Acoustic and Microwave Resonances Applied to Measuring the Gas Constant and the Thermodynamic Temperature

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Abstract—Techniques are being developed for simultaneously measuring the frequencies of microwave and acoustic resonances in a spherical cavity. They will permit the determination of the thermodynamic temperature with unprecedented accuracy. Progress to date includes: a new value for the universal gas constant:

\[ R = 8.314.471 \pm 0.000.014 \text{ J/(mol.K)} \] (1.7 ppm)

with a five-fold reduction in its standard error, a new value of the thermodynamic temperature of the triple point of gallium \(302.9169 \pm 0.000.5 \text{ K} \), and a microwave measurement of the volumetric thermal expansion of an acoustic resonator with an error of about 1.5 ppm. Improved values of the Boltzmann constant, \( 1.380.6513 \pm 0.000.0025 \text{ J/K} \), and the Stefan–Boltzmann constant, \( 5.670.399 \pm 0.000.038 \text{ W/(m².K)} \), were obtained from \( R \), and further studies of the temperature scale are in progress.

I. INTRODUCTION

In the near future, the present international practical temperature scale (IPTS-68) that is used to calibrate thermometers will be replaced with a new scale that better approximates the Kelvin thermodynamic temperature \( T \) for which all thermodynamic calculations and relationships are exactly true. In preparation for this change, standards laboratories are determining the thermodynamic temperature of highly reproducible fixed points such as the \( \lambda \) point of helium, triple points of hydrogen, neon, etc. The standards laboratories are also developing new instruments for interpolating between fixed points.

The present work reviews certain experimental and theoretical developments in acoustic [1]–[6] and microwave techniques [7], [8] and the progress in combining them to measure accurately \( u/c \), the ratio of the speed of sound in a gas to the speed of light. Measurements of \( u/c \) in dilute monatomic gases can be used to determine the temperature of fixed points with unprecedented accuracy and to interpolate between them. This work also refers to the recent application of acoustic techniques to the redetermination of the universal gas constant.

II. ACOUSTIC THERMOMETRY

Elementary considerations of hydrodynamics and the kinetic theory of dilute gases lead to relations between the average kinetic energy \( E \) in one degree of freedom, the speed of sound \( u \), and the thermodynamic temperature:

\[ 3E = \frac{1}{2} m u_{\text{rms}}^2 = \frac{3}{2} kT, \quad u^2 = \frac{\gamma}{3} v_{\text{rms}}^2 \] (1)

where \( u_{\text{rms}} \) is the root mean square speed of a gas molecule, \( m \) is its mass, \( k \) is the Boltzmann constant, and \( \gamma \) is the ratio of the specific heat capacities, which is \( 5/3 \) for dilute monatomic gases. The International System of Units assigns the value 273.16 K to the temperature of the triple point of water \( T_t \). From this specification and (1), it follows that \( T \) may be determined from measurements of the speed of sound as a function of pressure \( p \) in a monatomic gas at the temperatures \( T \) and \( T_t \). \( T \) is calculated from the relation:

\[ \frac{T}{T_t} = \lim_{p \to 0} \left[ \frac{u^2(p, T)/u^2(p, T_t)}{u_0^2(T)/u_0^2(T_t)} \right] \] (2)

In the program reviewed here, the speed of sound is deduced from measurements of the frequencies \( f_N \) of the radially symmetric acoustic resonances in argon contained within a thick spherical shell. These frequencies are insensitive to geometric imperfections of the shell that leave the internal volume \( V \) of the shell unchanged. In terms of the frequencies and the volume, the ratio \( T/T_t \) is given by

\[ \frac{T}{T_t} = \lim_{p \to 0} \left[ \frac{f_N(p, T) - f_N(p, T_t)}{f_N(p, T_t)} \right] \] \[ \cdot \frac{V(p, T)}{V(p, T_t)} \] \[ \cdot \left[ 1 + \frac{\Delta V(p, T - T_t)}{V(p, T_t)} \right]^{2/3} \] (3)

The small corrections \( \Delta f_N \) to the resonance frequencies will be discussed in the section below. The term \( \Delta V(p, T - T_t) \) is the integrated thermal expansion of the volume of the spherical cavity between \( T \) and \( T_t \), which can be determined from the frequencies of microwave resonances within the spherical cavity.

III. THE BOLTZMANN CONSTANT AND THE GAS CONSTANT

The Boltzmann constant can be considered a conversion factor between two units of energy. One is twice the kinetic energy in a degree of freedom and is measured in
A. Spherical Acoustic Resonators

by geometrically perfect spherical cavity of radius $a$ bounded by rigid, thermally insulating shell have frequencies given by

$$f_n = \frac{u_0 a}{\pi} \left( 2n + 1 \right).$$

(Here $u_0$ is the speed of sound in a monatomic gas at $T_r$, if the mass of an atom $m$ were known accurately. In this program the speed of sound was measured at $T_r$ in a sample of isotopically enriched $^{40}$Ar for which the molar mass $M = N_A m$ was determined from measurements of the relative abundances of chemical and isotopic impurities. Thus a new value was obtained for the universal gas constant $R$ from the ratio $N_A \text{mole}^2/\left(\gamma T_r\right)$ where $N_A$ is the Avogadro constant.

IV. The Program

This program, initiated in 1979 [1], has achieved the following objectives: 1) develop an accurate theoretical model and confirming experiments to facilitate the application of spherical acoustic resonators to metrology, 2) assemble a 3-1 resonator designed for measuring $R$, 3) measure the volume of the resonator with an accuracy of $\pm 1.2$ ppm by weighing the mercury required to fill it, 4) determine $R$ with an accuracy of $\pm 1.7$ ppm by measuring the speed of sound in a sample of argon of known chemical and isotopic composition at $T_r$, 5) use mercury dilatometry to measure the volumetric expansion of the resonator between $T_r$ and $T_p$, the temperature of the triple point of gallium, 6) determine $T_p$ from measurements of the speed of sound in argon, and 7) measure the volumetric expansion of the resonator using the frequencies of microwave resonances and establish the accuracy of the results by comparison with mercury dilatometry between $T_r$ and $T_p$.

In the near future we hope to complete the following tasks: 8) use existing techniques to compare IPTS-68 with the thermodynamic temperature in the range 220–310 K and to determine the temperature of the triple point of mercury, 9) develop an accurate theoretical model and confirming experiments to facilitate the application of spherical microwave resonators to metrology, 10) develop acoustic waveguides suitable for coupling sound to a resonator located in an oven, and 11) fabricate a spherical cavity that acts as both an acoustic and a microwave resonator and use the cavity for studying the temperature scale at high temperatures. (From the evidence presented in [8] and in Section IV-G below, it appears that task 9) is not essential for the completion of tasks 8) and 11).)

The first seven enumerated tasks comprise the outline for the remainder of this manuscript. We conclude with a brief discussion of our plans.

A. Spherical Acoustic Resonators

1) Theory: The theory of acoustic resonances in a spherical cavity has been developed in great detail [2], [5], [6]. The normal modes of the acoustic field within a geometrically perfect spherical cavity of radius $a$ bounded by rigid, thermally insulating shell have frequencies given by

$$\delta_h = \left( k/(\rho C_p T_f) \right)^{1/2}.$$

(Here $k$ is the thermal conductivity of the gas, $\rho$ is its density, and $C_p$ is its constant-pressure heat capacity.)

Under the conditions of the measurement of $R$, $\delta_h$ was in the range 10–95 $\mu$m, the radius $a$ was 90 mm, and the heat capacity ratio $\gamma$ was very nearly 5/3. $\Delta f$ ranged from 40 to 360 ppm, and it could be calculated with adequate accuracy from published values of the thermal conductivity and heat capacity of argon.

For the nonradial acoustic modes, a perturbation of comparable magnitude results from the viscous penetration length.

Perturbation theory can be used to calculate the effects of spatially smooth departures from perfect spherical geometry. In general, such shape changes remove the degeneracy of each multiplet; however, the average frequency of each multiplet is independent of volume-preserving deformations of the cavity, in the first order of perturbation theory. Thus a spherical cavity manufactured to machine-shop tolerances (say 1 part in 2000) can be used for extremely accurate (part per million) speed of sound measurements without making any dimensional measurements other than the volume of the resonator. To exploit this fact, the speed of sound must be deduced from either the frequency of a radially symmetric mode or the arithmetic average of the frequencies of all $2l + 1$ components of a nonradial multiplet. In practice, the frequencies of many modes or multiplets are measured and the redundancy is used to test for systematic errors.

There are other factors that can shift the real and the imaginary components of the acoustic resonance frequencies of practical resonators. These factors include: 1) sound dissipation in the bulk of the gas, 2) the elastic response of the shell to the motion of the gas within it, 3) ducts used to admit gas into the shell, 4) transducers, 5) the seam where the two hemispheres comprise the resonator...
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donator are joined, 6) effects on the order of a mean free path divided by the wavelength of sound which include imperfect thermal accommodation and departures from the Navier-Stokes dispersion relations, 7) effects that are nonlinear in the acoustic amplitude, and 8) roughness of the interior surface of the shell. Usually these factors produce perturbations that are smaller than the perturbation produced by the thermal boundary layer. In the most accurate work, it was necessary to correct the resonance frequencies for some of these factors using a combination of theory and/or auxiliary experiments.

2) Tests of Acoustic Resonators: In the context of the present program, the most extensive tests of the theory of spherical acoustic resonators occurs in [5]. In that work, the frequencies and half-widths of the first 9 radially symmetric acoustic resonances were measured with argon in a 1-l aluminum resonator at pressures ranging from 0.1 to 1 MPa. Similar data were acquired for all three components of the first 9 modes with \( l = 1 \).

The frequencies were corrected for the thermal and viscous boundary layers to obtain values of \( u/a \). These in turn were fitted by polynomial functions of pressure and extrapolated to zero pressure to obtain \( u_0/a_0 \). The values of \( u_0/a_0 \) for six \( l = 0 \) modes had a standard deviation of the mean of 1.8 ppm (see Fig. 1). The values of \( u_0/a_0 \) for the \( l = 1 \) modes had a standard deviation of the mean of 200 ppm, a result consistent with the deviations of the resonator's shape from a perfect sphere. However, when the three values of \( u_0/a_0 \) for each \( l = 1 \) triplet were averaged, the averages differed by only 3.8 \( \pm 1.8 \) ppm from the \( l = 0 \) modes. The dramatic difference between 200 and 3.8 ppm confirms the applicability of shape perturbation theory to practical resonators.

For three \( l = 0 \) modes and two \( l = 1 \) triplets the zero-pressure values of \( u/a \) deviated greatly from the data on Fig. 1 for readily identifiable reasons. In one case the deviant mode coupled strongly to a duct leading from the spherical cavity to a transducer. In the other two cases, the frequencies of the deviant modes happened to occur near the frequencies of mechanical resonances of the shell.

This experience was employed in the design of the 3-1 resonator used to measure \( R \) and \( T_g \). Ducts were not used; the resonator was made from a stiff alloy. The acoustic modes whose frequencies occurred near mechanical resonances were not used. In the measurement of \( R \), the standard deviation of \( u_0/a_0 \) determined from the first five radial modes was 0.34 ppm, five times smaller than the standard deviation from the mean of the \( l = 0 \) modes in Fig. 1.

The measurements of the half-widths of the acoustic resonances provided an independent test of the theories for the boundary layer and the bulk attenuation of sound. In the measurement of \( R \), the experimental half-widths exceeded the calculated half-widths by only 2 ppm of the resonance frequencies at the highest pressures. Furthermore, the excess half-widths declined as the pressure was reduced. This added to the confidence that systematic errors in the acoustic model were very small.

In [6], acoustic measurements were extended to low pressures, and were able to confirm the applicability of theory for thermal accommodation. Thus an allowance for the thermal accommodation length was used in the redetermination of \( R \).

B. The 3-1 NBS Resonator and Related Apparatus

Fig. 2 shows a cross section of the 3-1 spherical resonator installed in its pressure vessel. The fabrication and the assembly of the resonator were described in [2]. The hemispheres were machined from type 316L stainless steel bar stock. This material was chosen for compatibility with mercury as well as for dimensional stability, ease of machining, and high stiffness. The interior surfaces were hand polished to a near mirror finish with \( \gamma \)-alumina paste of 0.05-\( \mu \)m particle size. From dimensional measurements, the nominal interior radii of the "northern" and "southern" hemispheres were found to be 88.918 and 88.938 mm, respectively.

The hemispheres were initially machined with cylindrical extensions from the equatorial plane. These were removed after the final polishing; however, dimensional measurements were not available to establish the accuracy with which this operation was performed. If the extensions were not completely removed, the cavity would have had an axisymmetric shape perturbation. (The cavity had another axisymmetric perturbation because the hemispheres had unequal sizes.) Evidence for the presence of an axisymmetric perturbation appears in the splitting of the \( l = 1 \) acoustic [2] and microwave [8] triplets (see Section IV-G).

The mating surfaces of the hemispheres were lapped to a local flatness of 0.5 \( \mu \)m. Then the hemispheres were "soldered" together with a layer of "Apiezon-W" wax approximately 3-\( \mu \)m thick. The hemispheres were joined...
together while in a jig which maintained the alignment of the outer cylindrical surfaces at the equator.

Three capsule platinum resistance thermometers were used to measure the temperature of the resonator. The calibration procedures and the history of the thermometers are documented in [2]. The pressure vessel shown in Fig. 2 was immersed in a rapidly stirred water bath that maintained a stable, nearly isothermal environment. During the measurements near $T_i$, the “north pole” of the resonator was 0.6 mK warmer than the “south pole”. During measurements near $T_f$, the south pole was 0.1 mK warmer than the north pole.

Commercially manufactured microphones were used as acoustic transducers. They were mounted in housings that fit snugly into ports in the northern hemisphere. When installed, the interior surfaces of the transducers were nearly flush with the interior of the resonator.

A port in the top of the resonator was used to admit gas to the cavity. The port was closed with a remotely operated valve that had a flat tip. In the closed position, the tip was flush with the interior of the resonator.

The resonance frequencies were determined from measurements of the in-phase $u$ and quadrature $v$ voltages produced by the detector transducer as a function of the frequency of the drive transducer. As in previous work [5], the voltages were measured at 11 equally spaced, synthesized, discrete frequencies within ±1 half-width of the resonance under study. The complex voltages $u + iv$ were fitted using the function of frequency expected from theory

$$u + iv = \frac{ifa}{\left[f^2 - (f_N + ig_N)^2\right]} + B + C(f - f_N) \tag{7}$$

Here, $f_N + ig_N$ is the complex resonance frequency under study, $A$ is the complex amplitude, and $B$ and $C$ are complex constants which account for the “tails” of the modes other than the one under study. The deviations from the fit were less than 0.1 percent under most conditions. They were always random and resulted from noise in the instrumentation.

C. Volume Determination

The volume of the resonator was measured by weighing the quantity of mercury required to fill it while it was maintained at $T_f$ and had equal external and internal pressures of $p_0 = 101.325$ kPa at the equator. Additional measurements were made of the compliance of the resonator’s volume. These compliance measurements served three purposes: 1) they determined the change in the resonator’s volume with hydrostatic pressure; 2) they tested our understanding of the elastic response of the resonator to the acoustic field; and 3) they were a diagnostic tool used to search for bubbles or voids in the mercury during the determinations of the volume.

Three independent volume determinations at $T_i$ in a period of 8 months had a range of 0.85 ppm [2] from which one can estimate a standard deviation of 0.51 ppm for a single volume determination. The mercury that was used was traced to Cook who had measured its density at 20°C with an uncertainty of 0.42 ppm [9]. The total standard error of the volume measurement was 1.2 ppm at $T_i$, a result dominated by Cook’s estimate that the uncertainty in the volumetric thermal expansion of mercury between 20°C and $T_i$ is 1 ppm [10].

It was not practical to weigh the resonator. Instead, the mercury required to fill it at $T_i$ was transferred from a special weighing bottle. The bottle was weighed in a balance room before and after the transfer and once again when the mercury was returned to the weighing bottle from the resonator.

When ready for filling with mercury, the resonator was configured to look very much like a volume dilatometer. The valve at the top of the resonator was replaced with a glass capillary and expansion volume assembly. The electroacoustic transducers were replaced by plugs of special design that were compatible with mercury. The volume changes resulting from these configuration changes were measured separately.

When the resonator was filled, the mercury level extended into the glass capillary tube where its level, relative to a fiducial mark, was measured with a cathetometer. The capillary was long enough to allow for variation in the pressure above the mercury from 50 to 250 kPa, and the resulting curve of mercury level as a function of applied pressure constituted a compliance measurement.

D. Determination of $R$

The new value for $R$ is based on measurements of the speed on sound in a sample of isotopically enriched $^{40}$Ar that was obtained from the Mound Facility [1]. The supplier had measured the relative abundances of the $^{36}$Ar and $^{38}$Ar in the sample. The sample was chemically purified by ex-
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Exposure to a heated zirconium-aluminum getter. The concentrations of the remaining noble gas impurities were determined by gas chromatography. Limitations of the concentration measurements led to a 0.7-ppm uncertainty in $M/\gamma_0$.

The acoustic resonance frequencies were measured near $T_g$ for the first five $l = 0$ modes. The data spanned the frequency range 2.5-9.5 kHz and the pressure range 25-500 kPa. The errors in the measurement of the acoustic resonance frequencies were on the order of 0.2 ppm and the errors in the measurement of pressure were negligible.

In order to obtain $(u_0/a_0)^2$, the resonance frequencies were corrected for the boundary layer and the compliance of the shell and then fitted using a physically based function of pressure. The correlations among the fitted parameters contributed an error to comparable to the errors in determining the temperature, the volume of the resonator, and $M/\gamma_0$ (see Table I).

The new value of $R$ that was obtained with the spherical resonator [2] is

$$R_{\text{new}} = 8.314471 \pm 0.000014 \text{ J/(mol-K)} \quad (1.7 \text{ ppm})$$

This value of $R$ is in agreement with the value

$$R_{\text{1986}} = 8.314510 \pm 0.000070 \text{ J/(mol-K)} \quad (8.4 \text{ ppm})$$

accepted in the 1986 adjustment of the fundamental physical constants [11]. The new value of $R$ leads to more accurate values of the Boltzmann constant,

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

and the Stefan–Boltzmann constant,

$$\sigma = 2\pi^2k^4/15h^2c^2 = 2\pi^4R^4/15N_A(N_Ah)^3c^2$$

$$= (5.670399 \pm 0.000038) \times 10^{-8} \text{ W/(m}^2\text{K}^4) \quad (6.8 \text{ ppm})$$

The standard errors of the new values of $R$, $k$, and $\sigma$ are a factor of 5 smaller than the standard error for these constants in the 1986 adjustment of the fundamental physical constants. (To obtain $k$ and $\sigma$ the 1986 values of the Avogadro constant $N_A$, the Planck constant $h$, and the more accurately known molar Planck constant $N_Ah$ were used [11].)

E. Mercury Dilatometry

Compared with the absolute determination of the resonator's volume, measurement of the volume ratio $V(T_g)/V(T)$ was a straightforward task [4]. After the second measurement of the resonator's volume at $T_g$ [2] and before the resonator was emptied of mercury, the bath temperature was raised to nearly $T_g$. With the resonator now behaving like a thermometer bulb, mercury rose in the capillary and filled a portion of the expansion volume. Mercury was then withdrawn by syringe until the meniscus was once again about midway up the glass capillary.

The mass of mercury that had been withdrawn was weighed. The volume of the resonator at 302.927 K and 101.325 kPa was then determined from the mass of mercury remaining in the resonator. Finally, the new meniscus height was measured as a function of pressure to determine the compliance of the resonator at $T_g$.

F. Triple Point of Gallium

The frequencies of the first 5 radially symmetric acoustic modes were measured with argon in the cavity at pressures in the range 25-380 kPa at $T_g$. These frequencies were corrected and fitted by a function of pressure as described in Section IV-D. The resulting value of $(u_0/a_0)^2$ was combined with the radius change determined by the mercury dilatometry and with $u_0/a$ data at $T_g$ to obtain

$$u_0^2(T_g)/u_0^2(T) = 1.108935 \pm 0.0000020 \quad (1.8 \text{ ppm})$$

and $T_g = (302.9169 \pm 0.0005) \text{ K} [4]$. Among recent determinations of $T_g$ on IPTS-68, the one from NBS [12] and those from "the three laboratories with the smallest estimated measurement uncertainties" [14] fall in the range from 302.923 71 to 302.923 98 K. This range can be combined with the present result to conclude that $T - T(IPTS-68) = (-6.9 \pm 0.5) \text{ mK}$ near 303 K. In Fig. 3, the present result is compared with those of other recent studies [14], [16] of the relation between the thermodynamic temperature scale and IPTS-68. The present result falls near the average of the earlier studies and may be more accurate than some of them.

Table II summarizes the main contributions to the error in $T_g$. The largest entry in Table II is the result of the imperfect knowledge of the ratio of the densities of mercury. The standard error in this ratio has been estimated at 1 ppm [11] in the temperature range 0–20°C. The error was assumed to be 1.5 ppm in the larger temperature range 0–30°C; however, this may be an overestimate because of correlations among the sources of error. Equation (3) demonstrates that $T_g/T$ is proportional to the volume

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<th>TABLE I</th>
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<tr>
<td>Uncertainties in parts per million from various sources in the redetermination of $R$</td>
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<td>Constant</td>
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<td>Density of mercury at 30°C</td>
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<td>Storage and handling of argon</td>
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<td>Thermal expansion of argon</td>
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<td>44Ar standard</td>
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<tr>
<td>Comparison of working gas to 44Ar</td>
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<td>Zero pressure limit of $(u_0/a_0)^2$</td>
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<tr>
<td>S. D. of $(u_0/a_0)^2$ 70 observations at 14 pressures</td>
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<tr>
<td>Thermal boundary layer correction</td>
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<td>Possible error in location of transducers</td>
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<td>Square root of the sum of the squares</td>
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the identical speed of sound, within +0.3 ppm. Finally, detected. Nevertheless, it would be desirable to develop the capability of flowing the sample gas through a heat exchanger and the resonator. Then one could avoid possible temperature-dependent sorption phenomena that are slow compared to the acoustic period but rapid compared with the two hours required for thermal equilibration.

Fig. 3. Comparison of the thermodynamic temperature scale and IPTS-68 in the vicinity of the triple point of gallium. The data for NBS Gas Thermometry are from [14], NML Gas Thermometry from [15], and NPL Total Radiation Thermometry from [16].

G. Volumetric Expansion from Microwave Resonances

1) Microwave Theory: The theory of microwave resonances in a spherical cavity is discussed in [17]. The normal modes of the electromagnetic field within a perfectly spherical cavity of radius $a$ bounded by perfectly conducting nonmagnetic walls fall into two classes. The electric (TM) and magnetic (TE) modes have frequencies given by

$$f_m = c z_{in} / (2\pi a)$$  \(8\)

where $z_{in}$ is the $n$th root of $j_1(z) = 0$ for the TM case, and $z_{in}$ is the $n$th root of $d[z_j(z)]/dz = 0$ for the TE case. In contrast to the acoustic resonances, radially symmetric ($l = 0$) modes do not occur. The microwave modes are also characterized by an index $m$ which appears in the associated vector spherical harmonic. For a geometrically perfect sphere, the frequencies are independent of $m$, and each class of modes is comprised of $(2l + 1)$-fold degenerate multiplets. This paper discusses the results for two 3-fold degenerate triplets, one with $l = 1$ and $n = 1$ (denoted TM11) and a second with $l = 1$ and $n = 2$ (denoted TM12).

When the wall of the cavity has a finite conductivity $\sigma$ the electromagnetic field decays exponentially within the wall. The decay is characterized by a skin depth $\delta$

$$\delta = (\pi \mu_0 \sigma)^{-1/2}$$  \(9\)

where $\mu_0$ is the magnetic permeability of free space. The penetration of the field results in a contribution to the half-widths of the resonances $g$ as well as an equal reduction in the frequencies of the resonances. The size of these effects for the TM multiplets is given by

$$\Delta f + i g = (1 + i) \frac{\delta}{2a} \left[ 1 - \frac{l(l+1)}{(z_{in})^2} \right].$$  \(10\)

For the TM11 triplet in the 3-1 stainless-steel resonator, $\delta = 11 \mu m$ and $a = 90 mm$. Thus this mode has a theoretical $Q = f/(2g)$ of 6700. The theoretical $Q$ of the TM12 mode is 11 000. If copper or gold plating had been used, these $Q$’s would have been increased by a factor of 5.

As in the acoustic case, perturbation theory can be used to calculate the effects of spatially smooth departures from perfect spherical geometry [7]. In general, such shape changes remove the degeneracy of each multiplet in the first order of perturbation theory. However, in analogy with the $l > 0$ acoustic modes, the average frequency of each microwave multiplet is independent of volume-preserving deformation of the cavity, in the first order of perturbation theory [7]. The utility of this symmetry was demonstrated by simple microwave measurements that determined the volume of the 3-1 resonator within 30 ppm of the volume determined gravimetrically [8].

In addition to shape imperfection one should consider other perturbations to the microwave modes of a practical resonator. These include the probes used to couple microwaves into and out of the resonator, the annular insulators.
surrounding the probes, and a joint between the two hemispheres comprising the resonator. The theory for these perturbations has not yet been completed and tested. When this work is complete, it is expected that the accuracy of microwave volume measurements will be limited by the accuracy with which the interior surfaces of the resonator can be characterized. From published data [18], it is probable that oxide layers and residual surface roughness will lead to errors in the volume on the order of 1 ppm for 1-l cavities with solid copper or silver plated walls. Of course, it will be possible to measure small changes in volume with yet higher precision.

V. Microwave Apparatus

For the present measurements, the acoustic transducers and their housings described in [2] were removed from the transducer ports in the northern hemisphere and replaced with two microwave probes, one serving as a transmitter and the second serving as a receiver. The central copper conductor of each probe had a diameter of 1 mm and it protruded 4 mm into the spherical cavity. These straight conductors coupled efficiently to the TM modes of the cavity; however, they were not efficient in exciting the TE modes semi-rigid coaxial cable led from each probe via feedthroughs above the water bath to either a diode detector or the microwave synthesizer.

The microwave synthesizer that was available could generate a maximum frequency of 990 MHz. Thus one frequency doubler was required to excite the TM111 resonance at 1472 GHz and a second doubler combined with a 2–4 GHz amplifier were required to excite the TM12 resonance at 3283 GHz. The synthesizer was stepped through 51 equally spaced discrete frequencies within ±2 half-widths of the components of the triplets. At each frequency, the voltage rectified by the diode was measured. This voltage was assumed to be proportional to the frequency-dependent microwave power transmitted through the resonator $P(f)$. This procedure did not make use of the phase shift in the transmitted signal.

VI. Microwave Results

The TM11 and the TM12 triplets appeared to be split into only two overlapping peaks. This situation was remarkably similar to the splitting of the $l = 1, n = 3$, and $l = 1, n = 8$ acoustic triplets which had been observed in the same resonator during the measurement of $R$. A quantitative explanation of both the acoustic and the microwave splittings has been proposed [8]. The explanation assumed that the most important departure from a spherical figure was a cylindrical extension at the equator, and then applied shape perturbation theory. The proposed explanation accounted for most, but not all, details of the data.

In order to determine the volumetric expansion from the frequency dependence of the transmitted power $P(f)$, both a one-parameter analysis and a multiparameter analysis of the $P(f)$ data were used.

In the one-parameter analysis the $P(f)$ data that had been obtained at $T_i$ were used together with an interpolation rule to define a continuous function. Then a subset of the results near the center of each multiplet at $T_s$ was fitted by the function $P(f + \Delta f(T - T_s))$, where the frequency shift $\Delta f(T - T_s)$ was the only fitting parameter. Finally, the ratio of the volumes was computed for each multiplet:

$$\frac{V(T_s)}{V(T_i)} = \left[ \frac{\{f(T_i)\} + g(T_s)}{\{f(T_i)\} + g(T_s) - \Delta f(T - T_s)} \right]^3. \hspace{1cm} (11)$$

In (11), $\{f(T_i)\}$ is the average frequency of the multiplet at $T_i$ which was estimated with adequate precision from graphs of $P(f)$. For this analysis the half-widths $g(T_s)$ and $g(T_i)$ were calculated from the dc resistivity [19].

In the multiparameter analysis, it was assumed that, over the narrow frequency range spanned by each triplet, both the voltage applied to the resonator and the phase shifts in the microwave circuit were independent of the excitation frequency. Functions of the theoretically expected form (analogous to the absolute value squared of (7)) were fitted to the $P(f)$ data. For the TM11 multiplet 8 parameters were required: two resonance frequencies, two half-widths, two scalar amplitudes, and two "background" terms to account for the tails of the other multiplets. Although the TM11 mode is a triplet, the fit could not be improved by the addition of a third frequency or any other physically reasonable parameters. The data for the TM12 multiplet required a third "background" parameter.

The fitted half-widths exceeded the half-widths calculated from the published dc resistivity [19] and (10) by 15 percent of the calculated half-widths (10 ppm of the frequency of the TM11 mode and 6 ppm of the frequency of the TM12 mode). The origin of these excess half-widths is not yet known. It is larger than the excess half-widths found in the acoustic case; however, the derived values of $V(T_s)/V(T_i)$ are not sensitive to this problem.

Table III shows that $V(T_s)/V(T_i)$ obtained from microwave measurements is in agreement with $V(T_s)/V(T_i)$ obtained from mercury dilatometry. This is true for both the one-parameter and the multiparameter analyses. Comparable results were obtained using the calculated and the fitted values of the half-widths. In Table III the standard deviations of the fits (scaled by $10^3$ times the maximum power) are also listed. The standard deviations of the one-parameter fits are larger than those of the multiparameter

<table>
<thead>
<tr>
<th>Mode</th>
<th>$10^6 {f(T_s)}$</th>
<th>$10^6 {f(T_i)}$</th>
<th>$10^3$ of $g$</th>
<th>${f(T_i)}$</th>
<th>$g(T_s)$</th>
<th>$\Delta f(T - T_s)$</th>
<th>$V(T_s)/V(T_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM11</td>
<td>1420.1 + 0.7</td>
<td>1420.5 + 0.1</td>
<td>0.8</td>
<td>0.0</td>
<td>calc</td>
<td>calc</td>
<td>calc</td>
</tr>
<tr>
<td>TM12</td>
<td>1420.8 + 0.6</td>
<td>1420.5 + 0.3</td>
<td>0.8</td>
<td>1.1</td>
<td>calc</td>
<td>calc</td>
<td>calc</td>
</tr>
<tr>
<td></td>
<td>1420.3 + 0.3</td>
<td>1420.5 + 0.3</td>
<td>0.8</td>
<td>1.1</td>
<td>calc</td>
<td>calc</td>
<td>calc</td>
</tr>
<tr>
<td></td>
<td>1420.5 + 0.4</td>
<td>1420.5 + 0.5</td>
<td>0.8</td>
<td>1.1</td>
<td>calc</td>
<td>calc</td>
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<tr>
<td></td>
<td>1420.8 + 0.5</td>
<td>1420.5 + 0.5</td>
<td>0.8</td>
<td>1.1</td>
<td>calc</td>
<td>calc</td>
<td>calc</td>
</tr>
<tr>
<td></td>
<td>1421.3 + 0.6</td>
<td>1420.5 + 0.6</td>
<td>0.8</td>
<td>1.1</td>
<td>calc</td>
<td>calc</td>
<td>calc</td>
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<tr>
<td></td>
<td>1420.5 + 0.7</td>
<td>1420.5 + 0.7</td>
<td>0.8</td>
<td>1.1</td>
<td>calc</td>
<td>calc</td>
<td>calc</td>
</tr>
</tbody>
</table>
fits; however, the derived values of $V(T_k)/V(T_r)$ are nearly the same.

VII. Plans

The existing 3-l resonator will be used with microwave expansion measurements to study the IPTS-68 scale between 220 and 310 K. A new resonator and oven are being assembled to extend this work to higher temperatures. It appears feasible to improve the instrumentation and the modeling of the microwave resonances to the point where internal consistency achieved is comparable to that achieved with acoustic resonances. Microwave instrumentation for phase sensitive measurements is commercially available in the relevant frequency range. This may not be essential because of the encouraging agreement of mercury and microwave dilatometry; however, the agreement was demonstrated over a very limited temperature range.

In order to conduct acoustic thermometry at high temperatures, acoustic transmission lines and couplings must be manufactured and characterized. Then the acoustic source and detector can be outside the oven, as are the microwave source and detector. A final problem to be addressed is maintaining the purity of the test gas at high temperatures. A flowing gas system may be a good way to achieve this. Tests are in progress.

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REFERENCES


