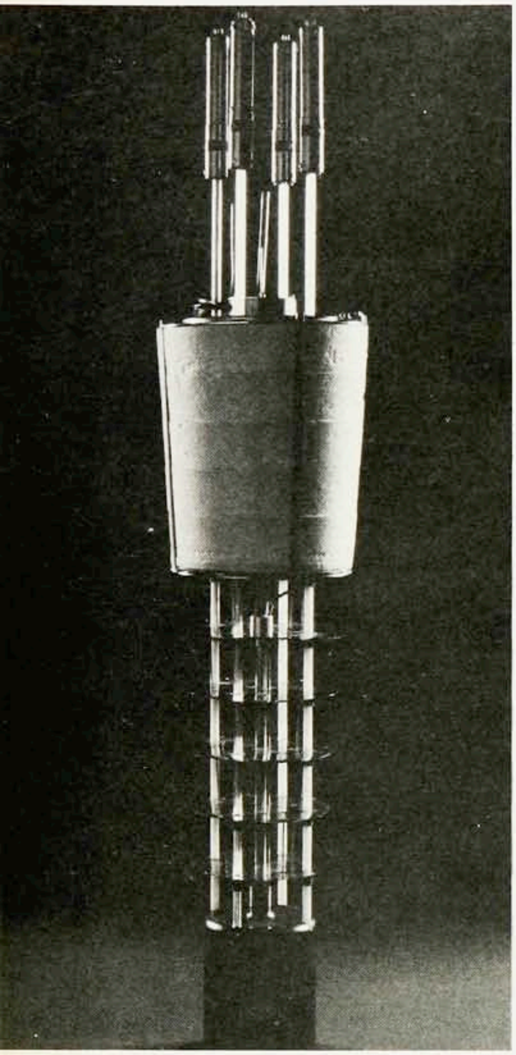
The measurement of thermodynamic temperature

Temperature is defined through thermodynamics, and values on practical temperature scales are derived from measurements with several thermometers based on fundamental thermodynamic or statistical-mechanical principles.

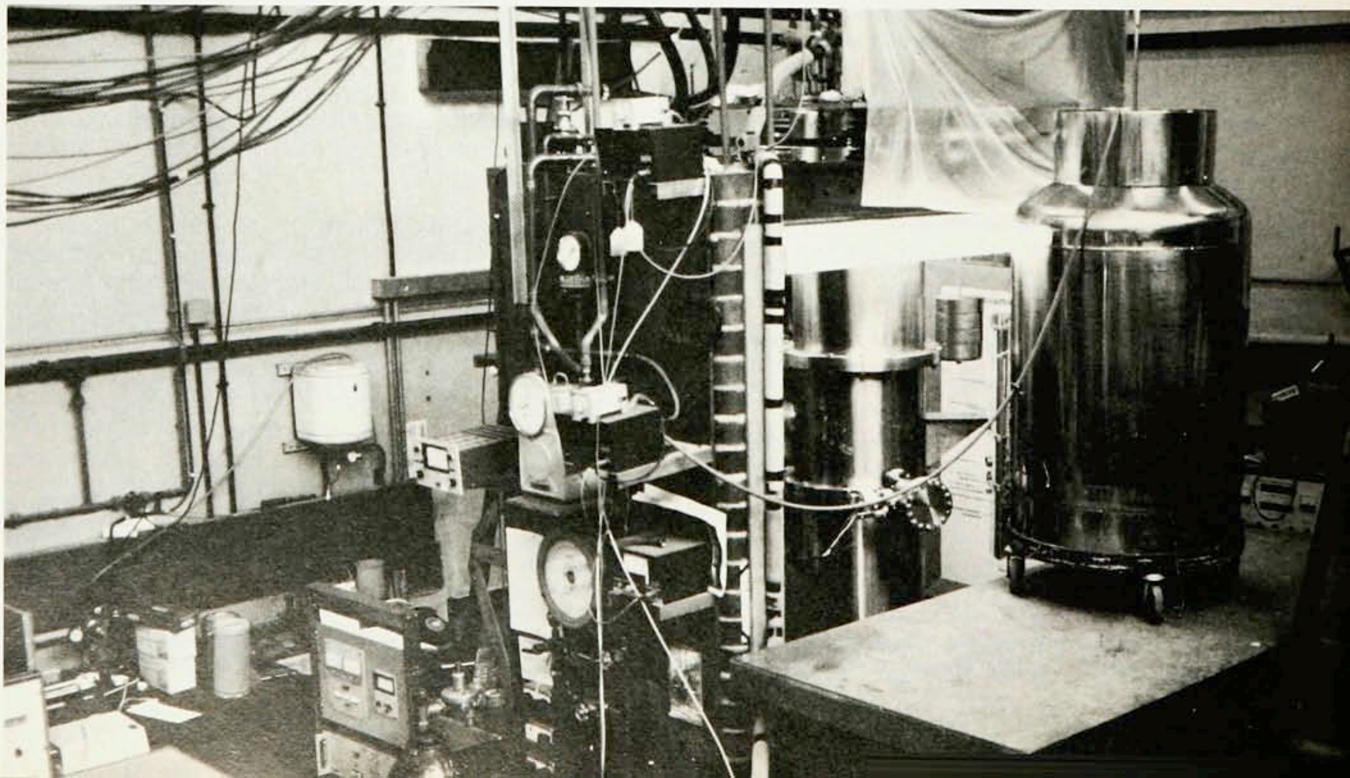
Leslie A. Guildner

We owe the concept of "thermodynamic temperature" to Sadi Carnot, William Thomson and Rudolf Clausius. This very basic property is measured in the Systeme Internationale of units by the kelvin, defined in terms of the thermodynamic temperature of the triple point of water. In principle, any other temperature may be determined by its ratio to this defined temperature. In practice, however, it is almost always more convenient to measure an approximation of the thermodynamic temperature by using one of the famil-



Constant-volume gas thermometer assembly at NBS. The gas bulb is at the bottom inside an inconel counter-pressure case. Four standard platinum-resistance thermometers extending to the midpoint of the case serve to compare the thermodynamic temperatures with those of a reproducible practical scale; the tube between them supports the bulb and case. Figure 1

Cryogenic radiometer used at NPL to obtain thermodynamic temperatures in the range − 40 °C to a + 100 °C to within a few millikelvins and to measure the Stefan–Boltzmann constant with a precision better than 1/10%. Figure 6 compares temperature measurements between 273L and 373K made with these two thermometers. Figure 2



iar thermometers (platinum resistance, thermocouple, radiation pyrometer, and so on).

Two "practical" scales defined with reference to practical thermometers cover most temperature measurements. Between 13.81 K and 1337.58 K, the International Practical Temperature Scale of 1968, referred to as the IPTS-68, is defined by a set of fixed points (given as the temperatures at which certain pure materials undergo first-order phase transitions), together with equations for interpolating between the fixed points by so-called "standard instruments." Above 1337.58 K (the gold point), the IPTS is realized by radiation measurements, extrapolated according to the Planck radiation equation, without restriction as to the standard instrument. The "1976 Provisional 0.5 K to 30 K Temperature Scale" (EPT-76) provides a standard practical scale for low temperatures. It overlaps the IPTS-68 between 13.81 K and 30 K to improve the thermodynamic accuracy and smoothness of temperatures in that region and to give continuity with the IPTS at 27.1 K. This scale lacks the relative simplicity of the IPTS-68, in particular because no satisfactory standard instruments have been found for the lower temperatures.

The values of temperature on the practical scales—both at the fixed points and in between—are continually subject to examination to see how closely they conform to thermodynamic temperature. The instruments needed for this purpose must of course depend for their interpretation only on basic thermodynamic (or statistical-mechanical) principles, and the purpose of this article is to discuss recent progress made with several of them. We shall examine particularly gas thermometers, noise thermometers, acoustic thermometers, spectral-radiation thermometers, dielectric-constant thermometers, and gamma-ray-anisotropy thermometers.

Over the temperature range from 5 K to the freezing point of gold (1337 K), gas thermometers, such as that shown in figure 1, presently offer the most accurate way to realize thermodynamic temperatures. But in the last ten years some of the previously existing thermodynamic thermometers have gained remarkably in accuracy, and some others that have appeared only within that period are already accurate and reliable instruments, to the extent that the advantage of gas thermometry is substantially diminished. Because of their totally different systematic errors, the results obtained with these various kinds of thermometers are useful for comparison to ensure the essential absence of systematic errors in the different measurements.

Certain of these instruments—the gamma-ray-anisotropy thermometer and the Josephson-junction noise thermometer—can operate at lower temperatures than is possible with a gas thermometer, with good accuracy. Others—the dielectric-constant gas thermometer, the acoustic thermometer, and the cross-correlated noise thermometers—can be used to measure thermodynamic temperatures between 2 K and 5 K with greater ease than, and at least comparable accuracy to, a gas thermometer. Above 5 K these instruments offer about the same accuracy as below, but the attainable accuracy of a gas thermometer improves. At higher temperatures the more usual noise thermometer and the total-radiation thermometer (figure 2) can approach the accuracy of good (but probably not the best) gas thermometry. Over the hotter part of the range, around 700 K to 1337 K, spectral-radiation thermometry can be used to make accurate measurements, but at a level of accuracy inferior to the best gas thermometry potentially available. Above the temperature of the gold point, the advantage in accuracy swings toward the spectral-radiation thermometers.

Much of the work I will be discussing here was reported at a recent International Symposium on Temperature, held in Washington, D.C., in March 1982. See the box on this page for more details of the symposium and its published proceedings.

Thermodynamic temperature

Carnot was considering a practical problem with great commercial implications, the amount of work that can be produced with steam engines, when he analyzed the operation of the generalized heat engine with the now well-known "Carnot cycle." He concluded that there is a theoretical maximum to the amount of work that can be extracted when a given quantity of heat flows from one temperature to another. He further deduced that this theoretical maximum is independent of the substance by which the cycle is effected and that it depends only upon some (at that time) undetermined function of the upper and lower temperatures. By present-day standards, the principles set forth by Carnot are remarkable; their development by him in the early 1820s rates as an act of creative genius that profoundly affected the development of science. This is all the more astonishing when one considers that Carnot was better known to his contemporaries as the son of his militarily successful father, Lazare Carnot, than as a scientist, and his little book *Reflexions sur la Puissance Motrice du Feu* (*Reflections on the Motive Power of Heat*), published in 1824, received scant notice.

Twenty-five years later, William Thomson recognized that Carnot's conclusions formed the basis of an "absolute thermometric scale," and he published articles on the subject in 1848 and 1849. At that time the idea of "caloric" persisted, and the interconvertibility of heat and work was, in Thomson's words, "probably impossible."

Both Carnot and Thomson recognized inconsistencies in their theories, the resolution of which was speedily provided by Rudolf Clausius in 1850 with two laws for the theory of heat. Whereas the prior considerations were based on ideas that approximate the First Law of Thermodynamics, Clausius accounted for the conversion of heat to work and showed that the Carnot cycle was strictly a creature of the hitherto unknown Second Law.

Although Thomson referred to "an absolute thermometric scale," the same concept is now referred to as "thermodynamic temperature," to de-

Leslie A. Guildner recently retired from the National Bureau of Standards, where he was the leader of the gas thermometry project.

Temperature: Its Measurement and Control in Science and Industry

The accompanying article is adapted from a paper presented at the Sixth International Temperature Symposium, held in Washington, D.C., 15–18 March 1982. The original paper, and the 1981 others presented at this conference (which is held only once per decade) are published in *Temperature: Its Measurement and Control in Science and Industry*, Volume 5. (Yes, the proceedings of the Sixth Symposium are published in Volume 5; the first symposium, held in 1920, had no published proceedings.)

Copies of the 1400-page, two-part publication can be obtained from:

Marketing Service Department
American Institute of Physics
335 East 45 Street
New York, NY 10017
The price is $110 per set, prepaid.

note that it is a "fundamental physical quantity," that is, it is measured and expressed as a coefficient times a unit. The unit, the kelvin with the symbol K, is one of the units adopted for the Système Internationale, and is defined as 1/273.16 of the thermodynamic temperature of the triple point of water. All other thermodynamic temperatures must be determined by their ratios to the assigned value of the triple point of water (273.16 K).

Other systems of temperature measurement that are constructed sequentially, such as the IPTS, are *scales* of temperature. The fixed points of these scales have highly reproducible temperatures to which values as closely thermodynamic as possible are assigned. The standard instruments used to realize the scales are practical thermometers of great precision and reproducibility, considered either in terms of a single instrument or between instruments. The text of the IPTS specifies that the standard instruments must possess certain characteristics (except that above the gold point, 1064.43 °C, no instrument is specified). The interpretation of their indications is made according to equations that are designed to approximate as closely as practicable the thermodynamic values as understood at a given time. Although thermodynamic temperature and the 1968 revision of the IPTS (the most recent full revision) have the triple point of water with an assigned value of 273.16 K in common, it must be clear that their units are not everywhere the same. This must be true since IPTS-68 values of temperature have been found not to agree with the corresponding thermodynamic values at many points. It is a measure of the success of the Comité Consultatif de Thermomètrie in its construction of the IPTS, however, that the kelvin of the IPTS varies with respect to the thermodynamic kelvin by no more than 0.4%.

Thomson was impressed by the consistency of values of temperature derived by gas thermometry. In his earliest paper involving the Carnot cycle, he used the observations from Victor Regnault's constant-pressure gas thermometry to calculate an absolute scale. It is rather ironic that the godfather of thermodynamic temperature was led to it by a statistical-mechanical instrument. In principle, thermodynamic temperatures can be determined by measurements involving any second-law process explicitly dependent on thermodynamic temperature, or equivalently, upon statistical-mechanical temperature. In fact, all of the techniques that give acurate results involve processes elucidated by statistics.

The determination of the thermodynamic temperature fundamentally involves a ratio measurement. Whenever temperature occurs in statistical-mechanical expressions, it is coupled with either R, the molar gas constant, or k, the Boltzmann constant (as RT or kT), so that statistical-mechanical (or thermodynamic) temperature can be measured at an isotherm by choosing a value of R. The identical isotherm techniques can be used to determine R at the temperature of the triple point of water. Thus selecting a value of R for calculating a temperature measured by a statistical-mechanical instrument amounts to employing a surrogate measurement at the triple point of water. Recent measurements of R have been made with considerably improved accuracy, but any of the techniques of thermodynamic thermometry carried out at the state of the art use an explicit ratio measurement that eliminates the uncertainty in R by cancellation.

Gas thermometry

The term "gas thermometry" is used here to denote thermodynamic measurements by those instruments that make direct use of the pressure-versus-volume relationship of a gas. Of the seven techniques we shall discuss in this article for thermodynamic temperature measurement, gas thermometry has been the mainstay, and it provided the basis of temperature standards even before the principles of thermodynamics were understood.

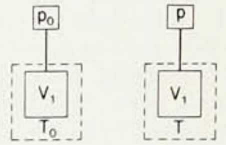
Given that the equation of state for a real gas is

$$pV = nRT[1 + B_V\, p/(RT) + \dots]$$

thermodynamic temperatures are identical to the ideal-gas temperatures obtained by extrapolating to zero pressure the gas thermometer temperatures, $pV/(nR)$. In the equation, p is the pressure, V the volume, n the number of moles of gas, R the molar gas constant, T the thermodynamic or ideal-gas temperature, and B_V the second volume virial coefficient. The expansion involves higher virial coefficients, but the range of pressure over which a gas thermometer is operated is usually restricted enough to make their effect insignificant.

Many gas thermometers are designated by those experimental parameters maintained constant in their operation, such as constant volume, constant pressure, constant bulb temperature, or the method of two bulbs, and in each type of thermometer a fixed quantity of gas is used. The essential feature of each thermometer is demonstrated by considering its equation for the idealized case, which is to say that the thermometers are filled with a perfect gas, that the gas thermometer bulb or bulbs are not subject to change in size, and that all connecting tubing is of insignificant volume. The use of constant-volume valves and a diaphragm pressure transducer effectively eliminates any concern for the volume of the manometer. (We will have more to say about this later.)

In an idealized constant-volume gas thermometer, a fixed amount of gas is confined in a bulb thermostated successively at temperatures T and T_0, with corresponding pressures p and p_0. The equation derived by equating the number of moles of gas in each state gives the temperature from $p/p_0 = T/T_0$.

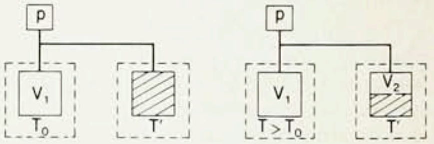


In an idealized constant-pressure gas thermometer, a bulb of volume V_1 is thermostated successivly at temperatures T and T_0. At the lower of these temperatures, all the gas is confined in V_1, but at the higher temperature, gas is allowed to flow into a second bulb thermostated at a temperature T', and its volume, V_2, is adjusted to a value that keeps the pressure constant. For highest accuracy, T' and T_0 should both be at the reference temperature, ordinarily 273.16 K. When $T > T_0$ and $T' = T_0$,

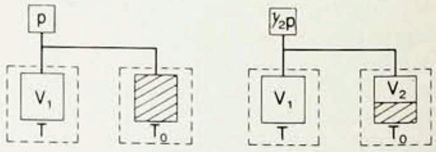
$$TV_1 = T_0(V_1 + V_2)$$

and when $T < T_0$ and $T' = T_0$,

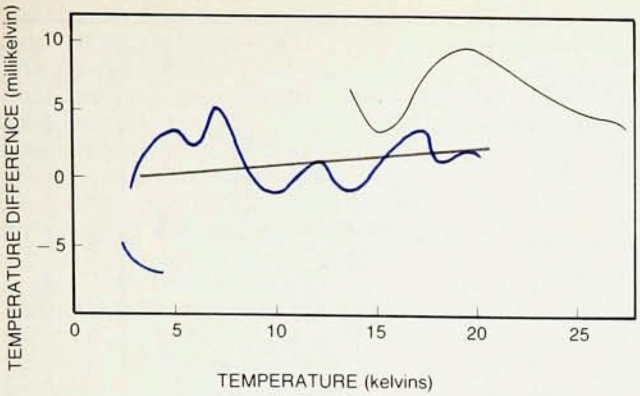
$$TV_1 = T_0(V_1 - V_2)$$



In an idealized constant bulb temperature gas thermometer, a fixed amount of gas is initially confined in a bulb of volume V_1 that is thermostated at a temperature T and pressure p. Then a portion of the gas is transferred to a second bulb of volume V_2 thermostated at a temperature T_0. When the volume V_2 is chosen so that the final pressure is $p/2$, maximum sensitivity is achieved. The resulting equation is $T_0V_1 = TV_2$.



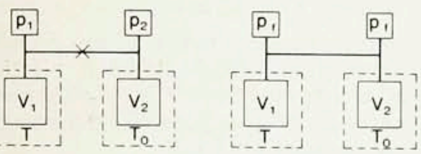
The method of two bulbs has one bulb of volume V_1 at temperature T and a second bulb of volume V_2 at temperature T_0. Initially the gas in V_1 is at pressure p_1 and the gas in V_2 is at pressure p_2. Then the bulbs are inter-



Variations between temperature scales in the cryogenic range 0–25 K, measured against a 1975 determination by Keith Berry at NPL with a gas thermometer. The curves represent scales known as NBS_{2-20} (solid color), T_{76} (grey), T_{58} (light color) and IPTS-68, the current international practical temperature scale (black). Figure 3

connected with a final pressure p_f. The resulting equation is

$$T_0 V_1 = T V_2 (p_2 - p_f)/(p_f - p_1).$$



The fundamental assumption in isotherm thermometry is that the gas is not ideal. For the absolute isotherm thermometer, gas is transferred from a volume V_2 at temperature T_0 and initial pressure $p_i^{\,1}$ to a volume V_1 at a final pressure $p_f^{\,1}$. The number of moles added to V_1, N_B, is the difference between the initial and final amounts in V_2. We may then express the gas-thermometer temperature of the gas in V_1, $T_{GT} = p_B^{\,1} V_1/(RN_B)$, in two ways, first by substitution of the value of N_B, so that

$$\frac{p_B^1 V_1}{(RN_B)} = \frac{p_B^1 V_1 T_0}{V_2}\left[\frac{p_i^1}{1 + B_r\, p_i^1/(RT_0)} - \frac{p_f^1}{1 + B_r\, p_f^1/(RT_0)}\right]^{-1}$$

and from the equation of state

$$p_B^1 V_1/(RN_B) = T_B\,[1 + B(T_B)\, p_B^1/(RT_B) + \ldots\,]$$

One may similarly add further increments of gas to V_1 and derive a series of values of T_{GT} as a function of $p_B^{\,n}$ to allow extrapolation to zero pressure. The gas thermometer temperature depends primarily upon the pressure ratios $p_i^{\,n}/p_B^{\,n}$ and $p_f^{\,n}/p_B^{\,n}$, and the volume ratio V_1/V_2; the effect of the uncertainty in R is insignificant.

Relative isotherm thermometry is equivalent to constant-volume gas thermometry performed at a series of gas densities. The gas-thermometer temperatures found can then be extrapolated to zero pressure to give the thermodynamic temperature.

All real gas thermometers fail to operate ideally because the have a "real" (that is, imperfect) gas for a thermometric fluid, together with numerous other practical problems:

▶ The thermometer bulbs are subject to thermal and pressure dilation and possibly significant mechanical creep. To account for thermal dilation, some of the most exact thermal-expansion measurements ever made have been performed for gas thermometry. Many modern gas thermometers are made with counter-pressure systems to avoid pressure dilation. Mechanical creep leads to error only to the extent that it occurs during the period of a single cycle of measurements, hence it can be kept small.

▶ Connecting lines have finite volumes, the choice of their diameter being a compromise between the need for a small value to minimize the amount of gas contained in the lines and the need for a large value to maximize high vacuum conductance and to reduce thermomolecular pressures. On balance, tubes with internal diameters of about 1 mm are satisfactory.

▶ There must be communication of the gas with a pressure-measuring device. All modern gas thermometers make use of pressure transducers. The thermometer proper is defined to end at a constant-volume valve; the connecting tube, bypass valve and pressure transducer are made as small in volume as possible. The gas thermometer must then be operated so as to cause insignificant changes in the amount of gas in the transducer section as a result of being connected with it.

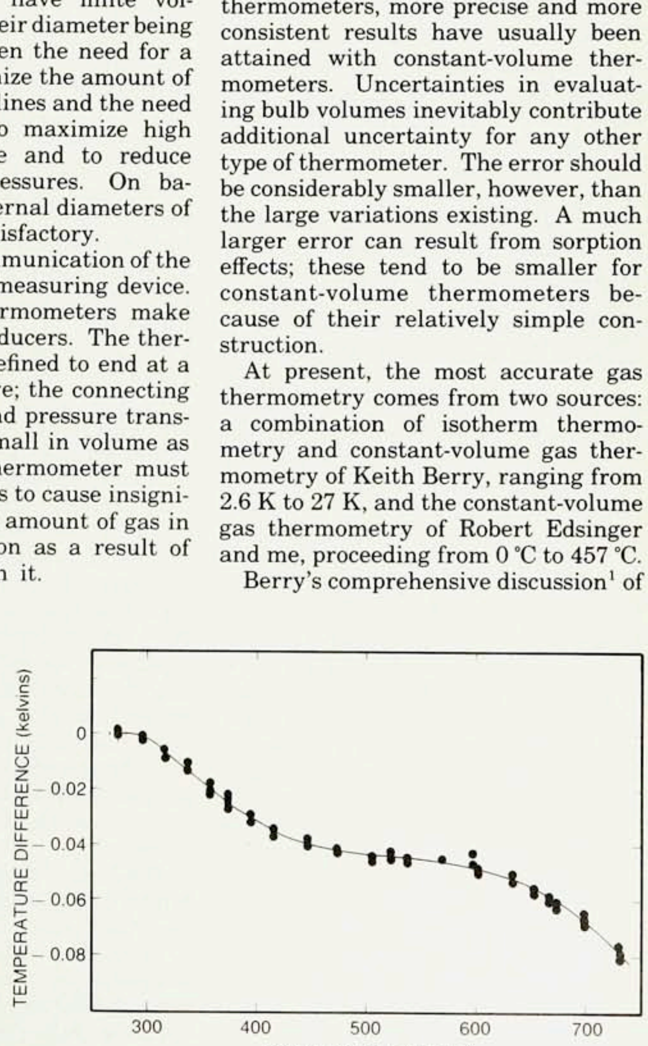
▶ The quantity of gas may vary because of sorption. Because of this, only helium qualifies as a satisfactory thermometric fluid. Helium will adsorb only at temperatures so low that the effect is not significant for currently attained uncertainties. Conversely, practically all of the older gas thermometry is flawed by choice of some other gas as the thermometric fluid. At higher temperatures, sorption—the desorption and resorption of various species, and, above 400 °C, the diffusion of hydrogen through the walls of the gas thermometer bulb—can cause, and almost surely has caused, major systematic errors in earlier gas thermometry. As an indication of the size of this effect, modern National Bureau of Standards gas thermometry shows that the value of 273.23 K (rather than 273.16 K) should have been assigned to the triple point of water! It is clear that there are no published results of gas thermometry above 500 °C in which hydrogen diffusion was correctly analyzed and controlled, yet the effects are pervasive and potentially large.

While in principle the values of thermodynamic temperatures should be in agreement for all types of gas thermometers, more precise and more consistent results have usually been attained with constant-volume thermometers. Uncertainties in evaluating bulb volumes inevitably contribute additional uncertainty for any other type of thermometer. The error should be considerably smaller, however, than the large variations existing. A much larger error can result from sorption effects; these tend to be smaller for constant-volume thermometers because of their relatively simple construction.

At present, the most accurate gas thermometry comes from two sources: a combination of isotherm thermometry and constant-volume gas thermometry of Keith Berry, ranging from 2.6 K to 27 K, and the constant-volume gas thermometry of Robert Edsinger and me, proceeding from 0 °C to 457 °C.

Berry's comprehensive discussion[1] of

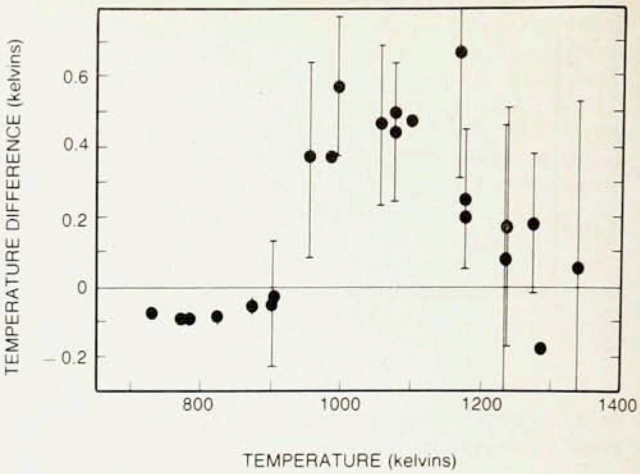
Gas-thermometer measurements in the range 273 K–730 K show differences between IPTS-68 and thermodynamic temperature. The measurements were made at the National Bureau of Standards. Figure 4



his work at the National Physical Laboratory in Teddington, UK, gives details and evaluation of the results. The scale based on this work, NPL-75, is recorded on three rhodium–iron thermometers and a platinum-resistance thermometer, in terms of fixed points and interpolating equations. The relationships to other scales for the low-temperature range are well-established. The differences between these scales and NPL-75 are shown in figure 3.

Results with our constant-volume gas thermometer at the National Bureau of Standards[2] have been recorded in terms of the differences from the IPTS-68, with the IPTS realized as an average from the indications of three, and sometimes four, calibrated standard platinum-resistance thermometers. The results from 0 °C to 457 °C are given in figure 4. The total uncertainty (99% confidence) is about 8 ppm over the range of measurement. Subsequently, preliminary measurements have been made at the aluminum point (660 °C) and higher. The goal of the project is to determine values of thermodynamic temperatures versus a precise practical scale every 50 °C up to the gold point.

Variations in spectral-radiation temperture measurements in the range 730–1337 K. The reference temperatures are the IPTS-68 values. The measurements are from experiments at NPL, BIPM and the Instituto di Metrologia. Figure 5



Noise thermometry

The measurement of thermodynamic temperature by noise thermometry depends upon the effect of the Brownian motion of the electrons of a conductor. The rms values of the voltage produced by the thermal agitation of the electrons, the Johnson noise, of a resistance R at a thermodynamic temperature T is given by Nyquist's equation, where the time average of the mean square voltage of the fluctuations $\langle V^2\rangle$, between the frequencies ν and $\nu + d\nu$ is

$$\langle V^2\rangle = 4Rh\nu d\nu\{\exp(h\nu/kT) - 1\}^{-1}$$

where h is Planck's constant and k is Boltzmann's constant. In the absence of significant quantum effects (at the radio frequencies used in these experiments, that is for temperatures above 30 mK), this expression reduces to

$$\langle V^2\rangle = 4RkTd\nu$$

which is the familiar equation.

The practical problems in noise thermometry arise because the fluctuation voltages are very small and require amplification over a frequency bandwidth; there are other sources of thermal noise that must be excluded from the evaluation of $\langle V^2\rangle$ and there are other kinds of noise to be excluded as well. Thus the measured quantity is represented by an integral

$$\langle V^2\rangle_{\rm meas} = \int_0^\infty (v_{\rm noise} + \Sigma\, v_i)^2 \alpha_A\, F_A\, d\nu$$

where the v_i are extraneous sources of noise voltage, α_A the amplification and F_A a filter by which the bandwidth is controlled. The fundamental imprecision of this thermometer, $\Delta T/T$, is given by $(t\Delta\nu)^{-1/2}$ where t is the time of actual averaging and $\Delta\nu$ is the frequency bandwidth. Thus for $\Delta T/T$ to be small, the measurements must continue over appreciable lengths of time, with high stability of α_A and F_A. For highest accuracy, thermodynamic temperatures must be evaluated by ratio measurements of the mean square voltages at the unknown temperature and at the temperature of the triple point of water, to cancel k and eliminate its attendant uncertainty.

The first measurements of thermodynamic temperature by noise thermometry, reported by John Garrison and Andrew Lawson, had uncertainties greater than 0.1% because of the noise instability of the amplifiers. Clive Pickup[3] at the National Measurement Laboratory in Sydney, Australia, is currently using a similar technique, but with much lower uncertainty: He evaluates the noise voltage balance between two resistors, R_1 and R_2, one at an unknown temperature and the other at a reference temperature, by means of synchronous switching. To compare identical noise voltages, one adjusts the resistances so that $R_1T_1 = R_2T_2$. With constant channel bandwidth (a requirement), the shunt capacitances C_1 and C_2 must be adjusted so that $R_1C_1 = R_2C_2$. In Pickup's experiments a typical bandwidth was 100 kHz; he subsequently introduced a second bandwidth in a higher range to permit a more exact balance of capacitance.

The improvement in electronic technology has allowed considerable reductions in the noise level and instability of amplifiers. Relative to a reference temperature measured on IPTS-68 near 25 °C, Pickup measured a thermodynamic value of the oxygen boiling point 3 mK above IPTS-68 (90 K), and a thermodynamic temperature 8 mK larger than IPTS-68 at 97 K. If the value reported from NBS gas thermometry for 25 °C is used, the differences are reduced by 2 mK.

H.-H. Klein, Günter Klempt and Leo Storm[4] at the University of Münster made use of an exceptionally high level of electronic technology to achieve low extraneous noise levels and long-term stability of the amplifiers. They measured the noise voltage first at one temperature and than at another. Their technique does not require that $R_1T_1 = R_2T_2$, but the effective shunt capacitances must be in the relation $R_1C_1 = R_2C_2$. In addition, Klein, Klempt and Storm used a cross-correlation technique that reduces the effect of amplifier noise by a factor perhaps exceeding a thousand, thus allowing accurate measurements at temperatures as low as 2 K. The noise voltage is sensed by two nearly identical amplifiers in parallel, so that random noise will very nearly cancel.

Klein, Klempt and Storm have reported measurements at seven cryogenic temperatures established by helium vapor pressures. From 2.1451 K to 4.2221 K, two of their values exceeded those of the NPL-75 scale by + 0.0004 K; the average difference of their values was + 0.0002 K higher than the NPL-75 values. Their estimates of uncertainty are consistent with this result, and they project a reduction in total temperature uncertainty from the presently attained 100 ppm to around 10 ppm at higher temperatures.

For temperatures so low that the noise from the cross-correlation technique is excessive, one can use amplifiers based on the Josephson effect, such as SQUID magnetometer noise thermometers or resistance SQUID noise thermometers for temperatures as low as 0.01 K and as high as 10 K. For such Josephson-effect devices, the upper temperature is necessarily limited because, except for the resistor, the components of the first-stage amplifier must be superconducting.

In the apparatus of Robert Soulen[5] at the National Bureau of Standards, the Josephson junction in a resistive SQUID noise thermometer is biased by a dc voltage, approximately 10^{-11} volts, which causes it to produce an ac signal according to the Josephson equation

$$V = (h/2e)\nu$$

The voltage V consists of the constant bias voltage plus the noise voltage generated across the resistance R; the frequency ν is in the audio-frequency range. This combined signal modulates the amplitude of an rf signal, from which one then obtains the voltage noise information in terms of frequency; the frequency information is in turn computer processed to give the variance

$$\sigma_\alpha{}^2 = \sum_1^N (\nu_i - \nu_{i+\alpha})^2/2N$$
$$\alpha = 1,2,3,\ldots$$

where ν_i is an individual frequency count and $\nu_{i+\alpha}$ is the frequency count α gate times later. When the measurements contain only the noise voltage of the resistor, the power spectrum is "white," as established by the fact that all the variances are equal. When that criterion is fulfilled, the variance can be related to temperature by

$$\sigma^2 = 2kRT/(\tau h^2/4e^2)$$

where τ is the gate time and $h/2e$ is the Josephson constant, whose value (which is very precisely known) is about 2.07 fV Hz^{-1}. Although this expression is free of the properties of any part of the system except the value of the resistance R, in reality the dc impedance of the SQUID is modified, thus affecting the apparent value of R. Furthermore, the Josephson junction adds noise to the circuit. Both effects are proportional to the ratio of the superconducting current to the biasing current, a fact that provides a means for eliminating them by extrapolation.

The present level of uncertainty of the resistive SQUID does not exceed 0.5% and is that large partly because of its very long averaging time. There is a possibility of a ten-fold reduction in averaging time (to achieve the same accuracy) which would allow a 1% statistical imprecision in 2000 seconds (τ of one second).

Acoustic thermometry

Sound is propagated adiabatically in an unbounded medium with a velocity given by $c^2 = B_s/\rho$, where the adiabatic bulk modulus is $B_s = -V(\partial p/\partial V)_s$ and ρ is the density. For an ideal gas, $B_s = \gamma p$, where γ is the the ratio of specific heats, c_p/c_v, and $\rho = pM/(RT)$, so that $c^2 = c_0{}^2 = \gamma RT/M$. For a real gas, used at pressures low enough that the equation of state is sufficiently accurate when written

$$pV = RT(1 + B_v\,\rho)$$

the speed of sound is

$$c^2 = c_0{}^2(1 + A_1(T)p + \ \ldots)$$

where

$$A_1(T) = (\gamma/M)[2BT + (4/3T\,dB/dT + (4/15)T^2\,d^2B/dT^2]$$

Thus acoustic thermometry, like noise thermometry, can be used to realize thermodynamic temperatures by isotherm measurements when the uncertainty in the value of R is acceptable. Acoustic thermometry, like gas thermometry, is affected by gas imperfections. This effect can be eliminated by evaluating c^2 as a function of p and extrapolating to zero pressure.

In reducing these principles to practice, one must take great care to balance competing choices to optimize the accuracy of the results. The speed of sound is typically determined in a cylindrical chamber, where the distances of resonance for a fixed frequency are determined by varying the path length. If one uses low frequencies, one can establish the mode of propagation, but the boundary effects are very large. If one uses high frequencies, the modes of propagation are mixed; the boundary-layer effects are smaller, but the overall uncertainty is probably larger because of the difficulty of interpreting the results, which rely on understanding the modes of propagation.

At the National Physical Laboratory, Anthony Colclough[6] has measured the speed of sound in helium gas in a cylindrical container at low frequencies. The resulting experimental system has well-defined modes, with large but accurately calculable boundary-layer effects. Thus, even though the relative value of the adjustment, $\Delta c/c$, was as high as 4000 ppm at the lowest pressures used, the error in Δc did not contribute significantly to the total uncertainty. Colclough measured the thermodynamic temperature of five cryogenic fixed points, with uncertainties evaluated at 1 to 4 mK (three standard deviations), and additional systematic uncertainties from 0.5 to 1.7 mK. The values agree with Berry's gas thermometry within 2.2 mK at 17 K, but otherwise within about 1 mK at temperatures from 4.2 K to 20.27 K.

The NPL acoustic thermometer represents the most careful execution and analysis of a customary acoustic device up to the present time. It will be necessary to improve its accuracy to yield more accurate values of the gas constant or higher thermodynamic temperatures.

The spherical resonator, constructed by James Mehl and Michael Moldover at the National Bureau of Standards, requires boundary adjustments only about 10% as large as those of the NPL instrument. The frequencies of 4 kHz to 13 kHz are in the same range that Colclough used (3.3 kHz to 7.25 kHz). The derived values of $c_0{}^2$ had standard deviations in the range of 100 ppm for either instrument. It is expected that the spherical instrument is also capable of greater accuracy, so that values of thermodynamic temperatures determined for higher temperatures may be useful.

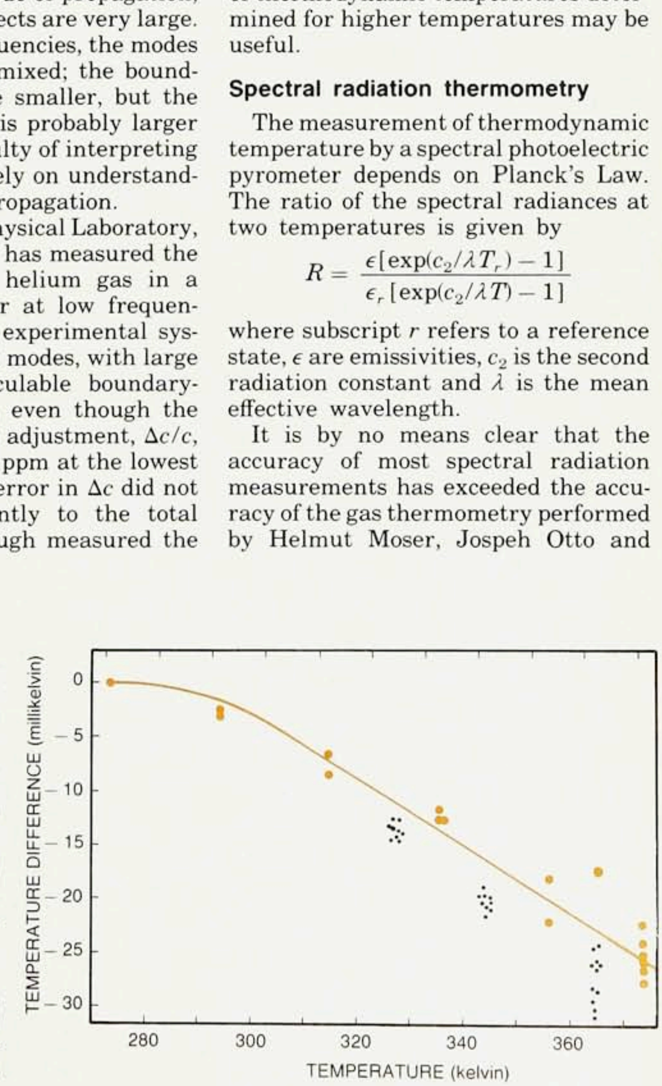
Spectral radiation thermometry

The measurement of thermodynamic temperature by a spectral photoelectric pyrometer depends on Planck's Law. The ratio of the spectral radiances at two temperatures is given by

$$R = \frac{\epsilon[\exp(c_2/\lambda T_r) - 1]}{\epsilon_r[\exp(c_2/\lambda T) - 1]}$$

where subscript r refers to a reference state, ϵ are emissivities, c_2 is the second radiation constant and λ is the mean effective wavelength.

It is by no means clear that the accuracy of most spectral radiation measurements has exceeded the accuracy of the gas thermometry performed by Helmut Moser, Jospeh Otto and



Comparison of total-radiation thermometry and gas thermometry with the practical temperature scale IPTS-68. The black dots indicate total-radiation measurements by T. J. Quinn and J. E. Martin at the NPL; the colored dots indicate gas-thermometer measurements by L. A. Guildner and R. E. Edsinger of NBS. The curve is Guildner and Edsinger's fit to their data. Figure 6

Wilhelm Thomas in the 1950s at the Physikalisch-Technische Bundesanstalt in Braunschweig. That work, however, was confined to the temperatures of the fixed points over the range from 0 °C to 1064.43 °C, and it is at temperatures between the fixed points, particularly above 630 °C, that the differences between the IPTS and thermodynamic values are large. Spectral radiation thermometry has given somewhat improved accuracy for the difference of the thermodynamic temperatures of the freezing points of silver and gold, and with the development of more sensitive and more stable detectors, there is a real prospect of much-increased accuracy overall in the near future.

Peter Coates, J. W. Andrews and M. V. Chattle have recently reported results of work on a spectral photoelectric pyrometer at the NPL. They determined the differences, $t - t_{68}$, between 457 °C and 630 °C, based on the NBS gas-thermometer value at 457 °C, and report an "overall uncertainty" increasing from 0.010 °C at 460 °C to 0.030 °C at 630 °C.

Jacques Bonhoure at the Bureau International des Poids et Mesures measured the differences between thermodynamic temperatures, as realized by a spectral photoelectric pyrometer, and the IPTS-68, as realized by type-S thermocouples, at six temperatures ranging from 720 °C to 1064.43 °C. As references, he used the assigned values of the IPTS-68 for the temperature of the antimony point (903.89 K) and for the second radiation constant, c_2 (0.014388 K m). The reported standard deviations for the silver point and for the gold point were 0.13 K and 0.16 K, respectively. Further work is underway at BIPM to compare values of thermodynamic temperatures and the IPTS between 420 °C and 630 °C by similar techniques.

Numerous measurements of the thermodynamic temperatures of the silver point and the gold point, have shown the thermodynamic interval to be less than the IPTS-68 interval. Terence Quinn, T. R. D. C. Chandler and Chattle reported a value as early as 1973; that value and the later results are in better agreement than would be expected from the estimated uncertainties. The determinations made in more recent measurements are reported to have less uncertainty. On the basis of the freezing point of gold as 1064.43 °C, the thermodynamic temperature of the freezing point of silver was reported by H.-J. Jung as 962.06 °C ± 0.1 °C, by Teresio Ricolfi and F. Lanza as 962.05 °C ± 0.04 °C, and by Trevor Jones and J. Tapping[7] as 961.98 °C ± 0.015 °C, whereas the IPTS-68 value is 961.93 °C.

In combination, this work on spectral radiation work covers the temperature interval from 457 °C to the gold point, although not as accurately as could be desired. These results with error bars for the total uncertainties estimated by the authors together with other work in the same range are presented in figure 5.

Total radiation thermometry

Total radiation thermometers are calorimeters capable of accurately measuring the radiant heat flow from a blackbody. Dafoe Ginnings, Les Nuttal and Martin Reilly have built such a device at NBS, as have Quinn and John Martin at NPL and Akira Ono at the National Research Laboratory of Metrology in Tokyo. The thermodynamic temperature is established from the Stefan–Boltzmann Law, where the radiant power transferred between two surfaces at temperatures T_2 and T_1 with an effective emissivity ϵ_{12} is

$$\dot{q} = A\epsilon_{12}\sigma(T_2^{\,4} - T_1^{\,4})$$

with A the area and σ the Stefan–Boltzmann constant. (It should be of interest that our "surrogate ratio" to the temperature of the triple point of water still exists, inasmuch as

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

which involves Boltzmann's constant k.) There are formidable experimental problems to overcome in this experiment. The radiant power is measured with a calorimeter at liquid-helium temperatures so that $T_1^{\,4}$ is insignificant compared with $T_2^{\,4}$. If the problems of achieving sensitivity, aperture alignment, ultrahigh vacuum and high emissivity are solved, there still remains the nearly intractable problem caused by diffraction of the radiation. The work at the NBS was dropped because of it. The instrument at the NRLM is still under construction. The NPL instrument incorporates a specially designed aperture system that appears to perform satisfactorily, and it is operational. Quinn and Martin[8] have reported the differences between thermodynamic temperatures and the IPTS-68 from −30 °C to 93 °C. These results and those of NBS gas thermometry in the same range are shown in figure 6. Because the operation of this instrument is in its early stages, no final judgment of its accuracy is yet possible, but an uncertainty of a few millikelvins at the steam point is a reasonable possibility.

Dielectric-constant gas thermometry

The temperature dependence of the dielectric constant of a gas on its density has been successfully used by Donald Gugan and J. W. Michel[9] for measurements of thermodynamic temperatures in the cryogenic region. The relative change in capacitance produced by the introduction of a gas at pressure p between the plates of a capacitor is $[C(p) - C(0)]/C(0)$, where $C(p)$ and $C(0)$ are the capacitances at pressure p and under vacuum. When the dielectric constant of the gas is ϵ, $\Delta C/C(0) = \epsilon - 1$. The observed value is related to the Clausius–Mossotti equation modified for the effect of gas imperfection:

$$(\epsilon - 1)/(\epsilon + 2) = (A_\epsilon/V)(1 + b/V + c/V^2 + \dots)$$

where A_ϵ is the polarizability of the gas and V is the molar volume. When V, derived from the Clausius–Mossotti expression, is substituted into the equation of state for a real gas,

$$pV = RT(1 + B/V + C/V^2 + \dots)$$

the resulting equation is

$$p = A_1\mu(1 + A_2\mu + A_3\mu^2 + \dots)$$

The expansion parameter, μ, is $(\epsilon - 1)/(\epsilon + 2)$ with a small additional term for the compressibility, K, of the capacitor. The coefficients are

$$A_1 = (A_\epsilon/(RT) + K/3)^{-1}$$

$$A_2 = B'/A_\epsilon,$$

$$A_3 = C'/A_\epsilon^2$$

$$A_4 = D'/A_\epsilon^3$$

where $B' = B - b$, and C', D' and so forth, are very nearly equal to the virial coefficients C, D and so forth.

Thus values of T can be determined from values of A_1 derived from the intercepts of isotherms, when values of A_ϵ, R and K are known. The polarizability of helium, A_ϵ, can be calculated from theory, with an estimated uncertainty of 1 ppm. In their laboratory at the University of Bristol, Gugan and Michel have determined thermodynamic temperatures, estimated to be accurate within 0.3 mK, in good agreement with Berry's NPL gas thermometry, from 4.2 K to 27.1 K. They anticipate that the method should be useful over the range from 2.6 to 400 K, with a total uncertainty of 10 parts per million when the uncertainty in R is eliminated.

Gamma-ray anisotropy thermometry

At temperatures between 12 mK and 35 mK, Harvey Marshak at the NBS has determined thermodynamic temperatures with a gamma-ray anisotropy thermometer. The measurements depend on the fact that at sufficiently low temperatures, the nuclear spin system of cobalt-60 is ordered when the nuclei are part of single crystal of Co^{59}. As a result, the gamma rays emitted in the process of nuclear decay are oriented with respect to the crystal axis. This anisotropy diminishes as the temperature increases. The degree of ordering with respect to a cylindrical axis is given by a set of parameters B_λ whose values are given as thermal averages, involving 6-j symbols, over the spin states of the system, that is with weights of the populations, a_m, of the spin states, with values of m between $-I$ and I. The population for thermal equilibrium follows the Boltzmann distribution

$$a_m = \frac{e^{-E_m/kT}}{\Sigma_m e^{-E_m/kT}}$$

where E_m is the energy of a nuclear m-state, k the Boltzmann constant and T the thermodynamic temperature. Experimentally, the ratio of intensity at angle θ with respect to the c-axis of Co^{59} for 1.17 and 1.33 MeV gamma-rays at the unknown low temperature and at a high temperature is determined, along with background counts according to

$$W(\theta) = \frac{C_c - B_c}{C_w - B_w}$$

where total counts either cold or warm (subscripts c and w) are labeled C and the background counts are labeled B. From the theory this ratio is given by

$$W(\theta) = \Sigma_\lambda B_\lambda(I,T) U_\lambda A_\lambda Q_\lambda P_\lambda(\cos\theta)$$

where θ is the angle between the axis of orientation and the gamma ray, U_λ and A_λ are angular coefficients depending on the decay path, the index λ runs from 0 to $2I$. The angular dependence is expressed by $Q_\lambda P_\lambda(\cos\theta)$, where the $P_\lambda(\cos\theta)$ are Legendre polynomials and Q_λ accounts for the geometry of the detector. The sensitivity depends on the value of E_m/kT. The useful range with cobalt is restricted to an upper limit of about 40 mK, with a total uncertainty somewhat less than 2%, and it can be extended to very low temperatures with an estimated uncertainty of 7.5% at 2 mK. The thermometer might be used with other elements at higher temperatures.

References

1. K. H. Berry, Metrologia **15**, 89 (1979).
2. L. A. Guildner, R. E. Edsinger, J. Res. Nat. Bur. Stds. **80A**, 703 (1976).
3. C. P. Pickup, Metrologia **11**, 151 (1975).
4. H.-H. Klein, G. Klempt, L. Storm, Metrologia **15**, 143 (1979).
5. R. J. Soulen Jr, Proc. Fifth Int. Conf. on Noise, Dietrich Wolf, ed., Springer, Berlin, (1978), page 249.
6. A. R. Colclough, Proc. Roy. Soc. (London) **A365**, 349 (1979).
7. T. Jones, J. Tapping, *Temperature, Its Measurement and Control in Science and Industry*, Vol. 5, AIP, New York (1982), page 169.
8. T. J. Quinn, J. E. Martin, *Temperature* etc, page 103.
9. D. Gugan, G. W. Michel, Metrologia **16**, 149 (1980).
10. H. Marshak, R. J. Soulen Jr, *Low Temperature Physics* LT-13, Vol. 4, Plenum, New York (1974) page 498. □