Simultaneous Measurements on Helium and Nitrogen with a Newly Designed Viscometer−Densimeter over a Wide Range of Temperature and Pressure[†]

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A newly designed apparatus for accurate simultaneous viscosity and density measurements on gases was assembled. The measuring system consists of a vibrating-wire viscometer and a single-sinker densimeter. Density values measured directly are a prerequisite for accurate viscosity measurements. For the relative measurements with the vibrating-wire viscometer, the wire radius was determined by means of a calibration with a theoretically based value for the viscosity of helium in the limit of zero density. In general, the viscosity measurements are characterized by a relative uncertainty of ± (0.25 to 0.3) %, whereas the relative uncertainty in the density is estimated to be less than ± 0.1 %, except for the low-density range. The working range of the instrument covers temperatures from (253 to 473) K at pressures up to 30 MPa. Some isothermal series of measurements on helium (293 K) and nitrogen [(293 and 423) K] were carried out to check the performance of the apparatus and to provide accurate $\eta\rho pT$ data. On the basis of comparisons with values calculated from the viscosity surface correlations and equations of state for helium and nitrogen as well as with selected experimental data from the literature, it is concluded that the new viscosity values are appropriate to improve the viscosity surface correlations available in the literature.

Introduction

Reliable thermophysical properties of working fluids based on equations of state and on transport property correlations are needed for a more accurate basic design of boilers, compressors, gas turbines, and gas pipelines. Such correlations require accurately measured data determined by means of high-precision experimental equipment.

Some years ago, Wilhelm et al.[1] designed a vibrating-wire viscometer and performed high-precision measurements on argon, krypton, and propane[2,3] as well as on sulfur hexafluoride.[4] A special measuring program was arranged to determine the viscosity of natural gas components and of natural gas mixtures to fulfill the needs of the gas industry. In addition to the investigation on propane, the viscosity of methane,[5,6] ethane,[7] nitrogen,[8] and two natural gases[6,9] was determined.

The density is needed in the working equations to evaluate the measurements with the vibrating-wire viscometer but also in the analysis of experiments with other types of viscometers. For that purpose, temperature and pressure measurements are performed generally to infer density values using a suitable equation of state. The uncertainties of the measured temperatures and pressures limit the accuracy of the final viscosity values, if the density is determined in this manner. Furthermore, the number of sufficiently accurate equations of state is restricted, particularly in the case of mixtures. Experimental equipment, in which the density is measured directly together with the viscosity, solves this problem. For the gaseous region, Docter et al.[10,11] and Evers et al.[12] developed an absolute measuring system, in which a single-sinker densimeter is combined with a rotating-cylinder viscometer, and reported measurements on a number of gases over a wide range of density and temperature. Another reason for determining simultaneously viscosity and density is that a viscosity correlation is reasonably formulated depending primarily on temperature and density.

In our group, an apparatus for the simultaneous measurement of viscosity and density combining a vibrating-wire viscometer and a single-sinker densimeter was also developed.[13] Apart from the low densities, the relative uncertainty in the density measurement with the single-sinker method is expected to amount to ± 0.1 %, so that the relative uncertainty in the viscosity could achieve ± 0.3 %. In this paper, measurements on helium and nitrogen intended to verify the performance of the new instrument are reported.

Experimental Section

Vibrating-Wire Viscometer. The details of the vibrating-wire viscometer have already been given by Seibt[13] considering the experience with the former instrument described by Wilhelm et al.[1] and Wilhelm and Vogel.[2] Here only the essential items of the design are summarized but supplemented by the description of new components. A thin wire with a length of 90 mm and a nominal diameter of 25 μm is arranged symmetrically in a magnetic field, whereas the length ratio of wire and magnetic field amounts to 1.5. In doing so, the first oscillation mode is initiated primarily, and the third as well as all even harmonics of the oscillation are suppressed. The wire material has been chosen to be Chromel because of its comparably smooth surface since it was found that a rough surface causes systematic errors in measurements on dilute and even dense gases.[1] The oscillation of the wire is initiated by a sinusoidal voltage pulse with a frequency close to the resonant frequency of the wire. The oscillation following the pulse is detected by amplifying the induced voltage and measuring it as a function of time. For that purpose, a new low-noise preamplifier SR560 (Stanford Research Systems, Sunnyvale, USA) with a gain of 5000 and a precise 16-bit I/O multifunction card (National Instruments Germany GmbH, Munich, Germany) are used. To improve the

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[†] Part of the "William A. Wakeham Festschrift".

10.1021/je900131q CCC: $40.75

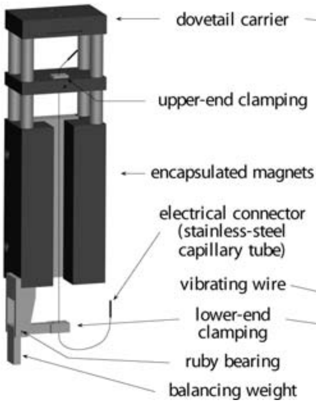

Figure 1. Viscometer models with different clamping of the lower end of the vibrating wire. Left, lever support; right, freely suspended weight.

signal-to-noise ratio, 100 oscillations are recorded, and the measured curves are averaged within a run. To obtain reasonably large measuring signals, it is necessary to generate comparably large displacements y of the wire compared to its radius R. This contradicts the requirements of the measuring theory that the displacement should be less than 1 % of the radius of the wire. Wilhelm et al. showed that the parameters of the oscillation curves, the logarithmic decrement Δ, and the frequency ω depend on the square of the relative initial amplitude $\varepsilon = y_{\max}/R$. Hence they used relatively large and different values of ε in the oscillation runs and determined the correct values of Δ and ω by extrapolation of the values for the different runs as a function of ε^2 when ε tends to 0.

The new equipment possesses three circumferentially arranged sites for three vibrating-wire viscometers so that alternative variants of the installation of the wires could be tested. Finally, two versions with different clamping of the lower end of the wire were used as shown in Figure 1. New planar glass-ceramic blocks made of Macor were applied to clamp the wire at the upper and partly at the lower ends. In the older version, shown on the right-hand side of the figure, the lower end of the wire is clamped between the halves of stubbed cones and stressed by a weight with a mass of about 1.1 g, all made of stainless steel. In the new version developed for this work shown on the left-hand side of Figure 1, the lower end of the wire is clamped between glass-ceramic blocks placed at the end of a rotatable lever support implemented by means of two ruby bearings. In this way, a superimposed precession movement due to the freely suspended weight, especially in vacuo, can be suppressed, and the direction of the oscillation is ensured to be perpendicular to the magnetic field. For the new device, the cobalt−samarium magnets were encapsulated in magnetic stainless steel to prevent them from corroding and to avoid the porous magnets absorbing gas molecules. These features improve the uncertainty of the vibrating-wire viscometer.

The theory of the vibrating-wire viscometer developed by Retsina et al.[14] relates the properties of the fluid, the density ρ, and the viscosity η to the measured values of the damped harmonic oscillation Δ and ω. The working equations needed to calculate the viscosity in an iterative way are given as

$$\Omega = \frac{\rho\omega R^2}{\eta} \tag{1}$$

$$A = (i - \Delta)\left[1 + \frac{2K_1(h)}{hK_0(h)}\right],\ h = [(i - \Delta)\Omega]^{1/2} \tag{2}$$

$$k = -1 + 2\mathrm{Im}(A),\ k' = \mathrm{Re}(A) + \Delta\mathrm{Im}(A) \tag{3}$$

$$\Delta_{\mathrm{cal}} = \frac{\Delta_0 + (\rho/\rho_{\mathrm{s}})k'}{1 + (\rho/\rho_{\mathrm{s}})k} \tag{4}$$

Here K_0 and K_1 are modified Bessel functions. The calculation procedure assumes that the density ρ of the fluid, the density ρ_{s} and the radius R of the wire, and the parameters of the oscillation in vacuo are known. The iteration is started by choosing different values for Ω and calculating the decrement Δ_{cal} according to eq 4. The correct value of Ω is inferred by comparison of Δ_{cal} with the experimental value Δ. The viscosity follows after all from

$$\eta = \frac{\rho\omega R^2}{\Omega} \tag{5}$$

An accurate wire radius R cannot be determined by direct measurements. Hence R was obtained by means of a calibration using a value for the zero-density viscosity coefficient of helium derived by Bich et al.[15] from an ab initio potential on the basis of the kinetic theory of dilute gases. The calibration was performed assuming the density of the wire material Chromel to be 8500 $\mathrm{kg \cdot m^{-3}}$ as given by the supplier. The reproducibility of the measurements was found to be lower than ± 0.05 %.

Single-Sinker Densimeter. The density measurements are carried out using an accurate single-sinker measuring device supplied by Rubotherm Präzisionsmesstechnik GmbH, Bochum, Germany, which covers a range of (1 to 2000) $\mathrm{kg \cdot m^{-3}}$. The single-sinker method based on the buoyancy principle was developed at the Ruhr-University Bochum by Brachthäuser et al.[16] and Wagner et al.[17] and further improved by Klimeck et al.[18,19] The most important part of the device is an electronically controlled magnetic suspension coupling developed by Lösch et al.[20,21] It enables a contactless transmission of the forces on the sinker within the pressure-tight measuring cell to a calibrated microbalance placed under ambient conditions.

The buoyant force on the sinker, which depends on the gas density, corresponds to the difference of the sinker mass in vacuo and its mass in the fluid, both measured with the precise microbalance. The density of the fluid surrounding the sinker follows from the working equation

$$\rho = \frac{m_{\mathrm{s,vac}}(T) - m_{\mathrm{s,fluid}}(p, T)}{V_{\mathrm{s}}(p, T)} \tag{6}$$

The ‘true’ sinker mass $m_{\mathrm{s,vac}}$ is determined accurately in the evacuated measuring cell as a function of temperature. The ‘apparent’ mass of the sinker in the fluid-filled measuring cell $m_{\mathrm{s,fluid}}$ is recorded as a function of pressure along isotherms. The sinker volume V_{s} has been calibrated by hydrostatic weighing in water at 293.15 K and atmospheric pressure, whereas the dependence on temperature and pressure can be calculated appropriately.

For most of the measuring series, a sinker made of quartz glass was used. Since in the case of helium the density determination is influenced distinctly by absorption processes on quartz glass (see Figure 3 and the discussion in subsection Density), a new sinker made of silicon was used for a further measuring series. These new measurements on helium are only marginally affected by adsorption on or absorption in silicon. Apart from this difficulty concerning only helium (see below), the density measurements on nitrogen and other gases to be published in further papers do not suffer from similar problems.

Temperature Measurements and Thermostat. The temperature was determined first with a 100Ω platinum resistance thermometer (Steffen Messtechnik GmbH, Dorsten, Germany) and later with a 25Ω platinum resistance thermometer (TP

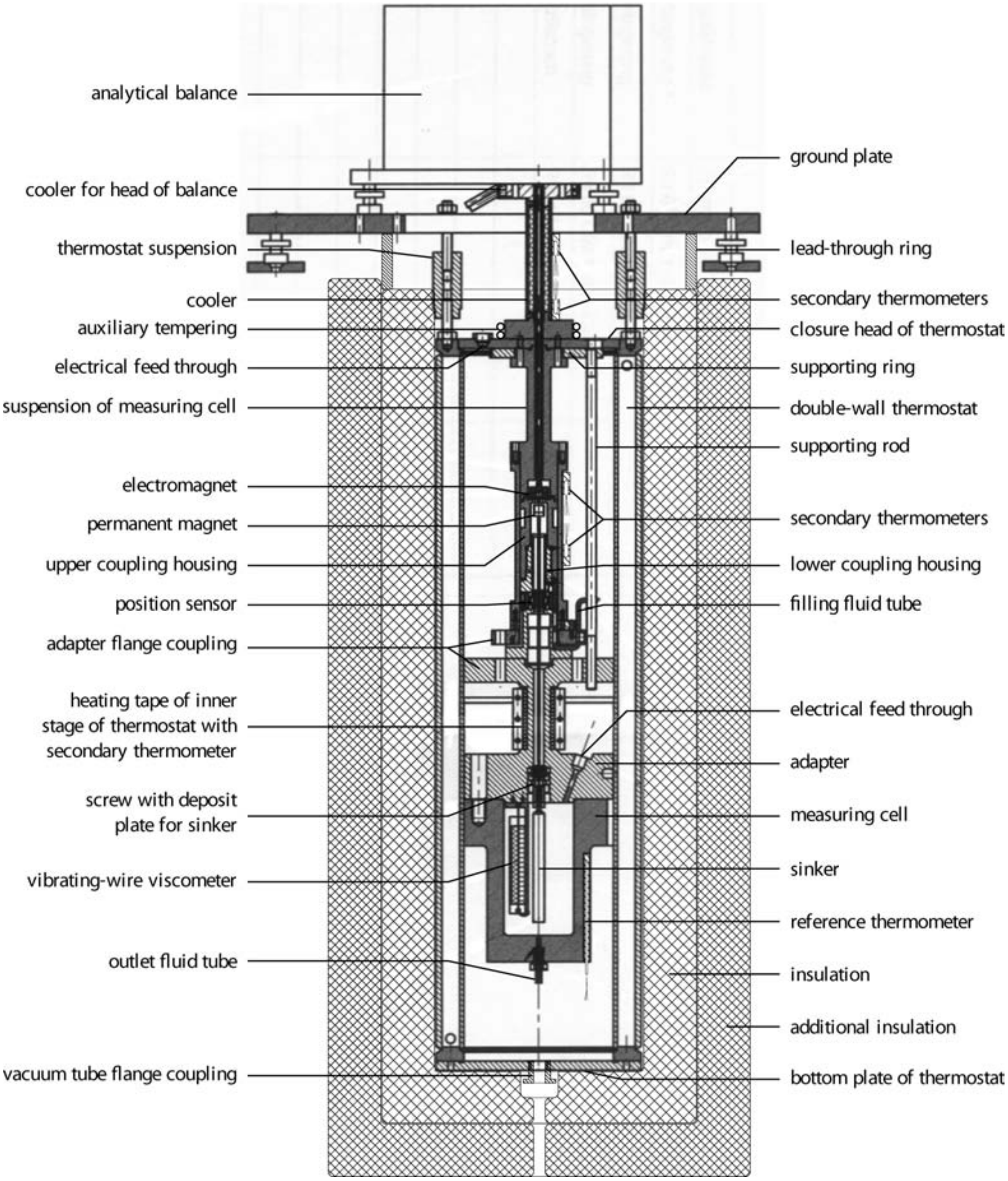

Figure 2. Sectional view of the combined apparatus with vibrating-wire viscometer and single-sinker densimeter (including schematic drawing of balance).

Temperature Products GmbH, Freigericht, Germany), in connection with a resistance measuring bridge F300 including a SB148 switchbox and an external reference resistor RR100 (ASL Automatic Systems Laboratory, Croydon, United Kingdom). The uncertainties of the platinum resistance thermometers are ± 26 mK for the 100Ω thermometer in the temperature range (235 to 429) K and ± 18 mK for the 25Ω thermometer between (235 and 505) K, whereas the measuring bridge is characterized by an uncertainty of ± 2 mK. Considering the control accuracy of the thermostat (± 2 mK) experimentally found for the time of one individual point of an isothermal series of measurements (see below), the total uncertainty in the temperature measurements with the two thermometers amounts to ± 30 mK and ± 22 mK, respectively.

Additional 100Ω platinum resistance thermometers (Electrotherm GmbH, Geraberg, Germany) are used to monitor temperature gradients and to control the temperature of the thermostat. For this purpose, they were calibrated in a metal block against the 100Ω platinum resistance thermometer with an uncertainty of ± 50 mK.

The temperature of the measuring cell is controlled by an oil-filled double-wall thermostat with a vacuum vessel for the insulation of the two-stage thermostat. The outer stage of the thermostat is operated by means of the oil thermostatted by a special thermostat Presto LH40 (Julabo GmbH, Seelbach, Germany) with a performance of ± (10 to 50) mK dependent on temperature. A heating tape regulated by a precise temperature controller LS 331 (Lake Shore Cryotronics, Westerville, USA) within ± 10 mK acts as the inner stage of the thermostat. These values are each given by the supplier.

Pressure Measurement and Gas System. The pressure is measured using four precise absolute pressure transmitters (Paroscientific, Redmond, USA) with ranges of (41.4, 13.8, 2.76, and 0.689) MPa characterized by an uncertainty of ± 0.01 % of full scale and of ± (0.03 to 0.05) % of reading. To prevent these transmitters from condensed fluid, they are operated in a nitrogen-filled gas system and separated from the measuring fluid-filled system by using a high-precision differential pressure transducer 3051S-CD (Rosemount, Chanhassen, USA). This transducer suitable to detect pressure differences of ± 5 kPa

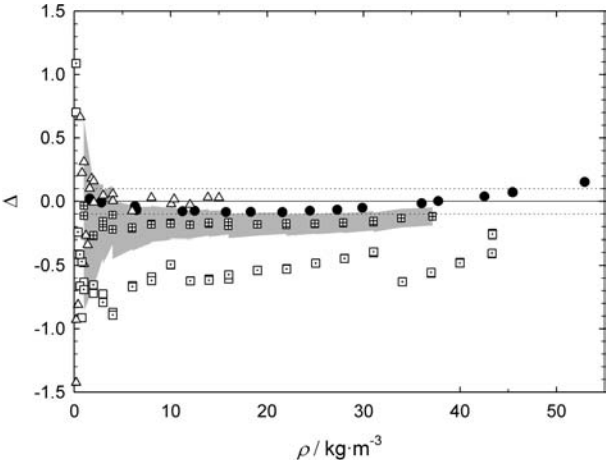

Figure 3. Comparison of the measured densities for helium at 293.15 K with values calculated for the equation of state of McCarty and Arp[23] using the measured temperature and pressure data as a function of density ρ. Deviations: $\Delta = 100 \cdot (\rho_{\text{exp}} - \rho_{\text{eos}})/\rho_{\text{eos}}$. Experimental data: □, this work, quartz-glass sinker (related to Table 1); ⊡, this work, quartz-glass sinker (related to Table 2); ⊞, this work, silicon sinker (Table 3); ●, McLinden and Lösch-Will,[25] two-sinker densimeter; △, Evers et al.,[12] single-sinker densimeter. ••••••, uncertainty of the equation of state of McCarty and Arp. The shaded area corresponds to the experimental uncertainty in this work using the silicon sinker.

has been calibrated with an uncertainty of ± 0.04 % from reading. This contributes ≤ ± 0.002 % to the uncertainty in the pressure measurement for pressures $p > 0.15$ MPa.

With respect to intended measurements on further fluids, the construction of the equipment had to be taken into account for a possible condensation of the measuring fluid. This occurs at subcritical temperatures and pressures higher than the saturation pressure in the connecting tubes to the measuring cell outside the thermostat which is situated at a higher temperature. For that purpose, a liquid-level indicator, which adjusted simultaneously the pressure in the measuring cell, is placed in a certain position of the connecting tubes. Its design and handling is described by Seibt[13] (see also Brachthäuser et al.[16]). The uncertainty of the hydrostatic pressure corrections particularly needed in the case of a condensable fluid is estimated to be within ± 0.001 % of the pressure p. In summary, the uncertainty for the pressure measurement amounts to ≤ ± 0.05 % of the determined pressure value.

The vacuum system consists of an XDS5 scroll fore-vacuum pump (BOC Edwards, Crawley, United Kingdom) and a high-vacuum turbomolecular pump Turbovac 50 (Leybold, Cologne, Germany). Pressures of $< 1 \cdot 10^{-4}$ Pa, determined outside the measuring cell with an ultrahigh vacuum gauge Ionivac ITR 90 (Leybold, Cologne, Germany), are achieved with this vacuum pump system. In this way, good conditions are prepared for the measurement of the logarithmic decrement and oscillation frequency in vacuo as well as of the sinker weight in vacuo.

Error Analysis. Using eq 6, the relative uncertainty in the measured density follows from that of the sinker mass measurements as well as from the calibration uncertainty in the sinker volume

$$\frac{\Delta\rho}{\rho} = \left|\frac{\Delta(m_{\text{s,vac}} - m_{\text{s,fluid}})}{m_{\text{s,vac}} - m_{\text{s,fluid}}}\right| + \left|\frac{\Delta V_{\text{s}}}{V_{\text{s}}}\right| \tag{7}$$

The uncertainty in the mass determinations results from the sum of $\Delta m_{\text{s,vac}} \le \pm 0.035$ mg for the measurement of the basic load in vacuo and of $\Delta m_{\text{s,fluid}} \le \pm 0.055$ mg for the measurement of the basic load in the fluid including a possible adsorption error of + 0.02 mg (Docter et al.[10]). Further, the relative error of the balancing system (6 ppm) as well as the force transmission error of the magnetic suspension coupling (20 ppm) dependent on the fluid have to be considered. Hence the uncertainty in the mass determinations is given as

$$\left|\frac{\Delta(m_{\text{s,vac}} - m_{\text{s,fluid}})}{m_{\text{s,vac}} - m_{\text{s,fluid}}}\right| \le \pm 0.0026\,\% + \frac{0.09\text{ mg}}{m_{\text{s,vac}} - m_{\text{s,fluid}}} \tag{8}$$

With the calibration uncertainty in the quartz-glass sinker volume ($\Delta V_{\text{s}}/V_{\text{s}} = \pm 0.05$ %) and after normalization to a fluid density of 10 kg·m^{-3}, the uncertainty for the density determination results as

$$\frac{\Delta\rho}{\rho} \le \pm \left|0.0526\,\% + \frac{0.07\,\%}{\rho/(10\text{ kg}\cdot\text{m}^{-3})}\right| \tag{9}$$

The total uncertainty of the $p\rho T$ data consists of the uncertainty in the measured density according to eq 9 as well as of the allocation errors of the temperature and pressure measurements considering the temperature and pressure dependence of the density of the fluid

$$\left(\frac{\Delta\rho}{\rho}\right)_{\text{tot}} \le \pm \sqrt{\left(\frac{\Delta\rho}{\rho}\right)^2 + \left(\frac{\partial\rho}{\partial T}\right)_p^2 \frac{\Delta T^2}{\rho^2} + \left(\frac{\partial\rho}{\partial p}\right)_T^2 \frac{\Delta p^2}{\rho^2}} \tag{10}$$

The partial derivatives of the density with respect to temperature and pressure needed in this equation can approximately be taken from an equation of state, even if only a preliminary one is available. The total uncertainty is assumed to be < ± 0.1 % for $\rho > 15$ kg·m^{-3} due to small uncertainties in the measured temperature and pressure values in wide thermodynamic regions.

The relative uncertainty in the viscosity measurements is estimated using an analysis of multivariate functions. In doing so, only the error propagation factors for the wire radius R and for the frequency ω are constant, whereas due to the complexity of the working eqs 2 to 5 the other factors, such as $|(\partial\eta/\partial\Delta)(\Delta/\eta)|$, are dependent on density

$$\frac{\Delta\eta}{\eta} \approx 2\frac{\Delta R}{R} + \frac{\Delta\omega}{\omega} + \left|\frac{\partial\eta}{\partial\Delta}\frac{\Delta}{\eta}\right|\frac{\Delta\Delta}{\Delta} + \left|\frac{\partial\eta}{\partial\Delta_0}\frac{\Delta_0}{\eta}\right|\frac{\Delta\Delta_0}{\Delta_0} + \left|\frac{\partial\eta}{\partial\rho}\frac{\rho}{\eta}\right|\frac{\Delta\rho}{\rho} + \left|\frac{\partial\eta}{\partial\rho_{\text{s}}}\frac{\rho_{\text{s}}}{\eta}\right|\frac{\Delta\rho_{\text{s}}}{\rho_{\text{s}}} \tag{11}$$

The uncertainties of wire density and wire radius are coupled and partly cancel each other by using a constant wire density to obtain the wire radius by calibration (see above). Their sum could be approximated by the uncertainty of the helium value (estimated conservatively by the authors of this work to be ± 0.05 %) used for the calibration. However, because the error propagation factor for the wire density increases up to 1.6 at higher densities, the contributions of the wire radius and of the wire density to the uncertainty in the viscosity are estimated conservatively to be ± 0.08 % in all. The uncertainty in the logarithmic decrement (± 0.05 %), in connection with a propagation factor $1 < |(\partial\eta/\partial\Delta)(\Delta/\eta)| < 2$, results in a contribution of ± 0.075 % to the relative uncertainty in the viscosity. The contribution of the circular frequency is negligibly small. Assuming an uncertainty of < ± 0.1 % for the density determination in regions > 15 kg·m^{-3} and an error propagation factor of 0.5, the contribution of the uncertainty in the density amounts to ± 0.05 %. Further, it is to be considered that the uncertainty in the density is increased in the low-density region, whereas the propagation factor decreases.

The total uncertainty in the viscosity consists of the uncertainty in the viscosity measurements according to eq 11 as well as of the allocation errors of the temperature and density measurements considering the temperature and density dependence of the viscosity

$$\left(\frac{\Delta\eta}{\eta}\right)_{\text{tot}} = \left|\sqrt{\left(\frac{\Delta\eta}{\eta}\right)^2 + \left(\frac{\partial\eta}{\partial T}\right)_\rho^2 \frac{\Delta T^2}{\eta^2} + \left(\frac{\partial\eta}{\partial\rho}\right)_T^2 \frac{\Delta\rho^2}{\eta^2}}\right| \tag{12}$$

The small uncertainties of the experimental temperature and pressure values reduce the contribution of the allocation errors to $\Delta\eta/\eta \leq \pm\ 0.02\ \%$ in wide thermodynamic regions. In summary, the preceding conservative analysis leads to a total uncertainty of ± (0.25 to 0.3) % for the viscosity determination in the range of (6 to 150) μPa·s.

Measurements and Results

The combined apparatus for the precise simultaneous measurements of viscosity and density is shown in Figure 2. As already mentioned above, two different sinkers made of quartz glass or of silicon were employed in the measurements. One wire with a freely suspended weight and two wires with lever support were applied together with the quartz-glass sinker to test different suspension systems. In principle, all wires gave the same results. The better handling, when comparing freely suspended weight and lever support, led to the decision to use in combination with the silicon sinker three suspension wires with lever support.

The procedure of an isothermal series of measurements is started with the determination of the decrement Δ_0 and of the sinker mass $m_{\text{s,vac}}$ in vacuo. In contrast to the measurement in a fluid, only one oscillation is detected within a run to obtain Δ_0 with a break of about five minutes between the runs at different relative initial amplitudes ε. The determination of $m_{\text{s,vac}}$ is performed five times at least and averaged.

At the beginning of the measurement series, the measuring apparatus is filled with the fluid up to the highest pressure, and the first experimental point is performed. The further individual points of the isothermal series are carried out after reducing the pressure by a discharge of the fluid according to the measuring program. After attaining the thermodynamic equilibrium which needs about two hours at the highest densities and reduces to about half an hour at low densities, the determination of the logarithmic decrement Δ and of the frequency ω on the basis of runs of a hundred oscillations at different initial amplitudes ε as well as of three or more weighings of the sinker mass $m_{\text{s,fluid}}$ are performed in the fluid, whereas temperature T and pressure p are measured simultaneously. A series of measurement are completed by a second determination of the measuring values in vacuo.

Several isothermal series of measurements on helium and nitrogen were carried out at 293.15 K and at 423.15 K (nitrogen) to test the performance of the single-sinker densimeter and of the vibrating-wire viscometer. In the framework of the measurements on helium at 293.15 K, the calibration of the different viscometers was performed, which means the determination of the radii of their vibrating wires. The certified purities of helium and nitrogen, both supplied by Air Liquide Deutschland GmbH, Düsseldorf, Germany, were 99.996 % and 99.999 %, respectively.

The individual points of the isothermal series of measurements were not measured exactly at the nominal temperature, but the deviations of the experimental temperatures were kept within approximately ± 130 mK for each of the isotherms. The experimental viscosity values were adjusted to the nominal temperature using a Taylor series expansion restricted to the first power in temperature. For that purpose, the following values of the coefficient $(\partial\eta/\partial T)_\rho$ were used: 0.046 $\mu\text{Pa}\cdot\text{s}\cdot\text{K}^{-1}$ for helium and (0.039 to 0.046) $\mu\text{Pa}\cdot\text{s}\cdot\text{K}^{-1}$ for nitrogen, both reported by Vogel.[22] In this procedure, the densities, measured directly or derived from the experimental values of temperature and pressure using an equation of state (see below), correspond to the densities for the isotherm. Hence the pressures at the nominal temperature were recalculated from the densities for the nominal temperature.

The results of three series of measurements on helium at 293.15 K are summarized in Tables 1 to 3, and those of two series of measurements on nitrogen at 293.15 K and of one series on nitrogen at 423.15 K are summarized in Tables 4 to 6, all listed according to increasing pressure. The characteristics of the sinkers and vibrating wires used in the measurements are also given in these tables. In the case of the density measurements on helium with the quartz-glass sinker, the resulting experimental density values are not reported in Tables 1 and 2 due to the absorption effects discussed below. In addition, the tables present values for the density calculated by means of the equation of state by McCarty and Arp[23] for helium and of that by Span et al.[24] for nitrogen. Furthermore, the pressures at the nominal temperature are listed in the tables.

The values of the viscosity at relatively low densities are characterized by a tendency to be too low which is caused by the slip effect. In this case, the fluid does not behave as a continuum since the molecular mean free path becomes comparable to the wire diameter. The data influenced by slip are included in the tables, but marked. They were excluded from further evaluation.

Discussion and Comparison with Literature

Density. The results for the density of helium at 293.15 K obtained with the two different sinkers in the three series of measurements are compared in Figure 3 with values calculated by means of the equation of state by McCarty and Arp[23] as well as with the experimental data by Evers et al.[12] and by McLinden and Lösch-Will.[25] The equation of state by McCarty and Arp is characterized by an uncertainty of up to ± 0.1 % in the temperature range (2 to 1500) K and up to pressures of 2000 MPa.

Figure 3 illustrates that the experimental density data measured with the quartz-glass sinker deviate systematically by about −0.5 % from the values calculated with the equation of state and that discontinuities occur within the course of these two series of measurements. The negative deviations show that the quartz-glass sinker absorbed obviously helium molecules so that the difference of the mass resulting from the measurements in vacuo and in the fluid became too small. This effect increased in the course of the series of measurements with decreasing density since the absorption−desorption equilibrium was not achieved during the measurement periods in the daytime and the difference between the masses in vacuo and in the fluid decreased. The discontinuities correspond to rest periods overnight and indicate that a slow desorption of helium occurred and the absorption−desorption equilibrium was reached in some degree. Weighings of the sinker in vacuo after completion of the series of measurements showed that its mass reduced with time. This makes it evident that absorbed helium molecules were removed in the course of the evacuation.

Table 1. Experimental $\eta\rho pT$ Data for Helium at 293.15 K[a]

T K	p MPa	$p_{293.15\ \mathrm{K}}$ MPa	ρ_{eos} $\mathrm{kg \cdot m^{-3}}$	η $\mu\mathrm{Pa \cdot s}$	$\eta_{293.15\ \mathrm{K}}$ $\mu\mathrm{Pa \cdot s}$
293.279	0.12133	0.12128	0.19905	19.548[b]	19.542[b]
293.277	0.24414	0.24404	0.40030	19.577[b]	19.571[b]
293.281	0.36670	0.36654	0.60090	19.592[b]	19.586[b]
293.269	0.48997	0.48977	0.80245	19.595	19.590
293.269	0.61345	0.61321	1.0041	19.600	19.595
293.243	1.2206	1.2202	1.9924	19.594	19.590
293.257	1.8273	1.8266	2.9741	19.594	19.589
293.144	2.4660	2.4661	4.0034	19.585	19.585
293.166	3.7426	3.7424	6.0394	19.581	19.581
293.150	4.9959	4.9959	8.0159	19.568	19.568
293.166	6.2734	6.2731	10.006	19.569	19.569
293.170	6.2737	6.2733	10.006	19.572	19.571
293.158	7.5870	7.5868	12.029	19.573	19.573
293.182	8.8702	8.8692	13.980	19.573	19.572
293.151	10.227	10.227	16.021	19.568	19.568
293.177	12.237	12.236	18.996	19.577	19.576
293.150	14.320	14.320	22.025	19.589	19.589
293.187	16.436	16.434	25.041	19.612	19.611
293.172	18.562	18.561	28.020	19.624	19.623
293.198	20.757	20.753	31.033	19.657	19.654
293.149	22.973	22.973	34.026	19.675	19.675
293.162	25.225	25.224	37.004	19.709	19.708
293.129	27.527	27.529	39.997	19.749	19.750
293.164	30.150	30.149	43.330	19.799	19.798
293.210	30.175	30.168	43.354	19.793	19.790
293.213	30.175	30.169	43.354	19.789	19.786

[a] The density relates to 293.15 K. (Quartz-glass sinker: $m_{\mathrm{s,vac}} = 31.84128$ g; wire with freely suspended weight: $\Delta_0 = 3.64 \cdot 10^{-5}$.) [b] Influenced by slip.

Table 2. Experimental $\eta\rho pT$ Data for Helium at 293.15 K[a]

T K	p MPa	$p_{293.15\ \mathrm{K}}$ MPa	ρ_{eos} $\mathrm{kg \cdot m^{-3}}$	η $\mu\mathrm{Pa \cdot s}$	$\eta_{293.15\ \mathrm{K}}$ $\mu\mathrm{Pa \cdot s}$
293.277	0.12130	0.12125	0.19901	19.544[b]	19.538[b]
293.278	0.24419	0.24408	0.40037	19.581[b]	19.575[b]
293.277	0.36666	0.36650	0.60084	19.586[b]	19.580[b]
293.273	0.49002	0.48982	0.80253	19.599	19.594
293.257	0.61330	0.61308	1.0039	19.597	19.592
293.253	1.2207	1.2203	1.9925	19.596	19.591
293.251	1.8271	1.8265	2.9739	19.588	19.584
293.155	2.4662	2.4662	4.0036	19.585	19.585
293.177	2.4666	2.4663	4.0038	19.588	19.587
293.157	3.7423	3.7423	6.0393	19.581	19.580
293.159	4.9962	4.9961	8.0161	19.571	19.571
293.162	6.2732	6.2729	10.006	19.569	19.569
293.168	7.5873	7.5869	12.029	19.572	19.571
293.173	8.8698	8.8691	13.980	19.567	19.566
293.175	10.228	10.227	16.021	19.579	19.578
293.173	12.237	12.236	18.996	19.584	19.583
293.162	14.320	14.320	22.025	19.590	19.590
293.182	16.436	16.434	25.042	19.608	19.607
293.181	18.563	18.561	28.020	19.638	19.637
293.191	18.564	18.561	28.020	19.631	19.629
293.196	20.756	20.753	31.032	19.653	19.651
293.160	22.974	22.973	34.026	19.675	19.675
293.183	22.975	22.973	34.026	19.681	19.679
293.153	25.224	25.223	37.004	19.721	19.721
293.141	27.529	27.530	39.998	19.747	19.747
293.161	30.149	30.148	43.328	19.797	19.797
293.208	30.174	30.168	43.354	19.797	19.794
293.218	30.175	30.169	43.354	19.801	19.798

[a] The density relates to 293.15 K. (Quartz-glass sinker: $m_{\mathrm{s,vac}} = 31.84128$ g; wire with lever support: $\Delta_0 = 3.56 \cdot 10^{-5}$.) [b] Influenced by slip.

Further, Figure 3 shows that the experimental data obtained with the silicon sinker deviate only by −0.1 % from the values calculated for the equation of state by McCarty and Arp as well as from the high-precision experimental data by McLinden and Lösch-Will. This demonstrates that the absorption of helium molecules in the silicon sinker is distinctly reduced and practically negligible. Nevertheless, the viscosity measurements on helium were evaluated in the case of all three series of measurements with the densities resulting from the experimental values of temperature and pressure using the equation of state by McCarty and Arp.

The results of the density measurements on nitrogen at 293.15 K with the quartz-glass and the silicon sinkers and at 423.15 K with the quartz-glass sinker are presented in Figure 4. They are compared with values calculated by means of the equation of state by Span et al.[24] as well as with the experimental data by

Table 3. Experimental $\eta\rho pT$ Data for Helium at 293.15 K[a]

T / K	p / MPa	$p_{293.15\ \mathrm{K}}$ / MPa	ρ / $\mathrm{kg \cdot m^{-3}}$	ρ_{eos} / $\mathrm{kg \cdot m^{-3}}$	η / $\mu\mathrm{Pa \cdot s}$	$\eta_{293.15\ \mathrm{K}}$ / $\mu\mathrm{Pa \cdot s}$
293.150	0.12225	0.12225	0.19885	0.20065	19.541[b]	19.541[b]
293.151	0.12225	0.12225	0.19885	0.20065	19.540[b]	19.540[b]
293.156	0.24573	0.24572	0.40445	0.40307	19.576[b]	19.576[b]
293.155	0.24573	0.24572	0.40368	0.40306	19.576[b]	19.576[b]
293.150	0.36653	0.36653	0.60087	0.60089	19.590[b]	19.590[b]
293.150	0.36651	0.36651	0.59858	0.60085	19.587[b]	19.587[b]
293.155	0.48300	0.48299	0.79119	0.79138	19.586[b]	19.586[b]
293.154	0.48299	0.48299	0.79042	0.79137	19.587[b]	19.587[b]
293.158	0.61317	0.61315	1.0037	1.0040	19.591	19.591
293.158	0.61318	0.61316	1.0029	1.0040	19.592	19.592
293.151	1.2199	1.2199	1.9866	1.9919	19.586	19.586
293.151	1.2199	1.2199	1.9866	1.9920	19.587	19.587
293.151	1.8276	1.8276	2.9711	2.9757	19.583	19.583
293.151	1.8275	1.8275	2.9695	2.9755	19.583	19.583
293.157	2.4475	2.4475	3.9693	3.9736	19.578	19.577
293.157	2.4475	2.4474	3.9647	3.9735	19.576	19.576
293.150	3.7143	3.7143	5.9827	5.9949	19.564	19.564
293.150	3.7142	3.7142	5.9819	5.9948	19.567	19.567
293.151	4.9786	4.9786	7.9740	7.9886	19.561	19.561
293.151	4.9787	4.9787	7.9747	7.9888	19.561	19.561
293.160	6.2639	6.2636	9.9737	9.9914	19.555	19.554
293.160	6.2639	6.2637	9.9745	9.9914	19.557	19.556
293.150	7.5642	7.5642	11.972	11.994	19.553	19.553
293.149	7.5641	7.5641	11.972	11.994	19.552	19.552
293.152	8.8429	8.8428	13.917	13.940	19.550	19.550
293.152	8.8429	8.8428	13.915	13.940	19.550	19.550
293.167	10.198	10.197	15.951	15.977	19.553	19.552
293.172	10.198	10.197	15.945	15.976	19.553	19.552
293.149	12.231	12.231	18.954	18.988	19.560	19.560
293.148	12.231	12.231	18.954	18.988	19.556	19.557
293.147	14.296	14.296	21.953	21.991	19.569	19.569
293.147	14.295	14.295	21.949	21.990	19.574	19.574
293.146	16.374	16.374	24.913	24.957	19.581	19.582
293.145	16.374	16.374	24.912	24.957	19.584	19.584
293.149	18.460	18.460	27.833	27.880	19.600	19.600
293.149	18.460	18.460	27.831	27.879	19.602	19.602
293.147	20.744	20.744	30.973	31.021	19.625	19.626
293.145	20.744	20.744	30.969	31.020	19.623	19.623
293.152	22.883	22.883	33.861	33.906	19.656	19.656
293.148	22.880	22.880	33.856	33.901	19.655	19.655
293.152	25.329	25.329	37.097	37.142	19.688	19.688
293.152	25.329	25.329	37.099	37.142	19.690	19.690

[a] The densities relate to 293.15 K. (Silicon sinker: $m_{\mathrm{s,vac}} = 31.82474$ g; wire with lever support: $\Delta_0 = 1.29 \cdot 10^{-5}$.) [b] Influenced by slip.

Evers et al.[12] and by McLinden and Lösch-Will.[25] The equation of state by Span et al. is characterized by an uncertainty of up to ± 0.02 % in the temperature and pressure ranges of the measurements of this work. Apart from two points, the deviations of our experimental data do not exceed ± 0.02 % at densities $> 10\ \mathrm{kg \cdot m^{-3}}$. It is important to mention that measurements using a single-sinker densimeter are generally hampered at densities $< 10\ \mathrm{kg \cdot m^{-3}}$ (see subsection Error Analysis). Hence our results at these densities possess deviations up to ± 0.15 %. This holds also for the measurements of Evers et al. at densities of about $1\ \mathrm{kg \cdot m^{-3}}$ whose results deviate by more than + 1 % from the equation of state (not shown in the figure). On the contrary, measurements with a two-sinker densimeter as used by McLinden and Lösch-Will lead to very small uncertainties as demonstrated in Figure 4. In principle, densities $> 10\ \mathrm{kg \cdot m^{-3}}$ determined with the single-sinker densimeter can be used for the evaluation of the viscosity measurements, whereas at lower densities values derived from experimental temperatures and pressures using a reliable equation of state, if available, should be preferred.

For nitrogen, the series of measurements with the silicon sinker at 293.15 K was analyzed with the experimental densities, whereas the densities calculated with the equation of state were still used to obtain the viscosity data for the other two measurements with the quartz-glass sinker.

Viscosity. As already mentioned in the subsection Vibrating-Wire Viscometer, the wire radius was determined within the framework of a calibration with a theoretically based value for the viscosity of helium in the limit of zero density. For that purpose the value $\eta_{0,\mathrm{He}}(293.15\ \mathrm{K}) = 19.600\ \mu\mathrm{Pa \cdot s}$ with an uncertainty of ± 0.02 %, according to the estimation by Bich et al.,[15] was used. Since experiments in this limit are not feasible and, in addition, measurements with the vibrating-wire viscometer at low densities are influenced by slip, results obtained at somewhat higher densities for the isotherms at 293.15 K had to be extrapolated to the limit of zero density. With regard to the calibration, this means that the wire radius had to be determined in an iterative procedure in which a power series expansion of the viscosity as a function of density was used to fit the experimental results in such a way that the first coefficient of the polynomial series corresponds to the calibration value by Bich et al. Criteria of the fit were the weighted standard deviation σ of the series of measurements and the individual standard deviations s.d. of the coefficients in the power series expansion, particularly at low densities.

The experimental results of each isotherm for helium, but also for nitrogen, were correlated as a function of the reduced density δ by means of a power series representation restricted to the fourth or a lower power depending on the density range and on the reduced temperature τ

$$\eta(\tau,\delta) = \sum_{i=0}^{n} \eta_i(\tau)\delta^i,\ \delta = \frac{\rho}{\rho_{\mathrm{c,fluid}}},\ \tau = \frac{T}{T_{\mathrm{c,fluid}}},$$
$$\text{with } T_{\mathrm{c,He}} = 5.1953\ \mathrm{K},\ T_{\mathrm{c,N_2}} = 126.192\ \mathrm{K},$$
$$\rho_{\mathrm{c,He}} = 69.641\ \mathrm{kg\cdot m^{-3}},\ \rho_{\mathrm{c,N_2}} = 313.30\ \mathrm{kg\cdot m^{-3}} \tag{13}$$

Weighting factors of η_{exp}^{-2} were used in the multiple linear least-squares regression to minimize the relative deviations for the different isotherms. The coefficients $\eta_i(\tau)$ of eq 13 are given in Table 7 for helium and nitrogen. Furthermore, the values of the radii R of the vibrating wires obtained by the calibration are also given in this table.

The experimental results for one of the isotherms of helium (Table 1) are presented in Figure 5 as a function of the density ρ. The relative deviations plotted in the inset of the figure reveal that the experimental data at low densities are influenced by slip. Further, the figure makes obvious that the initial density dependence of the viscosity of helium at 293.15 K features a negative slope.

The comparison of our values for the initial-density viscosity coefficient η_1 at room temperature in Table 8 with results reported by other groups shows a reasonably good agreement with the exception of the value given by Evers et al.[12] In addition, the table makes it clear that there exists a close agreement between our experiments and the value resulting from

Table 4. Experimental $\eta\rho pT$ Data for Nitrogen at 293.15 K[a]

T / K	p / MPa	$p_{293.15\ \mathrm{K}}$ / MPa	ρ / kg·m^{-3}	ρ_{eos} / kg·m^{-3}	η / μPa·s	$\eta_{293.15\ \mathrm{K}}$ / μPa·s
293.176	0.069618	0.069612	0.79943	0.80020	17.487[b]	17.485[b]
293.164	0.087057	0.087053	1.0006	1.0007	17.504[b]	17.503[b]
293.163	0.17408	0.17407	2.0011	2.0014	17.531	17.530
293.153	0.26016	0.26016	2.9879	2.9919	17.545	17.545
293.170	0.34738	0.34736	3.9950	3.9955	17.559	17.558
293.151	0.43463	0.43463	4.9978	5.0003	17.565	17.565
293.166	0.43486	0.43484	5.0007	5.0027	17.573	17.572
293.146	0.86769	0.86771	9.9877	9.9920	17.634	17.634
293.107	1.7373	1.7375	20.040	20.040	17.760	17.762
293.125	3.4565	3.4569	39.956	39.950	18.067	18.069
293.119	5.1884	5.1891	60.007	60.000	18.427	18.429
293.124	6.9321	6.9329	80.084	80.078	18.843	18.844
293.114	8.6841	8.6854	100.062	100.052	19.307	19.309
293.161	10.467	10.466	120.042	120.041	19.832	19.831
293.109	12.288	12.291	140.108	140.099	20.393	20.395
293.130	14.176	14.177	160.309	160.309	21.009	21.010
293.118	16.079	16.081	180.081	180.076	21.680	21.682
293.144	18.079	18.080	200.088	200.079	22.383	22.383
293.159	20.166	20.166	220.109	220.101	23.165	23.165
293.118	22.359	22.363	240.226	240.215	23.994	23.995
293.116	24.666	24.671	260.273	260.254	24.902	24.903
293.158	27.067	27.066	279.916	279.903	25.851	25.851
293.164	30.306	30.304	304.692	304.680	27.134	27.133
293.166	30.306	30.304	304.691	304.681	27.137	27.136

[a] The densities relate to 293.15 K. (Quartz-glass sinker: $m_{\mathrm{s,vac}} = 31.84015$ g; wire with lever support: $\Delta_0 = 3.30\cdot10^{-5}$.) [b] Influenced by slip.

Table 5. Experimental $\eta\rho pT$ Data for Nitrogen at 293.15 K[a]

T / K	p / MPa	$p_{293.15\ \mathrm{K}}$ / MPa	ρ / kg·m^{-3}	ρ_{eos} / kg·m^{-3}	η / μPa·s	$\eta_{293.15\ \mathrm{K}}$ / μPa·s
293.151	0.16817	0.16809	1.9327	1.9336	17.545	17.545
293.151	0.16817	0.16809	1.9327	1.9336	17.544	17.544
293.151	0.25704	0.25712	2.9569	2.9560	17.553	17.553
293.151	0.25703	0.25732	2.9592	2.9559	17.550	17.550
293.149	0.34860	0.34876	4.0116	4.0098	17.563	17.563
293.149	0.34859	0.34830	4.0063	4.0097	17.571	17.571
293.149	0.43844	0.43844	5.0442	5.0442	17.579	17.579
293.149	0.43845	0.43851	5.0450	5.0443	17.577	17.577
293.152	0.86504	0.86470	9.9572	9.9611	17.630	17.630
293.152	0.86503	0.86463	9.9564	9.9610	17.631	17.631
293.145	1.7417	1.7417	20.088	20.088	17.752	17.752
293.141	1.7417	1.7417	20.088	20.089	17.755	17.755
293.154	3.4523	3.4519	39.892	39.897	18.048	18.048
293.154	3.4523	3.4519	39.892	39.897	18.046	18.046
293.143	5.1913	5.1920	60.033	60.027	18.402	18.402
293.140	5.1910	5.1915	60.028	60.024	18.408	18.409
293.156	6.9173	6.9178	79.905	79.898	18.813	18.813
293.145	6.9198	6.9207	79.938	79.930	18.811	18.811
293.139	6.9199	6.9206	79.937	79.933	18.811	18.811
293.159	8.6834	8.6835	100.03	100.03	19.276	19.275
293.154	8.6834	8.6844	100.04	100.03	19.280	19.280
293.159	10.724	10.725	122.91	122.90	19.870	19.870
293.159	10.724	10.724	122.90	122.90	19.867	19.867

[a] The densities relate to 293.15 K. (Silicon sinker: $m_{\mathrm{s,vac}} = 31.82481$ g; wire with lever support: $\Delta_0 = 1.19\cdot10^{-5}$.)

Table 6. Experimental $\eta\rho pT$ Data for Nitrogen at 423.15 K[a]

T K	p MPa	$p_{423.15\ \mathrm{K}}$ MPa	ρ $\mathrm{kg \cdot m^{-3}}$	ρ_{eos} $\mathrm{kg \cdot m^{-3}}$	η $\mu\mathrm{Pa \cdot s}$	$\eta_{423.15\ \mathrm{K}}$ $\mu\mathrm{Pa \cdot s}$
423.105	0.10056	0.10057	0.79993	0.80052	22.935[b]	22.936[b]
423.107	0.12569	0.12570	0.99956	1.0005	22.949[b]	22.950[b]
423.114	0.25145	0.25147	1.9998	2.0007	22.985[b]	22.987[b]
423.103	0.37731	0.37735	2.9994	3.0009	23.010[b]	23.012[b]
423.115	0.50326	0.50331	3.9997	4.0010	23.029	23.030
423.097	0.62965	0.62973	5.0007	5.0039	23.036	23.038
423.094	1.2614	1.2616	9.9995	10.003	23.089	23.091
423.086	2.5335	2.5339	20.001	20.003	23.201	23.204
423.097	5.1175	5.1182	40.010	40.008	23.473	23.475
423.086	7.7606	7.7619	60.009	60.006	23.815	23.817
423.106	10.470	10.472	79.969	79.969	24.197	24.199
423.108	13.263	13.264	99.939	99.933	24.643	24.644
423.119	16.171	16.173	120.044	120.036	25.134	25.136
423.089	19.172	19.175	140.043	140.032	25.686	25.688
423.098	22.320	22.323	160.186	160.161	26.293	26.295
423.090	25.569	25.574	180.070	180.048	26.946	26.949
423.158	30.225	30.224	206.975	206.955	27.911	27.910
423.151	30.228	30.228	206.995	206.978	27.915	27.915
423.154	30.257	30.257	207.176	207.141	27.916	27.915

[a] The densities relate to 423.15 K. (Quartz-glass sinker: $m_{\mathrm{s,vac}} = 31.83943$ g; wire with freely suspended weight: $\Delta_0 = 3.60 \cdot 10^{-5}$.) [b] Influenced by slip.

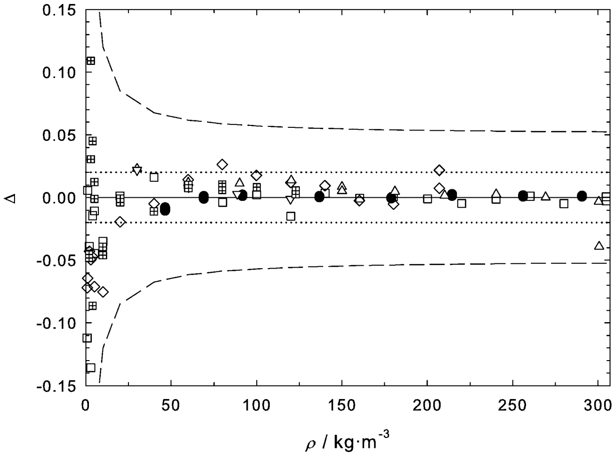

Figure 4. Comparison of the measured densities for nitrogen at 293.15 K and at 423.15 K with values calculated for the equation of state of Span et al.[24] using the measured temperature and pressure data as a function of density ρ. Deviations: $\Delta = 100 \cdot (\rho_{\mathrm{exp}} - \rho_{\mathrm{eos}})/\rho_{\mathrm{eos}}$. Experimental data: □, this work, quartz-glass sinker, 293.15 K (Table 4); ⊞, this work, silicon sinker, 293.15 K (Table 5); ◇, this work, quartz-glass sinker, 423.15 K (Table 6); ●, McLinden and Lösch-Will,[25] two-sinker densimeter, 293.15 K; △, Evers et al.,[12] single-sinker densimeter, 293.15 K; ∇, Evers et al., single-sinker densimeter, 423.15 K. − − −, uncertainty in the density measurement of this work; ••••••, uncertainty of the equation of state of Span et al.

the Rainwater−Friend theory for the initial density dependence of transport properties.[30,31]

The density dependence of the viscosity of helium at 293.15 K should be compared with viscosity surface correlations as well as with directly measured experimental data. As shown in the inset of Figure 6, surprisingly large deviations of our experimental data result with respect to the correlations by Bammert and Klein[32] and by Arp et al.[33] which are available in the open literature for the complete fluid range. Hence it is better to compare our values with experimental data. In this context, the viscosity value in the limit of zero density has to be discussed primarily, since the calibration datum used for our measurements differs by −(0.15 to 0.20) % from the values considered by Kestin and Leidenfrost[26] and by Kestin et al.[27] to be correct. Furthermore, it is taken into account that the uncertainty of experimental data, even at room temperature, amounts to ± (0.1 to 0.2) % at best. Figure 6 reveals that the density dependence of the viscosity found by Kestin and Leidenfrost,[26] Kestin et al.,[27] Flynn et al.,[28] and Gracki et al.[29] agrees within ± 0.1 % with that derived from the three series of measurements of this paper. The data by Evers et al.[12] show a different behavior of the density dependence what has already become obvious by the discriminative value of the initial-density viscosity coefficient (see Table 8). Finally, it is to be stated that the density range is distinctly extended by the new experimental results.

In the case of nitrogen, a reliable viscosity surface correlation was recently reported by Lemmon and Jacobsen[34] who estimated the uncertainty of their correlation to be ± 2 % in the complete range between (50 and 2000) K and at pressures up to 2200 MPa, reduced to ± 0.5 % in the low-density range. The uncertainty of the correlation should also be decreased in the thermodynamic region of the present measurements. In Figures 7 and 8, values calculated by means of the viscosity correlation by Lemmon and Jacobsen are compared with our experimental data as well as with reliable data from the literature.

It is again taken into account that some of the earlier data were obtained by relative measurements based on viscosity values at room temperature which are higher by about 0.2 %. This explains that the low-density viscosity data of the present paper at 293.15 K, shown in Figure 7, deviate by −0.3 % from the values calculated for the correlation and by −(0.2 to 0.3) % from the experimental data by Kestin and Leidenfrost,[26] Kestin et al.,[27] and Seibt et al.[8] The relative measurements by Seibt et al. were also performed with a vibrating-wire viscometer in our laboratory, but using an experimentally based calibration value, 0.2 % higher than ours. Flynn et al.[28] and Gracki et al.[29] carried out absolute measurements with a capillary viscometer whose results are 0.2 % lower than our new experimental data in the low-density region. Figure 7 makes additionally evident that the results for the density dependence of the viscosity of nitrogen at 293.15 K, derived from the measurements of Flynn et al., of Gracki et al., and of Seibt et al., as well as from the present ones, agree within ± 0.1 %, apart from one point of Gracki et al. at 263 $\mathrm{kg \cdot m^{-3}}$. However, there exist differences in the density dependence resulting from the experimental data of Kestin and Leidenfrost and of Kestin et al. increasing with

Table 7. Coefficients of Equation 13 for the Viscosity Measurements on Helium and Nitrogen Including the Results of the Calibration with Helium[a]

	R_{cal}	$\rho_{\max}$	$\eta_0 + \mathrm{s.d.}_{\eta_0}$	$\eta_1 + \mathrm{s.d.}_{\eta_1}$	$\eta_2 + \mathrm{s.d.}_{\eta_2}$	$\eta_3 + \mathrm{s.d.}_{\eta_3}$	$\eta_4 + \mathrm{s.d.}_{\eta_4}$	σ
Table and wire supension	μm	kg·m^{-3}	μPa·s	μPa·s	μPa·s	μPa·s	μPa·s	(weighted)
1 and free weight	12.9623	43.354	19.600 ± 0.002	−0.375 ± 0.015	1.096 ± 0.023			0.020
2 and lever support	12.9594	43.354	19.600 ± 0.002	−0.368 ± 0.014	1.096 ± 0.022			0.019
3 and lever support	12.9667	37.142	19.600 ± 0.001	−0.485 ± 0.007	1.224 ± 0.013			0.009
4 and lever support	12.9594	304.68	17.512 ± 0.002	3.436 ± 0.049	7.557 ± 0.243	−2.650 ± 0.403	1.759 ± 0.211	0.023
5 and lever support	12.9667	122.91	17.521 ± 0.001	3.287 ± 0.025	6.902 ± 0.069			0.023
6 and free weight	12.9623	207.14	22.980 ± 0.003	3.094 ± 0.024	6.620 ± 0.037			0.026

[a] All series of measurements at 293.15 K, apart from the third series for nitrogen at 423.15 K.

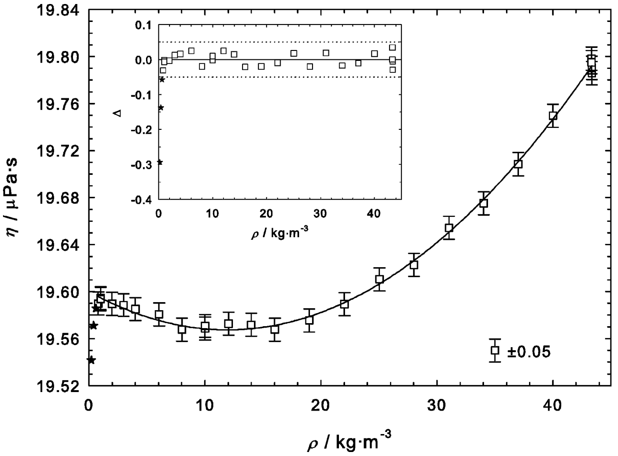

Figure 5. Viscosity of helium at 293.15 K as a function of density ρ. □, experimental data using a wire with freely suspended weight (Table 1); ★, experimental points influenced by slip; −, fitted with a power-series expansion of second order in the reduced density δ (eq 13, Table 7). Deviations: $\Delta = 100 \cdot (\eta_{\mathrm{exp}} - \eta_{\mathrm{fit}})/\eta_{\mathrm{fit}}$.

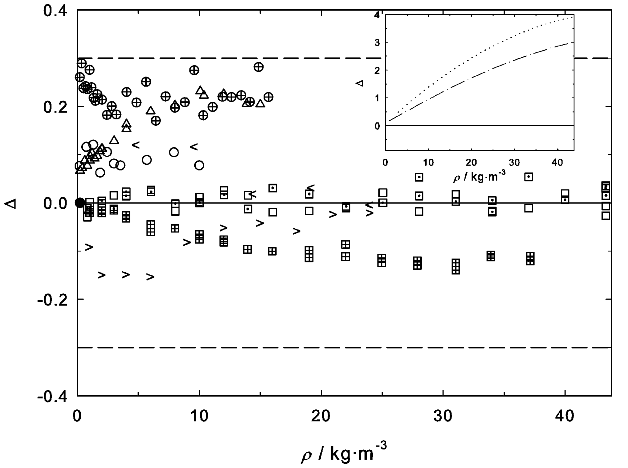

Figure 6. Comparison of experimental and correlated viscosity data with values fitted to the data of Table 1 using eq 13 for helium at 293.15 K (see Table 7). Deviations: $\Delta = 100 \cdot (\eta_{\mathrm{exp,cor}} - \eta_{\mathrm{fit}})/\eta_{\mathrm{fit}}$. Experimental data: □, this work, freely suspended weight (Table 1); ⊡, this work, lever support (Table 2); ⊞, this work, lever support (Table 3); ○, Kestin and Leidenfrost;[26] ⊕, Kestin et al.,[27] 298.15 K (adjusted to 293.15 K); <, Flynn et al.,[28] 298.15 K (adjusted to 293.15 K); >, Gracki et al.,[29] 298.15 K (adjusted to 293.15 K); △, Evers et al.[12] Calibration: ●, theoretically calculated value of Bich et al.[15] − − −, uncertainty in the viscosity measurement of this work. Inset: correlations available in the literature: ·······, Bammert and Klein;[32] − · − ·, Arp et al.[33]

Table 8. Coefficient for the Initial Density Dependence of the Viscosity of Helium at 293.15 K[a]

	η_1		η_1
Reference	μPa·s	Reference	μPa·s
Table 1 & free weight	−0.375	Kestin and Leidenfrost[26]	−0.395
Table 2 & lever support	−0.368	Kestin et al.[27] (298.15 K)	−0.741
Table 3 & lever support	−0.485	Flynn et al.[28] (298.15 K)	− 0.528
		Gracki et al.[29] (298.15 K)	−0.293
Rainwater−Friend theory[30,31]	−0.334	Evers et al.[12]	0.020

[a] Comparison of the measurements of this work with theoretical and experimental values from the literature.

the density as well as differences concerning the data by Evers et al.[12] at the highest densities.

Figure 8 reveals that the low-density viscosity value at 423.15 K calculated with the correlation by Lemmon and Jacobsen is further increased by 0.3 % compared with the new experimental data as well as with those measured by Seibt et al. This increase by 0.3 % is certainly due to the fact that Lemmon and Jacobsen based their correlation in the limit of zero density on data by Kestin and co-workers which are influenced by a temperature measurement error discussed extensively by Vogel et al.[35] In addition, there are comparably small differences to the correlated viscosity values concerning the density dependence. The close agreement between the values calculated for the correlation and the experimental data by Evers et al. is due to the fact that these data were included in the correlation.

Conclusions

A vibrating-wire viscometer and a single-sinker densimeter were combined in an apparatus to perform quasi-simultaneously accurate measurements of viscosity and density of gases over wide ranges of temperature and pressure. The absolute density determination is based on the buoyancy principle and characterized by an uncertainty of $< \pm\ 0.1$ % for $\rho > 15$ kg·m^{-3} increasing with decreasing densities. Using these density data, the well-engineered vibrating-wire technique enables us to achieve uncertainties of about ± (0.25 to 0.3) % in relative viscosity measurements. For that purpose, the wire radius was determined by calibration of the viscometer by means of a theoretically based value for the zero-density viscosity coefficient of helium at room temperature. The combined apparatus is designed for measurements between (253 and 473) K at pressures up to 30 MPa. Although the installation of the densimeter in the immediate vicinity of the vibrating wire has advantageous effects, the uncertainty in the viscosity measurement is expected to increase distinctly in the near-critical region of the fluids due to the increased uncertainty in the density determination.

Three isothermal series of measurements on helium at 293.15 K as well as two series at 293.15 K and one series at 423.15 K on nitrogen were carried out to check the performance of the apparatus and to provide accurate $\eta\rho pT$ data. Since the individual points of the isotherms were not measured exactly at the nominal temperature, the experimental viscosity values were adjusted to nominal isotherms using a first-order correction in temperature and at last correlated as a function of the reduced

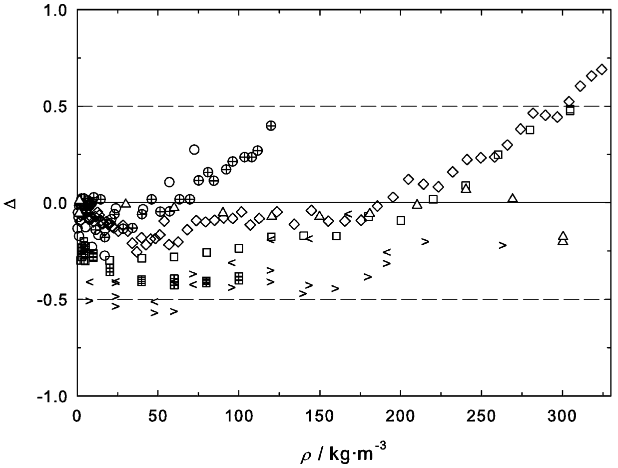

Figure 7. Comparison of experimental viscosity data with the correlation of Lemmon and Jacobsen[34] for nitrogen at (293.15 and 298.15) K. Deviations: $\Delta = 100\cdot(\eta_{\text{exp}} - \eta_{\text{cor}})/\eta_{\text{cor}}$. Experimental data: ◇, Seibt et al.,[8] freely suspended weight, 298.15 K; □, this work, lever support, 293.15 K (Table 4); ⊞, this work, lever support, 293.15 K (Table 5); ○, Kestin and Leidenfrost,[26] 293.15 K; ⊕, Kestin et al.,[27] 298.15 K; <, Flynn et al.,[28] 298.15 K; >, Gracki et al.,[29] 298.15 K; △, Evers et al.,[12] 293.15 K.

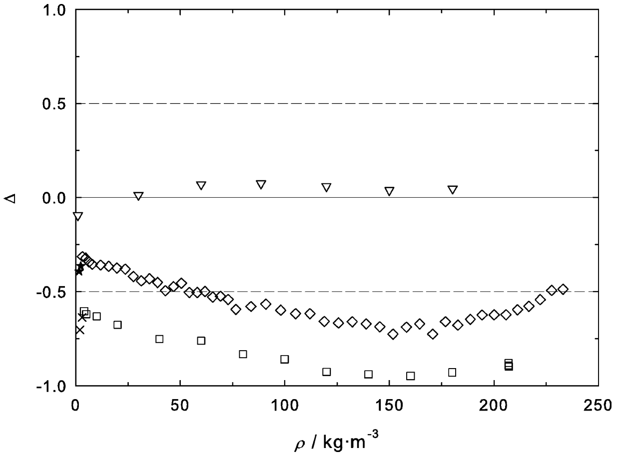

Figure 8. Comparison of experimental viscosity data with the correlation of Lemmon and Jacobsen[34] for nitrogen at 423.15 K. Deviations: $\Delta = 100\cdot(\eta_{\text{exp}} - \eta_{\text{cor}})/\eta_{\text{cor}}$. Experimental data: ◇, Seibt et al.,[8] freely suspended weight; ★, Seibt et al.,[8] freely suspended weight, influenced by slip; □, this work, lever support (Table 6); ×, this work, lever support, influenced by slip (Table 6); ∇, Evers et al.[12]

density δ by means of a power series representation restricted to the fourth or a lower power depending on the density range and on the reduced temperature τ. As a result of these fits, the internal consistency of our data is estimated to be lower than ± 0.05 %.

The density values measured directly for helium and nitrogen were compared to values calculated by means of reliable equations of state from the values of temperature and pressure determined experimentally. Due to effects of absorption, the values determined for helium with a quartz-glass sinker differ systematically by about −0.5 % from the equation of state by Arp et al. Replacing this sinker with one of silicon, the differences decreased to about −0.1 %. The density determinations for nitrogen with both sinkers were not influenced by absorption effects so that the measured and the calculated density values agree within ± 0.03 % at densities > 10 kg·m^{-3}. However, the measurements with the single-sinker densimeter are less reliable at densities < 10 kg·m^{-3}, although the error propagation factor for the density decreases with decreasing density.

The viscosity data for helium and nitrogen were compared to viscosity surface correlations as well as to selected experimental data available in the literature. At low densities, the majority of other data is about 0.2 % higher than our values which is mainly due to our calibration with a value calculated theoretically for the viscosity coefficient of helium in the limit of zero density at room temperature.

Differences of more than 3 % at the highest densities between the experimental data of this work and the viscosity surface correlations from the literature prove the necessity to develop a new viscosity correlation for helium. Since the deviations between our experimental data and those of the literature are < 0.3 %, a reliable database exists already which could be used for an improved viscosity surface correlation. The new measurements extend this database, particularly in the high-pressure region.

The comparison of the new experimental results for the viscosity of nitrogen at (293.15 and 423.15) K with the correlation by Lemmon and Jacobsen reveals that the density dependence is in reasonably good agreement of ± 0.3 % taking into account the deviations in the low-density region which are due to distinct calibration procedures used in different measurements. Larger differences occur only at the highest densities > 250 kg·m^{-3}. Further, the results of earlier measurements in our laboratory by Seibt et al. are confirmed by the new experiments. With regard to the development of a new viscosity surface correlation, all available experimental data in the literature should be reviewed critically.

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Received for review January 30, 2009. Accepted May 26, 2009.

JE900131Q