Measurement of the Universal Gas Constant Using an Acoustic Resonator

Competition is a great motivator. The 1988 measurement of the universal gas constant R at NIST [1] was stimulated by an error made at a rival national metrology institute, Great Britain's National Physical Laboratory (NPL). In 1976, a group at NPL reported a "new" value for the universal gas constant R that had a standard uncertainty of 8.4 ppm (1 ppm = 1 part in 10^6). The "new" value was 159 ppm larger than the "older" 1972 value of R that had an uncertainty of 31 ppm (See Fig. 1.).
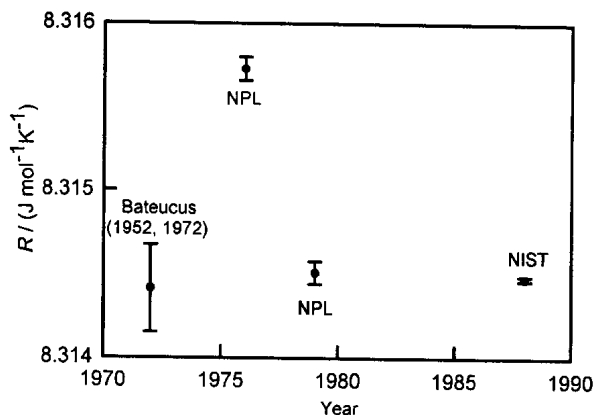
Fig. 1. History of measurements of R. The standard uncertainty of NIST's 1988 measurement is 14 μJ mol^{-1} K^{-1}, a value that is approximately the size of the plotted symbol.

The mutually inconsistent "old" and "new" values of R troubled many scientists, including Ralph Hudson, Chief of the Heat Division of NBS. Ralph solicited proposals to redetermine R in novel ways. In response, Mike Moldover proposed to determine R by measuring the speed of sound in argon using a spherical acoustic resonator [2]. This proposal was never formally funded; it was never a milestone in a performance plan. However, Moldover was encouraged to proceed on a part-time basis. Soon, Jim Mehl at the University of Delaware became a collaborator. Guest scientists Martin Trusler and Terry Edwards joined in the mid 80s, followed by Rich Davis, NBS' expert in mass metrology.

Twelve years after research began, the measurements were successfully completed. As shown in Fig. 1, NIST's 1988 value of R (and NPL's corrected 1978

value) are consistent with the "old" value of R albeit with the much smaller standard uncertainty of 1.7 ppm. The NIST result $R = 8.314\,472(15)$ J mol^{-1} K^{-1} was recommended by CODATA in 1999, and the research effort was honored with NIST's Stratton Award.

After completing the measurement of R in 1988, Moldover and his collaborators [3] used the same acoustic resonator in the temperature range 217 K to 303 K to measure the thermodynamic inconsistency of the ITS-90, the International Temperature Scale of 1990. (The ITS-90 is a set of carefully crafted recipes for accurately determining the temperature from procedures such as measuring the resistance of very pure platinum wire.)

In characteristic NBS/NIST fashion, the insights gained from measuring R and studying the ITS-90 are being applied to industrial problems. NIST's Fluid Science Group uses acoustic resonators to measure the thermodynamic and transport properties of gases, including environmentally acceptable refrigerants and semiconductor process gases. In 1997, the spherical resonator was given to NIST's Temperature Group where Dean Ripple and his collaborators rebuilt it to study the ITS-90 up 800 K.

In order to place the 1988 measurement of R in context, we shall describe the role that R plays in temperature metrology, the connection between R and the speed of sound, and the remarkable symmetry that made the accurate acoustic measurement of R possible. Then, to convey the flavor of the metrology, we describe the measurement of the resonator's volume. We conclude with a few remarks concerning acoustic thermometry.

With commercially available thermostats, platinum resistance thermometers, and triple point cells, it is much easier to reproduce any particular temperature than it is to measure any of the fundamental statistical mechanical quantities that characterize that temperature (e.g., the average kinetic energy E in a mechanical degree of freedom). Simply put, it is much easier to measure a "T" than E. This very practical consideration led the designers of the International System of Units (SI) to define temperature as an independent physical quantity. The definition specifies that the kelvin (K) is the unit of the temperature and that the temperature of the triple point of water T_w is exactly 273.16 K. In this context, the Boltzmann constant is $k_B = 2E/T_w$ and the

universal gas constant is $R = N_A k_B = 2EN_A/T_w$, where N_A is the well-known Avogadro constant, which relates the atomic mass unit to the kilogram. Thus, the 1988 measurement of R was equivalent to measuring E at the temperature T_w.

The 1988 measurement of R immediately led to a 5-fold reduction in the uncertainty of both the Boltzmann constant k_B and the Stefan-Boltzmann constant σ. [$\sigma \equiv 2\pi^5 k_B^4/(15h^3c^2)$ is used in radiation measurements. Here, h is Planck's constant and c is the speed of light.] The more accurate values of R, k_B, and σ will be used by national metrology institutes for calibrating a few vital primary thermometers that have designs that do not permit their use at T_w. (Primary thermometers, such as gas, noise, acoustic, and radiation thermometers measure E or its equivalent, and are used to calibrate other thermometers, such as platinum resistors.)

The most common use of R is in calculating gas densities ρ from the virial equation of state:

$$pV = \rho RT[1+b(T)\rho+ \ldots$$

Today, the uncertainty of R is much smaller than the uncertainties of the other quantities in this equation.

The 1988 measurement of R was based on measuring the speed of sound in argon. The speed of sound u was deduced from the resonance frequencies f_n of radially symmetric acoustic oscillations of argon enclosed by a thick spherical shell that had a carefully measured internal volume ($V \approx 3$ L. See Fig. 2.) An exactly known eigenvalue z_n connects these quantities through $u = V^{1/3} f_n/z_n$. A detailed theory correcting this equation had to be derived and tested by rigorous measurements [4].

In a dilute gas, the speed of sound u is connected to E by kinetic theory and hydrodynamics:

$$E = \tfrac{1}{2}m v_{rms}^2 = \tfrac{3}{2}k_B T, \qquad u^2 = \gamma v_{rms}^2$$

(Here, v_{rms} is the root mean square speed of a gas molecule, m is the mass of one molecule, and γ is the heat capacity ratio that has the zero-pressure limit 5/3 for the monatomic gases.) These equations can be rewritten in terms of the molar quantities $M = N_A m$ and $R = N_A k_B$ to get a simple equation for R:

$$R = \frac{M}{T} \lim_{p \to 0} \frac{u^2}{\gamma} = \frac{M}{273.16\ K} \frac{3}{5} \lim_{p \to 0} \left(\frac{V^{1/3} f_n}{z_n} \right)^2$$

Thus, to measure R one must measure M, V, and f_n, all at T_w, and extrapolate to the limit of low pressure.
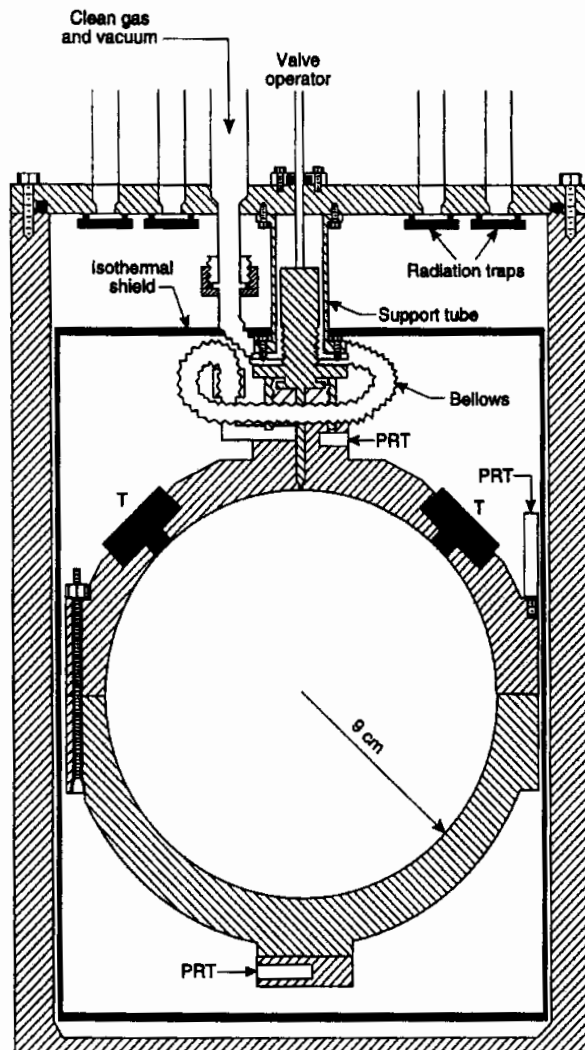

Fig. 2. Cross-section of the resonator and pressure vessel. "T" indicates the acoustic transducers; "PRT" indicates the platinum resistance thermometers. The pressure vessel was immersed in a thermostatted bath (not shown). The isothermal shield was installed after the measurement of R to reduce the temperature gradients when the resonator was used for thermometry at temperatures down to 217 K.

The thermodynamic temperature of a dilute, monatomic gas can be deduced from the ratio of two speed of sound measurements, one at T and a second at T_w:

$$T = 273.16\ K \times [u(T)/u(T_w)]^2$$

In some respects, primary acoustic thermometry is easier than measuring R. Neither V nor M must be measured accurately. For thermometry, the thermal expansion of V must be measured accurately, and this is done using microwave resonances.

The frequencies f_n are sensitive to small, smooth departures from perfect spherical geometry *in the second order,* provided that the volume is unchanged. Thus, a spherical shell built to machine-shop tolerances, e.g., one part per thousand, could be used to measure R with an uncertainty on the order of the square of (one part per thousand) = 1 ppm. In fact finer tolerances were achieved in this work. This was confirmed by the 0.34 ppm internal consistency of the speed-of-sound results obtained using five different radially symmetric acoustic modes spanning the frequency range 2.5 kHz to 9.5 kHz.

The weak dependence of the frequencies on shape imperfections appears in S. A. Moszkowski's 1955 calculation of energy levels in deformed nuclei. In the course of the gas constant work, Mehl and Moldover generalized this symmetry to vector (electromagnetic) fields confined by a conducting sphere [5]. Their generalization made it practical to determine the thermal expansion of spherical shells from the resonance frequencies of a few, selected microwave modes within the shell.

The 1988 paper concerning R took a year to write and filled 60 pages of the *Journal of Research of the NBS* [1]. It took 43 pages to describe the experimental procedures and the analysis of the data. Instead of summarizing this exhaustive work, we shall convey its flavor by outlining only the measurement of the resonator's volume V.

The principle of the volume measurement was simple. The mercury required to fill the resonator was weighed and the known density of mercury was used to convert the weight to a volume. To implement this principle with the required accuracy, the resonator was reconfigured to resemble a dilatometer. The valve in the top of the resonator was replaced with a glass capillary tube and the acoustic transducers were replaced with carefully designed plugs. The reconfigured resonator was immersed in a bath thermostatted at T_w.

For the weighings, the mercury was held in an especially designed weighing vessel. For each volume determination, the vessel was weighed when it was full of mercury and again after the mercury required to fill the resonator had been pumped out of it. As a check, the vessel was weighed again after the mercury was returned to it.

If a bubble were in the mercury inside the resonator, the weighings would have underestimated the volume of the resonator. Concern about this led to a delicate test for bubbles. After the mercury was pumped into the resonator, it overflowed, partially filling the glass capillary tube atop the resonator. A measured overpressure of argon was applied to the mercury meniscus in the glass capillary causing the meniscus to move downward. The change of the meniscus' height was compared with that expected from the known compressibility of mercury and the calculated compliance of the 19 mm-thick, stainless steel shell. Because bubbles are much more compliant than mercury and steel, this test would have detected a bubble with a volume of 3×10^{-7} V.

The calculation of the shell's compliance used its dimensions, the tabulated properties of stainless steel, and a simple model. However, this calculation is not completely trustworthy because the shell was a complex, assembled object. Thus, the calculation was checked by a measurement. This was done while gas was sealed within the shell. The pressure outside the shell was reduced, causing the shell to expand slightly and the acoustic resonance frequencies to decrease by $(-12.8 \pm 0.4) \times 10^{-6}$ MPa^{-1}. The compliance determined in this way was 6 % larger than the calculated compliance; however, this difference was within the combined uncertainties.

The effect of the mercury's pressure on the volume and the sagging of the resonator when it was filled with 40 kg of mercury were taken into account.

When the acoustic transducers were replaced with mercury-compatible plugs for the weighings, the volume of the resonator changed. This volume change was measured in an auxiliary experiment where the plugs and transducers were interchanged in a small acoustic coupler. These coupler experiments also accounted for the effective volume that resulted from the transducers' compliance.

Because mercury is a mixture of isotopes, the density of mercury varies slightly, depending on its source and how it is handled (e.g., purified by multiple distillation). The mercury used in the volume determination was taken from a vault at NBS where it had been stored since A. H. Cook had standardized it in 1961. Thus, its density near 20 °C was well known 24 years before it was used. A sample of this mercury was compared to a sample from a similar stock maintained at the Australian national metrology laboratory, CSIRO. Within the uncertainty of the comparison, any changes that might have occurred during 24 years of storage were identical at NBS and CSIRO.

Cook's recommended data for the thermal expansion of mercury between T_w and 20 °C was used; however, the uncertainty of the thermal expansion data was the largest contributor to the uncertainty of the volume. (See Table 1.) Several years later, Moldover and several colleagues showed that the thermal expansion of the spherical cavity, as deduced from microwave resonances within it, was consistent with that deduced from mercury dilatometry.

Two complete volume determinations were made in September 1985 and a third was made in April 1986. The standard deviation of their mean was 0.29 ppm. The weighings were extraordinarily reproducible.

The measurements of the temperature T, molar mass M, and the resonance frequencies f_n, received as much attention as the measurement of the resonator's volume V. Thus, it was not an accident that the uncertainties of T, M, f_n, and V were approximately equal (0.8 ppm; see Table 1.).

Table 1. Relative standard uncertainties in parts per million from various sources in the redetermination of R

$(\text{Volume})^{2/3}$	
Density of mercury at 20 °C	0.28
Storage and handling of mercury	0.20
Thermal expansion of mercury (0 °C to 20 °C)	0.67
Random error of volume determination from weighings	0.20
Temperature	
Random error of calibrations	0.8
Temperature gradient	0.4
Molar Mass	
^{40}Ar standard	0.7
Comparison of commercial argon to ^{40}Ar	0.26
Zero-pressure limit of $(f_n/z_n)^2$	
Standard deviation of u_0^2 from 70 observations (at 14 pressures)	0.68
Thermal boundary-layer correction	0.30
Possible error in positions of transducers	0.55
Square root of the sum of the squares	1.7

After the 1988 measurement of R was completed, Moldover and his collaborators used the resonator to measure $(T - T_{90})$, the difference between the thermodynamic temperature and ITS-90. In Fig. 3, their results in the range 217 K to 303 K are highlighted by a solid curve and are labeled "NIST Acoustic (1999)."

The "NIST Acoustic (1999)" data had a standard uncertainty of 0.6 mK, which is approximately 2 ppm of T. This uncertainty is much smaller than that of any other method of measuring $(T - T_{90})$. In Fig. 2, the "UCL Acoustic (1994)" results were obtained by Ewing and Trusler using a smaller, less elaborately characterized, spherical acoustic resonator. It is very reassuring that the NIST and UCL results agree, within combined uncertainties.

Fig. 3 implies that ITS-90 can be improved with the help of primary acoustic thermometry. It is possible that
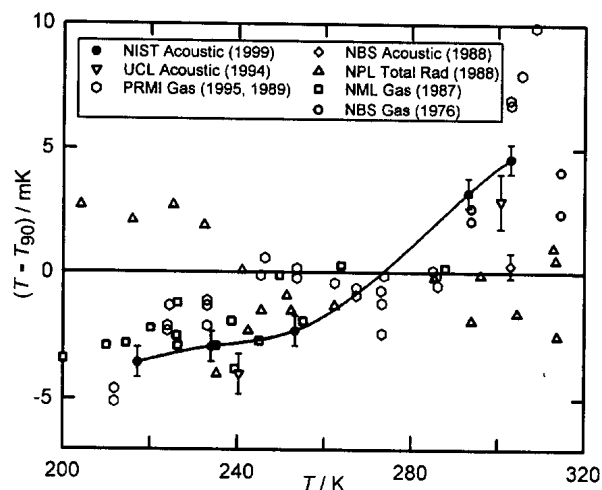

Fig. 3. Comparison of the Kelvin thermodynamic temperature T and the International Temperature Scale of 1990 T_{90}. The "NIST Acoustic (1999)" data were obtained using the gas-constant resonator.

this will be done after primary acoustic thermometry is extended to 800 K, perhaps in the next few years.

Mike Moldover joined the Heat Division at NBS in 1972 and began working with acoustic resonators in the late 1970s. He has made accurate measurements of many thermophysical properties, including density, heat capacity, viscosity, dielectric constant, speed of sound, surface tension, and refractive index. Many of these measurements were made very near liquid-vapor critical points. Moldover is now developing an atomic standard of pressure that will require measurements of the dielectric constant of helium with part per billion uncertainties. He is a NIST Fellow and Leader of the Fluid Science Group of the Process Measurements Division.

Martin Trusler and Terry Edwards were postdoctoral guest researchers at NIST during the redetermination of R. Trusler is now on the Chemical Engineering Faculty of Imperial College in London and Edwards is now on the Faculty of the Centre for Oil and Gas Engineering of the University of Western Australia. Jim Mehl has maintained a strong collaboration with NBS/NIST since 1979. During this interval he has been a Professor of Physics, Department Chair, and Associate Dean at the University of Delaware. Now retired from Deleware, Jim continues to collaborate with the NIST group. Rich Davis was a physicist in the Length and Mass Division of NIST. He is now Head of the Mass Section at the BIPM in Sevres, France.

Prepared by Michael R. Moldover.

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