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**Review of methods for
a redetermination of the
Boltzmann constant**

**A Report for the DTI
Quantum Programme**

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Review of methods for a redetermination of the Boltzmann constant

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ABSTRACT

The Boltzmann constant, k , is the fundamental constant of thermal metrology, which links temperature and thermal quantities with quantities in other branches of physics. As part of a wider move to define the units of the SI in terms of fundamental constants, it is now proposed that the unit of temperature, the kelvin, should be defined not by reference to a particular state of matter, but by specifying the value for the Boltzmann constant. This report reviews methods for the determination of k with high accuracy and considers the options for NPL to carry out such a determination and so contribute to the derivation of the best value. Following this, NPL will be well placed to undertake thermodynamic measurements based on the new definition.

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EXECUTIVE SUMMARY

This review was commissioned under the DTI National Measurement System Quantum Programme, to examine the feasibility and desirability of starting a programme of work at NPL to determine a value for the Boltzmann constant, k , and to identify the most appropriate technique to be adopted. This would have regard to potential benefits beyond the immediate aim of the project.

The Boltzmann constant is the fundamental constant of thermal metrology. It enters physics as the link between the random thermally-activated motions of particles (atoms and molecules) on a microscopic scale and the observable macroscopic properties of matter. The statistical analysis leads to the Boltzmann distribution of particles among the available energy states, which follows the exponential $e^{(-\mu/kT)}$, where μ is the excitation energy and kT the characteristic thermal energy at temperature T .

Thus k , in J K^{-1} , is the link between the kelvin, the unit of thermodynamic temperature, and the joule, the SI unit of energy.

Temperature scales have historically been set up empirically using an arbitrarily chosen interval, such as that between the melting point of ice and the boiling point of water, to fix the ‘size of the degree’. With the adoption in 1954 of thermodynamic temperature as a base quantity in what became the SI, and the definition of the unit, the kelvin, by specifying the value 273.16 K for the thermodynamic temperature of the triple-point of water, thermometry has been brought into line with other branches of metrology (even though, for reasons of convenience and everyday familiarity, the Celsius scale is still officially recognised).

The CIPM now proposes to redefine four of the base units (the kilogram, the ampère, the kelvin and the mole) by specifying values for the relevant fundamental constants (h , e , k and N_A) and has called for work to be carried out to determine the best values for these constants in preparation for the change, scheduled for 2011. Since the current CODATA value for the Boltzmann constant is effectively derived from a single determination of R dating from 1988, it is imperative that new experiments are undertaken to confirm (or otherwise) this value, before the change is made.

The need for a better value of the Boltzmann constant was highlighted by B N Taylor of NIST, joint author of the CODATA evaluations of fundamental constants, and T J Quinn, Director-emeritus of the BIPM, at a meeting at the Royal Society, London, on the *Fundamental constants of physics, precision measurements and the base units of the SI*, February 2005. New data was needed for the redefinition of the kelvin, and Dr Taylor considered this to be next in significance to the need for data from watt-balances in supporting the proposed revision of the SI.

The Royal Society meeting followed soon after a PTB workshop on *Methods for new determinations of the Boltzmann constant*. This was held in association with the CCT and EUROMET, in January 2005. At its meeting in June 2005, the CCT adopted a recommendation to the CIPM that ‘national laboratories initiate and continue experiments to determine values of thermodynamic temperature and the Boltzmann constant’.

After an introduction and a brief résumé of previous determinations, we review the five techniques which seem to be capable of achieving uncertainties of 10 parts in 10^6 (10 ppm) or better. Since such a measurement will extend our capabilities and will necessarily involve other fields of metrology (mechanical, optical or electrical), we consider the wider implications of the project and the synergies which may bring additional benefit in the longer term. Finally we summarise our conclusions and recommend possible courses to follow.

We are grateful to many colleagues at NPL, and contacts elsewhere in the UK and overseas, for many discussions during this project. We believe that we have presented the options fairly, but naturally we take responsibility for the analysis.

1 INTRODUCTION

Since its inception in 1960, the *Système International d'Unités*, the SI, has progressively moved toward basing physical units on atomic phenomena and fundamental constants. Thus the second is defined in terms of a hyperfine transition in caesium, and the metre by the distance travelled by light in vacuum in a given fraction of a second. Electrical units are in practice based on conventional values for ratios of fundamental constants, although the SI definition of the ampère has not yet been amended. In recent years it has become possible to consider a new definition for the kilogram itself, and so replace the last remaining material artefact in the SI, by specifying a value of the Planck constant.

For over 50 years the unit of thermodynamic temperature, the kelvin, has been based on an assigned value for the thermodynamic temperature of a particular state of matter, the triple point of water, 273.16 K. Water is a material substance, but this is not an artefact definition, since it is not necessary to refer to a central authority, such as the BIPM, for its realisation. Instead, the triple point can be set up independently, using a sample of water closely approximating the stated isotopic composition of ocean water.

However, the definition is arbitrary, and the value was adopted for consistency with previous practice, in which the 'fundamental interval' was that between the melting point of ice, 0 °C, and the boiling point of water, 100 °C. (In fact, on the present definition it is now believed that the boiling point of water is more nearly 99.98 °C.) The definition has provided an acceptable basis for thermometry, but it leaves temperature, and other thermal quantities, apart from the rest of the SI. They are linked only through the Boltzmann constant, k , and related thermal constants, whose values are subject to experimental determination.

It is now suggested that this situation should be reversed: the value for k should be assigned in the SI, and the unit of temperature thereby fixed. The advantages of making this change are:

- that the unit would be simply related to a fundamental constant, much as has been done for other units
- that the unit becomes independent of any particular substance, or temperature, or measurement method
- that by linking the unit directly to energy, it is more fully integrated with mechanical, electrical, optical and other units in the SI
- that determinations of thermodynamic temperature can be made directly, without the need to refer to the triple point of water.

The change would not of itself alter any temperature values currently adopted in the International Temperature Scale of 1990.

At its meeting in October 2005, the CIPM passed Recommendation 1 (CI-2005), see Appendix 1. This paves the way for new definitions of the kilogram, the ampère, the kelvin and the mole, in terms of fundamental constants, h , e , k and N_A , respectively. It will be the most substantial change in the history of the SI. In support of this, the CIPM calls for the National Metrology Institutes (NMIs) to pursue work 'aimed at providing the best possible values of the fundamental constants needed for the re-definitions', and to prepare for the long-term maintenance of those experiments that will be necessary for

the practical realisation of the new definitions. It is proposed that the changes should be approved by the CIPM in 2010, and adopted by the CGPM in 2011.

For thermometry, the requirement is to define a value for k which is as consistent as possible with the current definition of the kelvin, so that future determinations of the temperature of the triple point of water, when it is no longer defined, will return a value very close to 273.16 K. The precision with which the triple point can be realised is now something less than 50 μK , or < 2 parts in 10^7 , 0.2 ppm. There is no possibility of a determination of k matching this uncertainty (the realisation of the triple point would in any case be part of such an experiment), and in fact the uncertainty of the current CODATA value is 1.8 ppm. This value comes almost exclusively from the 1988 determination of the universal gas constant, $R = N_A k$, by acoustic thermometry in argon at NIST [1].

In anticipation of the CIPM recommendation, work is under way in a number of NMIs to confirm the current value. Notable examples are a project in dielectric constant gas thermometry at PTB and acoustic thermometry at IEN/IMGC, which aim to achieve uncertainties in the region of 2 ppm. Thus they are not expected to improve on the current value, but confirmation by different experimenters and, for PTB, by a different method, would give greater confidence in the value adopted.

These two experiments are based on the properties of gases. Two alternative systems are being investigated: photons in absolute radiometry in the NPL ARD experiment, and electrons in noise thermometry at NIST. A third radically different experiment using molecular spectroscopy is in progress at LPL in Paris. None of these is expected to reach uncertainties less than 10 ppm by 2010.

Against this backdrop, the present report surveys the options for an NPL experiment which could achieve competitive uncertainties in the time available, and so contribute to the derivation of an adopted value for k . It covers all systems and methods which can fulfil the following necessary conditions:

- that the physical system is well-characterised, so that the measurement can lead to an unambiguous value of kT or RT
- that the uncertainty in its application can be better than 10 ppm
- that the system can be operated at or near 273.16 K, so that the temperature can be accurately known.

These rule out many phenomena in which kT is certainly a fundamental parameter, but where the behaviour of the system is not ideal or exact enough, for example:

- Brownian motion or diffusion of particles in a fluid
- the density gradient in an ‘atmosphere’ of mesoscopic particles in a fluid
- the thermal vibrations of the probe in a scanning probe microscope
- chemical kinetics.

Sensors based on cryogenic phenomena, for example superconductors, or the use of semiconductors or tunnel junctions, are also ruled out. Such systems may have applications in thermometry, but they are not relevant to this survey.

2 PREVIOUS DETERMINATIONS

No accurate direct determinations of k have been made to date, and the value is usually inferred from values of R , or occasionally σ . We therefore present historic data in terms of R .

In 1972 Batuecas [2] reviewed values of R based on classical p - v - T measurements, and this led to the then-accepted best value, $8.31441 \pm 0.00028 \text{ J mol}^{-1} \text{ K}^{-1}$. Since then there have been no further determinations by this method, but four values from acoustic measurements have been published, and one based on radiometry, as follows:

- an ultrasonic value, $8.31479 \pm 0.00035 \text{ J mol}^{-1} \text{ K}^{-1}$, by Gammon [3] in 1976, later thought to require a significant boundary-layer correction [4]
- a low-frequency acoustic value, $8.31573 \pm 0.00017 \text{ J mol}^{-1} \text{ K}^{-1}$, by Quinn, Colclough and Chandler [5], which was revised to $8.31448 \pm 0.00021 \text{ J mol}^{-1} \text{ K}^{-1}$ in 1979 [6]
- a radiometric determination of σ by Quinn and Martin in 1985, $5.66967 \pm 0.00076 \text{ W m}^{-2} \text{ K}^{-4}$ [7], which translates to $R = 8.31420 \pm 0.00028 \text{ J mol}^{-1} \text{ K}^{-1}$
- the NIST (Moldover *et al*) low-frequency acoustic determination in a spherical resonator in 1988 [1], $8.314471 \pm 0.000014 \text{ J mol}^{-1} \text{ K}^{-1}$.

The history since 1972 is presented graphically in Figure 1, as published, with Colclough's assessment of results and uncertainties up to 1980 [4].

The NIST value has much smaller uncertainties than the others, and the CODATA 2002 value, $8.314472 \pm 0.000015 \text{ J mol}^{-1} \text{ K}^{-1}$, [8] is almost entirely based on it. No determinations have been made since 1988, and it is the lack of high-quality published data, confirming the NIST value or otherwise, which gives the urgency to new determinations, before the value becomes fixed in the SI.

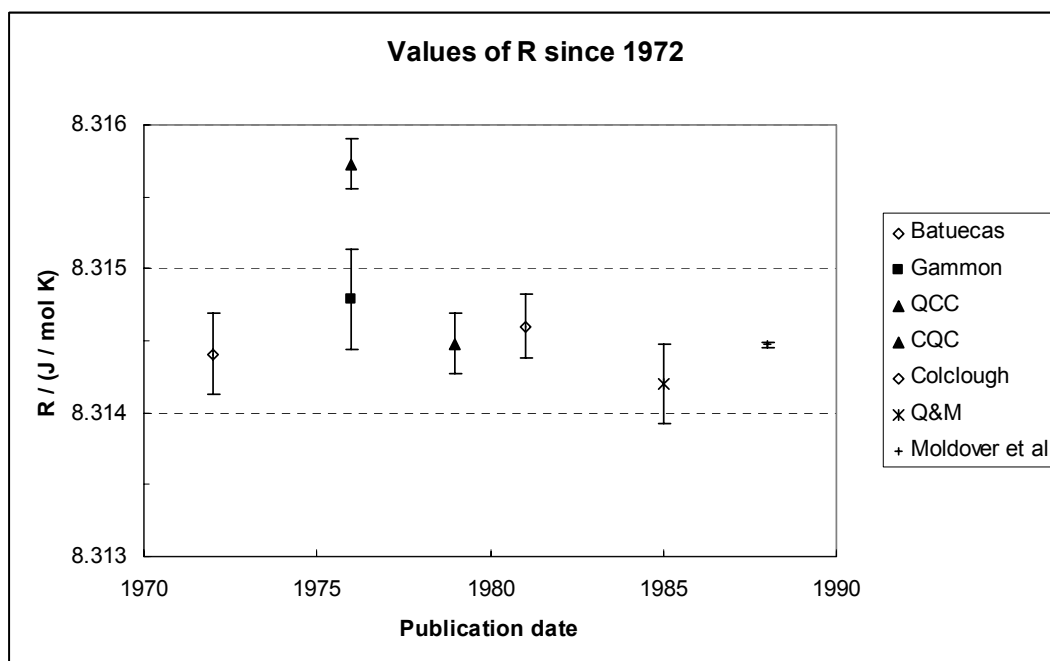


Figure 1: Values of R determined since 1972, with bars at one standard uncertainty

3 ANALYSIS OF TECHNIQUES

This section outlines the essential features of the five techniques which offer the best prospects for determining k . The first two are based on absolute measurements of the properties of gases and lead to the universal gas constant, R . They are the classical method of p - v - T gas thermometry, and acoustic gas thermometry, on which the current CODATA value is based. The third is by radiometric determination of the Stefan-Boltzmann constant, σ , and the fourth is by a measurement of the electronic noise in a resistor. The last method again uses a gas, in this case through measurement of the Doppler broadening of a molecular absorption line.

These are the only methods which currently appear capable of reaching uncertainties at the level of 10 ppm or better.

A review ‘*Towards a new definition of the kelvin: ways to go*’ has recently been published by Fischer *et al* [9].

3.1 P - V - T GAS THERMOMETRY

The classical method of limiting density

The virial equation of state of a gas is

$$pV = nRT [1 + B(T)(n/V) + C(T)(n/V)^2 + \dots],$$

where n is the number of moles of the gas in volume V at pressure p . $B(T)$ and $C(T)$ are the second and third virial coefficients, expressing the non-idealities of real gases due to two- and three-particle interactions. The product RT is seen to be the limiting value of $p(V/n)$ at low density, and consequently it can be obtained by extrapolating an isotherm to $(n/V) = 0$. This is the classical method, which was last practised in the 1950s and was the basis of the accepted value for R until about 25 years ago.

In this procedure, a bulb of known volume is set up, into which a measured quantity of gas is introduced at the required temperature, and its pressure is measured. The quantity of gas is found by weighing, so the molecular mass, M , is also needed. These quantities (M , n , V , p and T) are all required to full accuracy, and each set of data leads to a single point on the isotherm.

Traditionally the pressure was measured using a mercury barometer and the temperature was fixed at the ice point, 0 °C. The mass of the gas sample was measured by weighing the bulb first empty and then when charged, and its volume was determined by weighing the mass of water required to fill it. (Thus the density of the gas was measured relative to the density of water.) In many cases the gas used was oxygen, whose molecular mass was 32 g mol⁻¹ by definition, though nitrogen was also used. The pressures were typically in the range 25 to 101 kPa.

The uncertainties in these experiments are many and formidable. Apart from the weighing and the barometry, the density of the water must be known, and there are important secondary effects to account for, such as distortions to the bulb under the different filling conditions, and adsorption of gas on the bulb walls, which adds to the mass and reduces the pressure. Prior to 1954 there was additional uncertainty about the (kelvin) temperature to be assigned to the ice point.

Colclough [4] has reviewed five experiments published between 1924 and 1978, and he also estimated the uncertainties which might be achievable in a modern (1984)

experiment. He arrived at a combined standard uncertainty of 9 ppm, with the largest component coming from adsorption. This may be realistic, but improvements in technique in the last 20 years are unlikely to enable the overall uncertainty to be significantly less than this.

One interesting new idea follows from improvements in weighing technology [10]. It is now possible to make accurate measurements of air density by comparing the buoyancies of nearly equal masses with matched surface areas but significantly different volumes, in a temperature-controlled chamber. Application to argon at a range of pressures would permit an isotherm to be plotted, as above. However, the buoyancy is rather small, at least for modest pressures. The pressures and volumes must still be measured accurately, and adsorption would need to be investigated, in this case using masses of equal volumes but different surface areas. A measurement to 10 ppm seems not yet possible.

In summary, the classical method has been superseded by other options in which the gas density is measured directly rather than being separated into its two extensive components, mass and volume. These are discussed next, but before proceeding we point out that many of the above problems, including that of weighing, are avoided in constant-volume gas thermometry by taking ratios of pressures at two temperatures. The volume V then drops out to first order: that is, one only requires to know the *change* in the bulb volume between the two states. Similarly one only requires to know how n changes, due to migration of gas up or down the pressure sensing tube, and to estimate any changes in the adsorbed layer. It is still necessary to plot isotherms, but starting from a known temperature, typically the triple-point of water, one can use these ‘relative isotherms’ to establish thermodynamic temperatures over the range of operation. Even with these simplifications, however, constant-volume gas thermometry is no longer practised.

Dielectric constant gas thermometry

Gugan and Michel [11] pioneered the technique of dielectric constant gas thermometry (DCGT) at the University of Bristol about 30 years ago. It is based on the equation of state, but avoids the complication of working with extensive quantities by making a direct measurement of the density. This is achieved by measuring the dielectric constant of the gas, which is related to the density by the Clausius-Mossotti equation:

$$(\varepsilon - 1)/(\varepsilon + 2) = A_\varepsilon(n/V) [1 + b(T)(n/V) + c(T)(n/V)^2 + \dots]$$

where ε is the dielectric constant (relative dielectric permittivity) of the gas, and A_ε is the molar polarisability. The dielectric virial coefficients $b(T)$ and $c(T)$ take account of dipole-dipole interactions between the gas molecules at finite density.

The density can be eliminated between this equation and the virial equation of state given above, the leading term being

$$p = T(R/A_\varepsilon)(\varepsilon - 1)/(\varepsilon + 2).$$

Hence the temperature can be determined from measurements of p and ε , given the constant R/A_ε , or by taking the ratio to a known reference temperature. A determination of R , and hence k , at the triple-point of water, requires in addition that the polarisability be known.

The great advantage of the method is that there is no need to maintain fixed amounts of gas in a known volume, or account for ‘dead volumes’ along the sensing tube, which

can therefore be of any size. Gas can be admitted or removed at will, and analysed for purity, and adsorption is only a minor concern. The pressure must still be measured to full accuracy, however, and the main penalty is the additional requirement for a measurement of ε .

This is done by incorporating a capacitor in the gas cell, since the capacitance will be proportional to ε . Specifically, the relative change in capacitance

$$\Delta C/C(0) = (C(p) - C(0))/C(0)$$

between the value at pressure p and at $p = 0$ is proportional to $\varepsilon - 1$, apart from a second-order change due to the compressibility of the capacitor. Following Guggen and Michel, we can write

$$\gamma = \Delta C/C(0) = (\varepsilon - 1) + \kappa \varepsilon p,$$

where κ is the effective linear compressibility of the capacitor, ideally one third of the volume compressibility of the material.

From the equation of state and the Clausius-Mossotti equation, and using μ in place of $\gamma/(\gamma + 3)$ as the measured polarisation parameter broadly proportional to the gas density, the full expression can now be written, with sufficient accuracy, as

$$p / \mu = (A_\varepsilon/RT + \kappa/3)^{-1} [1 + ((B(T) - b(T))\mu/A_\varepsilon + C(T)(\mu/A_\varepsilon)^2 + \dots)]$$

and the quantity of interest, A_ε/RT , is seen to be the intercept of an isotherm, after the compressibility correction has been made. Provided that the measurement precision is sufficient over a wide enough pressure range, the isotherm can be extrapolated reliably.

However, the compressibility effect is not so tractable. It is not separable from the dielectric effect, since both scale with pressure: for copper the linear compressibility is about $2.5 \cdot 10^{-12} \text{ Pa}^{-1}$, which is about 0.3 % of the dielectric effect of helium at 273 K. The compression would need to be accounted for to 1 part in 3300 for a determination of RT to 1 ppm. Reference data are not accurate enough, and a non-trivial ancillary experiment would be needed. Moreover, the model assumes that the capacitor in the gas cell undergoes a truly isotropic compression when subjected to the pressure.

The dimensional stability of the cell can be improved if it is constrained, for example if the walls and end-faces are of substantial thickness and the design is such that they define the relevant length. In this case the internal dimensional changes can be significantly smaller but they are also more difficult to model.

The DCGT technique was first used by Guggen and Michel [11, 12] in the temperature range 4.2 K to 27.1 K, using a single reference point at 20.27 K, taken from the NPL-75 constant-volume gas thermometry [13] to determine the polarisability. Relative to this point, the uncertainty of the experiment was estimated to be in the region of 0.3 mK, or 1 part in 10^4 to 10^5 . The correction for the compressibility of the copper capacitor was accounted for, within this uncertainty.

Later, experiments were conducted in a similar range at PTB [14], with improvements in design and measurement. A second-generation system is currently being assembled at PTB, which will be used first for primary thermometry at low temperatures, and later for a determination of the Boltzmann constant [15].

Experiments in the region of 273 K suffer from the disadvantage that gas density, and hence the sensitivity, scales with $1/T$ and consequently is relatively low. However, more gases are available for use: argon and xenon, for example have polarisabilities which

are 8 and 20 times that of helium, respectively. Starting from the defined triple-point of water, one could use the technique to determine other temperatures with good accuracy [16]. Unfortunately, for an absolute measurement of RT one requires to know A_ϵ accurately, and experimental values are not accurate enough (not surprisingly, since they would most likely come from similar experiments, with RT assumed). On the other hand, in the particular case of helium, the polarisability has recently been calculated from first principles [17] with an uncertainty of less than 1 ppm. Thus a determination of RT by this method has become possible, albeit only with helium.

To see what is entailed, we calculate the sensitivity for helium at 101 kPa and 273 K. The parameter $\epsilon - 1$ is approximately $7 \cdot 10^{-5}$, and to see 10^{-6} of the change in capacitance on introducing the gas, the bridge must have a resolution of $7 \cdot 10^{-11}$ (but it need only be ‘accurate’, or linear, to $1 \cdot 10^{-6}$). This is some way beyond the current state of the art at PTB, given as $3 \cdot 10^{-9}$ [18]. The solution is to improve on this by a factor of 3, and to extend the isotherms to 1 MPa and beyond. The pressures are to be measured using a pressure balance, the goal being to reduce the uncertainties in this to $1 \cdot 10^{-6}$, leading to a combined standard uncertainty in k of $2 \cdot 10^{-6}$ by 2008.

At these pressures the virial expansion becomes quite significant, but fortunately $B(T)$ for helium has also been calculated with sufficient accuracy [19]. The third density virial coefficient $C(T)$ has a measurable effect, but the dielectric virials are still not important. A correction for dimensional changes is needed as discussed above.

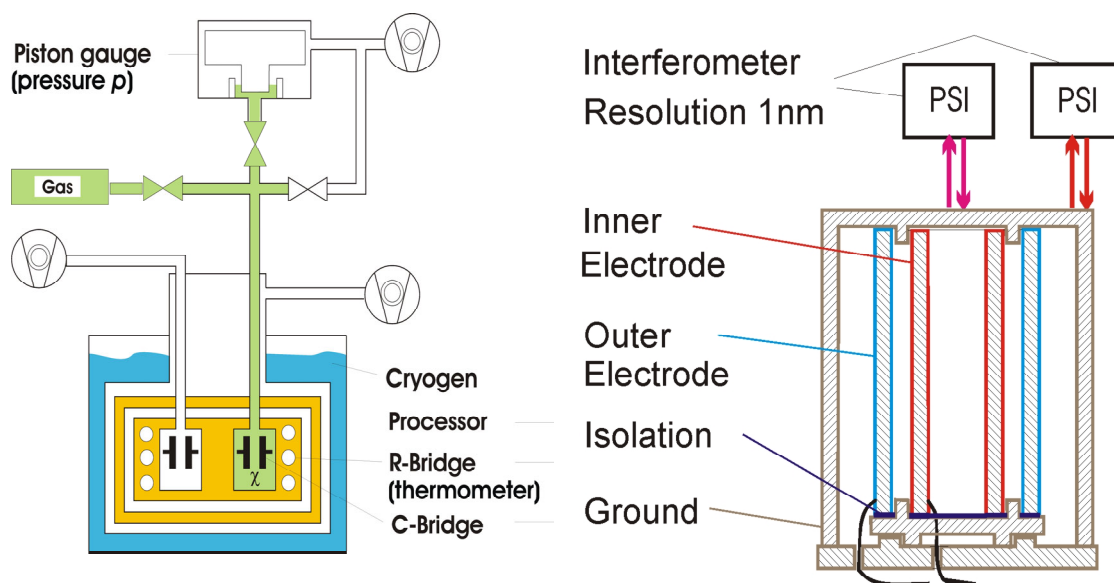


Figure 2: Schematic diagram of the new PTB apparatus and the gas cell, courtesy of B Fellmuth.

The new PTB capacitor is of coaxial cylindrical design made of copper, Figure 2, and it is housed in a massive copper block. An interferometer (PSI) is included to monitor changes in dimension. The capacitance bridge measures the ratio of the capacitance in the cell to a reference capacitor, and for reasons of electrical similarity the latter is a permanently evacuated duplicate of the former, located in the same block of copper.

This also ensures that dimensional changes due to thermal expansion (about $15 \cdot 10^{-6} \text{ K}^{-1}$) are compensated between the two, provided that there are no relative changes in temperature between them. These should be no more than 5 μK (at $p = 101 \text{ kPa}$) if thermal expansion effect is to be less than 1 ppm of the dielectric effect.

The refractive index alternative

The optical analogue of dielectric constant gas thermometry, using a laser interferometer to measure the refractive index n , was proposed by Colclough [20] and considered also by Rusby [16]. Since $\epsilon = n^2$, and $(\epsilon - 1) \sim 2(n - 1)$, the analysis is closely similar to the above, though experimentally the two methods are very different.

In the simplest form of refractive index gas thermometry the laser beam passes through a gas cell, length l_0 , and interference fringes are counted as the gas is admitted. The change in optical path $(l - l_0)$ is proportional to $(n - 1)p/T$, and this must be measured with the required accuracy ($\sim 1 \text{ ppm}$). Thus the resolution of the interferometer (allowing for two passes, go and return) must again be $\sim 7 \cdot 10^{-11}$ of l_0 , for helium at 273 K and 101 kPa. In optical terms, the fringe count is $2(n - 1)l_0/\lambda$, so for a laser wavelength of 633 nm and a cell length of 0.1 m, the count is about 10 and the discrimination must be 10^{-5} of a fringe. Unfortunately, for measurements of RT , rather than temperature ratios, one also needs to know l_0 absolutely.

The solution for absolute measurements is to replace the interferometer by an optical cavity which can be locked to an accurately measurable resonant frequency, f_0 . As the gas enters the cavity, the frequency shifts and the shift is measured as a function of pressure. We have, in principle,

$$\Delta f / f_0 \sim (n - 1) \sim (3/2)(A_\epsilon / RT) (1 + \kappa n) p,$$

where a compressibility effect is now shown. Thus at a frequency of 473 THz ($\lambda = 633 \text{ nm}$) and a pressure of 101 kPa the frequency shift is about 17 GHz. The precision of the method can be very high, better than the required $3.6 \cdot 10^{-11}$ (17 kHz). The concept is shown in Figure 3.

In practice one would not track a given resonance: one would lock on to a new resonance and calculate the frequency shift, knowing how many resonances have passed and their separation in frequency ($\sim 2 \text{ GHz}$).

However, the cavity must have great thermal and mechanical stability. As for the dielectric capacitors, a second, evacuated, cavity would be needed to counteract the effect of thermal expansion, and in effect frequency ratios (f_1 / f_2) and $(f_1 + \Delta f_1) / f_2$ would be taken.

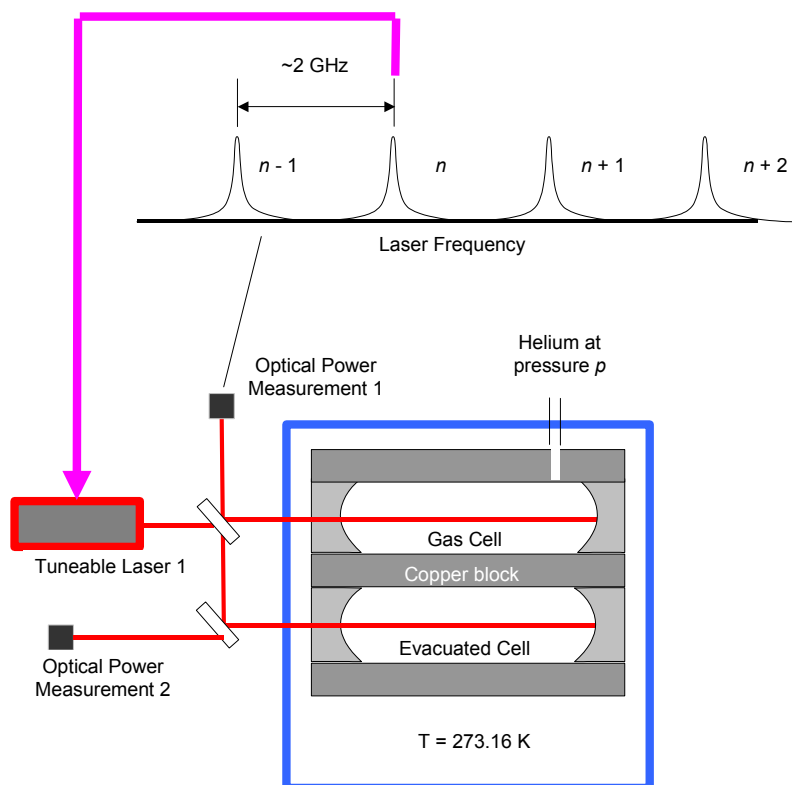


Figure 3: Illustration of a refractive-index gas thermometer concept. The cells are cylindrical bores in a large copper block, and the spherical reflectors are located against lips in the walls, not shown. Also not shown are the ‘o’-ring vacuum seals to the reflectors, and retaining brackets to keep them in place. The output is shown as a series of resonances, to one of which the frequency is locked (n is here a counting variable).

If the cavity is contained totally *within* the gas cell, it will suffer a quasi-hydrostatic compression, which must be estimated accurately (a correction is needed to 1 part in ~ 7000 for 1 ppm in R). Alternatively, if the cavity is a narrow channel in a substantial copper cell which contains the gas and supports the mirrors at each end, as shown in Figure 3, then the length will extend under pressure, but only by a modest amount. The correction is still likely to be needed to 1% or more, and in this case the exact mechanical response to pressure is not so easily predicted. In both cases, the compression of the mirrors themselves must also be considered.

We conclude that on mechanical grounds alone, the technique will be very difficult to realise at the level of a few ppm. Added to this, the current limitation of pressure metrology at NPL is in the region of 5 ppm, though with some possibility of reducing this to 2-3 ppm in the next few years. While either the dielectric constant or the refractive index method would stretch our metrology in useful directions, we conclude that at present neither is likely to lead us to a determination of R to better than 3-5 ppm.

The dielectric constant method in microwave cavities

The final option under this heading is to apply the same principles but in the microwave regime. May *et al* at NIST [21] have used microwave resonances in quasi-spherical copper resonators to measure the dielectric constant of helium and argon, and they have considered the possibilities of using such data in dielectric constant gas thermometry (to

measure temperature given accurate pressure measurement) or as a primary pressure standard in the range up to 7 MPa (at a known temperature).

In this case the relative permittivity is proportional to the square of the resonant frequency, and it is determined from the frequency ratio or change in the frequency on admitting the gas. In a carefully made cavity, the microwave resonances are well resolved and can be determined with high accuracy, < 1 in 10^8 . However, this must be pushed significantly further if it is to match the low-frequency method discussed earlier.

The NIST work includes a number of innovations, including making the cavity ‘quasi-spherical’, *ie* with slightly unequal principal radii so as to resolve the triple-degeneracy of the microwave modes, and the inclusion of a low-frequency cross-capacitor for comparison. (The cross-capacitor is an alternative to the coaxial cylindrical design used at PTB. It has excellent electrical and dimensional properties, but a rather low capacitance per unit length.)

As for other methods of this class, a measurement of RT requires the pressure to be measured to first order accuracy, and a compressibility correction is needed. Thermal expansion is a significant factor, especially as here there is no reference cavity to compensate for temperature changes. In conclusion, we note that the method has been presented as much as a potential new high pressure standard and for the measurement of polarisability, as it has for thermometry.

3.2 ACOUSTIC GAS THERMOMETRY

Background

The speed of sound, u , in an isotropic medium is given by $u^2 = B/\rho$, where B , the adiabatic bulk modulus, is given by $-(\delta p/\delta v)_s$, and ρ is the density. It follows for an ideal gas that

$$u^2 = \gamma RT/M,$$

where M is the molar mass of the gas. Departure from adiabatic propagation occurs, but is small at low density. Imperfections due to non-ideality of the gas can be accounted for in a virial expansion:

$$u^2 = \gamma RT/M \{1 + B_a(T) \rho + C_a(T) \rho^2 + \dots\},$$

where $B_a(T)$ and $C_a(T)$ are the second and third acoustic virial coefficients, which are directly related to the virials $B(T)$ and $C(T)$ in the equation of state for the gas. This shows the need for plotting an isotherm which can be extrapolated to $\rho = 0$ to recover the ideal relation.

The utility of measuring the speed of sound in gases as a primary means of measuring temperature has long been appreciated. The parameters are all intensive, so in principle there is no need to measure quantities such as volumes and the amounts of gas contained in them. Moreover, pressure is not required to be measured to first order of accuracy, being only needed for evaluating the non-idealities.

The main challenge of the method is the measurement of u with the necessary uncertainty, and in spite of significant advances this is still the limitation. Firstly, velocity decomposes into two extensive quantities, length and time. Time (or frequency) is in principle not difficult, but the length has always been problematical. This can be easily understood in the simple time-of-flight method in which a pulse is

launched into the gas at one point and detected at another. Better results can be achieved interferometrically, for example in a cylindrical cavity in which the frequency is fixed and the distance traversed by a piston between successive resonances is measured, each separation corresponding to half of the acoustic wavelength.

Fixed-frequency variable-path interferometry was undertaken in the 1960s and 1970s at NBS (NIST) and NPL for temperature measurement in the range 2 K to 20 K [22, 23], to provide a much-needed primary scale in the liquid-helium-to-liquid-hydrogen temperature range. While these experiments achieved significant advances and reached uncertainties in the region of 1 in 10^4 , some second-order acoustic effects had to be overcome, by design or by correction.

One particular effect is that at high frequencies (eg ~ 1 MHz, as used at NBS), which can readily be excited by quartz crystal oscillators, many different modes of propagation are possible and are not easily resolved. The velocity measured is likely to be a group velocity constituted of the phase velocities of the different modes. It is very difficult, or impossible, to analyse the situation well enough to make a valid correction.

Consequently a low frequency (few kHz) instrument was preferred at NPL, in which the higher modes are excluded and the propagation is truly plane wave. It has the compensating disadvantage of larger boundary layer losses due to viscous and thermal effects at the cavity walls, but in this case the effects can be modelled and corrections calculated [24].

Although the NBS and NPL acoustic experiments were successful up to a point, parallel advances in constant-volume gas thermometry [13], relative to the triple-point of water, pushed the target uncertainty to a few parts in 10^5 , and the acoustic scales were superseded. The particular application where acoustic interferometry of this era was still pre-eminent was in the determination of the gas constant, R , at the triple-point of water, since at that point absolute pressure and gas density measurements are unavoidable in other gas-based methods (see Section 4.1). This was exploited by Quinn, Colclough and Chandler (QCC) who published the results of the first modern determination of R , using a low-frequency variable-path interferometer in a cylindrical plated-brass cavity of radius 1.5 cm [5], see Figure 4. Their final value was $8.31448 \pm 0.00021 \text{ J mol}^{-1} \text{ K}^{-1}$ [6], 8 ppm higher than the previously accepted value [2].

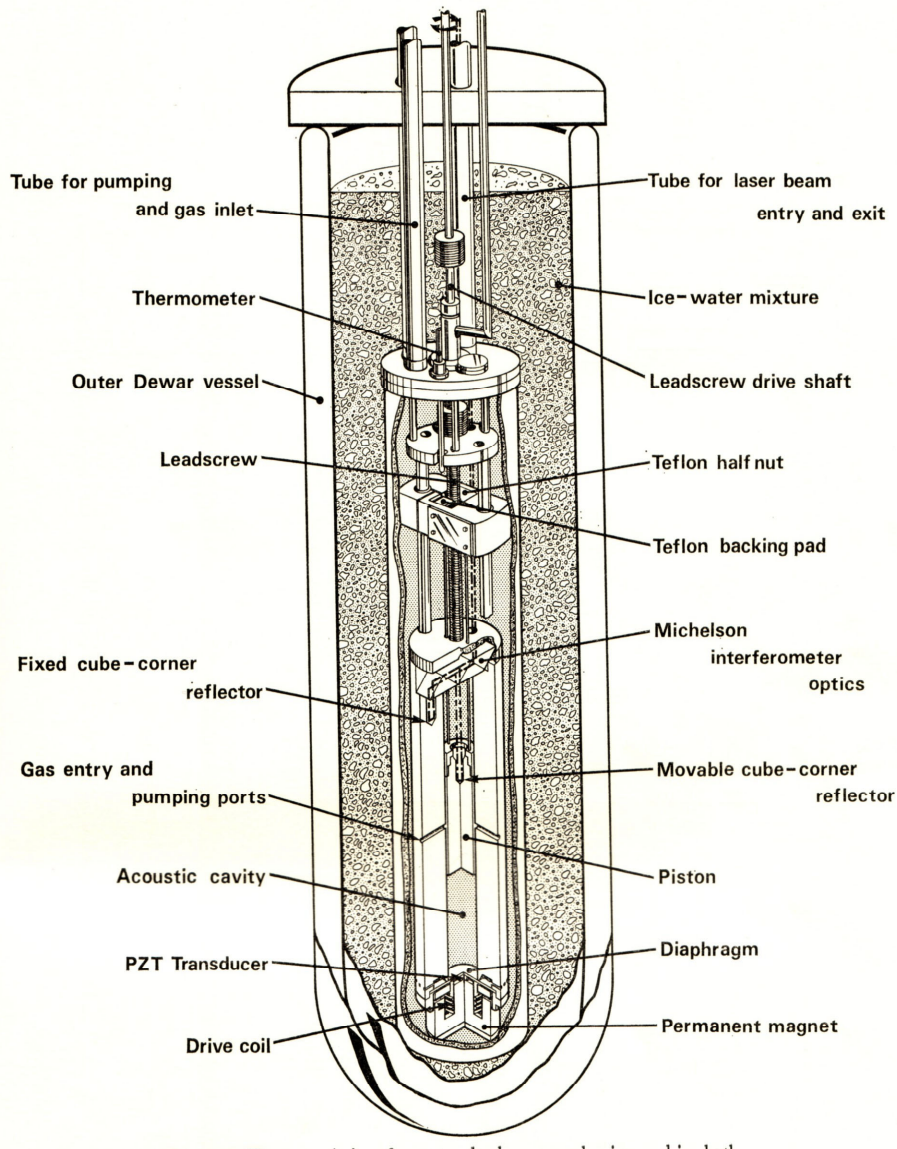


Figure 4: A cut-away diagram of the QCC cylindrical interferometer in an ice bath [5].

Acoustic thermometry in spherical resonators

The logical next step in acoustic interferometry would be to increase the cavity diameter to reduce the effect of the boundary layer. The feasibility of a design for such an instrument was investigated at NPL, but it was not pursued. Instead, at NIST, Moldover and his colleagues took an alternative route of using spherical cavities, ‘resonators’, which possess better-controlled acoustic properties. They are made by carefully machining matched pairs of hemispheres to the required tolerances, which are then joined at the equator.

In spherical resonators the sound is excited by a transducer at one point on the cavity wall, and detected using a second transducer at another point on the wall, typically at a rotation of 90° from the first. Solutions of the wave equation

$$\nabla^2 \psi(r, \theta, \phi) + k^2 \psi(r, \theta, \phi) = 0$$

have the form

$$\Psi(r, \theta, \varphi) = j_l(kr)Y_{lm}(\theta, \varphi),$$

where $j_l(kr)$ is a spherical Bessel function and $Y_{lm}(\theta, \varphi)$ is a spherical harmonic. The eigenfrequencies, f_{lm} , are such as to satisfy the boundary condition that the normal component of the particle velocity is zero at the resonator wall.

In this situation one must vary the frequency, rather than the path, and in practice the frequency is swept through a series of resonances corresponding to the different modes and harmonics propagated. Each of these can be used for determining the velocity, especially the non-degenerate radial modes, where $l = 0$ and very high Q-values can be achieved. Moving parts are avoided, and a further advantage is the smaller and well-modelled boundary-layer corrections. The compensating disadvantages are the construction of the resonators, including the transducers, with minimal surface imperfections and, for absolute measurements of RT , the need to determine of the radius in order to convert the frequencies to velocity.

During the 1980s, spherical resonators were used for the first time at the triple-point of water, 273.16 K, to measure RT , and hence R , the radius having been determined by weighing the mass of mercury required to fill the 3 l cavity [1]. The value for the gas constant resulting from this work, at NIST, was $8.314471 \pm 0.000014 \text{ J mol}^{-1} \text{ K}^{-1}$. This is still the most accurate determination, by a factor of about 15. Figure 5 shows a cross section of the resonator in its enclosure, and a photograph of the assembly.

Later uses of spherical resonators at NIST and elsewhere have been to measure temperature ratios T/T_w , where T_w is the triple point of water. Hence the value of R is not required. Remarkable consistency, within ± 10 ppm, has been achieved in six sets of temperature measurements in the range between 90 K and 400 K [25-30]. In addition, NIST has published new values for the freezing points of indium and tin (near 429 K and 505 K, respectively) [26], and a recent publication has extended the range down to 7 K [29]. Note that in measuring T relative to the triple-point of water, it is only the *change* in radius with temperature which must be determined.

Other notable applications of spherical acoustic resonators have included p - v - T studies in hydrocarbons such as synthesised natural gases.

Two recommended textbooks on physical acoustics are by Trusler [31] and Blackstock [32].

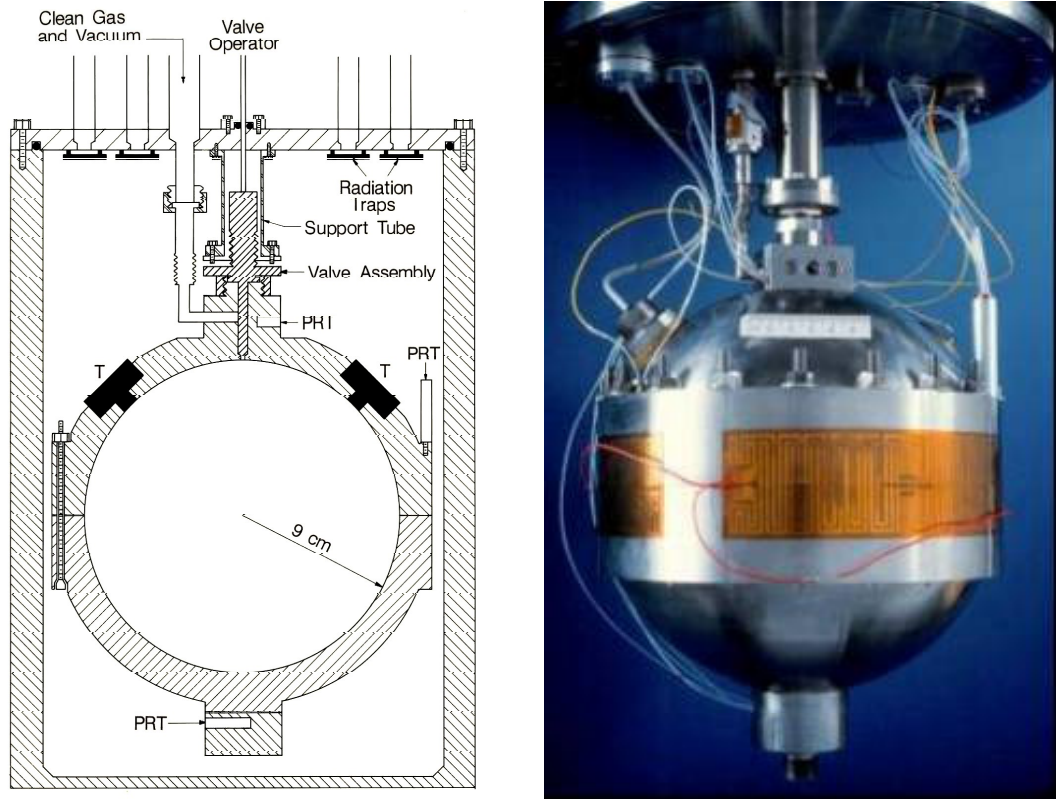


Figure 5: Cut-away diagram and photograph of the NIST gas-constant spherical resonator [1], courtesy of M. Moldover

Prospects for a new determination of R

In [1], Moldover *et al.* identified several ways in which their experiment could be refined to achieve an uncertainty in the value of R in the region of 1 ppm. The main components of uncertainty are associated with f_{in} , V , M , and T , and all of them could be reduced, as follows.

Frequency measurement is inherently accurate, but the determination of eigenvalues at the zero-pressure limit (extrapolation of the isotherm) is dependent on the signal-to-noise at low pressures, and this could now be improved. Eigenvalue imperfections also arise due to departures from the ideal spherical shape: for smooth departures they cause errors which are quadratic in the distortion, and therefore fractional errors of (say) 5 parts in 10^4 can be tolerated. For a resonator of radius 10 cm, this calls for precisions in machining and alignment at the level of 50 μm . An uncertainty in the NIST resonator arising from ambiguity in the position of the transducers could be reduced or eliminated through improved design.

The main acoustic corrections to be applied come from the containment of the gas (the boundary layer effect) and the elasticity (*ie* acoustic admittance) of the container. In particular, continuity of temperature and heat flow at the boundary requires that the temperature fluctuations associated with the propagation of the sound are counteracted by a thermal wave in the gas close to the boundary. The effect leads to a reduction in

the resonant frequency by an amount which is dependent on the cavity radius and the diffusivity of the gas. The magnitude in the NIST resonator (using argon in a stainless steel resonator of radius 9 cm) ranged from 40 to 360 parts in 10^6 , depending on the pressure. This was accurately modelled, and the resulting contribution to the uncertainty in R was 0.3 parts in 10^6 .

The correction due to the acoustic admittance of the resonator shell depends on the ratio of the elasticities (compressibilities) of the gas and the shell. This is also modelled and a correction can be applied, but the magnitude goes to zero in the limit of zero density so there is no contribution to the uncertainty.

The uncertainty in the determination of the resonator volume at NIST, by weighing the mercury required to fill it, led to an uncertainty of 1 part in 10^6 , mainly due to uncertainty in the density of mercury at 0 °C. This could be improved by making the measurement at 20 °C and correcting for the expansion of the resonator using microwave resonances. The projected overall uncertainty from this source is then reduced to 0.4 parts in 10^6 .

However, a more elegant solution would be to use microwave resonances to determine the absolute dimensions of the cavity, so avoiding the use of mercury altogether, if this can be done with the required uncertainty. In essence RT is then directly related to the ratio u^2/c^2 at the limit of zero density, where c is the speed of light. Thus the ratio of the acoustic and microwave frequencies is required, on the assumption that the effective cavity radius is the same in both measurements. In fact, corrections must be applied for the acoustic boundary layer, as already discussed, and for the microwave skin depth. This is discussed again later.

A further refinement is to use not a near-perfect sphere, but a ‘quasi-sphere’ in which the diameters in the x , y and z directions are slightly but distinctly different. The 3-fold degeneracy of the microwave modes in a true sphere is then lifted, and each resonance can be resolved independently, with greater precision. The mean radius is accurately calculated from the mean of the three frequencies.

The temperature T of the resonator comes from a platinum resistance thermometer calibrated at the triple point of water. The uncertainty clearly depends on the quality of the realisation of the triple point, on its transfer to the experiment and on the equivalence between the thermometer temperature and that of the gas. In practice, several thermometers are required, to provide redundancy and to explore possible temperature gradients in the resonator. The main recommendation for reducing this component of uncertainty from 0.9 to 0.4 parts in 10^6 is to use removable thermometers, which can be checked at regular intervals. Even so, it will not be trivial to ensure the accuracy of the thermometry at the required level of less than 0.2 mK.

Finally, it is expected that the uncertainty in the molar mass of the gas can be reduced from 0.8 to 0.4 parts in 10^6 by improving the detection limit for Xe in the reference argon against which the working gas was calibrated. It is of course necessary to bake out the resonator, pump it and flush it, and to guard against contamination of the gas.

In sum, Moldover estimates that these improvements could lead to an overall uncertainty of 1 part in 10^6 , compared with the 1.7 parts in 10^6 achieved in 1988 [1]. Other variations are possible, involving different materials, gases and procedures, etc, and these are now considered.

Summary and practical considerations

The use of spherical acoustic resonators in thermodynamic metrology has many advantages, and the theory and practice have been thoroughly developed and documented. However, some incremental development is still needed to reach absolute uncertainties of 1 ppm, and there are some choices to be made. These are now discussed.

Choice of gas: argon has much to commend it, but so does helium. The velocity and frequencies would be higher, so limiting the number of modes before encountering resonances in the shell, but this is compensated by a much smaller boundary-layer correction. A further alternative gas would be nitrogen. This has the advantage of being relatively insensitive to contamination by air and water vapour. Being diatomic, it has two rotational degrees of freedom, and this would provide a new test of the theoretical model. It is an advantage of the method that different gases are available with which to test the robustness of the model and results, and ideally all three gases should be used.

Materials: stainless steel is well suited for the resonator shell, as it has good elastic properties. It was necessary for the NIST gas-constant determination, in which the materials had to be compatible with mercury. Aluminium and copper are generally preferred for thermal reasons, because the higher diffusivity leads to better temperature uniformity, but this is not such a major consideration at 273 K. The higher electrical conductivity is important in reducing the microwave skin depth, see below.

Pressure range: this is constrained by the deterioration of signal-to-noise at the lower pressures, and the practicalities of working at higher pressures. For this work (as distinct from possible applications in pressure metrology) an upper limit of 0.3 MPa should be sufficient, though this could be increased for helium, for which the second virial coefficient is known. The uncertainty in the pressure measurement need be no better than 0.1 %.

Gas inlet: A technical detail is the gas inlet for the resonator. A large orifice is better for baking and pumping, but this must be plugged when the resonator is in use. The possibility of using a small flow of gas, to provide a continuous purge of the impurities from the sample, should be considered, though the half-life of an impurity atom in the resonator is likely to be quite long. Alternatively, tests can be carried out for progressive contamination of a static sample, and purging used only if necessary – in which case, it may be preferable periodically to replace the complete sample.

Many other practical points must be considered, ranging from the acoustic design (optimising the size, the environment, and the transducer design, location and installation), the gas handling, thermal control, temperature measurement, etc.

Cavity radius

We conclude this section with a discussion of issues related to the measurement of the cavity radius, which is needed to convert the measured frequency to the speed of sound. The expected uncertainty in this is one factor affecting the choice of radius, another being the need to excite well-defined modes of propagation. A radius in the region of 0.1 m is envisaged, being a compromise between the uncertainty in its measurement and design practicalities. Several options are in principle available for its measurement.

The first is to use a coordinate measuring machine, or an optical profiling technique, and such measurements should certainly be made, to demonstrate the quality of the

spherical surfaces before any experiments begin. The requirements for sphericity are not great, being proportional to the square of the deviations. However, it is likely that the uncertainty in the absolute radius will be some way short of the 1 ppm target (0.1 μm in 0.1 m).

The second option is to use microwave resonances, as indicated earlier. This is needed in any case to monitor the thermal expansion of the resonator, and it is attractive in that the measurements are carried out *in situ*, during the main acoustic experiments (even if gas is present, corrections can be made for the relative permittivity). Good resolution can be expected, especially if the cavity is made slightly non-spherical so as to split the triply-degenerate radially-symmetric modes [33]. However, some corrections must be applied, and the presence of the microwave transducers must not perturb the acoustic propagation unduly.

The most significant effect is due to the penetration of microwaves into the shell, the skin effect. This is characterised by the skin depth, δ , which is proportional to $(f\sigma)^{-0.5}$ where f is the frequency and σ is the (ac) electrical conductivity. For oxygen-free high-conductivity copper at a few GHz, δ should be about 1 μm , and its magnitude would be required to about 10 %. For stainless steel, the conductivity is about 50 times lower, leading to a skin depth of about 7 μm .

However, the surface of a machined sample of copper is bound to be disordered, even if it is annealed, and the uncertainty in its conductivity will be considerable. The effect could be mitigated by polishing it, or plating it with gold and then polishing it. This would also improve the chemical stability.

Previous practice has been to model the microwave line-widths, and deducing the conductivity from the excess line-widths. However, to date, the technique has only been used to determine *changes* in cavity radius due to thermal expansion, for which the requirements are less stringent. To put the correction on a firmer basis, it is recommended in addition that the conductivity is measured on the bench, using a microwave probe.

The final option for determining the cavity radius, is by weighing the amount of liquid which is required to fill it, as was done by Moldover et al [1] using mercury in their steel resonator. It is not an attractive option, but it may be the best available, in which case the resonator material is dictated. Using another liquid, compatible with a copper or gold-plated resonator, such as water, alcohol or a silicone fluid, would be more difficult experimentally. The density of these liquids should be measured before and afterwards, from the buoyancy of a sinker, but there will be difficulties with fully filling the cavity, with pressure and temperature effects, dissolved gases and, for some liquids, with evaporation.

To summarise, the microwave method of determining the radius is much preferred, and should be acceptable. Failing this, other options can be investigated, or it could be necessary to reconsider the cavity geometry: that is, to consider whether a variable-path cylindrical cavity might after all be chosen.

3.3 ABSOLUTE RADIOMETRY

Thermally-emitted radiation represents, in the ideal case, a well understood system whose measurement can be used to deduce the temperature of the radiator. We now consider the possibilities for using this method to determine kT .

Spectral methods

The spectral intensity of radiation inside an isothermal cavity, $I(\lambda, T)$, is described by the well-known Planck law:

$$I(\lambda, T) d\lambda = (2\pi c^2 h / \lambda^5) (e^{hc/\lambda kT} - 1)^{-1} d\lambda,$$

where λ is the wavelength and other symbols have their usual meanings. Thus a measurement of $I(\lambda, T)$ over a known wavelength interval can be used to determine kT .

This is the basis of spectral radiation thermometry, which has long been practised in metrology and industry. The method has very good intrinsic sensitivity, particularly at short wavelengths, provided that the intensity is large enough for accurate measurement (hence it has traditionally been a high-temperature technique, though infrared thermometry is now commonly used down to ~ 230 K). In almost all cases, including its application in the International Temperature Scale (above 1235 K), the thermometer is calibrated against a blackbody source at one or more known temperatures, so as to avoid the need to know the absolute response of the detector and the solid angle of view. Note that the inclusion of an aperture to allow observation necessarily implies that the radiation from a real cavity is never truly Planckian, though good practical approximations can be achieved.

In recent years absolute measurements have become possible using ‘filter radiometers’ traceable to the SI through cryogenic radiometry, but so far not at temperatures below about 750 K, and the best uncertainties have been ~ 20 mK (~ 30 ppm) [34]. At lower temperatures it is necessary to operate over broader wavebands well into the infrared, but suitable well-characterised spectral radiometers are not available for this. Thus a radiometric determination of kT at the triple point of water is not yet in prospect: instead it is necessary to use non-selective thermal detectors and measure the *total* radiant exitance of the cavity.

Total radiometry

The Stefan-Boltzmann T^4 law for the total radiant exitance $M(T)$ of a blackbody at temperature T was originally deduced from thermodynamic arguments but is now seen as the integration of the Planck law over all wavelengths. The full equation is:

$$M(T) = 2\pi^5 k^4 T^4 / 15 h^3 c^2 = \sigma T^4,$$

where σ / ($\text{W m}^{-2} \text{K}^{-4}$) is the Stefan-Boltzmann constant. For a determination of σ and hence k , one requires to measure the energy emitted from a blackbody at a known temperature through an aperture of known area, in a known solid angle. The detector must absorb all the radiation emitted without itself radiating significantly, and in practice this means it must be a blackbody at a sufficiently low temperature. The measurement is made by shutting off the radiation and substituting a measured electrical power in the detector cavity so as to maintain the same heat flow.

Ideally the radiating and the absorbing blackbodies would be located either side of a thin aperture, the latter absorbing all the radiation transmitted from the former. In practice, mainly for thermal reasons, the two blackbodies are separated by a structure (a radiation trap) in which two apertures are separated by a measured distance, the radiation transfer (geometrical factor) between them being accurately characterised. All radiation not in the geometrical beam must be trapped and absorbed. However, for a measurement of blackbody radiance to a few ppm at the triple-point of water, the wavelength range must extend to ~ 1 mm, and unless the aperture is isotropically

irradiated (which is very difficult to engineer) diffraction at the aperture is very significant.

Among many features critical to the performance of the radiometer, the radiation trap has been the most difficult component of the two absolute cryogenic radiometers built at NPL. The first radiometer, due to Quinn and Martin (QM), was set up in the 1970s and produced a value for σ in 1985 [7], see Section 3. This compared well with the then current value, and had a stated standard uncertainty of 130 ppm (32 ppm in k).

The second generation Absolute Radiation Detector, ARD, has been built at NPL and is undergoing final preparations for a new determination of σ . Many design improvements have been made, following experience gained in the earlier work, with the aim of making the radiation transfer as ‘diffraction-free’ as possible (it is now thought that the QM experiment suffered from larger scattering and diffraction effects than was estimated at the time). A schematic illustration of ARD is shown in Figure 5.

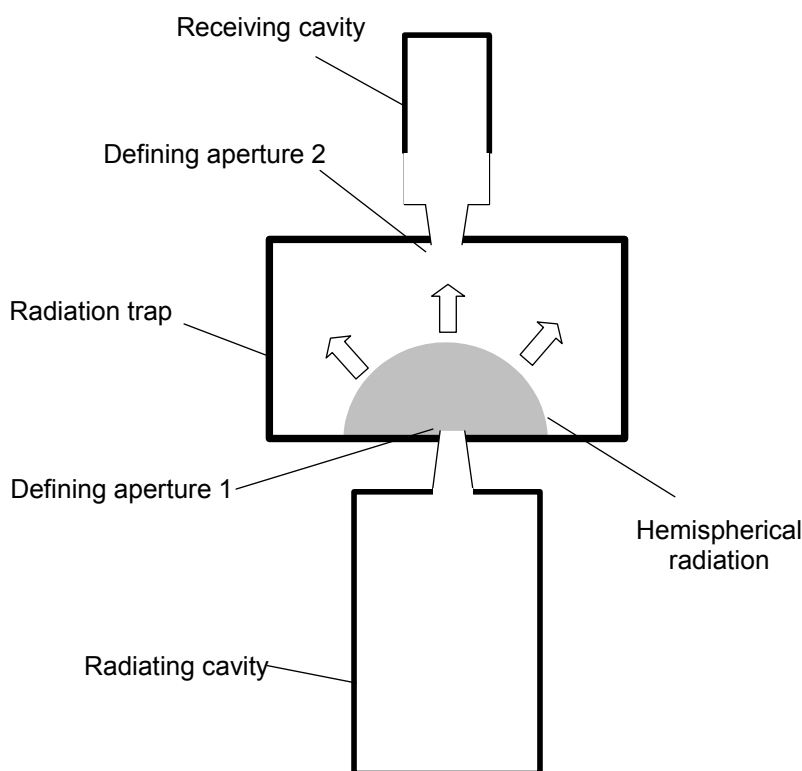


Figure 5: A schematic illustration of ARD.

The current aim is to achieve a measurement of σ with an uncertainty of ~ 40 ppm, giving k to ~ 10 ppm. This would represent a major advance in absolute radiometry, but it is a factor of 5 short of the current uncertainty in k . Thus the question here is whether the technique offers the prospect of further improvements in the near future.

In principle diffraction effects and cavity emissivities can be improved by increasing the dimensions, and to the extent that ARD is limited by these factors, a larger apparatus should give smaller uncertainties. The thermal and mechanical difficulties in

building and operating such an apparatus would be formidable, however, and the costs might not be affordable. Moreover, the improvements which could realistically be expected will only become clearer when the present experiments in ARD are completed, and it is therefore premature to commit to this course.

As a footnote to this discussion, and because the radiation transfer creates such difficulties with absolute total radiometry, we consider again whether a design with a single aperture might after all be possible. The radiating cavity would approach the aperture as closely as possible, and its emission profile should be made nearly lambertian, so as to cause minimal diffraction at the exit aperture, and eliminate reliance on high accuracy diffraction calculations. The receiving cavity would be required to absorb all the radiation passing through the aperture.

The practical difficulties of realising this may be insurmountable. Apart from producing radiating and receiving cavities of the required high emissivity, and a thin stable aperture of known area, the hot radiator must be isolated from the cold aperture, and it must be possible to shut off or remove the radiator while the electrical substitution is done, etc.

If such a system is really impossible to engineer within acceptable limits, then it seems that absolute total thermal radiometry at these temperatures has reached a plateau and cannot presently proceed much further.

3.4 JOHNSON NOISE THERMOMETRY

Introduction

Given the appeal that a practical thermodynamic thermometer based on an electrical measurement has, it is not surprising that Johnson noise thermometry already has a long history. Although it has only found limited application to date, significant improvements have been made following advances in electronics, computing and measurement technique, and it is now possible to consider making absolute measurements for the determination of the Boltzmann constant. Some of the advantages of the technique and its application as outlined in this section are:

- Johnson noise thermometry gives access to thermodynamic temperature measurement over a continuous range using just an electrical measurement
- by measuring the noise in terms of the voltage generated by the Josephson effect, the temperature can be related to an electrical quantum standard
- by relating the sensor resistance to the quantum Hall effect, the two energy quantities hf and kT can be compared, leading to a measurement of k directly in electrical units
- a novel Josephson-based analogue to digital converter for the noise measurement is proposed, which will greatly simplify the measurement set-up
- the construction of parallel measurement channels is therefore possible, leading to a significant reduction in the measurement time required to achieve a given temperature resolution
- Type B uncertainties of 40 mK (130 ppm) and Type A uncertainties of 10 mK (30 ppm) have been published, and improved on. Now 3 mK (10 ppm) is within reach with modest research, with scope to push the uncertainty lower

- by establishing a collaborative project with other institutes such as NIST and MSL in New Zealand, existing knowledge in this area can rapidly be brought together to facilitate the next steps in this area of research.

Background

Johnson noise thermometry is based on the Nyquist formula [35]

$$\overline{V_T^2} = 4kTR(T)\Delta f$$

where $\overline{V_T^2}$ is the mean-square Johnson noise voltage measured in a bandwidth Δf across a resistor R at a temperature T and k is Boltzmann's constant.

Noise thermometry is attractive in that it gives access to thermodynamic temperature through the measurement of an electrical noise signal which is independent of all the material properties of the sensor except its resistance [36]. Thus no calibration is needed and the technique can be used over a very wide range of temperature.

In addition, the availability of reference voltages based on the Josephson effect ($V_J = nhf/2e$) and reference resistances based on the quantised Hall effect ($R_H = h/ie^2$) leads to the possibility of measuring the Johnson noise from a resistor in terms of the fundamental constants h and e and thus providing a route to the determination of Boltzmann's constant through the direct comparison of the two energy units hf and kT .

Measurement challenges

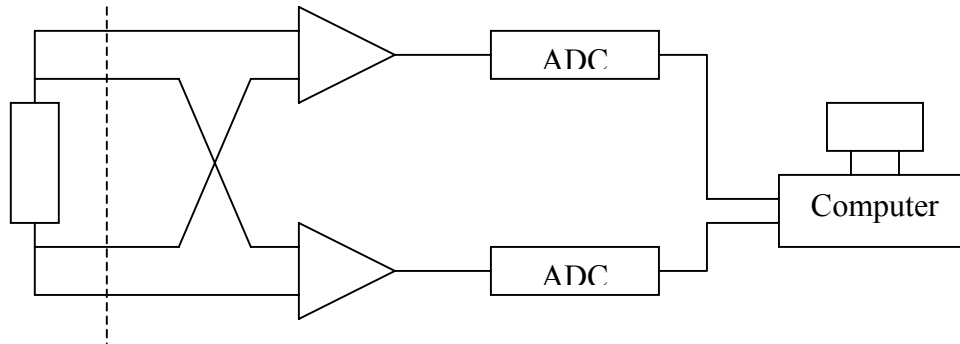
The signal levels generated by a typical noise thermometer are small. For example, the noise generated by a 100 Ω sensor at a temperature of 300 K observed in a bandwidth of 100 kHz is about 0.4 μ V rms. Effective measurement of such signal levels requires low-noise amplifiers with gains typically in the region of 10^6 . However, amplifiers with carefully designed input stages based on field effect transistors have been developed with input noise contributions which are negligible for temperature accuracies at the mK level [36].

The mean-square voltage, since it is a noise signal, fluctuates about its expected value and the resulting uncertainty σ in a single measurement is given by Rice's equation

$$\frac{\sigma^2}{\overline{V_T^2}^2} \geq \frac{1}{\tau_m \Delta f_c}$$

where τ_m is the measurement time and Δf_c is the correlation bandwidth of the thermometer. To achieve an uncertainty of 3 mK at 300 K with a 100 kHz bandwidth requires a measurement time of at least 27 hours (in contrast, an industrial measurement with an uncertainty of 1 K at 1000 K requires only 10 seconds) [36]. In order to shorten this measurement time, either a higher measurement bandwidth is required or a number of parallel measurement systems whose results are combined.

The noise generated by the wires which connect the sensor to the amplifiers has to be eliminated from the measurement. This is conveniently done by making a four-wire connection to the sensor and two amplifier chains as shown in the figure below:



If the product of the output signals from the amplifiers is taken, then only noise signals shared by both channels give a non-zero expectation in the output. Noise voltages in the leads and voltage noise in the amplifiers are eliminated. Current noise from the amplifiers is not eliminated and has to be made sufficiently small by design. Recent developments in analogue-to-digital converters and computer processing mean that the multiplication is most effectively carried out by digitising the signal and calculating the product in a computer. Note that the four-wire sensor configuration also gives an accurate definition of the resistance value of the sensor.

The frequency response of the signal path has a direct effect on the accuracy of the measurement and this effect is most easily reduced by switching between two sensors (at, for example, two temperatures whose ratio is to be measured) at the reference plane indicated by the dotted line in the figure. The noise powers need to be matched: thus the resistances need to be such that the product $T R(T)$ is the same for both. With such a technique, it is important that the sensors and their connecting wires also have the same frequency characteristic.

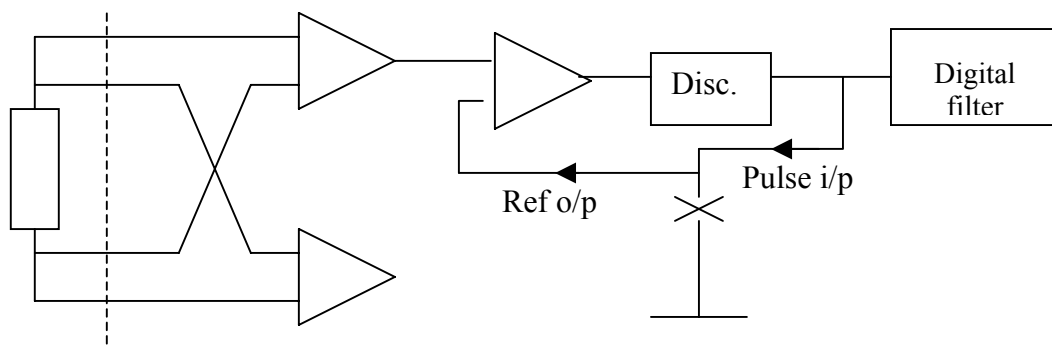
Making an absolute thermometer

Carrying out ratio measurements with two sensors, with one at the triple point of water, only establishes a temperature scale relative to the current definition. To make a noise measurement traceable back to the maintained quantum electrical units (through the Josephson and quantised Hall effects) a known electrical signal has to be substituted at the reference plane.

This has been done very effectively at NIST using an array of Josephson junctions biased with a high-speed pulse train having a pseudo-random pattern chosen to emulate the noise produced by a resistive sensor [37]. The Josephson-based noise source was substituted for the resistive sensor at 100 second intervals and the authors reported a type-A uncertainty of 10 mK on a measurement at the gallium triple-point (302 K) using data collected over 16 hours and a 100 kHz signal bandwidth. The measured temperature differed by 44 mK from the ITS-90 value. A critical factor with this method is the exactness of the substitution of the noise source for the sensor, and the measurement data showed some non-ideal frequency response behaviour. In a recent private communication of yet unpublished work [38], NIST have indicated that they have made significant improvements in the understanding of the frequency response behaviour of their system, leading to lower uncertainties than those given above.

Proposal for an alternative electrical measurement

The method presented above uses a Josephson-based noise generator to provide reference signals for the measurement system. A new approach is now proposed in which a Josephson reference is used in a closed-loop system to form an analogue to digital converter as shown (for one channel) below:



The analogue to digital conversion uses a delta-sigma modulation loop. The noise signal from the sensor is compared with the reference voltage from a single Josephson junction (indicated by the cross) and a discriminator determines whether the next high speed pulse sent to the array is of positive or negative sign. The Josephson junction acts as a perfect reference because it quantises the input pulses in multiples of $h/2e$ Vs [39]. The advantage of this technique is that the delta-sigma pulse train is automatically generated by the control loop and the hardware required is relatively simple. In the case of the NIST Josephson-based noise source, a pulse pattern generator is required to store a very long delta-sigma code which has been artificially generated by a computer beforehand.

Implementation as a collaborative project

A successful measurement of kT in terms of the maintained electrical quantum units with an uncertainty (in temperature) of 10 mK or better would be best achieved by bringing together relevant skills from several laboratories. D R White of MSL in New Zealand has developed a great deal of expertise in the area of noise thermometry and is already working in collaboration with the NIST who have experience in Josephson-based signal sources. NPL has recently pioneered new methods of using Josephson references with delta-sigma modulation techniques to make a quantum-based analogue to digital converter. NPL also has leading expertise in impedance measurement to 10 MHz [40] which is required to relate the sensor impedance over a wide band of frequencies to the maintained electrical unit of resistance in terms of the quantised Hall effect at dc. A collaboration between NPL, MSL and NIST would facilitate an effective experiment to make an absolute thermometer based on Johnson noise measurements in a limited amount of time.

The apparatus is sufficiently simple that experiments could be undertaken in all three (and other) NMIs, and the results pooled. This would be an efficient way to reduce the statistical uncertainties, and lead to an international consensus value. In future the same principle could be applied to other fixed points in the temperature scale.

3.5 DOPPLER BROADENING

Background

Atomic and molecular spectra can be used for temperature measurement in discharges and plasmas, etc, or in active spectroscopic techniques such as coherent anti-Stokes Raman spectroscopy or laser-induced fluorescence. These rely on the temperature dependent relative populations of excited states which is proportional to $\exp(-E/kT)$ for an excitation energy E . However, the experimental conditions are usually difficult, and uncertainties are rather large.

Absorption data can also be used, and this has potential for measurements in cold gases. In particular, measurements of Doppler broadening at the Laboratoire de Physique des Lasers, LPL, at the Université Paris-Nord, in association with LNE, have been demonstrated with good accuracy in ammonia at 273 K. Since the absorption process can be accurately modelled, in principle a value of k can be deduced.

The absorption is proportional to $\exp(-(\omega_L - \omega_0)^2/k_L u)$, where ω_L is the laser frequency, ω_0 is the frequency of resonance, $k_L = \omega_L/c$, and u is the root mean square velocity of the molecules, $\sqrt{(2kT/m)}$. This leads to the basic equation for kT :

$$kT = (mc^2 / 8 \ln 2)(\Delta / \omega_L)^2,$$

where $\Delta = 2 k_L u \sqrt{\ln 2}$ is the full width at half maximum.

The LPL-LNE group have built a gas cell which is a tube of 38 mm diameter and overall length of about 1200 mm [41]. This passes through a bath of ice at 273.15 K, and the central region, 360 mm long, contains ammonia at pressures typically between 1 and 10 Pa. The conditions are arranged such that there is sufficient absorption when a laser beam is passed through the cell, but the unwanted pressure broadening of the line is not excessive. A CO₂ laser is used, at ~30 THz (wavelength near 10 μ m). The frequency is modulated at 8-18 GHz and a Fabry-Perot optical cavity is used to filter out unwanted sidebands. The beam is split in two, one channel passing through the cell, the other going straight to the HgCdTe detector, so that the relative difference between the beam intensities can be measured. Temperature measurements are made using 100 Ω platinum resistance thermometers attached to the cell. A schematic diagram is shown in Figure 6.

The absorption measurement is made by fitting the line profile against the theoretical model, and determining the width at half-height. A key component of the uncertainty in the experiment is the quality of the fit obtained: noise in the measurements, and errors or uncertainties in the model, affect both the width and the location of the half-height. Various other effects must be considered in order to reduce the uncertainties to the level of 10 ppm, which is the current objective of the LPL project.

Firstly, it is necessary to be sure that the gas in the cell is at equilibrium at the temperature of the cell wall, and that the Maxwell-Boltzmann velocity distribution properly applies. The mean-free-path of molecules of ammonia at 1 Pa and 273 K is approximately 10 mm, or about one quarter of the cell diameter. Many molecules interacting with photons in the beam will have come directly from the cell wall, and may not be fully equilibrated with the gas, particularly with regard to the axial velocity component. This will show up as a pressure-dependence in the absorption, as well as other pressure effects (eg line broadening). Tests using a non-absorbing 'buffer' gas in addition to the ammonia would help to investigate this.

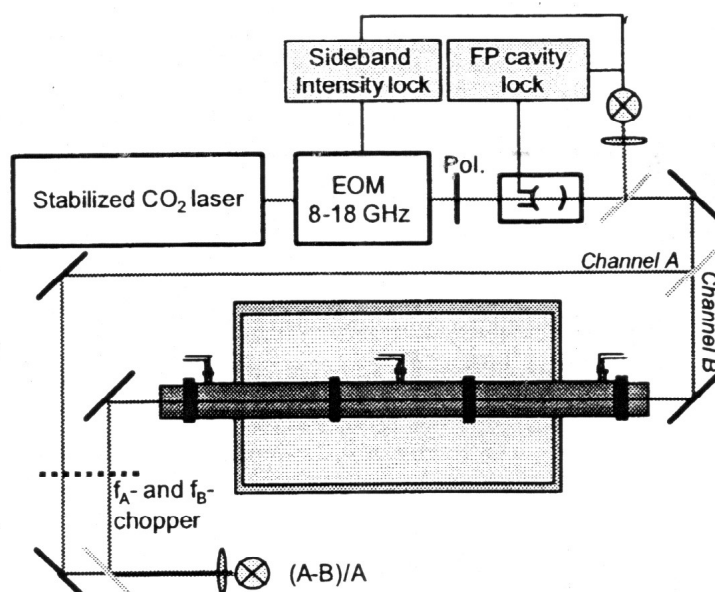


Figure 6: Schematic layout of the LPL-LNE apparatus for the measurement of Doppler broadening in ammonia: from Chardonnet and Briaudeau [38].

Other thermal effects will include the heating effect of the absorption and heating of the gas by thermal radiation entering through the windows at each end of the cell. Calculations suggest that the laser energy absorbed in the gas ($\sim 1 \mu\text{W}$) can be dissipated without setting up a temperature gradient greater than 0.1 mK . However, a further effect is that after interaction, the gas molecule must move out of the beam: double interactions are a perturbation in the effect. The temperature rise due to thermal radiation is also calculated to be small for the geometry adopted, and it can be tested by introducing (or adjusting) apertures in the cell.

A possibly significant optical effect concerns the linearity and uniformity of the HgCdTe detector. These detectors are known to have limitations, and their characterisation and alignment will be important.

In summary, the technique is an innovative one which uses the properties of gases to give a value for k by a non-classical method. It requires significant improvements to laser spectroscopy and may have potential to give interesting uncertainties, $\sim 10 \text{ ppm}$, in the near future. This will not be low enough to affect the adopted value, but if it is consistent with other values it will provide additional confirmation from a new source, as well as validating the technology used.

4 SYNERGIES

Fundamentally, a measurement of the Boltzmann constant requires the measurement of an energy and a temperature. The latter is conveniently taken directly from the definition of the kelvin, by operating at or near the triple-point of water: no other temperature is known well enough to achieve the desired or even useful uncertainties. Since thermal energy is not directly measurable as such, the energy measurement necessarily brings in some other branch of metrology, mechanical, optical or electrical,

in which a property of a system is determined by its thermal state in equilibrium, or a change in the property is measured between two equilibrium states. Therefore thermal metrology is dependent on the existence of systems in which such properties are manifested in well-understood ways, and are capable of accurate measurement.

In many cases the requirements of temperature measurement provide the most demanding application of the metrology, and in these circumstances innovations in temperature metrology call for a corresponding innovation in the related field. Sometimes it is temperature metrology which can provide the stimulus for a development in another field. Since we are considering measurements at the current limit of thermal metrology, it is useful to identify where the related fields also stand to benefit. In this section we briefly summarise the ‘spin-offs’ for each of the options considered in Section 4.

1. p - v - T , dielectric-constant and refractive-index measurements

Ideally these call for the pressure measurement to ~ 1 ppm at pressures up to ~ 1 MPa. This is not currently available at NPL, though advances in pressure balance metrology can be envisaged and would need to be implemented.

The measurement of gas density from the buoyancy of sinkers has developed in recent years, and further improvements would be needed, if the classical method is adopted.

The dielectric-constant method demands capacitance measurements of the highest order, and would stretch our current capabilities. Correspondingly, the refractive-index method would be a demanding application of optical cavities, though in this case the limitations are not likely to be in the frequency measurement but in the dimensional stability, which both of these options require.

There is a strong link between high accuracy measurements using gases and the calculation of properties such as viscosity, conductivity, diffusivity, polarisability and the virial coefficients. Currently these calculations are only reliable for helium, and consequently only this gas can be used in the dielectric-constant and refractive-index methods. Once done, the polarisabilities of other gases could be determined experimentally, by comparison with helium.

2. Acoustic thermometry.

NPL currently has no experience with spherical acoustic resonators for high-accuracy measurements in fluids, and this would be a very useful extension of its capability. Apart from the gas constant determination there would be applications in thermodynamic thermometry in establishing values for the next International Temperature Scale, and the resonator could be set up on a semi-routine basis as an alternative temperature reference for the calibration of Standard Platinum Resistance Thermometers.

Since the speed of sound depends on the mean molecular mass of the gas, the technique has application in fundamental gas analysis. A practical example is in humidity, where moisture content is conveniently measured by determining the dew point temperature. This is indirect, but reference to a primary standard linked to the SI, such as the gravimetric hygrometer, is extremely time-consuming. The acoustic

method is a potential alternative, which could have interesting accuracy over a wide range of humidity.

The need to measure the radius of the resonator will be a factor in the success of an acoustic determination of R . Direct dimensional measurements at the limit of current capability will be required, using CMM or optical techniques, but it is also envisaged that microwave resonances will be obtained. The line profiles will be analysed to estimate the skin depth, so that a correction can be made for it. The conductivity of the resonator surface, on which the skin depth depends, will also be probed using microwaves. NPL has good expertise in both dimensional and microwave metrology to bring to bear.

3. *Radiometry*

The technique of cryogenic radiometry has been pioneered at NPL, and the necessary theoretical and experimental expertise is available to achieve a result at the current state of the art. This is also a multi-disciplinary technique, involving high accuracy electrical, optical, dimensional and thermal metrology in its realisation.

Apart from providing the fundamental verification of standards in radiometry, the method can be used as a thermodynamic thermometer. Moreover, as the basis for the absolute characterisation of filter radiometers, cryogenic radiometry enables absolute spectral radiation thermometry to be carried out at high temperatures.

4. *Johnson noise thermometry*

Since electrical metrology is generally an order of magnitude more precise than thermal metrology, and is linked directly to fundamental constants, converting from a thermal energy to an electrical one should be highly advantageous. In the case of noise thermometry, it is the smallness of the signal (which is normally a large nuisance) which provides the main limitation. The development of low-noise amplification techniques involving Josephson technology can be expected to have applications in electrical metrology.

5. *Doppler broadening*

Similar considerations apply to the Doppler broadening method. Frequency is an even more desirable parameter for measurement, but nevertheless the accurate measurement of the broadening requires innovations in spectroscopy. These can then be applied in other experiments in the field.

5 SUMMARY OF FINDINGS

Having reviewed the techniques available, as far as seems profitable, we can now summarise their advantages and disadvantages. This is done from the technical point of view, but comments are included regarding other factors, where appropriate: costs, risks, innovation, synergies within NPL, longer-term implications, partnerships, etc.

Classical gas thermometry

In this method, the determination of R requires full accuracy in pressure measurement, weighing samples of gas, and volumetric determinations. The resulting uncertainty is not likely to be less than 10 ppm. The technique is well established, in principle, but has limited potential for future exploitation. It has not been used for many years.

Dielectric-constant gas thermometry

This technique has been developed to avoid measurement of the extensive quantities of classical gas thermometry, but the measurement of (helium) gas density through the dielectric constant calls for high-resolution capacitance measurement (~ 1 part in 10^9 in ~ 10 pF). Measurement of pressures up to or beyond 1 MPa is needed to full accuracy (~ 1 ppm). These two requirements mean that 5 ppm is likely to be achievable with our present capabilities, but to improve on this would require significant advances in the pressure metrology at the necessary high pressures.

Similar considerations apply to the optical alternative, refractive-index gas thermometry, but here the basic sensitivity of the method (optical frequency measurements versus pressure) is such that only modest gas pressures (up to 101 kPa) need be used. These pressures should be measurable with uncertainties of a few ppm.

Dielectric constant gas thermometry using microwaves also has good potential, as the resonances in a high-Q spherical resonator can be resolved to $<10^{-8}$. However, this is not sufficient for a measurement of RT with helium to <10 ppm. Pressures well in excess of 101 kPa will again be needed, and they must be measured to full accuracy. Experimentally there is a strong link between this method and the acoustic gas thermometry discussed next.

Apart from the requirement for measurement of the key parameters at or beyond the present state of the art, all these methods suffer from a significant (up to 0.3%) effect due to compressibility (or other dimensional change) under pressure, and due to thermal expansion. Overcoming these will require careful design and construction, and possibly ancillary experimentation.

Any project under this heading would be built around a close collaboration between thermal and pressure metrologists, plus electrical or optical colleagues, with benefits in all fields. The methods all call for significant innovation, and have good potential for the measurement of thermodynamic temperature and pressure over ranges set by the limitations of the apparatus design.

Acoustic gas thermometry

Acoustic thermometry again avoids the need to measure the gas density but is also independent of pressure to first-order accuracy. Instead the speed of sound must be measured. With the development of spherical acoustic resonators the method seems capable of giving 1 ppm in RT , provided that the resonator dimensions are known well enough. These should be obtainable from microwave resonances, which can also be measured with high precision (see above), after the necessary correction for skin-effect can be made.

This is therefore the most promising gas-based method. A major new investment would be required to set up a project at NPL, but there is already good expertise in the UK to draw on, at IC and UCL as well as in NPL Acoustics. Within Europe, an acoustic determination of R is currently under way at IEN/IMGC in Italy, and a copper resonator

is being set up for thermometry at LNE-INM, Paris. From our discussions, the LNE group are keen to collaborate in a new determination of R , as that would complement their measurements of temperature over the cryogenic range.

Finally, there is good potential for exploitation in thermometry, and in humidity. A combined acoustic and microwave resonator could be used to investigate a possible new primary pressure standard, as indicated above. The links in the chain are as follows:

1. Spherical acoustic/microwave resonator $\rightarrow u \rightarrow RT$ ($p < 101$ kPa)
2. Microwave resonator + acoustics or SPRT* $\rightarrow \varepsilon_r \rightarrow (n/V)RT \rightarrow p$, up to ~ 7 MPa.

*SPRT = Standard platinum Resistance Thermometer (ITS-90).

The interest in humidity is in the possibility of determining moisture content in air or other gases through a measurement of the effective molecular mass. It is a potentially absolute method which might replace the present gravimetric apparatus.

Radiometry

The ARD project is in progress, aiming to obtain a value of σ to ~ 40 ppm, leading to k with an uncertainty of about 10 ppm. The main limitation is in characterising the optical throughput of the aperture system, rather than in measuring the energy. While possibilities may exist for improvements, it is premature to embark on a major new project in this area.

Noise thermometry

The fundamental detection limit for a noise thermometer using a resistor of $100\ \Omega$ at 273 K and an amplifier bandwidth of 100 kHz is about 10 ppm in a measurement time of 27 h. It is possible to consider an experiment conducted over a period of months in which this might be reduced by a factor of 10, provided that the amplifier performance is near-ideal. However, for a determination of kT (rather than a temperature ratio) one also requires to know the bandwidth accurately – that is, the amplifier system must be ‘calibrated’ in some way.

The Josephson Quantum Noise Voltage Source, developed at NIST, has been used as a calculable reference source, with interesting results. The suggestion made in Section 4.4 uses a novel method to implement Josephson technology. It has the potential to simplify the hardware and allow the operation of several amplifier chains in parallel, with significant reductions in time taken for a given precision. This offers the possibility of breaking through the 10 ppm barrier for noise thermometry at quite modest cost. If it is successful, the measurement times could be extended so that k can be determined with an uncertainty of only a few ppm. The proposal in Section 4.4 envisages a collaboration with NIST and MSL, New Zealand, and this would lead naturally to reducing the statistical uncertainties by setting up similar experiments in these three, and possibly other, laboratories. Each would obtain its own result, which would then be combined to give the first accurate direct determination of the Boltzmann constant.

Doppler broadening

The Doppler broadening technique relies critically on the ability to model and fit the measured absorption in the gas, and so determine the half width. This must take account of other broadening mechanisms. The method also relies on the gas having the Maxwell-Boltzmann velocity distribution, *i.e.* being properly thermalised internally and

with the cell wall, which is held at a known temperature. Other important aspects of the experiment relate to laser stability, sources of heating, window absorption and detector uniformity.

These are being addressed at LPL, where the objective in the medium term is to achieve uncertainties of 10 ppm. This will be challenging, but it is a field in which LPL has great expertise. We have held discussions with the LPL team, and see no advantage in setting up a similar project at NPL.

6 CONCLUSIONS AND RECOMMENDATIONS

On the basis of the above, we conclude that gas-based techniques are still hard to beat for high-accuracy fundamental thermodynamic measurements, and that acoustic thermometry still offers the best option for making a determination of the gas and Boltzmann constants. Among the other techniques, developments in noise thermometry are very interesting and well worth following up.

A combined acoustic and microwave resonator would give NPL useful new capability in temperature measurement, and offers the prospect of providing new primary pressure and humidity standards in due course.

Expertise in the acoustic technology exists in the UK (at IC, UCL and NPL Acoustics), and colleagues in France, Italy and also Spain are active in the field. Microwave expertise is available at NPL.

Compared with this, the dielectric constant or refractive index methods have drawbacks (due to the electrical or optical measurement, pressure measurement and dimensional stability) which make them less likely to achieve the best accuracy, being likely to give a result to 3-5 ppm. The refractive index method would be an innovative choice, and could be adopted in the interest of diversity. Otherwise, dielectric constant measurements in a combined acoustic/microwave cavity would keep this option open for the future.

We therefore recommend

1. that a project is commissioned to set up a combined acoustic and microwave resonator which can operate from 273 K to 303 K (and possibly over a wider range) with the purposes of
 - determining k with an uncertainty of 1-2 ppm within 5 years
 - enabling measurements to be made of the thermodynamic temperature of the melting point of gallium, and possibly of other temperatures, also within 5 years
 - in a third phase, undertaking comparisons with NPL pressure balances in the range up to 7 MPa, to establish a possible alternative basis for the primary standards of pressure
 - informing a study of options to replace the primary gravimetric hygrometer as the basis for traceability of humidity standards to the SI.
2. that a pilot project in noise thermometry is set up to investigate the feasibility of using sigma-delta modulation with a Josephson junction to measure the mean-square noise voltages in a direct manner, in collaboration with NIST and MSL.

Finally, we note that PTB has taken the initiative to coordinate information and technical exchange between European laboratories active in determinations of the Boltzmann constant, in a EUROMET iMERA project. NPL has expressed interest in participating, and starting a new experiment would therefore be highly opportune.

7 ACKNOWLEDGEMENTS AND CONTACTS MADE

The survey covers a broad spectrum of metrology, and many people have contributed to it. The authors are pleased to acknowledge their inputs and identify them.

Three meetings provided useful opportunities to hear talks by experts in the field and for discussions with them and many others. They were

- the PTB Workshop on *Methods for New Determinations of the Boltzmann Constant*, in January 2005,
- a meeting at the Royal Society, London, on the *Fundamental constants of physics, precision measurements and the base units of the SI*, in February 2005,
- the meeting of the Comité Consultatif de Thermométrie, and Working Group 4, at the BIPM in June 2005.

The PTB workshop was attended by RLR and MdeP, and included the following talks:

- M Moldover (NIST) on the acoustic determination of the Boltzmann constant
- Marcarino and Benedetto (IEN/IMGC) on an acoustic/microwave determination of the universal gas constant
- Szalewicz (University of Delaware) on *ab initio* calculations of intermolecular potentials and electric properties of gases
- Fellmuth (PTB) on dielectric constant gas thermometry at PTB
- Fox (NPL) on the radiometric determination of the Stefan-Boltzmann constant
- Briaudeau (LNE) and Chardonnet (LPL) on the feasibility of a determination of the Boltzmann constant by Doppler broadening

The meeting led to discussion chaired by the organiser, J Fischer of PTB, and informal discussions were held with M Moldover, K Hill (NRC), L Pitre (LNE), M Stock (BIPM), B Fellmuth and C Gaiser (PTB) among others.

The Royal Society meeting was more broadly-based, but comments on the need for new determinations of the Boltzmann constant were made by B N Taylor (NIST) and T J Quinn (BIPM), and this was taken up with them and others privately, notably A Steele (NRC), W Buck and B Fellmuth (PTB).

CCT Working Group 4 (Chairman R Rusby, members M Moldover, J Fischer, D R White (MSL), M Durieux (Leiden University), L Pitre (LNE), PPM Steur (IMGC), K Hill, O Tamura and M de Podesta) discussed the redefinition of the kelvin, and its implications for thermometry. The CCT was advised of the proposal to be put to the CIPM.

The opportunity was taken to visit LPL, to see the Doppler broadening experiment and discuss it with the experimenters (Chardonnet, Briaudeau, Bordé and colleagues).

Other visits were as follows:

L Pitre (LNE) to NPL for a seminar on acoustic thermometry

D R White (MSL) to NPL including discussions on noise thermometry

S Briaudeau (LNE) to NPL for a seminar on the Doppler broadening experiment

S Nam (NIST) to NPL for discussions on electrical metrology, including noise

To Professor J P M Trusler, Imperial College, to discuss acoustic thermometry.

Other contacts made outside NPL by e-mail and telephone include

Professor A R Colclough, on acoustic thermometry

M B Ewing, University College, and M Moldover, NIST, on microwave measurements in spherical cavities

Among colleagues at NPL who have contributed we acknowledge

J Flowers, B Petley and J Gallop (general aspects)

I Severn, J Greenwood and colleagues (pressure metrology)

S Davidson (density measurement)

R Barham, R Lord and B Zeqiri (acoustic metrology)

A Lewis, N Cross and D Putland (dimensional metrology)

N Fox and E Usadi (radiometry)

W R C Rowley and H Margolis (laser interferometry)

R Clarke, A Gregory and J Gallop (microwave metrology)

The authors apologise for any omissions from these lists

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APPENDIX 1

Recommendation of the International Committee for Weights and Measures

Preparative steps towards new definitions of the kilogram, the ampere, the kelvin and the mole in terms of fundamental constants

RECOMMENDATION 1 (CI-2005)

The International Committee for Weights and Measures (CIPM),

considering

- Resolution 7 of the 21st General Conference on Weights and Measures (CGPM), 1999, concerning a future definition of the kilogram;
- the recent, 2005, Recommendations of the Consultative Committee for Mass and Related Quantities (CCM), the Consultative Committee for Electricity and Magnetism (CCEM), the Consultative Committee for Amount of Substance - Metrology in chemistry (CCQM) and the Consultative Committee for Thermometry (CCT) concerning proposals for and matters related to changes in the definitions of the kilogram, the ampere and the kelvin;
- the Recommendation of the CCU [Recommendation U 1 (2005)] which brings together all of the major points of these other recommendations and which requests that the CIPM:
 - approve in principle the preparation of new definitions and *mises en pratique* of the kilogram, the ampere and the kelvin so that if the results of experimental measurements over the next few years are indeed acceptable, all having been agreed with the various Consultative Committees and other relevant bodies, the CIPM can prepare proposals to be put to Member States of the Metre Convention in time for possible adoption by the 24th CGPM in 2011;
 - give consideration to the possibility of redefining, at the same time, the mole in terms of a fixed value of the Avogadro constant;
 - prepare a Draft Resolution that may be put to the 23rd CGPM in 2007 to alert Member States to these activities;
 - further encourages National Metrology Institutes to pursue national funding to support continued relevant research in order to facilitate the changes suggested here and improve our knowledge of the relevant fundamental constants, with a view to further improvement in the International System of Units;
- the need for careful consideration to be given to both the form and content of possible new definitions of these units, not only individually but also taken as an ensemble;

approves, in principle, the preparation of the new definitions, as requested by the CCU in its Recommendation cited above;

invites all Consultative Committees

- particularly the CCM, CCEM, CCQM and CCT, to consider the implications of changing the definitions of the above-mentioned base units of the SI, and to submit a report to the CIPM not later than June 2007;

- to monitor closely the results of new experiments relevant to the possible new definitions, to identify necessary conditions to be met before proceeding with changing the definitions, and to consider, in particular, the alternative ways of redefining the above mentioned units;
- to solicit input from the wider scientific and technical community on this important matter;

recommends that National Metrology Institutes

- should pursue vigorously their work presently underway aimed at providing the best possible values of the fundamental constants needed for the redefinitions now being considered;
- should prepare for the long term maintenance of those experiments that will, in due course, be necessary for the practical realization of the new definitions.