

On the Calculation of the Thermal Diffusion Constant from Viscosity Data

In a recent issue of this journal a letter¹ appeared in which the value of the thermal diffusion constant² α for various gases was computed from the experimentally determined variation of viscosity with temperature. The method of computation was to assume that all of the molecules in question interact with a force which varies as the inverse s th power of the distance. If the viscosity varies as T^n , then s is given by the relation³

$$s = (2n+3)/(2n-1). \quad (1)$$

The experimental fact that n does vary with the temperature indicates that the assumption of an inverse power law of force is only an approximation to the actual situation. The number s having been determined from viscosity data by Eq. (1), the value of α was then computed from the equation

$$\alpha = \frac{105}{118} \cdot \frac{m_2 - m_1}{m_2 + m_1} \cdot \frac{s-5}{s-1}. \quad (2)$$

This relation is rather questionable, however. It was apparently obtained by noting that for the limiting case in which the lighter molecule is rare, and in which the mass of the lighter molecule is *negligible* in comparison with the mass of the heavier molecule, the value of α is given by $\frac{1}{2}(s-5)/(s-1)$, and then assuming that the expression $(s-5)/(s-1)$ should be a suitable correction factor to apply to the value of α as determined² for the case of isotopes with $s = \infty$. In the case of isotopes, however, the masses are in general *nearly equal*, so that it is preferable to use an expression valid for an inverse power field in this limiting case.

Let the lighter isotope be termed species 1, and the heavier, species 2. We assume that the interactions between two molecules of species 1, between two of species 2, and between one molecule of species 1 and one of species 2, are all identical, and are of the form Kr^{-s} . We may now expand the expression for α given by Enskog⁴ and by Chapman^{5,6} in ascending powers of $(m_2 - m_1)/(m_2 + m_1)$. In the notation of reference 6, we find for the first term of this expansion,⁷

$$\alpha = \frac{(45/2) \{ (m_2 - m_1)/(m_2 + m_1) \} \cdot \{ 2\Omega(1,2) - 5\Omega(1,1) \} \{ 15\Omega(1,1) + 2\Omega(2,2) \}}{\Omega(2,2) \{ 165\Omega(1,1) - 60\Omega(1,2) + 12\Omega(1,3) + 16\Omega(2,2) \}}, \quad (3)$$

where the $\Omega(l,n)$'s are as defined by (26'') and (27'') of reference 6. This expression for α is homogeneous and of order zero in the Ω 's, so that if we wish we may multiply simultaneously all of the Ω 's by any expression whatever that does not depend on l or n . One of the simple choices consistent with this possibility and with (26'') is

$$\begin{aligned} \Omega(1,1) &\rightarrow 1, \\ \Omega(1,2) &\rightarrow 3 - 2/(s-1), \\ \Omega(1,3) &\rightarrow \{ 3 - 2/(s-1) \} \{ 4 - 2/(s-1) \}, \\ \Omega(2,2) &\rightarrow 3 \{ I_2(s)/I_1(s) \} \{ 3 - 2/(s-1) \} = 3f(s), \end{aligned} \quad (4)$$

where $I_1(s)$ and $I_2(s)$ are functions of s defined by certain definite integrals; they have been evaluated⁸ for the following values of s : 2, 3, 5, 7, 9, 11, 15, and ∞ .

The substitution of (4) in (3) yields:

TABLE I. Values of $C(s)$ and $f(s)$ for various values of s .

s	$f(s)$	$C(s)$
3	1.500	0.714
4.5		0.800*
5	1.2918	0.8156
6		0.831*
7	1.2335	0.8431
8		0.852*
9	1.1957	0.8629
10		0.874*
11	1.1631	0.8823
12		0.894*
13		0.898*
14		0.902*
15	1.1248	0.9064
∞	1.	1.

* Obtained by graphical interpolation.

$$\alpha = \frac{105}{118} \cdot \frac{m_2 - m_1}{m_2 + m_1} \cdot \frac{s-5}{s-1} \cdot C(s), \quad (5)$$

where $C(s)$ is the correction factor to be applied to the formula (2) used by Brown:

$$C(s) = \frac{59}{21} \cdot \frac{(15/f) + 6}{43 + 16 \{ f - 1/(s-1) + 1/(s-1)^2 \}}. \quad (6)$$

This function, as well as $f(s)$, is tabulated in Table I. The values indicated by an asterisk were obtained by graphical interpolation from the remaining values.

The correction factor $C(s)$ should be applied to the values of $R_T = \alpha(s)/\alpha(\infty)$ tabulated by Brown.¹ For the only case in which comparison with experiment is possible—that of methane⁹—the experimental value of R_T is 0.29 ± 0.03 ; the value obtained by Brown from (2) is 0.46, and the corrected value (5) is 0.39. The difference between (5) and (2) is not sufficient to invalidate any of the qualitative arguments presented by Brown.

The derivation of (6) of course depends not only on the assumption of an inverse power field, but also on the use of classical theory for the collision processes. Dimensional arguments indicate that, for s considerably larger than two, the wave-mechanical collision cross sections will be practically the same as the classical if the de Broglie wave-length is very small compared with the effective molecular diameter. For thermal energies the ratio λ/d is very roughly equal to $0.2m^{-1/2}$, where m is the molecular weight.

Equation (5) indicates that, within the limitation of the assumptions used in its derivation, the constant α is independent of the temperature.

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¹ Harrison Brown, Phys. Rev. **57**, 242(L) (1940).

² W. H. Furry, R. Clark Jones, and L. Onsager, Phys. Rev. **55**, 1083 (1939).

³ J. H. Jeans, *Dynamical Theory of Gases*, fourth edition (Cambridge, 1925), p. 282.

⁴ D. Enskog, Doctoral Dissertation, Upsala (1917).

⁵ S. Chapman and W. Hainsworth, Phil. Mag. **48**, 593 (1924).

⁶ S. Chapman, Phil. Mag. **7**, 1 (1929).

⁷ This expression was obtained from Eqs. (9) to (16) and (24'') to (27'') of Chapman, reference 6. In making this derivation it is essential to note that according to our assumption about the identical character of the forces one has $(2\mu_2)^{-3}\Omega_{11}(l,n) = (2\mu_1)^{-3}\Omega_{22}(l,n) = \Omega_{12}(l,n) = \Omega(l,n)$. We have received a private communication from Professor H. M. Mott-Smith (University of Illinois) containing a formula equivalent to (3) which he obtained from the formulation of Enskog, reference 4.

⁸ S. Chapman, *Memoirs and Proc. of the Manchester Lit. and Phil. Soc.* **66**, No. 1 (1922).

⁹ A. O. Nier, Phys. Rev. **56**, 1009 (1939).