Recommended Viscosities of 11 Dilute Gases at 25 °C

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Commercially manufactured meters that measure the flow of a process gas are often calibrated with a known flow of a surrogate gas. This requires an accurate model of the flow meter and accurate values of the relevant thermophysical properties for both gases. In particular, calibrating a "laminar" flow meter near ambient temperature and pressure requires that the ratio (process gas viscosity)/(surrogate gas viscosity) be known to approximately 0.1%. With this motivation, we critically reviewed measurements of viscosity conducted with 18 instruments near 25 °C and zero density for 11 gases: He, Ne, Ar, Kr, Xe, H_2, N_2, CH_4, C_2H_6, C_3H_8, and SF_6. For these gases and this single state, we determined viscosity ratios with relative standard uncertainties ranging from 2.7 $\times 10^{-4}$ to 3.6 $\times 10^{-4}$ at a 68% confidence level. Anchoring the ratios to the value $(19.8253 \pm 0.0002) \times 10^{-6}$ Pa s for the viscosity of helium calculated *ab initio* at 25 °C and zero density yields recommended values for the other ten gases and establishes a scale for gas viscosities that is more accurate than most of the reported values. To facilitate the extension of this scale, we recommend that researchers who calibrate gas viscometers (1) use helium as a calibration gas when possible, (2) report the values of all calibration data, and (3) report the uncertainties of their measured viscosity ratios. Similarly, we recommend that data archives capture this relevant calibration information. © 2012 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [http://dx.doi.org/10.1063/1.4765368]

Key words: argon; dilute gases; ethane; helium; krypton; methane; neon; nitrogen; propane; reference viscosities; sulfur hexafluoride; viscosity; xenon.

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bin 0.5 u_r(ratio) wide, where u_r(ratio) is the estimated standard deviation of ratios measured with each instrument.................................

1. Introduction

The present work was stimulated by three observations about the viscosity of gases at low density: (1) accurate values of viscosity ratios are needed to calibrate certain flow meters; (2) the uncertainty of measured viscosity ratios is much smaller than the uncertainty of measured absolute viscosities; and (3) the viscosity of helium η_{He} at zero density is known from theory with a relative standard uncertainty $u_r(\eta_{He}) \approx 10^{-5}$ near ambient temperature.[1]

In response to these observations, we critically reviewed viscosity measurements[2–40] conducted with 18 instruments for 11 gases: He, Ne, Ar, Kr, Xe, H_2, N_2, CH_4, C_2H_6, C_3H_8, and SF_6. These gases have been frequently studied, either for their commercial importance or for their interest to theorists. We calculated 235 viscosity ratios from those measurements, simultaneously fit them to obtain the most accurate values of the ratios at 25 °C and zero density, and then anchored the fitted ratio values to the most accurate value of η_{He}. (See Table 1.) The resulting recommended viscosities, supplemented by the temperature and pressure derivatives of the viscosities, successfully address the calibration need mentioned above. The scope of the present correlation is more limited than that of many other correlations that reproduce measured viscosity values over wide ranges of temperature and density. However, this correlation can be extended to other gases and to wider ranges of states by reconsidering published viscosity

data from a ratio perspective. Thus, this work is a step towards a more accurate viscosity scale.

Often, commercially manufactured gas-flow meters are calibrated using one gas at one temperature and pressure and then used to measure flows of another (process) gas at other temperatures and pressures. For so called "laminar" flow meters, the calibration adjustment relies on published values of the viscosity ratios $\eta_{process}/\eta_{calibration}$. Recently, Wright et al.[44] critically tested this practice by calibrating three types of laminar flow meters with five different gases. They detected small inconsistencies that could be reduced by slightly altering the viscosity ratios generated by a widely used database.[45] Thus, their calibrations would have benefitted from the accurate values of viscosity ratios reported here. When the viscosity of two gases is measured using a single instrument, the ratio of the viscosities is often more accurately determined than the viscosity of either gas because the linearity and the reproducibility of the instrument is often significantly smaller than its absolute uncertainty. This is illustrated in panels (a)–(f) of Fig. 1. In these panels, the data from the various instruments are concentrated along the diagonal lines that represent viscosity ratios calculated from the viscosities recommended in Table 1. The concentration of the ratio data demonstrates that the uncertainties are correlated and that viscosity ratios are more accurately determined than viscosities themselves. (If the uncertainties were uncorrelated, the data would scatter in a roughly circular pattern.) In Sec. 2 below, we discuss why the measured viscosity ratios are highly correlated.

We anchor the measured viscosity ratios to the remarkably accurate result $\eta_{0,He} = (19.8253 \pm 0.0002)$ μPa s calculated ab initio by Cencek et al.[1] (Unless otherwise stated, all uncertainties are standard uncertainties with 68% confidence level.) This result for the viscosity of helium at 25 °C and zero density is consistent with earlier calculations that had larger uncertainties.[46–48] As discussed in Ref. 1, the ab initio result

TABLE 1. Reference viscosities obtained by fitting 235 viscosity ratios measured using 18 instruments. (A): Recommended values of η_0 (the viscosity at 25 °C and zero density) and their absolute $u(\eta_0)$ and relative standard ($k = 1$) uncertainties $u_r(\eta_0)$. The uncertainty was calculated by multiplying the standard uncertainty returned by the fitting program by the standard deviation σ of the normalized deviations ($\sigma = 1.89$, see Sec. 6). (B): Values of the isothermal density derivative of the viscosity that we used to adjust measurements of η to zero density. (C): Values of the exponent b in the expression $\eta = \eta_0(T/298.15 \text{ K})^b$ that we used to adjust η_0 to 25 °C.

	(A)			(B)		(C)	
	η_0 μPa s	$u(\eta_0)$ μPa s	$10^4 u_r(\eta_0)$	$10^4 (d\eta/d\rho)/\eta_0$ $\text{m}^3 \text{ kg}^{-1}$	Refs.	b	Ref.
H_2	8.8997 $\pm$ 0.0030		3.4	19.2 $\pm$ 4.7	3,14,15	0.69	39
He	19.8253[a] $\pm$ 0.0002[a]		0.1	−1.1 $\pm$ 1.3	3,4,13,15,37	0.69	22
CH_4	11.0631 $\pm$ 0.0035		3.1	19.2 $\pm$ 1.9	14,30,37	0.88	17
Ne	31.7088 $\pm$ 0.0100		3.1	1.4 $\pm$ 0.1	3,4,13,37	0.68	22
N_2	17.7494 $\pm$ 0.0048		2.7	6.3 $\pm$ 0.6	3,13,15,32	0.77	22
C_2H_6	9.2305 $\pm$ 0.0030		3.3	8.2 $\pm$ 2.0	35,41,42	0.94[b]	35
Ar	22.5666 $\pm$ 0.0060		2.7	4.9 $\pm$ 0.5	3,13,15,29,37	0.85	22
C_3H_8	8.1399 $\pm$ 0.0028		3.5	−4.9 $\pm$ 2.0	26,29,35,42	0.99[b]	35
Kr	25.3062 $\pm$ 0.0080		3.2	3.6 $\pm$ 0.5	3,29,37,43	0.92	22
Xe	23.0183 $\pm$ 0.0072		3.1	2.7 $\pm$ 0.2	3	0.98	22
SF_6	15.2234 $\pm$ 0.0054		3.6	0.6 $\pm$ 0.6	24,31	0.89	24

[a]Calculated in Ref. 1.

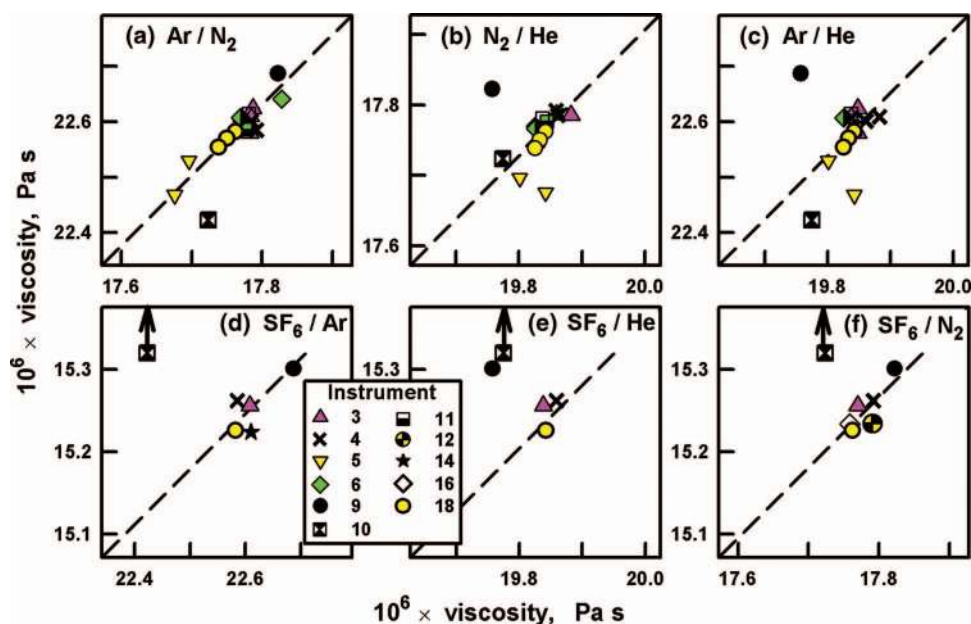[b]Value not needed for adjustment to 25 °C but included here for completeness.

FIG. 1. (Color online) Viscosities of six pairs of gases measured with 11 instruments. For each gas pair such as Ar/N$_2$, the viscosity of Ar, η_{Ar}, is plotted on the vertical axis and η_{N2} is plotted on the horizontal axis. Each axis ranges from 99% to 101% of the viscosity recommended in Table 1. The diagonal, dashed lines represent the recommended ratios of viscosities. The instruments are identified by numbers listed in Table 2. The value of η_{SF6} measured with instrument 10 is 15.507 μPa s, which is off the scale, as indicated by arrows on panels (d)–(f).

agrees also with the best available measurements[3,37,38] to within twice the measurement uncertainty, which is at least 20 times larger than the uncertainty of the *ab initio* result. For completeness, we note that *ab initio* calculations predict the viscosity as a function of the thermodynamic temperature T. In contrast, viscosities are measured as a function T_{90}, the temperature on the International Temperature Scale of 1990. Near 25 °C, $(T - T_{90}) \approx 0.0029$ K (Ref. 49) and $(d\eta_{He}/dT)/\eta_{He} \approx 2.3 \times 10^{-3}$ K^{-1}. Therefore, the fractional correction of η for $(T - T_{90})$ is 7×10^{-6}, which is only slightly smaller than the relative uncertainty $u_r(\eta_{He}) \approx 10 \times 10^{-6}$ of the *ab initio* result.

In previous work at NIST, we used capillary viscometers to measure gas viscosity ratios, and we claimed that the results had uncertainties of approximately 0.02%.[38–40] Our uncertainty claims were based on a rigorous analysis of the uncertainties of the measurements, but the comparisons of our ratios to those measured elsewhere were not comprehensive. Here, we examine published measurements of viscosities made with 17 other instruments based on capillaries, oscillating disks, vibrating wires, and rotating cylinders. After excluding outliers, the NIST viscosity ratios (Instrument 18 in Table 2) are consistent, within combined uncertainties, with the ratios obtained with the other instruments, provided that the uncertainties of all 18 instruments are multiplied by a factor of 1.89. (Section 6 explains the origin of this factor.)

The remainder of this paper is organized as follows. In Sec. 2, we show that measured viscosity ratios are expected to be more accurate than individual viscosity measurements. Section 3 describes the criteria for selecting the 18 instruments discussed here. We mention our criteria for selecting the data, the technique used by each research group, and the processing of the

published data to deduce viscosities at 25 °C and zero density. Section 4 describes the method of simultaneously fitting to all of the data, Sec. 5 discusses discrepant data (outliers), and Sec. 6 describes the deviations and uncertainties of the final fit. In Sec. 7, we discuss the present results and briefly consider their implications concerning a viscosity scale.

2. Measured Ratios Have Small Uncertainties

We consider four types of instruments that have been used to accurately measure the viscosities of dilute gases: (1) capillary flow, (2) oscillating disk, (3) rotating cylinder, and (4) vibrating wire. As shown in Fig. 2, the first three instruments are arranged so that most of the viscous dissipation occurs in a confined space that is well defined and geometrically stable, while the vibrating-wire instrument operates so that dissipation occurs mainly in a layer whose thickness δ_v is comparable to or smaller than the wire radius. (Here $\delta_v \equiv [\eta/(\pi f \rho)]^{1/2}$ is the viscous penetration length, where ρ is the density of the gas and f is the oscillation frequency.) Consequently, all four instruments have an important dimension that is small and difficult to measure accurately: the internal diameter a of a capillary, the external radius a of a wire, or the distance a between a rotating cylinder or an oscillating disk and its stationary surroundings. However, the ratio of two viscosities measured with the same instrument is only weakly sensitive to the small dimension, as we now show explicitly.

When the viscosity of a dilute gas is measured with a capillary viscometer and a mass flow meter, an approximate
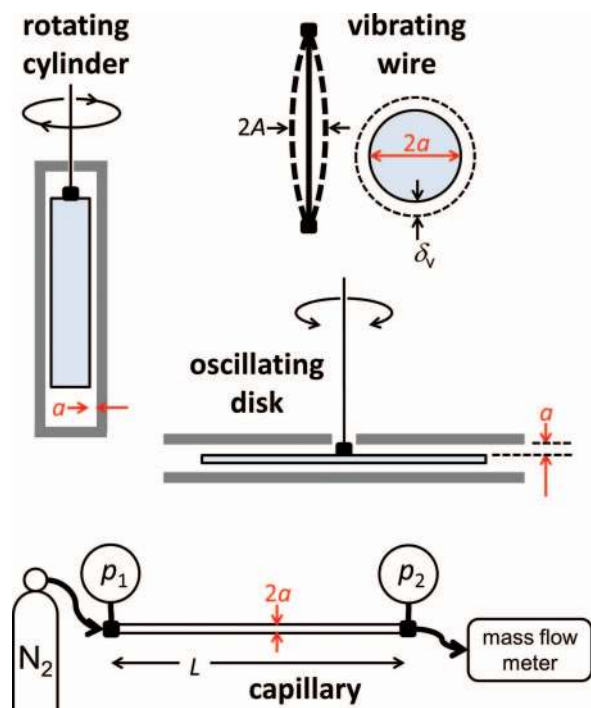
FIG. 2. (Color online) Four types of instruments that have been used to accurately measure the viscosities of dilute gases. Each instrument has a small length (a) that is difficult to measure accurately.

working equation is[50]

$$\eta \cong \frac{\pi a^4}{16L} \frac{(p_1^2 - p_2^2)}{\dot{n}RT}, \tag{1}$$

where a and L are the radius and length of the capillary, p_1 is the pressure upstream of the capillary, p_2 is the pressure downstream of the capillary, $\dot{n}$ is the molar flow rate, and R is the universal gas constant. If the same capillary is used to measure the viscosities of two gases, the ratio of the viscosities is insensitive to a, L, and the scale factors for the flow meter and pressure gauges. The ratio is sensitive to the capillary dimensions only through small correction terms not shown in Eq. (1).[38]

The oscillating disk viscometer, as refined by Kestin and Leidenfrost to measure the viscosity of dilute gases,[3] operates in the regime $\delta_v \gg a$, where a is the geometric mean of the distances between the top and bottom surfaces of the oscillating disk and the stationary plates above and below the disk. An approximate working equation for this instrument is

$$\eta \approx 2Iaf\Delta/r^4, \tag{2}$$

where $2\pi\Delta$ is the logarithm of the amplitude decrement during one oscillation period, and I and r are the moment of inertia and radius of the disk. The length a will cancel out of a viscosity ratio determined with Eq. (2). A more sophisticated working equation, such as Eq. (1) in Ref. 8, also has little sensitivity to a because each of its terms can be written as a function of ratio δ_v/a multiplied by a function of aspect ratios such as r/a.

The vibrating wire viscometer, as developed by Tough et al.,[51] operates in the regime $\delta_v < a$ and $A < \delta_v$, where a

is the radius of the wire and A is the amplitude of the oscillation. (Measurements are sometimes made as a function of A^2 and extrapolated to $A = 0$.) In the approximation that the hydrodynamic mass of the wire is small, the working equation is

$$\eta = \frac{\pi a^2 f \rho}{2[m(k')]^2}, \tag{3}$$

where

$$k' \equiv \rho_{\text{wire}}/(\pi\rho f\tau). \tag{4}$$

Here ρ_{wire} is the density of the wire material, $\tau = (\omega\Delta)^{-1}$ is the measured damping time of the free vibrations, and the function $m(k')$ describes the hydrodynamics of a cylinder oscillating transversely in a fluid at small amplitude. A viscosity ratio obtained by using Eqs. (3) and (4) does not depend on the wire radius a. More generally, a viscosity ratio obtained with any oscillating-body viscometer operating at small amplitude will depend only weakly on a length such as a because the viscometer's response depends on viscosity only through a function of the ratio δ_v/a.[52]

The magnetically suspended, rotating-cylinder instrument developed by Docter et al.[53] operated as a viscometer and a densimeter. It was refined by Evers et al.,[37] who determined the viscosity of a gas in the narrow annular volume surrounding the rotating cylinder by measuring the free decay of the cylinder's rotation about its symmetry axis. They used the working equation [Eq. (4) in Ref. 37],

$$\eta = (zD - D_R)/C, \tag{5}$$

where D^{-1} is the time constant for the exponential decay of the rotational motion; D_R^{-1} is the time constant when the cylinder is in vacuum; C is the "apparatus coefficient"; and z is a correction for the momentum of the rotating fluid. The parameter C depends upon the moment of inertia of the cylinder and the geometry of the flow field and is approximately inversely proportional to the thickness a of the annular volume surrounding the cylinder. When this apparatus is used to determine viscosity ratios, the values of the ratios are independent of C (and thus a) and only weakly dependent on z.

3. Selecting and Adjusting the Data

Table 2 lists the selected viscosity values obtained from Refs. 2–40. We considered only data published since 1959, the year of the landmark paper by Kestin and Leidenfrost.[3] Publications that included multiple gases, especially helium, were favored. Publications that did not specify clearly the calibration values were rejected. Often, a laboratory published data that were obtained with a viscometer that had been modified only slightly over the course of a few years. We assumed that the viscosity values obtained during those years were sufficiently reproducible to yield consistent viscosity ratios, and we, therefore, grouped such publications into a single "instrument."

TABLE 2. Selected values of viscosity that were used to calculate the viscosity ratios. Each of the 18 instruments is identified by an author and a range of years in bold face. When instruments comprise multiple publications from one laboratory, each publication is identified by the year of publication and the first author. The relative uncertainty u_r(ratio) of the viscosity ratios was estimated from the scatter of the measurements of both gases. The typical uncertainty for each instrument is the average of individual uncertainties. Ratios derived from values in parentheses were excluded as outliers.

Inst	Reference	Ref.	Method	$10^4 \times$ u_r(ratio)	H₂ μPa s	He μPa s	CH₄ μPa s	Ne μPa s	N₂ μPa s	C₂H₆ μPa s	Ar μPa s	C₃H₈ μPa s	Kr μPa s	Xe μPa s	SF₆ μPa s
1	**1959 Rietveld**	2	Oscillating disk	**28**[a]	8.9644	19.8395		31.3266							
2	1959 Kestin	3		4[a]	(8.9675)	19.8482		31.7494	17.7870		22.6240		25.3196	23.0580	
2	1964 Kestin	4		4[b]		19.8374		31.7949			22.6074				
2	1966 Kestin	5		4[b]		19.8486			17.7826		22.5800		25.3432		
2	1968 Kestin	6		7[a]	(8.9332)	19.8486	11.0870		17.7826				25.3656		
2	**1959–1969 Kestin**		Oscillating disk	**5**											
3	1971 Kestin	7		4[c]		19.8825			17.7850		22.6090				
3	1971 Kestin	8		6	8.9080	19.8382	11.0740	31.7508	17.7698	9.2367	22.6079	8.1492	25.3546		15.2560
3	1972 Kestin	9		4[a]		19.8593		31.7733	17.7861						
3	1972 Kestin	10		4[a]		19.8610		31.7520			22.6010		25.3600	23.0510	
3	**1971–1972 Kestin**		Oscillating disk	**5**											
4	1977 Kestin	11		6[c]		19.8590	11.0990	31.7700	17.7920		22.5850				15.2620
4	1978 Abe	12		6[c]		19.8610	11.1000	31.7520	17.7850	9.2500	22.6010	8.1500		23.0510	
4	**1977–1978 Kestin**		Oscillating disk	**6**											
5	1963 Flynn	13		9[a]		19.8422		31.6919	17.6758		22.4680				
5	1964 Barua	14		10[a]	8.8890	19.8422[d]	(10.9910)								
5	1969 Gracki	15		5[a]	8.8550	19.8010			17.6960		22.5300				
5	**1963–1969 Flynn**		cap. 0.19 mm	**8**											
6	**1968 Smith**	16	cap. 0.44 mm	**22**[c]					17.8280		22.6410		25.3900	23.0830	
7	**1969 Smith**	17	cap. 0.33 mm	**22**[a]		19.8908	11.1129	31.8242	17.8055						
8	**1989 Smith**	18	cap. 0.44 mm	**20**[c]	8.9255						22.6586				
9	1970 Dawe	19		20[b]		19.7573		31.6804	17.8224		22.6869		25.4952	23.2249	
9	1970 Dawe	20		50[b]		19.7573[e]	11.1762		17.8224						15.3008
9	**1970 Smith**		cap. 0.44 mm, high T	**35**											
10	**1983 Lukin**	21	cap. 0.5 mm, transient	**14**[a]	8.8925	19.7748		(31.2349)	17.7235		22.4228		25.1170	22.9887	(15.5074)
11	**1984 Vogel**	22	Oscillating disk	**6**[a]		19.8441		31.7801	17.7766		22.5861		25.3701	23.0471	
12	1989 Vogel	23							17.7912						
12	1989 Strehlow	24							17.7912[f]						15.2340
12	1992 Hendl	25							17.7912[f]	9.2471					
12	**1989–1992 Vogel**		Oscillating disk												
13	1995 Vogel	26		14[a]					17.7693		22.6071	8.1460			
13	2011 Vogel	27		15[b]		19.8260	11.0830								
13	2012 Vogel	28		15[b]		19.8260			17.7662						
13	**1995–2012 Vogel**		Oscillating disk	**15**											

TABLE 2. Selected values of viscosity that were used to calculate the viscosity ratios. Each of the 18 instruments is identified by an author and a range of years in bold face. When instruments comprise multiple publications from one laboratory, each publication is identified by the year of publication and the first author. The relative uncertainty u_r(ratio) of the viscosity ratios was estimated from the scatter of the measurements of both gases. The typical uncertainty for each instrument is the average of individual uncertainties. Ratios derived from values in parentheses were excluded as outliers.—Continued

Inst	Reference	Ref.	Method	$10^4 \times$ u_r(ratio)	H_2 μPa s	He μPa s	CH_4 μPa s	Ne μPa s	N_2 μPa s	C_2H_6 μPa s	Ar μPa s	C_3H_8 μPa s	Kr μPa s	Xe μPa s	SF_6 μPa s
14	2000 Wilhelm	29		7[a]							22.6100	8.1410	25.3470		
14	2004 Schley	30		7[a]			11.0790				22.6100				
14	2005 Wilhelm	31		7[a]							22.6100				15.2240
14	2006 Seibt	32		7[a]					17.7880		22.6100				
14	2006 Wilhelm	33		7[a]						9.2380	22.6100				
14	**2000-2006 Vogel**		Vibrating wire, 25 μm	**7**											
15	2009 Seibt	34		11[a]		19.8260			17.7416						
15	2011 Seibt	35		25[b]		19.8260				9.2272		8.1350			
15	**2009–2011 Vogel**		Vibrating wire, 25 μm	**18**											
16	**1985 Hoogland**	36	cap. 0.20 mm	**6[a]**					17.7584						15.2336
17	**2002 Evers**	37	Rotating cylinder	**4[b]**		19.8374	(11.1120)	(31.6878)	17.7812		22.6144		25.3539		
18	2005 Berg	38		2[b]		19.8420			17.7620		22.5820	8.1480			15.2260
18	2007 May	39		2[b]	8.9032	19.8330	11.0630		17.7501	9.2346	22.5700			23.0257	
18	2012 Berg	40		3[b]		19.8253		31.6880	17.7381		22.5539		25.2812		
18	**2005–2012 NIST**		cap. 0.31 mm	**2**											

[a]Estimated u_r(ratio) as experimental scatter $\times 2^{1/2}$.
[b]Used authors' value of u_r(ratio).
[c]Assumed u_{ratio} equal to that of a similar publication.
[d]Used η_{He} value from Ref. 13 to calculate η_{gas}/η_{He} viscosity ratios.
[e]Used η_{He} value from Ref. 19 to calculate η_{gas}/η_{He} viscosity ratios.
[f]Used η_{N2} value from Ref. 23 to calculate η_{gas}/η_{N2} viscosity ratios.

All of the data in Table 2 are at the standard condition of $T_0 = 25\,°C$ in the limit of zero density ρ. Some publications reported viscosity values only at 20 °C or at 1 atm, and our adjustments to the standard condition used the form

$$\eta(\rho, T) = \eta_0 \left[1 + \frac{\rho}{\eta_0} \left(\frac{d\eta}{d\rho} \right)_{\rho=0} \right] \left(\frac{T}{T_0} \right)^b, \qquad (6)$$

with the temperature and density dependences listed in Table 1. Other publications reported viscosity values over a range of temperature or density. When it was available, we used the authors' fit to those values to obtain the viscosity at the standard condition; otherwise we used our own fit. When the original authors used a temperature or density derivative to adjust the viscosity to 25 °C or to zero density, we made no correction when the value differed from those listed in Table 1. The effects of the differences between the original temperature scale and ITS-90 are too small to require corrections.

4. Calculating and Fitting to the Viscosity Ratios

After adjusting the values to the standard condition, we calculated the viscosity ratios among the gases for each of the publications listed in Table 2. For four of the publications,[13,19,24,25] we calculated the gas/helium ratios by using the helium viscosity value reported by the same group in a contemporary publication. Frequently, there were multiple viscosity ratio measurements for common gas pairs, such as N_2/Ar; for such pairs we combined the multiple ratio measurements into an unweighted average for that instrument. After dropping unity ratios, such as η_{Ar}/η_{Ar}, and redundant ratios, such as η_{Ar}/η_{N2} (while keeping η_{N2}/η_{Ar}), there were 266 independent viscosity ratios.

The viscosity values were obtained from a simultaneous fit to the viscosity ratios using the open source statistical package R.[54] We assumed that the viscosity of helium was

$\eta_{He} = 19.8253$ μPa s (Ref. [1]) and then used a linear model to fit the viscosities η_{gas} of the other ten gases to the 266 ratios r_{ixy}. Here, i denotes the instrument (1–18), and x and y denote the gas (1–11, where 2 is helium). The fit minimized the squared sum of the weighted deviations defined by

$$\sum_{i=1}^{18} \sum_{x=1}^{11} \sum_{y=1, y \neq x}^{11} \left[\frac{\ln(r_{ixy}) - \ln(\eta_x/\eta_y)}{u(r_{ixy})/r_{ixy}} \right]^2, \quad (7)$$

where $u(r_{ixy})$ is the ratio uncertainty. Consistent with the assumption of linearity, the fit used logarithms of the ratios instead of the ratios themselves so that, for example, $\ln(r_{ixy}) + \ln(r_{iyz}) + \ln(r_{izx}) = 0$.

The published estimate of the ratio's uncertainty was used whenever it was available. Typically, only the absolute viscosity's uncertainty and the reproducibility of the measurement were stated. In those cases, we assumed that the ratio uncertainty was due only to the reproducibility, and we estimated the ratio uncertainty by multiplying the reproducibility typical for one gas by $2^{1/2}$. In some cases, we estimated the reproducibility from the typical deviations of a curve fitted to the authors' tabulated data. In a few publications,[7,11,12,16,18] the limited information led us to assume that the viscosity ratios had the same uncertainty as a similar, earlier publication from the same group.

5. Outliers

After a preliminary fit to all 266 ratios, we looked for outliers by comparing the measured ratios r_{ixy} to the ratios η_x/η_y calculated from the fitted viscosities. In particular, we looked for values of the absolute normalized deviation

$$D_i(x,y) = \left| \frac{\ln(r_{ixy}) - \ln(\eta_x/\eta_y)}{u(r_{ixy})/r_{ixy}} \right| \quad (8)$$

that exceeded 5 and were correlated with one gas and one instrument. Such a correlation suggests that the deviation was caused by an impurity in the gas. Table 3 lists six gas-instrument combinations where such deviations were identified as outliers. The rows of Table 3 indicate the order in which the outliers were identified and removed. After removing the outliers indicated in the first and second rows (Instrument 10

TABLE 3. Gas-instrument combinations identified as outliers in the preliminary fit. The rows are in order of decreasing absolute normalized deviation $D_i(x,y)$, as defined by Eq. (8).

Instr.	Year	Group	Ref.	$D_i(x,y)$
10	1983	Lukin	21	$D_{10}(gas, SF_6) \approx 16$
10	1983	Lukin	21	$D_{10}(gas, Ne) \approx 10$
2	1959–1969	Kestin[a]	3,6	$D_2(gas, H_2) \approx 10$
5	1963–1969	Flynn[b]	14	$D_5(gas, CH_4) \approx 8$
17	2002	Evers[c]	37	$D_{17}(gas, CH_4) \approx 7$
17	2002	Evers[c]	37	$D_{17}(gas, Ne) \approx 5$

[a]Time dependent η_{H2}/η_{N2} and η_{H2}/η_{Ar} (Fig. 3).
[b]Large nonlinear extrapolation to $p = 0$.
[c]Viscosity-dependent deviations from fit (Fig. 4).

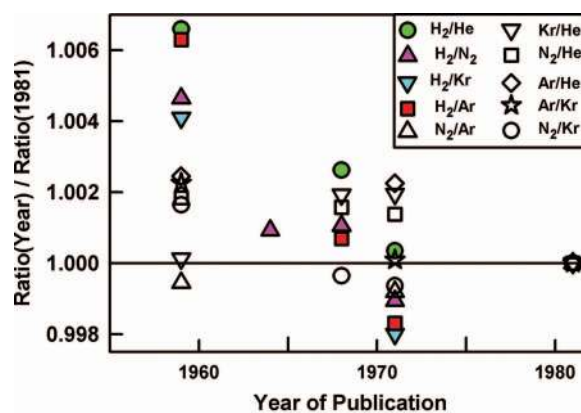FIG. 3. (Color online)Viscosity ratios for H_2, He, N_2, Ar, and Kr reported by Kestin's group in 1959,[3] 1964,[4] 1968,[6] 1971,[8] and 1981.[55] Before plotting, every ratio was divided by its value reported in 1981. All four ratios involving H_2 (filled symbols) were anomalously high in 1959. (The data from the 1981 paper did not clearly specify the calibration values for He and Ar and, therefore, were not used in the correlation.)

with SF_6 and Ne), we refit the data before identifying and removing the outliers indicated in the third row (Instrument 2 with H_2). Continuing in that fashion, we removed a total of 31 outliers and then fit the remaining 235 viscosity ratios to yield the final viscosity values in Table 1.

Because removing data from a correlation has a subjective aspect, we point out that the first two entries of Table 3 comprise data with deviations that are large enough to be seen easily in plots such as Fig. 1, and below we provide graphical evidence that supports the outlier status of the other entries.

The third entry of Table 3 is Instrument 2 (Kestin 1959–1969) with H_2. Figure 3 plots the ten viscosity ratios computed from Kestin's values for the viscosities of H_2, He, N_2, and Ar during the years 1959 through 1981, all divided by their 1981 values. Between 1959 and 1981, the ratios involving hydrogen decreased, while the other ratios on average did not change. (The corresponding papers do not mention the decrease.) This suggests that the values of η_{H2} measured in 1959 were anomalously large (and not that the values of η_{H2} measured in subsequent years were anomalously small), confirming the identification of this data set as outliers.

The fourth entry of Table 3 is Instrument 5 (Flynn) with CH_4. An error in the CH_4 value at zero pressure[14] is plausible because it was estimated by a nonlinear extrapolation of data obtained above 28 bar.

The fifth and sixth entries of Table 3 are Instrument 17 (Evers, Ref. [37]) with CH_4 and Ne. Figure 4 displays the deviations between Evers' measurements and the results of a trial fit to 242 ratios that included Evers' measurements while excluding the other outliers indicated in Table 3. The deviations appear to have a viscosity dependence which suggests that the theory of the instrument [Eq. (5)] can be improved. Nine of Evers' 15 viscosity ratios involve Ne and CH_4. Removing these nine changed the fitted viscosities by the fraction 2.7×10^{-4}, in the worst case. (See Table 4.)
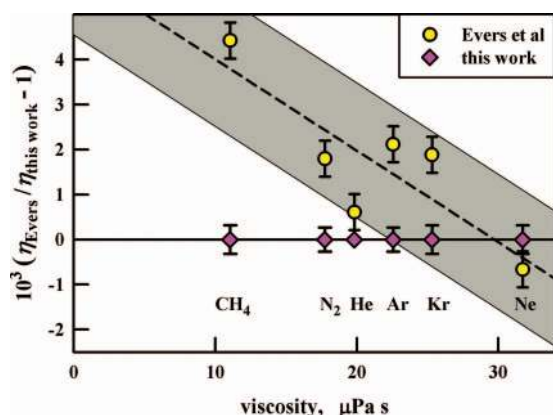
FIG. 4. (Color online)Deviations of measurements of Evers *et al.*[37] from the results of a trial fit to 242 ratios that included Evers' measurements while excluding the other outliers indicated in Table 3. The shaded band represents the uncertainty of the instrument of Evers *et al.*: $\pm 0.0015 \eta$. The uncertainty bar for each point is our estimate of that ratio's uncertainty; it neglects the common uncertainty due to the calibration. The dashed line is a linear fit to Evers' deviations, which appear to depend on viscosity.

6. Deviations and Uncertainties of the Final Fit

After we removed the outliers indicated in Table 3, the final fit to the remaining 235 ratios yielded the viscosity values in Table 1. Figure 5 summarizes the resulting fractional deviations. The upper panel shows two histograms, one for the ratios measured using all 18 instruments and one for the ratios measured using the 4 more precise instruments (u_r(ratio) < 0.0005). The histogram for the more precise instruments shows that 79 of the 108 ratios fall within the range ± 0.0007, which is consistent with our conclusion that the recommended

values of the viscosities have fractional uncertainties on the order of 0.0003. (See Table 1 and the discussion below.) The histogram for all 18 instruments shows a larger spread, with 23 of the 235 ratios falling outside the range ± 0.0040. The larger spread is due partly to the range of instrument uncertainties ($0.0002 < u_r$(ratio) < 0.0036) and partly to outliers that were included in the fit because their normalized deviations were smaller than those in Table 3.

The lower panel of Fig. 5 compares a histogram of the deviations (normalized by their estimated uncertainties) to a normal distribution (curve) with no free parameters. The normal distribution's mean is zero and its width is the standard deviation ($\sigma = 1.89$) calculated directly from the normalized deviations. The normalized deviations are close to the normal distribution, which, by definition, has no outliers. Therefore, we made no attempt to identify additional outliers.

The standard deviation of the normalized deviations, $\sigma = 1.89$, is larger than the expected value of 1.00. One interpretation of this discrepancy is that any remaining outliers are hidden because they have deviations that are normally distributed. An equivalent interpretation is that some of the estimated instrument uncertainties are too small. The uncertainties given in Table 1 account for this discrepancy by multiplying the standard uncertainties returned by the fitting program by 1.89.

We examined the sensitivity of the fit to the input data by removing various subsets of the data and refitting. Table 4 shows that the sensitivity was small except for CH_4, Kr, and SF_6. The largest sensitivity occurs for η_{SF_6}; upon removing the data from Instrument 18 (NIST), η_{SF_6} increases by the fraction 0.0010; upon removing the data from Instruments 3 and 4 (Kestin), η_{SF_6} decreases by the fraction 0.0007. In Fig. 1, panels (d)–(f) display three ratios involving SF_6. For each panel, the plotted ratio for Instrument 18 is on the right of the

TABLE 4. Sensitivity of the fitted values η_{fit} to data selection. Each column lists the fractional changes $10^4[\eta_{fit}/\eta_{ref}-1]$ from η_{ref} in Table 1 for alternative selections of data: (1) include outliers listed in Table 3; (2) omit outliers and all ratios with estimated uncertainties greater than 0.0005; (3) omit outliers and all Kestin data (Instruments 2–4); (4) omit outliers and all Vogel data (Instruments 11–15); (5) omit outliers and all Evers data (Instrument 17); (6) omit outliers and all NIST data (Instrument 18). The first three rows give the number of fitted ratios N, the standard deviation σ of the normalized deviations D, and the maximum value of $|D|$.

| Omitted data	None	Outliers & u_r(ratio) > 0.0005	Outliers & all Kestin	Outliers & all Vogel	Outliers & all Evers	Outliers & all NIST
N	264	108	133	202	243	198
σ	4.0	1.5	2.0	1.9	1.9	1.8
$|D_{max}|$	23.1	4.0	6.9	6.9	6.9	7.1
H_2	7.7	−0.1	0.4	−0.2	−0.6	0.1
He	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	3.7	−2.4	−3.1	−0.3	−0.6	7.0
Ne	−6.5	−0.4	−0.8	−1.1	−0.7	4.0
N_2	0.2	−0.2	−2.1	−0.4	−0.8	4.5
C_2H_6	1.4	−0.5	0.9	−0.1	−0.6	0.0
Ar	0.0	1.1	−1.8	−0.3	−1.0	3.7
C_3H_8	1.1	2.0	0.0	0.3	−0.6	−0.3
Kr	−1.7	−0.6	−3.1	−1.6	−1.0	6.4
Xe	−0.5	0.3	−0.1	0.0	−0.6	2.2
SF_6	6.2	0.0	−7.4	0.1	−0.6	10.3
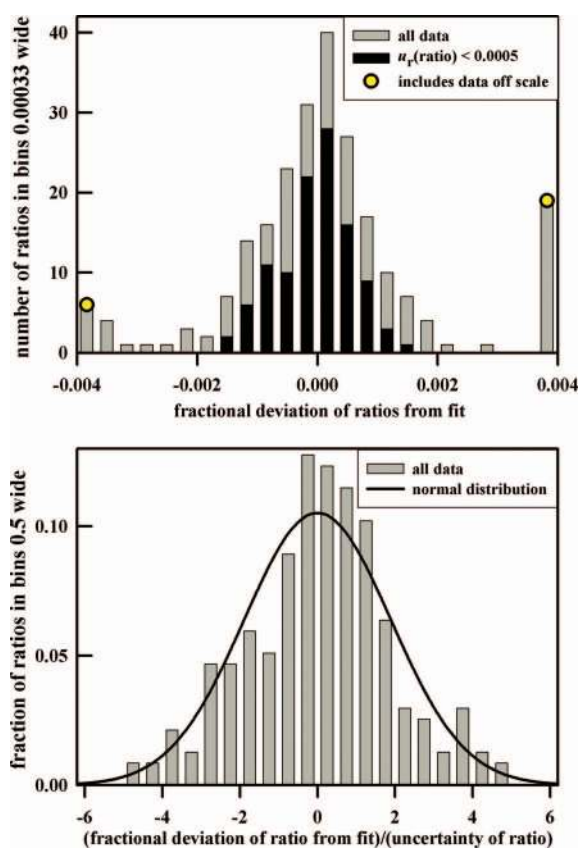
FIG. 5. (Color online)(Top) Histogram showing the distribution of fractional deviations (ratio$_{meas}$/ratio$_{fitted}$ −1). (Outliers are excluded.) The height of each bin is the number of instances that (ratio$_{meas}$/ratio$_{fitted}$ −1) falls into the bin. (Bottom) Histogram showing the fraction of ratios in each bin 0.5 u_r(ratio) wide, where u_r(ratio) is the estimated standard deviation of ratios measured with each instrument. The solid curve is a normal distribution whose width is the standard deviation ($\sigma = 1.89$) calculated directly from the normalized deviations.

dashed line and the plotted ratio for Instrument 3 is on the left of the dashed line. For SF$_6$, ratio measurements from instruments other than 3, 4, and 18 are not sufficiently accurate to resolve this inconsistency. Therefore, the fractional uncertainty $u_r(\eta_{SF6}) = 3.6 \times 10^{-4}$ is the largest uncertainty in Table 1.

7. Discussion

We have demonstrated that the ratios of gas viscosities at 25 °C and zero density are known from measurements with standard relative uncertainties on the order of 0.03%. There is nothing in the present demonstration that is specific to 25 °C other than the abundance of accurate measurements. Similar fits to viscosity ratios at other temperatures are possible because accurate *ab initio* values of η_{He} are available from 1 K to 10 000 K. Therefore, we suggest that future correlations of gas viscosity data multiply the correlation results by the factor needed to make the results consistent with Table 1. This will address the calibration problem mentioned in the Introduction under a wider range of conditions.

More generally, we encourage researchers to use helium as a calibration gas and to explicitly use ratio techniques when acquiring, analyzing, and correlating viscosity data. If this is done, it will be easy to add new gases to Table 1. For example, Vogel recently used a quartz oscillating-disk viscometer to measure the viscosities of CO and N$_2$ over a wide temperature range.[28] He calibrated the apparatus using the *ab initio* value of η_{He} at 25 °C. Vogel's Table 4 includes three values of η_{N2} near 25 °C. When adjusted to exactly 25 °C, their average differs from the value in Table 1 by the small relative fraction -0.00017 ± 0.00044, where the uncertainty is the quadrature sum of the relative uncertainty in Table 1 and the standard relative deviation of Vogel's values from their mean. This agreement gives us confidence in Vogel's instrument. We interpret Vogel's CO results at 25 °C to yield $\eta_{CO} = 17.755$ µPa s with the fractional uncertainty 4×10^{-4}, the same fractional uncertainty we estimated for Vogel's value of η_{N2} near 25 °C. (Vogel reviewed the literature data for η_{CO} and found that previous measurements had much larger uncertainties than his own measurements.)

Acknowledgments

8. References

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