Polarizability of Helium and Gas Metrology

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(Received 26 March 2007; published 21 June 2007)

Using a quasispherical, microwave cavity resonator, we measured the refractive index of helium to deduce its molar polarizability A_ε in the limit of zero density. We obtained $(A_{\varepsilon,\mathrm{meas}} - A_{\varepsilon,\mathrm{theory}})/A_\varepsilon = (-1.8 \pm 9.1) \times 10^{-6}$, where the standard uncertainty (9.1 ppm) is a factor of 3.3 smaller than that of the best previous measurement. If the theoretical value of A_ε is accepted, these data determine a value for the Boltzmann constant that is only 1.8 ± 9.1 ppm larger than the accepted value. Our techniques will enable a helium-based pressure standard and measurements of thermodynamic temperatures.

DOI: 10.1103/PhysRevLett.98.254504 PACS numbers: 51.30.+i, 06.20.F−, 47.80.Fg

Fundamental gas metrology, such as determining the Boltzmann constant or developing a calculable pressure standard, requires a physical property amenable to both precise measurements and a thorough theoretical understanding. One such property is the molar polarizability $\wp$ of helium. Its density expansion

$$\wp \equiv \frac{\varepsilon_r - 1}{\varepsilon_r + 2}\frac{1}{\rho} = A_\varepsilon[1 + b(T)\rho + c(T)\rho^2 + \ldots], \quad (1)$$

is important for gas metrology for three reasons: (i) the coefficients A_ε, $b(T)$, and $c(T)$ are accurately calculated *ab initio*, (ii) the relative dielectric permittivity, ε_r, often called the "dielectric constant", can be accurately measured, and; therefore, (iii) the molar density ρ can be accurately determined from electrical measurements. During the last decade, the relative uncertainty of the *ab initio* value of A_ε, has been reduced from 20 [1] to 2 ppm [2], and then to 0.2 ppm [3]. (The uncertainties are one standard uncertainty and 1 ppm $\equiv$ 1 part in 10^6). Here, we report a new measurement of A_ε that reduces its experimental uncertainty from 30 [1] to 9.1 ppm. Our result, $A_\varepsilon = 0.517\,253\,5\,(47)\ \mathrm{cm}^3/\mathrm{mol}$, is 1.8 ± 9.1 ppm smaller than the most accurate theoretical value [3].

The present measurements are a step towards realizing a pressure standard that combines the virial equation of state of helium gas

$$p = RT\rho[1 + B_\rho(T)\rho + C_\rho(T)\rho^2 + D_\rho(T)\rho^3 + \ldots], \quad (2)$$

with electrical measurements of the density. The present techniques will lead to accurate determinations of the thermodynamic temperature and may lead to a more accurate value of the Boltzmann constant.

We determined A_ε and the refractive index $[n^2(p,T) \equiv \varepsilon_r\mu_r]$ of helium as a function of temperature and pressure, by measuring the microwave resonance frequencies of a helium-filled cavity. To calculate $n(p,T)$, Eqs. (1) and (2) are combined with the leading term of the density expansion of the relative magnetic permeability μ_r

$$(\mu_r - 1)/(\mu_r + 2) = \rho A_\mu(1 + \ldots) \quad (3)$$

($A_\mu \equiv 4\pi\chi_0/3$, where χ_0 is the diamagnetic susceptibility of one helium atom from the *ab initio* calculation in [4].) Solving for n^2 while neglecting small terms gives

$$(n^2_{\mathrm{calc}} - 1)/3\rho = (A_\varepsilon + A_\mu) + (A_\varepsilon b + A_\varepsilon^2)\rho + A_\varepsilon(A_\varepsilon^2 + A_\varepsilon b + c)\rho^2 + \ldots \quad (4)$$

Figure 1 shows that the measured values $n^2{}_{\mathrm{meas}}$ and the calculated values $n^2{}_{\mathrm{calc}}$ differ by, at most, 25×10^{-9}. However, they overlap when just one component (the isothermal compressibility of the resonator κ_T) of $n^2{}_{\mathrm{meas}}$ is changed by only 1.1 times its uncertainty. Table I lists the values, uncertainties, and sources of the virial coefficients needed to convert $n^2(\rho,T)$ to $n^2(p,T)$ as well as the parameters in Eqs. (2)–(4) that relate n^2 to A_ε. At 273 K, each of the tabulated components of $u_r(A_\varepsilon)$ in Table I is connected to the corresponding uncertainty component of the refractive index by $u_r(A_\varepsilon) \approx u(n^2) \times 1460/p^*$ where $p^* \equiv p/(\mathrm{MPa})$. In the virial equation, p and T are thermodynamic pressure and temperature; thus, they do not have uncertainties. However, their corresponding standards

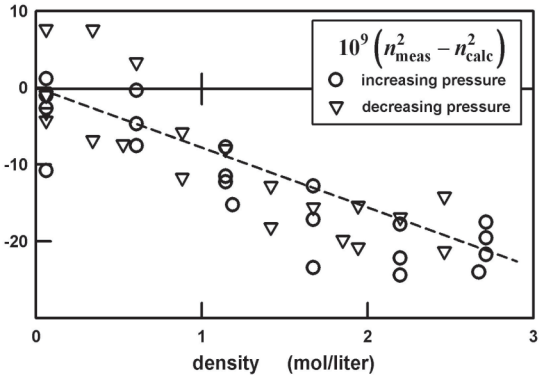

FIG. 1. Differences $n^2{}_{\mathrm{meas}} - n^2{}_{\mathrm{calc}}$. The values of n^2 range from 1 to 1.004. The dashed curve coincides with the baseline if the value of the resonator's isothermal compressibility, κ_T in Table I, is decreased by 1.1 times its estimated uncertainty, $u(\kappa_T)$.

TABLE I. Components of the uncertainty of A_ε [or, equivalently, of $(n^2-1)/(3\rho)$] as a function of $p^* \equiv p/(\mathrm{MPa})$ at 273.16 K.

Quantity/(unit)	Value (uncert.)	$10^6 u_r(A_\varepsilon)$	Reference
	Type B uncertainties from theory		
$A_\varepsilon/(\mathrm{cm^3\,mol^{-1}})$	0.517 254 19 (10)	0.2	[3]
$A_\mu/(\mathrm{cm^3\,mol^{-1}})$	−0.000 008 03 (17)	0.4	[4]
$B_\rho/(\mathrm{cm^3\,mol^{-1}})$	11.9301 (39)	$1.6p^*$	[5]
$b/(\mathrm{cm^3\,mol^{-1}})$	−0.098 (04)	$1.6p^*$	[6]
$c/(\mathrm{cm^6\,mol^{-2}})$	−1.34 (36)	$0.07(p^*)^2$	[7]
	Type B uncertainties from measurements		
$R/(\mathrm{J\,mol^{-1}\,K^{-1}})$	8.314 472 (15)	1.8	[8]
$C_\rho/(\mathrm{cm^6\,mol^{-2}})$	112.7 (20)	$0.36(p^*)^2$	[9]
$D_\rho/(\mathrm{cm^9\,mol^{-3}})$	820 (70)	$0.006(p^*)^3$	[9]
$p_{\mathrm{lab}}/(\mathrm{Pa})$		$[4.3^2+(1.1p^*)^2]^{1/2}$	[a]
$T_{\mathrm{lab}}/(\mathrm{mK})$	(0.6)	2.0	[a]
$10^{12}\kappa_T/(\mathrm{Pa^{-1}})$	6.0370 (46)	4.8	[a]
Impurities		<0.5	[a]
	Type A uncertainties from the present measurements		
$\Delta T_{\mathrm{res}}/(\mathrm{mK})$	(0.18)	$0.7\lvert 1-8.1/p^*\rvert$	[a]
$(f_0/f)^2$	$(1.7\times10^{-9}$	$2.5/p^*$	[a]
$P_{\mathrm{lab}}/(\mathrm{Pa})$		0.6	[a]

[a]This work.

(p_{NIST} and ITS-90) and their laboratory realizations (p_{lab} and T_{lab}) are approximations that have significant uncertainties. In accord with [10], we determined the type A uncertainties by statistical methods and the type B uncertainties by other means.

The uncertainty $u(n^2{}_{\mathrm{calc}})$ was calculated from only those components in Table I that have references to the published literature. At low pressures, $u(n^2{}_{\mathrm{calc}})$ is dominated by the 1.8 ppm uncertainty of the universal gas constant R [8]. Between 1 and 5 MPa, the uncertainty of the *ab initio* values of B_ρ [5] and b [6] are dominant; above 5 MPa the uncertainty of the measured value of C_ρ is dominant [9]. The uncertainty contributions from c [7] and D_ρ [9] are less important.

We measured $n^2(p, T)$ using a quasispherical microwave cavity resonator. These cavities were invented at NIST to simplify acoustic gas thermometry [11]. As sketched in Fig. 2, they have just enough asymmetry to separate the triply degenerate microwave resonances of a perfectly spherical cavity into three easily measured components. In common with spherical cavities, quasispherical cavity resonators have high microwave Qs. Their TE modes are insensitive to the dielectric constants of thin surface films (such as oxides) and their TM modes are insensitive to the magnetic permeability of thin surface films [12]. Finally, the average frequency of each microwave multiplet is insensitive to volume-preserving deformations of the cavity [13]. Because of this property, the values of $n^2{}_{\mathrm{meas}}$ averaged over the triplets had mutually consistent pressure dependencies, even though the deformation of the cavity under hydrostatic pressure was slightly anisotropic.

We deduced the refractive index of the helium gas filling the cavity from the relation

$$n^2_{\mathrm{meas}}(p,T) = [\langle f_0 + g_0\rangle(1+\kappa_T p/3)/\langle f_p + g_p\rangle]^2, \quad (5)$$

where, f_0 and f_p are the frequencies of a microwave resonance mode measured under vacuum and at pressure p and the brackets "$\langle\rangle$" indicate averaging over a triplet. In Eq. (5), κ_T is the isothermal compressibility of the cavity and g_0 and g_p are corrections to the frequencies that account for the penetration of the microwave fields into the inner surface of the cavity.

We designed the quasispherical shell to make the correction terms g_0, g_p, and κ_T small and easily measurable. In use, the resonator was enclosed by a pressure vessel and immersed in helium at pressures up to 6.4 MPa ($\approx$63 atm). The resonator was uncoupled from the deformation of the pressure vessel; however, the helium pres-

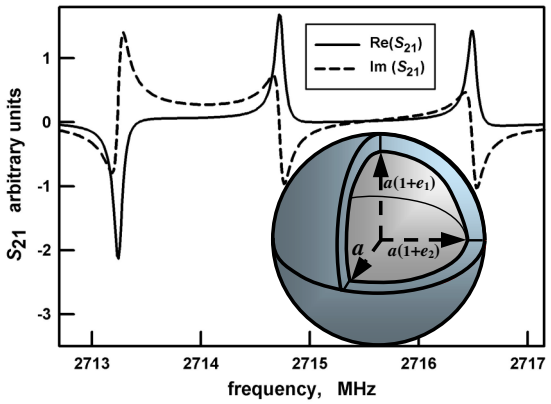

FIG. 2 (color online). Quasispherical cavity resonator and its spectrum near the TM11 mode. The dimensions of the cavity were: radius, $a \approx 4.82$ cm, $e_1 = 0.0013$, $e_2 = 0.0029$.

sure caused its dimensions to decrease by the factor $\kappa_T p/3$ ($=1.3 \times 10^{-5}$ at 6.4 MPa). We made the resonator from maraging steel because this alloy has a small value of κ_T and low ultrasonic absorption that facilitates the determination of κ_T with resonance ultrasound spectroscopy [14]. Five, nearly cubical, samples were cut out of the steel billet used to manufacture the resonator. These samples were heat treated simultaneously with the resonator. We determined the adiabatic compressibility k_S of these samples from measurements of their dimensions, mass, and approximately 50 ultrasonic resonance frequencies. The values of κ_S, combined with the measured thermal expansion ($\alpha_T = 9.85 \times 10^{-6}$ K^{-1}) and the constant-pressure heat capacity, determined κ_T. The scatter among the κ_S values accounts for 40% of the uncertainty of κ_T. Most of the remaining uncertainty came from the deviations of the resonance frequencies from the elastic model. Despite the effort devoted to determining κ_T, its uncertainty is a large component of the uncertainty of A_ε in this work.

The corrections to the resonance frequencies, g_0 and g_p, range from 9 to 17 ppm. We calculated them assuming that the cavity was spherical and that its copper-plated surface had the conductivity σ_{copper} reported for pure copper at low frequencies [15]. We tested these assumptions by measuring the quality factor Q_i of each component of the 4 microwave triplet resonances. The values of Q_i/Q_{theory} ranged from 0.91–0.94 implying that $\sigma \geq 0.82\sigma_{\text{copper}}$. Multiplying σ_{copper} by 0.82 in the calculation of g_0 and g_p decreased ${n^2}_{\text{meas}}$ by, at most 2×10^{-9}, which is negligible.

Impurities in helium raise its refractive index. (^{3}He effects are negligible; they will be discussed elsewhere). The supplier of the helium claimed that its purity was "99.9999% by volume." A metal manifold led the helium from the supplier's cylinder through a liquid-helium-cooled trap, a pressure regulator, and a chemically reactive getter to the resonator. Before use, the resonator was repeatedly flushed. When the flushing was not sufficient, $\Delta n^2 \equiv {n^2}_{\text{meas}} - {n^2}_{\text{calc}} > 0$ and Δn^2 decreased as the impurities were diluted by admitting helium into the resonator; however, Δn^2 was unchanged as the helium was withdrawn. This impurity effect was visible on plots such as Fig. 1. We searched for outgassing by monitoring the microwave frequencies for 20 h under constant conditions and by comparing a 30 h pressure cycle with a 90 h pressure cycle. No outgassing was found.

The resonator was maintained within a few millikelvins of T_{TPW}, the temperature of the triple point of water. (The SI defines $T_{\text{TPW}} \equiv 273.16$ K). The resonator's temperature was measured with a standard capsule platinum resistance thermometer inside the pressure vessel. Systematic uncertainties (≈ 0.6 mK) in relating our resistance thermometry to ITS-90 led to the term T_{lab} in Table I. The thermal expansion of the resonator and of the helium converted random uncertainties of the resonator's temperature ($\Delta T_{\text{res}} \approx 0.18$ mK, r.m.s.) into random uncertainties of the microwave frequencies. This effect dominated the experimental uncertainty at low pressures and led to the term ΔT_{res} in Table I.

The helium pressure was raised in steps (typically, $\sim$1 MPa) from 0.1 to 6.3 MPa and then lowered in similar steps. Following each step, five hours elapsed while the temperature of the resonator equilibrated with the bath. Then, the pressure, temperature, and resonance frequencies were recorded.

A network analyzer measured the microwave spectra in frequency intervals spanning the triplet modes TM11, TE11, TM12, and TE12. The average frequency of each triplet was determined with a fractional uncertainty between 1 and 2×10^{-9}. As expected at these frequencies (2.7–7.6 GHz), the experimental result for A_ε was independent of the mode. For helium, Ref. [16] reports $A_\varepsilon(f)/A_\varepsilon(f=0) - 1 = 22.6 \times 10^{-14}(f/\text{GHz})^2$. The mutual consistency of the results from TE and TM modes is evidence that any possible contamination of the cavity's surfaces did not affect the results.

The pressures p_{lab} were measured with a pressure balance (piston and cylinder) that had been calibrated by comparison with one of NIST's primary pressure standards [17]. At low pressures, $u_r(p_{\text{lab}})$ was dominated by the 4.3 ppm uncertainty of the effective area of the piston near 100 kPa. The effective area is a scale factor for every pressure measurement. The imperfect model of the deformation of the piston and cylinder under pressure increases the type B uncertainty at the higher pressures. Fluctuations of the pressure balance's temperature generated a type A uncertainty of $\sim 0.6 \times 10^{-6}\ p_{\text{lab}}$.

The data acquired at low pressures indicated that $\langle f_0 + g_0 \rangle$ continuously decreased, as if the average radius of the cavity were growing by the fraction 0.3×10^{-6}/year. Comparable dimensional changes have been observed in steel gauge blocks [18]. We accounted for this by fitting $\langle f_0 + g_0 \rangle$ with a linear function of time. This time dependence is the only property of the quasisphere determined by fitting data. Figure 1 displays the data acquired during 4 successive pressure cycles. After correcting for the cavity growth, the data taken with increasing and decreasing pressures are indistinguishable.

Equations (2) and (5) were used to determine $n^2_{\text{meas}}(\rho, T)$ from the frequency, pressure, temperature, and κ_T data. A quadratic polynomial in density fits the values of $n^2_{\text{meas}}(\rho, T)$ with the standard deviation $\sigma(n^2) = 4.1 \times 10^{-9}$. The coefficient of the polynomial's linear term is $3(A_\varepsilon + A_\mu)$ and its statistical uncertainty (1.8 ppm) accounts for the correlations among the coefficients of the polynomial and for the type A uncertainties in Table I. The sum in quadrature of the remaining uncertainties in Table I is 8.9 ppm or less below 2 MPa. Thus, the total uncertainty of $3(A_\varepsilon + A_\mu)$, as determined below 2 MPa, is 9.1 ppm. Using the value of A_μ from [4], we interpret this result as $A_{\varepsilon,\text{meas}} = 0.517\,253\,5\ (47)\ \text{cm}^3\ \text{mol}^{-1}$, which is equivalent to $(A_{\varepsilon,\text{meas}} - A_{\varepsilon,\text{theory}})/A_\varepsilon = (-1.8 \pm 9.1) \times 10^{-6}$. Fig-

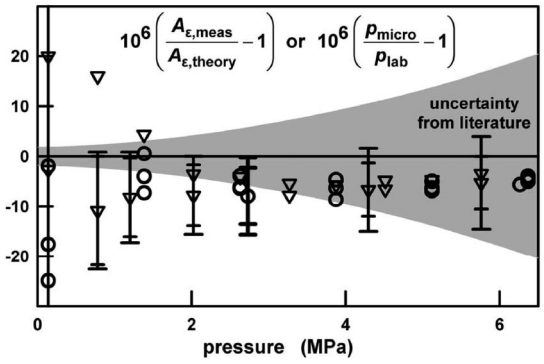

FIG. 3. Fractional deviations of A_ε from theory (outer error bars) and fractional deviations of the microwave-determined pressure p_{micro} from laboratory standards (inner error bars). The vertical coordinates from Fig. 1 are divided by $3\rho A_\varepsilon$. The outer error bars span "This work." uncertainties in Table I. The shaded area spans the literature-referenced uncertainties in Table I.

ure 3 separates the uncertainty components of A_ε at each pressure into those that come from the literature data (shaded area) and those that come from this work (outer error bars).

There are two alternative interpretations of the present results. Both alternatives rely on the theoretical values of A_ε and A_μ. The first alternative treats the molar gas constant R as the unknown with the result $R = 8.314\ 487\ (76)\ \mathrm{J\,mol\,K^{-1}}$. This value of R (and the value of the Boltzmann constant k deduced from it) is 1.8 ± 9.1 ppm larger than the currently accepted value and its uncertainty is 5 times larger than currently accepted uncertainty [8]. Notably, this determination of R is the only one since 1941 that does not rely on measurements of the speed of sound in argon. [8,19].

The second alternative interpretation of these results treats the pressure as the unknown that we deduced from microwave resonances: $p_{\mathrm{micro}} = (n^2{}_{\mathrm{meas}} - 1)RT/(3A_\varepsilon + 3A_\mu) + \ldots$ In effect, we implemented a helium-based pressure standard defined by solving Eqs. (2)–(4) for the pressure. Our microwave data at T_{TPW} in the range 0.8–2.8 MPa determine the pressure with the uncertainty $u_r(p_{\mathrm{micro}}) \leq 8 \times 10^{-6}$, as indicated by the inner error bars on Fig. 3. To reduce $u(p_{\mathrm{micro}})$ to $u(p_{\mathrm{NIST}})$, we must reduce the uncertainties of κ_T and ΔT_{res} by a factor of 3, and others must reduce the uncertainties of B_ρ, C_ρ, and b.

The present resonator techniques can determine the thermodynamic temperature T nearly as precisely as the best method available (acoustic thermometry in argon) while relying on a different property and on a different gas. To determine the temperature T "near" T_{TPW} (e.g., $0.7 < T/T_{\mathrm{TPW}} < 1.5$), the present measurements must be repeated in the same pressure range at the temperature T. State-of-the-art pressure measurements are not necessary if two resonators are operated simultaneously at identical pressures generated by a common gas supply. With one resonator operating at T_{TPW} and the second operating at T, the temperature ratio is computed from

$$\frac{T}{T_{\mathrm{TPW}}} = \lim_{p\to 0}\left(\frac{\rho_{\mathrm{TPW}}}{\rho_T}\right) = \lim_{p\to 0}\left(\frac{n^2_{\mathrm{TPW}} - 1}{n^2_T - 1}\right),$$

where n^2 is determined from frequencies using Eq. (5). Because the uncertainties of $n^2{}_{\mathrm{meas}}$ from p_{lab}, κ_T, B_ρ, and C_ρ are correlated at T and T_{TPW}, $u(T/T_{\mathrm{TPW}})$ will be significantly less than $u_r(A_\varepsilon) = 9.1$ ppm. Furthermore, one can eliminate the need to measure κ_T at T_{TPW} and T by measuring the microwave resonance frequencies while each cavity is immersed in helium gas and then again while each is immersed in, for example, neon.

We thank J. Hurly, J. Mehl, M. McLinden, and C. Lösch-Will for providing their results to us prior to publication. We thank L. Pitre for continuing interest and suggestions. While at NIST, E. F. M. was supported in part by the American Australian Association.

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