

# Densimetry for primary temperature metrology and a method for the *in situ* determination of densimeter sinker volumes\*

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## Abstract

The feasibility of using gas-phase pressure–density–temperature ( $p$ – $\rho$ – $T$ ) measurements as a method of determining thermodynamic temperatures is evaluated. Densities are measured at the unknown and reference temperatures at identical pressures, and the resulting density ratios are extrapolated to zero pressure to yield the ratio of the temperatures. The method utilizes a two-sinker densimeter with a magnetic suspension coupling to separate the sinkers (in the working gas) from the balance (in atmosphere). Numerical studies investigate the optimum working gas and the effects of experimental uncertainties on the uncertainty in temperature. The method is demonstrated using an existing densimeter over the range of 234–505 K with argon, neon or nitrogen as the working gas. Experimental protocols and data analysis techniques are developed. New experimental  $p$ – $\rho$ – $T$  data for argon and neon are reported. The technique is shown to be feasible, although the present densimeter has uncertainties which are too high for temperature metrology. In particular, the uncertainty in the sinker volumes is relatively large. The method is inverted to determine, *in situ*, the sinker volumes as a function of temperature, reducing their uncertainties, and thus the uncertainties of fluid densities measured with this apparatus.

**Keywords:** argon, density, gas thermometer, neon, temperature, two-sinker densimeter, volume

## 1. Introduction

Temperature is among the most important quantities in a vast array of applications. Temperature is a well-defined thermodynamic quantity, but the temperature scales in practical use, such as ITS-90, are only approximations of the thermodynamic temperature. In many applications, it is sufficient to use a temperature scale which is merely consistent and reproducible. In thermodynamics, however, it is often important that the temperature scale represents true

thermodynamic temperatures. Two of the primary sources of thermodynamic temperatures on which ITS-90 is based, namely the gas-thermometer work of Edsinger and Schooley (1989) and Guildner and Edsinger (1976), differ from each other by 30 mK at 730 K. Recent work by Strouse *et al* (2002) and Ripple *et al* (2002) provides strong evidence that ITS-90 differs from the true thermodynamic temperature by 11 mK at 505 K. Thus, temperature metrology offers room for improvement, and an additional, independent technique would be valuable.

We have recently put into operation at NIST a new apparatus for the determination of fluid density. This densimeter operates on the familiar Archimedes (buoyancy)

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principle and provides an absolute determination of density. Several twists on the conventional Archimedes experiment—including a differential weighing with two sinkers and a magnetic suspension coupling to separate the balance from the fluid being measured—reduce the uncertainties and allow operation over a wide range of temperature and pressure. Repeatabilities at the level of a few parts per million (ppm) are routinely obtained for the densities of liquids and dense gases. Such a densimeter could create a new type of gas thermometer, while avoiding many of the headaches of the traditional constant-volume gas thermometer (CVGT).

The pressure of a low-density gas is given by a simple virial expansion:

$$p = \frac{RT\rho(1 + B\rho + C\rho^2 + D\rho^3)}{M}, \quad (1.1)$$

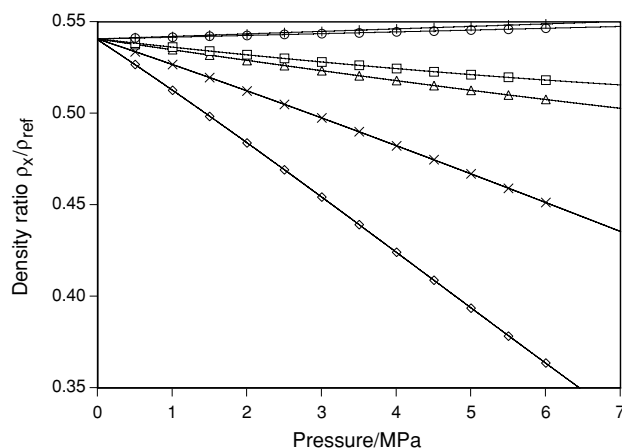
where  $T$  is temperature,  $R$  is the molar gas constant,  $\rho$  is the mass density,  $M$  is the molar mass, and  $B$ ,  $C$  and  $D$  are the second, third and fourth virial coefficients on a mass basis.

With a constant-volume gas thermometer, the temperature is derived from the pressure ratio of a fixed quantity of gas measured at some unknown temperature  $T_x$  and at a reference temperature, usually  $T_{\text{ref}} = 273.16$  K. With the densimeter, the pressure would be held constant for measurements at the two temperatures; the density ratio is then extrapolated to zero pressure to yield the temperature:

$$\frac{T_x}{T_{\text{ref}}} = \lim(p \rightarrow 0) \frac{\rho(T_{\text{ref}})}{\rho(T_x)}. \quad (1.2)$$

The densimeter operating as a ‘density-ratio gas thermometer’ (DRGT) offers several advantages over a CVGT. The ‘reference volume’ is that of the sinkers, rather than a thin-walled gas bulb and its associated plumbing; the thermal expansion corrections would be simpler. Pressure would be generated and held constant with a piston gauge. Leaks and outgassing are potential problems with CVGT, but a small leak would be of little consequence with the DRGT, and a small flow of gas may be desirable to maintain gas purity. CVGT corrects for non-ideal behaviour by either extrapolating multiple experiments at different gas densities to zero pressure or by applying corrections based on accurate knowledge of the virial coefficients. With the density approach, measurements are made at multiple pressures and extrapolated to zero pressure. This extrapolation circumvents the need for the virials (or alternatively, provides a simultaneous fit of the virial coefficients for the particular gas being used), with the benefit of reduced sensitivity to gas purity. Note that the gas constant and molar mass drop out of (1.2). While the gas constant is well known ( $u = 1.7$  ppm with  $k = 1$ , Mohr and Taylor 2005), the molar mass is dependent on sample purity and isotopic variations. With the density method the working gas need not be of unusually high purity; it need only be the same for all the tests. CVGT usually uses helium, but argon can also be used. With the DRGT, measurements with different gases would provide an additional check on the results.

The work presented here is exploratory in nature and is intended to investigate the feasibility of this approach. It combines analytical and experimental investigations. Numerical studies are used to determine the optimum working gas and the effects of measurement uncertainties. Experiments with our present densimeter over the range of 234–505 K



**Figure 1.** Simulated density ratios for  $T_x = 505.078$  K and  $T_{\text{ref}} = 273.16$  K for several fluids (+) helium; (O) neon; (□) nitrogen; (Δ) argon; (×) krypton and (◇)  $\text{CF}_4$ .

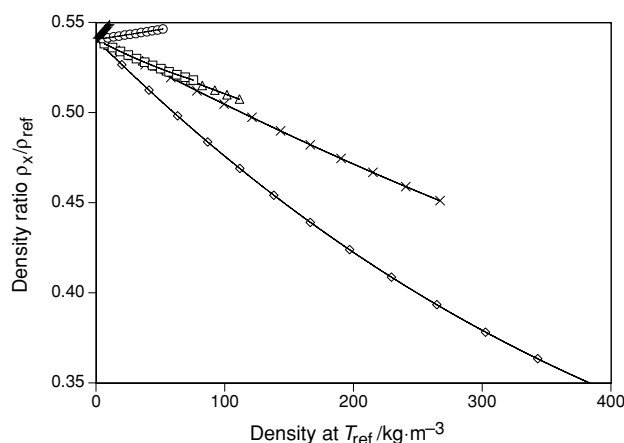
with argon, neon and nitrogen as the working gases have been carried out. These demonstrate experimental protocols, examine data analysis techniques and explore systematic errors. While these experiments have demonstrated the feasibility of the method, the present densimeter has uncertainties which are too high for temperature metrology—in particular, the uncertainty in the sinker volumes is large compared to the uncertainty in temperature. The method was, thus, inverted and used with the measured data to determine, *in situ*, the sinker volumes as a function of temperature.

## 2. Numerical study

### 2.1. Model

The density-ratio gas thermometer involves density measurements of a working gas at two temperatures and multiple pressures. The ratios of the densities at each pressure are computed and these ratios are extrapolated to zero pressure (or density) to give the temperature ratio according to (1.2). In principle, any gas could be measured over any range of pressures. But what is the optimum working gas, optimum pressure range and best extrapolation model? The basic assumption behind the method is that any real gas will approach ideal-gas behaviour in the limit of zero pressure, but measurements must be carried out at finite pressures, so nearly ideal behaviour at higher pressures is desirable. This argues for a very simple fluid with a low critical temperature, and helium is the most obvious example. But since mass densities are measured, large relative uncertainties in the densities would result from light gases and/or measurements at low pressures. Thus one should consider operation at higher pressures and with gases which are heavier, but which still retain a simple, symmetrical structure.

Figure 1 shows simulated results for several gases measured at  $T_x = 505.078$  K and  $T_{\text{ref}} = 273.16$  K over the pressure range 0.5–6 MPa. In addition to helium, the noble gases neon, argon and krypton are considered as well as nitrogen and the quasi-spherically symmetric  $\text{CF}_4$ . The densities were computed using the equations of state in the NIST REFPROP database (Lemmon *et al* 2002). (REFPROP



**Figure 2.** Simulated density ratios over the pressure range 0.5–6 MPa for  $T_x = 505.078$  K and  $T_{\text{ref}} = 273.16$  K for several fluids, plotted as a function of the density at  $T_{\text{ref}}$ : (+) helium; (○) neon; (□) nitrogen; (△) argon; (×) krypton and (◇)  $\text{CF}_4$ .

implements accurate equations of state from the literature for industrially important fluids and fluid mixtures. It provides a convenient means of calculating properties at any desired  $(T, p)$  state point.) All of the fluids are seen to extrapolate to the same zero-pressure limit of 0.540 827; this, of course, is the ideal-gas limit. Helium ( $M = 4.0026$  g mol $^{-1}$ ) and neon ( $M = 20.179$  g mol $^{-1}$ ) show the most ideal behaviour, as indicated by density ratios which are nearly constant over a range of pressures. The variation of the density ratio with pressure increases with molar mass for nitrogen ( $M = 28.013$  g mol $^{-1}$ ), argon ( $M = 39.948$  g mol $^{-1}$ ), krypton ( $M = 83.804$  g mol $^{-1}$ ) and  $\text{CF}_4$  ( $M = 88.01$  g mol $^{-1}$ ). Plotting these same data versus the density at the reference temperature (figure 2) shows the same trend with molar mass but emphasizes the large difference in densities for the different gases.

Figures 1 and 2 suggest that the density ratios could be extrapolated to zero using a simple function, such as a polynomial in pressure or density:

$$\frac{\rho_x}{\rho_{\text{ref}}} = a_0 + a_1 p + a_2 p^2 \quad (2.1)$$

$$\frac{\rho_x}{\rho_{\text{ref}}} = b_0 + b_1 \rho_{\text{ref}} + b_2 \rho_{\text{ref}}^2 \quad (2.2)$$

But a simple polynomial discards the knowledge of how gases behave at low pressures. A more physically based model is obtained by recasting the virial equation (1.1) in terms of densities and density ratios to provide the basic working equation for the DRGT:

$$\frac{\rho(T_x, p)}{\rho(T_{\text{ref}}, p)} = \frac{f(T_x, p, B_x, C_x)}{f(T_{\text{ref}}, p, B_{\text{ref}}, C_{\text{ref}}, D_{\text{ref}})}, \quad (2.3)$$

where the function in the numerator of the right-hand side is the virial equation recast in terms of a cubic equation and solved explicitly for density. The denominator of (2.3) is the virial equation at the reference temperature; by including the fourth virial coefficient  $D_{\text{ref}}$ , an iterative solution is required to give the density as a function of the temperature and pressure.

Equations (2.1)–(2.3) were studied for the six gases shown in figure 1 at temperatures of 83.8058 K, 234.3156 K,

302.9146 K, 429.7458 K, 505.078 K and 692.677 K, with all the ‘unknown’ temperatures referenced to 273.16 K. These temperatures are fixed points on ITS-90. Multiple cases of temperature, fluid and maximum pressure were considered. For each case, ten ‘data points’ over a range of pressures were simulated up to a maximum pressure ranging from 0.5 MPa to 20 MPa. Eight pressure ranges were simulated for each maximum pressure, with  $p_{\text{max}}/p_{\text{min}} = 2$ –20.

The ‘data’ (the density ratios and pressures or densities) were input to an orthogonal distance regression using the package ODRPACK (Boggs *et al* 1992). (Orthogonal distance regression allows for uncertainties in both the independent and dependent variables; in contrast, ordinary least squares assumes that all uncertainties are in the dependent variable.) The density ratio at zero pressure or density is given by the fitted parameters  $a_0$  and  $b_0$  for (2.1) and (2.2), respectively. For (2.3), the unknown temperature  $T_x$  is one of the fitted parameters, along with the virial coefficients  $B_x$ ,  $C_x$ ,  $B_{\text{ref}}$ ,  $C_{\text{ref}}$  and  $D_{\text{ref}}$ . In some cases, it will be more convenient to discuss the results in terms of  $T_x$  and in others the density ratio will be more convenient. The two are equivalent and can be converted by (1.2).

In principle, all the parameters in (2.3) could be fitted simultaneously. But this approach resulted in virial parameters which lost all connection with reality—some were even of the wrong sign. In other words, (2.3) was essentially equivalent to a completely empirical model with a large number of fitted parameters. To avoid this, the  $p$ – $\rho$ – $T$  data at  $T_{\text{ref}}$  were first fitted separately to generate  $B_{\text{ref}}$ ,  $C_{\text{ref}}$  and  $D_{\text{ref}}$ ; these were then input as fixed parameters to the fit of the density-ratio data where  $T_x$ ,  $B_x$  and  $C_x$  were determined. The fourth virial coefficient at  $T_x$  was not included in (2.3) to avoid overfitting.

For densities computed directly from the equations of state, the optimum test conditions for all the fluids, models and temperatures were the smallest maximum pressure ( $p_{\text{max}} = 0.5$  MPa) and largest pressure range ( $p_{\text{max}}/p_{\text{min}} = 20$ ). At these conditions, the fitted  $T_x$  was within 0.01 mK of the expected value with an uncertainty of less than 0.01 mK. This result is expected; the gases are most nearly ideal at the lowest pressures, and even the simple polynomial models correctly extrapolate to zero at these conditions.

## 2.2. Effects of experimental uncertainties and optimal experimental parameters

The more interesting results come from simulating experimental uncertainties. The simulated data were varied by an estimated standard deviation multiplied by a normal distribution (evaluated at a random number). Standard deviations of 2 mK in temperature, 5 Pa in pressure and 0.0002 kg m $^{-3}$  in density were assumed. In addition, a systematic offset of 20 ppm in pressure was also included. These are typical uncertainties for the present densimeter. Four ‘replicates’ for each data point were simulated with the random number generator.

With these ‘uncertainties’ the optimum fluid (as indicated by the lowest uncertainty in the fitted  $T_x$ ) was neon at 83 K, argon at 234 K (with neon a close second), krypton at 303 K, 430 K and 505 K (with argon a close second), and argon at 693 K (with krypton a close second). The optimum maximum

**Table 1.** Simulation results for different fluids in a density-ratio gas thermometer; listed are the standard uncertainties in the fitted value of  $T_x$  (in mK) at the optimum maximum pressure (MPa) for the experiment, and the fitting equation giving the lowest uncertainty.

Fluid	$T_x$					
	83 K	234 K	303 K	430 K	505 K	693 K
(a) Results for uncertainties in the input data of $T_\sigma = 2$ mK, $p_\sigma = 5$ Pa, $\rho_\sigma = 0.0002$ kg m <sup>-3</sup> and a systematic offset in pressure of 20 ppm						
Helium	2.42 @ 12 (2.1)	5.45 @ 20 (2.2)	7.60 @ 20 (2.2)	12.9 @ 20 (2.2)	16.8 @ 20 (2.2)	29.2 @ 20 (2.2)
Neon	0.80 @ 6 (2.3)	1.35 @ 12 (2.2)	1.50 @ 20 (2.1)	3.01 @ 20 (2.1)	3.77 @ 20 (2.1)	5.71 @ 20 (2.3)
Nitrogen	n.a.	2.06 @ 6 (2.3)	2.52 @ 8 (2.3)	2.97 @ 12 (2.3)	4.81 @ 12 (2.3)	6.60 @ 12 (2.1)
Argon	n.a.	1.32 @ 6 (2.3)	1.77 @ 8 (2.3)	2.17 @ 12 (2.3)	2.59 @ 12 (2.3)	3.81 @ 16 (2.2)
Krypton	n.a.	n.a.	1.11 @ 6 (2.3)	1.86 @ 6 (2.3)	2.47 @ 6 (2.3)	4.04 @ 8 (2.2)
CF <sub>4</sub>	n.a.	n.a.	3.09 @ 2 (2.2)	3.32 @ 4 (2.1)	4.12 @ 4 (2.1)	6.84 @ 4 (2.1)
(b) Results for uncertainties in the input data of $T_\sigma = 0.5$ mK, $p_\sigma = 1$ Pa, $\rho_\sigma = 0.00005$ kg m <sup>-3</sup> and a systematic offset in pressure of 10 ppm						
Helium	1.02 @ 6 (2.1)	1.33 @ 20 (2.2)	1.82 @ 20 (2.1)	3.28 @ 20 (2.1)	4.34 @ 20 (2.1)	7.30 @ 20 (2.1)
Neon	0.34 @ 4 (2.3)	0.39 @ 12 (2.2)	0.42 @ 20 (2.1)	1.18 @ 20 (2.1)	1.40 @ 12 (2.3)	2.02 @ 16 (2.3)
Nitrogen	n.a.	0.62 @ 6 (2.2)	0.89 @ 6 (2.3)	0.99 @ 10 (2.3)	1.51 @ 8 (2.3)	1.85 @ 10 (2.1)
Argon	n.a.	0.34 @ 6 (2.2)	0.63 @ 6 (2.2)	0.93 @ 8 (2.3)	0.92 @ 10 (2.3)	1.36 @ 10 (2.3)
Krypton	n.a.	n.a.	0.35 @ 4 (2.3)	0.56 @ 6 (2.3)	0.66 @ 6 (2.3)	1.12 @ 6 (2.3)
CF <sub>4</sub>	n.a.	n.a.	1.19 @ 2 (2.3)	1.29 @ 2 (2.3)	1.72 @ 2 (2.3)	5.76 @ 1 (2.1)

n.a.: not applicable,  $T_x$  is at or below the triple point temperature of the fluid or near the critical temperature.

pressure was 6–16 MPa. The best pressure ratio was a broad optimum with  $p_{\max}/p_{\min}$  between 6 and 12. In all cases, helium showed the largest uncertainties; however, the best pressure for helium may lie above the maximum of 20 MPa simulated here. CF<sub>4</sub> was the second-worst fluid in all cases. The best model was (2.3) at five of the six temperatures. The polynomial in density was the best at 693 K, but only by a small margin. Under the optimum conditions, the standard uncertainty ranged from 0.80 mK for neon at 84 K to 3.81 mK for argon at 693 K. This standard uncertainty is the standard deviation in the  $T_x$  parameter returned by the ODRPACK fitting routine. These results are summarized in table 1(a).

A second set of cases with standard deviations of 0.5 mK in temperature, 1 Pa in pressure and 0.00005 kg m<sup>-3</sup> in density, along with a systematic offset of 10 ppm in pressure, was also considered. These were intended to simulate an improved densimeter. The optimums were very similar. Krypton was now the best fluid, and by a wider margin, at 303 K, 430 K, 505 K and 693 K. Neon was the second best at 303 K, but, as before, argon was a good choice at all temperatures except for 84 K. The optimum  $p_{\max}$  was lower at 4–6 MPa. The optimum pressure represents a balance between the ability of the numerical model to represent the data and the minimization of experimental errors. The virial model is nearly exact at low pressures, but here the relative experimental uncertainties are large. With smaller experimental uncertainties the optimum moves to lower pressures. The best model was again (2.3) in most cases. The standard uncertainty ranged from 0.34 mK for neon at 84 K to 1.12 mK for krypton at 693 K. These results are summarized in table 1(b).

### 3. Experimental details

An experimental exploration of the density-ratio gas thermometer was carried out using a two-sinker densimeter. Measurements were carried out over the temperature range 234.316–505.078 K using argon, neon or nitrogen as the

working gas. Argon was used as the primary gas in these tests because it was identified as the best or second best fluid over this temperature range by the numerical studies described above and it is readily available in high purity. Krypton was the optimum gas at temperatures between 303 K and 505 K, but it is much more expensive than argon. Nitrogen was ranked lower, but previously measured data (McLinden and Lösch-Will 2006) were available which could be analysed by the present method. Limited tests using neon provided a check on the method using an additional gas.

#### 3.1. Apparatus description

The key elements of the densimeter are two sinkers which are immersed in the fluid of interest inside a measuring cell (pressure vessel). The sinkers are weighed with a high-precision balance which is separated from the fluid by a magnetic suspension coupling consisting of an electromagnet (in air) hung from the balance and a permanent magnet and ‘lifting fork’ assembly (in the fluid) which pick up the sinkers for weighing. The sinkers are made of titanium and tantalum and have the same mass (60 g) and surface area but very different volumes. The use of two sinkers greatly reduces the effects of any systematic errors in the weighings. The loading on the balance is nearly the same for the two weighings, reducing errors from any nonlinearity in the balance. More importantly, the loading on the magnetic suspension coupling is nearly the same, largely cancelling the ‘force transmission error’ associated with the coupling. Two-sinker densimeters are further described by Wagner and Kleinrahn (2004), and force transmission errors are discussed in this reference as well as by McLinden *et al* (2006).

A thermostat consisting of multiple layers of passive and actively controlled shields provides a uniform temperature. The temperature of the measuring cell was measured with a standard platinum resistance thermometer read by a resistance bridge. For this work, pressures were measured with a gas-operated piston gauge.

For the two-sinker technique, the density is given by

$$\rho = \frac{(m_1 - W_1) - (m_2 - W_2)}{(V_1 - V_2)}, \quad (3.1)$$

where  $m$  and  $V$  are the mass and volume of a sinker and  $W$  is the balance reading; the subscripts refer to the two sinkers. The sinker volumes were determined at 293.15 K by a hydrostatic comparator technique relative to silicon density standards; the technique and procedures detailed by Bowman *et al* (1974) were followed closely in this determination. The sinker volumes as functions of temperature were calculated from measured values of the thermal expansion coefficients. The ( $k = 1$ ) uncertainty in the sinker volumes varies from 12 ppm at 293 K to 125 ppm at 505 K. A complete description of the apparatus and a detailed uncertainty analysis are provided by McLinden and Lösch-Will (2006).

### 3.2. Test procedure

Tests were run along isotherms starting at the highest pressure. Four to six replicate density determinations were made at each ( $T, p$ ) state point. The sample was then vented to the next lowest pressure, and the process was repeated for six pressures per isotherm. After each isotherm, the cell was evacuated and the sinkers were again weighed; just as the zero of any instrument will drift, the calculated density in vacuum differed slightly from zero (average value of  $0.005 \text{ kg m}^{-3}$ ), and this ‘apparatus zero’ was subtracted from the measured densities.

The pressures were both measured and regulated with the piston gauge. (That is, the measuring cell and piston gauge were directly connected; there was no pressure-separating diaphragm.) For each pressure, the gas sample was vented to a pressure 1–2% higher than desired (with a valve between the measuring cell and the piston gauge closed) and allowed to come to within 0.01 K of temperature equilibrium. The piston gauge was floated and the valve connecting the piston gauge and measuring cell was opened. This caused the piston to rise, and the gas volume was adjusted using a manual pressure controller to return the piston to the reference position. (The piston gauge used the same working gas as was being measured. Nevertheless, we were careful to allow gas flow only from the cell to the piston gauge while adjusting pressures to avoid contamination of the sample.) A further 30–60 min of equilibration time was allowed with the piston gauge connected and floating before commencing the density determinations. This resulted in temperatures which were steady to within 1 mK. The height and the rotation speed of the piston were adjusted only between density determinations. This arrangement provided exceptionally steady pressures during a test and also made it easy to replicate pressures from one temperature to the next. Very small day-to-day variations in pressure (on the order of 10 ppm) arose from changes in room temperature.

### 3.3. Experimental samples

The argon was ‘ULSI-grade’ (Matheson Tri-Gas, Inc.)<sup>1</sup> with a certified purity of 99.9999%. A cylinder analysis by the

<sup>1</sup> Certain trade names and products are given to adequately document the experimental equipment and procedures. This does not constitute a recommendation or endorsement of these products by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

supplier indicated impurities of nitrogen at 0.49 ppm, oxygen at 0.11 ppm and water at 0.17 ppm. Carbon dioxide, carbon monoxide and methane were not detected at the level of 0.1 ppm. The nitrogen was ‘VLSI-grade’ (Scott Specialty Gases). The specification for this gas is 99.9995% purity, and a cylinder analysis by the supplier indicated concentrations of oxygen, carbon dioxide, carbon monoxide, water and total hydrocarbons of 0.2–0.5 ppm. The concentration of hydrogen was 1 ppm for an overall purity of 99.9997%. The supplier’s batch analysis for the research grade neon (Air Products and Chemicals, Inc.) indicated helium, nitrogen, oxygen and carbon monoxide at levels of 1–5 ppm; water, total hydrocarbons and carbon dioxide were at levels of 0.2–0.5 ppm for an overall purity of 99.999%. Our own analysis by gas chromatography was consistent with the suppliers analysis. We also checked for the presence of argon in the nitrogen and neon samples and found none at the 1 ppm level.

### 3.4. Results

Measurements were made with argon at 234 K, 273 K, two series at 293 K, 360 K, two series at 430 K and 505 K; nitrogen was measured at 293 K, 340 K, 400 K, 440 K and 480 K and neon was tested at 293 K and 430 K. Several of these temperatures will be recognized as fixed points on ITS-90. Measuring at these temperatures minimizes the temperature uncertainty since the PRT was calibrated at these points. The sinker volumes were determined at 293.15 K, and this will serve at the reference temperature for the present experimental results.

The measured  $p$ – $\rho$ – $T$  data for argon and neon are given in tables 2 and 3. Densities are given based both on sinker volumes determined from the thermal expansion data (designated as  $\rho_{\text{CTE}}$  in the tables) and also using the ‘corrected’ volumes described in section 3.7. The nitrogen measurements have been previously reported (McLinden and Lösch-Will 2006); that reference reports only the ‘corrected’ densities. The actual sequence of the argon and neon tests is noted in tables 2 and 3. The nitrogen tests at 293 K were carried out in June 2003; the other temperatures were measured in October 2003 in the sequence 480 K, 400 K, 340 K and 440 K. The uncertainties ( $k = 1$ ) for the data are 2 mK in the temperatures and  $\pm(0.0011\% + 2 \text{ Pa})$  in pressure. The uncertainties in the ‘corrected’ densities are given by

$$u = \{[12 + 0.28|T - 293|]^2 + [0.62p]^2\}^{0.5} \times \text{ppm} + (0.0003 + 0.9 \times 10^{-6}|T - 293|) \times \text{kg m}^{-3}, \quad (3.2)$$

where  $T$  is the temperature in K and  $p$  is the pressure in MPa. The terms inside the braces arise from the uncertainties in the sinker volumes at  $T_{\text{ref}}$  and also the uncertainties in the sinker volumes as functions of temperature and pressure; these result in a constant relative error in density at a given  $T$  and  $p$ . The final terms arise from uncertainties in the weighings, which result in an absolute error in the density.

The argon data have an average absolute deviation of 34 ppm compared to the equation of state of Tegeler *et al* (1999). This EOS was fitted to extensive high-accuracy data for argon and has an uncertainty in gas-phase densities of 200 ppm for temperatures up to 340 K and 300 ppm for temperatures up to 520 K. Thus, the present data are consistent

**Table 2.** Experimental  $p$ - $\rho$ - $T$  data for argon with a comparison to the equation of state of Tegeler *et al* (1999). Densities are computed using sinker volumes based on the coefficient of thermal expansion ( $\rho_{\text{CTE}}$ ) and using the ‘corrected’ sinker volumes discussed in section 3.7 ( $\rho_{\text{corrected}}$ ).

$T$ (K)	$p$ (MPa)	$\rho_{\text{CTE}}$ (kg m <sup>-3</sup> )	$\rho_{\text{corrected}}$ (kg m <sup>-3</sup> )	$(\rho_{\text{corrected}} - \rho_{\text{EOS}})/\rho_{\text{EOS}}$ (ppm)
$T = 234.32$ K; 10–11 February 2005				
234.3162	5.994 459	136.0194	136.0254	16.3
234.3162	5.994 454	136.0196	136.0257	18.6
234.3188	5.994 450	136.0178	136.0239	22.2
234.3183	5.994 446	136.0173	136.0233	15.8
234.3163	5.994 442	136.0188	136.0249	16.0
234.3170	3.996 244	87.7084	87.7123	42.1
234.3173	3.996 242	87.7075	87.7114	34.1
234.3185	3.996 241	87.7067	87.7106	31.8
234.3181	3.996 240	87.7065	87.7104	27.4
234.3168	3.996 238	87.7067	87.7106	23.7
234.3166	2.997 160	64.6734	64.6763	49.9
234.3170	2.997 159	64.6725	64.6753	38.1
234.3188	2.997 159	64.6718	64.6747	37.8
234.3178	2.997 158	64.6717	64.6746	31.3
234.3167	2.997 157	64.6720	64.6749	29.9
234.3182	1.998 081	42.3852	42.3871	38.5
234.3173	1.998 082	42.3852	42.3871	34.2
234.3186	1.998 082	42.3851	42.3870	38.8
234.3187	1.998 083	42.3851	42.3870	38.0
234.3176	1.998 083	42.3852	42.3871	35.2
234.3165	0.999 045	20.8360	20.8369	87.4
234.3164	0.999 046	20.8356	20.8365	64.3
234.3182	0.999 046	20.8353	20.8363	62.9
234.3184	0.999 046	20.8351	20.8361	54.0
234.3167	0.999 046	20.8352	20.8361	48.7
234.3189	0.499 520	10.3296	10.3300	60.9
234.3175	0.499 520	10.3297	10.3302	69.7
234.3168	0.499 520	10.3295	10.3300	46.2
234.3182	0.499 520	10.3294	10.3299	47.1
234.3182	0.499 520	10.3295	10.3300	57.0
$T = 273.16$ K; 31 January–2 February 2005				
273.1597	6.993 345	130.4092	130.4122	6.8
273.1587	6.993 341	130.4096	130.4125	5.4
273.1606	6.993 340	130.4087	130.4117	7.9
273.1615	6.993 340	130.4081	130.4111	7.7
273.1591	6.993 333	130.4089	130.4118	3.2
273.1598	5.994 235	110.9715	110.9740	10.1
273.1605	5.994 239	110.9715	110.9740	12.4
273.1611	5.994 242	110.9709	110.9734	9.7
273.1598	5.994 244	110.9714	110.9739	7.2
273.1592	5.994 246	110.9717	110.9742	7.4
273.1602	4.995 205	91.7693	91.7714	29.5
273.1587	4.995 204	91.7691	91.7712	21.5
273.1597	4.995 203	91.7686	91.7707	20.7
273.1619	4.995 203	91.7677	91.7698	20.7
273.1602	4.995 203	91.7679	91.7700	14.8
273.1585	3.996 145	72.8255	72.8272	52.7
273.1611	3.996 144	72.8239	72.8255	41.3
273.1603	3.996 145	72.8232	72.8248	27.9
273.1587	3.996 145	72.8231	72.8247	19.9
273.1602	3.996 144	72.8230	72.8246	25.1
273.1596	2.997 088	54.1577	54.1590	24.2
273.1596	2.997 089	54.1578	54.1590	24.9
273.1612	2.997 090	54.1574	54.1587	24.2
273.1610	2.997 092	54.1575	54.1588	25.0
273.1596	2.997 094	54.1577	54.1590	22.5

Table 2. (Continued.)

$T$ (K)	$p$ (MPa)	$\rho_{\text{CTE}}$ (kg m <sup>-3</sup> )	$\rho_{\text{corrected}}$ (kg m <sup>-3</sup> )	$(\rho_{\text{corrected}} - \rho_{\text{EOS}})/\rho_{\text{EOS}}$ (ppm)
273.1615	1.998 056	35.7920	35.7928	68.5
273.1599	1.998 055	35.7916	35.7924	52.0
273.1611	1.998 055	35.7909	35.7918	38.5
273.1620	1.998 055	35.7908	35.7916	37.5
273.1608	1.998 056	35.7907	35.7915	31.3
273.1602	0.999 032	17.7354	17.7358	51.6
273.1596	0.999 032	17.7353	17.7357	46.4
273.1619	0.999 032	17.7348	17.7352	26.1
273.1624	0.999 032	17.7349	17.7354	36.8
273.1604	0.999 032	17.7352	17.7356	40.8
273.1615	0.499 515	8.8271	8.8273	58.0
273.1602	0.499 515	8.8271	8.8273	59.1
273.1608	0.499 515	8.8270	8.8272	50.0
273.1617	0.499 515	8.8271	8.8273	59.0
273.1617	0.499 515	8.8269	8.8271	36.1
$T = 293.15$ K (series 1); 19–20 October 2004				
293.1521	5.994 107	101.8247	101.8247	27.7
293.1549	5.994 101	101.8227	101.8227	20.9
293.1522	5.994 096	101.8227	101.8227	10.6
293.1539	5.994 091	101.8220	101.8220	11.8
293.1531	5.994 085	101.8218	101.8218	7.3
293.1494	3.996 026	67.1623	67.1623	28.6
293.1520	3.996 024	67.1615	67.1615	27.4
293.1526	3.996 025	67.1611	67.1611	23.9
293.1501	3.996 022	67.1613	67.1613	18.0
293.1517	3.996 021	67.1608	67.1608	16.8
293.1517	2.997 004	50.0775	50.0775	38.3
293.1500	2.997 004	50.0772	50.0772	26.3
293.1518	2.997 003	50.0769	50.0769	26.8
293.1538	2.997 003	50.0764	50.0764	24.0
293.1517	2.997 003	50.0765	50.0765	18.1
293.1516	1.997 958	33.1788	33.1788	23.1
293.1532	1.997 957	33.1787	33.1787	27.9
293.1541	1.997 958	33.1784	33.1784	21.1
293.1525	1.997 958	33.1786	33.1786	22.3
293.1517	1.997 958	33.1787	33.1787	20.1
293.1511	0.998 986	16.4833	16.4833	34.5
293.1523	0.998 986	16.4833	16.4833	36.3
293.1553	0.998 985	16.4830	16.4830	34.4
293.1535	0.998 985	16.4831	16.4831	28.5
293.1521	0.998 985	16.4832	16.4832	35.3
293.1515	0.499 494	8.2146	8.2146	58.7
293.1536	0.499 494	8.2146	8.2146	61.1
293.1539	0.499 494	8.2143	8.2143	35.5
293.1519	0.499 494	8.2143	8.2143	23.4
293.1535	0.499 494	8.2143	8.2143	28.9
$T = 293.15$ K (series 2); 28–29 January 2005				
293.1527	5.994 233	101.8259	101.8259	21.1
293.1547	5.994 230	101.8253	101.8253	22.9
293.1546	5.994 226	101.8247	101.8247	17.5
293.1537	5.994 221	101.8247	101.8247	14.6
293.1536	5.994 216	101.8245	101.8245	13.7
293.1538	3.996 110	67.1632	67.1632	38.3
293.1533	3.996 106	67.1627	67.1627	29.9
293.1552	3.996 103	67.1620	67.1620	27.3
293.1552	3.996 100	67.1617	67.1617	23.8
293.1540	3.996 098	67.1618	67.1618	20.4
293.1538	2.997 057	50.0776	50.0776	30.3
293.1558	2.997 057	50.0772	50.0772	29.7
293.1546	2.997 057	50.0771	50.0771	24.1
293.1530	2.997 057	50.0773	50.0773	20.4
293.1541	2.997 058	50.0770	50.0770	19.3

Table 2. (Continued.)

$T$ (K)	$p$ (MPa)	$\rho_{\text{CTE}}$ (kg m <sup>-3</sup> )	$\rho_{\text{corrected}}$ (kg m <sup>-3</sup> )	$(\rho_{\text{corrected}} - \rho_{\text{EOS}})/\rho_{\text{EOS}}$ (ppm)
293.1536	1.998 017	33.1796	33.1796	25.8
293.1522	1.998 018	33.1794	33.1794	14.1
293.1530	1.998 019	33.1794	33.1794	16.4
293.1542	1.998 020	33.1794	33.1794	18.8
293.1530	1.998 021	33.1795	33.1795	18.6
293.1530	0.999 012	16.4835	16.4835	26.6
293.1542	0.999 012	16.4834	16.4834	27.3
293.1528	0.999 013	16.4834	16.4834	21.5
293.1519	0.999 013	16.4836	16.4836	27.5
293.1534	0.999 013	16.4835	16.4835	25.9
293.1513	0.499 507	8.2148	8.2148	59.3
293.1539	0.499 507	8.2148	8.2148	68.1
293.1542	0.499 507	8.2146	8.2146	43.9
293.1521	0.499 507	8.2147	8.2147	42.7
293.1526	0.499 508	8.2146	8.2146	31.6
$T = 360.00$ K; 15–17 September 2004				
360.0007	5.994 233	80.5817	80.5738	1.8
360.0015	5.994 247	80.5814	80.5735	-1.5
360.0011	5.994 239	80.5813	80.5735	-1.9
360.0024	5.994 234	80.5809	80.5730	-2.9
360.0009	5.994 230	80.5810	80.5731	-4.8
360.0000	3.996 117	53.6394	53.6341	-3.2
360.0021	3.996 115	53.6392	53.6339	0.2
360.0022	3.996 113	53.6391	53.6339	-1.0
360.0004	3.996 112	53.6392	53.6340	-3.2
360.0020	3.996 111	53.6390	53.6338	-2.1
360.0001	2.997 064	40.1855	40.1816	-0.2
360.0020	2.997 063	40.1854	40.1814	2.3
360.0026	2.997 063	40.1853	40.1814	2.6
360.0014	2.997 062	40.1852	40.1813	-2.7
360.0011	2.997 062	40.1853	40.1813	-2.1
360.0021	1.998 047	26.7550	26.7524	-8.5
360.0010	1.998 047	26.7552	26.7526	-6.3
359.9999	1.998 047	26.7551	26.7525	11.1
360.0014	1.998 047	26.7552	26.7526	-3.5
360.0019	1.998 047	26.7551	26.7525	-6.3
360.0002	0.999 026	13.3574	13.3561	-1.6
360.0014	0.999 026	13.3574	13.3561	-1.4
360.0026	0.999 025	13.3573	13.3560	-5.2
360.0013	0.999 024	13.3573	13.3560	-8.0
360.0004	0.999 024	13.3574	13.3561	-2.4
360.0013	0.499 511	6.6733	6.6726	26.4
360.0007	0.499 510	6.6731	6.6725	2.4
360.0027	0.499 510	6.6731	6.6725	8.6
360.0034	0.499 510	6.6732	6.6725	18.5
360.0013	0.499 510	6.6731	6.6725	5.8
$T = 429.75$ K (series 1); 20–21 September 2004				
429.7483	5.994 172	66.6498	66.6389	48.3
429.7495	5.994 170	66.6497	66.6388	50.2
429.7483	5.994 169	66.6495	66.6386	44.7
429.7496	5.994 168	66.6493	66.6384	44.2
429.7498	5.994 166	66.6495	66.6386	47.8
429.7481	3.996 090	44.5412	44.5339	50.0
429.7479	3.996 100	44.5414	44.5341	51.2
429.7485	3.996 085	44.5411	44.5339	49.8
429.7479	3.996 083	44.5411	44.5338	47.6
429.7477	3.996 081	44.5412	44.5339	49.4
429.7486	3.996 079	44.5410	44.5337	48.8
429.7484	3.996 076	44.5409	44.5336	46.1
429.7473	2.997 039	33.4392	33.4338	39.7
429.7460	2.997 040	33.4393	33.4338	37.0
429.7468	2.997 041	33.4391	33.4336	32.4



Table 2. (Continued.)

$T$ (K)	$p$ (MPa)	$\rho_{\text{CTE}}$ (kg m <sup>-3</sup> )	$\rho_{\text{corrected}}$ (kg m <sup>-3</sup> )	$(\rho_{\text{corrected}} - \rho_{\text{EOS}})/\rho_{\text{EOS}}$ (ppm)
429.7478	2.997 042	33.4392	33.4337	39.3
429.7468	2.997 043	33.4392	33.4337	35.1
429.7458	1.998 041	22.3131	22.3094	58.5
429.7461	1.998 039	22.3126	22.3090	38.1
429.7443	1.998 039	22.3128	22.3091	42.7
429.7446	1.998 037	22.3128	22.3091	42.8
429.7460	1.998 036	22.3128	22.3092	48.9
429.7454	0.999 020	11.1647	11.1629	46.7
429.7441	0.999 020	11.1647	11.1629	44.2
429.7453	0.999 019	11.1646	11.1627	32.2
429.7469	0.999 019	11.1648	11.1630	56.9
429.7457	0.999 019	11.1648	11.1630	58.4
429.7444	0.499 510	5.5844	5.5834	78.7
429.7462	0.499 510	5.5842	5.5833	57.1
429.7464	0.499 510	5.5841	5.5832	38.9
429.7448	0.499 510	5.5841	5.5832	34.7
429.7456	0.499 510	5.5840	5.5831	19.2
429.7468	0.499 510	5.5840	5.5831	21.4
$T = 429.75$ K (series 2); 26–27 October 2004				
429.7490	5.993 982	66.6469	66.6360	38.5
429.7486	5.993 978	66.6471	66.6362	40.4
429.7487	5.993 973	66.6468	66.6359	37.1
429.7486	5.993 968	66.6470	66.6361	40.0
429.7492	5.993 965	66.6469	66.6360	40.9
429.7501	3.995 944	44.5392	44.5319	44.8
429.7483	3.995 939	44.5392	44.5320	43.2
429.7493	3.995 936	44.5391	44.5318	42.4
429.7509	3.995 933	44.5390	44.5317	46.0
429.7498	3.995 929	44.5390	44.5317	43.2
429.7498	2.996 930	33.4378	33.4324	40.2
429.7476	2.996 929	33.4379	33.4324	38.0
429.7487	2.996 928	33.4379	33.4324	40.6
429.7508	2.996 926	33.4377	33.4322	40.1
429.7501	2.996 925	33.4378	33.4323	40.0
429.7503	1.997 995	22.3119	22.3082	38.6
429.7495	1.997 991	22.3119	22.3082	38.2
429.7487	1.997 987	22.3120	22.3084	43.2
429.7498	1.997 983	22.3116	22.3080	31.1
429.7500	1.997 980	22.3115	22.3079	29.2
429.7506	0.998 987	11.1638	11.1620	12.5
429.7488	0.998 985	11.1641	11.1622	29.3
429.7499	0.998 983	11.1640	11.1622	28.0
429.7518	0.998 983	11.1639	11.1621	28.7
429.7509	0.998 981	11.1639	11.1621	24.0
429.7502	0.499 488	5.5837	5.5828	27.7
429.7493	0.499 487	5.5837	5.5828	25.3
429.7502	0.499 487	5.5837	5.5828	27.7
429.7515	0.499 487	5.5838	5.5829	50.0
429.7506	0.499 487	5.5836	5.5827	9.8
$T = 505.08$ K; 5–7 October 2004				
505.0837	5.994 050	56.3608	56.3561	221.7
505.0823	5.994 046	56.3613	56.3565	227.7
505.0833	5.994 042	56.3610	56.3563	225.8
505.0847	5.994 039	56.3604	56.3557	219.0
505.0841	5.994 037	56.3601	56.3554	213.2
505.0858	3.995 991	37.7340	37.7308	198.2
505.0849	3.995 990	37.7336	37.7304	186.0
505.0841	3.995 988	37.7341	37.7310	199.6
505.0850	3.995 987	37.7341	37.7309	200.8
505.0859	3.995 987	37.7338	37.7306	194.1

Table 2. (Continued.)

$T$ (K)	$p$ (MPa)	$\rho_{\text{CTE}}$ (kg m <sup>-3</sup> )	$\rho_{\text{corrected}}$ (kg m <sup>-3</sup> )	$(\rho_{\text{corrected}} - \rho_{\text{EOS}})/\rho_{\text{EOS}}$ (ppm)
505.0834	2.996 966	28.3556	28.3533	123.3
505.0830	2.996 968	28.3555	28.3532	118.2
505.0836	2.996 969	28.3556	28.3533	122.5
505.0847	2.996 967	28.3555	28.3531	121.8
505.0836	2.996 975	28.3555	28.3531	114.8
505.0821	1.997 984	18.9398	18.9382	77.1
505.0842	1.997 983	18.9400	18.9384	91.5
505.0848	1.997 984	18.9398	18.9383	84.4
505.0839	1.997 984	18.9398	18.9382	79.9
505.0819	1.997 984	18.9397	18.9381	73.1
505.0835	0.998 998	9.4874	9.4866	52.2
505.0824	0.998 998	9.4873	9.4865	39.5
505.0828	0.998 998	9.4874	9.4866	50.8
505.0842	0.998 997	9.4874	9.4866	58.7
505.0842	0.998 997	9.4875	9.4867	63.6

with the EOS and, indirectly, the literature data. The deviations for neon are larger (AAD = 162 ppm), but the EOS for neon is older, and it is based on fewer and less accurate data compared to argon.

Table 4 presents a detailed analysis of the argon results for the first measurement series at 293 K and 430 K as an example. The data at the reference temperature of 293 K and the ‘test’ temperature of 430 K are presented as two side-by-side groups. All of the measurements are averaged to obtain 293.1524 K and 429.7468 K for the reference and test temperatures. The replicates at each of the pressures are averaged over both temperatures to obtain average pressures. The experimental  $p$ – $\rho$ – $T$  points are then adjusted to the average ( $T$ ,  $p$ ) using an equation of state:

$$\rho_{\text{adjusted}} = \rho_{\text{exp}} \frac{\rho_{\text{EOS}}(T_{\text{avg}}, p_{\text{avg}})}{\rho_{\text{EOS}}(T_i, p_i)}, \quad (3.3)$$

where  $\rho_{\text{exp}}$ ,  $\rho_{\text{EOS}}$  and  $\rho_{\text{adjusted}}$  are the experimental density, the density calculated from the equation of state and the density adjusted to the average temperature and pressure  $T_{\text{avg}}$ ,  $p_{\text{avg}}$ .  $T_i$  and  $p_i$  are the experimental temperature and pressure. The equations of Span *et al* (2000), Tegeler *et al* (1999) and Katti *et al* (1986) were used for nitrogen, argon and neon, respectively. The adjusted densities and the magnitudes of the adjustment (in parts per million) are given as the last two columns for each temperature in table 4. The average adjustment is 10.0 ppm and the maximum adjustment is 42.6 ppm, so the uncertainties in the equation of state will have negligible effect on the final results. For each set of ( $T_{\text{avg}}$ ,  $p_{\text{avg}}$ ), the adjusted densities were averaged to calculate the density ratios.

Table 5 presents the results for all cases. Figure 3 shows the extrapolation in pressure for neon and the two replicates for argon at 429 K. Both gases extrapolate to nearly the same zero-pressure limit.

### 3.5. Uncertainty analysis

The numerical study presented above considered the effects of measurement uncertainties. A more detailed analysis of uncertainties is presented here for the actual experimental measurements. The ODRPACK software used in fitting the

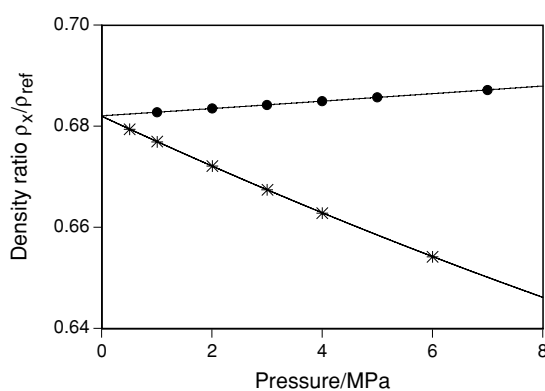


Figure 3. Extrapolation to zero pressure of the experimental density ratios at 429.749 K and 293.15 K for (●) neon and the two replicates (+) and (×) for argon.

data provides an estimate of the uncertainties in the fitted parameters, but this is based only on the actual scatter in the data and deviations from the fitted model. Significant systematic errors are possible, and these could be highly reproducible and, thus, ‘invisible’ to the fitting software. These include calibration uncertainties in the thermometer, piston gauge and sinker volumes. The weighings at higher temperatures are observed to have more scatter; there may be additional systematic effects on the balance, either due to temperature effects or because the measurements at  $T_{\text{ref}}$  and  $T_x$  are separated in time. The working gas is assumed to be the same for all tests, but its purity may vary with time; this is simulated by varying the molar mass. (As argued above, a pure gas is not required and ‘purity’ is better interpreted as ‘constancy’.)

Table 6 lists these uncertainty sources, their estimated magnitude ( $k = 1$ ) for the present densimeter and their effect on the calculated density ratio at zero pressure. While these error sources and their magnitudes can be reasonably estimated, calculating their effects on the final extrapolation to zero pressure would be very complex. Thus, these effects were simulated by varying the measured data by the indicated magnitude for each of the error sources. The modified data were then fitted again to obtain the difference in the final

**Table 3.** Experimental  $p$ - $\rho$ - $T$  data for neon with a comparison to the equation of state of Katti *et al* (1986). Densities are computed using sinker volumes based on the coefficient of thermal expansion ( $\rho_{\text{CTE}}$ ) and using the ‘corrected’ sinker volumes discussed in section 3.7 ( $\rho_{\text{corrected}}$ ).

$T$ (K)	$p$ (MPa)	$\rho_{\text{CTE}}$ (kg m <sup>-3</sup> )	$\rho_{\text{corrected}}$ (kg m <sup>-3</sup> )	$(\rho_{\text{corrected}} - \rho_{\text{EOS}})/\rho_{\text{EOS}}$ (ppm)
$T = 293.15$ K; 28–29 October 2004				
293.1509	6.993 078	56.0230	56.0230	408.2
293.1497	6.993 077	56.0235	56.0235	412.0
293.1521	6.993 072	56.0233	56.0233	417.3
293.1534	6.993 065	56.0229	56.0229	417.1
293.1509	6.993 056	56.0233	56.0233	416.7
293.1520	4.994 988	40.3958	40.3958	375.3
293.1509	4.994 985	40.3956	40.3956	367.4
293.1515	4.994 982	40.3956	40.3956	368.8
293.1533	4.994 979	40.3954	40.3954	371.6
293.1521	4.994 977	40.3956	40.3956	371.8
293.1507	3.995 933	32.4687	32.4687	329.0
293.1513	3.995 937	32.4686	32.4686	327.1
293.1541	3.995 940	32.4687	32.4687	338.6
293.1528	3.995 943	32.4687	32.4687	335.0
293.1510	3.995 946	32.4688	32.4688	330.2
293.1498	2.996 941	24.4668	24.4668	294.8
293.1522	2.996 939	24.4666	24.4666	296.8
293.1534	2.996 937	24.4664	24.4664	293.3
293.1511	2.996 936	24.4667	24.4667	298.5
293.1512	2.996 934	24.4669	24.4669	305.6
293.1497	1.997 947	16.3880	16.3880	241.8
293.1525	1.997 947	16.3881	16.3881	251.9
293.1537	1.997 947	16.3879	16.3879	249.3
293.1503	1.997 947	16.3881	16.3881	247.5
293.1524	1.997 946	16.3881	16.3881	252.4
293.1515	0.998 978	8.2326	8.2326	175.9
293.1503	0.998 978	8.2327	8.2327	178.1
293.1526	0.998 978	8.2327	8.2327	185.6
293.1531	0.998 978	8.2328	8.2328	200.1
293.1503	0.998 978	8.2328	8.2328	196.7
$T = 429.75$ K; 4–5 November 2004				
429.7493	6.992 942	38.5084	38.5021	–35.2
429.7497	6.992 937	38.5084	38.5021	–32.9
429.7521	6.992 937	38.5081	38.5018	–35.7
429.7527	6.992 930	38.5082	38.5019	–30.7
429.7504	6.992 930	38.5082	38.5019	–36.2
429.7513	4.994 930	27.7061	27.7016	27.9
429.7521	4.994 929	27.7061	27.7015	27.7
429.7509	4.994 928	27.7060	27.7015	23.9
429.7497	4.994 927	27.7061	27.7016	25.9
429.7511	4.994 927	27.7060	27.7015	24.3
429.7491	3.995 957	22.2460	22.2424	59.9
429.7490	3.995 958	22.2459	22.2422	53.3
429.7480	3.995 958	22.2458	22.2422	48.9
429.7484	3.995 957	22.2459	22.2422	52.4
429.7496	3.995 957	22.2459	22.2423	57.1
429.7488	2.996 951	16.7457	16.7429	99.3
429.7478	2.996 949	16.7456	16.7429	95.3
429.7483	2.996 947	16.7453	16.7426	78.5
429.7500	2.996 945	16.7453	16.7426	84.8
429.7491	2.996 944	16.7451	16.7424	71.7
429.7492	1.997 949	11.2045	11.2027	118.5
429.7476	1.997 948	11.2047	11.2028	129.4
429.7484	1.997 947	11.2045	11.2026	111.8
429.7500	1.997 946	11.2044	11.2025	107.7
429.7493	1.997 945	11.2042	11.2023	88.4

**Table 3.** (Continued.)

$T$ (K)	$p$ (MPa)	$\rho_{\text{CTE}}$ (kg m <sup>-3</sup> )	$\rho_{\text{corrected}}$ (kg m <sup>-3</sup> )	$(\rho_{\text{corrected}} - \rho_{\text{EOS}})/\rho_{\text{EOS}}$ (ppm)
429.7508	0.998 974	5.6228	5.6219	141.6
429.7497	0.998 973	5.6226	5.6217	103.8
429.7490	0.998 973	5.6226	5.6216	93.3
429.7505	0.998 973	5.6226	5.6217	97.8
429.7512	0.998 972	5.6226	5.6217	108.7

**Table 4.** Example for data reduction: argon at  $T_{\text{ref}} = 293.15$  K and  $T_x = 429.75$  K showing experimental measurements, average temperatures and pressures, densities adjusted to average ( $T, p$ ) and resulting density ratios.

Experimental values			Adjusted to ( $T_{\text{avg}}, p_{\text{avg}}$ )		Experimental values			Adjusted to ( $T_{\text{avg}}, p_{\text{avg}}$ )		$\rho_x/\rho_{\text{ref}}$
$T_{\text{ref}}$ (K)	$p$ (kPa)	$\rho$ (kg m <sup>-3</sup> )	$\rho_{\text{adjusted}}$	$\Delta$ (ppm)	$T_x$ (K)	$p$ (kPa)	$\rho$ (kg m <sup>-3</sup> )	$\rho_{\text{adjusted}}$	$\Delta$ (ppm)	
293.1521	5994.107	101.8247	101.8250	3.1	429.7483	5994.172	66.6498	66.6496	-3.0	
293.1549	5994.101	101.8227	101.8243	15.5	429.7495	5994.170	66.6497	66.6497	0.3	
293.1522	5994.096	101.8227	101.8232	5.4	429.7483	5994.169	66.6495	66.6493	-2.5	
293.1539	5994.091	101.8220	101.8233	13.1	429.7496	5994.168	66.6493	66.6494	0.9	
293.1531	5994.085	101.8218	101.8229	10.9	429.7498	5994.166	66.6495	66.6496	1.7	
Avg	293.1524	5994.133		101.8238	429.7468	5994.133		66.6495		0.654 558
293.1494	3996.026	67.1623	67.1621	-3.1	429.7481	3996.090	44.5412	44.5410	-4.6	
293.1520	3996.024	67.1615	67.1620	7.4	429.7479	3996.100	44.5414	44.5411	-7.6	
293.1526	3996.025	67.1611	67.1617	9.5	429.7485	3996.085	44.5411	44.5410	-2.4	
293.1501	3996.022	67.1613	67.1613	0.6	429.7479	3996.083	44.5411	44.5410	-3.3	
293.1517	3996.021	67.1608	67.1613	7.0	429.7477	3996.081	44.5412	44.5411	-3.3	
					429.7486	3996.079	44.5410	44.5410	-0.7	
					429.7484	3996.076	44.5409	44.5409	-0.4	
Avg	293.1524	3996.059		67.1617	429.7468	3996.059		44.5410		0.663 190
293.1517	2997.004	50.0775	50.0777	3.5	429.7473	2997.039	33.4392	33.4391	-4.5	
293.1500	2997.004	50.0772	50.0771	-2.9	429.7460	2997.040	33.4393	33.4390	-7.9	
293.1518	2997.003	50.0769	50.0771	4.2	429.7468	2997.041	33.4391	33.4389	-6.4	
293.1538	2997.003	50.0764	50.0770	11.7	429.7478	2997.042	33.4392	33.4391	-4.3	
293.1517	2997.003	50.0765	50.0767	3.8	429.7468	2997.043	33.4392	33.4390	-7.0	
Avg	293.1524	2997.022		50.0771	429.7468	2997.022		33.4390		0.667 750
293.1516	1997.958	33.1788	33.1794	17.3	429.7458	1998.041	22.3131	22.3126	-23.9	
293.1532	1997.957	33.1787	33.1795	23.6	429.7461	1998.039	22.3126	22.3121	-22.2	
293.1541	1997.958	33.1784	33.1793	26.4	429.7443	1998.039	22.3128	22.3122	-26.5	
293.1525	1997.958	33.1786	33.1793	20.6	429.7446	1998.037	22.3128	22.31225	-24.8	
293.1517	1997.958	33.1787	33.1793	17.7	429.7460	1998.036	22.3128	22.3123	-20.9	
Avg	293.1524	1997.998		33.1793	429.7468	1997.998		22.3123		0.672 476
293.1511	998.986	16.4833	16.4835	11.9	429.7454	999.020	11.1647	11.1645	-21.0	
293.1523	998.986	16.4833	16.4836	16.1	429.7441	999.020	11.1647	11.1644	-24.0	
293.1553	998.985	16.4830	16.4835	27.7	429.7453	999.019	11.1646	11.1644	-20.2	
293.1535	998.985	16.4831	16.4835	21.3	429.7469	999.019	11.1648	11.1646	-16.5	
293.1521	998.985	16.4832	16.4835	16.4	429.7457	999.019	11.1648	11.1646	-19.3	
Avg	293.1524	999.002		16.4835	429.7468	999.002		11.1645		0.677 314
293.1515	499.494	8.2146	8.2147	14.3	429.7444	499.510	5.5844	5.5843	-20.3	
293.1536	499.494	8.2146	8.2148	21.6	429.7462	499.510	5.5842	5.5841	-16.1	
293.1539	499.494	8.2143	8.2145	22.6	429.7464	499.510	5.5841	5.5840	-15.6	
293.1519	499.494	8.2143	8.2144	15.7	429.7448	499.510	5.5841	5.5840	-19.3	
293.1535	499.494	8.2143	8.2145	21.3	429.7456	499.510	5.5840	5.5839	-17.5	
					429.7468	499.510	5.5840	5.5839	-14.7	
Avg	293.1524	499.503		8.2146	429.7468	499.503		5.5840		0.679 772

result. All the differences were summed (by the root sum of squares) together with the uncertainty resulting from the actual experimental scatter to arrive at the overall uncertainty.

Uncertainties in the weighings are seen to have the largest impact. This indicates where effort should be concentrated

to improve the DRGT technique. The effect of experimental scatter is next in importance. The effect of sample purity is relatively small. Any zero offset in the pressure, such as an incorrect reference pressure for the piston gauge, has a significant effect. It is also interesting to note factors which

**Table 5.** Fitted  $T_x$  and experimental density ratios extrapolated to zero pressure and relative deviations from the measured temperature ratio.

$T_{\text{ref}}$ measured on ITS-90	$T_x$ measured on ITS-90	$T_x$ fitted by (2.3)	$\text{Lim}(p \rightarrow 0) \rho_x/\rho_{\text{ref}}$	$10^6[\rho_x/\rho_{\text{ref}} - T_{\text{ref}}/T_x]/(T_{\text{ref}}/T_x)$
Argon				
293.1536	234.3176	234.3245	1.2510 58	−29.4
293.1536	273.1605	273.1661	1.073 170	−20.2
293.1536	360.0014	359.9787	0.814 364	63.0
293.1524	429.7468	429.6758	0.682 264	165.4
293.1524	429.7497	429.6920	0.682 238	134.3
293.1524	505.0838	505.0621	0.580 428	43.1
Neon				
293.1503	429.7498	429.6722	0.682 265	180.6
Nitrogen				
293.1395	339.9764	339.9536	0.862 292	67.1
293.1395	399.9729	399.9351	0.732 968	94.5
293.1395	439.9788	439.8757	0.666 414	234.5
293.1395	480.0027	479.9188	0.610 811	175.0

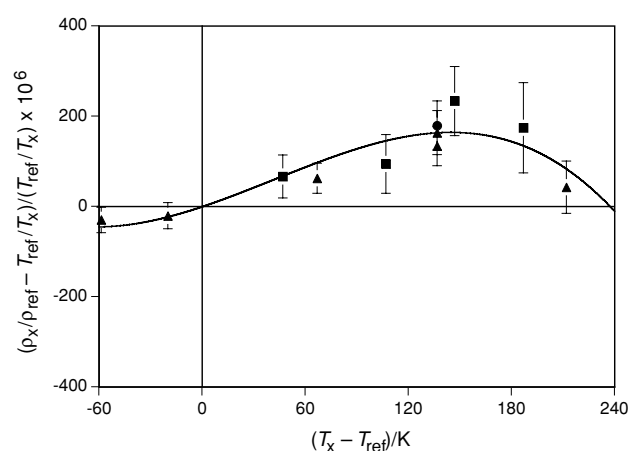
have virtually no effect on the result. A constant relative error in the measured pressures has no effect since the measurements at  $T_x$  and  $T_{\text{ref}}$  are carried out at the same pressures. In other words, a piston gauge area which is in error will not affect the final extrapolation. (Of course, this assumes that the same piston gauge is used for all of the measurements.) Likewise, an error in the sinker volumes at the reference temperature has no effect. Density ratios are the important quantity, and any error in the sinker volumes at  $T_{\text{ref}}$  would affect the calculated density at  $T_x$  and  $T_{\text{ref}}$  the same and thus cancel in taking the ratio.

### 3.6. Force transmission error and the effect of magnetic fluids

The magnetic suspension coupling in the densimeter is influenced by the magnetic properties of the materials of construction and by any external magnetic fields. These give rise to a force transmission error (FTE). The magnetic properties of the fluid under study also affect the measurement. The fluids used here are slightly diamagnetic with magnetic susceptibilities of  $-6.1 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$ ,  $-4.3 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$  and  $-5.4 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$  for argon, neon and nitrogen, respectively (Lide 2004). For the two-sinker densimeter used here, the differential nature of the measurement largely cancels these effects, but small errors in density—on the order of 20 ppm—are experienced. With a two-sinker densimeter, the force transmission error is nearly the same for the corresponding weighings at the two temperatures so it nearly cancels. The present two-sinker densimeter incorporates two balance calibration masses which are weighed in addition to the two sinkers for each density determination. An analysis developed by McLinden *et al* (2006) makes use of these additional weighings to determine and compensate for the force transmission error and the effects of magnetic fluids. With this analysis the uncertainty associated with magnetic effects is reduced to about 2 ppm in density.

### 3.7. In situ determination of sinker volumes

The final column in table 5 gives the relative difference (in ppm) between the measured temperature ratio and the extrapolated density ratio; the same data are shown in figure 4.



**Figure 4.** Relative difference between the extrapolated density ratio and the measured temperature ratio for (▲) argon, (●) neon and (■) nitrogen; the solid line is a polynomial fit of the points. This difference is interpreted as either the error in the measured temperature relative to the thermodynamic temperature or the error in the sinker volumes. Error bars are for  $k = 1$ .

The density ratio at zero pressure should be equal to the ratio of the thermodynamic temperatures. If the densimeter were operating as a gas thermometer this difference would indicate the difference between the temperature (measured on ITS-90) and the thermodynamic temperature. However, as explained above, the uncertainties in the sinker volumes for the present densimeter are much greater than those in the temperature: as much as 125 ppm in volume at 505 K versus 2 mK in temperature (equivalent to 4–8 ppm over the temperature range of 234–505 K). Clearly, the present instrument cannot be used as a thermometer. But, by inverting the method, the sinker volumes can be calibrated *in situ*. The sinker volumes are adjusted by the difference between the measured temperature ratio and the extrapolated density ratio. Figure 4 depicts the correction applied to the sinker volumes compared to the volumes computed from the thermal expansion data. The experimental points are fitted to a cubic polynomial (shown by the solid line in figure 4), and the sinker volumes are multiplied by this correction for use in (3.1). The resulting sinker volumes, and thus also the measured densities, have an

**Table 6.** Effects of experimental uncertainties and systematic errors on the density ratios extrapolated to zero pressure.

Source	Magnitude ( $k = 1$ )	Effect on $\lim (p \rightarrow 0) (\rho_x/\rho_{\text{ref}})$ (ppm) at $T_x$ (K)										
		Argon						Neon	Nitrogen			
		234	273	360	430 (no. 1)	430 (no. 2)	505	430	340	400	440	480
Fit to model	(Scatter in data)	12.9	11.6	4.7	9.2	5.2	41.0	16.4	6.0	19.8	16.8	42.2
$p$ (zero offset)	2 Pa	8.1	8.3	8.5	8.6	8.6	5.7	5.3	8.7	8.8	8.8	8.8
$p$ (const % error)	10 ppm	0	0	0	0	0	0	0	0	0	0	0
Sinker $V$ @ $T_{\text{ref}}$	10 ppm	0	0	0	0	0	0	0	0	0	0	0
Weighings	+1 $\mu\text{g}$ @ $T_{\text{ref}}$ -1 $\mu\text{g}$ @ $T_x$	21.9	24.3	28.9	32.3	32.3	23.7	39.7	41.0	45.3	48.0	50.7
$T$ -dependent weighing error	0.02 $\mu\text{g}$ ( $T_x - T_{\text{ref}}$ )	5.7	2.3	10.7	33.3	26.3	31.8	32.2	20.8	40.4	56.1	74.0
Molar mass (sample purity)	+1 ppm @ $T_{\text{ref}}$ -1 ppm @ $T_x$	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
$T_{\text{ref}}$	2 mK @ $T_{\text{ref}}$	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8
Root sum of squares		28.1	29.1	33.1	48.6	43.4	57.8	54.4	47.8	64.9	76.6	99.8

estimated standard uncertainty of 60 ppm at 505 K or one-half the uncertainty of the volumes computed from the thermal expansion data.

The corrected sinker volumes are based on ITS-90 temperatures. No attempt was made to include any errors in ITS-90. The suspected error of 11 mK at 505 K (Strouse *et al* 2002, Ripple *et al* 2002) is 22 ppm, and it is lower at the other temperatures investigated here. Any error in ITS-90 is significantly less than the uncertainty in the present measurements.

#### 4. Discussion—feasibility of the method

This work has shown that a densimeter can, in principle, be used as a density-ratio gas thermometer. The necessary experiments have been demonstrated, and the data analysis techniques have been developed. The densimeter measurements typically required two or three days for each  $T_{\text{ref}}$  or  $T_x$ , comparing very favourably with other methods. The main question remaining is whether the uncertainties can be reduced to a level comparable to other methods. Edsinger and Schooley (1989) report typical uncertainties for a CVGT of 5 mK at 505 K and 15 mK at 933 K. Uncertainties ( $k = 1$ ) for acoustic thermometry range from 0.6 mK at 303 K to 3.0 mK at 505 K (Strouse *et al* 2002). Expressed as relative uncertainties, these range from 2 ppm for the acoustic thermometer at 303 K to 16 ppm for the CVGT at 933 K.

The numerical study indicated that the uncertainties in temperature for the DRGT are on the order of 1–5 mK for reasonable values of experimental uncertainties. A more detailed analysis of the present experimental results, including consideration of likely systematic uncertainties, resulted in combined uncertainties on the order of 50 ppm in the density ratio or roughly 25 mK in temperature at 505 K. Can the uncertainties in the present densimeter be reduced by an order of magnitude in an instrument designed explicitly as a gas thermometer?

The largest uncertainty in the present densimeter is in the sinker volumes. They are so large, in fact, that the present data were analysed to determine the sinker volumes assuming the temperatures were known, rather than vice versa. A gas thermometer would require very accurate sinker volumes, and these could be determined by direct measurement of the sinker dimensions by interferometry over the temperature range of interest. Interferometric systems can measure lengths to sub-nanometre resolution or coefficients of thermal expansion (CTE) with uncertainties of  $10^{-8} \text{ K}^{-1}$  or less. One commercial testing company claims  $10^{-8} \text{ K}^{-1}$  uncertainty in CTE for temperatures from 20 K to 1300 K using a Michelson interferometer according to the ASTM test method E289 (ASTM 2004). At 505 K this would correspond to 7 ppm uncertainty in volume. An academic group (Dudik *et al* 2003) has developed a system operating from 30 K to 310 K with uncertainties in CTE of  $2 \times 10^{-9} \text{ K}^{-1}$ ; they thought that their system could be extended to higher temperatures as well (Halverson 2003).

More accurate weighings will be required. This implies either a more sensitive balance with sinkers of the current size or larger sinkers weighed to microgram uncertainties. The present 60 g sinkers are made of titanium

and tantalum for a volume difference of  $9.74 \text{ cm}^3$ . The volume difference could be more than doubled to  $22.96 \text{ cm}^3$  with silicon and platinum sinkers of the same 60 g mass. Commercial balances can directly weigh objects up to 310 g with a precision of  $1 \mu\text{g}$ . Special ‘kilogram comparator’ balances weigh 1 kg objects with  $1 \mu\text{g}$  uncertainty (1 part in  $10^9$ ). However, these balances have a very limited electronic weighing range and would require tare weights to compensate for the different buoyancy forces on the sinkers. Weighings of the required sensitivity are thus feasible using larger sinkers. One of the largest uncertainties in a high-accuracy mass determination arises from uncertainties in the air density in the weighing chamber. The present densimeter has calibration masses inside the balance chamber which are weighed as part of each density determination; these masses have nearly identical volumes so that air buoyancy effects on the balance calibration cancel. The present 1 ppm uncertainty in the masses of the sinkers and calibration masses could be easily improved.

The uncertainties in temperature will need to improve to the 0.5 mK level for  $T_{\text{ref}}$  near 273.16 K, and this is routinely achieved by temperature metrologists. The resistance of the PRT at  $T_x$  will need to be measured with uncertainties corresponding to 0.5 mK in temperature. Just as important will be a very stable thermostat with small temperature gradients. A stability of 0.5 mK or better should be readily achievable with careful design of the thermostat.

The measurement of pressure presents no particular difficulties. Commercially available piston gauges would be suitable. Care will be required, however, to minimize any zero offset, for example as the result of errors in the reference pressure for the piston.

The use of a magnetic suspension coupling brings with it effects due to magnetic materials and diamagnetic fluids but these can be compensated for (McLinden *et al* 2006). Glos *et al* (2004) describe a two-sinker densimeter where the balance is ‘immersed’ in the test fluid. Such an approach avoids the need for a magnetic suspension coupling, but brings with it many other complications.

The improvements necessary to realize a density-ratio gas thermometer with uncertainties comparable to acoustic or constant-volume gas thermometers would require state-of-the-art temperature, mass and dimensional metrology, but all are feasible with present technologies.

#### 5. Conclusions

A new technique for the determination of thermodynamic temperature based on gas density measurements has been presented and shown to be feasible. Further development of this method into a temperature standard would require a significant effort involving a collaboration among temperature, pressure, dimensional and mass metrologists, but no insurmountable obstacles are foreseen.

The method was inverted and used to determine *in situ* the volume of the densimeter sinkers for the case where the relative uncertainty in the sinker volumes was substantially higher than that in temperature.

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