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Reference Viscosities of Gaseous Methane and Hydrogen Sulfide at Low Density in the Temperature Range from (292 to 682) K

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ABSTRACT: An all-quartz oscillating-disk viscometer of very high precision was used to measure the temperature dependence of the viscosities of methane and hydrogen sulfide at low densities. The measurements were based on a single calibration at room temperature with a value theoretically calculated using an accurate ab initio pair potential for helium and the kinetic theory of dilute monatomic gases. The uncertainty of the experimental data is conservatively estimated to be ± 0.15 % at room temperature increasing to ± 0.20 % at the highest temperature of 682 K. The new data are compared with experimental data from the literature as well as with values obtained from the Quiñones-Cisneros correlation for methane (2010) and the Schmidt correlation for hydrogen sulfide (2008) both implemented in the REFPROP computer program of the National Institute of Standards and Technology (NIST). The comparison shows that the low-density values of the Quiñones-Cisneros correlation for methane, primarily based on measurements in the range from (211 to 392) K performed at NIST in 2007, can be considered as reference values. On the contrary, the new experimental data for hydrogen sulfide are (2 to 6) % lower than the low-density values of the Schmidt correlation and should be taken into account for an improvement of the viscosity correlation for hydrogen sulfide. Furthermore, the temperature dependence of the viscosities calculated theoretically using ab initio intermolecular potential energy hypersurfaces for methane and hydrogen sulfide and the extended kinetic theory of dilute molecular gases should be used to extrapolate the viscosity correlations to low and high temperatures.

INTRODUCTION

Methane and hydrogen sulfide are relevant in a wide variety of engineering contexts. Methane is the main constituent of natural gas, which will be a primary energy source at least for the next 50 years. Methane is a very important working fluid in various industries, for example, in the petrochemistry and in the natural gas industry. In addition, it is a significant greenhouse gas which effects strongly the climate. Hydrogen sulfide is also of importance for processes that involve natural gas, since H_2S can be a major constituent. It is highly toxic, flammable, and corrosive in the presence of water so that its handling requires special care.

Accurate and reliable thermophysical property data including viscosity are essential for designing, operating, maintaining, or retrofitting purposes of technical equipment dealing with methane and hydrogen sulfide. The data are strongly needed for the simulation of such processes as well as in computational fluid dynamics. In principle, viscosity data for methane are available, but they are of high accuracy only between (211 and 392) K (see below). On the contrary, experimental viscosity data for hydrogen sulfide are rather scarce and characterized by large uncertainties. The present work provides accurate viscosity data of methane and hydrogen sulfide in the dilute-gas limit between room temperature and 680 K. These data should be used to test the available viscosity values for both gases and to improve them, particularly in the case of H_2S. The development of improved viscosity correlations can be supported by theoretically calculated viscosity values, even if experimenters and practitioners may have doubts about the trustworthiness of such state-of-the-art calculations. The temperature dependence of the theoretical values could help to resolve the problem of extrapolation to low and high temperatures, at which the measurements are more difficult.

The Standard Reference Data Program REFPROP of the National Institute of Standards and Technology (NIST)[1] uses a viscosity correlation for methane based on unpublished work by Quiñones-Cisneros et al.[2] Its uncertainty is estimated to be < ± 0.3 % between (200 and 400) K for pressures less than 30 MPa and < ± 2 % over the rest of the fluid surface up to 100 MPa and for temperatures to 625 K. The correlation makes use of the equation of state by Setzmann and Wagner,[3] which covers the range from the melting line to 625 K at pressures up to 1000 MPa. The present paper is dealing with the low-density region and particularly with the limit of zero density so that the equation of state is without importance. The low-density contribution of the Quiñones-Cisneros correlation, for which experimental data in the temperature range (90.7 to 1022) K in the literature were available, has been additionally extended to 2000 K.[1] According to Quiñones-Cisneros,[4] the low-density contribution was primarily based on measurements of May et al.[5] carried out with very low uncertainty in the temperature range (211 to 392) K at NIST in 2007, whereas most other data sets could only be considered for the correlation with lower weights. To develop a reliable correlation in a possibly large temperature range, Quiñones-Cisneros included between (1000 and 1500) K viscosity values calculated theoretically by our group[6] using the ab initio intermolecular potential energy hypersurface for methane[7] and the extended kinetic theory of dilute molecular gases.[8] In principle, the theoretically calculated temperature dependence of viscosity could also have been used for an improvement at

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temperatures below 200 K, where no experimental data characterized by low uncertainty are available in the literature.

To decrease the uncertainty of their measurements on methane with single-capillary and two-capillary viscometers, May et al.[5] based the evaluation of their data at each of the measured temperatures on viscosity values for helium, derived theoretically by Hurly and Moldover[9] and by Hurly and Mehl[10] using an ab initio helium−helium interatomic potential and the kinetic theory of dilute monatomic gases. May et al. estimated the uncertainty of their methane data to be ± 0.096 % so that reference zero-density viscosities became available in the temperature range (211 to 392) K, but not in a larger one.

Schmidt et al.[11] developed a correlation for the viscosity of hydrogen sulfide which was implemented in the REFPROP computer program by NIST.[1] This correlation is characterized by an average deviation of ± 1 % from the available experimental data over the temperature range (190 to 600) K at atmospheric pressure and along the liquid saturation boundary. At pressures of 100 MPa the uncertainty is estimated to be of the order of ± 10 %. The short fundamental equation of state by Lemmon and Span[12] covering the range from the melting line to 760 K at pressures up to 170 MPa is needed for the high-density range of the Schmidt correlation. It is to note that the comparably good representation of the experimental data at low density by means of the Schmidt correlation does not give any evidence about its uncertainty, since high-precision measurements could not be taken into account by Schmidt et al. at that time. The present measurements of the low-density viscosity of hydrogen sulfide carried out over a large temperature range are intended to test the Schmidt correlation. Furthermore, the temperature dependence of viscosity values, very recently theoretically calculated by our group[13] analogously to methane, is included in the comparison with the Schmidt correlation and with the other experimental viscosity data.

■ EXPERIMENTAL SECTION

Experimental Equipment. The experiments of the present work on methane and hydrogen sulfide have been performed using an all-quartz oscillating-disk viscometer with small gaps newly constructed for measurements on argon[14] with the aim of determining reference values in a large temperature range. Principles concerning the construction of the viscometer were described in a previous paper.[15] Some details of the building design were changed over the years to facilitate the assembly of the instrument. The construction drawing and the characteristics of the new viscometer were given in Figure 1 and Table 1 of ref 14. Advantages of the use of fused quartz glass consist in the small thermal expansion coefficient and the small internal logarithmic decrement of the suspension strand to enable measurements in a large temperature range. Furthermore, quartz glass does not support the catalytic decomposition of the substances under discussion and owns a high chemical stability. But due to the construction and the assembly of the oscillating-disk viscometer, which are specified in ref 14, the dimensions of the viscometer cannot be determined with an accuracy needed for absolute measurements.

An opto-electronic system is used for measuring the period τ (of about 25 s) and the decrement Δ of the damped harmonic oscillation by time measurements. The relative uncertainty in Δ is ± 0.05 %, whereas that in τ is ± 0.005 %. The temperature of the oscillating-disk viscometer is regulated by a specially designed air-bath thermostat consisting of three heating zones operated separately. The vertical temperature profile of the thermostat generates a stable density stratification and avoids convection inside the viscometer. The temperature is determined with a 10 Ω platinum resistance thermometer and a resistance measuring bridge, each calibrated. The uncertainty of the temperature measurements is ± 50 mK at 300 K and ± 150 mK at 700 K.

Experimental Procedure. As already stated, instead of an absolute determination of the viscosity, relative measurements have to be performed with our viscometer. Their implementation in conjunction with a completely changed calibration and with a sound error analysis has already been reported in ref 14. In principle, the measuring theory of Newell,[16] designed for absolute measurements using an oscillating-disk viscometer with small gaps, had to be applied. In doing so, the Newell constant C_N had to be calculated absolutely from the dimensions of the specific viscometer. Then the experimentally known density of the fluid ρ and the measured quantities Δ and τ (including Δ_0 and τ_0 in vacuo) result in the viscosity η. With respect to our measurements it is to be noted that the gaseous density ρ is comparably small so that the contributions of higher terms to C_N are negligible. Consequently, the approximately known characteristics of the all-quartz oscillating-disk viscometer are used together with the working equation of the Newell theory to determine C_N. For that purpose the viscosity and the density of the gas used for the calibration are needed independently. It is to note that one reference viscosity value at room temperature and at low density is sufficient to calibrate the apparatus, since the derived Newell constant C_N will not change with temperature due to the properties of quartz glass mentioned above.

In our discussion of theoretically calculated viscosity coefficients for argon[17] and somewhat earlier for helium,[18] we demonstrated that the recommended reference values by Kestin et al.[19] were not derived from absolute measurements and do not possess the claimed uncertainty of ± 0.1 % at room temperature, but that they are slightly too high, for both gases by about +0.2 %. Therefore, the zero-density viscosity coefficient $\eta^{(0)}$ at 298.15 K, resulting from the new ab initio argon−argon interatomic potential[20,21] and using the kinetic theory of dilute gases,[17] was adopted as a reference value together with its temperature derivative near room temperature for the calibration of the oscillating-disk viscometer in ref 14. Then the evaluation of the measurements on argon in the complete temperature range was accomplished with the obtained Newell constant. After all, experimental reference values for argon resulted between (291 and 682) K and were compared with the theoretical argon viscosity values and with argon viscosities obtained by May et al.[5] at NIST with the same capillary viscometers as in the case of methane. The comparison revealed that the experimental reference values of NIST (203 to 394 K) and those of our group as well as the theoretically calculated argon values are consistent within ± 0.1 %, notwithstanding that a different calibration was used by NIST and Rostock University. Hence the excellent agreement of the experimental argon data and of the theoretical argon values at all temperatures proves the performance of our viscometer as well as the consistency of the temperature functions of the viscosity values calculated theoretically for the helium and argon pair potentials. The theoretical values for the different thermophysical properties have been found to be often more accurate than all available experimental data and suitable to be used for the calibration of high-precision measuring instruments.

For the measurements of the present paper we changed the evaluation insofar that the single calibration at room temperature was carried out with a theoretically calculated viscosity value for

Table 1. Old and New Reference Data of Helium for the Calibration of the Viscometer

ref	$\eta^{(0)}_{298.15}$	$(\partial\eta = \partial T)_\rho$	$(\partial\eta = \partial\rho)_T$
	μPa·s	μPa·s·K^{-1}	nPa·s·m^3·kg^{-1}
Vogel et al.[55] using ref 19	19.861 ± 0.02	0.0449	-10.644
present paper using ref 18	19.826 ± 0.004	0.0455	-10.644

helium,[18] which is based on a highly accurate ab initio pair potential for helium.[22] It is to note that the theoretical values for helium are characterized by a lower uncertainty in comparison with that for argon, ± 0.02 % compared to ± 0.1 %. The resulting value $C_N = 1.34758$ was used for the evaluation of the measurements of the present paper.

The reference data for the viscosity of helium in Table 1 used to calibrate the oscillating-disk viscometer, applied for our earlier measurements on the noble gases and on nitrogen in 1984,[23] and the present viscometer make evident that the difference consists mainly in the zero-density viscosity coefficient.

The values used for the calibration follow from

$$\eta(T,\rho) = \eta^{(0)}_{298.15} + (T - 298.15)(\partial\eta/\partial T)_\rho + \rho(\partial\eta/\partial\rho)_T \tag{1}$$

According to the error analysis for the all-quartz oscillating-disk viscometer in ref 14 the relative uncertainty of the viscosity measurements is given by

$$\frac{\Delta\eta}{\eta} = \frac{\Delta C_{\mathrm{cal}}}{C_{\mathrm{cal}}} + \frac{\Delta\Delta}{\Delta} + \frac{\Delta\tau}{\tau} \tag{2}$$

The relative uncertainty of C_{cal}, which corresponds to a product of the Newell constant C_N and of characteristics of the viscometer, amounts to ± 0.02 % and is determined by that of the helium reference value used for the calibration. The uncertainties of Δ and τ have already been given as ± 0.05 % and ± 0.005 %. Nevertheless, in agreement with the analysis of the argon measurements,[14] the relative uncertainty, compared with that following from eq 2, is conservatively estimated to be ± 0.15 % at room temperature and up to ± 0.20 % at higher temperatures. This is due to closing the viscometer by fusing the filling tube by means of a hydrogen−oxygen flame. The reproducibility does not exceed ± 0.1 % in the measured temperature range.

The total uncertainty in the viscosity consists of the uncertainty in the viscosity measurements according to eq 2 as well as of the allocation errors of the temperature and density measurements considering the temperature and density dependencies of the viscosity:

$$\left(\frac{\Delta\eta}{\eta}\right)_{\mathrm{tot}} = \left[\left(\frac{\Delta\eta}{\eta}\right)^2 + \left(\frac{\partial\eta}{\partial T}\right)^2_\rho \frac{\Delta T^2}{\eta^2} + \left(\frac{\partial\eta}{\partial\rho}\right)^2_T \frac{\Delta\rho^2}{\eta^2}\right]^{1/2} \tag{3}$$

Using the values of the applied density and of the measured viscosity (see below) as well as of the temperature and density derivatives of the viscosity according to the Quiñones-Cisneros[2] and Schmidt[11] correlations and considering the uncertainties of the temperature measurement ΔT (given above) and of the density determination $\Delta\rho$ (see below), the contributions of the allocation errors to $(\Delta\eta/\eta)_{\mathrm{tot}}$ are practically without influence on the total uncertainty of the viscosity.

■ MEASUREMENTS AND RESULTS

The temperature function of the period $\tau_0(T)$ in vacuo was determined in separate measurements, and the values for the logarithmic decrement in vacuo Δ_0 were taken from Whitelaw.[24]

The viscometer is filled with the gases to a pressure less than atmospheric at room temperature. The density of the isochoric series of measurements results from pressure and temperature measured during the filling process and from the volume of the viscometer body. The uncertainty of the density determination is ± 1 % caused by the procedure to close the viscometer by fusing its filling pipe.

A sample (methane 5.5) supplied and certified by Linde AG, Berlin, Germany, with a mole fraction $x_{\mathrm{CH_4}} \geq 0.999995$ was used for the measurements on methane. Its impurities consist of $x_{\mathrm{O_2}} \leq 0.5\cdot10^{-6}$, $x_{\mathrm{N_2}} \leq 4\cdot10^{-6}$, $x_{\mathrm{H_2}} \leq 0.1\cdot10^{-6}$, $x_{\mathrm{C_nH_m}} \leq 1\cdot10^{-6}$, and $x_{\mathrm{H_2O}} \leq 2\cdot10^{-6}$.

For hydrogen sulfide a sample by Linde AG, Berlin, Germany, with a certified purity of $x_{\mathrm{H_2S}} \geq 0.995$ was used. Its impurities according to the gas chromatographic analysis by Linde AG are $x_{\mathrm{COS}} \leq 3\cdot10^{-3}$, $x_{\mathrm{H_2O}} \leq 2\cdot10^{-3}$, $x_{\mathrm{N_2}} \leq 0.5\cdot10^{-3}$, $x_{\mathrm{CO_2}} \leq 0.5\cdot10^{-3}$, and $x_{\mathrm{CH_4}} \leq 0.5\cdot10^{-3}$. The effect of the impurities is small, since the viscosities of carbonyl sulfide and of water vapor are of the same order of magnitude as that of hydrogen sulfide (at ambient temperature: $\eta_{\mathrm{H_2S}} \approx 12.0\ \mu$Pa·s, $\eta_{\mathrm{COS}} \approx 12.3\ \mu$Pa·s, and $\eta_{\mathrm{H_2O}} \approx 9.5\ \mu$Pa·s).

Two series, for methane somewhat differing in density, were performed on both gases for at least 15 different temperatures between 292 K (290 K for methane) and 682 K. Five oscillation runs were carried out for each individual measuring point and the measured values for temperature, logarithmic decrement, and period were averaged. In particular, near to room temperature, some individual measuring points were replications to test for a possible electric charging of the quartz glass during the filling process. Such electric charging provokes an increased damping of the oscillating disk and consequently somewhat increased viscosity values. The discharge is dependent on the time elapsed after filling and is accelerated at higher temperatures. The results are summarized in Table 2 for methane and in Table 3 for hydrogen sulfide. The further evaluation has revealed that the first two measuring points for the second series on methane and for the first series on hydrogen sulfide are influenced by electric charging. These points are marked in Tables 2 and 3.

All experimental $\eta(T,\rho)$ data of the present paper were recalculated to the limit of zero density to compare them on a common basis with the reference values (η_{ref}) of the Quiñones-Cisneros correlation for methane[2] and the Schmidt correlation for hydrogen sulfide[11] as well as with values derived theoretically using the ab initio intermolecular potential energy hypersurfaces for methane[6] and hydrogen sulfide[13] and the extended kinetic theory of dilute molecular gases. For that purpose the values of the Quiñones-Cisneros and the Schmidt correlations were calculated for the comparison at pressures of $1\cdot10^{-6}$ MPa, which corresponds practically to the limit of zero density.

Whereas the theoretical values conform to the zero-density limit, experimental data are not directly accessible for it. For the moderately low densities under discussion, the correction is based on a first-order expansion for the viscosity, in terms of density, where B_η is the second viscosity virial coefficient:

$$\eta(T,\rho) = \eta^{(0)}(T)[1 + B_\eta(T)\rho] \tag{4}$$

Table 2. Viscosity of Methane at Low Density

series 1			series 2		
ρ = 0.344 kg·m^{-3}			ρ = 0.498 kg·m^{-3}		
T	η	$\eta^{(0)}$	T	η	$\eta^{(0)}$
K	μPa·s	μPa·s	K	μPa·s	μPa·s
292.96	10.926	10.921	289.05	10.813[a]	10.806[a]
297.08	11.062	11.057	296.57	11.048[a]	11.041[a]
323.86	11.914	11.909	323.43	11.886	11.878
350.55	12.735	12.729	350.64	12.725	12.717
378.15	13.562	13.556	378.25	13.552	13.543
405.88	14.365	14.358	406.03	14.360	14.350
433.83	15.149	15.142	434.02	15.141	15.131
461.85	15.912	15.906	461.75	15.901	15.891
490.13	16.663	16.656	490.15	16.649	16.640
518.83	17.398	17.391	518.80	17.403	17.393
542.60	17.996	17.990	542.36	17.981	17.971
565.38	18.564	18.557	565.10	18.544	18.534
594.08	19.261	19.254	593.84	19.239	19.229
623.33	19.953	19.947	623.05	19.934	19.925
652.41	20.626	20.620	652.07	20.605	20.596
682.14	21.310	21.303	681.93	21.273	21.264
291.93	10.891	10.886	290.41	10.833	10.826
			296.43	11.029	11.022

[a] Influenced by electric charging.

Table 3. Viscosity of Hydrogen Sulfide at Low Density

series 1			series 2		
ρ = 0.740 kg·m^{-3}			ρ = 0.740 kg·m^{-3}		
T	η	$\eta^{(0)}$	T	η	$\eta^{(0)}$
K	μPa·s	μPa·s	K	μPa·s	μPa·s
291.61	11.856[a]	11.879[a]	292.77	11.880	11.904
296.89	12.069[a]	12.091[a]	297.01	12.059	12.081
323.96	13.181	13.197	323.94	13.186	13.202
350.47	14.287	14.298	350.59	14.296	14.307
378.01	15.430	15.437	378.19	15.443	15.450
405.76	16.562	16.566	405.86	16.574	16.577
433.66	17.693	17.693	433.81	17.700	17.700
461.72	18.808	18.806	461.92	18.818	18.817
490.09	19.926	19.923	490.20	19.920	19.917
518.68	21.004	20.999	518.75	21.005	21.000
542.61	21.901	21.894	542.48	21.901	21.894
565.19	22.737	22.729	565.29	22.750	22.743
594.02	23.794	23.786	593.95	23.789	23.781
623.07	24.816	24.806	623.19	24.822	24.812
652.30	25.835	25.825	652.32	25.845	25.834
682.03	26.842	26.831	681.36	26.824	26.813
292.46	11.866	11.889	292.30	11.863	11.886

[a] Influenced by electric charging.

The zero-density viscosity coefficient $\eta^{(0)}$ is obtained after rearranging eq 4. The needed B_η values can be calculated by means of the Rainwater-Friend theory,[25−28] which models B_η in reduced form using the Lennard−Jones 12−6 potential for the interactions in the moderately dense gas.

$$\eta^{(0)}(T) = \frac{\eta(T,\rho)}{1 + N_A\sigma^3 B_\eta^*(T^*)\rho},$$
$$B_\eta^*(T^*) = \frac{B_\eta(T)}{N_A\sigma^3}, \quad T^* = \frac{k_B T}{\varepsilon} \tag{5}$$

Here N_A and k_B are Avogadro's and Boltzmann's constants, respectively. T^* is the reduced temperature, $B_\eta{}^*$ is the reduced second viscosity virial coefficient, σ and ε/k_B are the Lennard−Jones 12−6 potential parameters. Vogel et al.[29] recommended an improved empirical expression for $B_\eta{}^*$ as a function of T^* between $0.5 \le T^* \le 100$, which can be extrapolated down to $T^* \approx 0.3$ and for which the coefficients b_i are listed in ref 29.

$$B_\eta^*(T^*) = \sum_{i=0}^{6} b_i T^{*-0.25i} + b_7 T^{*-2.5} + b_8 T^{*-5.5} \tag{6}$$

The Lennard−Jones 12−6 parameters for methane, σ = 0.3706 nm and ε/k_B = 159.7 K, needed for the computation were taken from Bich and Vogel.[28] In the case of hydrogen sulfide, σ = 0.3565 nm and ε/k_B = 355.8 K as well as $\eta^{(0)}$ were derived together in an iterative process. In a first step, the experimental $\eta(T,\rho)$ data were directly used to derive start values for σ and ε/k_B. In a second step, preliminary $\eta^{(0)}$ values were determined with these start values using eqs 5 and 6 and the experimental $\eta(T,\rho)$ data. In a further step, the preliminary $\eta^{(0)}$ values were applied to calculate improved Lennard−Jones 12−6 parameters σ and ε/k_B. The procedure was repeated until no improvement was found.

The $\eta^{(0)}$ values resulting for both gases with eqs 5 and 6 from the experimental $\eta(T,\rho)$ data are listed in the third and sixth columns of Tables 2 and 3. The correction is very small for methane and reduces the measured values by 0.07 % to 0.04 %, systematically decreasing with temperature. The situation is somewhat more complicated for hydrogen sulfide, because the initial density dependence of its viscosity is negative at lower temperatures and increases to positive values with rising temperature. Hence the correction amounts to +0.20 % at room temperature and to −0.04 % at the highest temperature. The correction is of importance when comparing with the theoretically calculated temperature dependence of viscosity.

COMPARISON AND REFERENCE VALUES

Methane. The comparison between the results of the best measurements, available in the literature[5,30−43] including the data of the present paper, and the reference values (η_{ref}) of the Quiñones-Cisneros correlation for methane[2] is illustrated in Figure 1. The literature values were also recalculated to the limit of zero density. Either isothermal values as a function of density were extrapolated to this limit or individual values at low density were corrected to it using the Rainwater−Friend theory for the initial density dependence of the viscosity (see above). If necessary, the experimental temperature values were corrected to the temperature scale ITS-90 (International Temperature Scale of 1990). Without anticipating any conclusion, the discussion will be focused on the most recent data.

The figure illustrates that the experimental data of May et al.,[5] which already have been mentioned in the Introduction, deviate

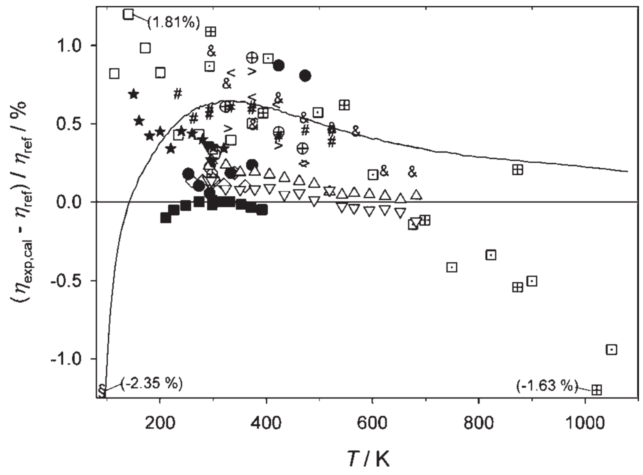

Figure 1. Deviations of experimentally based (η_{exp}) and of theoretically calculated (η_{cal}) zero-density viscosity coefficients for CH_4 from reference values (η_{ref}) of the Quiñones-Cisneros correlation[2] implemented in the REFPROP computer program (NIST 23, version 9.0),[1] as a function of temperature. Experimental data: ○, Kestin and Yata;[30] □, Clarke and Smith;[31] ⊡, Dawe et al.;[32] ⊙, Kestin et al.;[33] ⊕, Hellemans et al.;[34] ⊞, Maitland and Smith;[35] §, Sluysar et al.;[36] &, Timrot et al.;[37] ★, Gough et al.;[38] >, Kestin et al.;[39] <, Abe et al.;[40] #, Evers et al.;[41] ◊, Schley et al.;[42] ■, May et al.;[5] ●, El Hawary;[43] △, present paper, first series of measurements; ▽, present paper, second series of measurements; ▼, present paper, second series of measurements, influenced by electric charging. Calculated values: —, theoretically computed with the new intermolecular CH_4 potential.[6]

from the Quiñones-Cisneros reference values only within ± 0.05 %, apart from the datum at the lowest temperature of 211 K. This is in agreement with the Quiñones-Cisneros correlation being based on these data. Over a more limited temperature range, (260 to 360) K with 20 K intervals, Schley et al.[42] performed isothermal measurements up to maximum pressures of 29 MPa with a vibrating-wire viscometer in a relative manner and estimated the uncertainty of their results at low densities to be ± 0.2 %. The temperature dependence of the viscosity data of Schley et al. is consistent with that of the experiments by May et al., although the values of Schley et al. are higher by about 0.15 %. The difference arises mainly because Schley et al. used for the calibration of their vibrating-wire viscometer at 20 °C, an old reference value of Kestin and Leidenfrost[44] for the viscosity of argon. This datum is increased by 0.15 % compared with the theoretically calculated viscosity value for the viscosity of argon at this temperature (see Figure 4 and its discussion in ref 17). In the mutually overlapping temperature range (298 to 392) K, the experimental data of the first measurement series of the present paper are characterized by deviations of about +0.25 % from the May et al. values, whereas the data of the second series differ by about +0.15 %. Hence the data of May et al. and of the present paper are mutually consistent within their uncertainties of ± 0.096 % and ± (0.15 to 0.20) %. In addition, the differences between the two series of the present paper do not exceed ± 0.1 % at all temperatures up to 682 K (apart from the points influenced by electric charging). This means that the changes of the viscometer are small, even if measurements up to high temperatures are carried out, followed by refilling and performing a further series of measurements including the evaluation of both series with the same Newell constant. In this way the performance of the viscometer, the reproducibility of the measurements, and the conservative error analysis are approved.

In 2002, Evers et al.[41] performed at the Ruhr-Universität-Bochum, Germany, absolute measurements with a rotating-cylinder viscometer between (233 and 523) K up to pressures of 30 MPa and estimated the uncertainty of their data at low density to be ± 0.15 %. But Figure 1 reveals that their experimental data are too high by about (0.7 to 0.4) % compared with the Quiñones-Cisneros correlation. In the mutually overlapping temperature ranges each, the Evers et al. data are higher by about 0.6 % than the experimental data of May et al. and higher by about 0.4 % than the present values. Although the results of the measurements on helium and neon reported by Evers et al. in the same paper are in close agreement with reliable data of other investigators (see refs 18, 45, and 46), the same is not the case for methane as well as for argon.[17] Hence the Evers et al. data cannot be considered as reference values. In 2009, El Hawary[43] reported about new measurements with an improved rotating-cylinder viscometer at the Ruhr-Universität-Bochum and claimed for his low-density viscosity data in the temperature range (253 to 473) K the uncertainty to be ± 0.06 %. Figure 1 makes evident that the data of El Hawary are on average higher by 0.15 % than the Quiñones-Cisneros values and within ± 0.1 % with the results of the present paper, but only between (253 and 373) K. The reason why the experimental data of El Hawary are too high at (423 and 473) K by about (0.8 to 0.9) %, related to the Quiñones-Cisneros correlation, remains unclear. Nonetheless, the El Hawary data in the temperature range (253 to 373) K can be taken as reference values.

Furthermore, Figure 1 makes evident that the temperature dependence of the present viscosity data deviates a little from that of the Quiñones-Cisneros correlation. Thus the present data decrease systematically by about 0.2 % between room temperature and 682 K. On the contrary, the temperature dependencies of the May et al. reference values and of the present viscosity data are in excellent agreement with that of the viscosity values calculated theoretically by means of the intermolecular potential hypersurface of methane and the extended kinetic theory for dilute molecular gases.[6−8] This is very important, although the theoretical values exceed on average by 0.6 % the May et al. data and by 0.4 % (Series 1) and 0.5 % (Series 2) the present results. The difference between experimental data and theoretical values indicates that either the rigid-rotor assumption of the kinetic theory needs to be relaxed or the intermolecular potential needs some minor improvement. But when accounting for the difference of about 0.5 %, the temperature dependence of the theoretically calculated values can be used to create very reliable reference values for methane down to 90 K and up to 2000 K.

In accordance with the reference values accepted for the viscosity of the rare gases[19] in the 1970s, the experimental data reported by Kestin and co-workers[30,33,34,39,40] differ at ambient temperature from the values of May et al. by about + (0.1 to 0.3) %. However at temperatures between (330 and 380) K the Kestin data,[34,39,40] whose uncertainty was estimated to be < ± 0.3 %, exceed the experiments of May et al. up to +0.9 %. Although the Kestin data agree at higher temperatures better with the theoretically calculated values, they are definitely incorrect. The differences from the reference values of May et al.,[5] Schley et al.,[42] El Hawary,[43] and the present paper are due to a temperature measurement error in the experiments of Kestin and co-workers with their high-temperature oscillating-disk viscometer.[47] This error was extensively discussed by Vogel et al.[29] and was confirmed by comparison of viscosity data for helium, neon, and argon, measured with the same viscometer by Kestin and co-workers, with reference viscosity values for these rare gases,[17,18,45,46] which were derived from ab initio calculations of the interatomic pair potentials and by using the kinetic theory of dilute monatomic gases.

The experimental values of Smith and co-workers[31,32,35,38] measured with capillary viscometers, of Slyusar et al.[36] obtained by means of a falling-cylinder viscometer, and of Timrot et al.[37] using an oscillating-disk viscometer of the same kind as in the present paper are characterized by uncertainties of > ± 0.5 %. Hence they are not appropriate to be included in the group of qualified reference values, even though they extend to low temperatures (90.7 K) as well as to high temperatures (1050 K). The comparably small differences between (200 and 600) K from the theoretically calculated values are most likely fortuitous.

Hydrogen Sulfide. In principle, only primary viscosity data should be considered for a reliable correlation. Primary data require high-precision instruments, for which a full working equation including necessary corrections can be applied. They are characterized by a low uncertainty and a proven compatibility with data obtained from other methods or at least in other instruments. These requirements do not hold for the seven viscosity data sets of hydrogen sulfide at low pressures, which were available in the literature for the development of the Schmidt correlation.[11] The uncertainty of the very old measurements with capillary viscometers by Graham,[48] Rankine and Smith,[49] and Jung and Schmick[50] was already estimated by Schmidt et al.[11] to be of the order of ± (3 to 5) %. Pal, Bhattacharyya, and co-workers[51−54] claimed for their measurements with oscillating-disk viscometers around 1970 an uncertainty of ± (0.6 to 1.0) %, which seems to be very optimistic.

The Schmidt correlation is compared in Figure 2 with the data sets from the literature and with the experimental data of the present paper in the limit of zero density. Although the literature data suffer from a high uncertainty, they were also corrected for the effect of the initial density dependence[28,29] based on the information given in the papers. In addition, the experimental temperature values were again corrected to the temperature scale ITS-90. The correction to the zero-density limit is reasonable with respect to the further comparison with viscosity values calculated theoretically using the ab initio intermolecular potential energy hypersurface of hydrogen sulfide and the extended kinetic theory of dilute molecular gases.[13]

The figure illustrates that the Schmidt correlation is based on the experiments of Pal, Bhattacharyya, and co-workers.[51−54] The data of Pal and Barua and of Pal and Bhattacharyya measured from room temperature to 483 K, the highest temperature of these papers, are described by the correlation within ± 1.0 %. But the measurements of Bhattacharyya et al.[53,54] including experimental points at low temperature (the lowest at 221 K) are characterized by differences from the Schmidt correlation, which increase systematically with rising temperature and come up to −3.3 % at 308 K. In addition, the four earlier experimental data points[48−50] exceed the Schmidt correlation by + 2.5 to 5.1) %. All seven data sets from the literature cannot be regarded as reference data.

The situation seems to become more complicated regarding the data of the present paper. The new experimental values differ from the Schmidt correlation by −(1.9 to 6.9) %, increasing from ambient temperature up to 682 K. The reason that the data of the present paper are lower than practically all other data could be due to the fact that older experiments possibly suffer from an insufficient filling procedure so that the measured samples could be contaminated by some air. However, there is one decisive argument in favor of the present data. They agree within ± 0.1 % with the theoretically calculated values in the complete temperature range of the measurements (apart from the two data points influenced by electric charging). Although this excellent match is most likely fortuitous, the principal point is the consistent temperature dependence of the present experimental data and of the theoretical viscosity values. Hence the data of the present paper are claimed to be reference data.

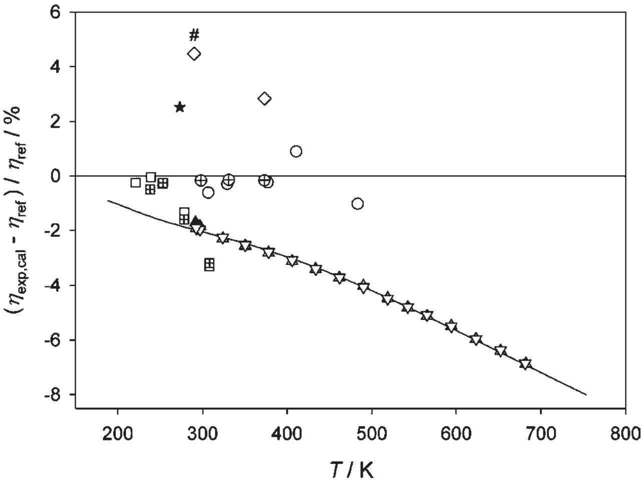

Figure 2. Deviations of experimentally based (η_{exp}) and of theoretically calculated (η_{cal}) zero-density viscosity coefficients for H_2S from values (η_{ref}) of the Schmidt correlation[11] implemented in the REFPROP computer program (NIST 23, version 9.0),[1] as a function of temperature. Experimental data: ★, Graham;[48] ◇, Rankine and Smith;[49] #, Jung and Schmick;[50] ○, Pal and Barua;[51] ⊕, Pal and Bhattacharyya;[52] □, Bhattacharyya et al.;[53] ⊞, Bhattacharyya;[54] △, present paper, first series of measurements; ▲, present paper, first series of measurements, influenced by electric charging; ▽, present paper, second series of measurements. Calculated values: —, theoretically computed with the new intermolecular H_2S potential.[13]

■ CONCLUSIONS

The relative viscosity measurements on gaseous methane and hydrogen sulfide with an all-quartz oscillating-disk viscometer, based on a calibration with only one theoretically calculated zero-density viscosity value for helium at 298.15 K, are characterized by an uncertainty of ± 0.15 % at room temperature increasing up to ± 0.2 % at 682 K. This low uncertainty qualifies the new data to be reference values for the viscosities of methane and hydrogen sulfide.

The comparison with data from the literature indicates for methane that reference data are already available. These are the experimental values of May et al.[5] between (211 and 392) K, Schley et al.[42] between (260 and 360) K, and El Hawary[43] between (253 and 373) K. But the new data extend the range to high temperatures by nearly 300 K. The four experimental data sets determined with different experimental methods (capillary, vibrating-wire, rotating-cylinder, and oscillating-disk viscometers) are mutually consistent and characterized by the same temperature dependence. The data of the present paper are also in close agreement with the Quiñones-Cisneros correlation[2] implemented in the REFPROP computer program by NIST,[1] whereas the temperature dependence of the present viscosity data differs by about 0.2 % between room temperature and 682 K from that of the Quiñones-Cisneros correlation. Although viscosity values, calculated theoretically[6] using the ab initio intermolecular potential energy hypersurface for methane[7] and the extended kinetic theory of dilute molecular gases,[8] are about 0.5 % higher than the four reference data sets, the temperature dependencies of the experimental data and of the theoretical values are consistent within ± 0.1 % for the complete temperature range of the measurements. When accounting for the difference, the temperature dependence of the theoretically calculated values can be used to create very reliable viscosity values down to 90 K and up to 2000 K and to improve further the Quiñones-Cisneros correlation for methane.

In the case of hydrogen sulfide, the seven data sets available in the literature for the development of the Schmidt correlation[1,11] are not characterized by reference quality. Although the new experimental data are (2 to 6) % lower than the Schmidt correlation between (292 and 682) K, they agree within ± 0.1 % with viscosity values calculated theoretically[13] using the ab initio intermolecular potential energy hypersurface for hydrogen sulfide and the extended kinetic theory of dilute molecular gases. The new experimental values are claimed to be reference data so that they should establish the basis for an improved viscosity correlation. Whereas the fortuitous exact agreement between experimental and theoretical values is insignificant, the consistent temperature dependence of the theoretical viscosity values should be used to extrapolate the future correlation to low and high temperatures.

The comparison with experimental reference data makes evident that state-of-the-art calculations of zero-density viscosity values using ab initio intermolecular hypersurfaces and the extended theory of dilute molecular gases are rational and trustworthy. The development of improved viscosity correlations is supported by theoretically calculated viscosity values, since their temperature dependence enables to extrapolate reliably to low and high temperatures, at which accurate measurements are difficult and often impossible.

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