Viscosity-ratio measurements with capillary viscometers

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Abstract

Viscosity-ratio measurements made with capillary viscometers exploit the accurate values of the viscosity of helium calculated *ab initio*. Accurate values of the argon-to-helium viscosity ratio are now used for primary acoustic gas thermometry and for the most accurate redeterminations of the Boltzmann constant. Accurate viscosity ratio measurements enable the calibration of laminar flow meters with surrogate gases and their use with process gases. We review ratio viscometers that comprise one, two, and four capillaries. A single capillary is a ratio viscometer when it is used to measure multiple gases sequentially, while two- and four-capillary viscometers are instruments intended for ratio measurements. We consider gases and Newtonian liquids, with a focus on the two-capillary gas viscometer and its extension to pressures up to 100 MPa. A single-capillary viscometer could measure the ratio (viscosity of liquid water)/(viscosity of gaseous helium) thereby reducing the uncertainty of the liquid-viscosity scale relative to the international system of units.

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1. Introduction

The ratio of two viscosities can be measured more accurately than either viscosity by using a viscometer with a reproducibility that is smaller than its absolute uncertainty. An absolute measurement requires accurate knowledge of the flow field, which, for most viscometers, requires an accurate measurement of a small length such as the inner diameter of a capillary or the gap between a rotating cylinder and a surrounding stationary cylinder. Such lengths can be determined accurately by using the viscometer to measure the viscosity of helium and comparing the result with the viscosity of helium gas calculated *ab initio* (using only quantum mechanics, statistical mechanics, and fundamental constants) [1]. Often, the comparison leads to a smaller uncertainty than that achievable by direct measurement. Once the viscometer is calibrated with helium, it can be used for other, accurate viscosity-ratio measurements. In this review article, we will discuss the use of capillaries to measure viscosity ratios. The discussion will cover measurements of gases and Newtonian liquids, with a focus on the two-capillary gas viscometer recently devised by May *et al*. [2,3] and subsequently used by Zhang et al. [4]. In addition to the review, we make two suggestions for research to be carried out by other laboratories. One is to extend the two-capillary technique to high pressures, and the other is to use a single-capillary viscometer to measure the ratio (viscosity of liquid water)/(viscosity of gaseous helium).

The low-pressure Ar-to-He gas viscosity ratios measured by May *et al*. have proved useful for primary acoustic thermometry [5] and acoustic redeterminations of the Boltzmann constant [6-8]. These acoustic measurements require accurate values of the thermal conductivity of low density argon, which can be obtained by combining

the measured Ar-to-He viscosity ratio with theoretical values for the viscosity of helium and the Prandtl number for argon. The measured Ar-to-He viscosity ratio also has been used in the temperature range $200\,\text{K} < T < 400\,\text{K}$ to test *ab initio* calculations of the viscosity and thermal conductivity of argon [9,10]. The uncertainty of the viscosity calculated from the Ar-Ar interatomic potential is estimated to be less than 0.1 % at temperatures as low as 80 K [10]; however, the uncertainty from the use of classical (rather than quantum-mechanical) calculation has not been quantified, and there may be uncertainties from anomalous bound-state effects [5]. Thus, accurate gas viscosity-ratio measurements at temperatures below 200 K would be a useful guide to theory. Similar measurements above 400 K would help resolve the current tension between measurements and the theory of the viscosity of hydrogen [11].

The widespread practice of calibrating laminar flow meters with surrogate gases (such as helium or argon) and then using them to meter process gases requires accurate surrogate-to-process gas viscosity ratios [12]. With this application in mind, Berg and Moldover [13] reviewed several hundred viscosity measurements near 25 °C and zero density for 11 gases and determined the viscosity ratios among the gases with an uncertainty less than 0.04 %, which is smaller than the uncertainty of the absolute measurements. They then anchored the measured viscosity ratios to the remarkably accurate value,

$$\eta_{0,298}^{\text{He}} = \left(19.8253 \pm 0.0002\right)\ \mu\text{Pa s}\,, \tag{1}$$

calculated *ab initio* by Cencek *et al* [1] for helium at 25 °C and in the limit of zero density. (Unless otherwise stated, all uncertainties are standard uncertainties with 68 % confidence level.)

Table 1 reproduces the viscosities recommended in [13]. The small uncertainty of the

viscosity ratios and the negligible uncertainty of the *ab initio* value means that one

can now use helium gas to calibrate a gas viscometer with an uncertainty limited only

by the reproducibility of the viscometer. The rarity of accurate absolute measurements

of gas viscosity supports the significance of the *ab initio* results. Before 2006, the

calibrations of viscometers, including those with oscillating disks and vibrating wires

as well as capillaries, often traced to measurements by Kestin and Leidenfrost [14],

which in turn traced to Bearden's 1939 measurement of dry air [15].

Table 1. Reference viscosities, reproduced from [13], obtained by fitting 235 viscosity ratios measured using 18 instruments. The first column gives the recommended value of $\eta_{0,298}^{\text{gas}}$, the viscosity at 25 °C and in the limit of zero density, and its standard ($k = 1$) uncertainty. The value for helium was calculated in [1]. The second column gives the corresponding ratios relative to helium. The third column gives the isothermal density derivative of the viscosity that was used to adjust measurements of viscosity to zero density. The fourth column gives the exponent b in the expression $\eta_{0,T}^{\text{gas}} = \eta_{0,298}^{\text{gas}} \left(T / 298.15 \text{ K} \right)^{b}$ that was used to adjust $\eta_{0,298}^{\text{gas}}$ to 25 °C. See [13] for details and references.

	$\eta_{0,298}^{\text{gas}}$ (μPa s)	$\eta_{0,298}^{\text{gas}} / \eta_{0,298}^{\text{He}}$	$10^{4} \left(d\eta / d\rho \right) / \eta$ (m^{3} kg^{-1})	b
H_2	8.8997 $\pm$ 0.0030	0.44891 $\pm$ 0.00034	19.2 $\pm$ 4.7	0.69
He	19.8253 $\pm$ 0.0002	1.00000 $\pm$ 0.00001	-1.1 ± 1.3	0.69
CH_4	11.0631 $\pm$ 0.0035	0.55803 $\pm$ 0.00031	19.2 $\pm$ 1.9	0.88
Ne	31.7088 $\pm$ 0.0100	1.59941 $\pm$ 0.00031	1.4 $\pm$ 0.1	0.68
N_2	17.7494 $\pm$ 0.0048	0.89529 $\pm$ 0.00027	6.3 $\pm$ 0.6	0.77
C_2H_6	9.2305 $\pm$ 0.0030	0.46559 $\pm$ 0.00033	8.2 $\pm$ 2.0	0.94
Ar	22.5666 $\pm$ 0.0060	1.13827 $\pm$ 0.00027	4.9 $\pm$ 0.5	0.85
C_3H_8	8.1399 $\pm$ 0.0028	0.41058 $\pm$ 0.00035	-4.9 ± 2.0	0.99
Kr	25.3062 $\pm$ 0.0080	1.27646 $\pm$ 0.00032	3.6 $\pm$ 0.5	0.92
Xe	23.0183 $\pm$ 0.0072	1.16106 $\pm$ 0.00031	2.7 $\pm$ 0.2	0.98
SF_6	15.2234 $\pm$ 0.0054	0.76788 $\pm$ 0.00036	0.6 $\pm$ 0.6	0.89

Capillary viscometers are simple to construct, and a meter-long glass capillary can be

made with a cross section that is close to circular and uniform over its length. The

inner surfaces of glass capillaries are nearly flat on an atomic scale [16]. Dandeneau

and Zerenner [17] extended these advantages to much longer capillaries in 1979,

when they discovered that a glass capillary could be rugged and flexible enough to bend into a tight coil if it had a thin wall and was made of silica. A long capillary has the advantage that hydrodynamic end corrections are proportional to the radius-to-length ratio of the capillary. Metal capillaries, though less circular and uniform, are even more robust, and the development of electroformed nickel capillaries in 1984 [18] led to commercially available capillaries with smooth walls and diameters as small as 25 μm.

Capillary viscometers can tolerate Reynolds numbers up to at least 100 while retaining stable, laminar flows [19]. In the first approximation, the flow is governed by the Hagen-Poiseuille equation with no-slip boundary conditions [19]. For accurate results, several small, well-understood corrections must be applied. For dilute gases, the capillary dimensions and flow conditions can be chosen so that the relative magnitudes of the corrections are only a few percent.

The next three sections of this article discuss viscometers for gases that comprise respectively one, two, and four capillaries. A single capillary is a ratio viscometer when it is used to measure multiple gases sequentially, while two- and four-capillary viscometers are instruments intended for ratio measurements. The section on two-capillary viscometers discusses how the present low-pressure techniques could be extended up to 100 MPa. The final section discusses single-capillary viscometers for liquids, whose calibrations almost always trace to the viscosity of water. That section includes a proposal to use a single-capillary viscometer to measure the ratio of the viscosity of liquid water to that of gaseous helium.

2. Single-capillary viscometers for gases

The molar flow rate $\dot{n}$ of a gas through a capillary with internal radius r and length L depends on temperature T and the pressures just upstream (p_1) and downstream (p_2) of the capillary as follows [20]:

$$\dot{n} = \frac{\pi r^4 \left(p_1^{\,2} - p_2^{\,2} \right)}{16 L R T \eta_{0,\mathrm{T}}^{\mathrm{gas}}} C^{\mathrm{gas}} \left(T, p_1, p_2 \right) \qquad (2)$$

Here, R is the universal gas constant, and $\eta_{0,T}^{\mathrm{gas}}$ is the viscosity determined at T in the limit of zero pressure. The first factor in Eq. (2) comes from combining ideal-gas compressibility with the Hagen-Poiseuille equation for incompressible flow through a capillary [19], and it estimates the flow rate to within a few percent for a gas near ambient temperature and pressure. The second factor,

$$C^{\mathrm{gas}} \left(T, p_1, p_2 \right) \equiv \left(1 + \sum_{i=1}^{5} c_i^{\mathrm{gas}} \right) f_{\mathrm{cent}} \left(De, r / R_{\mathrm{coil}} \right), \qquad (3)$$

contains five terms c_i^{gas} that are usually small corrections to the flow of an ideal gas through a straight capillary. They account for: (1) the density virial coefficients and the viscosity virial coefficient, (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 function f_{cent} accounts for the centrifugal effect that occurs when the capillary is coiled. It depends on the geometric ratio r / R_{coil}, where R_{coil} is the radius of curvature of the capillary coil, and the Dean number $De \equiv (r/R_{\mathrm{coil}})^{1/2} Re$, where $Re \equiv 2 M \dot{n} / \left(\pi r \overline{\eta} \right)$ is the Reynolds number; M is the molar mass, and $\overline{\eta}$ is the viscosity at the average pressure defined by Eq. (7) of [20]. Further details about each of the correction terms are given in [20].

Table 2 is a list of single-capillary viscometers that were selected to illustrate the ranges of temperature, pressure, geometry, and construction materials that have been used to measure gas viscosities.

Table 2. Examples of single-capillary viscometers that have been used to measure gas viscosities. Here P_{max}, T_{min}, and T_{max} denote, respectively, the maximum pressure and the minimum and maximum temperatures at which the viscometer was used. The last column gives the calibration, which was either absolute (*e.g.* the radius r was measured by mercury intrusion), relative to another gas, or relative to the same gas at a fixed reference temperature T_{ref}.

reference		$2r$	L	$2R_{coil}$	material	T_{min}	T_{max}	P_{max}	cal
		mm	m	mm		K	K	MPa	
1931 Michels	[21]	0.10	0.8		glass	298	348	101.	abs
1959 Eakin	[22]	0.23	0.9		Pyrex	298	644	69.	abs
1963 Flynn	[23]	0.19	0.4		Pb glass	195	373	18.	abs
1964 Reynes	[24]	0.25	3.2	20	s. steel	373	473	81.	abs
1964 Barua	[25]	0.19	0.4		Pb glass	223	423	17.	abs
1968 Clarke	[26]	0.44	1.5	55	Pyrex	114	374	0.2	N_2
1969 Guevara	[27]	0.51	0.1		W	283	2150	0.1	T_{ref}
1970 Dawe	[28]	0.44	1.0	47	Pt	293	1530	0.1	N_2
1970 Dawe	[29]	0.44	1.6	9	silica	450	1100	0.1	N_2
1983 Lukin	[30]	0.50	0.2		glass	77	293	0.01	abs
1985 Hoogland	[31]	0.20	0.2		Pyrex	298	333	12.	abs
1989 Hunter	[32]	0.44	1.5	55	Pyrex	118	353	0.2	Ar
2005 Berg	[20]	0.31	6.4	200	silica	298	298	0.3	abs
2007 May	[3]	0.31	3.9	174	silica	298	298	0.3	He

The most accurate gas viscosity ratios have been measured near room temperature; here we pay special attention to viscosity ratios at 25 °C of dilute gases relative to that of helium, which we denote as $\eta_{0,298}^{gas}/\eta_{0,298}^{He}$. (The first subscript is the pressure in kPa, and the second subscript is the temperature in K.) In general, determining $\eta_{0,T}^{gas}/\eta_{0,T}^{He}$ with a single-capillary viscometer requires measurements of the molar flow rate $\dot{n}$ for both gases and the upstream pressure, downstream pressure, and temperature T of the capillary. One then applies Eqs. (2) and (3) twice, once for the test gas and once for helium, and forms the ratio of these two equations:

$$\frac{\eta_{0,T}^{gas}}{\eta_{0,T}^{He}} = \frac{\left(p_1^{\;2} - p_2^{\;2}\right)_{gas}}{\left(p_1^{\;2} - p_2^{\;2}\right)_{He}} \frac{\left(1 + \sum\limits_{i=1}^{5} c_i^{gas}\right)}{\left(1 + \sum\limits_{i=1}^{5} c_i^{He}\right)} \frac{f_{cent}\left(De_{gas}, r/R_{coil}\right)}{f_{cent}\left(De_{He}, r/R_{coil}\right)} \frac{\dot{n}_{He}}{\dot{n}_{gas}} \qquad (4)$$

Equation (4) is accurate when the capillary's geometry is consistent with the assumptions used to develop the hydrodynamic model. If the capillary is straight, small deviations of the capillary bore from circularity and uniformity are acceptable because the effective radius r is fit to the helium measurement. Three of the corrections in Eq. (3) are proportional to r/L, so the radius-to-length must be small. If a long capillary is made compact by winding it into a coil, the coil radius R_{coil} be uniform and well known to calculate accurately the correction function f_{cent}. The correction function will have errors at large Dean number De if the bore is not circular and uniform along its length. A non-circular capillary whose bore has a flatness $\varepsilon \equiv 1 - b/a$, where a and b are the bore's (unknown) semi-radii, will have an error proportional to εDe^4 [2,33].

Equation (3) includes a correction for slip flow that is proportional to the ratio of the mean free path to the capillary's radius: λ/r. The radius must be large enough, and the pressure high enough, to apply this correction, which assumes $\lambda/r \ll 1$. Helium requires special attention because, for a given temperature and pressure, its mean free path is the largest of any gas. More importantly, the momentum accommodation for helium on smooth quartz glass deviates from unity and was observed to drift from year to year in the same capillary [20].

Determining $\eta_{0,298}^{gas}/\eta_{0,298}^{He}$ with a capillary viscometer requires a flow meter whose nonlinearity and reproducibility are smaller than the uncertainty desired for the

viscosity ratio. The flow meter's absolute uncertainty is less important because an incorrect calibration factor will cancel out of the factor $\dot{n}_{\text{He}} / \dot{n}_{\text{gas}}$ in Eq. (4) and affect only the corrections that are proportional to *Re* and *De*.

3. Two-capillary viscometers for gases

A two-capillary viscometer, comprising two capillaries in series, can be used to measure the temperature dependence of viscosity ratios with small uncertainty and without the need for a flow meter. May *et al*. [2,3] developed and used such a viscometer to measure the viscosities of hydrogen, methane, argon, and xenon in the temperature range from 200 K to 400 K. They analysed their measurements with the relation,

$$\eta_{0,T}^{\text{gas}} = \eta_{0,298}^{\text{He}} \left(\frac{\eta_{0,T}^{\text{He}}}{\eta_{0,298}^{\text{He}}} \right)_{\text{ab initio}} \left(\frac{\eta_{0,298}^{\text{gas}}}{\eta_{0,298}^{\text{He}}} \right) R_{T,298}^{\text{gas,He}}. \tag{5}$$

Equation (5) has four factors: (i) a reference value $\eta_{0,298}^{\text{He}}$ for the viscosity of helium at zero density and 298.15 K, calculated *ab initio* from quantum mechanics and statistical mechanics [1], (ii) the temperature-dependent ratio $\left(\eta_{0,T}^{\text{He}} / \eta_{0,298}^{\text{He}} \right)_{\text{ab initio}}$, also calculated *ab initio* [1], (iii) a reference value for the viscosity ratio $\eta_{0,298}^{\text{gas}} / \eta_{0,298}^{\text{He}}$ measured at 298.15 K [13], and (iv) a measurement of the temperature-dependent ratio of viscosity ratios,

$$R_{T,298}^{\text{gas,He}} \equiv \left(\frac{\eta_{0,T}^{\text{gas}}}{\eta_{0,T}^{\text{He}}} \right) \bigg/ \left(\frac{\eta_{0,298}^{\text{gas}}}{\eta_{0,298}^{\text{He}}} \right). \tag{6}$$

May *et al*. used a single-capillary viscometer to measure $\eta_{0,298}^{\text{gas}} / \eta_{0,298}^{\text{He}}$ and a two-capillary viscometer to measure $R_{T,298}^{\text{gas,He}}$. Such an approach is effective because the uncertainties of the theoretical quantities $\eta_{0,298}^{\text{He}}$ and $\left(\eta_{0,T}^{\text{He}} / \eta_{0,298}^{\text{He}} \right)_{\text{ab initio}}$ are less than

0.01 % [1] and the uncertainties of the measured values of the ratios $\eta_{0,298}^{gas}/\eta_{0,298}^{He}$ and

$R_{T,298}^{gas,He}$ are nearly equal to their precisions.

The reference ratio $\eta_{0,298}^{gas}/\eta_{0,298}^{He}$ was measured by a single-capillary viscometer using

the techniques and analysis described in [2,3,20], while $R_{T,298}^{gas,He}$ was measured over the

temperature range of interest by the two-capillary viscometer shown in Figure 1. With

the upstream capillary's temperature controlled at the reference temperature 298.15 K,

and the downstream capillary's temperature controlled at the measurement

temperature T, helium and the test gas were flowed alternately through the two-

capillary viscometer while the pressures were measured at the ends of both capillaries.

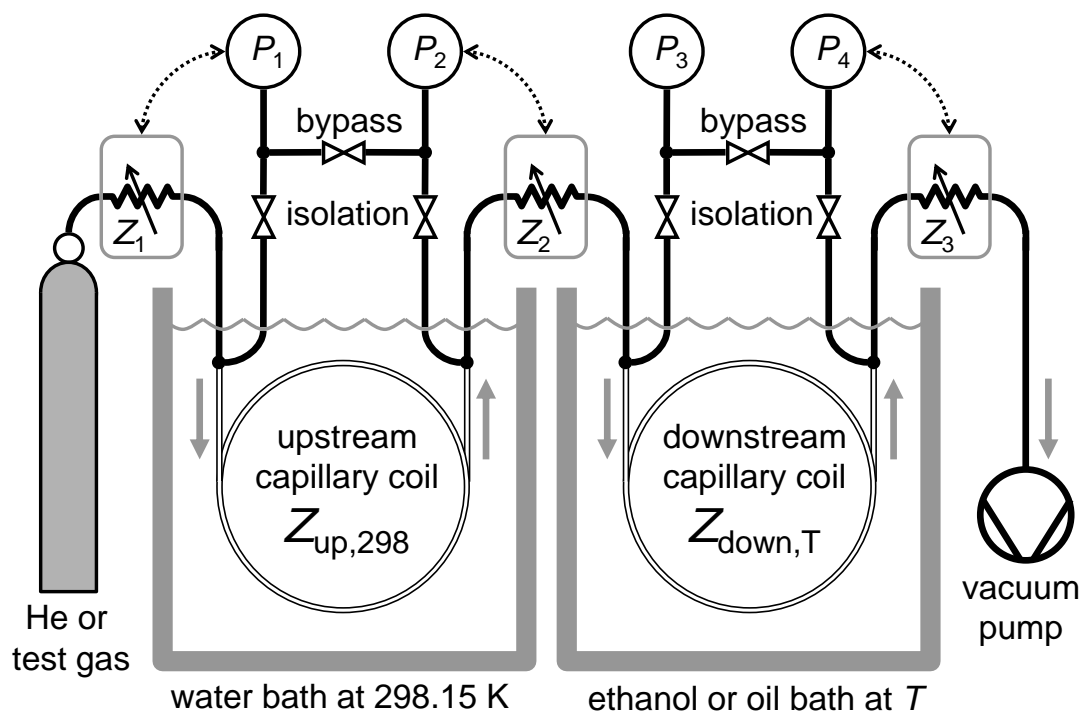Importantly, no flow rate measurements were required to determine $R_{T,298}^{gas,He}$.

Figure 1. Schematic diagram of the two-capillary viscometer used by May *et al*
[2,3]. The impedances Z_{up} and Z_{down} were coiled nickel capillaries with a length of 7
m and an inside diameter of 0.8 mm. The variable impedances Z_1 and Z_3 were
piezoelectric gas leak valves, and Z_2 was either a leak valve or a mass flow controller.
(Reprinted from [3] with permission of Springer.)

Figure 1 indicates five flow impedances: the upstream and downstream capillaries, denoted respectively as $Z_{\text{up,298}}$ and $Z_{\text{down,T}}$, and the variable impedances denoted as Z_1, Z_2, and Z_3. During a measurement p_1 and p_2 were maintained at constant, predetermined values by controlling Z_1 and Z_2. This established a stable but unknown gas flow rate $\dot{n}$ that was identical through both capillaries. If both $\dot{n}$ and $Z_{\text{down,T}}$ were known, Eq. (2) could be used to determine the viscosity at the temperature T from accurate measurements of p_3 and p_4. However, $\dot{n}$ and $Z_{\text{down,T}}$ were unknown, and therefore Eq. (2) was applied separately to the upstream and downstream capillaries to eliminate $\dot{n}$ and obtain an expression for the viscosity ratio $\eta_{0,T}^{\text{gas}}/\eta_{0,298}^{\text{gas}}$ in terms of p_1, p_2, p_3 and p_4. Combining that expression for the test gas with a similar expression for the helium measurements yields the working equation:

$$R_{\text{T,298}}^{\text{gas,He}} = \frac{\left(p_3^2 - p_4^2\right)^{\text{gas}}}{\left(p_1^2 - p_2^2\right)^{\text{gas}}} \frac{\left(p_1^2 - p_2^2\right)^{\text{He}}}{\left(p_3^2 - p_4^2\right)^{\text{He}}} \frac{C^{\text{gas}}(T, p_3, p_4)}{C^{\text{He}}(T, p_3, p_4)} \frac{C^{\text{He}}(298.15\ \text{K}, p_1, p_2)}{C^{\text{gas}}(298.15\ \text{K}, p_1, p_2)} \quad (7)$$

Equation (7) does not contain the impedance ratio $Z_{\text{up,298}}/Z_{\text{down,298}}$, which depends on temperature through the thermal expansion of the downstream capillary. Instead, Eq. (7) contains the viscosity ratio $\eta_{0,T}^{\text{He}}/\eta_{0,298}^{\text{He}}$, which is known from *ab initio* calculations. The dimensions of the capillaries appear only in the correction terms of Eq. (3); therefore, approximate values of the dimensions are sufficient for Eq. (7). May *et al.* used two coils of electroformed nickel tubing, each with a nominal internal diameter of 0.762 mm, a length of about 7.45 m, in a helical coil with a 0.1 m radius of curvature and a length of 0.04 m.

Stability and accurate measurements of temperature and pressure are central to the determinations of $\eta_{0,298}^{\text{gas}}/\eta_{0,298}^{\text{He}}$ and $R_{\text{T,298}}^{\text{gas,He}}$. The nickel capillaries used by May *et al.*

were immersed in stirred liquid baths that controlled their temperatures with an uncertainty of 0.01 K. The flow rates and the viscometer's design ensured that the flowing gas reached the bath's temperature before the gas entered the capillaries. The pressure transducers had full scales of 300 kPa or 150 kPa, an uncertainty of 0.008 % of full scale (±24 or ±12 Pa), and a resolution of 0.16 Pa. The experimental quantities of primary importance are the difference pressures across the capillaries, $\Delta p_{12} \equiv p_1 - p_2$ and $\Delta p_{34} \equiv p_3 - p_4$. Several important refinements were used to measure Δp_{12} and Δp_{34} with relative uncertainties of order 10^{-4}. The two pairs of transducers ($\{p_1, p_2\}$ and $\{p_3, p_4\}$) and the two bypass valves were housed in a temperature controlled enclosure. Before and after every measurement the bypass valves were opened to measure the zero-offsets of Δp_{12} and Δp_{34} near the average operating pressure. The measured zero-offsets were used to tare the readings of Δp_{12} and Δp_{34} made while the bypass valves were closed. The pressures p_1, p_2 and p_4 were controlled at their set points using the variable impedances Z_1, Z_2 and Z_3 and digital proportional-integral algorithms. The pressure set-points were chosen so that for both gases the flow rates and average pressures within the two capillaries were similar. The first (upstream) capillary's upstream pressure p_1 was usually fixed near 125 kPa, and its downstream pressure p_2 was set to four values between about 100 and 120 kPa to produce four flow rates ranging from about 4 μmol·s^{-1} to 80 μmol·s^{-1}. The second (downstream) capillary's downstream pressure p_4 was then controlled sequentially at six set points between 13 kPa and 75 kPa for each of the four flow rates. This array of 24 measurements per gas per temperature was used to estimate the dependence of the measured values of $R_{\text{T},298}^{\text{gas,He}}$ [Eq. (7)] on the Dean number and the small pressure-dependence of the viscosity, as described below. Automation of the entire apparatus and experimental method, including the taring of the pressure transducers, was

essential because the measurements of $R_{T,298}^{gas,He}$ at each temperature required several hours while the apparatus stepped through two identical sets of $\{p_2, p_4\}$ conditions, one for helium and one for the test gas. These refinements to the apparatus and experimental method enabled the pressure differences Δp_{12} and Δp_{34} to be controlled and measured to within 0.01 %, with the dominant uncertainty due to the instability (≈ 2 Pa) in the uncontrolled pressure p_3. See Figure 2.
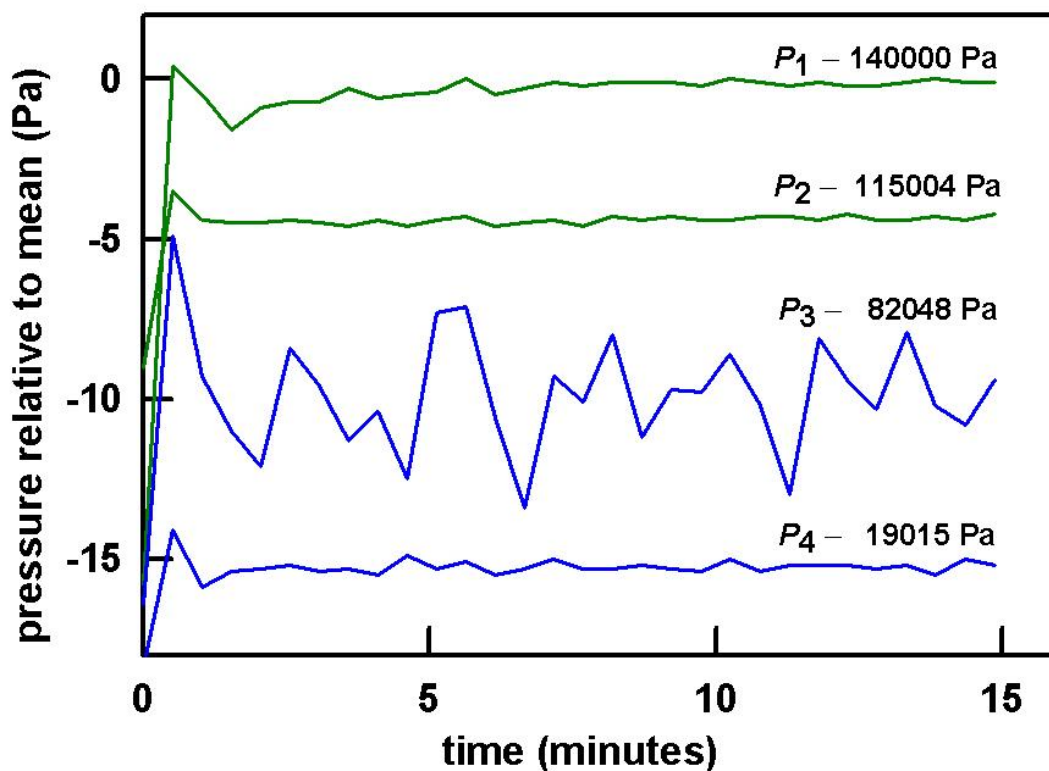
Figure 2. Time dependence of the pressures measured by May *et al*. [2] during a typical helium flow through the two-capillary viscometer; each curve is plotted relative to the pressure in the label, which is the mean pressure. The r.m.s. noise in the controlled pressures, p_1, p_2 and p_4 is equal to the 0.16 Pa resolution of the transducers.

In many cases the correction factor $C^{gas}(T, p_1, p_2)$ can be determined with sufficient accuracy so that Eq. (7) can be used directly to calculate $R_{T,298}^{gas,He}$. Such cases require that (a) the Dean number and, hence, the centrifugal flow correction be sufficiently small, and (b) that the following parameters required to evaluate the c_i^{gas} terms for the

gas are sufficiently well known: the molar mass M, the zero-density viscosity $\eta_{0,T}^{\text{gas}}$, the density virial coefficients B and C, the thermal conductivity, the temperature derivative of the zero-density viscosity $d\eta_{0,T}^{\text{gas}}/dT$, and the viscosity virial coefficient $B_\eta \equiv \lim_{\rho \to 0}(\partial\eta/\partial\rho)_T$. Of these, it is B_η that is least well known, but under certain circumstances the equivalent quantity $b_T^{gas} \equiv \lim_{p \to 0}(\partial\eta/\partial p)_T / \eta = B_\eta (\partial\rho/\partial p)_T / \eta$ can be measured with a modest uncertainty by the two-capillary viscometer itself.

To determine whether the correction terms in $C^{\text{gas}}(T, p_1, p_2)$ are sufficiently accurate, it is useful to calculate the quantity

$$\Xi^{gas}(T) \equiv \frac{\Delta p_{34} \bar{p}_{34}}{\Delta p_{12} \bar{p}_{12}} \frac{C^{gas}(T, p_3, p_4)}{C^{gas}(298\ \text{K}, p_1, p_2)} \tag{8}$$

and test its dependencies on the mean pressure in the downstream capillary, $\bar{p}_{34} \cong (p_3 + p_4)/2$ and on the Dean number of the flow through the downstream capillary. (The temperature dependence of viscosity causes the value of De in the downstream capillary to depend on temperature as well as flow rate. However, the value of De is nearly independent of the pressure decrease that occurs from the inlet to the outlet of each capillary.) Figure 3 shows two examples from experiments with xenon where systematic trends were observed for both quantities.
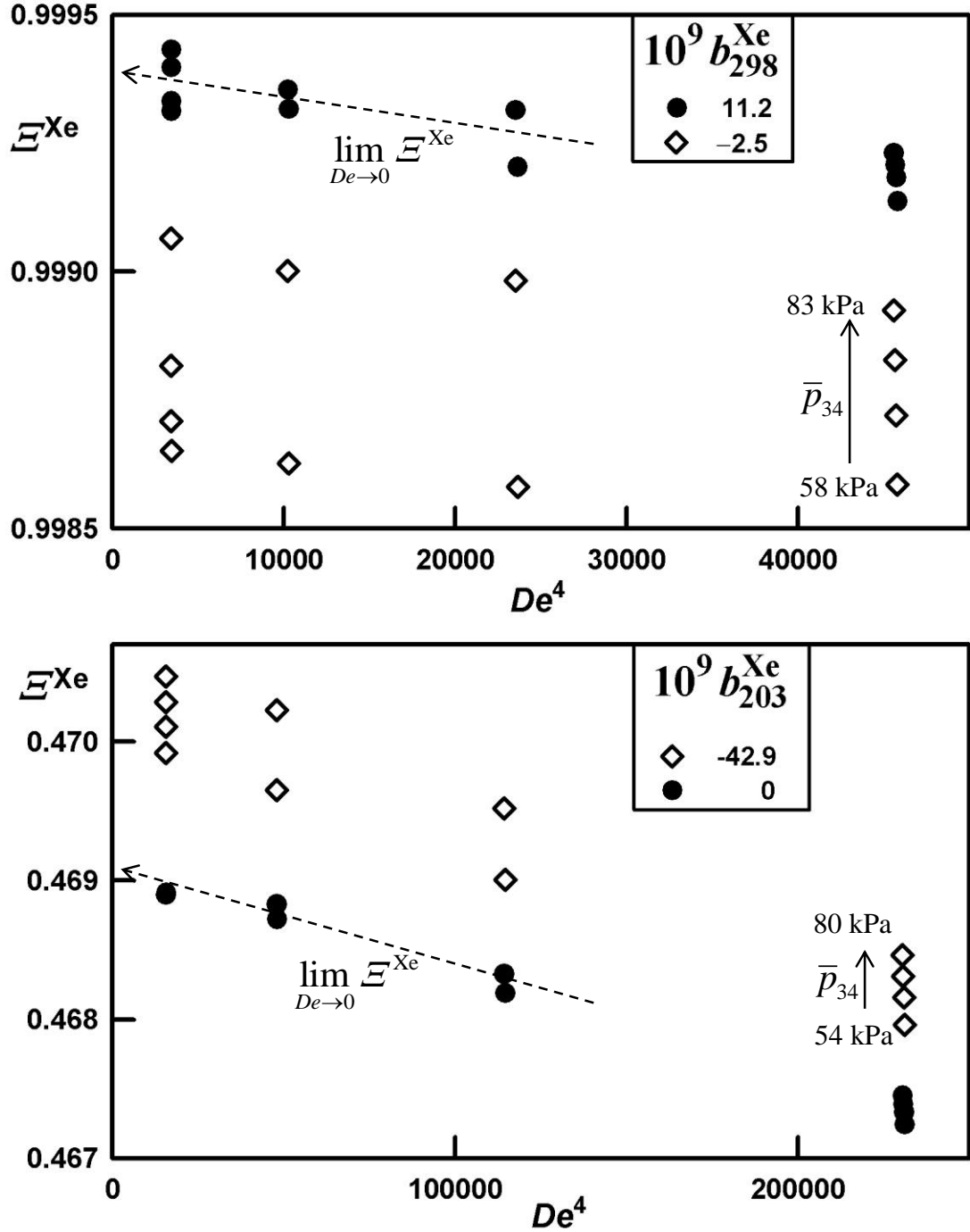
Figure 3. Values of Ξ^{Xe} measured by May *et al* [3] at 298 K (top) and 203 K (bottom), indicating the effects of the two most significant systematic limitations of the hydrodynamic model and the methods by which they can be mitigated. The variation of Ξ^{Xe} with pressure can be significantly reduced by adjusting the viscosity virial coefficient, which is generally poorly known, to minimise that variation. Afterwards, errors due to the centrifugal correction can be minimised by estimating Ξ^{Xe} in the limit $De \to 0$.

In both sets of measurements shown in Figure 3 the hollow symbols correspond to values of b_T^Xe that were estimated using corresponding states models [34-36], which results in a clear variation in the values of $\varXi^\mathrm{Xe}$ with $\bar{p}_{34}$. The solid symbols correspond to values of b_T^Xe that minimize that variation; in the top panel a value of b_{298}^Xe derived from the measurements of Kestin and Leidenfrost [14] was used, while in the bottom panel the optimised value $b_{203}^\mathrm{Xe} = (0 \pm 5.2) \times 10^{-9}\ \mathrm{Pa^{-1}}$ was taken as a measure of the viscosity virial coefficient.

For gases that have accurately known density and viscosity virial coefficients, the pressure dependence of $\varXi^\mathrm{gas}$ can be taken into account when calculating the c_i^gas correction terms. However, accounting for the dependence on the Dean number, De, is more complicated. The correction for centrifugal flow in the hydrodynamic model assumes that the capillary bore is circular and uniform. Capillaries that are robust enough to operate over a wide range of temperatures are unlikely to satisfy this criterion, especially at $De > 16$, and the lowest order correction to the centrifugal function f_cent in Eq. (2) for a capillary with a slightly elliptical bore is proportional to De^4 [2,33]. Such a dependence is evident in the xenon data shown in Figure 3 for which $7 < De < 22$. Under these circumstances, the value of $R_\mathrm{T,298}^\mathrm{gas,He}$ should not be estimated directly from Eq. (7) but rather from

$$R_{T,298}^{gas,He} = \lim_{De \to 0} \varXi^{gas}(T) \Big/ \lim_{De \to 0} \varXi^{He}(T) \tag{9}$$

The principles underlying the viscosity ratio measurements of low pressure gases with the two-capillary apparatus could be applied to determine viscosity ratios at higher pressures. Such an instrument would be similar to that shown in Figure 1 except with

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capillary impedance Z_{up} operated at high pressure and immersed in a bath at the test temperature T, and Z_{low} operated at low pressure (around 100 kPa) in a bath maintained at the reference temperature 298.15 K. Such an apparatus could be used to measure the quantity

$$
\begin{aligned}
\left(R_{T,298}^{gas,He}\right)_{p,0} &\equiv \left(\frac{\eta_{p,T}^{gas}}{\eta_{p,T}^{He}}\right)\Bigg/\left(\frac{\eta_{0,298}^{gas}}{\eta_{0,298}^{He}}\right) \\
&= \frac{\left(p_3^2 - p_4^2\right)^{He}}{\left(p_1^2 - p_2^2\right)^{He}}\frac{\left(p_1^2 - p_2^2\right)^{gas}}{\left(p_3^2 - p_4^2\right)^{gas}}\frac{C^{*\,gas}(T,p_1,p_2)}{C^{*\,He}(T,p_1,p_2)}\frac{C^{He}(298.15\ \text{K},p_3,p_4)}{C^{gas}(298.15\ \text{K},p_3,p_4)}.
\end{aligned} \tag{10}
$$

which is the generalization of Eq. (6) to high pressures. The modified correction function C^* in Eq. (10) does not include the viscosity virial correction but is otherwise the same as Eq. (3). The validity of the density virial correction would establish a pressure limit at which a measurement could be made accurately, which would vary with temperature and the test gas. We note that Hoogland $et\ al.$ [22] developed a more complex hydrodynamic model to analyze gas viscosity measurements at high pressures with a straight capillary with an uncertainty of 0.1 %. Using a small pressure drop in the high pressure capillary, $i.e.$ p_1 - p_2 << p_2, would simplify the analysis. The test gas viscosity at the temperature and pressure of Z_{up} could then be determined from

$$
\eta_{P,T}^{gas} = \eta_{0,298}^{He}\left(\frac{\eta_{0,T}^{He}}{\eta_{0,298}^{He}}\right)_{ab\ initio}\left(\frac{\eta_{0,298}^{gas}}{\eta_{0,298}^{He}}\right)\left(\frac{\eta_{p,T}^{He}}{\eta_{0,T}^{He}}\right)\left(R_{T,298}^{gas,He}\right)_{p,0} \tag{11}
$$

This measurement scheme has the advantage that corrections due to the changes in capillary dimensions with pressure and temperature are unnecessary as they are replaced by the helium viscosity ratios $\left(\eta_{0,T}^{He}/\eta_{0,298}^{He}\right)_{ab\ initio}$ and $\left(\eta_{p,T}^{He}/\eta_{0,T}^{He}\right)$. The former is known from theory with very small uncertainty [1], and the latter is close to unity for a wide pressure range because helium's B_η is small for $T > 130$ K [34-36]: $e.g.$ the

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values of $\left(\eta_{p,293}^{\mathrm{He}} / \eta_{0,293}^{\mathrm{He}} \right)$ measured by Seibt *et al.* [37] with a vibrating wire viscometer ranged from a minimum of 0.9976 at 8.8 MPa to 1.0047 at 25.3 MPa.

The required values of $\left(\eta_{p,T}^{\mathrm{He}} / \eta_{0,T}^{\mathrm{He}} \right)$ could be obtained with a two-capillary viscometer by setting both baths at temperature T and operating the upstream capillary first at low pressure and then at high pressure p. The low pressure measurements would be used to determine the capillary impedance ratio,

$$
\begin{aligned}
\frac{Z_{\mathrm{up},T}(p)}{Z_{\mathrm{down},T}(0)} &= \left[\frac{Z_{\mathrm{up},T}(p)}{Z_{\mathrm{up},T}(0)} \right] \frac{Z_{\mathrm{up},T}(0)}{Z_{\mathrm{down},T}(0)} \\
&= \left[\frac{Z_{\mathrm{up},T}(p)}{Z_{\mathrm{up},T}(0)} \right] \frac{\left(p_1^2 - p_2^2 \right)^{\mathrm{He}}}{\left(p_3^2 - p_4^2 \right)^{\mathrm{He}}} \frac{C^{\mathrm{He}}(T, p_1, p_2)}{C^{\mathrm{He}}(T, p_3, p_4)},
\end{aligned}
\tag{12}
$$

where the factor $Z_{\mathrm{up},T}(p)/Z_{\mathrm{up},T}(0)$, calculated from the dimensions and elastic modulus of the capillary, corrects for the dilation of the upstream capillary's inner diameter with pressure. For nickel capillaries similar to those used by May *et al.*, which had a wall thickness of 0.4 mm, the dilation correction would be small, *e.g.* 0.04 % at $p = 100$ MPa and $T = 298$ K.

After the impedance ratio was measured, the high pressure measurements would be used to determine the desired helium viscosity ratio from

$$
\left(\frac{\eta_{p,T}^{\mathrm{He}}}{\eta_{0,T}^{\mathrm{He}}} \right) = \frac{Z_{\mathrm{down},T}(0)}{Z_{\mathrm{up},T}(p)} \frac{\left(p_1^2 - p_2^2 \right)^{\mathrm{He}}}{\left(p_3^2 - p_4^2 \right)^{\mathrm{He}}} \frac{C^{* \mathrm{He}}(T, p_1, p_2)}{C^{\mathrm{He}}(T, p_3, p_4)}.
\tag{13}
$$

This one-time set of helium measurements would facilitate accurate high-pressure viscosity ratio measurements for other gases and stimulate calculations of helium's properties at higher densities.

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The capillaries, variable impedances, flow rates and operating pressures selected for such high-pressure viscosity ratio measurements would need to be chosen to best satisfy the constraints of stable flow control, good signal-to-noise ratios, and small corrections associated with high Re and De numbers. Small molar flow rates similar to those used at low pressures by May et $al.$ [2,3] should be used. The pressure drop Δp_{12} of the high-pressure capillary would then be small and decreasing with increasing pressure For example, operating at $p_1 = 10$ MPa would cause the volumetric flow rate in the upstream capillary to be approximately 100 times smaller than in the downstream capillary, with a similar decrease in Δp_{12}. An adequate measurement of Δp_{12} would then require either a sensitive differential pressure gauge or an upstream capillary with a smaller diameter.

4. Four-capillary viscometers for gases and liquids

Figure 4 shows how four capillaries can be arranged to measure small differences in viscosity. Such viscometers were first used by Engelhardt and Sack [38] and by Becker [39] to investigate the viscosity difference between ortho and para hydrogen. The arrangement of Figure 4 is analogous to an electrical Wheatstone bridge. As described by Korving et $al.$ [40], fluid flows through impedance Z_5, splits and flows through the bridge, and then recombines before exiting through impedance Z_6. The four capillaries Z_1, Z_2, Z_3, and Z_4 have approximately equal impedances, and the impedances Z_5 and Z_6 are adjustable, which allows the pressure in the bridge to be regulated. Korving et $al.$ used heaters on Z_3 and Z_4 to slightly increase the temperatures of these capillaries, thereby decreasing the molar flow rate because the density of the gas decreased and the viscosity increased. The heating adjustment allowed the bridge to be nulled in a standard condition. Once the bridge was nulled,

the condition at Z_1 could be changed, for example, by applying a magnetic field to study the visco-magnetic effect. The resulting change of viscosity of the fluid in Z_1 was then inferred from the change of the differential pressure Δp. The resolution possible with this technique is remarkable. Van Ditzhuyzen *et al*. [41] observed the viscomagnetic effect in hydrogen by using a bridge with all four capillaries at the same temperature, and they were able to measure fractional viscosity changes smaller than 10^{-6}.
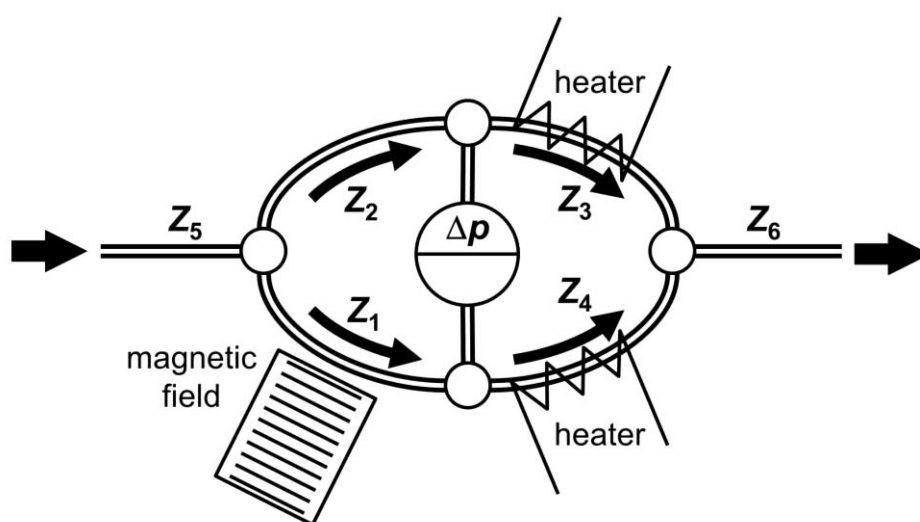

Figure 4. Schematic diagram of the four-capillary viscometer used by Korving *et al*. [40] to measure the viscomagnetic effect of 13 gases.

Wheatstone bridge viscometers have been used for liquids also. Haney [42] developed such a viscometer to measure the derivative of viscosity with respect to the concentration of a solute in a solvent. While flowing solvent through the bridge, he injected a solution into one arm of the bridge while observing the differential pressure. Some commercial liquid chromatographs have a viscosity detector that comprises a capillary bridge in which one of the arms has a delay volume. When a solution pulse enters the bridge, the delay volume causes a temporary imbalance of the bridge [43].

5. Capillary viscometers for liquids and the viscosity of water

Most viscosity measurements, for both scientific as well as industrial purposes, are made on liquids using calibrated viscometers. The calibrating liquid is either water or a more viscous liquid whose viscosity was compared to that of water by a ratio technique. The most accurate ratio technique is to measure the flow rate of the liquid, with unknown viscosity η, through a glass capillary "master" viscometer and then make another measurement with water to obtain the ratio of the two viscosities. For a capillary of internal radius r and length L, the volume flow rate is approximately

$$\frac{\Delta V}{\Delta t} \cong \frac{\pi r^4 \left(p_1 - p_2 \right)}{8 \eta L} \tag{14}$$

where p_1 and p_2 are respectively the entrance and exit pressures. Gravity drives the flow through a master viscometer, so that $p_1 - p_2 = \rho g L$, and

$$\frac{\Delta V}{\Delta t} = \frac{\pi \rho g r^4}{8 \eta} \left(1 + C^{\text{liq}} \right) \tag{15}$$

Here, ρ is the liquid density, g is the gravitational acceleration, and C^{liq} is the sum of small correction factors that account for effects such as air buoyancy, surface tension, and the change of kinetic energy at the capillary entrance [19]. To within those correction factors, two liquids will have a kinematic viscosity ratio given by the ratio of their volume flow rates through the same viscometer.

If the unknown liquid is very viscous, one compares its viscosity to that of water by using multiple viscometers to make a series of ratio measurements on liquids of intermediate viscosities. The accuracy possible with this method was demonstrated

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most recently by Fujita *et al*. [44], who used nine master viscometers with overlapping viscosity ranges that extended from that of water to 10^5 times larger. Each step between viscometers increased the ratio uncertainty; the ratio uncertainty for the largest viscosity was 0.08 %, and for liquids similar to water it was only 0.02 %. The small uncertainty of liquid viscosity ratios seems unlikely to improve significantly in the near future due to the maturity of the techniques and the lack of a need for smaller uncertainty.

The document ISO 3666 [45] recommends the value (1.0016 ± 0.0009) mPa s for the viscosity of liquid water at 20 °C and 101.325 kPa. The ISO could not assign a smaller uncertainty because the two best studies yielded values that differ by more than their combined uncertainties [46]; the 1952 study by Swindells *et al*. [47] used the pressure drop caused by steady flow through a capillary, and the 1988 study by Berstad *et al*. [48] used the decrement of an immersed oscillating cylinder. Thus, the viscosity of water has an uncertainty that is larger than the uncertainty of the best ratio measurements. The opposite is true for gas viscosity ratios because the uncertainty of helium's viscosity is so small.

We suggest that the use of a single-capillary ratio measurement could decrease the uncertainty of the viscosity of water. One could flow gaseous helium and then liquid water through the same capillary while measuring the entrance and exit pressures with the same pressure transducers. This procedure would reduce errors due to the capillary radius and the transducer calibrations. Using a long, coiled capillary would reduce end corrections. Care would be needed to avoid errors due to surface tension at the capillary ends and in the connections to the pressure transducers. As a check on

the working equation, the pressures, and thus the flow rates, could be varied for both fluids; the measured ratio η_{H2O}/η_{He} should depend only on the fluid densities and temperatures and not on the flow rate. Most of the corrections to Eq. (2) are proportional to the Reynolds number Re, so measuring the two fluids at the same value of Re would be valuable. The associated ratio is approximately

$$\frac{Re_{He}}{Re_{H2O}} \cong \left(\frac{\rho_{He}}{\rho_{H2O}}\right)\left(\frac{\eta_{H2O}}{\eta_{He}}\right)^2 \frac{(p_1 - p_2)_{He}}{(p_1 - p_2)_{H2O}} \cong \frac{(p_1 + p_2)_{He}}{(475 \text{ kPa})} \frac{(p_1 - p_2)_{He}}{(p_1 - p_2)_{H2O}}. \quad (16)$$

Choosing the same p_1 and p_2 for both flows would eliminate errors due to the pressure transducers. Furthermore, the experimentally convenient choice $p_1 = 375$ kPa and $p_2 = 100$ kPa would cause both flows to have the same Re, thereby making negligible any error associated with Re. At those pressures, using a capillary with $r = 0.1$ mm and $L = 10$ m would give flow rates of 7 cm^3/min for He and 200 g/min for H_2O, both of which could be measured accurately.

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