Thermodynamic gas thermometry in the range 230 °C to 660 °C

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Thermodynamic values of temperature were obtained in the range 230 °C to 660 °C by constant-volume gas thermometry. The apparatus and techniques employed in the experiments were substantially those developed by Guildner and Edsinger. In the present work, observed differences in temperature between the thermodynamic Kelvin scale and the International Practical Temperature Scale of 1968, t(KTTS) − t(IPTS-68), ranged from −0.03 °C at 230 °C to −0.11 °C at 660 °C. The estimated random uncertainty of the results ranged from ±0.005 °C to ±0.008 °C. The KTTS value of the freezing temperature of aluminum was found to be 660.342 °C ±0.015 °C. The major uncertainties in these results appear to lie in the determination of the volume of the gas bulb and the determination of its IPTS-68 temperature. Where they overlap in temperature, the present results differ noticeably from the earlier studies by Guildner and Edsinger. No explanation was found for this level of disagreement.

INTRODUCTION

In 1976, Guildner and Edsinger (1) reported on the use of constant-volume gas thermometry to determine the deviation of the International Practical Temperature Scale of 1968 (IPTS-68) from the Kelvin Thermodynamic Temperature Scale (KTTS) from 0-457 °C. Their results indicated that the IPTS-68 scale provided temperatures that were too large over the whole range, with the difference reaching 0.08 °C at 457 °C.

Since that time, the NBS results have been corroborated by total radiation thermometry (2) in the range 0-100 °C and by acoustic thermometry (3) at 30 °C. The studies have been extended to considerably higher temperatures by means of spectral radiation thermometry experiments (4-6).

In order to provide reference temperatures substantially above 457 °C that are referred to the KTTS defining temperature at 0.01 °C, we continued the work begun by Guildner and Edsinger, utilizing the existing equipment and a high-temperature furnace built for the gas thermometry project (7). We were able to make useful measurements up to temperatures as high as 660 °C. These measurements and the resulting determinations of the differences between the IPTS-68 and the KTTS from 230 °C to 660 °C have been presented in the journal Metrologia (8).

APPARATUS

The apparatus and procedures used in these studies have been fully described in our earlier paper (8). Here we provide only enough detail to allow an understanding of the work without recourse to other publications.

The construction of the gas thermometer was as follows: A thin-walled (~1 mm) right circular cylinder of volume ~400 ml made from a Pt-Rh alloy was connected by a Pt-Rh alloy capillary to a constant-volume valve block and thence to a source of very pure ^{4}He gas. The gas bulb also could be connected directly to a highly accurate mercury manometer (9), although in use it was separated from the manometer by the diaphragm of a capacitance-based differential pressure gage. The gas bulb was protected by a heavy-walled Inconel (10) jacket. The purified helium gas also could be admitted to the annular space between the gas bulb and its jacket; the pressure of this gas was held very close (within 1 kPa) to the gas-bulb pressure to minimize pressure deformation of the bulb. Four vertical holes drilled entirely within the thick walls of the jacket were utilized for the insertion of standard long-stem platinum resistance thermometers (PRT) near the bulb so as to allow estimation of its IPTS-68 temperature. Through the use of rotatable joints in the gas and pumping lines, the whole gas-bulb/jacket assembly could be removed from the high-temperature furnace by a hydraulic lift and placed into an ice bath for reference measurements without disconnecting it from the gas-handling and manometer systems.

The furnace was constructed with a set of baffles for thermal stability, and with a set of eight heaters for thermal homogeneity. In use, the furnace was connected to a source of dried argon gas at a slightly higher pressure than atmospheric in an effort to exclude water vapor from the system.

The mercury manometer was installed in a subterranean room where the temperature was stabilized and measured at the millikelvin level. The manometer itself was thought to be capable of measurement of absolute pressure in the range 10-130 kPa with an uncertainty not exceeding 2 ppm, and of somewhat more accurate measurement of pressure ratios. Great care went into the construction of the manometer so that it could achieve these uncertainty levels in daily operation.

The resistances of the set of four PRT commonly used for gas-bulb temperature measurements were measured with a self-balancing, computer-controlled resistance bridge of local design (11). Another PRT was placed near a fine-control heater in the

furnace. This control PRT was monitored by a manually adjustable resistance bridge whose output controlled the heater current. PRT measurements also were employed to measure the manometer temperature and the temperature of a resistance-bridge resistance standard.

The gas-handling system could be evacuated by an ion pump. Its cleanliness was monitored routinely by use of a residual gas analyzer, as was the proportion of impurity gases present in the ^{4}He working gas. The helium, drawn from a well-characterized supply, was purified before use by passage through a heat exchanger held at 4.2 K. The flow of the helium gas always was maintained in the same direction; from the supply through the 4.2-K heat exchanger, to the gas bulb, and thence to the manometer.

A necessary complement to the gas thermometer itself was a separate apparatus for measurement of the linear thermal expansion of the Pt-Rh alloy used in constructing the gas bulb. The thermal expansion of the bulb amounted to about 0.6% between 0 °C and 660 °C; thus it was necessary to correct the measured pressure ratios by about 2% at the higher temperature. To avoid errors in the determination of thermodynamic temperatures that would be greater than ±0.011 °C at the aluminum point, we therefore needed thermal expansion data accurate within about 4 ppm. The thermal expansion apparatus (12) employed a Fizeau interferometer, a thermally homogeneous sample furnace, and a calibrated PRT in order to measure the thermal expansion of the material from which the gas bulb used in the gas thermometer experiments was constructed. Analysis of the results obtained with this apparatus indicated that it met the accuracy requirement stated above.

A laboratory microcomputer was used to record several readings during gas thermometer measurements. These readings included the resistance bridge standard, the resistances of up to four PRT located in the jacket of the gas bulb, the resistance of the PRT in the manometer room, and the output of a digital voltmeter. The voltmeter could be connected via a set of low-thermal switches in a four-deck scanner to a set of thermocouples ranged along the gas-bulb capillary of the gas thermometer, to another set of thermocouples placed on the lines and cells of the manometer, to the capacitance diaphragm gage that monitored the pressure difference between the gas bulb and the manometer, or to the voltage settings on the eight furnace heaters. Calibration data stored in the computer memory was used to convert all thermometer readings into temperatures and the pressure gage readings into pressures.

EXPERIMENTAL

We incorporated into the laboratory microcomputer all of the programs that had been developed, principally by Guildner, to calculate the quantity t(KTTS) - t(IPTS-68). Thus we could evaluate very quickly the results of a given measurement. We verified the accuracy of these programs by re-calculating several of the published results (1) using the original input data.

At the beginning of our study, we filled the gas bulb while it was maintained at 0 °C in the ice bath. Both the bulb and the manometer were filled with purified ^{4}He gas, usually at 13.3 kPa (about 100 mm Hg). After filling, we closed off the gas bulb, exchanged the ice bath for the furnace, and heated the furnace to a temperature in the range 231 °C to 660 °C. After measuring the gas-bulb pressure and the IPTS-68 temperature of the upper point, we returned the gas thermometer to the ice bath for re-measurement of the initial pressure.

However, this process, which typically lasted seven days, invariably led to a final gas-bulb pressure that was lower than its starting value, the discrepancy being the larger, the higher the intervening furnace temperature and the duration of the high-temperature portion of the measurement. Typically, this effect amounted to -0.027 Pa/day at 231 °C, -0.067 Pa/day at 420 °C, and -0.27 Pa/day at 660 °C. In terms of the thermodynamic temperature of the gas bulb, these quantities correspond to -0.54 mK/day, -1.3 mK/day, and -5.4 mK/day, respectively. No such drift in the gas-bulb pressure occurred while the gas thermometer was maintained at 0 °C, even for a period of several weeks.

We could not explain this effect. To diminish the possibility of high-temperature creep of the gas bulb, we modified the rather thin-walled (~1 mm) gas bulb by replacing its bottom cap with thicker material (~2.5 mm). Subsequently we found that the high-temperature drift, while still observable, was diminished by at least by a factor of two at 660 °C.

Then we adopted the following practice: we evacuated the gas bulb and its protective jacket at a temperature at least as high as that which we desired to measure; we filled the gas bulb, jacket, and the manometer to a pressure that corresponded to 13.3 kPa (or some other chosen base pressure) at 0 °C; and we attempted to minimize (usually within ±0.003 °C) both radial and vertical gradients in the gas bulb before closing off the gas-bulb/capillary from the capacitance diaphragm gage. After equilibration, we measured the offset in the capacitance gage and turned off all power to the furnace. After this step, an ice-bath reference measurement could be performed, and thus a determination of t(KTTS)-t(IPTS-68) at the chosen high temperature could be accomplished within about 48 hours. We estimated the maximum temperature uncertainty from drift during this sequence of measurements as less than -0.0006 °C for our measurements at 230 °C and -0.006 °C for those at 660 °C.

RESULTS

The results of 26 determinations of t(KTTS)-t(IPTS-68), obtained over the temperature range 230 °C to 660 °C, are shown by the diamond-shaped points in Fig. 1. For comparison, we show the earlier results of Guildner and Edsinger (1) as a continuous line. Also included in Fig. 1 are radiation thermometry determinations of Jung (4); these determinations, shown as plus signs, were based upon the 457 °C results of Guildner and Edsinger.

We estimated the magnitudes of both random and systematic uncertainties associated with our determinations of the scale differences. These are shown in Table I.

Uncertainties in the manometer pressure ratios arose from uncertainties in the manometer temperature, in the differences in height of the mercury columns, and in the magnitude of the acceleration due to gravity at

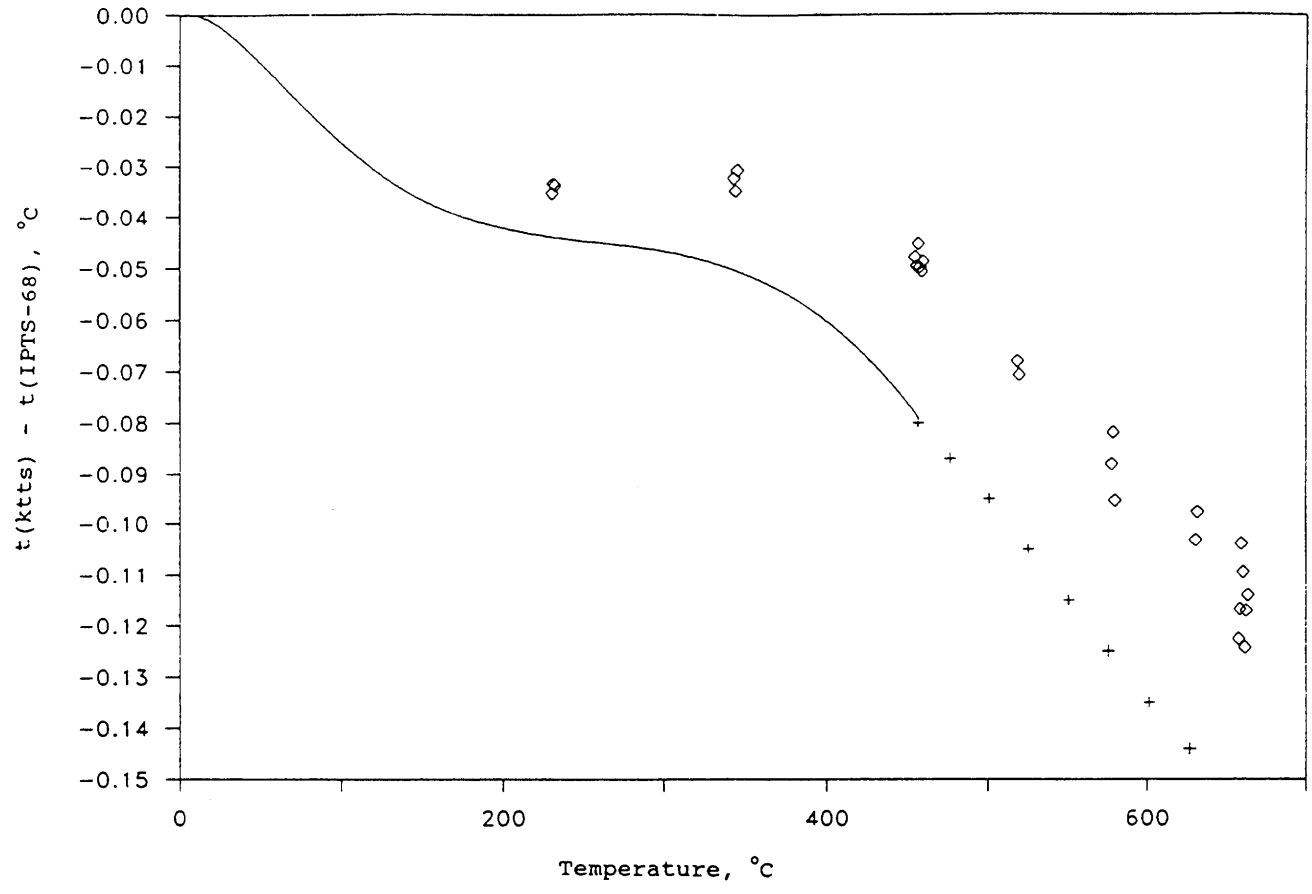

Fig. 1. Differences t(KTTS) - t(IPTS-68) as determined by Guildner and Edsinger (1) (continuous line); by Jung (4), using the 457 °C difference from Ref 1 as the reference temperature (plus signs); and by Edsinger and Schooley (8) (diamonds).

Table I.

Estimated uncertainties of present results.

Source	Type[a]	Magnitude, °C	
		230 °C	660 °C
Manometer pressure-ratio accuracy	C	±0.001	±0.0015
Gas-bulb thermal expansion/creep	S	-0.0006	-0.006
Gas bulb thermal expansion measurements	R	±0.003	±0.006
Gas-bulb thermostat temperature inhomogeneity	R	±0.003	±0.005
PRT resistance-temperature relation	R	±0.001	±0.002
^{4}He purity	S	Unknown	
^{4}He virial correction	S	±0.001	±0.004
Thermomolecular pressure correction	S	<0.001	<0.001
Capacitance diaphragm gage imbalance	C	±0.0002	±0.0002

[a] S=Systematic; R=Random; C=Combination

the manometer. The high-temperature drift noted above contributed an uncertainty that we have ascribed to creep. Uncertainties in the thermal expansion of the gas bulb reflected both experimental uncertainties in the dilatometer and possible differences in properties between the samples as measured and the gas bulb when it was used as a gas thermometer. Uncertainties in the gas-bulb temperatures arose from two sources: temperature gradients between the gas bulb and the jacket that housed the PRT; and temperature gradients within the gas bulb. The latter was estimated as by far the dominant contribution. Frequent re-calibration of the PRT and the resistance bridge reduced the estimated uncertainties in the PRT resistance-vs-temperature relations. We were unable to form a useful estimate of the uncertainties arising from impurities in the helium working gas; the impurity levels consistently fell below the minimum sensitivity levels of our residual gas analyzer. Uncertainties in the ^{4}He virial correction up to 660 °C were estimated on the basis of recent data (13). Uncertainties in the magnitude of the thermomolecular corrections for our experiments were estimated by varying the filling pressure by a factor of

four at 660 °C and by a factor of two at 580 °C; in neither case was there a significant discrepancy that could be attributed to an improperly evaluated thermomolecular correction. As described above, the difference of pressure between the manometer and the gas bulb was monitored by a capacitance diaphragm gage; we estimated the uncertainty in its readings as ±7 mPa, leading to an uncertainty in t(KTTS) that nowhere exceeded ±0.0002 °C.

DISCUSSION OF RESULTS

One notes in Fig. 1 that the 26 determinations of the differences t(KTTS) - t(IPTS-68) were made at seven temperatures. We repeated three of the determinations of the differences t(KTTS) - t(IPTS-68) reported earlier by Guildner and Edsinger for the range 0 °C to 457 °C (1). The experimental scatter of our results ranged over 0.002 °C at 231 °C (three determinations) and 0.021 °C at 660 °C (seven determinations), with the scatter increasing somewhat in proportion to the temperature of the determination. It is also easy to see by examining Fig. 1 that our results did not agree particularly well with those of Guildner and Edsinger; our values of t(KTTS) at 230 °C, 340 °C, and 457 °C exceed those of Guildner and Edsinger by 0.01 °C, 0.02 °C, and 0.03 °C, respectively. We could not account for these differences, although we considered possible systematic errors arising in the use of the manometer system, the calculational techniques, the composition of the gas bulb, the new high-temperature thermostat furnace, new PRTs, and certain changes in handling the working gas. A thorough review of the NBS/NIST gas thermometry program was presented recently (14); this review included summary discussions of the similarities and differences in the program over the years.

In the range 457 °C to 660 °C, on the other hand, we found a similar relationship between the two scales to that determined by Jung and by Coates, Andrews, and Chattle--the data would coincide but for the choice of the Guildner-Edsinger value as the radiation thermometry reference temperature.

In assessing the relationship between the KTTS and the IPTS-68 between 230 °C and 457 °C, we concluded that the KTTS is uncertain at least to the extent indicated by the discordant data pictured in Fig 1. For the purpose of formulating a thermodynamic basis for replacement of the IPTS-68 by a new international scale, we suggested, in the absence of other determinations of the KTTS in this range, that t(KTTS) - t(IPTS-68) values be chosen so as to lie between those of Refs (1) and (8). This suggestion followed from the premise that the two studies were in large measure independent ones--only the manometer, which contributes but a minor component to the uncertainty analysis, was common to the two efforts.

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