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$R_3 \perp uv$, then the particular integral counting double does belong again to $E = 0$; etc.

Finally $V_4 (f = 0)$ may possess a double space, which then is common to the two polar spaces $\frac{\partial f}{\partial u} = 0, \frac{\partial f}{\partial v} = 0$ (cf. § 5). Every $R_3 \perp uv$ cuts this double space along a curve, and every π' contains a double curve, the latter of which fill the whole space R_{xyz} ; the result of the elimination E disappears now identically.

Observation. Following up this method, and without encountering other difficulties but those which arise from the increasing number of dimensions, one can obtain an insight into the singular solution of the partial differential equation of the first order with an arbitrary number of independent variables.

Physics. — “*The diffusion-coefficient of gases and the viscosity of gas-mixtures*”. By Prof. J. P. KUENEN

(Communicated in the meeting of March 28, 1914).

In a previous communication ¹⁾ on the diffusion-coefficient D of gases it was shown, that the contradiction between O. E. MEYER'S theory on the one hand and that of MAXWELL-STEFAN-LANGEVIN on the other can be largely removed by taking into account in the former theory the *persistence* of molecular movement. By doing this the limiting values for the two components, i. e. for $n_1 = 0$ and $n_2 = 0$, become equal, which involves a much smaller change in D with the composition of the mixture than according to the incomplete theory, while the second theory mentioned makes the coefficient entirely independent of the composition, observation also gives only a small variation of D .

In order to further compare the improved theory with observation I have calculated D for two pairs of gases viz. carbon dioxide—hydrogen and argon—helium, which seemed specially suitable for this test owing to the great difference in the molecular masses. For this purpose it is necessary to give a further modification to the formulae in order to express the influence of the mutual attraction of the molecules: in the former theoretical paper this influence had to be left out of account, seeing that in STEFAN'S theory the molecules are likewise regarded as free from attraction.

Using SUTHERLAND'S well-known formulation of the attraction by means of a factor $\left(1 + \frac{C}{T}\right)$ the formulae become for $0^\circ (T = 273)$.

¹⁾ J. P. KUENEN, Proc. XV p. 1152. 1913.

$$\begin{aligned}
l_1 = 1 : & \left\{ \sqrt{2} n_1 \pi s_1^2 \left(1 + \frac{C_1}{273} \right) + n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left(1 + \frac{C_{12}}{273} \right) \right\} \\
l_2 = 1 : & \left\{ \sqrt{2} n_2 \pi s_2^2 \left(1 + \frac{C_2}{273} \right) + n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left(1 + \frac{C_{12}}{273} \right) \right\} \\
f_1 = 1 : & \left\{ 1 - \sqrt{2} n_1 \pi s_1^2 \left(1 + \frac{C_1}{273} \right) l_1 \times 0.406 - \right. \\
& \left. - n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left(1 + \frac{C_{12}}{273} \right) l_1 \frac{m_1 - 0.188 m_2}{m_1 + m_2} \right\} \\
f_2 = 1 : & \left\{ 1 - \sqrt{2} n_2 \pi s_2^2 \left(1 + \frac{C_2}{273} \right) l_2 \times 0.406 - \right. \\
& \left. - n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left(1 + \frac{C_{12}}{273} \right) l_2 \frac{m_2 - 0.188 m_1}{m_1 + m_2} \right\} \\
D = & \frac{1}{3n} (n_2 u_1 l_1 f_1 + n_1 u_2 l_2 f_2).
\end{aligned}$$

Possibly in the last formula the coefficient $\frac{1}{3}$ might be replaced by a slightly different one, but the uncertainty involved in this has but a small influence on the result.

A difficulty in the calculation arises from the constant C_{12} , which measures the attraction of unlike molecules. Experiments on the viscosity of mixtures have shown, that the influence of temperature may in that case, as with pure substances, be represented by means of a factor $\left(1 + \frac{C}{T} \right)$, but the constant C in this factor is not identical with the C_{12} in the above formulae, for in the viscosity of a mixture not only the attraction of unlike molecules but also that between like molecules plays a part. If the observations could be represented by a rigorous theoretical formula, the various attractions could be separated and thus the C_{12} in question determined. As this is not the case, however, an estimation has to be resorted to; it seems simplest to take for C_{12} the value which holds for the mixture of composition 1:1 as a whole: fortunately a small change in C_{12} does not involve more than a small change in the result.

For the mixture of equal parts of CO_2 and H_2 ($n_1 = n_2 = \frac{1}{2}n$), I have calculated from BREITENBACH's experiments ¹⁾ $C_{12} = 116.2$.

The molecular diameters s_1 and s_2 were found from the viscosities of the pure components at 0° using the formula

¹⁾ P. BREITENBACH, Wied. Ann. 67. p. 808, 1899.

$$\eta = 0.44 d u l \frac{1}{1 + \frac{C}{273}} = \frac{0.44 d u}{\sqrt{2} n \pi s^2 \left(1 + \frac{C}{273}\right)},$$

in which n was taken equal to 2.76×10^{19} and further

	d	u	η_0	C
carbon-dioxide	0.00197	36250	0.0001388	239.7
hydrogen	0.0008987	169200	0.0000841	87
mixture	1:1		0.0001423	116.2

The result of the calculation is $s_1 = 3.136 \times 10^{-8}$ and $s_2 = 2.217 \times 10^{-8}$, and hence

$$\sigma = \frac{1}{2}(s_1 + s_2) = 2.676 \times 10^{-8}.$$

For $n_1 = n_2 = \frac{1}{2} n$ I find $D_{1/2} = 0.453$, whereas the limiting values for pure CO_2 and H_2 become: $D_1 = D_2 = 0.551$. Observation has given $D = 0.53$.

The agreement with observation may be considered satisfactory. The difference between $D_{1,2}$ and D_1 or D_2 which was discussed in the previous communication, is rather large: probably, as observed, this is owing to the imperfections of the method of calculation by averages followed in the theory.

For argon and helium the following constants hold ¹⁾:

	d	u	η_0	C
Argon	0.001781	38080	0.0002119	164.1
Helium	0.0001784	120400	0.0001819	80.3
Mixture 3:2			0.0002207	
„ 1:1			0.0002203	105

which give

$s_1 = 2.674 \times 10^{-8}$ $s_2 = 1.775 \times 10^{-8}$ hence $\sigma = 2.224 \times 10^{-8}$
and

$$D_{1/2} = 0.535 \quad D_1 = D_2 = 0.597 \quad D(\text{observed}) = 0.70^2).$$

The agreement with observation is less close here than in the former case; it may be added, that STEFAN'S formula (after correction for the molecular attraction) would, as the previous communication shows, give a result closely agreeing with $D_1 = D_2$ according to our formula and therefore also differing from the experimental value.

¹⁾ K. SCHMITT, Ann. d. Phys. (4) 30, p. 393, 1909.

²⁾ R. SCHMIDT, Ann. d. Phys. (4) 14 p. 801, 1904. A. LONIUS ib. 29 p. 664 1909.

The further question arises, whether the theory is capable of explaining the viscosity of gas-mixtures, in particular the interesting fact, that, e.g. for the two above combinations, the viscosity goes through a maximum. In order to derive a formula for the viscosity of mixtures it is necessary first to consider the case of a pure substance. The coefficient 0.44 in the formula for η , used above, is the result of the multiplication of the factor 0.35 which is obtained, when the *persistence* is left out of account, and a persistence-factor $\frac{1}{1 - \frac{1}{2}\vartheta}$, where $\vartheta=0.406$

represents the persistence.

The coefficient $\frac{1}{2}$ in the denominator which is absent in the persistence-factor of the diffusion-formula may be justified as follows¹⁾. When a molecule is traced on its way from the moment that it collides, it is found, that on the average it does not describe a distance l in the direction of motion, before its velocity in this direction is exhausted and therefore all directions become equally probable, but a distance:

$$l + l\vartheta + l\vartheta^2 + \dots = \frac{l}{1-\vartheta}.$$

In the case of viscosity however we are dealing with the transport of momentum: it would on the one hand be incorrect to assume, that the momentum of a molecule at each collision immediately assumes the value belonging to the point where the collision occurs; if that were the case, the persistence would have no influence on the viscosity and would have to be left out of account. On the other hand it cannot be assumed, that the molecule keeps its momentum till the moment, when it has lost its velocity in the direction of motion, and then suddenly, as regards momentum, goes into equilibrium with the neighbouring molecules. It is much more reasonable to assume, that at each collision the excess of momentum is equally distributed over the two molecules: on this supposition the persistence-factor will obviously be given by the series

$$1 + \frac{1}{2}\vartheta + \frac{1}{4}\vartheta^2 + \dots = \frac{1}{1-\frac{1}{2}\vartheta}$$

by which JEANS's result is obtained.

If we now apply this principle to mixtures, it seems natural to suppose, that for collisions between unlike molecules the persistence

¹⁾ J. H. JEANS. Theory of gases p. 249-250. 1904.

has to be multiplied, instead of by the factor $\frac{1}{2}$, by the mass-ratio $\frac{m_1}{m_1+m_2}$ or $\frac{m_2}{m_1+m_2}$ respectively. A rigorous treatment of the problem is impossible, but it would seem that an approximately correct result will be obtained, if in the above formulæ for f the first term in the denominator which refers to collisions between like molecules is given the factor $\frac{1}{2}$, and the second term which depends on the unlike collisions is multiplied by the aforesaid mass-ratio. In this manner the persistence-factors f' which apply in the case of viscosity assume the following form

$$f'_1 = 1 : \left\{ 1 - \frac{1}{2} \sqrt{2} n_1 \pi s_1^2 \left(1 + \frac{C_1}{273} \right) l_1 \times 0.406 - \right. \\ \left. - \frac{m_1}{m_1+m_2} \times n_2 \pi \sigma^2 \sqrt{\frac{m_1+m_2}{m_2}} \left(1 + \frac{C_{12}}{273} \right) l_1 \frac{m_1 - 0.188 m_2}{m_1+m_2} \right\}$$

$$f'_2 = 1 : \left\{ 1 - \frac{1}{2} \sqrt{2} n_2 \pi s_2^2 \left(1 + \frac{C_2}{273} \right) l_2 \times 0.406 - \right. \\ \left. - \frac{m_2}{m_1+m_2} \times n_1 \pi \sigma^2 \sqrt{\frac{m_1+m_2}{m_1}} \left(1 + \frac{C_{12}}{273} \right) l_2 \frac{m_2 - 0.188 m_1}{m_1+m_2} \right\},$$

while the viscosity of the mixture is given by the formula

$$\eta = 0.35 \frac{n_1}{n} d_1 u_1 l_1 f'_1 + 0.35 \frac{n_2}{n} d_2 u_2 l_2 f'_2.$$

For CO_2 and H_2 with $n_1 = n_2 = \frac{1}{2} n$ calculation gives $\eta = 0.0001482$.

The theory therefore actually gives a maximum in the viscosity, in accordance with observation which had not been explained hitherto. The observed maximum lies at 70% CO_2 and is not quite so high viz. about 0.000144, but a nearer agreement could not really be expected.

For argon and helium calculation gives

$$\text{for the mixture } 3:2 \quad \eta = 0.0002294$$

$$,, \quad ,, \quad ,, \quad 1:1 \quad \eta = 0.0002321.$$

Observation gives a maximum near the first named mixture with $\eta = 0.0002207$; in this case the theory gives again too high a value. Whereas therefore a numerical agreement is absent, we may conclude from the investigation that the ordinary gas theory which treats the molecules as mutually attracting elastic spheres can without being strained explain the occurrence of a maximum in the viscosity of the above mixtures.