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Low Temperature Transport Properties of Gases. I. Helium

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Values have been computed for the viscosity, thermal conductivity, and coefficient of self-diffusion of gaseous helium for temperatures below 200°K by application of classical scattering theory within angular regions where diffraction effects are absent. Values of classical total collision cross sections are obtained which are used to evaluate classical cross sections for viscosity, thermal conductivity, and self-diffusion appropriate to a Maxwellian gas. Numerical values of the transport properties are obtained by substitution of the appropriate classical cross sections into the exact transport property formulas of Chapman and Enskog.

In the region 200°–14°K, the average absolute deviations between calculated and experimental values are 1.9 percent for viscosity and 4.6 percent for thermal conductivity. Extrapolation of calculated viscosity values to 1.64°K appears to be justified on the basis of agreement with experimental values. It cannot be stated that similar extrapolation in the case of thermal conductivity is valid because of possible uncertainties in the experimental values between 3.95° and 1.62°K. Values of the self-diffusion coefficient have been calculated between 200° and 5°K, but experimental values are not available for comparison.

VISCOSITY AND THERMAL CONDUCTIVITY

IN recent years the viscosity and thermal conductivity of helium gas at low temperatures have been calculated by applying the quantum theory of scattering to the computation of the appropriate transport cross sections. Massey and Mohr¹ were able to reproduce observed viscosities between 15° and 300°K with a maximum deviation of 7 percent, by treating the helium atom as a hard sphere with a diameter of 2.10Å. In a later paper,² they eliminated the undesirable feature of assuming an arbitrary hard sphere diameter by using an approximation to the Slater-Kirkwood interaction potential between two helium atoms.³ The calculated viscosities in this case exceed the measured values by 6 percent at 300°K and by 22 percent at 15°K. Massey and Buckingham⁴ assumed that the interaction potential was 1.30 times that computed by Slater and Kirkwood and computed viscosities in the range 0–26°K on the basis of Bose-Einstein and Fermi-Dirac statistics. Their values agree within 3 percent above 15°K, but are in error by 16 percent at 4.23°K and by 36 percent at 1.64°K. On the basis of a Lennard-Jones type

potential deduced from equation of state measurements, Uehling and Hellund⁵ were able to predict viscosities at 4.23°K and at 273°K within 0.6 percent and 2.6 percent, respectively. A previous calculation by Uehling⁶ of viscosities in the range 15°–300°K, using a hard sphere model, gave results in agreement with those obtained by Massey and Mohr.¹ He also calculated thermal conductivities in the range 20°–320°K with the same model, but was unable to obtain agreement closer than 33 percent at the lowest temperature. Much better agreement, about 3 percent, was obtained by deBoer⁷ who calculated thermal conductivities in the narrow temperature region, 1.6°–2.8°K, using a Lennard-Jones form of potential, although his value for the viscosity at 1.64°K is in error by 25 percent.

It is the purpose of the present paper to show that a proper application of classical methods can be used to calculate viscosities and thermal conductivities for helium in the range 14°–200°K with good accuracy, and possibly to obtain values down to 1.62°K by extrapolation. The method involves the calculation of classical transport cross sections, taking into account the range of interaction distance in which classical theory does not apply. These cross sections are then inserted into classical expressions developed

¹ H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A141**, 434 (1933).

² H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A144**, 188 (1934).

³ J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

⁴ H. S. W. Massey and R. A. Buckingham, Proc. Roy. Soc. **A168**, 378 (1938); **A169**, 205 (1938).

⁵ E. A. Uehling and E. J. Hellund, Phys. Rev. **54**, 479 (1938).

⁶ E. A. Uehling, Phys. Rev. **46**, 917 (1934).

⁷ J. deBoer, Physica **10**, 348 (1943).

by Chapman⁸ and by Enskog⁹ to obtain numerical values of the transport properties as functions of temperature.

Classical values for the cross sections effective in viscosity and thermal conductivity can be obtained from classical values of the total collision cross section whose significance can be illustrated as follows: if a stream of N atoms per unit area per second impinges upon a single atom, the number of atoms from the stream deflected per second between angles Θ and $\Theta + d\Theta$ is equal to $2\pi NG(\Theta)d\Theta$, where $G(\Theta)$ is the solid angle scattering coefficient, and Θ , the angle through which the direction of the relative initial velocity, v , of the colliding particles, is turned by collision. The use of the relative coordinates, Θ and v , is equivalent to considering the single scatterer held fixed at all times, instead of free to move before and after collision. The classical total collision cross section, S , may be defined^{1,10} as

$$S = 2\pi \int_{\Theta_c}^{\pi} G(\Theta) \sin \Theta d\Theta \\ = 2\pi \int_{b \text{ at } \Theta_c}^{b \text{ at } \pi} b db = \pi [b(\Theta_c)]^2, \quad (1)$$

where Θ_c is the critical relative angle below which classical theory does not apply. This angle may be set equal to $\lambda/(2r_0)$ where λ is the de Broglie wave-length of the colliding system and r_0 the distance of closest approach of the center of a particle in the stream to the center of the scatterer. The wave-length, λ , is equal to $h/(\mu v)$ where h is Planck's constant and μ the reduced mass of the colliding system. For like particles of mass m , μ is $m/2$. The defining equation for $b(\Theta_c)$, the impact parameter, is

$$\left[1 - \frac{V(r_0)}{\frac{1}{2}\mu v^2} \right] r_0^2 = [b(\Theta_c)]^2. \quad (2)$$

In the present application, the mutual potential energy at the distance of closest approach, $V(r_0)$ will be small compared with the relative

kinetic energy, $\frac{1}{2}\mu v^2$, so that r_0 will be nearly equal to $b(\Theta_c)$.

Since the critical angle, Θ_c , is small, it is permissible to use the small angle formula given by Kennard,¹⁰ namely

$$\Theta_c = 2r_0/(uv^2) \int_{r_0}^{\infty} \frac{[V(r_0) - V(r)]r dr}{(r^2 - r_0^2)^{\frac{3}{2}}}. \quad (3)$$

Substituting $\Theta_c = h/(2\mu v r_0)$ into Eq. (3), we obtain

$$v = 4r_0^2/h \int_{r_0}^{\infty} \frac{[V(r_0) - V(r)]r dr}{(r^2 - r_0^2)^{\frac{3}{2}}}. \quad (4)$$

In order to calculate the classical total collision cross section, S , as a function of the relative velocity, v , it is necessary to express the potential energy $V(r)$ as a suitable function of the separation distance, r . Margenau¹¹ has computed such functions for helium by extending the calculations of Slater and Kirkwood to include second-order exchange forces as well as dipole-quadrupole and quadrupole-quadrupole interactions. The potential which will be used for the present calculations is that given by Margenau in his 1939 paper, with an additional small quadrupole-quadrupole term computed by him in the earlier paper. It has the form

$$V(r) = \left[7.70e^{-4.60r} - 5.60e^{-5.33r} \right. \\ \left. - \frac{0.0139}{r^6} - \frac{0.030}{r^8} - \frac{0.035}{r^{10}} \right] \times 10^{-10} \text{ erg}, \quad (5)$$

where r is in angstrom units. This function should be quite accurate for separation distances near the minimum, about 2.9A, and should yield accurate cross sections corresponding to distances not too far removed from this value. It is this fact which limits the present calculations to an upper temperature limit of 200°K corresponding to a separation distance of 2.34A. Since the function in Eq. (5) was evaluated largely from theoretical considerations without recourse to experimental results on the equation of state or transport properties of helium, it seems preferable to limit the present calculations to temperatures

⁸ S. Chapman, Phil. Trans. Roy. Soc. **A211**, 433 (1912); **A216**, 279 (1915); **A217**, 115 (1917).

⁹ D. Enskog, Inaug. Diss. Upsala, 1917.

¹⁰ E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), Chapter III.

¹¹ H. Margenau, Phys. Rev. **38**, 747 (1931); **56**, 1000 (1939).

TABLE I. Classical total collision cross section of helium.

r_0 , Å	v , 10^6 cm/sec.	$b(\Theta_c)$, Å	S , Å ²
2.30	3.18	2.28	16.33
2.33	2.66	2.31	16.78
2.35	2.32	2.33	17.09
2.38	1.87	2.37	17.60
2.40	1.60	2.39	17.97
2.43	1.23	2.45	18.87
2.45	1.02	2.49	19.43
2.48	0.729	2.61	21.37
2.50	0.559	2.75	23.83

below 200°K rather than to extend the range by empirical variation of the potential energy function. Agreement between calculated and experimental values of viscosity and thermal conductivity will then tend to serve as independent confirmation of the accuracy of Margenau's calculations.

The potential given by Eq. (5) is of the general form

$$V(r) = Ae^{-ar} - Be^{-br} - \frac{C}{r^x} - \frac{D}{r^y} - \frac{E}{r^z}. \quad (6)$$

Methods for evaluating the integral in Eq. (4) for a potential of this form have been worked out by Amdur and Pearlman¹² and by Kennard¹⁰ and lead to the result

$$v = \frac{Aa^{\frac{1}{2}}(2r_0)^{\frac{1}{2}}e^{-ar_0}}{h} \sum_{n=0}^{\infty} (-1)^n \binom{-\frac{1}{2}}{n} \times \frac{1}{(2ar_0)^n} \Gamma(n + \frac{1}{2}) - \frac{Bb^{\frac{1}{2}}(2r_0)^{\frac{1}{2}}e^{-br_0}}{h} \times \sum_{n=0}^{\infty} (-1)^n \binom{-\frac{1}{2}}{n} \frac{1}{(2br_0)^n} \Gamma(n + \frac{1}{2}) - \frac{4xK_x C}{h(r_0)^{x-1}} - \frac{4yK_y D}{h(r_0)^{y-1}} - \frac{4zK_z E}{h(r_0)^{z-1}}, \quad (7)$$

where K_x , K_y , and K_z may be computed from the general relation

$$K_i = \frac{2 \cdot 4 \cdots (i-1 + \delta_i^1)}{1 \cdot 3 \cdots i} \text{ for odd } i$$

$$(\delta_i^1 = 1 \text{ if } i = 1 \text{ but otherwise} = 0),$$

$$= \frac{1 \cdot 3 \cdots (i-1)}{2 \cdot 4 \cdots i} \frac{\pi}{2} \text{ for even } i. \quad (8)$$

¹² I. Amdur and H. Pearlman, J. Chem. Phys. 9, 503 (1941).

The summations in Eq. (7) do not converge, but the first part of each series is an asymptotic expression for the contribution of the corresponding portions of the interaction potential to the relative velocity. By taking only the first few terms of each series, therefore, this portion of the relative velocity may be computed quite accurately for values of ar_0 or br_0 greater than about 3. For example, in the present case, only two terms of each series are required for an accuracy better than 0.15 percent, since the values of ar_0 and br_0 which are of interest lie between 7 and 14.

Under these conditions, Eq. (7) reduces to

$$v = \left(\frac{\pi r_0}{8a} \right)^{\frac{1}{2}} \frac{A}{h} (8ar_0 - 1) e^{-ar_0} - \left(\frac{\pi r_0}{8b} \right)^{\frac{1}{2}} \frac{B}{h} (8br_0 - 1) e^{-br_0} - \frac{4xK_x C}{h(r_0)^{x-1}} - \frac{4yK_y D}{h(r_0)^{y-1}} - \frac{4zK_z E}{h(r_0)^{z-1}}. \quad (9)$$

The calculation procedure may be outlined as follows:

(A) Values of v are computed from Eq. (9) for given values of r_0 by substituting the numerical values of the constants as given in Eq. (5).

(B) Since Eq. (9) is valid only for $\Theta = \Theta_c$, the values of r_0 chosen in (A) are substituted into Eq. (2) to obtain values of $b(\Theta_c)$.

(C) The above values of $b(\Theta_c)$, as functions of v , are inserted into Eq. (1) to yield values of S as functions of v .

A summary of such calculations for helium is given in Table I.

In order to compute values of the viscosity, η , and the thermal conductivity, K , it is necessary to obtain values for the classical cross section for viscosity and thermal conductivity, $S_{\eta, K}$, as a function of the relative velocity, v . For *hard spheres*^{1,10} the classical total collision cross section is given by

$$S = 2\pi \int_0^\pi G(\Theta) \sin \Theta d\Theta$$

$$= 2\pi \int_0^\pi \left(\frac{1}{4} r_0^2 \right) \sin \Theta d\Theta = \pi r_0^2 \quad (10)$$

and the classical cross section for viscosity and

thermal conductivity by

$$S_{\eta, K} = 2\pi \int_0^\pi G(\Theta) \sin^3 \Theta d\Theta \\ = 2\pi \int_0^\pi (\frac{1}{4} r_0^2) \sin^3 \Theta d\Theta = \frac{2}{3} \pi r_0^2. \quad (11)$$

It will be assumed that, for any given value of v , the above ratio of $S_{\eta, K}/S = \frac{2}{3}$ holds for particles which do not possess a hard sphere interaction potential. Actually, this assumption is implied in the concept of *equivalent hard sphere* diameters which depend upon the relative velocity. Since it is possible to represent the results of Table I with an average absolute deviation of 0.8 percent and a maximum deviation of 1.6 percent by the relation

$$S = 14.70 + \frac{5.06 \times 10^5}{v} \text{ A}^2 \quad (v \text{ in cm/sec.}), \quad (12)$$

the dependence of $S_{\eta, K}$ upon v will be given by

$$S_{\eta, K} = 9.80 + \frac{3.37 \times 10^5}{v} \text{ A}^2. \quad (13)$$

For a single gas, the classical expression for the viscosity is^{8,9}

$$\eta = \frac{5}{16} \frac{(1 + \epsilon)(\pi MRT)^{\frac{1}{2}}}{NQ_{\eta, K}}, \quad (14)$$

where M is the molecular weight, R , the gas constant per mole, N , Avagadro's number, and $Q_{\eta, K}$, the classical cross section for viscosity and thermal conductivity for a Maxwellian gas at temperature, T , defined by

$$Q_{\eta, K} = \frac{M^4}{512 R^4 T^4} \int_0^\infty v^7 S_{\eta, K} e^{-Mv^2/(4RT)} dv. \quad (15)$$

The quantity ϵ is 0 for a gas whose molecules possess an inverse fourth power repulsive potential (inverse fifth power repulsive force) and 0.016 for a gas of hard spheres. The latter value will be used as the more suitable approximation for helium. If the expression for $S_{\eta, K}$ given in Eq. (13) is substituted into Eq. (15) with appropriate numerical values for the constants, evaluation of the integral gives the dependence of $Q_{\eta, K}$ in the form

$$Q_{\eta, K} = 14.70 + \frac{30.80}{T^{\frac{1}{2}}} \text{ A}^2. \quad (16)$$

The final equation for η is obtained by combining Eqs. (14) and (16) to give

$$\eta = \frac{1.16 \times 10^{-5} T}{2.10 + T^{\frac{1}{2}}} \frac{\text{g}}{\text{sec. cm}}. \quad (17)$$

For a monatomic gas, the thermal conductivity,

TABLE II. Comparison of calculated and observed values of viscosity and thermal conductivity.

T (°K)	$Q_{\eta, K}$ (A ²)	$\eta_{\text{exp}} \times 10^5$ ($\frac{\text{g}}{\text{sec. cm}}$)	$\eta_{\text{cal}} \times 10^5$ ($\frac{\text{g}}{\text{sec. cm}}$)	$100 \left \frac{\Delta \eta}{\eta_{\text{exp}}} \right $ (%)	$K_{\text{exp}} \times 10^5$ ($\frac{\text{cal}}{\text{sec. cm deg.}}$)	$K_{\text{cal}} \times 10^5$ ($\frac{\text{cal}}{\text{sec. cm deg.}}$)	$100 \left \frac{\Delta K}{K_{\text{exp}}} \right $ (%)
200	16.87	14.960	14.29	4.5			
194.6	16.91				26.09	26.6	2.0
190	16.93	14.460	13.88	4.0			
180	17.00	13.950	13.45	3.6			
170	17.06	13.430	13.02	3.0			
160	17.13	12.900	12.58	2.5			
150	17.21	12.365	12.12	2.1			
140	17.30	11.815	11.66	1.4			
130	17.40	11.255	11.17	0.8			
120	17.51	10.680	10.67	0.1			
110	17.64	10.095	10.14	0.4			
100	17.78	9.470	9.59	1.3			
90	17.95	8.845	9.01	1.9			
89.4	17.96				16.5	16.9	2.4
80	18.14	8.205	8.41	2.5			
76.3	18.23				14.6	15.2	4.1
70.9	21.44				6.35	6.83	7.6
20.38	21.52	3.523	3.51	0.4			
20.1	21.57				6.24	6.66	6.7
18.0	21.96				5.85	6.19	5.8
16.8	22.21				5.61	5.91	5.3
16.55	22.27	3.147	3.11	1.2			
14.7	22.73				5.26	5.40	2.7
14.21	22.87	2.846	2.81	1.3			
4.23	(29.68)	1.277	(1.18)				
3.94	(30.22)				1.95	(2.10)	
3.25	(31.78)				1.58	(1.82)	
2.78	(33.17)				1.33	(1.61)	
2.00	(36.48)				0.92	(1.24)	
1.64	(38.75)	0.549	(0.56)				
1.62	(38.90)				0.79	(1.05)	

K , may be written

$$K = (1 + \delta)^{\frac{5}{2}} \eta c_v^{8.9}, \quad (18)$$

where c_v is the specific heat at constant volume which will be set equal to $3R/2M$. The value of δ lies between zero, for a gas with an inverse fourth power repulsive potential, and 0.01, for a gas of hard spheres. The hard sphere value will be used, as in the case of viscosity, so that, upon inserting values for R and M ,

$$K = 1.88 \eta \frac{\text{cal}}{\text{sec. cm deg.}} \quad (19)$$

where η is in $\frac{\text{g}}{\text{sec. cm}}$.

In Table II values of η and K , calculated from Eqs. (17) and (19) are compared with experimental viscosity values of van Itterbeek and Keesom¹³ (1.64°–20.38°K) and of Johnston and Grilly¹⁴ (80°–200°K), and with experimental thermal conductivity values of Ubbink and de Haas¹⁵ (1.62°–89.4°K) and of Eucken¹⁶ (194.6°K). In the range 1.62°–4.23°K, calculated values appear in parentheses since they represent extrapolations beyond the region of demonstrable validity of Eq. (3), the small angle formula which is the basis of the present calculations.

Above the extrapolated region, the average absolute deviation of the calculated η values is 1.9 percent and that of the calculated K values, 4.6 percent. It is interesting that the agreement of the extrapolated thermal conductivities is considerably poorer than that of the extrapolated viscosities. This may be due to several causes, such as low experimental K values, appreciable departure of c_v from the ideal gas value of $(3/2)(R/M)$, or failure of the relation in Eq. (18). In the opinion of the author, it is quite likely that the experimental values are low since the helium pressures (1–4 mm) in the thermal conductivity apparatus may well have

been insufficient to yield pressure independent values of K . In fact, Ubbink and de Haas state that, in the liquid helium temperature region, they were unable to test their measured values properly for pressure independence. Although extrapolation seems justified for viscosity, additional experimental results on the thermal conductivity below 4°K appear necessary to determine the validity of extrapolation in the case of thermal conductivity.

COEFFICIENT OF SELF-DIFFUSION

Although experimental values of the coefficient of self-diffusion of helium are not available, it seems desirable, for the sake of completeness, to obtain calculated values by procedures similar to those used for viscosity and thermal conductivity.

The classical expression for the coefficient of self-diffusion, $D(1, 1)$, is^{8,9}

$$D(1, 1) = -\frac{3(1+\epsilon)(\pi MRT)^{\frac{1}{2}}}{8 N \rho Q_{D(1,1)}}, \quad (20)$$

where ϵ is the small correction term previously encountered in the expression for η , ρ , the gas density in grams per unit volume, and $Q_{D(1,1)}$, the classical cross section for self-diffusion for a Maxwellian gas at temperature T defined by

$$Q_{D(1,1)} = \frac{M^3}{32R^3T^3} \int_0^\infty v^5 S_{D(1,1)} e^{-Mv^2/(4RT)} dv. \quad (21)$$

The classical cross section for self-diffusion, $S_{D(1,1)}$, which appears in Eq. (21) is given, for hard spheres, by^{1,10}

$$\begin{aligned} S_{D(1,1)} &= 2\pi \int_0^\pi G(\Theta) \sin^2 \frac{\Theta}{2} \sin \Theta d\Theta \\ &= 2\pi \int_0^\pi \left(\frac{1}{4}r_0^2\right) \sin^2 \frac{\Theta}{2} \sin \Theta d\Theta = \frac{1}{2}\pi r_0^2, \end{aligned} \quad (22)$$

and since it will be assumed that the hard sphere ratio, $S_{D(1,1)}/S = \frac{1}{2}$, is valid for helium, the dependence of $S_{D(1,1)}$ upon v is obtained simply from Eq. (12) in the form

$$S_{D(1,1)} = 7.35 + \frac{2.53 \times 10^5}{v} A^2, \quad (23)$$

¹³ A. van Itterbeek and W. H. Keesom, *Physica* 5, 257 (1938).

¹⁴ H. L. Johnston and E. R. Grilly, *J. Phys. Chem.* 46, 948 (1942).

¹⁵ J. B. Ubbink and W. J. de Haas, *Physica* 10, 465 (1943).

¹⁶ A. Eucken, *Physik. Zeits.* 12, 1101 (1911).

TABLE III. Calculated values of the self-diffusion coefficient at 1 atmos.

$T, ^\circ\text{K}$	$Q_{D(1,1)} \text{ A}^2$	$D(1, 1), \text{ cm}^2/\text{sec.}$
200	17.30	0.687
180	17.45	0.582
160	17.61	0.483
140	17.81	0.391
120	18.07	0.306
100	18.39	0.229
80	18.82	0.160
60	19.46	0.100
40	20.53	0.0518
20	22.95	0.0164
15	24.22	0.0101
10	(26.37)	(0.00504)
5	(31.20)	(0.00151)

where v is in cm/sec. Upon combining Eqs. (23) and (21), inserting values for R and M , and integrating, the following relation is obtained

for $Q_{D(1,1)}$:

$$Q_{D(1,1)} = 14.70 + \frac{36.89}{\sqrt{T}} \text{ A}^2. \quad (24)$$

If Eq. (24) is combined with Eq. (20), with ϵ set equal to 0.016, the final relation for $D_{1,1}$ becomes

$$D(1, 1) = \frac{1.39 \times 10^{-5} T \text{ cm}^2}{\rho [2.51 + (T)^{\frac{1}{2}}] \text{ sec.}} \quad (25)$$

where ρ is in g/cc, or

$$D(1, 1) = \frac{2.89 \times 10^2 T^2 \text{ cm}^2}{P [2.51 + (T)^{\frac{1}{2}}] \text{ sec.}} \quad (26)$$

where P is in dynes/cm², since $\rho = PM/RT$.

Values of $Q_{D(1,1)}$ computed from Eq. (24) and of $D(1, 1)$ computed from Eq. (26) for $P = 1.01 \times 10^6$ dynes/cm² (1 atmos.) are listed in Table III.