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Polarizability of Helium, Neon, and Argon: New Perspectives for Gas Metrology

Christof Gaiser* and Bernd Fellmuth
Physikalisch-Technische Bundesanstalt Abbestr. 2-12, 10587 Berlin, Germany

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With dielectric-constant gas thermometry, the molar polarizability of helium, neon, and argon has been determined with relative standard uncertainties of about 2 parts per million. A series of isotherms measured with the three noble gases and two different experimental setups led to this unprecedented level of uncertainty. These data are crucial for scientists in the field of gas metrology, working on pressure and temperature standards. Furthermore, with the new benchmark values for neon and argon, theoretical calculations, today about 3 orders of magnitude larger in uncertainty, can be checked and improved.

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Electric dipole polarizability is a fundamental property of an atomic or molecular system. It describes the response of an atom or molecule to an external electric field. In the last decades, a large amount of progress has been achieved with *ab initio* calculations for the polarizability of helium, where relativistic and quantum-electrodynamical corrections can be treated. The level of uncertainty of 0.1 parts per million (ppm) [1,2] is unachievable via experimental techniques, even though the present work reduces the experimental uncertainty by almost a factor of 5 compared to the best previous work [3]. Therefore, it is an important touchstone for the detailed theoretical understanding of the helium system. On the other hand, *ab initio* calculations for larger rare-gas atoms like neon and argon reveal much larger uncertainties on the tenth of a percent level due to the more complex electronic structure. Thus, these calculations must be checked by comparison with reliable experimental data, which serves not only as a reference value for one special atom, but also as a benchmark value to prove the efficiency of different calculation techniques. Furthermore, the present results are a step towards primary gas thermometry [4] or a pressure standard [5] with helium (He), neon (Ne), and argon (Ar) [6]. They will allow for an accurate density measurement via an electrical or optical measurement.

The method of dielectric-constant gas thermometry (DCGT) [7] has recently been used very successfully to determine the Boltzmann constant k [8], the thermodynamic temperature T [4], and particle interactions [9], as well as the polarizability of Ne [10]. For understanding the results presented here, it is only necessary to know the following facts on DCGT. The determination of the molar polarizability A_ε is based on the measured pressure dependence of the capacitance C of a capacitor containing the measuring gas at constant temperature, i.e., on measuring isotherms. The data pairs of pressure p and relative capacitance change $[C(p)-C(0)]/C(0)=\gamma$, scaled to $\mu=\gamma/(\gamma+3)$, are fitted applying a virial expansion, which includes A_ε as one of the parameters:

$$p=A_1(\mu+A_2\mu^2+A_3\mu^3+A_4\mu^4\ldots). \tag{1}$$

The fitting coefficient of the first linear term is given by

$$A_1=\left(\frac{A_\varepsilon}{RT}+\frac{\kappa_{\mathrm{eff}}}{3}\right)^{-1}, \tag{2}$$

where R is the molar gas constant, and κ_{eff} denotes the effective compressibility of the capacitor, which describes the change of the capacitance only due to the mechanical deformation caused by the measuring gas. With T traceable to the temperature of the triple point of water (TPW) and κ_{eff} independently determined, the ratio A_ε/R is deduced from A_1.

The results presented here were obtained in two completely different setups. The first one (DCGTk [8]) was built for the determination of the Boltzmann constant at the TPW applying three 10 pF cylindrical tungsten carbide capacitors (TC1 to TC3), and traceably calibrated special pressure balances for pressures up to 7 MPa (for more details see Ref. [11]). The second setup (DCGT2 [4]) was originally established for the cryogenic temperature range, but for this experiment operated at the TPW. The 10 pF cylindrical copper-beryllium capacitors (C1 and C2) are operated at pressures up to 0.3 MPa using traceably calibrated pressure balances (for more details see Ref. [4]). In both setups, an autotransformer ratio capacitance bridge [12] and a high-purity gas-handling system including a mass spectrometer [8] are used, and the TPW temperature was realized with a standard uncertainty of order 0.1 mK [4,8].

For each of the five capacitors C1, C2, and TC1 to TC3, 8 to 10 TPW isotherms have been measured. The individual pressure ranges as well as the gases used are shown in Fig. 1. The data evaluation is straightforward according to Eq. (1), with the only limitation that the truncation of the series expansion at a certain order must be done. In the case of the low-pressure experiments with DCGT2, the A_1 value

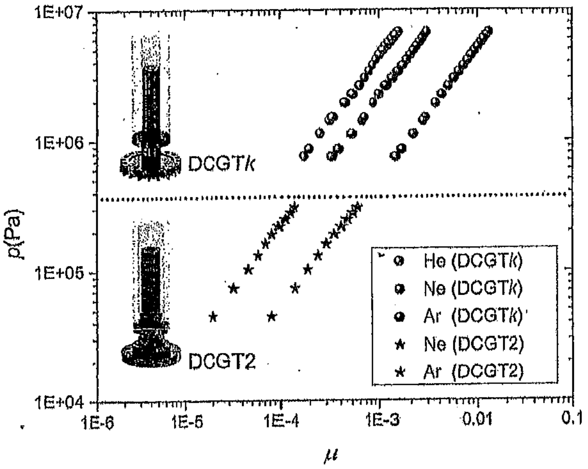

FIG. 1. Upper part above the grey dotted line: Typical measuring data pairs of pressure p and scaled relative capacitance change μ of high-pressure isotherms for He (black dots), Ne (red dots) and Ar (blue dots) measured with setup DCGTk [8]. The picture shows a tungsten carbide capacitor. Lower part below the grey dotted line: Typical measuring data pairs of p and μ of low-pressure isotherms for Ne (red stars) and Ar (blue stars) obtained with setup DCGT2 [4]. The picture shows a copper-beryllium capacitor.

of an isotherm is the weighted mean from fits of orders two to four (maximum power μ^2 to μ^4), whereby A_1 from the second-order fit was corrected with an estimate of the influence of the neglected third-order coefficient A_1A_3, using *ab initio* calculations (for more details see Ref. [4]). In the case of DCGTk, an independent approach was used. The results of third-order fits were taken considering a correction due to the influence of the neglected fourth-order coefficient A_1A_4. This influence was evaluated via overall fits of fourth and fifth order to the complete data set (for more details see Ref. [8]). The evaluation procedures lead to certain correlations of the type A uncertainties (uncertainty components of statistical nature) listed in Table I. According to Eq. (2), using the respective isotherm temperature and effective compressibility, the A_1 term can be transferred to the essential result of the measurement, namely, the ratio A_ϵ/R. The results for the individual capacitors as well as weighted-mean A_1 values are listed in Table II, and the uncertainties for these quantities in Table I. One of the most relevant uncertainty components arises from the measurement of capacitance changes, having a relative uncertainty of order 1 ppb and causing the type B component (nonstatistical, usually systematical) for μ in Table I. But since several pairs of p and μ are fitted on an isotherm, also a contribution to the type A component arises from the short-range nonlinearities of the inductive voltage divider used for balancing the capacitance bridge. The measurement of absolute pressures up to 7 MPa with an uncertainty of 1 ppm is a second, equally crucial challenge for the setup DCGTk. For this purpose, a system of two pressure-balance platforms, three piston-cylinder units with effective areas of 20 cm^2, and three of 2 cm^2 was designed, constructed, and evaluated [11]. Against this system, the piston-cylinder unit used in setup DCGT2 was calibrated with a relative standard uncertainty of 3.6 ppm leading to p correlations between both setups (see Table I). An additional component p_{head} for the pressure measurement is caused by the so-called head correction due to the gas column. For the light He atom, this component is very small, but for measurements with the heavier gases Ne and especially Ar, it becomes one of the dominating components. Maybe the most challenging quantity for measurements with He is κ_{eff}. Besides deformation and relative displacement, κ_{eff} may also be influenced by an

TABLE I. Uncertainty budgets of the DCGT results A_ϵ/R for He, Ne, and Ar. The estimates are given in ppm. At the end, weighted-mean values considering correlations (as listed in the last column) are given. The uncorrelated weighted-mean values are just included for comparison purposes. "Sum" means the root of the sum of the squared values.

Component	He			Ne				Ar				Correlation
	TC1	TC2	TC3	TC2	TC3	C1	C2	TC2	TC3	C1	C2	
Type A	2.6	1.6	1.9	2.2	2.1	9.1	11.2	1.2	1.2	11.2	9.2	partial
μ	1.0	0.4	0.4	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	complete
κ_{eff}	2.4	0.7	1.5	0.3	0.8	1.5	2.3	0.1	0.2	0.4	0.5	partial
T	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	complete
p	1.0	1.0	1.0	1.0	1.0	3.6	3.6	1.0	1.0	3.6	3.6	complete
p_{head}	0.2	0.2	0.2	1.0	1.0	2.5	2.5	2.0	2.0	5.0	5.0	complete
Impurities	1.0	1.0	1.0	0.8	0.8	0.8	0.8	0.1	0.1	0.1	0.1	No (independent)
Layers	0.5	0.5	0.5	0.3	0.3	0.3	0.3	0.1	0.1	0.1	0.1	No (independent)
M				0.1	0.1	0.1	0.1					complete
Sum	4.0	2.4	2.9	2.8	2.8	10.2	12.2	2.5	2.6	12.8	11.1	
Weighted mean		1.7			1.9				1.8			Without correlation
Weighted mean		1.9			2.4				2.4			With correlation

TABLE II. Results for the gases He, Ne, and Ar obtained with the three different capacitors TC1–TC3 applying setup DCGTk and the capacitors C1 and C2 applying setup DCGT2. The individual thermodynamic temperatures T, the effective compressibilities of the capacitors κ_{eff}, and the values of the fit coefficient A_1 according to Eq. (1) are listed. Furthermore, the individual results for the derived quantity A_ε/R for each capacitor and the final weighted mean for A_ε/R are given.

	He			Ne				Ar			
Capacitor	TC1	TC2	TC3	TC2	TC3	C1	C2	TC2	TC3	C1	C2
T (K)	273.149 0	273.157 6	273.157 6	273.158 6	273.158 6	273.159 4	273.159 3	273.160 9	273.160 9	273.159 3	273.159 4
$\kappa_{\mathrm{eff}} \times 10^{13}(\mathrm{Pa}^{-1})$	−9.370	−9.352	−9.895	−9.352	−9.895	−24.91	−24.59	−9.352	−9.895	−24.91	−24.59
$A_1 \times 10^{-8}$ (Pa)	43.966 96	43.968 09	43.971 71	22.848 65	22.849 67	22.875 59	22.875 26	5.485 979	5.486 049	5.487 553	5.487 506
$A_\varepsilon/R \times 10^8$ (m^3 K/J)	6.221 128	6.221 148	6.221 132	11.963 64	11.963 61	11.963 77	11.963 65	49.801 08	49.800 93	49.800 66	49.800 83
$A_\varepsilon/R \times 10^8$ (m^3 K/J)	6.221 140(12)			11.963 63(28)				49.801 00(12)			

eccentricity of the capacitor electrodes and a relative tilt of them. Furthermore, a rigid capacitor is a complicated geometrical object because electrically isolating pieces and stabilizing screws are necessary. Thus, the isothermal compressibility of a composite must be determined. For the tungsten-carbide capacitors of DCGTk (design see Fig. 1 upper part), direct determinations with relative standard uncertainties of κ_{eff} ranging from 0.05% to 0.17% were achieved (for more details, see Ref. [8]). In the case of DCGT2, the compressibilities of the copper-beryllium capacitors C1 and C2 (for design see Fig. 1, lower part) have been determined from low-pressure He isotherms equivalent to the ones shown for Ne and Ar in Fig. 1 (for more details see Ref. [4]). This approach led to uncertainties for κ_{eff} ranging from 0.08% to 0.12%. The use of ultrapure gases in combination with purifiers, getters, a mass spectrometer, and an appropriate gas-handling system [7] reduced the uncertainty component arising from impurities to a very small level (see Table I). The isotopic composition of the gases has generally a very small effect. For He, the natural abundance of the isotope ^{3}He is only 1.3 ppm and the relative deviation of the polarizabilities of the two isotopes amounts only to about 0.01%. Thus, for He the effect is negligible. The effect of finite mass of the nucleus on the polarizability can be estimated by the scaling factor $(1 + m_e/M)^3$, where M is the mass of the nucleus and m_e the electron mass. Applied to Ar, with a natural abundance of ^{40}Ar of 99.6% and the very small ratio m_e/M, this leads to a negligible effect on the polarizability. Only for Ne, with a difference for the polarizability between ^{22}Ne and ^{20}Ne of about 7.5 ppm, the maximum variation of the natural composition described in Ref. [13] leads to an additional component of 0.08 ppm. For several individual uncertainty components listed in Table I, correlations between the different groups of capacitors have been considered following the procedure explained in Ref. [8]. For T and p also correlations between the two different setups exist. The consideration of correlations increases the uncertainty of the weighted-mean A_ε/R value of Ar by 30%. The weighted-mean A_ε/R values given in Table II are the essence of the DCGT measurement. For all three noble gases, the DCGT determinations have the lowest experimental uncertainties ever achieved. In the case of He, three high-pressure results obtained with the capacitors TC1 to TC3 are combined to a weighted-mean value. For Ne and Ar, two high-pressure results (obtained with TC2 and TC3) and two low-pressure results (C1 and C2) are considered, respectively. To enable a comparison with literature data for the molar polarizability A_ε, the ratios have been converted to A_ε values using the k and N_{A} values published recently by CODATA [14] as a basis for the redefinition of the units kelvin and mole. The individual DCGT results are shown in the left-hand plots of Fig. 2 and Table III.

The following comparison between the DCGT results and literature data is not intended to be complete, but just to give an impression of existing information and level of uncertainty. For Ne and Ar the spread of the theoretical data in literature is substantial. Most state-of-the-art calculations

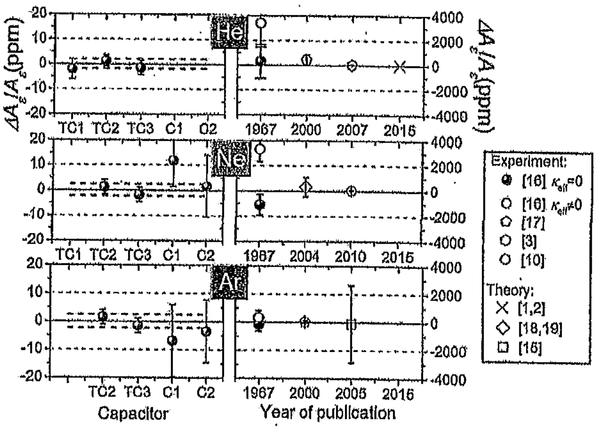

FIG. 2. Three plots on the left: Black dots: Relative deviations $\Delta A_\varepsilon/A_\varepsilon$ in ppm of the individual results obtained with capacitors TC1, TC2, TC3, C1, and C2, respectively, from the correlated weighted mean of them are shown for He, Ne, and Ar. Dashed red lines: Confidence intervals of the correlated weighted-mean values corresponding to the relative standard uncertainties. Three plots on the right: Relative deviations in ppm of different theoretical and experimental literature results (for more details see text) from the correlated weighted-mean values are shown.

TABLE III. The final weighted mean of A_ε for He, Ne, and Ar of this work as well as the experimental and the theoretical values plotted in Fig. 2 are given. The uncertainties given in parentheses are standard uncertainties (for Ref. [15], see text).

	$A_\varepsilon^{\mathrm{He}}$(cm^3/mol)	$A_\varepsilon^{\mathrm{Ne}}$(cm^3/mol)	$A_\varepsilon^{\mathrm{Ar}}$(cm^3/mol)
This work	0.517 254 4(10)	0.994 711 4(24)	4.140 686(10)
Experiment	0.517 40(70) [16]	0.993 60(80) [16]	4.140 0(20) [16]
	0.517 47(20) [17]	0.994 727(11) [10]	4.140 78(39) [17]
	0.517 253 5(47) [3]		
Theory	0.517 254 079(52) [1,2]	0.995 03(75) [18,19]	4.140(11) [15]

have been perfomed with so-called coupled-cluster methods (CCMs). The idea is to include two-, three-, and possibly higher-electron excitations by assuming the wave function in an exponential form and calculating the exponent directly. Another approach, with no restrictions on the multiplicity of excitations, used for a few electron systems like Ne, is the so-called full configuration interaction (FCI). Here, all possible combinations of occupied virtual excitations and related Slater determinants are taken into account. The combination of CCM calculations with separate relativistic corrections [18] and a benchmarking considering FCI results [19] lead to a value of 2.661 7(20) atomic units (a.u.) for Ne, which corresponds to 0.99503 cm^3/mol (details see in Ref. [10]). For Ar, FCI benchmarking is not yet available, due to the high number of electrons. As a nonrelativistic estimate, the value of 11.065(3) a.u. from Ref. [15] is taken (the upper and lower bound, estimated in Ref. [15] by comparing CCM results of different groups, was transferred to a standard uncertainty applying a rectangular distribution). Finally, a comparison of three different calculations of the relativistic effects [20–22] lead to a correction of $+0.01(1)$ a.u. and, therefore, to a final CCM value of 11.075(30) a.u. or 4.140(11) cm^3/mol. In summary, the uncertainties from theory for Ne and Ar are almost 3 orders of magnitude larger than the experimental ones presented here. Within the uncertainty estimates of theory, the values are in good agreement with this work.

On the contrary for He, stimulated by experimental activities, e.g., Ref. [5], the *ab initio* calculations, including relativistic and higher order QED corrections, have been improved drastically by the group of Refs. [1,2] and are now on a sub-ppm level of uncertainty. This work is the first experimental test of these calculations on the ppm level and, therefore, crucial for the use of helium as a standard in metrology.

Concerning the experimental data, the agreement between former experiments, one of them 50 years old [16], is quite impressive. Thereby, it must be emphasized that the data in Ref. [16], listed in Table III, is the low-pressure data without correction of the pressure distortion of the capacitors. In Fig. 2, both the uncorrected and the corrected data are shown, which supposes a wrong compressibility correction. A careful measurement of the dielectric constant with capacitors [17] achieved uncertainties of 100 ppm for Ar and 400 ppm for He. The results are in very good agreement with the present work. Two highly accurate determinations on the 10 ppm level have been achieved by a microwave technique in 2007 for He [3] and by DCGT1, a forerunner setup of DCGT2, in 2010 for Ne [10]. Both measurements agree with the new determinations within the expanded combined uncertainties.

The uncertainty level of 2 ppm for the polarizabilities of neon and argon is a completely new situation for gas metrology. Theoretical calculations and approaches for many electron systems can now be tested and improved. In addition, for the first time, this allows the use of another gas besides helium in a dielectric-constant or refractive-index measurement to determine T with a relative uncertainty of only a few ppm. This is a major step towards a gas-based standard of pressure, temperature, etc. [5,6], with an easily manageable gas like argon.

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*christof.gaiser@ptb.de

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