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

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M. J. Assael, S. Mixafendi, and W. A. Wakeham



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

M. J. Assael and S. Mixafendi

Department of Chemical Engineering, Aristotle University of Thessaloniki, GR 540.06 Thessaloniki, Greece

and

W.A. Wakeham

IUPAC Transport Properties Project Centre, Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London SW7 2BY, United Kingdom

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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.

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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

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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-workers⁷ 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 collaborators¹⁰ 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 (%) | |
|------------------------------|--------------------|--------------------------|------------------------------|--|
| | Viscosit | у | | |
| Kestin et al ^{5,6} | Oscillating disk | 293-308 | ± 0.2 | |
| Coremans et al? | Oscillating disk | 20-80 | ± 2.0 | |
| Menabde ⁸ | Oscillating disk | 70-300 | ± 2.0 | |
| Michels et al? | Capillary | 290-400 | ± 0.2 | |
| Guevara et al.0 | Capillary | 1100-2200 | ± 2.0 | |
| | Thermal Condu | ctivity | | |
| 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 viscometers¹⁵⁻¹⁷ 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 temperature¹⁸⁻²⁰ 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 hydrogen²¹ 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 Diller²² made with a parallel-plate instrument, and the high-temperature data of Saxena and Saxena²³ 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 form³²

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

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,

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

it can readily be shown³² 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

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

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

| - | | <u></u> | the second s | No |
|----|------------------------------|---------------------------------|--|----------------------------------|
| | Coefficients of equation (3) | Coefficients of equation (9) | Coefficients of equation (11) | Coefficients of equation (12) |
| 1 | ^a i | ^b i | °1 | ¢i |
| 0 | 0.354125 | | 435 | 0.49145 |
| 1 | -0.427581 | -8.13854095 x 10 ⁻⁹ | ~8.6 | 0.16246 |
| 2 | 0.149251 | 3.97854897 x 10 ⁻⁶ | 0.1 | -0.0075 |
| 3 | -0.037174 | -7.62127455 x 10 ⁻⁴ | | |
| 4 | +0.003176 | +7.8169885 x 10 ⁻² | | |
| 5. | | 0 | | |
| 6 | | 0 | | |
| 7 | | 1 14136996 x 10 ¹ | | |
| 8 | | 4.75486954 $\times 10^{1}$ | | |
| 9 | | 0 | | |
| 10 | | -4.18040384×10^2 | | |
| 11 | | 4.60945792×10^2 | | |
| 12 | | 0 | | |
| 13 | | -4.10534450×10^2 | | |
| 14 | | 6.03774849×10^2 | | |
| 15 | | -3.92633104×10^2 | | |
| 16 | | 9.99743666 x 10 ¹ | | |
| 17 | | 0 | | |
| 18 | | 1.36830122×10^4 | | |
| 19 | | 1.79687156 x 10 ² | | |

 $\epsilon/k = 33.3$ K $\sigma = 0.2968$ nm

= 0.2908 mm

In the fitting procedure, each viscosity datum has been assigned a temperature-dependent statistical weight in the

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

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

where

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

Here, λ denotes the thermal conductivity, M the molar mass of the gas, $C_{\nu,int}$ 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

$$\frac{C_{\nu,\text{int}}}{\zeta} = \frac{C_{\nu,\text{rot}}}{\zeta_{\text{rot}}} + \frac{C_{\nu,\text{vib}}}{\zeta_{\text{vib}}}$$
(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,

$$\frac{C_{\nu,\text{int}}}{D_{\text{int}}} = \frac{C_{\nu,\text{rot}}}{D_{\text{rot}}} + \frac{C_{\nu,\text{vib}}}{D_{\text{vib}}}.$$
(8)

Because for hydrogen, $C_{\nu,vib} \leq C_{\nu,rot}$ and $\zeta_{vib} \geq \zeta_{rot}$,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





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the thermal conductivity of hydrogen can be achieved by utilizing our correlation for the viscosity together with independent correlations of the collision number $\zeta_{\rm rot}$ and the internal heat capacity $C_{v,\rm int}$. These correlations leave only the group ($\rho D_{\rm int}/\eta$) to be determined from the experimental thermal conductivity by application of Eqs. (4) and (5) to each datum. Because the group ($\rho D_{\rm int}/\eta$) 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

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

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

$$C_{\rm vint}/R = C_{\nu}/R - 5/2. \tag{10}$$

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

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

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 ($\rho D_{int}/\eta$) 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

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

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.

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).

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 Smith¹ 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 Watson² 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).



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

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 $\leq T$ \leq 400 K (3 $\leq T$ * \leq 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 ŋ/µPa s | T/K | Viscosity η/μPa s | T/X | Viscosity η/μPa s | T/K | Viscosity ŋ/µPa s |
|-----|----------------------|-------------|----------------------|------|----------------------|------|----------------------|
| 20 | 1 039 | 510 | 12.86 | 1080 | 21.67 | 1650 | 29.23 |
| 20 | 1 319 | 520 | 13 03 | 1000 | 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 | 2 684 | 570 | 13.88 | 1140 | 22.51 | 1710 | 29.98 |
| 55 | 2.685 | 580 | 14.05 | 1150 | 22.00 | 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 | 13/0 | 25.63 | 1940 | 32.76 |
| 240 | 7.715 | 810 | 17.71 | 1380 | 25./6 | 7920 | 32.88 |
| 250 | 7.930 | 820 | 17.87 | 1390 | 25.89 | 1960 | 33.00 |
| 260 | 8.143 | 830 | 18.02 | 1400 | 26.03 | 19/0 | 33.12 |
| 270 | 8.353 | 840 | 18.17 | 1410 | 20.10 | 1980 | 33.24 |
| 280 | 8.361 | 850 | 10.32 | 1420 | 26.42 | 2000 | 33.47 |
| 200 | 8 949 | 870 | 18.67 | 1440 | 26.55 | 2010 | 33.59 |
| 110 | 0.707 | 890 | 18 77 | 1450 | 26 69 | 2020 | 33 71 |
| 320 | 0 360 | 800 | 18.97 | 1460 | 26.81 | 2030 | 33.82 |
| 320 | 9.566 | 900 | 19.07 | 1470 | 26.94 | 2040 | 33.94 |
| 340 | 0 761 | 910 | 10 22 | 1480 | 27.07 | 2050 | 34-06 |
| 350 | 0.054 | 920 | 19.22 | 1400 | 27 30 | 2060 | 34.10 |
| 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 | 99 0 | 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 | | |
| | | | | | | | |

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| Table 4 | . The | thermal | conduc | tivity | of normal | hydrogen |
|---------|-------|----------|---------|--------|-----------|----------|
| | 2 | in the 1 | imit of | zero d | lensity | |

| т/к | 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 | 140.6 | 380 | 222.6 |
| 230 | 149.5 | 385 | 224.6 |
| 235 | 152.3 | 390 | 226.6 |
| 240 | 155.2 | 395 | 228.5 |
| 245 | 156.0 | 400 | 230.4 |

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 equation³²

$$\ln(\Omega_{\eta}^{*}) = 0.466 \ 49 - 0.570 \ 15(\ln T^{*})$$
$$+ 0.191 \ 64(\ln T^{*})^{2} - 0.037 \ 08(\ln T^{*})^{3}$$

 $+ 0.002 \, 41 (\ln T^*)^4 \, 1 - T^* - 90 \, (12)$

$$+ 0.002 41(\ln T^{*})^{*}, 1 \leq T^{*} \leq 90.$$
 (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_n^* 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 ($\rho D_{int}/\eta$). The exact evaluation of $\rho D_{int}/\eta$ for an appropriate nonspherical pair potential for hydrogen⁴⁴ 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 ($\rho D_{int}/\eta$). 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 that³²

$$\rho D_{\rm int} / \eta = \rho D / \eta = 6A * /5,$$
 (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 $(\rho D_{int}/\eta)$ 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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