

TOWARDS AN ELECTROMAGNETIC PRESSURE STANDARD: DIELECTRIC PERMITTIVITY OF HELIUM AND ARGON MEASURED WITH QUASI-SPHERICAL MICROWAVE RESONATORS AND CROSS CAPACITORS

R. Gavioso¹, E.F. May², J.W. Schmidt³, M.R. Moldover³ and Y. Wang⁴

¹Istituto Nazionale di Ricerca Metrologica, Torino, Italy

²School of Oil & Gas Engineering, Univ. of Western Australia, Perth, Australia

³NIST Process Measurements Division, Gaithersburg, MD 20899, U.S.A

⁴NIST Quantum Electrical Metrology Division, Gaithersburg, MD 20899, U.S.A

Abstract

To develop electrically based pressure standards, we measured the dielectric permittivity of helium $\varepsilon_{\text{He}}(p, T)$ and argon $\varepsilon_{\text{Ar}}(p, T)$ using two independent techniques (quasi-spherical microwave cavities and cross capacitors). At 7 MPa, the microwave results for helium differ from NIST's pressure standards by $(18 \pm 37) \times 10^{-6}$.

Introduction

For electrically based pressure standards to compete with conventional pressure standards, which at 7 MPa have relative uncertainties of 17×10^{-6} [1], we must measure $\varepsilon_{\text{He}}(p, T)$ with part-per-billion precision. This is a demanding requirement for which we have developed specialized apparatus: quasi-spherical microwave cavities and cross capacitors. We determined the dielectric permittivity of helium $\varepsilon_{\text{He}}(p, T)$ and argon $\varepsilon_{\text{Ar}}(p, T)$ from a quasi-spherical microwave cavity (2.5 cm radius) and the expression

$$\varepsilon\mu_T = \left[(f_0 + g_0) / (f_p + g_p) \right]^2 (1 + 2\kappa_T p / 3) . \quad (1)$$

Independently, we determined $\varepsilon_{\text{He}}(p, T)$ and $\varepsilon_{\text{Ar}}(p, T)$ from multi-ring toroidal cross capacitor measurements (10 pF) and the expression

$$\varepsilon(p, T) = (C_p / C_0) (1 + \kappa_T p / 3) . \quad (2)$$

Here, f_0 and g_0 are the frequency and half-width of a microwave resonance in vacuum; f_p and g_p are the frequency and half-width of the same microwave mode at pressure p ; C_0 and C_p are the capacitance of the cross capacitor in vacuum and at pressure p ; μ_T is the relative magnetic permeability, and κ_T is the isothermal compressibility of the microwave cavity or of the cross capacitor. (κ_T accounts for the deformation of the apparatus under hydrostatic pressure.) The data range from 273 K to 295 K and up to 7 MPa.

At present, the microwave results are more accurate than the capacitance results [2]. In a quasi-spherical cavity, the degenerate microwave modes of a spherical cavity are split into separate, easily measured components, while retaining the high quality factors typical of spherical cavity resonators. Using copper-plated steel cavities, we obtained Q s of 25,000 and thus measured frequencies to a few parts in 10^9 . The stability of cross-capacitors makes them more suitable for high accuracy measurements of $\varepsilon_{\text{He}}(p, T)$ than conventional coaxial capacitors [3]. We used a commercial

bridge to measure capacitance and obtained capacitance ratios with an uncertainty 100 parts in 10^9 . Within this comparatively large uncertainty, the capacitance results and the microwave results are consistent.

Helium used as a Pressure Standard

The pressure is obtained from electromagnetic measurements of ε_{He} by combining the dielectric virial equation for helium

$$\frac{\varepsilon_{\text{He}} - 1}{\varepsilon_{\text{He}} + 2} = \rho A_{e, \text{He}} (1 + b\rho + c\rho^2 + \dots) , \quad (3)$$

with the density virial equation of state for helium

$$p = RT\rho \left(1 + B_p \rho + C_p \rho^2 + \dots \right) , \quad (4)$$

to obtain

$$p_{\text{electro}} = \frac{RT}{A_e} \frac{\varepsilon - 1}{\varepsilon + 2} \left(1 + \frac{B - b}{A_e} \frac{\varepsilon - 1}{\varepsilon + 2} + \dots \right) . \quad (5)$$

where first principles calculations determine the polarizability $A_{e, \text{He}}$ [4-6], permeability μ_T [7], and the dielectric and density virial coefficients b [8] and B_p [9]. We used measurements from the literature to determine the third dielectric and density virial coefficients c [10] and C_p [11]. In Eq. (4), R is the molar gas constant [12] and T is the thermodynamic temperature [13].

Uncertainty

$u(\varepsilon_{\text{He}} - 1)$: We determined κ_T of the maraging steels used to make the resonator and the cross capacitor by combining our resonance ultrasound spectroscopy data [14] with published thermophysical property data. At 7 MPa, the uncertainty $u(\kappa_T)$ contributed 7.6×10^{-6} to the relative standard uncertainty $u_r(\varepsilon_{\text{He}} - 1)$ for the microwave cavity and 3×10^{-6} to $u_r(\varepsilon_{\text{He}} - 1)$ for the capacitor. Inconsistencies among microwave modes and hysteresis of the microwave cavity combined with $u(\kappa_T)$ give the total relative standard uncertainty $u_r(\varepsilon_{\text{He}} - 1) = 9.6 \times 10^{-6}$. For the capacitor the bridge uncertainty dominated the uncertainty in $(\varepsilon_{\text{He}} - 1)$ and was more than twice as large as for the microwave cavity based measurements.

$u_r(\rho)$: Near 7 MPa, the total relative standard uncertainty of the density obtained from Eqs. (1) and (3) is 10.2×10^{-6} .

The contribution from $u(b)$ is 3.3×10^{-6} . The contribution to $u_r(p)$ from the molar polarizability $A_{\epsilon, \text{He}}$ is $< 1 \times 10^{-6}$. [4-6]

$u_r(p)$: Near 7 MPa, the largest contributions to the relative standard uncertainty in pressures $u_r(p)$ deduced from Eq. (4) comes from $\rho u(B_p)$ and $\rho^2 u(C_p)$ and is 20×10^{-6} and 23×10^{-6} respectively. Smaller uncertainties come from the gas constant ($u_r(R) = 1.7 \times 10^{-6}$ [9]), the temperature of the stirred bath ($u(T) = 1.5$ mK, $u_r(T) = 5 \times 10^{-6}$), and the uncertainty of the thermodynamic temperature near 273 K, which we estimate as 0.9 mK ($u_r(T_K) = 3 \times 10^{-6}$) from Fig. 13 of [13]. The total standard uncertainty is displayed as the shaded region in Fig. 1. Near 7 MPa the total relative uncertainty in pressure is 33×10^{-6} . The minimum in the relative pressure uncertainty occurs at about 3.5 MPa and is 18×10^{-6} .

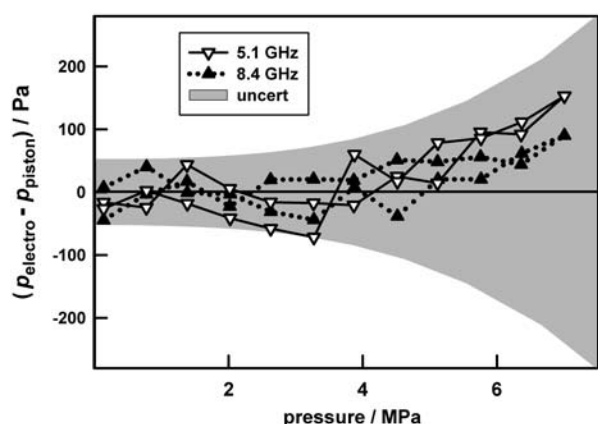


Figure 1. Comparison of pressure determined using the microwave resonator and the theory for $\alpha(p)$ at 273 K to a NIST pressure transfer standard (piston gauge). The shaded region indicates the total uncertainty of the present measurements.

Conventional Standards: At NIST, pressure standards near 7 MPa are piston gauges. They are calibrated against a mercury manometer at low pressures (0.02 to 0.36 MPa) and extrapolated to higher pressures. Figure 1 displays the difference between pressures obtained from the microwave measurements described above and a transfer piston gauge based on NIST's pressure standards. Near 7 MPa, the relative standard uncertainty, $u_r(p)$ is 17×10^{-6} for this gauge [1].

Comparison: We compared pressures obtained from ϵ_{He} to a piston gauge traceable to NIST's pressure standards; the difference was (123 ± 233) Pa at 7 MPa, or, fractionally, $(18 \pm 37) \times 10^{-6}$. At 3.5 MPa the fractional difference was $(0 \pm 25) \times 10^{-6}$.

Argon used as Secondary Standard

We also measured the ratio $(\epsilon_{\text{Ar}} - 1) / (\epsilon_{\text{He}} - 1) \approx 8$ under the same conditions that we measured $(\epsilon_{\text{He}} - 1)$; namely 273 K to 295 K and up to 7 MPa. Argon will become a convenient secondary pressure standard because the pressure dependence of its dielectric constant is 8 times larger than that of helium. When theory provides more

accurate values of B_p and C_p for helium, we will be able to reduce the uncertainty of the argon secondary standard without repeating the difficult measurements of $\epsilon_{\text{He}}(p, T)$. When a more accurate capacitance bridge becomes available, we shall repeat our comparison of the capacitor and the resonator with smaller uncertainties.

References

- [1] The BIPM key comparison data base; mass and related quantities (2002). <http://kcdb.bipm.org/AppendixC/>
- [2] E. May, L. Pitre, J.B. Mehl, M.R. Moldover and J.W. Schmidt, "Quasi-spherical cavity resonators for metrology based on the dielectric permittivity of gases", Rev. Sci. Instrum. Vol. 75, p3307 (2004).
- [3] J.W. Schmidt and M.R. Moldover, "Dielectric Permittivity of Eight Gases Measured with Cross Capacitors", Int. J. Thermophys. Vol. 24, p375 (2003).
- [4] W. Cencek, K. Szalewicz and B. Jeziorski, "Breit-Pauli and Direct Perturbation Theory Calculations of Relativistic Helium Polarizability", Phys. Rev. Lett. Vol. 86, P5675 (2001).
- [5] K. Pachucki, and J. Sapirstein, "Relativistic and QED corrections to the polarizability of helium", Phys. Rev. A., Vol. 63, p12504 (2000).
- [6] G. Lach, B. Jeziorski, and K. Szalewicz, "Radiative Corrections to the Polarizability of Helium", Phys. Rev. Lett, Vol. 92, p233001 (2004).
- [7] L.W. Bruch and F. Weinhold, "Diamagnetism of Helium", J. Chem. Phys. Vol. 113, p8667 (2000).
- [8] A. Rizzo, C. Hattig, B. Fernandez and H. Koch, "The effect of Intermolecular interactions on the electric properties of helium and argon. III Quantum statistical calculations of the dielectric second virial coefficients", J. Chem. Phys. Vol. 117, p2609 (2002).
- [9] J.J. Hurly, and M.R. Moldover, "Ab Initio Values of the Thermophysical Properties of Helium as Standards," J. Res. Natl. Inst. Stand. Technol. Vol 105, p667 (2000).
- [10] M.P. White and D. Guban, "Direct Measurements of the Dielectric Virial Coefficients of He⁴ between 3 K and 18 K," Metrologia, Vol. 29, p37 (1973).
- [11] A.L. Blancett, K.R. Hall and F.B. Canfield, "Isotherms for the He-Ar System at 50C, 0C and -50C up to 700 ATM", Physica Vol. 47, p 75 (1969).
- [12] M.R. Moldover, S.J. Boyes, C.W. Meyer and A.R.H. Goodwin, "Measurement of the Universal Gas Constant R Using a Spherical Acoustic Resonator," J.Res. Natl. Inst. Stand. Technol. Vol. 104, p11 (1999).
- [13] L. Pitre, M. R. Moldover, and W. L. Tew, "Acoustic Thermometry: New Results from 273 K to 77 K and Progress towards 4 K", Metrologia, Vol. 43, p142 (2006).
- [14] A. Migliori and J. Sarrao "Resonant Ultrasound Spectroscopy" (New York: Wiley) (1997).