawn my attention to the fact, that the expression given by me for the persistence cannot be correct. For, whereas for the case, that the masses m_1 and m_2 of the molecules are equal, it gives correctly the expression found by JEANS, on the other hand for m_2 infinite it gives a negative value, although a simple calculation shows that its value must be nought in this case.

In repeating the calculation it was found that on the former occasion an error had crept in which would have been noticed before, if the agreement with JEANS's value for $m_1 = m_2$ had not erroneously been taken as a proof of its being correct. The present calculation yielded the following expression for the mean persistence of a molecule m_1 colliding with a molecule m_2 :

$$\mathfrak{P}_1 = \frac{m_1}{2(m_1 + m_2)} + \frac{1}{4} \frac{m_1^2}{m_2^{1/2}(m_1 + m_2)^{3/2}} \log \frac{\sqrt{(m_1 + m_2)} + \sqrt{m_2}}{\sqrt{(m_1 + m_2)} - \sqrt{m_2}},$$

which is identical with that found by miss SNETHLAGE. The calculation may be shortly reproduced; with a view to an easy comparison with JEANS his notation and also, as far as possible, his method of calculation will be used.

We take two molecules with definite velocities a and b , which collide in all possible ways, and calculate for molecule a the mean velocity after the collision taken in the original direction of its motion. MAXWELL has proved, that this velocity is equal to that of the centre of mass projected on the same direction. Calling the angle between a and b \mathfrak{P} , this projection p is given by

$$p = \frac{am_1 + bm_2 \cos \mathfrak{P}}{m_1 + m_2}.$$

This projection has now to be averaged for all angles ϑ , taking into account, that the chance of a collision for each direction is proportional to the relative velocity r and to $\frac{1}{2} \sin \vartheta d\vartheta$. The mean is therefore given by

$$\frac{\int_0^\pi p r \sin \vartheta d\vartheta}{\int_0^\pi r \sin \vartheta d\vartheta}$$

As $r^2 = a^2 + b^2 - 2ab \cos \vartheta$, it follows, that $r dr = ab \sin \vartheta d\vartheta$. After substitution of $\sin \vartheta d\vartheta$ and of p and integration we obtain

$$\frac{(2m_1 + m_2) a^2 + m_2 b^2}{2(m_1 + m_2) a} - \frac{m_2}{m_1 + m_2} \frac{3}{10 a} \frac{5 a^4 + 10 a^2 b^2 + b^4}{3 a^2 + b^2} \text{ for } a > b$$

and

$$\frac{(2m_1 + m_2) a^2 + m_2 b^2}{2(m_1 + m_2) a} - \frac{m_2}{m_1 + m_2} \frac{3}{10 a} \frac{a^4 + 10 a^2 b^2 + 5 b^4}{a^2 + 3 b^2} \text{ for } a < b;$$

these expressions have to replace those given by JEANS (l.c. p. 239). With JEANS we may put $a = \kappa b$.

The chance per second, that a molecule with velocity a collides with a molecule with velocity b , the relative velocity being r , is

$$2 n_2 \sigma \sqrt{\pi h^3 m_2^3} e^{-h m_2 b^2} \frac{b}{a} db r^2 dr,$$

where n_2 is the number of molecules m_2 per unit volume, and as the number of molecules per unit volume with velocity a is equal to

$$4 n_1 \sqrt{\frac{h^3 m_1^3}{\pi}} e^{-h m_1 a^2} a^2 da$$

($n_1 =$ total number of molecules m_1 per unit volume), the total number of collisions of the kind considered will be

$$8 n_1 n_2 \sigma^2 h^3 \sqrt{m_1^3 m_2^3} e^{-h(m_1 a^2 + m_2 b^2)} ab da db r^2 dr.$$

Integrated with respect to r for $a > b$, when the limits of r are $a + b$ and $a - b$, this becomes

$$\frac{16}{3} n_1 n_2 \sigma^2 h^3 \sqrt{m_1^3 m_2^3} e^{-h(m_1 a^2 + m_2 b^2)} ab^2 (3a^2 + b^2) da db$$

and similarly for $a < b$

$$\frac{16}{3} n_1 n_2 \sigma^2 h^3 \sqrt{m_1^3 m_2^3} e^{-h(m_1 a^2 + m_2 b^2)} a^2 b (a^2 + 3b^2) da db.$$

In both expressions we may again put $a = \kappa b$.

To find the mean persistence the above expressions for the number of collisions have to be multiplied each by the corresponding mean persistence, separately for $a > b$ and $a < b$, then to be integrated with respect to b between 0 and ∞ , further with respect to z , in the former case between 1 and ∞ and in the latter between 0 and 1, and finally to be divided by the total number of collisions:

$$2 n_1 n_2 \sigma^2 \sqrt{\frac{\pi (m_1 + m_2)}{h m_1 m_2}}.$$

The result of this somewhat lengthy calculation which need not be detailed any further was given above. A corresponding expression is found for the m_2 -molecules viz.

$$\vartheta_2 = \frac{m_2}{2(m_1 + m_2)} + \frac{1}{4} \frac{m_2^2}{m_1^{1/2} (m_1 + m_2)^{1/2}} \log \frac{\sqrt{(m_1 + m_2)} + \sqrt{m_1}}{\sqrt{(m_1 + m_2)} - \sqrt{m_1}}.$$

The formulae given before for the *coefficient of diffusion* are now somewhat modified. Qualitatively there is no change, but the compensation at the limits referred to above is not so complete as before.

For D the same expression holds as before viz.:

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

where l_1 and l_2 keep their meaning, viz.:

$$l_1 = 1 : \left\{ \sqrt{2} n_1 \pi s_1^2 \left(1 + \frac{C_1}{273} \right) + n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left(1 + \frac{C_{12}}{273} \right) \right\}$$

and

$$l_2 = 1 : \left\{ \sqrt{2} n_2 \pi s_2^2 \left(1 + \frac{C_2}{273} \right) + n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left(1 + \frac{C_{12}}{273} \right) \right\},$$

but

$$f_1 = 1 : \left\{ 1 - \sqrt{2} n_1 \pi s_1^2 \left(1 + \frac{C_1}{273} \right) l_1 \times 0.406 - n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left(1 + \frac{C_{12}}{273} \right) l_1 \vartheta_1 \right\}$$

and

$$f_2 = 1 : \left\{ 1 - \sqrt{2} n_2 \pi s_2^2 \left(1 + \frac{C_2}{273} \right) l_2 \times 0.406 - n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left(1 + \frac{C_{12}}{273} \right) l_2 \vartheta_2 \right\}.$$

For $n_1 = 0$ and $n_2 = 0$ we now obtain:

$$D (n_1 = 0) = \frac{2}{3n \pi \sigma^2} \sqrt{\frac{m_2}{\pi h m_1 (m_1 + m_2)}} \left(1 + \frac{C_{12}}{273} \right) \frac{1}{1 - \vartheta_1}$$

and

$$D(n_2=0) = \frac{2}{3n\pi\sigma^2} \sqrt{\frac{m_1}{\pi l m_2(m_1+m_2)}} \left(1 + \frac{C_{12}}{273}\right) \frac{1}{1-\vartheta_2},$$

the ratio of which is :

$$\frac{D(n_1=0)}{D(n_2=0)} = \frac{m_2}{m_1} \frac{1-\vartheta_2}{1-\vartheta_1}.$$

Calculation gives for the persistence of carbon-dioxide in relation to hydrogen 0.942, for that of hydrogen in carbon-dioxide 0.239, so that for these two gases the above ratio becomes 0.77. According to the theory as corrected the ratio is therefore still much nearer unity than according to the uncorrected theory of O. E. MEYER which gives $\frac{\vartheta_2}{\vartheta_1} = 0.045$ in this case. As a complete agreement with MAXWELL'S theory is in any case lacking, the remaining difference between the two limiting values is not of any special consequence and no useful purpose would be served by communicating further numerical results. With combinations of gases which differ less in molecular weight the difference between the limiting values is smaller.

The formula for the *viscosity of a gas-mixture* undergoes a corresponding modification. As before the relation holds :

$$\eta = 0.35 \frac{n_1}{n} d_1 u_1 l_1 f_1' + 0.35 \frac{n_2}{n} d_2 u_2 l_2 f_2',$$

where f_1' and f_2' now have the values :

$$\begin{aligned} f_1' &= 1 : \left\{ 1 - \frac{1}{2} \sqrt{2} n_1 \pi s_1^2 \left(1 + \frac{C_1}{273}\right) l_1 \times 0.406 - \right. \\ &\quad \left. - \frac{m_1}{m_1 + m_2} \times n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left(1 + \frac{C_{12}}{273}\right) l_1 \vartheta_1 \right\} \\ f_2' &= 1 : \left\{ 1 - \frac{1}{2} \sqrt{2} n_2 \pi s_2^2 \left(1 + \frac{C_2}{273}\right) l_2 \times 0.406 - \right. \\ &\quad \left. - \frac{m_2}{m_1 + m_2} \times n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left(1 + \frac{C_{12}}{273}\right) l_2 \vartheta_2 \right\}. \end{aligned}$$

The numerical values which are now found for mixtures of carbon-dioxide and hydrogen, and of argon and helium respectively are somewhat lower than before, but the maxima which had to be explained by the theory remain. For the former pair of gases calculation for $n_1 = n_2 = \frac{1}{2} n$ gives $\eta = 0.0001470$ (observed 144), for the latter pair $\eta = 0.0002306$ for $n_1 = n_2 = \frac{1}{2} n$ and $\eta = 0.0002281$ for $n_1 = \frac{1}{3} n$, $n_2 = \frac{2}{3} n$, which results differ even a little less from the observed maximum 0.0002207 than according to the former calculation.

ERRATA.

In the Proceedings of the Meeting of September 26, 1914:

p. 528 line 9 and 10 from the top: For: "On plate IA of Comm. N^o. 107 α may be seen that part of the apparatus" read: "Part of the apparatus of Plate IA of Comm. N^o. 107 α is similar to that of our apparatus";

p. 532 line 6 from the bottom: for "the radius of molecular action is larger" read: "the sphere of molecular action reaches in the liquid to further layers of surrounding molecules".

In the Proceedings of the Meeting of December 30, 1914: p. 905 line 6 from the top: for 904 read 900.

February 27, 1915.