



Optical $n(p, T_{90})$ Measurement Suite 1: He, Ar, and N₂

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Abstract

An $n(p, T_{90})$ measurement suite is reported for the gases helium, argon, and nitrogen. The methodology is optical refractive-index gas metrology, operating at laser wavelength 633 nm and covering the temperature range ($293 < T < 433$) K and pressures $p < 0.5$ MPa. The measurement suite produces several things of thermophysical interest. First, the helium dataset deduces the effective compressibility of the apparatus with a relative standard uncertainty of 1.3×10^{-4} . Next, the argon dataset determines $T - T_{90}$ with a relative standard uncertainty of about $3 \mu\text{K} \cdot \text{K}^{-1}$. (The implementation is relative primary thermometry; $T - T_{90}$ is the difference between thermodynamic temperature and ITS-90.) Finally, the nitrogen dataset estimates the temperature dependence of polarizability within 3.5 % relative standard uncertainty. As a by-product of the nitrogen and argon measurements, values of the second density virial coefficient $B_\rho(T)$ are derived with uncertainties smaller than those of previous experiments. More broadly, the work enables conversion of a measured refractivity at known temperature to optical pressure within $3.5 \mu\text{Pa} \cdot \text{Pa}^{-1}$ across the stated range, albeit traceable to the diameter of a piston-gage.

Keywords Gas thermometry · Polarizability · Refractometry · Thermodynamic metrology

1 Introduction

Refractive-index gas metrology (RIGM) [1, 2] is a technique in which the density of a gas is inferred by measurement of refractivity $n - 1$ together with knowledge of polarizability. RIGM interests national metrology institutes because once density is inferred, gas pressure p (or thermodynamic temperature T) can be deduced (“realized”) when temperature (or pressure) is known. When helium gas is used,

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this realization of pressure (or temperature) is considered primary: that is, the physical quantity realized is described by fundamental equations, in which all parameters are known independent of the like-quantity. The equations describing the physical system [1, 2] of an RIGM implementation are the Lorentz–Lorenz relation and an equation of state. For pressure metrology, the appeal of RIGM is that it has potential to establish a scale based on a well-understood physical system, with a universal realization accessible to all via the optical properties of gases.

This article is part-one of a two-part series reporting highly-accurate $n(p, T_{90})$ measurements for several gases of metrological interest. (Throughout this article T_{90} is used to denote temperature measured on ITS-90 [3, 4].) The first part reports the datasets for helium, argon, and nitrogen; the second part will report datasets for gas-phase ordinary water and heavy water. Overall, the unifying theme is RIGM and the advancement of gas-based thermodynamic metrology; the water measurements are a subtopic, mostly of interest [5] to physical chemists. The work builds on old efforts [6, 7] employing a Fabry–Perot cavity. Section 2 therefore does not revisit the experimental details too deeply. After introducing the apparatus, the article explores the $n(p, T_{90})$ datasets. First, Sect. 3 uses helium as a standard of refractive index to calibrate the compressibility of the refractometer. Section 4 describes how the argon dataset provides a precise determination of $T - T_{90}$, the difference between thermodynamic temperature and ITS-90, which is a topic of ongoing international activity [8]. Unlike argon, nitrogen is an imperfect thermometric gas because its polarizability has a temperature dependence; Sect. 5 reports an estimate of this dependence, which is something of recent theoretical interest [9]. Finally, the article closes with Sect. 6, which discusses nonlinear effects in the relationship between pressure and refractivity—i.e., deviation from ideal gas behavior; the section accurately infers values for the second density virial coefficient for argon and nitrogen from the $n(p, T_{90})$ datasets.

2 Principle and Apparatus

The apparatus closely resembles Ref. [7], with the following thermal improvements: (i) Most of the cavity mode (the laser beam resonating between the mirrors of the cavity) has been enclosed inside a bored copper block, which does not touch the glass, and (ii) A capsule-type standard platinum resistance thermometer (cSPRT) was placed inside another bore in the copper block, about 13 mm above the cavity mode. A sketch of this arrangement is provided in Fig. 1. It is emphasized that the copper block is entirely passive to the *optical* performance of the cavity. The monolithic glass cavity suspended by wires delivers ultrahigh dimensional stability, ultralow thermal expansion, and ultralow hysteresis (in compressibility and expansivity). However, it is the passive copper block that vastly improves the *thermal* performance. For a 0.1 MPa charge of argon, the settling-time required to reach 0.1 mK gradients between the cavity mode and thermometer is within 1500 s [10]. This thermal performance is achieved because the majority of the cavity mode is enclosed in the same block of copper that houses the cSPRT. The copper block provides a rapidly-settling, isothermal volume that achieves minimal gradients in the

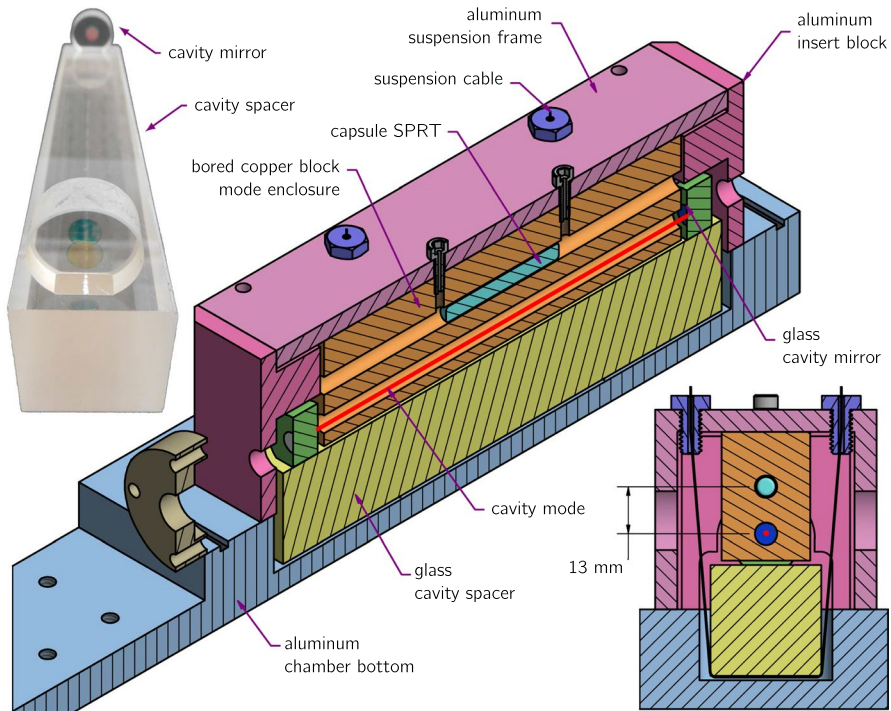


Fig. 1 A copper mode enclosure was placed between the mirrors of the FP cavity. The glass cavity remained suspended by wires, untouched by metal. See Fig. 2 of Ref. [7] for more details on the apparatus. A photograph of the cavity is shown in the top left of the figure

comparison of the two thermometers—cSPRT and cavity mode. The isothermal volume is immune to much slower time constants in the system, such as settling of the total system back to equilibrium after a gas charge, or thermal disturbance of the glass cavity. It is also noted that the gas thermometry occurs at the cavity mode, and thermal disturbance of the glass cavity only affects the gas thermometer via expansivity, which is near zero in titania-silicate glass. The apparatus is temperature-stabilized and operates $p < 0.5$ MPa and $(293 < T_{90} < 433)$ K.

The principle behind a measurement of refractivity in a Fabry–Perot cavity is to analyze the difference in frequency between a cavity resonance at vacuum ν_{vac} and a resonance in gas ν_{gas} . For operation at the few $10^{-6} \cdot (n - 1)$ level [6, 11], refractivity is adequately deduced via the simplified expression $n - 1 = \frac{\Delta f}{\nu_{\text{gas}}} + n\kappa\Delta p$, with Δf being the measured “effective difference frequency” and κ the one-dimensional compressibility (distortion coefficient) of the cavity. The compression of the cavity in length is proportional to the change in pressure Δp between vacuum and gas. For argon and nitrogen gases, this work demonstrates sub- 10^{-6} relative precision, which beckons the more accurate working-equation

$$n - 1 = \frac{\Delta f + \kappa \Delta p [\nu_{\text{gas}}(1 + \epsilon_d) + \epsilon_\tau(\nu_{\text{gas}} - \nu_c)]}{[\nu_{\text{gas}}(1 + \epsilon_d) + \epsilon_\tau(\nu_{\text{gas}} - \nu_c)](1 - \kappa \Delta p)}. \quad (1)$$

The effective difference frequency $\Delta f = (1 + \epsilon_\tau)[(\nu_{\text{vac}} - \nu_{\text{gas}}) + \Delta m \Delta \nu_{\text{fsr}}]$ has the frequencies ν_{vac} and ν_{gas} , which are measured by comparison to the absolute frequency of an iodine-stabilized laser. It is trivial to unambiguously identify the integer change in mode number Δm . The fractional effect on resonant frequency of the frequency-dependent reflection phase-shift ϵ_τ is needed to correct differences in absolute frequencies and multiples of the measured free-spectral range $\Delta \nu_{\text{fsr}} = \frac{c}{2L(T)(1+\epsilon_\tau)}$, with c the speed of light in vacuum. For a two-mirror cavity, the factor $\epsilon_\tau = \frac{\tau c}{L}$ is given by the group delay of each mirror $\tau = \frac{1}{2\pi} \frac{d\phi}{d\nu}$, and is always signed positive. The ϕ is the reflection phase-shift of a mirror. The magnitude of $\epsilon_\tau = 7.3(7) \times 10^{-6}$ is small enough that the thermal expansion and thermo-optic effects contributing to $\tau(T)$ can be ignored. However, the temperature dependence of cavity length $L(T) = L_{303} [1 + \int \alpha(T) dT]$ can not be ignored, and is governed by the thermal expansion coefficient of the cavity α . Since $\frac{d\nu}{\nu} \approx -\frac{dL}{L}$, the reference $\Delta \nu_{\text{fsr}}$ was established at 303 K, and updated for changes from the reference length via $\Delta \nu_{\text{fsr}}(T) = \Delta \nu_{303} \left(1 + \frac{\delta \nu_{\text{vac}}}{\nu}\right)$ with $\delta \nu_{\text{vac}}$ being the temperature-dependent change in cavity resonant frequency at vacuum relative to its reference value at 303 K.

So far, the explanation has not departed from Refs. [6, 11], but now two small corrections are added to the denominator of Eq. 1. The larger is $\epsilon_d = \frac{z_r}{r} \frac{1}{\pi m}$, which is a $0.3 \times 10^{-6} \cdot (n - 1)$ correction in the present system, and arises from diffraction—i.e., the change in Gouy phase-shift $\Phi(n) = \arctan [z\lambda/(\pi n w_0^2)]$ as a function of refractive index, with λ the wavelength, w_0 the beam waist radius, and z the geometric distance propagated in a medium of refractive index n . The term $z_r = \sqrt{(r - L)L}$ is the Rayleigh length in a plano-concave FP cavity of length L and mirror radius of curvature r . Division by the cavity integer mode number m makes ϵ_d small. The second correction to the denominator of Eq. 1 arises from mirror characteristics—i.e., the change the reflection phase-shift $\phi(n)$ as a function of refractive index. The correction is a consequence of the fact that the operating frequency of the laser resonating in the cavity ν_{gas} does not coincide with the center frequency of the mirror ν_c . (The center frequency of the mirror is the frequency at which $\phi = \pi$.) However, when mirror coatings are designed for a specific laser system, one can expect $\nu_{\text{gas}} - \nu_c < 10$ THz, such is the present system. Consequently, with $\epsilon_\tau \approx 7 \times 10^{-6}$ and $\nu \approx 474$ THz, this correction is below $0.2 \times 10^{-6} \cdot (n - 1)$. Details behind the derivation of Eq. 1 are in Appendix 1.

To summarize what has just been stated: a measurement of gas refractivity in Eq. 1 is obtained as simply the change in resonance frequency as the cavity is filled from vacuum to gas pressure. Additionally, the cavity length $L(T)$ is updated for all temperatures, based on auxiliary measurements of thermal expansion (that is, the change in vacuum resonance frequency as a function of temperature). The one unknown in Eq. 1 is compressibility $\kappa(T)$. This quantity will be deduced from measurement of helium refractivity at known pressure and temperature, discussed next.

3 Compressibility of Titania-Silicate Glass

In Eq. 1 there is one unknown: compressibility κ of the cavity. In this work, the compressibility is deduced

$$\kappa(T) \approx \frac{\frac{p}{T} \frac{3A_R}{2R} - \frac{\Delta f}{v}}{p \left(1 + \frac{p}{T} \frac{3A_R}{2R} \right)}, \quad (2)$$

by measurement of helium refractivity at known pressure p and temperature T . Equation 2 assigns compressibility to be the correction factor needed to make the calculated refractivity match the measured refractivity. The calculated refractivity $\frac{p}{T} \frac{3A_R}{2R}$ is obtained from theoretical knowledge [12] of molar refractivity A_R together with the measured p and T_{90} of the helium gas; R is the gas constant. The molar refractivity $A_R = A_e(\omega) + A_\mu$ is the combined physical properties frequency-dependent electronic polarizability $A_e(\omega)$ and magnetic susceptibility A_μ . The measured refractivity $\frac{\Delta f}{v}$ is the change in resonance frequency of the cavity when it is filled and compressed with helium gas. The approximation in Eq. 2 recognizes nonlinear terms which are a consequence of refractivity being nonlinear in density, and density being nonlinear in pressure. For this work, the calculated refractivity is third-order in $\frac{p}{T}$. Finally, note the framework above treats $\kappa(T)$ as an apparatus calibration factor. Consequently, the determination of $\kappa(T)$ by Eq. 2 may not be equivalent to a true material value, because the cavity is a mounted optical assembly. This point will be returned to below.

3.1 Measurement Details

The apparatus of Fig. 1 was filled with 99.9999 % purity helium. The cavity measured refractivity as the change in resonant frequency between vacuum and gas, via Eq. 1. A piston-gage generated the pressure [13]. Gas temperature was measured by the cSPRT carrying an ITS-90 calibration, and later converted to thermodynamic temperature using the consensus estimate [14].

Acquisition of isotherms was fully automated, and operated continuously. Acquisition of a single datapoint took about 2 h: evenly split between helium and pumpdown back to vacuum. (The cavity vacuum length was updated before every datapoint, a necessary strategy to contend with helium permeation. More details about helium permeation are in Appendix 2. Furthermore, large thermal gradients and time constants associated with pumpdown and heat transfer in vacuum were mitigated by a two-step procedure: a roughpump to 1 kPa, a wait for settling-time, then a turbopump to high vacuum.) Nine isotherms were acquired, each consisting of five repeats at eight set pressures. The helium $n(p, T_{90})$ dataset has 72 triplets repeated five times, took 44 days to complete, and is included in the supplemental material. The result for compressibility is discussed next.

3.2 Comparison with Literature

The present measurements of compressibility are plotted in Fig. 2(a). In the range ($293 < T < 433$) K, the data are described by the quadratic

$$\kappa(T) = \kappa_{303} + k_1 \cdot (T - 303) + k_2 \cdot (T - 303)^2,$$

with $\kappa_{303} = 9.8255(7) \times 10^{-12} \text{ Pa}^{-1}$, and $k_1 = -3.60(3) \times 10^{-15} \text{ Pa}^{-1} \cdot \text{K}^{-1}$ and $k_2 = 3.5(2) \times 10^{-18} \text{ Pa}^{-1} \cdot \text{K}^{-2}$. At 293.15 K, the present result agrees within 0.01 % with the initial characterization of Ref. [7]. Bracketed numbers on the fit coefficients cover statistical uncertainty only; measurement uncertainty in compressibility is detailed below.

Comparisons with literature now discussed can only be qualitative. Vitreous silica has thermophysical properties that can vary by recipe and process [17]; furthermore, for the mixture titania-silicate glass, the thermophysical properties exhibit a dependence on percentage-weight of titania [18, 19]. To continue qualitatively first requires an estimate of the cavity's titania mass fraction, which is correlated with the thermal expansion coefficient [18]. The expansivity of the cavity was characterized [20] by monitoring the change in cavity resonance frequency at vacuum as a

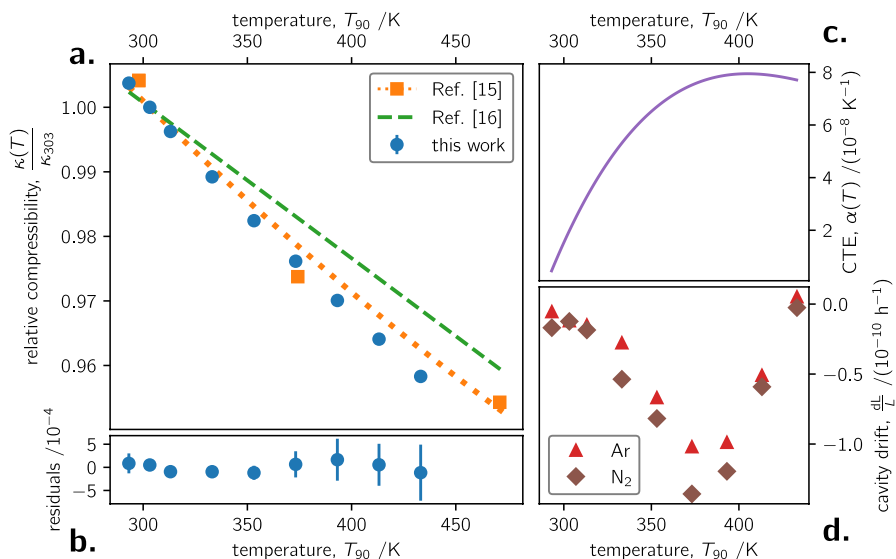


Fig. 2 Characteristics of the cavity. (a) Relative compressibility as a function of temperature. Errorbars on this work are smaller than the markers. Ref. [15] is also for low thermal expansion titania-silicate glass. Ref. [16] is a theoretical estimate for a pure silica glass. (b) Residuals from quadratic fit to compressibility. Errorbars span standard deviation on the estimated κ at each isotherm: each isotherm has eight $n(p, T_{90})$ triplets repeated five times. (c) Coefficient of thermal expansion (CTE) measured at vacuum. The $2 \times 10^{-9} \text{ K}^{-1}$ uncertainty in $\alpha(T)$ is thinner than the line. (d) Representative stability of the cavity during argon and nitrogen isotherms

function of temperature, and recognizing $\frac{dv}{v} \approx -\frac{dL}{L}$. The derivative of a quartic fit to expansivity gives

$$\alpha(T) = \alpha_{303} + a_1 \cdot (T - 303) + a_2 \cdot (T - 303)^2 + a_3 \cdot (T - 303)^3,$$

with $\alpha_{303} = 1.96(2) \times 10^{-8} \text{ K}^{-1}$, and $a_1 = 1.40(2) \times 10^{-9} \text{ K}^{-2}$, $a_2 = -1.01(3) \times 10^{-11} \text{ K}^{-3}$, and $a_3 = 2(2) \times 10^{-14} \text{ K}^{-4}$. The result is plotted in Fig. 2(c). Next, the known $\alpha(T)$ is combined with the correlation of Carapella et al. [18], based on an empirical additive law of composition $\alpha(10^{-9} \text{ K}^{-1}) = -55.1 \times \text{wt\%}[\text{TiO}_2] + 407.9$. This correlation is at unspecified temperature; by assuming the correlation is valid at room-temperature $T = 296 \text{ K}$, the optical cavity used in the present work has 7.2 wt% titania. Next, the work of Manghnani et al. [19] provides an estimate of compressibility as a function of the titania mass fraction: compressibility increases by 0.7 % per percentage-weight titania decrease. At 7.2 wt% titania and $T = 298 \text{ K}$, Manghnani et al. [19] estimated a compressibility of $9.72 \times 10^{-12} \text{ Pa}^{-1}$, which is 1.3 % lower than the present work. A second literature measurement is due to Scannell et al. [15], who found a compressibility of $9.48 \times 10^{-12} \text{ Pa}^{-1}$ at 8.2 wt% titania and $T = 303 \text{ K}$. To compare with the present work which has 7.2 wt% titania, the result of Scannell et al. is increased by 0.7 %, yielding $9.55 \times 10^{-12} \text{ Pa}^{-1}$. The adjusted result of Scannell et al. is 2.8 % lower than the present work. From these qualitative comparisons to the literature, the present work appears offset in the absolute value of compressibility. Moreover, as discussed next, the present work also differs from literature for the temperature dependence of compressibility.

Besides an absolute value of compressibility at a reference temperature, results presented later in this article also require accurate knowledge of the temperature dependence. The temperature-dependent compressibility inferred by this work is compared with the literature in Fig. 2(a). From above, at $T = 303 \text{ K}$ the present measurements exhibit $\frac{d\kappa}{dT} \frac{1}{\kappa} \approx k_1/\kappa_{303} = -3.64(2) \times 10^{-4} \text{ K}^{-1}$. The work of Scannell et al. [15], based on Brillouin spectroscopy, found a dependence $\frac{d\kappa}{dT} \frac{1}{\kappa} \approx -3.02 \times 10^{-4} \text{ K}^{-1}$, more than 20 % smaller than the present work. Scannell et al. do not provide a statement of measurement uncertainty; a crude analysis of their bulk modulus data suggest a statistical uncertainty of 20 % predicting slope on $\kappa(T)$. [This crude analysis uses the square-root of the covariance matrix for a quadratic fit to data in the range $(295 < T_{90} < 694) \text{ K}$. This fit is shown as the dotted line in Fig. 2(a) together with their three datapoints that overlap the present work.] Finally, the more studied system of pure SiO_2 glass is mentioned. The theory of Vukcevic [16] predicted $\frac{d\kappa}{dT} \frac{1}{\kappa} = -2.96 \times 10^{-4} \text{ K}^{-1}$, which was significantly larger than the then available experimental data. More recently, the temperature dependence predicted by Vukcevic has been better supported by the measurements of Le Parc et al. [21], who found $\frac{d\kappa}{dT} \frac{1}{\kappa} = -2.39 \times 10^{-4} \text{ K}^{-1}$. The measurements of Scannell et al. [15] do feature comparisons of $\kappa(T)$ for pure silica versus mass fraction of titania; arguably, their measurements (their Table 3) show an increase in $\frac{d\kappa}{dT} \frac{1}{\kappa}$ proportional to titania content, which would place the theory of Vukcevic [16] closer to the present experiment. However, the results of Scannell et al. are non-monotonic, which prevents any firm conclusion on the matter.

In summary, relative to literature, the present measurements show κ_{303} larger by about 2 %, and $\frac{d\kappa}{dT} \frac{1}{\kappa}$ larger by about 20 %. These disagreements should not be considered surprising. As mentioned above, Eq. 2 treats $\kappa(T)$ as an apparatus calibration factor, which may not be equivalent to the true material value, because the apparatus is a mounted optical assembly. In this context, a comparison of the present measurements to literature values is merely qualitative. Two further arguments are added. First, it is known that thermal expansion of pure silica glass can vary by as much as 2.5 % among samples taken from the same glass melt [22]. Expansivity is closely related to compressibility, embodied in the material equation of state. Therefore, it is unreasonable to assume an amorphous mixture of nominal silica composition will have a true material value of compressibility within 2.5 %, and imperfect agreement with literature values for $\kappa(T)$ is expected. Despite this ambiguity about a true material value, the second argument about $\kappa(T)$ in this work is that it should closely approximate the compressibility of the cavity material. The reason is because the cavity (optical assembly) consists of titania-silicate spacer with titania-silicate mirror substrates: there is no mismatch in elastic properties (other than the likely 2.5 % inhomogeneity mentioned above). The mirrors are silicate-bonded to the spacer: there is no epoxy or unpredictable bond effects. Finally, the cavity is suspended from wires at its Airy points: the mounting should not cause friction or stick/slip effects.

The above comparison with literature was qualitatively informative, and minor differences between literature and the $\kappa(T)$ determination of this work can be justified. Next, uncertainty in the $\kappa(T)$ determination is described.

3.3 Uncertainty in Compressibility

The uncertainty budget for the present measurement is listed in Table 1. Throughout this article, the notation $u(x)$ is used to denote the standard uncertainty of the quantity x . Unless otherwise stated, all uncertainties in this work are one standard uncertainty, corresponding to approximately a 68 % confidence level.

The dominant source of uncertainty in the determination of $\kappa(T)$ is permeation of helium into the glass cavity, which increases its length. Effectively, the change

Table 1 Relative standard uncertainty determining compressibility $\kappa(T)$ of the titania-silicate glass cavity

Component	$u_r(\kappa) (10^{-5})$
$\beta, 0.16 \text{ MHz} \cdot \sqrt{\text{h}}^{-1}$	10.4
$p, 1.9 \text{ } \mu\text{Pa} \cdot \text{Pa}^{-1}$	6.2
$T, 2.1 \text{ } \mu\text{K} \cdot \text{K}^{-1}$	4.8
$\frac{\Delta f}{\nu}, 3 \times 10^{-11}$	0.9
$n(p, T)_{\text{calc}}, 3 \times 10^{-17} \text{ Pa}^{-1}$	0.3
Impurity	1.8
Regression	1.2
Combined ($k = 1$)	13.3

The magnitude of the dominating component β is temperature-dependent and the entry covers characterization at 373 K; see text

in fractional frequency has the measurand—helium refractivity plus pressure-induced distortion—but the measurand is spoiled by transient elongation of the cavity length while exposed to helium. The correction to cavity length is based on extrapolating constant-density data to time-zero using a model that has a diffusion parameter and an initial frequency. However, in addition to statistical fitting, there is a dominating systematic error related to the diffusion model. The model error leads to large irreproducibility at higher temperatures, evident by the enlarged errorbars on the residuals shown in Fig. 2(b). Further details are in Appendix 2. The entry $u(\beta)$ in Table 1 includes the combined statistical and systematic contributions. The entry is temperature-dependent: the contribution of $u(\beta)$ ranges from $6.2 \times 10^{-5} \cdot \kappa$ at 293 K to $1.8 \times 10^{-4} \cdot \kappa$ at 433 K.

A calculated value of helium refractivity is only as accurate as the input measurements of pressure and temperature. Pressure was generated with a piston-gage, and the pressure was known within $1.9 \mu\text{Pa} \cdot \text{Pa}^{-1}$ uncertainty by calculation of force and area; Egan et al. [13] have the details. The cSPRT measured gas temperature T_{90} on the ITS-90, which was realized using the fixed-points of water and indium. More details about resistance thermometry and ITS-90 are in Sect. 4 and Appendix 4. The uncertainty on the cSPRT T_{90} was temperature-dependent, and at the representative temperature 373 K is at its maxima $1.6 \mu\text{K} \cdot \text{K}^{-1}$. The measured temperature T_{90} was converted to thermodynamic temperature T using the consensus estimate [14] covering this temperature range. Uncertainty in the conversion of T_{90} to T increases as a function of temperature, and the $u(T)$ entry adds in quadrature $1.6 \mu\text{K} \cdot \text{K}^{-1}$ with the cSPRT T_{90} uncertainty stated above.

Change in fractional frequency can be measured to very high accuracy. The present measurements are limited by the 5 kHz stability of the iodine-stabilized helium-neon laser frequency reference. This entry does not cover nonideal factors that perturb the resonant frequency, such as error in glass temperature or dimensional drift in cavity length. Nonideal factors are effectively absorbed into the entry $u(\beta)$.

Evaluation of Eq. 2 requires knowledge of the refractivity of helium at measured values of pressure and temperature. Since 2016 [12], calculation of $n - 1$ for helium within $10^{-7} \cdot (n - 1)$ has been possible for $p < 1$ MPa and T near ambient. Theoretical knowledge of the optical and thermophysical properties of helium is always improving [23]. Recent developments include improved accuracy in polarizability A_e [24, 25], more rigorous calculation of dielectric and refractivity virial coefficients [26, 27], and extension of the valid pressure range up to 10 MPa by improved accuracy in the density virial coefficients [28, 29].

Two helium cylinders from different suppliers were used. Gas chromatography revealed that the largest impurity was hydrogen, at a similar level $0.18(10) \mu\text{mol} \cdot \text{mol}^{-1}$ in both cylinders, which would be a $0.7 \times 10^{-6} \cdot (n - 1)$ error in the refractivity of helium. The effect of cylinder impurity in the characterization of compressibility is a small contributor to $u(\kappa)$. It is likely that outgassing, especially at elevated temperatures, contaminates the helium in the chamber much more than what is supplied direct from the cylinder. However, the effect of outgassing (gradual contamination of an initially pure sample) is effectively absorbed into $u(\beta)$, and the extrapolation of helium refractivity to time-zero. See Appendices 2 and 4.

Finally, there is an added regression component associated with fitting $\kappa(T)$ to a quadratic. Square-root of diagonal elements in the covariance matrix is used for the entry in the table.

4 Determination of $T - T_{90}$

Refractive-index gas thermometry (RIGT) [1, 30] determines thermodynamic temperature using the virial equation of state

$$p = \rho RT(1 + B_\rho \rho + C_\rho \rho^2 + \dots), \quad (3)$$

with the density virial coefficients B_ρ and C_ρ . The extended Lorentz-Lorenz equation links density ρ and refractive index n via molar refractivity A_R

$$\frac{n^2 - 1}{n^2 + 2} = \rho(A_R + B_R \rho + C_R \rho^2 + \dots), \quad (4)$$

with the refractivity virial coefficients B_R and C_R . In the limit of zero density, thermodynamic temperature T can be deduced [30] from Eq. 4 as $T \approx \frac{3A_R}{2R} \frac{p}{n-1}$. However, for a real gas at a measurable pressure p , the nonlinearities of Eqs. 3 and 4 come into play, and the simplified $T \approx \frac{3A_R}{2R} \frac{p}{n-1}$ produces large errors. To circumvent the problem of nonlinearity, the experimental method of isothermal regression is used, by which

$$p = (n - 1)\mathcal{A}[1 + (n - 1)\mathcal{B} + (n - 1)^2\mathcal{C}] + \epsilon_p, \quad (5)$$

is regressed to recover $\mathcal{A} = \frac{2RT}{3A_R}$ and find T . The units of $\mathcal{A}$ are J/m^3 , equivalent to Pa. Additional constraints are placed on the unitless coefficients $\mathcal{B}$ and $\mathcal{C}$ by the procedure of multi-isotherm fitting [31, 32]. A multi-isotherm fit is a global optimization in which the nonlinear terms of Eq. 5 are defined as smooth functions of temperature. In the temperature range of the present work, polynomials

$$\mathcal{B} = \sum_{i=0}^4 b_i(T - 303)^i \quad \text{and} \quad \mathcal{C} = \sum_{i=0}^1 c_i(T - 303)^i, \quad (6)$$

adequately describe the dependence. While $\mathcal{A}$ can be deduced by regressing each individual isotherm to Eq. 5, the benefit of the multi-isotherm fit is that it increases internal consistency and is (arguably) more physically justified. Finally, the term ϵ_p allows for an offset error related to pressure. There are several mechanisms that might contribute to ϵ_p , including: mass error in the piston-gage, scale error in the belljar vacuum-gage, residual pressure in the (vacuum state) refractometer, leaks (impurities) into the argon volume, dimensional instability of the glass cavity (i.e., imperfect compensation of thermal expansion or temporal drift), etc.

Two things are mentioned before moving onto the measurement details. First, this section concerns thermometry, so only coefficient $\mathcal{A}$ is of interest; some remarks on $\mathcal{B}$ and $\mathcal{C}$ and their temperature-dependencies are made in Sect. 6. Second, this

section concerns *relative primary* thermometry about a reference temperature T^* , and the determination

$$\frac{T}{T^*} = \frac{\mathcal{A}}{\mathcal{A}^*} \equiv \mathcal{A} \frac{3A_R}{2RT^*}, \quad (7)$$

employs “one key-parameter value determined from temperature fixed points, for which the thermodynamic temperature T^* is known *a priori*” [30]. The key-parameter is the molar refractivity of argon A_R , and details about its establishment at the gallium melting-point follow below.

4.1 $T - T_{90}$ over ($293 < T < 433$) K

Determination of the scale error $T - T_{90}$ was accomplished by measuring argon refractivity as a function of pressure on an isotherm. An isotherm consisted of 19 $n(p, T_{90})$ -triplets repeated 5 times. A 95-sample isotherm took 85 h to acquire. Nine isotherms were measured. The entire dataset were regressed to Eq. 5 using the multi-isotherm constraints in Eq. 6. The fit has 25 free parameters: nine independent $\mathcal{A}$ and ϵ_p , and the polynomials describing nonlinearity have five b and two c . The global optimization identified a value of $\mathcal{A}$ for each of the nine isotherms; these $\mathcal{A}$ were converted to relative thermodynamic temperature using Eq. 7. The argon $n(p, T_{90})$ dataset and analysis script are included in the supplementary material.

To use Eq. 7, a foundational statement must be made about the molar refractivity of argon. To do so, the $\mathcal{A}$ regressed from the 303 K isotherm was converted to molar refractivity $A_R = \frac{2RT^*}{3\mathcal{A}}$, using the consensus estimate [8] of $T^* = 302.9184(3)$ K, the thermodynamic temperature of the gallium melting-point. The result is $A_R = 4.195735(13) \text{ cm}^3 \cdot \text{mol}^{-1}$, operating at $\lambda = 632.9908(1) \text{ nm}$. The relative uncertainty in A_R is effectively described by Table 3 below. The present A_R increases $11.8 \times 10^{-6} \cdot A_R$ from the previous recommendation [33]. Uncertainty in the present value has been reduced by a factor of five because pressure has been generated by a dimensionally-characterized piston-gage [13]. The present value is within $5.3 \times 10^{-6} \cdot A_R$ of the recommendation of Lesiuk and Jeziorski [34], which is agreement within one-half of mutual standard uncertainty. The recommendation of Lesiuk and Jeziorski is based on a measurement of static polarizability [35] scaled in frequency by a theoretical estimate of dispersion, plus a theoretical estimate of magnetic susceptibility. Uncertainty in the recommendation of Lesiuk and Jeziorski is dominated by the frequency dependence of electronic polarizability. The stated disagreement uses the sixth-order Cauchy coefficient for dispersion [34]. The close agreement between the present A_R with what was estimated by Refs. [34, 35] adds confidence to the present relative primary results.

The present measurements of the scale error $T - T_{90}$ are listed in Table 2. This tabulation is shown graphically in Fig. 3 together with the literature [36–41] overlapping this range. Two consensus best-estimates of $T - T_{90}$ exist in this range, labeled “CCT”: the older Fischer et al. [14] covers all the range, but Gaiser et al. [8] is the newer recommendation for $T < 335$ K. This work has used Gaiser et al.

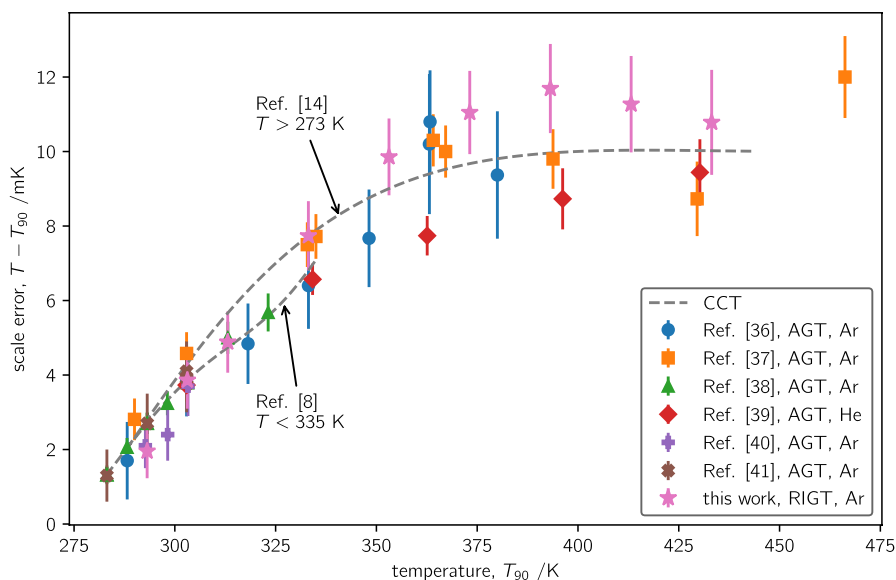


Fig. 3 Measurements of the scale error in the ITS-90. Errorbars span the standard uncertainties for each reference. CCT: consultative committee for thermometry. AGT: acoustic gas thermometry. RIGT: refractive-index gas thermometry

Table 2 Results of the scale error $T - T_{90}$ determined by optical refractive-index gas thermometry

T_{90} (K)	$T - T_{90}$ (mK)	$u(T - T_{90})$ (mK)
293.131	1.96	0.7
303.107	3.86 ^a	0.8
313.123	4.88	0.8
333.129	7.74	0.9
353.124	9.86	1.0
373.156	11.05	1.1
393.146	11.69	1.2
413.187	11.27	1.3
433.152	10.78	1.4

^aRelative primary thermometry referenced to $T - T_{90}$ at the gallium melting-point via Gaiser et al. [8]

for $T - T_{90}$ at the gallium melting-point T^* . Consequently, the scale error $T - T_{90}$ (and the molar refractivity of argon) is pinned to Gaiser et al., and future updates over Gaiser et al. to the thermodynamic temperature of the gallium melting-point will shift all $T - T_{90}$ results in Table 2 by that millikelvin change. Elsewhere in Fig. 3 are two notable things: (i) at $T = 333$ K, the present measurements agree better with the older consensus estimate [14] than the newer one [8], and (ii) there

Table 3 Standard uncertainty determining the temperature scale error $T - T_{90}$, expressed relative to T_{90}

component	$u(T - T_{90})/T_{90}$ ($\mu\text{K}\cdot\text{K}^{-1}$)
<i>T</i> relative RIGT	
p , $1.9 \mu\text{Pa}\cdot\text{Pa}^{-1}$	1.9
T^* datum [8], 0.4 mK	1.1
$\mathcal{A}$, 226 J/m^{-3}	0.4
$\kappa(T)$, $1.1 \times 10^{-15} \text{ Pa}^{-1}$	0.6
Impurity	0.2
T correlation, 10.0 mK	1.4
T_{90} cSPRT	
Fixed-point realization	0.2
Subrange inconsistency	1.1
Non-uniqueness	0.5
Self-heating	0.3
Nonlinearity	0.2
Reproducibility	0.2
Gradient	0.3
Combined ($k = 1$)	3.0

As described in the text, several entries are temperature-dependent, and the budget given is representative of operation at 373 K

is discrepancy between these moderate accuracy measurements compared to the work of Gavioso et al. [39], which appears to have the lowest uncertainty to date. The work of Gavioso et al. is also the only to employ helium for the thermometry, a gas more sensitive to contaminants than argon. Finally, the present measurements appear to be the first determination of $T - T_{90}$ in this range not employing an apparatus based on the speed-of-sound [42].

4.2 Combined Uncertainty $u(T - T_{90})$

Uncertainty for the $T - T_{90}$ is given in Table 3, and is split into two segments: uncertainty in relative refractive-index gas thermometry, and uncertainty in the realization of ITS-90. The entries in Table 3 are representative of operation at 373 K; the listing in Table 2 shows how uncertainty depends on temperature.

4.2.1 Uncertainty of Relative RIGT

For the relative RIGT, uncertainty is dominated by two entries, p and T^* . Uncertainty in the generated pressure has been described by Egan et al. [13]; the contributions of aerostatic head and thermal transpiration are insignificant. The present apparatus has the natural reference level of the piston-gage matched within 2 mm of the cavity mode altitude; the hot cavity mode communicates with the room-temperature piston-gage via 19 mm diameter tube. Uncertainty in the thermodynamic

temperature of the gallium melting-point (the datum) has been established by consensus [8].

The uncertainty on the fit parameter $\mathcal{A}$ was provided by the diagonal elements of $(\chi_v^2 \cdot \mathcal{I}^{-1})^{1/2}$, with χ_v^2 being the reduced chi-square statistic (i.e., the residual sum of squares result of the multi-isotherm regression divided by the degrees of freedom), and $\mathcal{I}$ is the information matrix (i.e., the negative-Hessian evaluated at the final-iteration estimate) [43]. Here, some remarks are added about robustness of the multi-isotherm regression, and the number of free parameters. The multi-isotherm regression has been implemented as a weighted nonlinear least squares (unconstrained multivariate optimization). The fractional difference in $\mathcal{A}$ between multi-isotherm and single-isotherm regression was $(0.3 \pm 18) \times 10^{-7}$, where the expression is mean difference plus-minus standard deviation on the mean for the nine isotherms. The single-isotherm regression was implemented as a total least squares reduction of Eq. 5 for each isotherm. Essentially, the difference is noise at the $1.8 \mu\text{K} \cdot \text{K}^{-1}$ level; see Fig. 6(a). A more familiar approach to multi-isotherm regression [31] would be described as ordinary least squares, with iteration on the estimator $T - T_{90}$ plus a pre-estimate of ϵ_p . The relative difference in the final $T/T_{90} - 1$ between the two multi-isotherm implementations was $(3.6 \pm 6.1) \times 10^{-7}$. In this work, complete preference is given to the results produced by the weighted nonlinear least squares multi-isotherm regression. Regarding the number of free parameters chosen for regression: The polynomial number chosen for $\mathcal{B}$ was guided by what was needed to adequately fit the theoretical estimate [26, 44]. The linear $\mathcal{C}$ was guided by the observation that a quadratic produced spurious results—that is, a quadratic $\mathcal{C}$ in the regression produced strong nonlinearity as a function of temperature, in contrast to the gentle trend predicted by theory [27, 45]. The polynomial choice for $\mathcal{C}$ has negligible influence on $u(T)$ —the relative difference in $\mathcal{A}$ using linear and quadratic $\mathcal{C}$ was $(0.1 \pm 2.6) \times 10^{-7}$. Finally, the choice to include ϵ_p is physically justified as mentioned above, but it could introduce a correlation error into $\mathcal{A}$. The multi-isotherm regression identified ϵ_p to have mean value 10 mPa on the nine isotherms, with average statistical uncertainty 41 mPa. This systematic error is within estimates of pressure offsets caused by mass error in the piston-gage (54 mPa) and refractivity offsets caused by error estimating temperature of the glass cavity (about 60 mPa, but smaller at temperatures with lower CTE). However, removing ϵ_p from the regression caused relative differences in $\mathcal{A}$ of only $(1.7 \pm 2.4) \times 10^{-7}$.

Next, the two other minor entries are accounted for. The measurement and uncertainty of compressibility $\kappa(T)$ has been detailed in Sect. 3. Its magnitude increases with temperature, and the entry in Table 3 is the mid-range value. Finally, impurity in 99.9999 % argon makes negligible contribution to the gas thermometry uncertainty, and the present system (fortuitously) outgasses a mixture of molar refractivity very similar to argon. However, noticeable outgassing was observed in two isotherms $T_{90} > 413 \text{ K}$; outgassing was corrected by linear extrapolation to time-zero. (More details about outgassing are in Appendix 3.)

The remaining entry in the relative RIGT segment is “ T correlation.” This entry manifests because Eq. 2 must use thermodynamic temperature to calculate helium refractivity and estimate $\kappa(T)$. But $\kappa(T)$ is also used in Eq. 1 for $n - 1$, and later

$n - 1$ is used to determine T via Eq. 5. In short, there is some circularity (correlation) between T used to calibrate the refractometer (in helium) and T determined by the calibrated refractometer (in argon). The correlation is weak: for example, if T_{90} were used to calculate helium refractivity, the later determination of $T - T_{90}$ in argon would be in error by no more than 0.8 mK at 433 K, and there would be no problem of circularity. This work has used Ref. [14] to evaluate all thermodynamic temperatures in the helium determination of $\kappa(T)$, but the entry in Table 3 allows for 100 % uncertainty in the estimate $T - T_{90}$ at the indium freezing-point. Alternatively stated, the present estimate of uncertainty bounds both thermodynamic and ITS-90 values for temperature of the indium freezing-point. This estimate of uncertainty is surely overestimated, but this cautious “100 % uncertainty” is a fair approach to handle the correlation.

4.2.2 Uncertainty in ITS-90

Contributors to uncertainty in the ITS-90 realization are familiar [46], and are briefly itemized.

The local ITS-90 realization at the temperature fixed-points water, gallium, and indium is claimed uncertain at 0.03 mK, 0.04 mK, and 0.09 mK, respectively. The entry in Table 3 has the local fixed-point uncertainty propagated to 373 K. It is noted that the (global) consensus recommendations for fixed-point uncertainties are considerably larger. For example, Ref. [4] suggests the “current best practical realization” for the indium freezing-point is eight times larger than what is used for Table 3. The recommendations of Ref. [4] were influenced by standard deviations observed in results for international intercomparisons of fixed-point realizations, and therefore fairly represent a global $u(T_{90})$. More recent intercomparisons [47] support the guiding principle of Ref. [4]. The argument whether the global or a local ITS-90 fixed-point uncertainty is more technically consistent to report in Table 3 is set aside. Table 3 lists the local uncertainty, which is customary in $T - T_{90}$ literature [36–41]. But this entry underestimates $u(T_{90})$ as compared to the current best practical realization.

Interpolating water–gallium or water–indium has a subrange inconsistency. For the particular cSPRT used in this work, the difference between the two linear interpolating equations is 0.2 mK at the gallium melting-point. The entry in Table 3 treats subrange inconsistency as a global property of the ITS-90 scale, and uses the function recommended in Ref. [46], which has a maxima near 373 K. To be clear, all resistance thermometry in this work used the subrange (0 to 156.5985) °C. The subrange deviation function was deduced at the defining points for the triple-point of water and freezing-point of indium. The mention here of gallium was only to crossvalidate the subrange inconsistency. Further mention of gallium below entails its use as a check standard to build confidence in the reproducibility of the resistance thermometry.

Additionally, non-uniqueness arises in the ITS-90 scale when different cSPRTs are used on the same subrange. Although this experiment used one cSPRT for all measurements, the non-uniqueness is also treated as a global property of the ITS-90

scale. The entry uses the recommendation of Ref. [46], which also has a maxima near 373 K.

Resistive self-heating in the cSPRT was about 0.4 mK, and its value changed less than 0.1 mK between conditions inside the copper bore versus inside a glass test-tube inserted into a (fixed-point cell) thermowell. All resistance measurements in this work were corrected to zero-power.

The resistance bridge is a mid-level instrument, with some nonlinearity. As mentioned above, the cSPRT was calibrated at the fixed-points water, gallium, and indium. This formal calibration was performed in an ITS-90 calibration lab. However, the lab in which the $T - T_{90}$ determination was performed also had actively maintained water and gallium fixed-points. These fixed-points were realized four times throughout the 6-month measurement campaign, to build confidence in the reproducibility and stability of the cSPRT plus bridge. Reproducibility details are in Appendix 4.

Finally, gradients between the cSPRT and the RIGT were less than 0.1 mK, and have been corroborated by finite-element modeling and indirect tests tracking the constant-density resonance frequency [10]. Extensive characterization was done in argon and helium. Validation at the 0.1 mK level was also performed by direct measurement with two thermistors in the copper block. However, direct measurement at this level is complicated by thermistor stability and reproducibility, and finite-element modeling has much to offer when estimating small and rapidly changing thermal effects. For example, the gradient of chief concern is that which exists between the cSPRT (average temperature of a small volume) and the cavity mode (average temperature of a line between the cavity mirrors); consider Fig. 1. Conventional resistance thermometry techniques can not easily estimate the average temperature of a line, especially in this system where a gas “hot spot” exists [10] in front of the mirrors (i.e., in the 1 mm space between the copper block and cavity mirror, where the laser beam exits the bore-hole). Finite-element modeling and indirect tests are an essential method to characterize such effects.

5 Nitrogen as a Thermometric Reference

Nitrogen is a candidate gas for refractive-index gas metrology. Nitrogen has the advantage of being widely available in ultrahigh purity. For the specific case of pressure standards, it also has tradition on its side—use of nitrogen gas as a force generator in manometers and piston-gages has a long history. However, one argument against nitrogen as a candidate gas is that hardly any aspect of the physical system can be calculated with an accuracy approaching measurement. For pressure standards, it is debatable if this technical weakness outweighs traditional practice. However, as a temperature standard, there is a strong argument against using nitrogen: polarizability of a molecule has a temperature dependence.

Next is described how nitrogen’s temperature-dependent molar refractivity was measured. A dataset of $n(p, T_{90})$ -triplets was acquired in 99.9999 % purity nitrogen. The nitrogen dataset has the same dimensions as argon: nine isotherms, nineteen generated pressures, repeated five times. The nitrogen $n(p, T_{90})$ dataset and analysis script are included in the supplementary material.

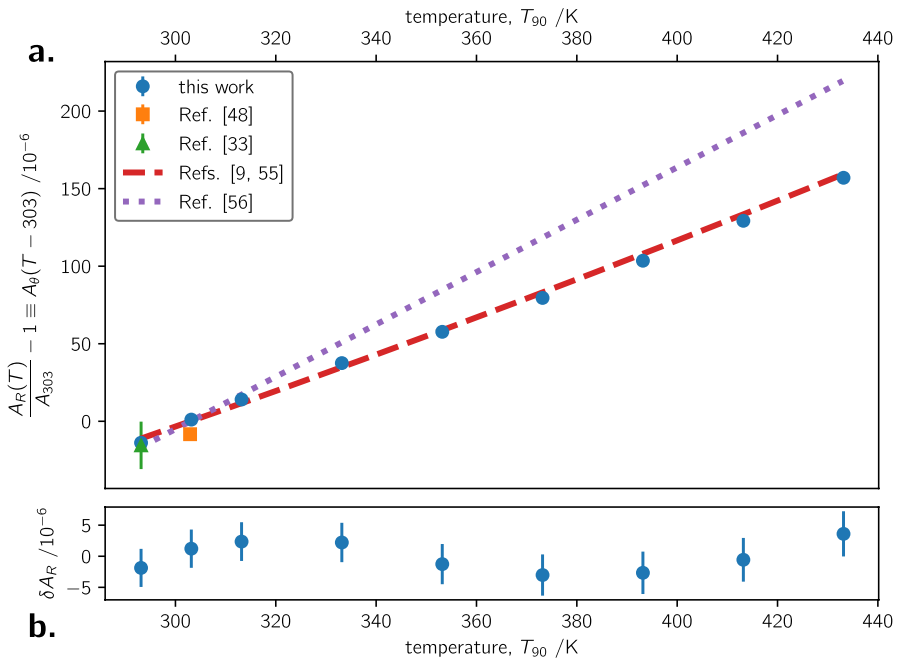


Fig. 4 (a) Temperature dependence for the molar refractivity of nitrogen gas. Errorbars span standard uncertainty, and on this scale most are smaller than the markers. (b) Residuals on the present work from Eq. 8. The errorbars span standard uncertainty

5.1 Temperature-Dependent Molar Refractivity

The multi-isotherm approach outlined in Sect. 4 was interpreted to have a linear temperature dependence:

$$A_R(T) = A_{303} [1 + A_\theta(T - 303)]. \quad (8)$$

The regression found $A_{303} = 4.446175(14) \text{ cm}^3 \cdot \text{mol}^{-1}$ and $A_\theta = 1.18(4) \times 10^{-6} \text{ K}^{-1}$ (at $\lambda = 632.9908 \text{ nm}$). The result is plotted in Fig. 4(a). Uncertainty on A_{303} adds in quadrature all entries in Table 3. The uncertainty on A_θ is dominated by the choice of $T - T_{90}$ (discussed below), which can change A_θ by more than two times the statistical (fit) uncertainty. Next follows discussion about A_{303} and A_θ in the literature context.

For individual temperature evaluations, the present $A_R(T)$ result can be compared with two previous measurements made in the same lab with different apparatus. These past measurements are also shown in Fig. 4(a). Reference [33] operated at $T_{90} = 293.15 \text{ K}$ with a cell-based refractometer and helium-calibrated pressure transducer; the two results agree within $3.7 \times 10^{-6} \cdot A_R$. Reference [48] operated at $T_{90} = 302.914 \text{ K}$ with a Fabry–Perot refractometer and mercury manometer; the two results agree within $8.0 \times 10^{-6} \cdot A_R$. These findings have an alternate interpretation: the molar refractivity of nitrogen has acted as

a reference property to establish equivalence between three different pressure scales. Reference [48] reported nitrogen molar refractivity relative to a mercury manometer [49]. Reference [33] reported nitrogen molar refractivity relative to the optical pressure scale [50]. The present work reports nitrogen molar refractivity relative to a dimensioned piston-gage [13]. Figure 4(a) and the measured temperature dependence of molar refractivity is the closure test, establishing equivalence at the $(5.9 \pm 4.3) \mu\text{Pa}\cdot\text{Pa}^{-1}$ level, where the $\pm 4.3 \mu\text{Pa}\cdot\text{Pa}^{-1}$ covers full range of disagreement between the three scales. This is a strong metrological result. In the broader context, claims below $10 \mu\text{Pa}\cdot\text{Pa}^{-1}$ equivalence to the mercury manometer are marred by historical problems [51] and recent nonlinearities observed by Egan et al. [48]; claims below $5 \mu\text{Pa}\cdot\text{Pa}^{-1}$ equivalence to a piston-gage are marred by historical disagreement in diameter metrology [52, 53]. For a nascent optical pressure scale, Fig. 4(a) reveals a small offset between Egan et al. [48] and this work, the two low uncertainty results near 303 K. The two $A_R(T)$ values are within mutual expanded uncertainty. Most of the disagreement between the two values is attributed to two or three small biases in Egan et al. [48]. One known bias concerns thermometry error: Egan et al. [48] operated under a validated 1.5 h settling-time to reach 0.5 mK gradients between the cavity mode and thermometer. About $2 \times 10^{-6} \cdot A_R$ can reasonably be attributed to insufficient wait time after a gas charge. A second bias is circumstantial: there is evidence that the dimensioned piston-gage used in the present work establishes a pressure scale about $3 \mu\text{Pa}\cdot\text{Pa}^{-1}$ lower than the mercury manometer scale [49, 54], upon which Egan et al. [48] was based. This possible offset (relative to Schmidt et al. [54]) is believed to originate in diameter metrology biases of about 70 nm. At present, this speculated bias is not well-supported, and needs further investigation.

The present measurement of A_θ can be compared with theoretical calculation. In the range ($293 < T < 433$) K, Sharipov et al. [9] calculate a relative change in (static) polarizability of $A_\theta = 1.14 \times 10^{-6} \text{ K}^{-1}$. The theoretical work of Sharipov et al. closely agrees with the older calculation of Buldakov et al. [55], which has a relative change in (optical) polarizability of $A_\theta = 1.07 \times 10^{-6} \text{ K}^{-1}$. The difference between these two theoretical estimates is not discernible on the scale of Fig. 4(a). The disagreement between the present measurement and theory for A_θ is 3.4 %, which is within experimental uncertainty; theoretical calculation has no formal estimate of uncertainty, but Buldakov et al. suggest it would be less than 1 %. Finally, two other experimental measurements are mentioned. Hohm [56] reported $A_\theta = 1.8(11) \times 10^{-6} \text{ K}^{-1}$ for optical measurements at $\lambda = 633 \text{ nm}$ and ($290 < T < 1100$) K; Hohm has 13 set temperatures, with standard deviation almost $10^{-3} \cdot A_R$. Schmidt and Moldover [57] reported $A_\theta = 1.4(3) \times 10^{-6} \text{ K}^{-1}$ for static (capacitance) measurements; Schmidt and Moldover have 3 set temperatures (273, 302, 323) K, but resolved A_θ as a statistically significant fit term.

Finally, extracting $A_R(T)$ from the $n(p, T_{90})$ dataset must decide how the measured T_{90} should be converted to T . That is, $A_R(T) \equiv \frac{2R(T_{90} + \Delta T)}{3A(T)}$, and the question is what to use for $\Delta T = T - T_{90}$. The analysis above derived A_{303} and A_θ using the old consensus estimate [14]. The choice was dictated by the fact that

the new consensus estimate [8] does not cover the range of the present measurements. Consequently, the values of A_{303} and A_θ produced by this $n(p, T_{90})$ dataset will change depending on what ΔT -function is used. Lastly, on a related note, residuals from Eq. 8 plotted in Fig. 4(b) are based on the old ΔT consensus estimate [14]. By contrast, residuals produced by a ΔT -function based on the argon measurements of the previous section (see Fig. 3) are 42 % smaller than what is plotted in Fig. 4(b). Naturally, this poses a question: does the theoretical calculation [9] of A_θ allow nitrogen to weight the $T - T_{90}$ estimate of Sect. 4? Answer: this work gives no weight to nitrogen as a viable gas for thermometry.

6 Coefficients $\mathcal{B}$ and $\mathcal{C}$

Section 4 outlined the multi-isotherm fitting. For the argon and nitrogen datasets, this procedure produced estimates of the nonlinear proportionality coefficients $\mathcal{B}$ and $\mathcal{C}$. These coefficients are described by the polynomials of Eq. 6 using the fit parameters listed in Table 4. These coefficients are anticorrelated and not uniquely identified by multi-isotherm regression. However, the combination recommended in Table 4 describes nonlinearity in Eq. 5 within $0.5 \mu\text{Pa}\cdot\text{Pa}^{-1}$ for the specified range.

The coefficients $\mathcal{B}$ and $\mathcal{C}$ describe deviation from ideal gas behavior, about 90 % of which is due to density virial coefficients B_ρ and C_ρ , and the remainder due to refractivity virial coefficients B_R and C_R . Since the density virial coefficients are so dominant, processing $\mathcal{B}$ and $\mathcal{C}$ can provide an accurate inference:

$$\begin{aligned} B_\rho &= \mathcal{B} \frac{3A_R}{2} + \frac{A_R}{4} + \frac{B_R}{A_R} \\ C_\rho &= \mathcal{C} \frac{9A_R^2}{4} + \frac{A_R B_\rho}{2} + \frac{2B_R B_\rho}{A_R} + \frac{A_R^2}{2} + \dots \end{aligned} \quad (9)$$

Table 4 Coefficients for Eq. 6, which describe the temperature dependence of the unitless nonlinear fit terms $\mathcal{B}$ and $\mathcal{C}$

Coefficient	Argon	Nitrogen
b_0	−2.5452(8)	−0.7827(6)
$b_1/(10^{-2} \text{ K}^{-1})$	3.105(5)	2.824(4)
$b_2/(10^{-4} \text{ K}^{-2})$	−1.169(8)	−1.125(6)
$b_3/(10^{-7} \text{ K}^{-3})$	3.39(9)	3.86(6)
$b_4/(10^{-10} \text{ K}^{-4})$	−4.3(4)	−6.9(3)
c_0	24.6(4)	30.7(3)
$c_1/10^{-2} (\text{K}^{-1})$	−5(2)	−10(2)

The numbers in brackets are statistical error only from the multi-isotherm regression. The $\mathcal{B}$ and $\mathcal{C}$ are anticorrelated, and care is required if one is used in Eq. 5 without relation to the other

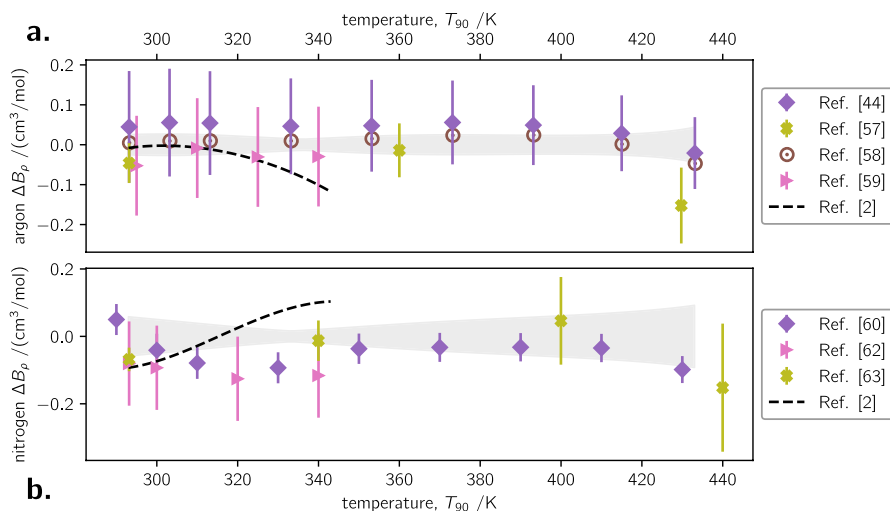


Fig. 5 Difference in the second density virial coefficient between literature and this work for (a) argon and (b) nitrogen. In all cases, ΔB_ρ is “literature value subtracted by this work.” The respective standard uncertainties are indicated by the errorbars (literature) and shaded area (this work)

The extra terms are listed in order of decreasing importance; $\frac{A_R}{4}$ is about $\frac{1}{10}B_\rho$; $\frac{A_R B_\rho}{2}$ is about $\frac{1}{30}C_\rho$; the truncated terms in C_ρ are fractionally $< 10^{-3}$. In this work, the operating pressure is too low to say anything meaningful about C_ρ . However, by fixing C *a priori* and re-performing the multi-isotherm regression, the deduced B_ρ tabulated in Table 5 are highly accurate. Next follows more detailed discussion on the argon and nitrogen gases. The comparisons with literature below use the convention $(\bar{x} \pm \sigma) \text{ cm}^3 \cdot \text{mol}^{-1}$, where $\bar{x}$ is mean difference and σ is standard deviation on the difference. The σ has no relevance to the mutual standard uncertainty in the statements below. The comparisons with literature are shown graphically in Fig. 5, where the difference ΔB_ρ is “literature value subtracted by this work.” The recommendations of Rourke [2] are illustrative only. For argon, Ref. [2] was weighted by temperatures down to 140 K, and well outside the present range. For nitrogen, Ref. [2] was weighted by a wide literature survey.

6.1 Argon

For argon, the fit coefficients can be compared with theoretical calculation. Estimates of B_{theory} and C_{theory} are synthesized via theoretical results for the refractivity [26, 27] and density [44, 45] virial coefficients, together with the experimental determination of the molar refractivity (Sect. 4). The comparison between this work (experimental) versus the current state of theory is shown graphically in Fig. 6. The figure also distinguishes the experimental values between those obtained by multi-isotherm (recommended) versus those of single-isotherm fitting. The agreement of the present results with theory is excellent for B , and not so good for C (as expected).

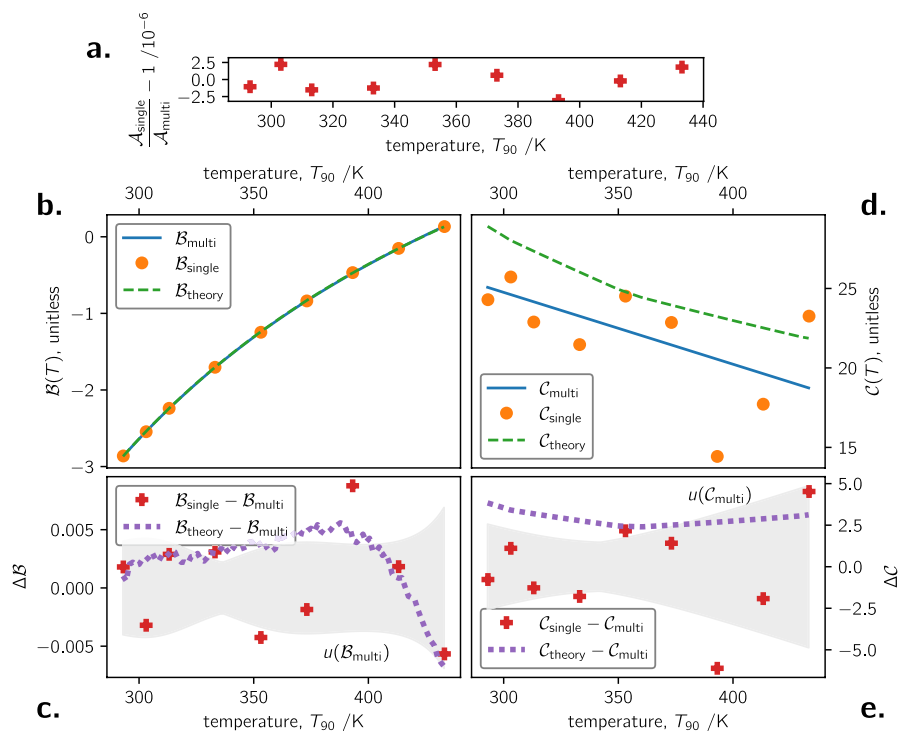


Fig. 6 The argon dataset. (a) Difference between the linear fit coefficient A determined by single-isotherm versus multi-isotherm regression. (b)–(e) Comparison of this work with theoretical [26, 27, 44, 45] estimates of the nonlinear parameters B and C . The shaded areas in (c) and (e) denote the Monte Carlo estimate of standard uncertainty

Table 5 Second density virial coefficient B_ρ deduced from B of the present measurements and Eq. 9

T_{90} (K)	Argon B_ρ (cm ³ ·mol ⁻¹)	Nitrogen B_ρ (cm ³ ·mol ⁻¹)
293.15	-16.595(26)	-5.869(59)
303.15	-14.565(27)	-3.920(46)
313.15	-12.684(25)	-2.119(34)
333.15	-9.316(15)	1.091(16)
353.15	-6.398(21)	3.867(31)
373.15	-3.846(26)	6.294(46)
393.15	-1.589(23)	8.444(57)
413.15	0.434(25)	10.370(69)
433.15	2.274(43)	12.108(92)

The numbers in brackets indicate standard uncertainty, estimated by Monte Carlo methods

The shaded area of Fig. 6 (c) and (e) shows the estimated standard uncertainty for $\mathcal{B}$ and $\mathcal{C}$ regressed in this work. The estimate of uncertainty used Monte Carlo analysis, as described at the end of this section.

To evaluate B_ρ in Eq. 9, the experimentally deduced A_R is used together with the theoretical estimate of B_R [26]. The multi-isotherm regression used $\mathcal{C}_{\text{theory}}$ as a known parameter, fixed by the theoretical estimates of B_R [26], C_ρ [45] and C_R [27]. (Note: inferring B_ρ is recursive, because $\mathcal{C}$ is also weakly dependent on B_ρ . The iterative solution was avoided by using a theoretical B_ρ [44] to fix $\mathcal{C}_{\text{theory}}$. This approximation incurs no significant error because the theoretical and “final” experimental values of B_ρ are so close.) The present measurements of B_ρ listed in Table 5 are $(0.04 \pm 0.02) \text{ cm}^3 \cdot \text{mol}^{-1}$ lower than theory [44], which is within one-third of the mutual standard uncertainty. The theoretical work of Lang et al. [44] is one of the first to assign uncertainty bounds on the calculated virial coefficients of argon; uncertainty in the calculation of Lang et al. is almost five times larger than the present measurements. The theoretical calculation of Jäger et al. [58] does not provide an uncertainty statement, but it is notable that its average disagreement from the present measurements is only $(0.006 \pm 0.019) \text{ cm}^3 \cdot \text{mol}^{-1}$. For experiment, the present work is $(0.07 \pm 0.06) \text{ cm}^3 \cdot \text{mol}^{-1}$ higher for the three temperatures overlapping the measurement section of Cencek et al. [45]; the agreement is within mutual standard uncertainty. For the four temperatures overlapping the experimental work of Tegeler et al. [59], the present measurements are $(0.03 \pm 0.02) \text{ cm}^3 \cdot \text{mol}^{-1}$ higher, and this disagreement is more than three times smaller than mutual standard uncertainty.

6.2 Nitrogen

Further analysis for nitrogen is hindered by lack of information with which to compare and enable additional evaluation. Estimates of $\mathcal{B}_{\text{lit}}$ and $\mathcal{C}_{\text{lit}}$ are synthesized from the calculated density virial coefficients [60], together with best-estimate (measurement) reference data in literature for the refractivity virial coefficients, which are scarce. It is emphasized that the second density virial coefficient of Subramanian et al. [60] is semi-empirical, not *ab initio*: the nitrogen pair potential [61] was adjusted so that the second density virial coefficient deduced from it matched experiment. Further, the three-body potential [61] for nitrogen is so approximate that experiment [62, 63] is likely more reliable than theory for C_ρ . For the second refractivity virial coefficient, $B_R(\text{cm}^6 \cdot \text{mol}^{-2}) = 0.741 - 1.29 \times 10^{-3} \cdot (T(\text{K}) - 303)$ uses the average of Montixi et al. [64] and Achtermann et al. [65] for the fixed value and the approximate calculation of Hohm [66] for the temperature dependence. (Compared to the rigorous theory of Garberoglio and Harvey [26], the approximate calculation of Hohm underestimates the temperature dependence of B_R for helium by 81 %, and for neon by 103 %. It is therefore unrealistic to expect the stated temperature dependence of nitrogen to be accurate within a factor of 2.) For the third refractivity virial coefficient, $C_R/(\text{cm}^9 \cdot \text{mol}^{-3}) = -97.3$, uses the average of Montixi et al. and Achtermann et al.; there is no information on the temperature dependence, but it would make negligible contribution at the densities of this work.

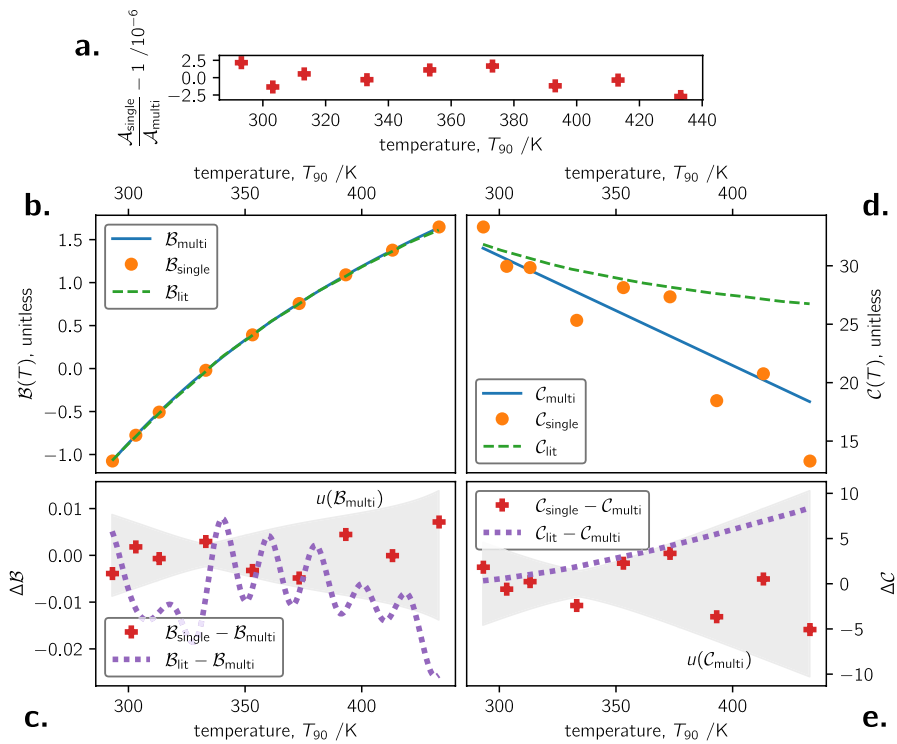


Fig. 7 The nitrogen dataset. (a) Difference between the linear fit coefficient A determined by single-isotherm versus multi-isotherm regression. (b)–(e) Comparison of this work with literature [60, 65] estimates of the nonlinear parameters B and C . The shaded areas in (c) and (e) denote the Monte Carlo estimate of standard uncertainty

The B and C of this work are compared to the synthesis B_{lit} and C_{lit} in Fig. 7. As with argon, agreement is excellent for B , and not so good for C . For the error plot in Fig. 7(c), the undulating trend on $B_{\text{lit}} - B_{\text{multi}}$ is caused by interpolation of the calculated tables of Subramanian et al. [60], because the temperature spacing used for calculation is too large. [By contrast, the undulation in Fig. 5(b) is not caused by interpolation error: the difference plot uses coincident temperatures.]

As mentioned, the results for B_ρ listed in Table 5 are affected by lack of quality information on the virial coefficients. Proceeding nonetheless, Eq. 9 was evaluated with $A_R(T)$ from this work and B_R as stated above. The multi-isotherm regression used a known C_{lit} set by the semi-empirical estimate for C_ρ [60] and the experimental B_R and C_R as stated above. (As with argon, recursion in B_ρ was avoided by using the semi-empirical B_ρ [60] to fix C_{lit} .) The result for the present work has B_ρ some $(0.041 \pm 0.020) \text{ cm}^3 \cdot \text{mol}^{-1}$ higher than calculation [60], which is generally within mutual standard uncertainty [see Fig. 5(b)]. For experiment, the present results are $(0.012 \pm 0.048) \text{ cm}^3 \cdot \text{mol}^{-1}$ higher at the three overlapping temperatures of McLinden and Lösch-Will [63]; agreement is within one-third of the mutual standard uncertainty. Also, for comparison to the four overlapping temperatures reported

by Nowak et al. [62], the present results are $(0.105 \pm 0.016) \text{ cm}^3 \cdot \text{mol}^{-1}$ higher, and agreement is within the mutual standard uncertainty.

6.3 Uncertainty in B_ρ

Briefly, the uncertainty in the second density virial coefficient of Table 5 has two sources: (i) fit statistics of the $n(p, T_{90})$ isotherms, and (ii) conversion of B to B_ρ via Eq. 9. In this work, the former is the dominant contributor.

Uncertainty in B and C is roughly described by scatter between single- and multi-isotherm fits seen in Figs. 6 and 7. A more sophisticated answer uses Monte Carlo analysis. The analysis simulated for variability in B and C caused by the following effects:

1. normally-distributed error in the $n(p, T_{90})$ triplets, as one or more of
 - $\pm 0.5 \times 10^{-6} \cdot (n - 1)$ error on every $n(p, T_{90})$ 5-sample average
 - $\pm 14 \%$ error on the distortion coefficient of the piston-gage [13]
 - $\pm 1.0 \mu\text{K} \cdot \text{K}^{-1}$ error on each 95-sample isotherm
2. $10\text{-}\sigma$ variation on the initial guess for the 25 free parameters in Eq. 5, where σ is statistical error on the “true values” of the 25 free parameters
3. adjustment of Eq. 6 to a cubic B or a quadratic C
4. addition of a known [58] or free D term to Eq. 5
5. insufficient data input to Eq. 5, tested by discarding one (of nineteen) randomly selected pressures from all isotherms

The result of the Monte Carlo simulation for $u(B)$ was converted to the equivalent uncertainty in B_ρ , and is used for the numbers in brackets in Table 5.

7 Conclusion and Outlook

Highly precise $n(p, T_{90})$ datasets for the gases helium, argon, and nitrogen were produced with an apparatus based on a Fabry–Perot cavity refractometer, a piston-gage, and a resistance thermometer with temperature fixed-points. The helium dataset allowed calibration of the refractometer compressibility. The argon dataset provided an estimate of error between thermodynamic temperature and ITS-90. The argon work is one of the few extending above $T > 400 \text{ K}$, and appears to be the first modern era estimate not based on a speed-of-sound technique. The nitrogen dataset produced an estimate of the temperature-dependent molar refractivity, which is in close agreement with theoretical calculation. The nitrogen work also served as a closure test, demonstrating $(5.9 \pm 4.3) \mu\text{Pa} \cdot \text{Pa}^{-1}$ equivalence between three independent pressure scales—a mercury manometer, a piston-gage, and a helium-based laser barometer. Finally, for argon and nitrogen, the datasets were analyzed to produce values for the second density virial coefficients, which have lower uncertainty than previous experimental determinations.

In fine distinctions of (pressure) metrology, this work has one fault: all gas properties reported are traceable to the diameter of a piston-gage. A truly absolute refractometer is needed which can measure the refractivity of helium within a few $10^{-6} \cdot (n - 1)$. When helium refractivity at known temperature is “generated” with a piston-gage, the generated pressure will be calculable based on fundamental properties of helium. Effectively, the refractometer will calibrate the piston-gage. At this point, the optical pressure scale will have superseded the mechanical one. Gas properties produced in a manner similar to this work would then be independent of the mechanical pressure scale. Semiprimary realization of the pascal would be possible in gases other than helium, with traceability to the kelvin provided by the optical properties of gas. It is hoped that the present contribution stimulates conversation about a *mise en pratique* for the new pascal, based on consensus values for the optical properties of gases. A blueprint might be the *mise en pratique* of the meter [67], a unit whose realization has been based on consensus values for the optical properties of gases for more than a generation.

Looking ahead for the current apparatus, $n(p, T_{90})$ datasets for gas-phase ordinary water and heavy water will next be undertaken. The temperature range will be the same as reported here, but the operating pressure will be limited $p < 2$ kPa (because the pressure transducer remains at room-temperature). Consequently, the water measurements are expected to be some 10^3 less accurate than what is reported in the present article. Nevertheless, $10^{-3} \cdot (n - 1)$ is near state-of-the-art for water vapor.

8 Supplementary Information

The supplementary material to this article is available from the NIST data repository at <https://doi.org/10.18434/mds2-3054>. The supplementary material is an archive file of research data containing:

- The $n(p, T_{90})$ dataset for helium. A Python script analyzes the data to produce the estimate of temperature-dependent compressibility, and reproduces Fig. 2.
- The $n(p, T_{90})$ dataset for argon. A Python script analyzes the data to determine $T - T_{90}$, and reproduces Fig. 3. Additionally, the output data $T - T_{90}$ (Table 2 in this article) are included in a separate text file, together with the estimated uncertainty in the determination. The Python script includes the further analysis undertaken on the nonlinear terms $\mathcal{B}$ and $\mathcal{C}$ to reproduce Fig. 6.
- The $n(p, T_{90})$ dataset for nitrogen. A Python script analyzes the data to reveal the temperature dependence of molar refractivity, and reproduces Fig. 4. The script includes the further analysis undertaken on the nonlinear terms $\mathcal{B}$ and $\mathcal{C}$ to reproduce Fig. 7.
- A Python script uses argon and nitrogen results from the present work to reproduce Fig. 5, a graphical depiction of difference with literature for the second density virial coefficient B_ρ .

Appendix 1: Derivation of Eq. 1

Resonance occurs in a two-mirror Fabry–Perot cavity when

$$2\pi m = \frac{4\pi L}{\lambda} + 2\phi + \Phi. \quad (10)$$

Here, m is the integer mode number, L is the separation between the front facets of the mirrors, $\lambda = \frac{c}{nv}$ is resonant wavelength, with c the speed of light in vacuum, ν the optical frequency, and n the refractive index of the medium between the mirrors. The treatment above includes phase-shifts caused by mirror reflection ϕ and Gouy phase Φ . It is the dependence of both these phase-shifts on refractive index that leads to small departures from Refs. [6, 11] mentioned in Sect. 2, as now explained.

The reflection phase-shift $\phi = \phi_0 + 2\pi\tau(\nu - \nu_c)$ can be modeled having a linear dependence on frequency near the center frequency of the mirror ν_c . Here, ϕ_0 is the phase-shift at the center frequency of the mirrors, and equals π when the high-index layer is outermost, and faces the incident laser. As one operates away from ν_c , the $\phi(\nu)$ dependence is described by the mirror group delay $\tau = \frac{1}{2\pi} \frac{d\phi}{d\nu}$. The group delay τ is customarily specified with vacuum as the incident medium. However, τ is medium dependent [68], and $\tau_{\text{gas}} = n\tau$ when the high-index layer is outermost.

For a Gaussian beam propagating in the z direction, the Gouy phase-shift is $\Phi(z) = \arctan(z/z_r)$ [69]. In Gaussian optics the Rayleigh length is defined $z_r = \pi n w_0^2 / \lambda$ by the beam waist w_0 at the focal point, and a related quantity is the beam-front radius of curvature $r(z) = z_r^2 / z + z$. When an input laser is mode-matched to a plano-concave FP cavity of length L , the cavity mode has a radius of curvature $r = z_r^2 / L + L$, which leads to the customary vacuum result $z_r = \sqrt{(r-L)L}$ in classic texts [69]. However, in operation a FP cavity refractometer adjusts frequency to maintain constant wavelength, and by definition $z_{r,\text{gas}} = n z_r$. So, when mode-matched in vacuum $\Phi = \arctan \left[\sqrt{L/(r-L)} \right]$ and in gas $\Phi_{\text{gas}} = \arctan \left[\frac{1}{n} \sqrt{L/(r-L)} \right]$. Taylor expansion of Φ_{gas} about the nominal geometry $\sqrt{L/(r-L)}$ shows $\Phi_{\text{gas}} = \Phi - (n-1) \frac{z_r}{r}$.

Returning now to Eq. 10, the resonance frequency at vacuum can be written

$$\nu_{\text{vac}} = \frac{c}{2L + 2\tau c} \left(m - \frac{\phi_0 - 2\pi\tau\nu_c}{\pi} + \frac{\Phi}{2\pi} \right). \quad (11)$$

From the $\phi(n)$ and $\Phi(n)$ explanations above, the resonance frequency in gas (ignoring compression of L) becomes

$$\nu_{\text{gas}} = \frac{c}{2nL + 2n\tau c} \left[m + \Delta m - \frac{\phi_0 - 2\pi n\tau\nu_c}{\pi} + \frac{\Phi - (n-1) \frac{z_r}{r}}{2\pi} \right], \quad (12)$$

with Δm being the integer change in mode number. Subtracting Eq. 12 from Eq. 11 and solving for refractivity yields

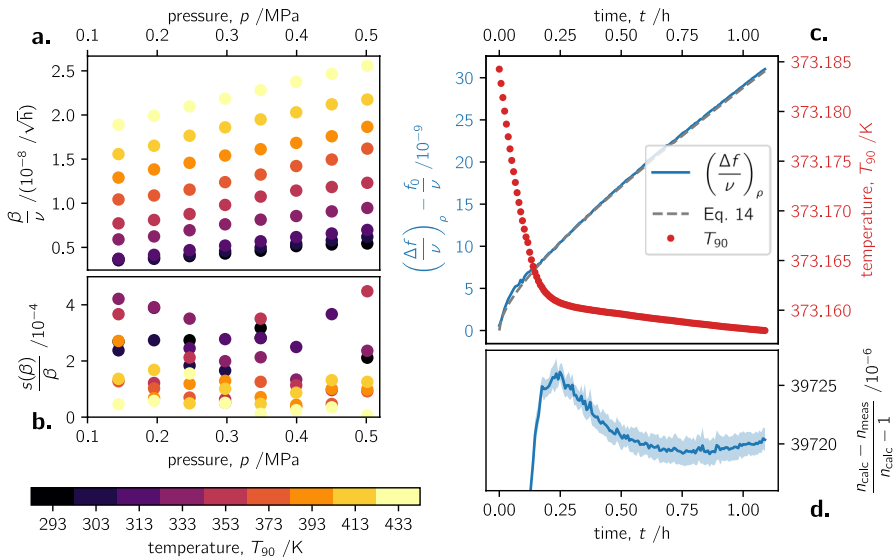


Fig. 8 (a) Fit coefficient β for the helium diffusion in Eq. 14, and (b) its statistical error as a function of pressure and temperature. (c) Change in constant-density fractional frequency and temperature immediately after a charge of 0.3 MPa helium. (d) Temporal evolution of difference between calculated $\frac{p}{T} \frac{3A_R}{2R}$ and measured $\frac{\Delta f}{\nu}$ refractivities. Deviation from constant value is attributed to systematic error in Eq. 14 describing the effect of diffusion on cavity length. The shaded area spans standard deviation on five repeat measurements

$$n - 1 = \frac{(\nu_{\text{vac}} - \nu_{\text{gas}})(1 + \epsilon_r) + \Delta m \frac{c}{2L}}{\nu_{\text{gas}} + \epsilon_r(\nu_{\text{gas}} - \nu_c) + \frac{c}{2\pi L} \frac{z_r}{r}}, \quad (13)$$

with the parameter $\epsilon_r = \frac{\tau c}{L}$ for two mirrors. The approximation $\nu_{\text{gas}} \approx m \frac{c}{2L}$ introduces the parameter $\epsilon_d = \frac{z_r}{r} \frac{1}{\pi m}$ to Eq. 1. Finally, Eq. 1 is produced from Eq. 13 by adding the distortion term $n \kappa \Delta p \equiv n \frac{\Delta L}{L}$ to the right-hand side of Eq. 13 and solving for $n - 1$.

Appendix 2: Details on the Helium Analysis

The constant density, fractional change in frequency was extrapolated to time-zero using a representative function

$$\left(\frac{\Delta f}{\nu}\right)_\rho(t) = \frac{1}{\nu} \left[f_0 + \beta \left(t^{\frac{1}{2}} - \frac{\pi}{16} \beta t \right) \right]. \quad (14)$$

This function is physically-motivated by the total amount of substance entering a solid absorbing rod, at short times, when exposed to constant surface concentration,

with the initial condition of a radially-distributed internal concentration [70]. Using Eq. 14, the effect of helium diffusion on cavity length is described by a single parameter β . The parameter is plotted in Fig. 8(a) for all pressures and temperatures in the helium $n(p, T_{90})$ dataset. The parameter was free for all pressures and temperatures, and any specific $\beta(p, T)$ exhibited deviation of about 2 % on the mean value. Deviation on the mean value β is expected; for example, because internal concentration changes, or because of correlation in the fit parameters. The purpose of the fit is to individually best describe (in the least squares sense) helium diffusion in each $(\frac{\Delta f}{\nu})_p$ data series. In this context, deviation on the mean value of β is not an uncertainty. Next follows discussion about $u(\beta)$.

Uncertainty in β is the largest part of $u(\kappa)$, and has three contributions. The first component is statistical error in the regression of Eq. 14, identifying f_0 and β . Relative statistical error in the fit parameter β is shown in Fig. 8(b). Combined, statistical uncertainty in f_0 and β contributes less than $2 \times 10^{-6} \cdot \kappa$. For any (p, T_{90}) , the statistical uncertainty in f_0 and β is considerably smaller than the standard deviation errorbars in Fig. 2(b). The combined statistical and systematic uncertainty in $\kappa(T)$ is now explained.

The second and largest component contributing to $u(\kappa)$ is error in the model of Eq. 14. This error shows as transient effects in the numerator of Eq. 2, the difference between calculated $n_{\text{calc}} \approx 1 + \frac{p}{T} \frac{3A_R}{2R}$ and measured $n_{\text{meas}} \approx 1 + \frac{\Delta f}{\nu}$ refractive indexes. The model error is visualized in Fig. 8(c) and (d), for representative helium data at $p = 0.3$ MPa and $T_{90} = 373$ K. Figure 8(c) shows the fractional change in resonant frequency and thermometer reading immediately after the helium charge. To be clear: β is signed positive, and diffusion causes cavity length to increase and the resonant frequency in gas to decrease; the increasing frequency of Fig. 8(c) is because the refractometer framework has $(\nu_{\text{vac}} - \nu_{\text{gas}}) \rightarrow \Delta f$. Figure 8(d) shows how the difference $n_{\text{calc}} - n_{\text{meas}}$ changes over time. Model error is the deviation of $n_{\text{calc}} - n_{\text{meas}}$ from constant value for times after settled. Model error may arise because Eq. 14 describes a rod; however, it is likely that thermal disturbance and gradients at $t < 0.2$ h have some influence, as well as gradual build-up of gas impurities. These transient effects and model error explain the large errorbars in Fig. 2(b), where it is clear deviation becomes larger at higher temperatures.

Finally, a third contributor to $u(\kappa)$ is irreproducibility in n_{meas} . Standard deviation for the five repeat n_{meas} measurements shows as the shaded band in Fig. 8(d). The contribution of irreproducibility in n_{meas} is about $3 \times 10^{-5} \cdot \kappa$.

To summarize combined $u(\kappa)$ by reference to Fig. 8(d): irreproducibility in n_{meas} plus statistical error f_0 and β is covered by the shaded area, and model error is covered by taking half the range of excursion for $(0.3 < t < 1.1)$ h.

[An aside: the wire suspension of Fig. 1 provides frictionless support of the cavity, and is an essential attribute of reproducible compressibility. Achieving the 1 mm clearance between metal surfaces and a swinging block of glass requires care. An initial characterization found semi-reasonable results for $\kappa(T)$, but some peculiarities in the $T - T_{90}$. It was found that one end of the cavity was resting on the bottom of the chamber. The effect was investigated more deliberately. The cavity was

taken off the suspension wires, and mounted on a pair of PTFE shims placed at the Airy points. The cavity rested on the bottom of the chamber, and the glass-to-aluminum contact was mediated by the two PTFE-to-PTFE mounting points. A full characterization in helium suggested κ_{303} increased 0.5 % and k_1 increased 7 %. The argon dataset was unreliable, exhibiting clear $\pm 2 \mu\text{Pa}\cdot\text{Pa}^{-1}$ quartic nonlinearity in the regression of Eq. 5, and temperature-cycle hysteresis of $11 \mu\text{K}\cdot\text{K}^{-1}$ in the estimate of $T - T_{90}$.]

Appendix 3: About Outgassing

Gases of purity 99.9999 % were employed for all measurements. The wait time between gas filling and the $(\Delta f, p, T_{90})$ sample acquisition allowed build-up of impurity in the initially pure gas volume. One way to observe the build-up of impurity is to study the resonant frequency of the cavity when filled with gas. The analysis is best done via the constant density effective difference frequency $(\frac{\Delta f}{\nu})_\rho$, which corrects fractional changes in resonant frequency to a condition of constant pressure and temperature. (Effectively, the correction is for changing temperature because the piston-gage generates nearly constant pressure by regulating volume.) At constant density, a pure volume would have constant refractivity, and $(\frac{\Delta f}{\nu})_\rho$ should be constant over time. Deviation from constant $(\frac{\Delta f}{\nu})_\rho$ means that refractivity is changing, most likely because of impurity build-up through outgassing. (The positive pressures of this work preclude leaks as a mechanism for impurity. Total gas volume was about 2 L, with 0.7 L in the chamber.)

Estimates of outgassing rates in the argon and nitrogen datasets are shown in Fig. 9. The ordinate is rate of change with respect to time on the constant density effective difference frequency $(\frac{\Delta f}{\nu})_\rho$, with correction for temporal drift in vacuum

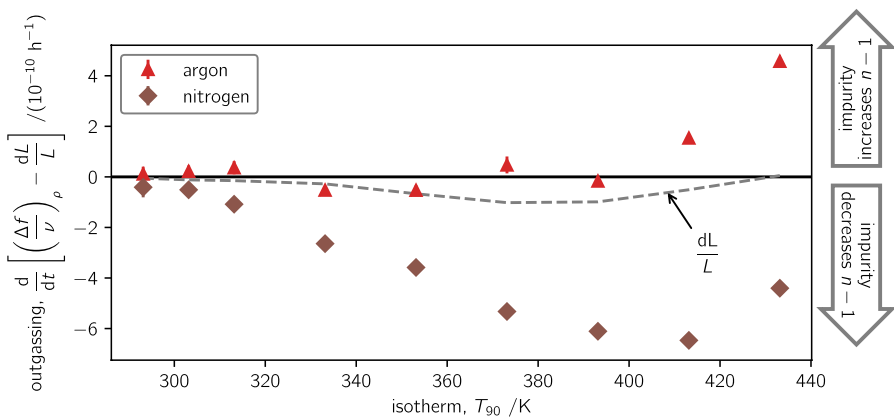


Fig. 9 Estimate of impurity build-up over time in the argon and nitrogen datasets. Each marker is the average over 5 repeats at the 19 generated pressures, and the barely visible errorbars show standard deviation

cavity length $\frac{dL}{L}$. The $\frac{dL}{L}$ is plotted as a dashed line; Fig. 2(d) shows that the $\frac{dL}{L}(T)$ trend was highly reproducible between the argon and nitrogen isotherms. Several qualitative comments can be made about Fig. 9:

- Outgassing is a minor problem in some cases. As a representative example: at 0.25 MPa and 373 K, nitrogen refractivity is $n - 1 \approx 5.4 \times 10^{-4}$, outgassing from Fig. 9 is $6 \times 10^{-10} \text{ h}^{-1}$, and the settling-time of the apparatus allows acquisition of a $(\Delta f, p, T_{90})$ sample within 1 h. So, without correction, outgassing would contribute $1.1 \times 10^{-6} \cdot (n - 1)$ error on the measurement of nitrogen refractivity.
- The major constituent of outgassing would be water vapor, which has a molar refractivity of $3.8 \text{ cm}^3 \cdot \text{mol}^{-1}$, relatively smaller compared to nitrogen $4.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ than compared to argon $4.2 \text{ cm}^3 \cdot \text{mol}^{-1}$. For all isotherms, Fig. 9 shows outgassing in nitrogen decreasing the refractivity of the initially pure gas volume. By contrast, argon isotherms $T_{90} < 393 \text{ K}$ show no observable outgassing. It appears that the impurity mixture outgassing in the sealed chamber is (fortuitously) very close to the molar refractivity of argon.
- For the $T_{90} = 433 \text{ K}$ isotherm (and to less extent the $T_{90} = 413 \text{ K}$ isotherm), impurities of molar refractivity larger than argon begin to build-up. The likely cause is polymeric hydrocarbon release [71], either from the elastomer o-rings or the wire insulation to the cSPRT.

Based on Fig. 9 and trends in $(\frac{\Delta f}{v})_\rho$, linear extrapolations to time-zero were applied to the argon and nitrogen datasets. For argon, corrections were applied to the two isotherms $T_{90} > 413 \text{ K}$. For nitrogen, corrections were applied to all isotherms. The linear extrapolation reduces error caused by outgassing and impurity to less than $0.2 \times 10^{-6} \cdot (n - 1)$.

Finally, as explained in Appendix 2, the $(\frac{\Delta f}{v})_\rho$ for helium is not constant because permeation changes the cavity length. Based on observations for argon and nitrogen

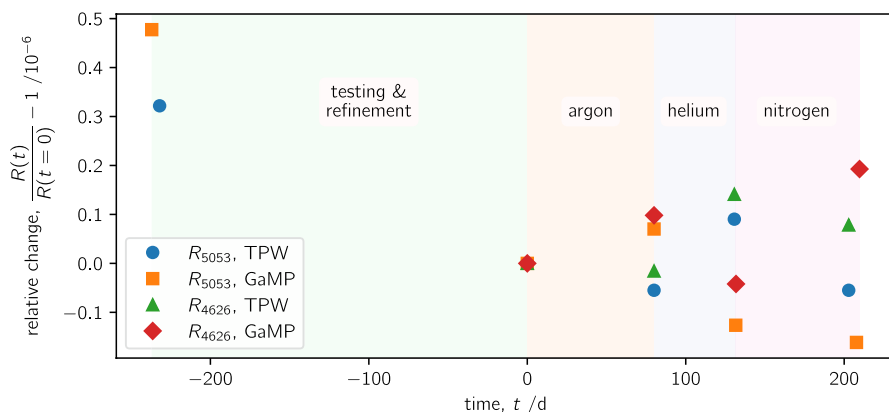


Fig. 10 Relative change in resistance of the two cSPRTs R_{5053} and R_{4626} at the ITS-90 fixed-points of water (TPW) and gallium (GaMP)

in Fig. 9, it is certain that the $(\frac{\Delta f}{\nu})_p$ of helium has a small additional component caused by outgassing, which could cause error up to $10^{-5} \cdot (n - 1)$. However, the helium data is also temporally corrected by a diffusion-motivated fit to $(\frac{\Delta f}{\nu})_p$. The diffusion correction simultaneously cancels most the effect of outgassing, but the correction is imperfect and residual (model) errors can be larger than $3 \times 10^{-6} \cdot (n - 1)$. More details in Appendix 2. Furthermore, helium diffusion presents a possible problem to the measurement sequence, because the cavity has absorbed so much gas that it takes a long time to return to its natural drift rate. Figure 10 shows nitrogen was measured after helium, which was not ideal. The cavity had to be left at 160 °C for 15 days for “all” the helium to be released. The reported measurement sequence could allow residual helium released from the glass to slowly contaminate the nitrogen (reduce its refractivity), which might explain some behavior in Fig. 9. This is not believed to be the case, because throughout extensive characterization of this system nitrogen has consistently been observed to have a weakly decreasing refractivity as a function of time. Furthermore, the drift rates on cavity length in Fig. 2(d) suggest that possible residual helium release would have been very small (i.e., because the vacuum drift rate during the nitrogen isotherms was similar to the vacuum drift rate during the argon isotherms).

Appendix 4: Crosschecks on Resistance Thermometry

Between the gas datasets, the resistance of the cSPRT used to infer gas temperature (R_{5053}) was repeatedly checked at the ITS-90 fixed-points of water and gallium. Two water triple-point cells were employed, one of which was capable of internal distillation. The water and gallium fixed-points were maintained in the same lab in which the RIGT took place. Therefore, repeated checks on the cSPRT resistance were accomplished with the same resistance bridge and cabling, and minimal disruption. Furthermore, a second cSPRT (R_{4686}) was repeatedly checked: this second cSPRT was not used in the RIGT, and stayed at room-temperature (when not cycled on the fixed-points). The combination of repeated checks of two cSPRTs in multiple fixed-points using the same (undisturbed) bridge allows reasonable assessment between drifts in the cSPRTs, the fixed-points, and the bridge.

The synopsis of the cSPRT crosschecks are shown in Fig. 10, and the plot is annotated with the activity ongoing between the resistance checks. The synopsis is shown as relative change from the initial resistance in either water or gallium. Before the initialization of R_{5053} , there was some 260 days refining procedure and system testing, in which system temperature was cycled between 293 K and 433 K multiple times. These data support the statement in Table 3 that reproducibility and stability for the cSPRT and resistance bridge was better than $0.2 \mu\text{K} \cdot \text{K}^{-1}$.

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