The Viscosity and Thermal Conductivity of Normal Hydrogen in the Limit of Zero Density

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This paper contains a new representation of the viscosity and thermal conductivity coefficients of normal hydrogen in the limit of zero density as a function of temperature. The correlation is based upon the semiclassical kinetic theory of polyatomic gases and a body of critically evaluated experimental data. In the temperature range 200–400 K the accuracy of the representation of the viscosity is estimated to be $\pm$ 0.5%. However, at the lowest temperature of 20 K and the highest temperature of 2200 K, the uncertainty rises to $\pm$ 2.0%. The available thermal conductivity data of high accuracy cover the much more restricted temperature range from 100 to 400 K and the correlation of this property is limited to that range. Above room temperature, the uncertainty in the correlated values is no more than $\pm$ 0.5%, but below room temperature it rises to one of $\pm$ 1.5%. An attempt has also been made to represent the viscosity data by means of a correlation universal among several other polyatomic gases but it has proven unsatisfactory. An extension of the temperature range of the thermal conductivity correlation based upon the Wang Chang and Uhlenbeck kinetic theory also fails to produce acceptable results.

Key words: corresponding states; hydrogen; thermal conductivity; viscosity.

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1. Introduction

The most recent critical assessments of the viscosity and thermal conductivity of hydrogen were performed in the early part of the last decade.[1-3] Since that time there have been significant improvements in the techniques of measuring transport properties which have led to increased accuracy in the results. Some new measurements of the transport properties of hydrogen have since been reported, so that in the new correlation of the properties presented here we make use of these more recent experimental data and, where appropriate, theoretical results to obtain a concise and accurate representation of the data.

2. Experimental Data

Since, for polyatomic gases, there are no independent sources of information that can be used to assess directly the accuracy of experimental values of the viscosity and thermal conductivity, the selection of the most reliable data to employ in a correlation must rest entirely upon an assessment of the measurement technique employed and the precision attained. To assist in this assessment, it is convenient to define two categories of experimental data.[4]

(i) Primary data. These are generally the results of measurements carried out with an instrument of high precision for which a complete working equation and a detailed knowledge of all corrections are available. The reproducibility of the results should be commensurate with the estimated precision. Exceptionally, in the case of hydrogen, data are included in the primary category which satisfy most, but not all, of the criteria, since otherwise the temperature range of the available data is too restricted to be useful.

(ii) Secondary data. These are the results of measurements that are of inferior accuracy to primary data. The inferior accuracy generally results from operation at extreme conditions or from the use of an ill-characterized apparatus for which neither high precision nor a complete working equation can be claimed.

For each transport coefficient, a survey of the available experimental data has been carried out and data have been assigned to one of the two categories. For the purposes of formulating the correlation, only the primary data have been considered, whereas the secondary data have been retained for comparison purposes.

2.1. Coefficient of Viscosity

The most accurate measurements of the viscosity of hydrogen in the limit of zero density have been performed with the oscillating disk viscometer at Brown University.[5,6] The measurements have been carried out with two different instruments of this type and confirmed by independent measurements over a number of years. The viscosity measurements are at room temperature and have an accuracy that is estimated to be $\pm 0.2\%$. As a complete working equation has been employed for the evaluation of these data, they evidently must be classified as primary data.

There are two further sets of data, obtained in oscillating disk viscometers, that we have also considered as primary data: one operated by Coremans and co-workers[7] and the other by Menabde.[8] It is estimated by the original authors that these instruments yield results with an uncertainty of $\pm 1\%$. In view of the fact that the data reduction was performed without the benefit of the full theory of the instrument, it is estimated that the accuracy may be worse than that claimed and may approach $\pm 2\%$. However, the measurements are among the small set which extend to low temperatures and because the results are consistent with the high-accuracy data at room temperature, we feel that their inclusion in the category of primary data is justified.

The remaining primary data for the viscosity of hydrogen have been obtained with capillary viscometers. Generally, the results are of inferior precision and accuracy to those from the oscillating-disk instrument, but the results of Michels *et al.*[9] and of Guevara and collaborators[10] enjoy a reasonable level of confidence. Furthermore, these results are especially valuable as they extend to higher temperatures than those available to the oscillating-disk instruments. For the work of Michels *et al.*,[9] it is estimated that the uncertainty is one of $\pm 0.2\%$, in accord with that claimed for the data.

Table 1. Primary experimental data for the viscosity and thermal conductivity of normal hydrogen

Reference	Technique	Temperature range (K)	Estimated uncertainty (%)
	Viscosity		
Kestin et al[5,6]	Oscillating disk	293-308	± 0.2
Coremans et al[7]	Oscillating disk	20-80	± 2.0
Menabde[8]	Oscillating disk	70-300	± 2.0
Michels et al[9]	Capillary	290-400	± 0.2
Guevara et al[10]	Capillary	1100-2200	± 2.0
	Thermal Conductivity		
Assael et al[18]	Transient hot-wire	308	± 0.3
Clifford et al[19]	Transient hot-wire	300	± 0.3
Clifford et al[20]	Transient hot-wire	311-385	± 0.5
Roder[21]	Transient hot-wire	100-300	± 1.5

However, for the work of Guevara *et al.*,[10] we have assigned an estimated uncertainty of $\pm 2\%$ to the data, which exceeds that claimed by the authors. It is felt that at temperatures above 1500 K the difficulty of temperature measurement may contribute significantly to the uncertainty in the reported viscosity. Table 1 lists the primary data used for the viscosity correlation.

The remaining viscosity data for normal hydrogen have been classified as secondary. Included among them were the results of the group of Ross,[11,12] obtained with a capillary viscometer, as well as those of Trautz and Kurz,[13] determined with a similar type of instrument. The former group's results deviate systematically from the high-accuracy data at room temperature by about 1%, which reveals a systematic error despite the high precision of the measurements. The latter work has already been shown to be in substantial error at high temperatures.[14] The early results obtained with oscillating-disk viscometers[15–17] have also been excluded because they are superseded by later work of the same group.[7]

2.2. Coefficient of Thermal Conductivity

The most accurate measurements of the thermal conductivity of normal hydrogen have been performed by the transient hot-wire technique,[18–21] and three independent measurements near room temperature[18–20] are essentially in agreement within their estimated uncertainty of $\pm 0.3\%$. Because a complete working equation exists for this instrument, the results of these measurements must be classified as primary data. A further set of measurements, also carried out with a transient hot-wire apparatus, has been reported by Roder.[21] Although these results have a greater uncertainty ($\pm 1.5\%$) they cover the temperature range from 100 to 300 K for normal hydrogen[21] and must also be regarded as primary. All of the primary data employed are included in Table 1.

The remaining measurements of the thermal conductivity of hydrogen have been carried out with steady-state instruments. In all cases, at the time the measurements were carried out, the instruments that were employed either lacked complete working equations or the importance of natural convection was not fully appreciated. Thus even the most reliable of these measurements, the low-temperature results of Roder and Diller[22] made with a parallel-plate instrument, and the high-temperature data of Saxena and Saxena[23] attained with a steady-state hot-wire apparatus, must be assigned uncertainties of $\pm 3\%$ and $\pm 5\%$, respectively. For these reasons we are forced to assign these results to our category of secondary data, even though it restricts the temperature range of our primary information. The remaining experimental data placed in the secondary category include the measurements reported by Ubbink,[24] Blais and Mann,[25] Keyes,[26] Gregory,[27] Geier,[28] Golubev,[29] Stoljarov,[30] and Johnston,[31] as well as those contained in Refs. 36–43.

3. Methodology

3.1. Viscosity

The viscosity of a pure gas in the limit of zero density may always be written in the form[32]

$$\eta = \frac{5}{16}\left(\frac{mkT}{\pi}\right)^{1/2}\frac{1}{\sigma^2\Omega^*(T)}, \tag{1}$$

in which m is the molecular mass, T the absolute temperature, and k is Boltzmann's constant. The symbol σ represents a length scaling parameter and Ω^* is a functional of the pair potential for the interaction between the molecules of the gas. In the case of spherically symmetric pair potentials between structureless particles, where the potential may be expressed in a universal reduced form,

$$U^*(r^*) = \frac{U(r/\sigma)}{\epsilon}, \tag{2}$$

it can readily be shown[32] that the functional Ω^* is a function only of the reduced temperature $T^* = kT/\epsilon$, and that it is universal among the same interactions. For polyatomic gases interacting through nonspherically symmetric pair potentials, the functional Ω^* depends not only upon the intermolecular pair potential but also upon the internal energy states of the molecules. Nevertheless, Eq. (1) provides a convenient means of representing experimental data, and the principle of corresponding states does retain some value for a particularly useful, although less accurate, correlation.

The primary data for the viscosity of hydrogen have been used to evaluate the functional $\Omega^*(T^*)$ over the temperature range 20–2200 K. For this purpose we have arbitrarily adopted for scaling parameters ϵ and σ for hydrogen, the values, obtained by a corresponding-states analysis (Sec. 5.1), $\sigma = 0.2968$ nm and $\epsilon/k = 33.3$ K. The experimental values of (Ω^*, T^*) have subsequently been fitted to an equation of the form

$$\ln \Omega^* = \sum_{i=0}^{\mu} a_i (\ln T^*)^i. \tag{3}$$

Table 2. The coefficients of the primary correlating equations for the viscosity and thermal conductivity of normal hydrogen

i	Coefficients of equation (3) a_i	Coefficients of equation (9) b_i	Coefficients of equation (11) c_i	Coefficients of equation (12) d_i
0	0.354125		435	0.49145
1	-0.427581	$-8.13854095 \times 10^{-9}$	-8.6	0.16246
2	0.149251	$3.97854897 \times 10^{-6}$	0.1	-0.0075
3	-0.037174	$-7.62127455 \times 10^{-4}$		
4	+0.003176	$+7.8169885 \times 10^{-2}$		
5		0		
6		0		
7		1.14136996×10^{1}		
8		4.75486954×10^{1}		
9		0		
10		$-4.18040384 \times 10^{2}$		
11		4.60945792×10^{2}		
12		0		
13		$-4.10534450 \times 10^{2}$		
14		6.03774849×10^{2}		
15		$-3.92633104 \times 10^{2}$		
16		9.99743666×10^{1}		
17		0		
18		1.36830122×10^{4}		
19		1.79687156×10^{2}		

ϵ/k = 33.3 K
σ = 0.2968 nm

In the fitting procedure, each viscosity datum has been assigned a temperature-dependent statistical weight in the fashion described by Cole and Wakeham.[4] The resulting correlation for the viscosity of normal hydrogen is presented and discussed in Sec. 4, while Table 2 lists the optimum values of the coefficients a_i.

3.2. Thermal Conductivity

The thermal conductivity and viscosity of a pure polyatomic gas are, to a first-order approximation in the Wang Chang and Uhlenbeck theory,[32] related by the equation

$$\frac{\lambda M}{\eta R} = \frac{5}{2}\left(\frac{3}{2} - \Delta\right) + \frac{\rho D_{\text{int}}}{\eta}\left(\frac{C_{v,\text{int}}}{R} - \Delta\right), \tag{4}$$

where

$$\Delta = \frac{2C_{v,\text{int}}}{\pi R\zeta}\left(\frac{5}{2} - \frac{\rho D_{\text{int}}}{\eta}\right) \times\left[1 + \frac{2}{\pi\zeta}\left(\frac{5C_{v,\text{int}}}{R} + \frac{\rho D_{\text{int}}}{\eta}\right)\right]^{-1}. \tag{5}$$

Here, λ denotes the thermal conductivity, M the molar mass of the gas, $C_{v,\text{int}}$ the internal energy contribution to the molar heat capacity, ρ the mass density of the gas, and ζ the collision number for internal energy relaxation.[32]

When the molecule possesses both rotational and vibrational degrees of freedom,[32] then

$$\frac{C_{v,\text{int}}}{\zeta} = \frac{C_{v,\text{rot}}}{\zeta_{\text{rot}}} + \frac{C_{v,\text{vib}}}{\zeta_{\text{vib}}} \tag{6}$$

and

$$C_{v,\text{int}} = C_{v,\text{rot}} + C_{v,\text{vib}}, \tag{7}$$

with obvious meanings for the various subscripts. In addition,

$$\frac{C_{v,\text{int}}}{D_{\text{int}}} = \frac{C_{v,\text{rot}}}{D_{\text{rot}}} + \frac{C_{v,\text{vib}}}{D_{\text{vib}}}. \tag{8}$$

Because for hydrogen, $C_{v,\text{vib}} \ll C_{v,\text{rot}}$ and $\zeta_{\text{vib}} \gg \zeta_{\text{rot}}$,[33] we can neglect the second term of Eq. (6) in preparing our correlation. However, no such simplification of Eq. (8) is possible so that we do not attempt to distinguish D_{rot} and D_{vib} and work only with D_{int}.

A convenient, theoretically sound representation of the thermal conductivity of hydrogen can be achieved by utilizing our correlation for the viscosity together with independent correlations of the collision number ζ_{rot} and the internal heat capacity $C_{v,\text{int}}$. These correlations leave only the group $(\rho D_{\text{int}}/\eta)$ to be determined from the experimental thermal conductivity by application of Eqs. (4) and (5) to each datum. Because the group $(\rho D_{\text{int}}/\eta)$ is a weak function of temperature, the representation of the derived values can be accomplished with a simple equation.

To implement this procedure we have employed a representation of the ideal gas, isobaric heat capacity of normal hydrogen, developed by Armstrong,[34] to represent the data listed by McCarty.[35] The representative equation is of the form

$$\frac{C_p}{R} = \sum_{i=1}^{5} b_i\left(\frac{1}{T^*}\right)^{i-5} + \sum_{i=6}^{11} b_i\left(\frac{1}{T^*}\right)^{(i-5)/3} + \sum_{i=12}^{17} b_i\left(\frac{1}{T^*}\right)^{i-9} + b_{18}\frac{\exp(b_{19}/T^*)}{[\exp(b_{19}/T^*) - 1]^2}\left(\frac{1}{T^*}\right)^2, \tag{9}$$

for which the coefficients are listed in Table 2. The correlation is valid over the temperature range 80–2500 K, and $C_{v,\text{int}}$ may be calculated from it with the aid of the simple relation

$$C_{v,\text{int}}/R = C_p/R - 5/2. \tag{10}$$

A compilation of rotational collision numbers for normal hydrogen has been given by Lambert.[33] These data have been represented by the simple correlation

$$\zeta_{\text{rot}} = c_0 + c_1 T^* + c_2 T^{*2}, \tag{11}$$

with the coefficients given in Table 2. Values of ζ_{rot} are not generally obtained from experiment with great accuracy.[33] However, the collision number for rotational relaxation for hydrogen is greater than 200 collisions and, in consequence, Eq. (4) is not very sensitive to its value. The correlation of Eq. (11) is therefore satisfactory for our present purposes.

With the aid of the correlations of Eqs. (3),(9), and (11) and the primary thermal conductivity data, we have evaluated the group $(\rho D_{\text{int}}/\eta)$ from Eq. (4). The results are plotted in Fig. 1, from which it can be seen that despite some small scatter the experimental values conform to a reasonably smooth curve in the temperature range 100–400 K. The data in this temperature range have been fitted to the equation

$$(\rho D_{\text{int}}/\eta) = d_0 + d_1 T^* + d_2 T^{*2}, \tag{12}$$

and Table 2 contains the optimum values of the coefficients. Equations (3), (4), and (9)–(11) then constitute our correlation of the thermal conductivity of normal hydrogen.

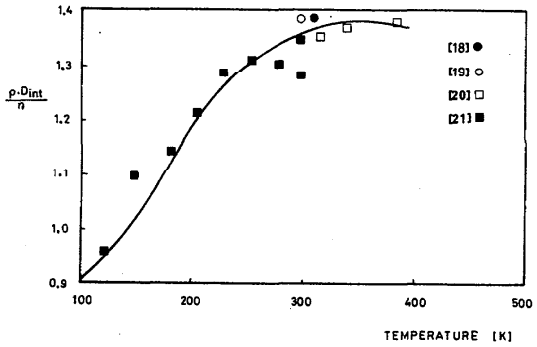

FIG. 1. The values of the group $(\rho D_{\text{int}}/\eta)$ deduced from the primary thermal conductivity data as a function of temperature.

4. Primary Correlations

4.1. Viscosity

The viscosity of normal hydrogen is represented by Eqs. (1) and (3) with the coefficients and parameters of Table 2 over the temperature range $20 \leqslant T \leqslant 2200$ K ($0.60 \leqslant T^* \leqslant 42$).

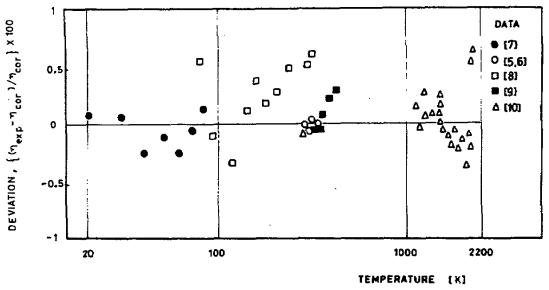

FIG. 2. Deviations of the primary experimental data for the viscosity of normal hydrogen from the present correlation of Eqs. (1) and (3).

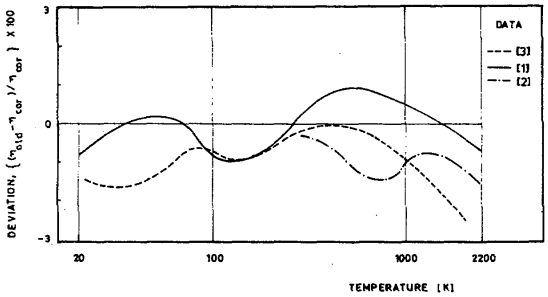

FIG. 4. The differences between the present correlation for the viscosity of normal hydrogen and earlier versions.

Figure 2 contains a plot of the deviations of the primary experimental data from this optimum correlation. The experimental data depart from the correlation by no more than $\pm 0.7\%$ over the entire temperature range. The results of different authors show some evidence of contradictory trends within the range of interest but no significance can be attached to this observation since the effects are often smaller than the uncertainty assigned to the data. It is estimated that, within the temperature range 200–400 K, the uncertainties in the viscosities generated by the correlation are no more than $\pm 0.5\%$; outside of this temperature range, the uncertainty rises to $\pm 2\%$ at the extremes of temperature.

Figure 3 contains a plot of the deviations of the secondary experimental data from the above correlation. The secondary data show a maximum deviation of as much as $\pm 5\%$ at the very low temperatures.

In Fig. 4, the present correlation is compared with previous correlations of the viscosity of normal hydrogen.[1–3] The correlation of Maitland and Smith[1] deviates by no more than $\pm 1\%$ from that of the present work over the entire temperature range, and this mainly reflects the different weights given to the results of various workers. The correlation of Watson[2] deviates from the present results by up to 2% at the highest temperatures, whereas the formulation of Hanley *et al.*[3] shows a more marked deviation at either temperature extreme.

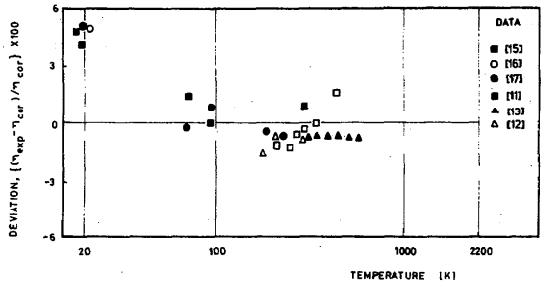

FIG. 3. Deviations of the secondary experimental data for the viscosity of normal hydrogen from the present correlation of Eqs. (1) and (3).

4.2. Thermal Conductivity

The thermal conductivity of normal hydrogen is represented by Eqs. (1), (3)–(5) and (9)–(12), with the coefficients of Table 2 over the temperature range 100 K$\leqslant T \leqslant$400 K ($3 \leqslant T^* \leqslant 12$). Figure 5 contains a plot of the deviations of the primary experimental data from this optimum correlation. The experimental data depart from the correlation by no more than $\pm 1\%$, except for one point at the lowest temperature where the deviation rises to 2%. Around

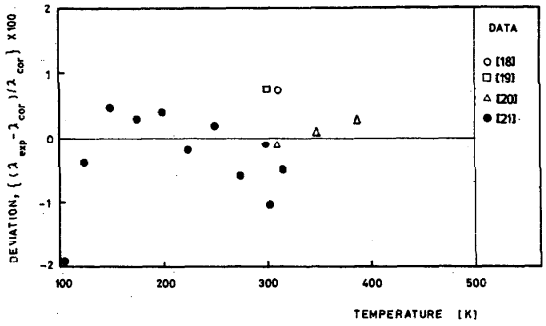

FIG. 5. Deviations of the primary experimental data for the thermal conductivity of normal hydrogen from the correlation of Eqs. (1), (3), and (9)–(11).

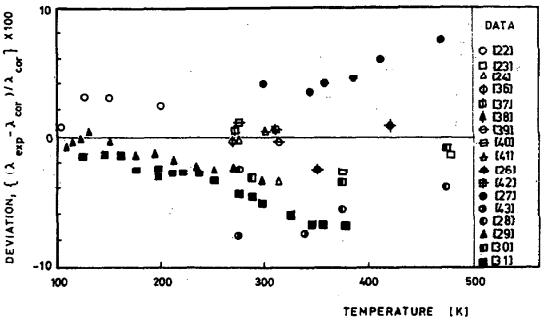

FIG. 6. Deviations of the secondary experimental data for the thermal conductivity of normal hydrogen from the correlation of Eqs. (1), (3), and (9)–(11).

room temperature the four independent measurements are consistent within a band of $\pm 0.5\%$, so that this is adopted as an estimate of the uncertainty in the correlated thermal conductivity at this temperature and above. At lower temperatures, the uncertainty in the correlated thermal conductivity rises to one of $\pm 1.5\%$.

Figure 6 compares the secondary thermal conductivity data with the present correlation and it can be seen that the deviations amount to as much as 8%, even near room temperature. On the one hand, this observation provides some confirmation of our decision to exclude these data from the formulation of the correlation. On the other hand, the same observation means that any extension of the temperature range of the present primary correlation cannot securely be based on experimental data.

4.3. Tabulation

The correlating equations for the viscosity and thermal conductivity of normal hydrogen have been used to generate the properties over the temperature range of their validity. Tables 3 and 4 list the values for viscosity and thermal conductivity at appropriate temperature intervals.

Table 3. The viscosity of normal hydrogen in the limit of zero density

T/K	Viscosity η/μPa s	T/K	Viscosity η/μPa s	T/K	Viscosity η/μPa s	T/K	Viscosity η/μPa s
20	1.039	510	12.86	1080	21.67	1650	29.23
25	1.318	520	13.03	1090	21.81	1660	29.35
30	1.579	530	13.21	1100	21.95	1670	29.48
35	1.824	540	13.38	1110	22.09	1680	29.60
40	2.055	550	13.55	1120	22.23	1690	29.73
45	2.275	560	13.72	1130	22.37	1700	29.85
50	2.484	570	13.88	1140	22.51	1710	29.98
55	2.685	580	14.05	1150	22.65	1720	30.10
60	2.877	590	14.22	1160	22.79	1730	30.22
65	3.063	600	14.38	1170	22.93	1740	30.35
70	3.242	610	14.55	1180	23.07	1750	30.47
75	3.416	620	14.71	1190	23.20	1760	30.59
80	3.585	630	14.88	1200	23.34	1770	30.71
85	3.749	640	15.04	1210	23.48	1780	30.84
90	3.909	650	15.20	1220	23.62	1790	30.96
95	4.066	660	15.36	1230	23.75	1800	31.08
100	4.219	670	15.52	1240	23.89	1810	31.20
110	4.515	680	15.68	1250	24.02	1820	31.32
120	4.801	690	15.84	1260	24.16	1830	31.44
130	5.077	700	16.00	1270	24.29	1840	31.56
140	5.345	710	16.16	1280	24.43	1850	31.69
150	5.605	720	16.32	1290	24.56	1860	31.81
160	5.859	730	16.48	1300	24.70	1870	31.93
170	6.107	740	16.63	1310	24.83	1880	32.05
180	6.349	750	16.79	1320	24.97	1890	32.17
190	6.587	760	16.94	1330	25.10	1900	32.29
200	6.820	770	17.10	1340	25.23	1910	32.41
210	7.049	780	17.25	1350	25.37	1920	32.53
220	7.274	790	17.41	1360	25.50	1930	32.64
230	7.496	800	17.56	1370	25.63	1940	32.76
240	7.715	810	17.71	1380	25.76	1950	32.88
250	7.930	820	17.87	1390	25.89	1960	33.00
260	8.143	830	18.02	1400	26.03	1970	33.12
270	8.353	840	18.17	1410	26.16	1980	33.24
280	8.561	850	18.32	1420	26.29	1990	33.35
290	8.766	860	18.47	1430	26.42	2000	33.47
300	8.969	870	18.62	1440	26.55	2010	33.59
310	9.170	880	18.77	1450	26.68	2020	33.71
320	9.369	890	18.92	1460	26.81	2030	33.82
330	9.566	900	19.07	1470	26.94	2040	33.94
340	9.761	910	19.22	1480	27.07	2050	34.06
350	9.954	920	19.36	1490	27.20	2060	34.18
360	10.15	930	19.51	1500	27.33	2070	34.29
370	10.34	940	19.66	1510	27.45	2080	34.41
380	10.52	950	19.80	1520	27.58	2090	34.52
390	10.71	960	19.95	1530	27.71	2100	34.64
400	10.90	970	20.10	1540	27.84	2110	34.76
410	11.08	980	20.24	1550	27.97	2120	34.87
420	11.27	990	20.39	1560	28.09	2130	34.99
430	11.45	1000	20.53	1570	28.22	2140	35.10
440	11.63	1010	20.67	1580	28.35	2150	35.22
450	11.81	1020	20.82	1590	28.47	2160	35.33
460	11.99	1030	20.96	1600	28.60	2170	35.45
470	12.16	1040	21.10	1610	28.73	2180	35.56
480	12.34	1050	21.25	1620	28.85	2190	35.67
490	12.51	1060	21.39	1630	28.98	2200	35.79
500	12.69	1070	21.53	1640	29.10		

Table 4. The thermal conductivity of normal hydrogen in the limit of zero density

T/K	Thermal Conductivity λ/mW m^{-1}K^{-1}	T/K	Thermal Conductivity λ/mW m^{-1}K^{-1}
100	68.62	255	163.5
105	71.72	260	166.2
110	74.84	265	168.9
115	77.98	270	171.6
120	81.14	275	174.2
125	84.33	280	176.8
130	87.52	285	179.4
135	90.72	290	181.9
140	93.93	295	184.4
145	97.14	300	186.9
150	100.35	305	189.3
155	103.5	310	191.8
160	106.7	315	194.2
165	109.9	320	196.5
170	113.1	325	198.9
175	116.2	330	201.2
180	119.4	335	203.4
185	122.5	340	205.7
190	125.6	345	207.9
195	128.7	350	210.1
200	131.7	355	212.3
205	134.7	360	214.4
210	137.7	365	216.5
215	140.7	370	218.6
220	143.6	375	220.6
225	146.6	380	222.6
230	149.5	385	224.6
235	152.3	390	226.6
240	155.2	395	228.5
245	158.0	400	230.4
250	160.7		

5. Secondary Correlations

5.1. Viscosity

The viscosity of many polyatomic gases has been successfully correlated, over a modest temperature range, by means of a universal scheme based upon the principles of corresponding states. The basic proposition of the corresponding-states correlation scheme is that the functional Ω^* of Eq. (1) is a universal function Ω_η^* of a reduced temperature $T^* = kT/\epsilon$ among all gases. Here, ϵ is again an energy scaling parameter and σ is the corresponding length scaling parameter.

As a result of a study of many monatomic and polyatomic gases, it has been shown that the universal functional may be represented by the equation[32]

$$\ln(\Omega_\eta^*) = 0.466\,49 - 0.570\,15(\ln T^*) + 0.191\,64(\ln T^*)^2 - 0.037\,08(\ln T^*)^3 + 0.002\,41(\ln T^*)^4, \quad 1 \leqslant T^* \leqslant 90. \qquad (13)$$

Because a corresponding-states correlation allows the temperature range of the viscosity for one gas to be extended outside of the region for which direct experimental information exists, we have attempted to represent the primary viscosity data for hydrogen by means of Eqs. (1) and (12). Accordingly, we have determined the values of ϵ/k and σ that secure the optimum representation of this kind. The optimum values are those quoted earlier and listed in Table 2.

Figure 7 shows the deviations of the primary viscosity data from this universal correlation. It is quite clear that the deviations are large, as much as 6%, lie well outside of experimental error, and have a systematic character. We therefore conclude that the universality of Ω_η^* found for some

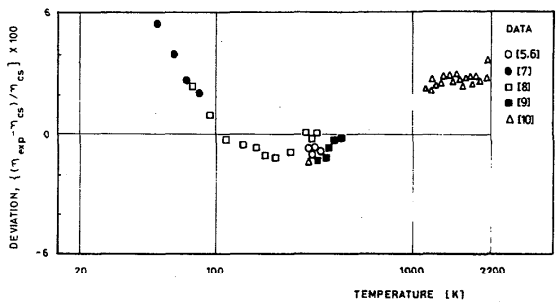

FIG. 7. Deviations of the primary experimental data for the viscosity of normal hydrogen from the universal correlation of Eqs. (1) and (12).

other polyatomic gases does not extend to hydrogen, and that any attempt to extrapolate viscosity data for this gas to lower and higher temperatures using this correlation will lead to rather large errors.

5.2. Thermal Conductivity

The desire to establish a reliable method of extrapolating the thermal conductivity of normal hydrogen to higher and lower temperatures is even stronger in view of the restricted temperature range of the present correlation. However, the poor quality of the experimental data means that any such extrapolation must be performed by theoretically based methods.

Given that the viscosity, heat capacity, and collision number are available over a wider temperature range than the reliable thermal conductivity data, the most sensible course of action would be to calculate the thermal conductivity through Eqs. (1), (3), and (9)–(11), combined with a calculation of the group $(\rho D_{\rm int}/\eta)$. The exact evaluation of $\rho D_{\rm int}/\eta$ for an appropriate nonspherical pair potential for hydrogen[44] has not yet been carried out and represents a substantial computational effort in itself.[44] Consequently, it is necessary to adopt a method of estimating $(\rho D_{\rm int}/\eta)$. The most common estimation method is based upon the Mason–Monchick approximation,[32] which leads to the result that

$$D_{\rm int} = D, \tag{14}$$

where D is the self-diffusion coefficient of the gas. It then follows that[32]

$$\rho D_{\rm int}/\eta = \rho D/\eta = 6A^*/5, \tag{15}$$

where A^* is a functional of the intermolecular pair potential. The advantage of this formulation is that A^* is generally weakly dependent on both the pair potential and temperature, so that almost any model suffices for its evaluation.

In order to attempt to extrapolate our correlation, we have adopted two methods of estimating A^*. In the first, we have employed, in the extrapolated region, values of A^* for a Lennard–Jones potential characteristic of hydrogen.[32] In the second, we have deduced a value of A^* empirically by application of Eq. (15) to the experimentally determined value of $(\rho D_{\rm int}/\eta)$ at the highest temperature of reliable thermal conductivity data. Then, we have maintained this value of A^* constant throughout the extrapolated temperature range. Either method of evaluating A^* together with Eqs. (1), (3), (9)–(11), and (15) enables us to calculate the thermal conductivity in the extended temperature range.

A comparison of the thermal conductivity calculated by either method with direct (secondary) experimental data in the temperature range 400–2000 K reveals large discrepancies amounting to $\pm 20\%$. Differences of this magnitude indicate either a large error in the application of the Mason–Monchick approximation to this system, or experimental errors substantially beyond those originally estimated. In view of the fact that it is not yet possible to make unequivocal statements about the validity of the Mason–Monchick approximation,[45] it would seem unwise to advocate, at this stage, its use for accurate extrapolations of data. We are therefore forced to conclude that it is not yet possible to produce accurate values of the thermal conductivity of hydrogen over an extended range of temperature.

6. Conclusion

A concise representation of the viscosity of normal hydrogen over the temperature range 20–2200 K has been developed. The correlation has an accuracy of $\pm 0.5\%$ between 200 and 400 K, which deteriorates to $\pm 2\%$ at the extremes of the temperature range. A consistent representation of the thermal conductivity has been possible only over the temperature range 100–400 K.

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