Noble gas viscosities at 25 °C

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Abstract
Near 25 °C, *ab initio* calculations of the zero-density viscosity of helium gas η_{He} have an uncertainty of approximately 0.001 %, which is 1/40th of the uncertainty of the best measurements. The uncertainties of the published calculations for neon [Bich et al. (2008)] and argon [Bich et al. (2007)] are probably much larger. We present new measurements of the viscosities of neon, argon, and krypton at 25 °C made with a capillary viscometer that was calibrated with helium. The resulting viscosity ratios are $\eta_{Ne}/\eta_{He} = 1.59836 \pm 0.00037$, $\eta_{Ar}/\eta_{He} = 1.13763 \pm 0.00030$, and $\eta_{Kr}/\eta_{He} = 1.27520 \pm 0.00040$. The argon ratio agrees with a recent, unpublished calculation [JB Mehl, private communication (2012)] to within the combined uncertainty (measurement plus calculation) of 0.032 %. The neon ratio is smaller than the calculated value by 0.13 %.

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1. Introduction

For most gases, one obtains the intermolecular potential by a fit to experimental data. Today, helium is exceptional because its intermolecular potential can be calculated *ab initio* to high accuracy using only quantum mechanics, fundamental constants, and the atomic mass. The calculated viscosity of helium η_{He} has an uncertainty that is so small (±0.001 % at 25 °C [1]) that, as anticipated [2], it has become a standard for calibrating viscometers. (All uncertainties here are standard uncertainties with coverage factor $k = 1$, which corresponds to a 68 % confidence level.) The disagreement between the most recent measurement [3] and the calculated value is 0.1 %, or twice the combined uncertainty. In contrast, the viscosities calculated by Mehl and coworkers [1,4] and by Bich et al. [5] differ by less than ±0.005 %.

Accurate *ab initio* calculations for other gases are desirable but more difficult. A group at the University of Rostock has published results for the viscosity, thermal conductivity, and second density virial coefficient of neon [6] and argon [7]. Their argon viscosity value differs from a more recent calculation by Mehl [8] by only 0.02 %. Their neon viscosity value motivated us to measure the low-density viscosity of neon. Anticipating additional calculations, we also measured the low-density viscosity of krypton at 25 °C.

Table 1 lists the values measured at NIST for the noble gases and those calculated for helium, neon, and argon. The measured values were obtained using an instrument that was calibrated with a recently calculated value for helium, η_{He} = 19.8253 μPa s [1]. The measured and calculated values of η_{Ar}/η_{He} agree within the combined uncertainty of 0.03 %. In contrast, the values for η_{Ne}/η_{He} differ by 0.13 %, which is more than the measurement uncertainty of 0.02 %. The significance of that difference is unclear because Reference [6] does not estimate the uncertainty of the calculation.

Table 1. Measurements at NIST and calculated viscosities of the noble gases at 25 °C in the limit of zero density. The apparatus was calibrated with the value 19.8253 μPa s calculated for helium [1]. For helium, the uncertainty of the measured ratio $u(\eta_{gas}/\eta_{He}) = 0.00022$ (indicated in the first row) includes contributions from irreproducibility and the uncertainty of the slip correction. The helium contributions are included in the uncertainties for all of the measured ratios.

	measured			**calculated**		
	η_{gas} **(μPa s)**	η_{gas}/η_{He}		η_{gas} **(μPa s)**	η_{gas} **(calculated) / η_{gas} (measured)**	
He	**19.8253**	**1.00000 ± 0.00022**	**a**	**19.8253 ± 0.0002**	**≡ 1**	**[1]**
				19.8245 ± 0.0004		[4]
				19.8262		[5]
Ne	31.6880	1.59836 ± 0.00037	a	31.728	1.00126	[6]
Ar	22.5539	1.13763 ± 0.00030	a	22.552		[7]
				22.556 ± 0.005	1.00009 ± 0.00031	[8]
Kr	25.2813	1.27520 ± 0.00040	a			
Xe	23.0162	1.16095 ± 0.00020	b [16]			

a: this work
b: used Table 2

2. Results for Ne and Kr

Figure 1 compares the NIST value for the neon ratio η_{Ne}/η_{He} with the calculated value and with selected values measured by other groups [10-14] at the standard condition of 25 °C in the limit of zero density. The plot is two-dimensional to efficiently compare the values for argon as well as neon. Each measurement point is derived from data for helium, neon, and argon in a single publication. We used only data that yielded small ratio uncertainties (< 0.0006). Most publications reported only the absolute uncertainty. In those cases we assumed that the ratio uncertainty was due only to the scatter of the measurements of both gases and that the scatter for each gas was the same and uncorrelated. We thus estimated the ratio uncertainty by multiplying the relative scatter typical for one gas by $2^{1/2}$.

Some publications reported viscosity values only at 20 °C or at 1 atmosphere and required adjustment to the standard condition. The adjustments to 25 °C used the temperature dependences measured by Vogel [13]; the adjusted value of η_{Ar}/η_{He} agrees with the value published by May *et al*. [16]. The adjustments to zero density used the viscosity virial coefficients listed in Table 2.

Table 2. Values of the initial density dependence of the viscosity. Each value is an average of several literature values, and, except for xenon, the uncertainty is estimated as the standard deviation of the literature values. The uncertainty for xenon is the measurement uncertainty of Kestin and Leidenfrost [10].

	$(d\eta/d\rho) / \eta$ (m^3 kg^{-1})	references
He	-0.00011 ± 0.00013	10,17,18
Ne	0.00014 ± 0.00001	10,14,19,20
Ar	0.00049 ± 0.00005	10,14,18,19,21
Kr	0.00036 ± 0.00005	10,14,21,22
Xe	0.00027 ± 0.00002	10

Although a general review of viscosity ratios is outside the scope of this article, we note that most of the measurements shown in Figure 1 are mutually inconsistent. We also note that the NIST value for argon agrees with the calculated value, has the smallest uncertainty, and, as described below, was checked by varying both pressure and flow rate. The disagreement between the measured and calculated values for Ne may not be significant because [6] does not give a calculation uncertainty.

The inconsistencies among these measurements suggest that we exclude the measurements of η_{Ar}/η_{He} that disagree with the calculated value. The remaining four points [11-13, this work] have neon ratios whose unweighted mean and standard deviation is $\eta_{Ne}/\eta_{He} = 1.5996 \pm 0.0014$.

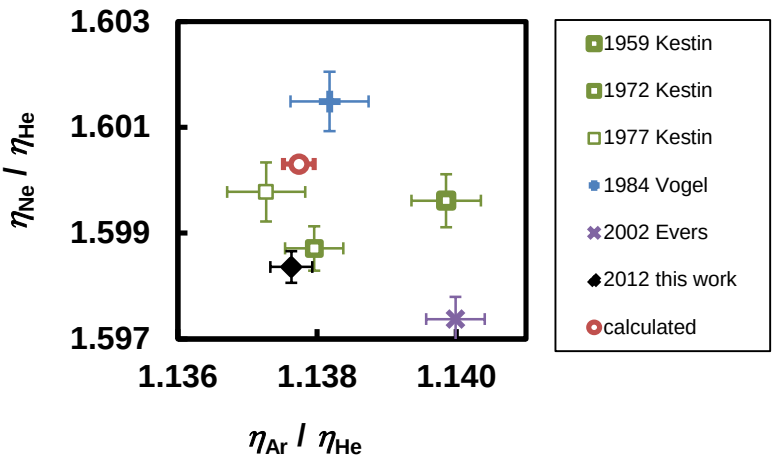

Figure 1. Measured values [10-14, this work], at 25 °C in the limit of zero density, of η_{Ne}/η_{He} plotted against η_{Ar}/η_{He}. The calculated point value was derived from References [1,5-8] and its uncertainty from [8].

Figure 2 is a similar plot for measurements of η_{Kr}/η_{He}. [10,11,13,14, this work]. Again we consider only the measurements from Refs. 11, 13, and this work because these references measured values of η_{Ar}/η_{He} that agree with the calculated ratio. The resulting unweighted mean and standard deviation of the krypton ratio is $\eta_{Kr}/\eta_{He} = 1.2768 \pm 0.0016$.

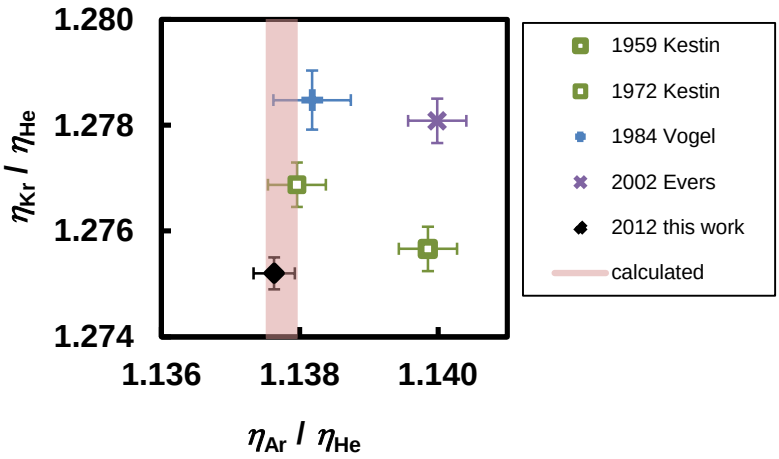

Figure 2. Measured values [10,11,13,14, this work], at 25 °C in the limit of zero density, of η_{Kr}/η_{He} plotted against η_{Ar}/η_{He}. The calculated value of argon [1,5-8] is given by the vertical band whose width indicates the uncertainty estimated in [8].

The following two sections discuss our experimental method and gas purity, which is a particular concern for neon.

3. Experimental method

We used the single-capillary technique described by May et al. [15,16] to determine the viscosities of neon and krypton relative to that of helium at 25 °C. This involved measuring the flow rates of helium and other gases through a coiled quartz capillary while measuring the pressures at the ends of the capillary. We then used a hydrodynamic model [3] that relates the pressures just upstream (p_1) and downstream (p_2) of the capillary to the molar flow rate of the gas through the capillary:

$$\dot{n} = \frac{\left(p_1^2 - p_2^2\right)\pi r^4}{16\eta_0 LRT} C^{gas}\left(T, p_1, p_2\right). \qquad (1)$$

Here R is the universal gas constant, T and η_0 are respectively the gas temperature and viscosity in the limit of zero density, and $r \cong 0.16$ mm and $L \cong 3.9$ m are respectively the bore radius and length of the capillary coil. The function C^{gas} contains a centrifugal factor due to coiling of the capillary and five terms that are small corrections to Poiseuille's law for the flow of an ideal gas through a straight capillary. The corrections account for: (1) the virial coefficients for density and viscosity, (2) slip at the capillary wall, (3) the increase in the kinetic energy of the gas as it enters the capillary, (4) gas expansion along the length of the capillary, and (5) the radial temperature distribution within the gas resulting from gas expansion and viscous dissipation.

The flow was measured by a "*PVTt*" primary flow meter based on measurements of pressure, volume, temperature and time [23]. Most of its fractional uncertainty of 0.02 % was due to static contributions that cancel when measuring a viscosity ratio, and the relevant uncertainty was the stability (< 0.01 %) during the interval needed to measure both gases. The capillary and its values of r and L were the same as those used by May et al.; the uncertainties of r and L introduced negligible uncertainty into the viscosity ratios. The viscosity ratio $\eta_{\mathrm{gas}}/\eta_{\mathrm{He}}$ was determined by applying Eq. (1) twice, once for the gas under study and once for a similar measurement with helium, and then taking the ratio of these two equations.

Slip was an important correction in Eq. (1) for helium and neon at all pressures. The correction term has the form $K_{\mathrm{slip}}\lambda/r$, where K_{slip} is a parameter that describes momentum accommodation and λ is the mean free path. As found previously with this quartz capillary, the data for the heavier gases were consistent with $K_{\mathrm{slip}} = 1$. For helium and neon the respective fitted values of K_{slip} were 1.20 and 1.165.

Figure 3 displays the relative deviations of the neon data (after fitting K_{slip} using the capillary flow model) from the flow measured by the primary flow standard.

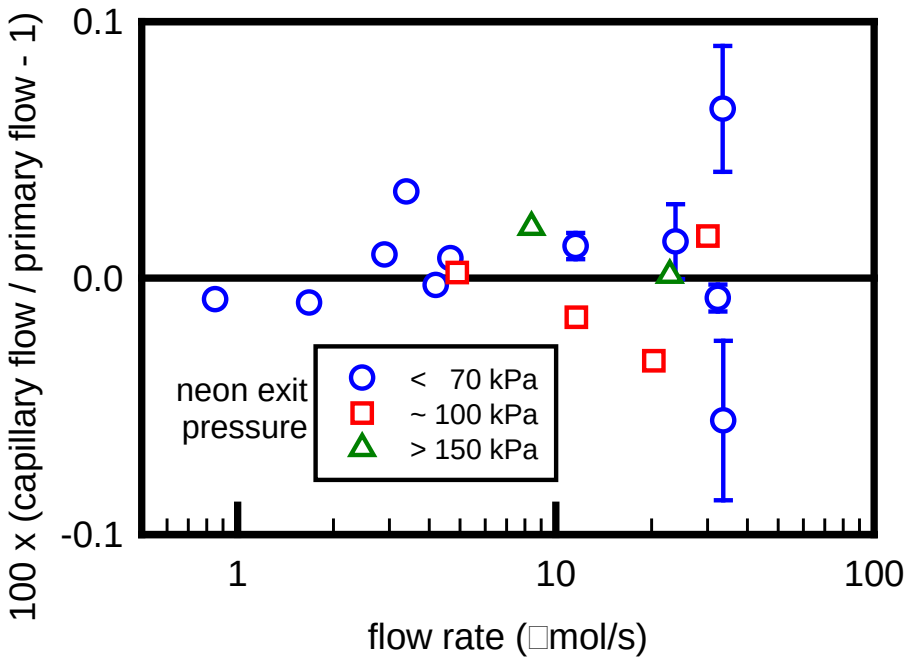

Figure 3. Relative deviations of the capillary flow model from the neon flow measured by the primary flow standard. The error bars for each point in the exit pressure range 32 kPa < p_2 < 70 kPa represent the uncertainty for that point. The error bars for the other points (~100, 152, and 200 kPa) are smaller than the symbols.

Contributions to the uncertainty of the viscosity ratio included the measurement reproducibility (Type A [24]), the uncertainty of K_{slip}, the uncertainty of the gas purity (Ne and Kr, see next section), and the uncertainty of the viscosity virial (adjustment to zero density, see previous section). For example, the uncertainty of the viscosity ratio $\eta_{\text{Ne}}/\eta_{\text{He}}$ was

$$u = \left[\left(u_{\text{A He}}^2 + u_{\text{slip He}}^2 + u_{\text{virial He}}^2 \right) + \left(u_{\text{A Ne}}^2 + u_{\text{slip Ne}}^2 + u_{\text{purity Ne}}^2 + u_{\text{virial Ne}}^2 \right) \right]^{1/2}. \qquad (2)$$

The values of the uncertainty components are listed in Table 3.

Table 3. Contributions, multiplied by 10^4, to the relative uncertainty of the measured viscosity ratios. For each gas, the total uncertainty $u(\eta_{\text{gas}}/\eta_{\text{He}})$ includes the components for helium. The xenon scatter from Reference [16] already includes the helium contributions.

source	He	Ne	Ar	Kr	Xe
scatter (type A)	1.9	2.6	1.5	1.9	1.4 [16]
slip	1.0	1.0	1.0	1.0	1.0
purity	0.1	1.2	0.1	1.6	0.3
viscosity virial	0.2	0.1	0.8	1.9	1.0
$u(\eta_{\text{gas}}/\eta_{\text{He}})$	**2.2**	**3.7**	**3.0**	**4.0**	**2.0**

We checked the accuracy of our results in three ways. First, we varied the flow rate and pressure. As was done by May et al. [16], we excluded data obtained at Dean numbers greater than 10 because those data had deviations that implied a small error in the centrifugal factor, perhaps

because the capillary coil was not perfectly circular. Due to this exclusion, there were only three useful krypton points, with flow rates spanning only a factor of 5; in contrast, the neon flow rates spanned a factor of 40. Most measurements were made with the exit pressure p_2 near 100 kPa, but others spanned the range 32 kPa < p_2 < 282 kPa, independent of the flow rate. The smaller values of p_2 were especially useful for determining the slip correction. For a second check of accuracy, we measured the viscosity ratios for argon and nitrogen and compared the results to those previously measured at NIST using the same apparatus [1,15,16]. The standard deviation of the three values was 0.020 % for nitrogen and 0.019 % for argon, which is comparable to the measurement reproducibility. (See Figure 3.) For our third check, we measured the viscosity of nitrogen before and after all of the other measurements. The ratio of the two sets of nitrogen viscosity measurements, 1.00010 ± 0.00011, is a strong indicator of the stability of the entire system.

4. Gas purity

Neon has the largest viscosity of any gas at room temperature; therefore, any contaminating gas will decrease its viscosity. The neon sample was specified by the manufacturer to have a purity of 99.999 %. Because outgassing of hydrogen from the wall of the 20-year-old cylinder was a concern, we used a mass spectrometer to measure the impurities in the neon. The dominant impurity was water (0.046 % mole fraction), followed by air (N_2 0.013 %, O_2 0.004 %, Ar 0.0001 %), both of which may have originated in the pressure regulator. The only other impurity detected was CO_2 (0.002 %). Contamination by H_2 was negligible (< 0.001 %).

We determined that the mass spectrometer was 1.7 times more sensitive to hydrogen than neon; that ratio led to the estimate that the uncertainty for each impurity was approximately 0.3 times its mole fraction. A viscosity mixing rule (Herning and Zipperer approximation in the Wilke method [25]) was used to estimate the effect of the impurities on the mixture viscosity η_{mix}. The result was $\eta_{\mathrm{mix}}/\eta_{\mathrm{Ne}} = 0.99960 \pm 0.00012$.

Neon has three stable isotopes whose distribution affects the viscosity approximately as the square root of the average atomic mass. Our mass spectrometer was unable to measure the isotopic distribution of our sample to the required accuracy. Fortunately, the distributions found in commercial neon are remarkably uniform worldwide [26,27], and our viscosity analysis used the average molar mass recommended by the Commission on Atomic Weights and Isotopic Abundances (CAWIA), (20.1797 ± 0.0006) g/mol [28]. The calculation by Bich et al. [6] also used the isotope distribution recommended by CAWIA.

Although the krypton cylinder was labelled “calibration gas”, its purity was not specified. Therefore, it was sent to a commercial laboratory for mass spectrometric analysis after the viscosity measurements were finished. Contamination by xenon was a particular concern due to its high concentration in crudely distilled krypton [29], but none was found within the spectrometer’s resolution of 0.01 % mole fraction. Unfortunately, useful measurements of nitrogen, oxygen, and argon in the krypton were not possible because air contaminated the krypton during shipment to the commercial laboratory. Because the absence of xenon suggested an overall good purity, we assumed that the krypton purity during the viscosity measurements was (99.9 ± 0.1) %, a range that conservatively spans the purities of the krypton used for the

measurements used in [10,11,13,14]. The resulting effect on the mixture viscosity was $\eta_{mix}/\eta_{Ne} = 0.99983 \pm 0.00016$.

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