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Viscosity and Diffusion Coefficients of Atomic Hydrogen and Atomic Deuterium*

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The viscosity of atomic hydrogen has been recalculated from Harteck's experimental values for the relative viscosity of atomic-molecular hydrogen mixtures, on the assumption that atomic hydrogen like molecular hydrogen may be regarded as a van der Waals gas. The numerical results confirm this assumption and permit the evaluation of diffusion coefficients for H-H₂, D-D₂, H-D₂, D-H₂ and D-H binary mixtures as well as the viscosity of atomic deuterium.

IN reaction kinetics investigations involving atomic hydrogen, it is often necessary to know the value of D_{12} , the diffusion coefficient of atomic-molecular hydrogen mixtures, in order to estimate the extent of a wall reaction (determined by the rate at which atoms diffuse to the wall). In dynamic systems, the rate at which atoms disappear by diffusion from a given volume element must be considered as well as the rate at which atoms are being removed by pumping. A knowledge of the value of D_{12} is required for such calculations.

It is the purpose of the present communication to reevaluate the existing data for the viscosity of atomic-molecular hydrogen mixtures in order to obtain the value of η_1 , the viscosity of atomic hydrogen, from which D_{12} may be calculated.

Harteck¹ has determined the viscosities of atomic-molecular hydrogen mixtures of known composition by applying Poiseuille's equation to the flow of such mixtures through a small tube. His measurements, in which molecular hydrogen was used as the reference gas, yielded relative values, η_{mix}/η_2 , at -80° , 0° and 100°C . In calculating the relative viscosity of atomic hydrogen, η_1/η_2 , from his experimental results Harteck used a formula derived by Pulu² which gives the relative viscosity of one component of a binary mixture in terms of the relative viscosities of the other component and of the mixture, and the composition. From the relative values, η_1/η_2 , obtained in this way, Harteck attempted to evaluate η_1 at the three temperatures from the known temperature variation of η_2 . If the viscosity of atomic hydrogen varies with tempera-

ture according to the Sutherland³ formula we have the relation

$$\eta_{1T} = \eta_{10} \frac{1 + (C/273.16)(T/273.16)^{\frac{1}{2}}}{1 + C/T} = \Phi(T/273.16)^{\frac{1}{2}}, \quad (1)$$

where η_{1T} is the viscosity of atomic hydrogen at the absolute temperature T and η_{10} that at 0°C (273.16°A). C is the Sutherland constant for atomic hydrogen. Harteck found that at the three temperatures Φ had the same value within his experimental error and concluded that the value of C was extremely small. He appears, however, to have forgotten the $(T/273.16)^{\frac{1}{2}}$ factor since he gives for the value of η_1 at 0°C the mean of the three Φ values. One gets the impression from this that the viscosity of atomic hydrogen does not vary with temperature whereas inclusion of the $(T/273.16)^{\frac{1}{2}}$ factor shows that η_1 actually does increase with temperature.

It has been considered advisable to recalculate Harteck's results since, in addition to the error indicated above, Pulu's formula does not give results which are in agreement with experiment.

In the present calculation it will be assumed that both atomic and molecular hydrogen are van der Waals gases (gases whose molecules are hard elastic spheres of invariable diameter with attractive forces varying as an inverse power of the distance). This is equivalent to the assumption that the viscosities of these gases can be represented by the Sutherland formula. For molecular hydrogen this is actually the case at the temperatures under consideration. Formulas for the viscosities of the mixtures and of the pure gases considered in these calculations will be consistent with the above assumption. In addi-

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¹ P. Harteck, *Zeits. f. physik. Chemie* **139**, 98 (1928).

² J. Pulu, *Wien. Ber.* **79**, 97, 745 (1879).

³ W. Sutherland, *Phil. Mag.* **36**, 507 (1893).

tion, the recombination of atomic hydrogen to molecular hydrogen need not be considered since the rate of recombination is negligibly slow compared to the rate of momentum transfer which determines the viscosity.

Chapman⁴ has obtained an expression for the viscosity of a binary gas mixture which, expressed in its general form, is independent of the laws of force governing the attraction and repulsion of the molecules. The derivations of Chapman have been subject to corrections by Enskog⁵ giving the expression⁶

$$\eta_{\text{mix}} = \frac{Ax^2 + B2x(1-x) + C(1-x)^2}{Ax^2/\eta_1 + D2x(1-x) + (C/\eta_2)(1-x)^2}, \quad (2)$$

in which

x = mole fraction of component 1 (atomic hydrogen),

$1-x$ = mole fraction of component 2 (molecular hydrogen),

$$A = 1 + kM_1/M_2, \quad (3)$$

$$C = 1 + kM_2/M_1, \quad (4)$$

$$B = (1-k) + \frac{1}{2G} \left(\frac{1}{\eta_1} + \frac{1}{\eta_2} \right), \quad (5)$$

$$D = \frac{(M_1 + M_2)^2 kG}{2M_1M_2} + \frac{1}{2G\eta_1\eta_2}, \quad (6)$$

where
$$\frac{1}{G} = \frac{(M_1 + M_2)}{2} \frac{PD_{12}}{RT}, \quad (7)$$

D_{12} is the diffusion coefficient (at the pressure P) for the mixture, R , the gas constant, M_1 and M_2 , the molecular weights of the respective components.

For elastic spheres with an attractive field (van der Waals molecules)

$$k = 0.600 \frac{1 + 2C_{12}/3T}{1 + C_{12}/T}, \quad (8)$$

where C_{12} , the Sutherland constant for the mixture, is given by^{5a}

$$C_{12} = \frac{\gamma(C_1C_2)^{\frac{1}{2}}}{[\frac{1}{2}((d_1/d_2)^{\frac{1}{2}} + (d_2/d_1)^{\frac{1}{2}})]^{\nu-1}}; \quad (9)$$

ν is the exponent in the expression for the

attractive force, $F = a/r^\nu$, and γ a constant which is a function of ν having the following values:

ν	3	4	5	7	9
γ	1.140	1.073	1.028	0.968	0.929.

C_1 and C_2 are the Sutherland constants for the pure gases and d_1 and d_2 , the respective molecular diameters. In order to use the above expressions in actual calculations it is necessary to know the value of D_{12} . As a first approximation Enskog^{5a} gives a formula in which it is considered as being independent of the composition of the mixture. Actually the value changes slightly with composition. If we let the approximate value be D_0 , then

$$D_{12} = D_0 f(x) = D_0 f'(\alpha),$$

where α is the degree of dissociation of molecular hydrogen into atoms, in which case $x = 2\alpha/(1+\alpha)$ and $1-x = (1-\alpha)/(1+\alpha)$. The actual dependence of D_{12} upon composition is quite small. Enskog^{5a} has evaluated $f(x)$ for the case of elastic spheres without attractive forces and finds that the calculated dependence is confirmed by experiments on real gas mixtures indicating that $f(x)$ is not appreciably different for a gas of van der Waals molecules than for a gas of elastic spheres without attractive forces. According to Enskog, when $(1-x)/x = 0 (\alpha = 1)$

$$D_{12} = D_0 \left(1 + \frac{M_1^2}{2(6M_1^2 + 8M_1M_2 + 15M_2^2)} \right) = 1.0061D_0$$

and when $x/(1-x) = 0 (\alpha = 0)$

$$D_{12} = D_0 \left(1 + \frac{M_2^2}{2(15M_1^2 + 8M_1M_2 + 6M_2^2)} \right) = 1.0364D_0.$$

Thus, the value of D_{12} changes by only three percent over the entire composition range. In view of this small variation it will be sufficiently accurate for the present purpose to let

$$f'(\alpha) = a + b\alpha,$$

where a and b , evaluated from the fact that $f'(\alpha) = 1.0016$ for $\alpha = 1$ and 1.0364 for $\alpha = 0$, are equal to 1.0364 and -0.0303 . Using Enskog's expression for D_0 for a van der Waals gas

⁴ S. Chapman, Phil. Trans. Roy. Soc. A211, 433 (1912); A216, 279 (1915); A217, 115 (1917).

⁵ D. Enskog, (a) Inaug. Diss. Uppsala, 1917; (b) Arkiv. for Mat., Astron. och Fysik 16, No. 16 (1921).

⁶ M. Trautz, Ann. d. Physik (5) 18, 816 (1933).

mixture we obtain finally

$$D_{12} = \frac{3R^{\frac{1}{2}}T^{\frac{1}{2}}}{8(2\pi)^{\frac{1}{2}}N((d_1+d_2)/2)^2(1+C_{12}/T)} \times \left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{\frac{1}{2}} \frac{1}{P}(1.0364 - 0.0303\alpha), \quad (10)$$

where N is Avogadro's number. Upon substituting the value of D_{12} from Eq. (10) into Eq. (7) we obtain

$$\frac{1}{G} = \frac{3(M_1+M_2)^{\frac{1}{2}}R^{\frac{1}{2}}T^{\frac{1}{2}}(1.0364 - 0.0303\alpha)}{16(2\pi)^{\frac{1}{2}}(M_1M_2)^{\frac{1}{2}}N\left(\frac{d_1+d_2}{2}\right)^2\left(1+\frac{C_{12}}{T}\right)}. \quad (11)$$

To evaluate $1/G$ it is necessary to know the values of d_1 and d_2 . The quantity d_2 may be computed directly from measured values of η_2 . In order to determine d_1 we shall assume as a first approximation that we are dealing with elastic spheres without attractive forces and solve for η_1 (using Harteck's measured values of η_{mix}/η_2). For this calculation it is possible to use rigorous expressions (analogous to Eq. (2)) derived by Enskog.^{5a} In such expressions C_{12} obviously does not appear so that by a series of successive approximations it is possible to calculate consistent values of η_1 and d_1 . In this manner it is found that at 0°C , $d_2 = 2.71 \times 10^{-8}$ cm and $d_1 = 2.49 \times 10^{-8}$ cm. The value of η_2 in this calculation is given by the relation

$$\eta_2 = \frac{5.882 \times 10^{-6} T^{\frac{1}{2}}}{1 + 35.8/T}, \quad (12)$$

obtained by F. G. Keyes (unpublished data) by applying the method of least squares to the existing viscosity data for hydrogen. Eq. (12), however, is the form assumed by the viscosity expression for attracting elastic spheres. The rigorous expression given by Enskog^{5a} is

$$\eta = \frac{5 \times 1.016}{16} \left(\frac{RTM}{\pi}\right)^{\frac{1}{2}} \frac{1}{Nd^2(1+C/T)}. \quad (13)$$

As a second approximation in determining d_1 we may determine d_2 from Eq. (13) (in this case, the diameter does not change with temperature), and assume that the ratio d_1/d_2 is the same for attracting elastic spheres as for nonattracting elastic spheres. This assumption is equivalent to

the assumption that the Sutherland constant for atomic hydrogen is essentially the same as that for molecular hydrogen. We may check our approximate value of d_1 (as well as C_1) when we have finally calculated η_1 from Eq. (2), by means of Eq. (13). This almost amounts to an independent check since Eq. (2) defines the composition dependence and Eq. (13) the temperature dependence of the viscosity coefficient.

In Keyes' expression for η_2 , the Sutherland constant, 35.8 is much smaller than the values found in the literature which vary from 70 to 83. There are two reasons for preferring 35.8 as the correct value. First, this value was obtained by the method of least squares applied to over 50 viscosity values in the temperature range -200° to $+300^\circ\text{C}$, whereas the high values in the literature are calculated from a small number of viscosity values over a narrow temperature range. Second, the relation between the Sutherland constant and equation of state data clearly indicates that the small value is more reasonable.

We may write the equation of state for a van der Waals gas at not too great pressure in the form⁷

$$P(V - B_0) = RT,$$

where B_0 is given by the expression

$$B_0 = -2\pi N \int_0^\infty (e^{-\text{Pot}/kT} - 1)r^2 dr. \quad (14)$$

In evaluating the integral it must be remembered that under the assumption of a van der Waals gas the intramolecular potential energy "Pot" becomes infinite on contact of two molecules making the integrand zero for all values of r from 0 to d , the diameter of a single molecule. A series integration of Eq. (14) gives the result

$$B_0 = \frac{2}{3}\pi Nd^3 - \frac{2\pi aN}{18d^3kT} + \dots \quad (15)$$

if the potential energy is represented by $-a/r^6$ in accordance with an attractive force a/r^7 . Since

$$B_0 = \beta - A/RT \quad (16)$$

we have the relations

⁷ F. G. Keyes, Chem. Rev. **6**, 175 (1929); F. G. Keyes, L. B. Smith and H. T. Gerry, Proc. Am. Acad. **70**, 319 (1936).

TABLE I.

$T(^{\circ}\text{A})$	η_{mix}/η_2	α	$\eta_2 \times 10^6$	$1/G \times 10^6$	k	A	B	C	D	$\eta_1 \times 10^6$
193.16	0.966	0.650	69.0	84.4	0.572	1.286	$1.040 + 42.2 \times 10^{-6}/\eta_1$	2.144	$1.525 \times 10^4 + 0.612/\eta_1$	65.3
273.16	0.883	0.637	86.0	104.8	0.579	1.290	$1.030 + 52.4 \times 10^{-6}/\eta_1$	2.158	$1.243 \times 10^4 + 0.609/\eta_1$	69.4
373.16	0.886	0.591	103.7	126.1	0.584	1.292	$1.024 + 63.0 \times 10^{-6}/\eta_1$	2.168	$1.042 \times 10^4 + 0.608/\eta_1$	83.2

$$\beta = \frac{2}{3} \pi N d^3, \quad A = \frac{1}{9} \frac{\pi a N^2}{d^3},$$

where higher series terms in Eqs. (15) and (16) have been neglected. To evaluate C in terms of β and A we make use of the relation derived by Enskog^{5a}

$$C = \frac{2\delta Na}{3(\nu-1)d^{\nu-1}R},$$

where, for the present case of $\nu=7$ ($F=a/r^7$), $\delta = \frac{1}{2} \times 0.5165$, so that

$$C = 0.5165 Na / 3 \times 6 R d^6 = 2.1 \times 10^{-9} A / \beta. \quad (17)$$

For hydrogen the values of A and β are 0.2001×10^{12} ergs \times cc per mole and 20.96 cc per mole, respectively,⁸ so that C calculated from Eq. (17) has the value 20.0.

From Eq. (12) we find that $\eta_2 = 86.0 \times 10^{-6}$ poises at 273.16 $^{\circ}$ A, so that d_2 calculated from Eq. (13) is 2.55×10^{-8} cm. The assumed value for d_1 , therefore, is $(2.55 \times 2.49 / 2.71) \times 10^{-8}$ cm or 2.34×10^{-8} cm. In order to evaluate C_{12} from Eq. (9) C_1 is determined from the relation indicated by Keyes,⁹ namely, that for nonpolar gases

$$C = K P_0,$$

where P_0 is the molecular polarization and K , a constant which is independent of the gas. For molecular hydrogen $P_0 = 2.00^{10}$ while for atomic hydrogen the calculated value is 1.68^{11} so that

$$C_1 = 35.8 \times 1.68 / 2.00 = 30.1.$$

Substituting the proper values in Eq. (9) we find that $C_{12} = 31.6$. We are now in position to calculate η_1 from Eq. (2). Table I contains the

results of this calculation as well as the values of the constants calculated from Eqs. (3), (4), (5), (6), (8) and (11). The values of η_{mix}/η_2 and α are taken from Harteck's paper.¹

It is now possible to use the calculated values of η_1 to determine C_1 and d_1 from Eq. (13) as a check upon the values assumed for use in Eq. (2). For this purpose only the η_1 values at 273.16 $^{\circ}$ and 373.16 $^{\circ}$ A will be used, since the value at 193.16 $^{\circ}$ A may be in considerable error as pointed out by Harteck.¹ At this temperature, the capillary used in the experiments became coated with a sheath of ice because of the fact that the atomic-molecular hydrogen mixture contained water vapor to poison the walls against recombination. In addition, Harteck states that at this low temperature the enhanced recombination prevented the gas mixture from assuming the temperature of the surrounding bath (-80° C). Both effects would tend to make η_{mix}/η_2 (and consequently, η_1) too high, in agreement with the high experimental value, 0.966. It is estimated that this value may be in error by as much as ten percent. Solving Eq. (13) simultaneously for C_1 and d_1 by substitution of the last two η_1 values of Table I, we find that $C_1 = 28.2$ and $d_1 = 2.42 \times 10^{-8}$ cm, in good agreement with the provisionally assumed values 30.1 and 2.34×10^{-8} cm. It is now possible to make a second calculation of η_1 values from Eq. (2), using the values of C_1 and d_1 obtained as a result of the first calculation. These approximations may be repeated until subsequent variations in C_1 and d_1 produce changes of less than one percent in the values of η_1 . This accuracy is at least as great as that of the experimental η_{mix}/η_2 values at 273.16 $^{\circ}$ and 373.16 $^{\circ}$ A. Table II summarizes the results of a series of such successive approximations, where approximation I is the calculation represented by Table I. Further approximations result in η_1 values that vary within the limits of the last three above approximations; accordingly, we may take as our final values for C_1 and d_1 those

⁸ J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. 63, 229 (1928).

⁹ F. G. Keyes, Zeits. f. physik. Chemie, *Cohen Festband*, 709 (1927).

¹⁰ This value is a weighted mean of many experimental values derived from dielectric constant measurements. References are given in J. H. Van Vleck's *Theory of Electric and Magnetic Susceptibilities* (Oxford Press, 1932), p. 67.

¹¹ J. H. Van Vleck, reference 10, p. 205.

TABLE II.

Approx.	$d_1 \times 10^8$	C_1	$\eta_1 \times 10^6$ (193.16°A)	$\eta_1 \times 10^6$ (273.16°A)	$\eta_1 \times 10^6$ (373.16°A)
I	2.34	30.1	65.3	69.4	83.2
II	2.42	28.2	66.7	70.9	85.4
III	2.37	34.0	66.1	70.2	84.3
IV	2.40	30.2	66.4	70.8	85.1
V	2.38	31.7	66.0	70.3	84.5
VI	2.39	31.4	66.2	70.5	84.9

values which most closely reproduce the mean of the last three sets of values (values at 193.16°A, of course, are not considered although they have been calculated for the sake of completeness). On this basis the best values are $d_1 = 2.39 \times 10^{-8}$ cm and $C_1 = 30.6$, corresponding to η_1 values of 70.5×10^{-6} and 84.7×10^{-6} .

On the basis of Harteck's experimental results, therefore, we may represent the viscosity of atomic hydrogen from 0° to 100°C by

$$\eta_1 = \frac{4.746 \times 10^{-6} T^{\frac{1}{2}}}{1 + 30.6/T}.$$

In like manner, we may calculate the diffusion coefficient for a mixture of atomic and molecular hydrogen from Eq. (10). For $d_1 = 2.39 \times 10^{-8}$ cm and $C_1 = 30.6$, C_{12} calculated from Eq. (9) is 31.9 so that the expression for the diffusion coefficient becomes

$$D_{12} = \frac{374.9 T^{\frac{1}{2}} (1.0364 - 0.0303\alpha)}{P(1 + 31.9/T)},$$

where P is expressed in dynes/cm².

Kinetic studies on the relative recombination rate of atomic hydrogen and atomic deuterium¹² indicate that the diameters and attractive forces are equal for hydrogen and deuterium atoms. The coefficient of viscosity for atomic deuterium, therefore, should be $\sqrt{2}$ times that of atomic hydrogen because of the greater mass of the deuterium atom, or

$$D = \frac{6.711 \times 10^{-6} T^{\frac{1}{2}}}{1 + 30.6/T}.$$

In the case of *molecular* hydrogen and deuterium this $\sqrt{2}$ ratio for the coefficient of viscosity has been experimentally verified¹³ indicating in this

TABLE III.

MIXTURE	DIFFUSION COEFFICIENT
D-D ₂	$\frac{265.1 T^{\frac{1}{2}} (1.0364 - 0.0303x)}{P(1 + 31.9/T)}$
H-D ₂	$\frac{342.2 T^{\frac{1}{2}} (1.0559 - 0.0541x)}{P(1 + 31.9/T)}$
D-H ₂	$\frac{306.1 T^{\frac{1}{2}} (1.0172 - 0.0x)}{P(1 + 31.9/T)}$
H-D	$\frac{400.4 T^{\frac{1}{2}} (1.0364 - 0.0303x)}{P(1 + 30.6/T)}$

case, also, an equality of molecular diameters and attractive forces for the two isotopes. With this information it is possible to calculate the diffusion coefficients for all possible binary mixtures of atomic and molecular hydrogen and deuterium by substituting the proper values for M_1 and M_2 in Eq. (10) and in the Enskog expressions giving the concentration dependence of the diffusion coefficient. The result of such substitution is given in Table III. In each case x represents the mole fraction of the first (lighter) component. Since the concentration dependence is small, it makes little difference that in the above expressions α , the degree of dissociation, has been replaced by x , the mole fraction. The quantity, α , was used previously since slightly better agreement with Enskog's rigorous elastic sphere formula was obtained thereby. In view of the fact that we have assumed that the concentration dependence for our van der Waals gas is the same as that for a gas of hard elastic spheres, and since the use of α or x gives values within 0.2 percent on either side of those obtained from Enskog's formula, it seems desirable to make Eq. (10) general by the use of x .

Although Harteck's relative viscosity values furnish an experimental basis for the present expressions only from 0° to 100°C, it seems quite probable that use of the formulas beyond this temperature range will give fairly accurate (one percent or better) values for the viscosity and diffusion coefficients. This prediction is based on the fact that the Sutherland expression for molecular hydrogen (with the corrected value of C) holds from -200° to +300°C and that atomic hydrogen may be regarded as a van der Waals gas with a diameter and attractive force almost equal to that of molecular hydrogen.

¹² I. Amdur, J. Am. Chem. Soc. **57**, 856 (1935).

¹³ I. Amdur, J. Am. Chem. Soc. **57**, 588 (1935).