Measurement of the Universal Gas Constant R Using a Spherical Acoustic Resonator

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We report a new value for the universal gas constant R: 8.314471 ± 0.000014 J mol^{-1} K^{-1}. The standard error of R has been reduced by a factor of 5, to 1.7 ppm. R was determined from the speed of sound in argon contained within a thick, spherical shell at the temperature of the triple point of water T_t. The volume of the shell was measured by our weighing the mercury required to fill it at T_t. The molar mass of the argon was determined relative to that of a standard with accurately known chemical and isotopic composition by use of speed-of-sound data.

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With readily available technology (e.g., triple-point cells and platinum resistance thermometers), it is possible to define and to reproduce states of particular temperatures with much greater precision than it is possible to measure the fundamental statistical mechanical quantities characterizing such states (e.g., the average kinetic energy E in a degree of freedom, or the derivative of the internal energy with respect to the entropy at constant volume). Accordingly, the International System of Units (SI) defines temperature as an independent physical quantity and the kelvin (K) as the unit of that quantity. The definition specifies that the temperature T_t of the triple point of water is exactly 273.16 K. With this specification, one can define Boltzmann's constant k, as the ratio $2E/T_t$, and one can define the universal gas constant R, as the ratio $2EN_A/T_t$. (Here N_A is Avogadro's constant.) In this work we have redetermined R with the result

$$R = 8.314471 \pm 0.000014 \text{ J/(mol K) (1.7 ppm)},$$

where the error quoted is a standard deviation. This new value of R is consistent with other recent determinations of R; however, it is 5 times more accurate than the best previous value.[1] The new value of R leads to more accurate values of Boltzmann's constant,

$$k = R/N_A = (1.3806513 \pm 0.0000025) \times 10^{-23} \text{ J/K (1.8 ppm)},$$

and of the Stefan-Boltzmann constant σ,

$$\sigma = 2\pi^5 k^4/15h^3c^2 = 2\pi^5 R^4/15N_A(N_A h)^3 c^2 = (5.670399 \pm 0.000038) \times 10^{-8} \text{ W/(m}^2\text{ K}^4\text{) (6.8 ppm)}.$$

Here we have used the values of N_A, Planck's constant h, and the more accurately known molar Planck constant $N_A h$ resulting from the 1986 adjustment of the fundamental physical constants.[2]

The more accurate values of R, k, and σ will be most useful for primary thermometry (e.g., gas, noise, acoustic, and radiation thermometry) with thermometers whose design does not permit them to be used at T_t where the temperature scale is defined. The other roles of R in metrology and the methods used in prior determinations of R have been reviewed by Colclough.[3]

The present redetermination of R is based on a new measurement of the speed of sound c in argon at T_t. Elementary considerations of hydrodynamics and the kinetic theory of dilute gases lead to the relations

$$\tfrac{1}{2} m v_{\text{rms}}^2 = \tfrac{3}{2} kT, \quad c^2 = \tfrac{1}{3} \gamma v_{\text{rms}}^2$$

(v_{rms}^2 is the mean square speed of the molecules, m is the mass of one molecule, and γ is the ratio of the specific heat capacities which has the value $\gamma_0 = \frac{5}{3}$ for dilute monatomic gases). Thus, a measurement of the speed of sound in a dilute monatomic gas at T_t is a measurement of v_{rms} at T_t and it would be a measurement of k if m were known accurately. Relative isotopic masses are extremely well known on a scale of atomic mass units; however, the knowledge of m for any *pure* gas is limited either by the uncertainty in the relative abundances of its isotopes or by the uncertainty in N_A, the constant[4] which relates the atomic mass unit to the kilogram.

We deduce the speed of sound from measurements of the frequencies $f_{0,n}$ of the radially symmetric acoustic resonances in argon contained within a thick spherical shell. These frequencies are insensitive to geometric imperfections that leave the internal volume of the shell unchanged. R is related to the frequencies, the volume, and the molar mass M by the highly simplified equations

$$R=\frac{c_0^2 M}{T_t \gamma_0}=\frac{1}{T_t}\left[\frac{f_{0,n}}{\nu_{0,n}}\right]^2 V^{2/3}\frac{M}{\gamma_0}. \tag{1}$$

($\nu_{0,n}$ is an eigenvalue which is known exactly.) Corrections to Eq. (1) have been derived[5-8] and confirmed by detailed experiments.[5-7] The complete theory, to be published elsewhere,[5] starts with the Navier-Stokes equations and treats the following phenomena exactly for the case of a geometrically perfect sphere: (1) the thermal boundary layer near the resonator wall, including imperfect thermal accommodation, (2) bulk dissipation, and (3) the coupling of the shell motion and the gas motion. Perturbation theory is used to account for surface roughness, effects of transducers, and imperfections in the geometry. Nonlinear effects are negligible at the low sound-pressure levels used here. The theoretical corrections to the Navier-Stokes dispersion relations resulting from mean-free-path effects at low pressures[9] or from the kinetic theory of moderately dense spheres[10] are also negligible. Indeed, the fact that we obtained consistent results at various frequencies can be viewed as a confirmation of the Navier-Stokes dispersion relations at the part-per-million level.

Table I lists the important contributions to the standard error of R from the measurements of the quantities in Eq. (1). We now consider them in turn.

For the determination of the volume, we weighed the mercury required to fill the resonator while it was maintained at T_t. The uncertainty in the volume is dominated by our imperfect knowledge of the thermal expansion of mercury[11] between T_t and 20 °C. Three volume determinations were made during an 8-month interval. The standard deviation of the mean volume is 0.29 ppm. We have followed Slogget, Clothier, and Ricketts[12] and included an entry in Table I for the uncertainty in the density of this batch of mercury introduced by handling and storage since Cook[11] standardized it in 1961. However, we have no reason to believe that any changes in density have occurred since then.

TABLE I. 1σ uncertainties (in parts per million) from various sources in the redetermination of R.

(Volume)$^{2/3}$	
Density of mercury at 20 °C	0.28
Storage and handling of mercury	0.20
Thermal expansion of mercury (0–20 °C)	0.67
Random error of volume measurements	0.20
Temperature	
Random error of calibrations	0.8
Temperature gradient	0.4
M/γ_0	
^{40}Ar standard	0.7
Comparison of working gas to ^{40}Ar	0.26
Zero-pressure limit of $(f_{0,n}/\nu_{0,n})^2$	
Standard deviation of c_0^2 from 70 observations at 14 pressures	0.68
Thermal boundary-layer correction	0.30
Possible error in location of transducers	0.55
Square root of the sum of the squares	1.7

During the volume determinations, we changed the pressure above the mercury to determine an effective compliance of the resonator. This compliance was used to show that any bubble which may have been in the mercury during the volume measurements was smaller than 0.3 ppm of the resonator's volume.

Capsule platinum resistance thermometers were calibrated at T_t and then inserted in the enclosed acoustic apparatus. (See Fig. 1.) The dominant uncertainty in the thermometry resulted from drifts in the thermometers and/or the bridge used with them during the weeks between calibrations.

We deduce M/γ_0 for a standard sample of ^{40}Ar from measurements of the small concentrations of isotopic and noble-gas impurities remaining in it after purification with a heated zirconium-aluminum getter. The limitations of the concentration measurements led to a 0.7-ppm uncertainty in M/γ_0. The speed of sound in the standard sample was compared with that in a working

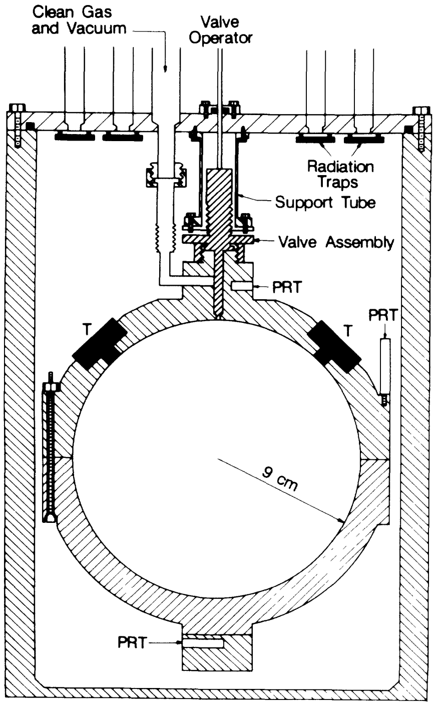

FIG. 1. Cross section of resonator and pressure vessel. The transducer assemblies are indicated by T, and the locations of the capsule thermometers are indicated by PRT. The pressure vessel is immersed in a stirred liquid bath (not shown) which is maintained at T_t.

sample of argon by use of the spherical resonator. The comparison established the ratios of M/γ_0 among the argon samples with an imprecision of 0.26 ppm. For the working sample, $M/\gamma_0 = 23.96868$ g/mol (± 0.8 ppm). It is notable that M/γ_0 of a second working sample, as received from another manufacturer, was only 0.56 ppm larger. These samples had an average molar mass of 39.94781 g/mol, in good agreement with the value derived by us[5] and by Cohen and Taylor[2] from Nier's measurements of relative isotopic abundance ratios in commercial argon.[13]

The resonance frequencies $f_{0,n}$ of the first five radial modes (designated 0,2–0,6) were determined from measurements of the in-phase and quadrature voltages produced by the detector transducer as a function of the frequency of the drive transducer. The data spanned the frequency range 2.5–9.5 kHz and the pressure range 25–500 kPa. The instrumentation for frequency measurement[6] led to a standard error of $f_{0,n}^2$ given by $1.4\times 10^{-7}\ f_{0,n}^2\{1+[(100\ \text{kPa})/P]^2[(6\ \text{kHz})/f_{0,n}]^2\}$. A second term contributiong to the standard error of $f_{0,n}^2$ corresponded to a random temperature error of 0.1 mK.

The resonance frequencies were converted to speed-of-sound observations by use of the volume determined gravimetrically and the corrections for the thermal boundary layer, the coupling of the gas and shell motion, and the unequal diameters of the hemispheres[8] comprising the resonator. Each speed-if-sound observation was weighted inversely by the square of its standard deviation and then fitted by the physically motivated function of pressure,

$$V^{2/3}(f_{0,n}/\nu_{0,n})^2_{\text{corr}} - A_3 p^3 = c_0^2 + A_1 p + A_2 p^2 + A_{-1} p^{-1}, \qquad (2)$$

from which we obtained the zero-pressure limit $c_0^2 = 94756.178 \pm 0.065$ m^2 s^{-2} with a standard error of 0.68 ppm.

Figure 2 shows fractional deviations of c^2 from the fit by Eq. (2). All but 13 of the 70 measurements deviate by less than 1 ppm and 11 of these 13 are in the narrow region below 100 kPa where the signal-to-noise ratio is reduced. All 70 observations fall within 2.6 standard deviations of the fit.

In using Eq. (2), we have assumed $A_3 = 1.45\times 10^{-18}$ m^2 s^{-2} Pa^{-3}, the value obtained by Goodwin[14] from speed-of-sound data at pressures up to 7 MPa where this term contributes 500 ppm to c^2. (If we had assumed $A_3 \equiv 0$, R would have been increased by 0.42 ppm.)

The value $A_{-1} = (2.7 \pm 2.9)\times 10^3$ m^2 s^{-2} Pa obtained from fitting by Eq. (2) is equivalent to a thermal accommodation coefficient $h = 0.93 \pm 0.07$, in agreement with other acoustic studies.[7] The value $A_1 = (2.2502 \pm 0.0035)\times 10^{-4}$ m^2 s^{-2} Pa^{-1} obtained from fitting by Eq. (2) agrees with values of A_1 obtained from earlier acoustic measurements,[1,7] a virial equation of state,[15] and recent redeterminations of the interatomic potential for argon.[16]

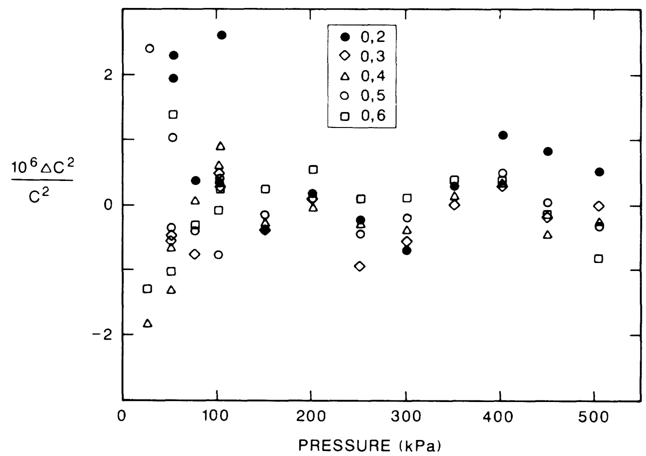

FIG. 2. Fractional deviations of 70 observations of c^2 from Eq. (2). ($\Delta c^2 = c^2_{\text{measured}} - c^2_{\text{fitted}}$.)

The values of A_2 from Refs. 1 and 7 are not consistent with our data. Both these earlier measurements yielded values of A_2 that are larger than the present value, $(5.321 \pm 0.062)\times 10^{-11}$ m^2 s^{-2} Pa^{-2}, and values of A_1 that are smaller. Perhaps these differences are correlated.

The resonance frequencies are perturbed by the presence of a thermal boundary layer (roughly 50 μm thick) in the gas in contact with the shell. This perturbation ranges from $(40$ to $360)\times 10^{-6} f_{0,n}$ and varies as $(f_{0,n} p)^{-1/2}$ at low pressures. The perturbation was calculated from independent information about the thermal conductivity of argon. The uncertainty in the thermal conductivity (0.3%) contributes 0.30 ppm to the uncertainty in the zero-pressure limit of $(f_{0,n}/\nu_{0,n})^2$. The boundary layer also makes the dominant contribution to the half-widths of the resonances $g_{0,n}$. At low pressures the measured $g_{0,n}$ agreed with the calculations. At the higher pressures, the measured $g_{0,n}$ exceed the calculated half-widths by only $2\times 10^{-6} f_{0,n}$, indicating that extraneous energy losses (perhaps associated with the motion of the shell) are quite small.

The final contribution to the uncertainty in the zero-pressure limit of $(f_{0,n}/\nu_{0,n})^2$ resulted from a possible displacement of one transducer during some of the frequency measurements and could have been eliminated if the opportunity to repeat these measurements were available.

The present value of R is 5 times more accurate than the best previous value,[1] which was also based on measurements of the speed of sound in argon. The high Q's of the radially symmetric resonances in the sphere enabled us to use small transducers which perturbed the resonances in a minor and easily calculable fashion while attaining an adequate signal-to-noise ratio. Thus, we avoided the nonlinear transducer behavior which occurred in the earlier work where a large transducer formed one end of a cylindrical resonator. Furthermore, the boundary-layer perturbations to the radial modes in the sphere could be calculated with the required accuracy because they were a factor of 10 smaller than the perturbations to the longitudinal modes in the cylinder.

Straightforward modifications of the present techniques might reduce the uncertainty in R somewhat, but probably by less than a factor of 2. Further reduction would require two developments: (1) transducers with improved signal-to-noise characteristics at low pressures, and (2) either a better value for the density of mercury at T_t or a better method of measuring the resonator's volume. Microwave resonance measurements are a promising alternative to the weighing of mercury for determining the volume of a practical resonator. A strategy for doing this was suggested by a theorem derived[17] by two of us.

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