Small Corrections to 1989 NIST Constant-Volume Gas Thermometry Data

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Abstract. Constant-volume gas thermometry data published in 1989 for the difference between the thermodynamic temperature and the International Practical Temperature Scale of 1968 are corrected in two ways. A refined estimate of the thermal expansivity of the material of the gas bulb, published in 1990, increases the thermodynamic temperature by amounts on the order of 1 mK to 3 mK. Better knowledge of the nonideality of helium gas reduces the uncertainty of the nonideality correction to near zero and decreases the thermodynamic temperature by amounts on the order of 0.1 mK to 0.5 mK. The net effect is a small increase in the thermodynamic temperature derived from the 1989 experiments. The magnitude of this increase is approximately 2 mK at 505 K, increasing to 3 mK at temperatures near 700 K, and then diminishing to near 0.5 mK at the highest temperature of the measurements (933 K). These corrections are smaller than the uncertainty of the experiments, but may be of significance for future recommendations for the relationship between the thermodynamic temperature and the consensus scale in this temperature range.

1. Introduction

In 1989, Edsinger and Schooley [1] of the National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards, NBS) published results obtained from constant-volume gas thermometry (CVGT) for the difference $(T - T_{68})$, where T is the thermodynamic temperature and T_{68} is the temperature on the International Practical Temperature Scale of 1968 (IPTS-68). The results extended from approximately 505 K to 933 K (we use K in this paper, although Ref. [1] mostly used °C). These results disagreed with those of similar experiments at NBS published in 1976 by Guildner and Edsinger [2] in the region where the two studies overlapped (505–730 K); the disagreement significantly exceeds the claimed uncertainties of the two studies. Because there was no clear reason to prefer one set of data or the other, the mean of the two studies was taken in order to construct values of $(T_{90} - T_{68})$ for construction of the International Temperature Scale of 1990 (ITS-90) [3].

Since the adoption of ITS-90, it has become generally accepted that the older NBS work [2] was in error for unknown reasons, and that the newer CVGT data of Edsinger and Schooley [1] should be preferred. Strong evidence for this has been provided by measurements of $(T - T_{90})$ by acoustic gas thermometry [4, 5]. This judgment was codified in the recommended estimates for the difference $(T - T_{90})$ published by the Consultative Committee for Thermometry (CCT) in 2011 [6].

The ability to determine thermodynamic temperature continues to improve due to advances in gas-based metrology based on acoustic, dielectric, and refractivity techniques, enabled in part by the ability to calculate thermophysical properties of helium gas from first principles [7]. Improved values of $(T - T_{90})$ were recently presented by a CCT working group [8], but this recommendation was limited to temperatures below 335 K where most of the new data have been measured. Any future recommendation for $(T - T_{90})$ at higher temperatures will likely rely in part on the data of Edsinger and Schooley [1], because there are still very few measurements of absolute temperature above approximately 505 K.

Two small improvements are now possible to the results for $(T - T_{68})$ presented in Table 1 of Ref. [1]. The first correction is due to better knowledge of the expansion of the gas bulb, as described in a 1990 review by Schooley [9]. The second is due to better knowledge of the nonideality of helium gas; the nonideality produces a correction on the order of 10 mK in these CVGT experiments and can now be calculated much more accurately than it was known in 1989. In the following, we present these two corrections and combine them to yield revised values of $(T - T_{68})$ for these experiments originally reported in 1989.

2. Correction for thermal expansion of bulb

The basic principle of CVGT is the accurate measurement of pressure for a fixed amount of gas in a bulb both at a well-known reference temperature (typically near 0 °C) and

at an unknown temperature. If the volume of the bulb is constant, a simple gas-law calculation (with a small correction for nonideality) relates the ratio of pressures to the ratio of thermodynamic temperatures. However, in reality the volume of the bulb is not constant because its material expands with temperature. CVGT therefore demands an accurate representation of this expansion.

In the NBS/NIST CVGT work, the thermal expansion of the bulb's volume V was described relative to the volume at 0 ℃ by

$$V(t)/V(0) = [1 + \epsilon(t)]^3 \,, \tag{1}$$

where t is the Celsius temperature and $\epsilon(t)$ is the linear thermal expansion coefficient defined by

$$\epsilon(t) = \frac{L(t) - L(0)}{L(0)}, \tag{2}$$

where $L(t)$ is the length of a uniform sample of the material at temperature t.

In the 1989 paper of Edsinger and Schooley [1], the thermal expansion was based on measurements of their bulb material that employed a precision dilatometer previously used by Guildner and Edsinger [2]. The results were described by

$$\begin{aligned} \epsilon(t) = {} & 8.707\,27 \times 10^{-6}t + 2.177\,349 \times 10^{-9}t^2 - 1.036\,845 \times 10^{-12}t^3 \\ & + 5.729\,291 \times 10^{-16}t^4 \end{aligned} \tag{3}$$

This is equation (3) in Ref. [1]; we note that the equation (29) given for this quantity in Schooley's 1990 review [9] should *not* be used because the coefficients were truncated too severely, altering the resulting temperatures by up to 1 mK.

In 1990, Schooley [9] described an improved apparatus for measuring thermal expansion, which was used to measure two samples from the bulb. Because the results were generally consistent with the previous measurements, Schooley recommended a "pooled-data" expression fitted to the two sets of expansion data obtained with the new apparatus and the one set obtained with the old apparatus. The result for the linear thermal expansion was given as equation (31) in Ref. [9]:

$$\begin{aligned} \epsilon(t) = {} & 8.704\,84 \times 10^{-6}t + 2.244\,55 \times 10^{-9}t^2 - 1.2136 \times 10^{-12}t^3 \\ & + 6.9642 \times 10^{-16}t^4 \end{aligned} \tag{4}$$

Schooley stated that this revised equation "will be used later to correct the observed gas thermometry results that were reported in [the 1989 paper]." However, to the best of our knowledge, no corrected results were ever presented. The only information about this correction is a comment later in Ref. [9] saying that the new expansivity equation "has the effect of increasing the calculated thermodynamic temperatures by 0.002 ℃ at 250 ℃, by 0.0033 ℃ at 400 ℃, and by 0.001 ℃ at 630 ℃."

We have derived this correction for all of the data points reported in Ref. [1]. This can be done in a straightforward way by using equation (1) to compute the relative volume when $\epsilon(t)$ is described by equation (3) (corresponding to the original 1989 results) and then again with $\epsilon(t)$ described by equation (4). To first order (which is adequate
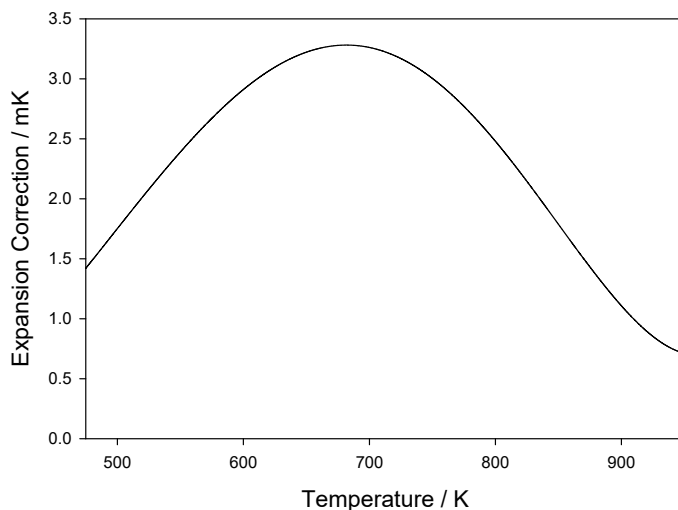
Figure 1. Correction to thermodynamic temperature from replacing the equation for linear thermal expansion used in Ref. [1] with the updated equation given by Schooley [9].

for such a small correction), the ratio of these volumes is proportional to the ratio of the original and corrected thermodynamic temperatures:

$$\frac{T}{T_{\text{Ref. [1]}}} = \frac{(V/V_0)_{\text{Eq. (4)}}}{(V/V_0)_{\text{Eq. (3)}}}, \tag{5}$$

where V_0 is the volume at the reference temperature for the CVGT datum; for these experiments the reference temperatures were always just a few mK below 0 °C. The resulting correction in thermodynamic temperature is plotted as a function of temperature in Figure 1. It will be denoted by ΔT_{expan} when we tabulate our results.

3. Gas nonideality correction

Temperatures derived from CVGT measurements must be corrected for deviations from ideal gas behavior (more specifically, for the change in nonideality between the reference state and the measured state). At the densities of the experiments in Ref. [1], it is sufficient to model the nonideality with the virial expansion truncated after the second virial coefficient, B; the contribution of the next term (proportional to the third virial coefficient, C) is smaller by more than four orders of magnitude. At that level of truncation, the volumetric behavior of the gas is described by

$$\frac{p}{\rho RT} = 1 + \frac{Bp}{RT}, \tag{6}$$

where p is the pressure, ρ is the molar density, and R is the molar gas constant which we take from the latest CODATA recommendation [10]. For a pure fluid, B is a function only of T.

The correction to the derived temperature for gas nonideality is then given by [2]

$$\Delta T_{\mathrm{vir}} = [B - B_0(p_0/p)(T/T_0)]\, p/R, \tag{7}$$

where the subscript 0 represents the reference state.

Edsinger and Schooley [1] used a correlation for $B(T)$ that had originally been fitted by Guildner and Edsinger [2] to some older experimental data. Its use at the higher temperatures of Ref. [1] was an extrapolation. Today, the most accurate values of $B(T)$ come from quantum statistical mechanics, where B is rigorously related to the pair potential between the atoms. For helium, because of the small number of electrons, this potential can be calculated with extraordinary accuracy from *ab initio* quantum mechanics. The current state-of-the-art pair potential was presented by Czachorowski *et al.* [11]; the standard uncertainties of B computed from this potential are less than 0.0001 cm^3/mol at the temperatures considered here, which is smaller than those from the best experiments by more than one order of magnitude.

Because the values of $B(T)$ tabulated in the Supplemental Material of Ref. [11] are on a grid that is rather sparse at high temperatures, we avoided interpolation errors by using values calculated at the specific temperatures of interest [12]. These were calculated by the traditional phase-shift methods described in Ref. [13], and agreement with the tabulated values of Czachorowski *et al.* [11] was verified. In principle, the relevant value of B is that at the true thermodynamic temperature, which would make calculating this correction iterative. Since the variation of B over a temperature range of a few mK is negligible, we calculated B at the thermodynamic temperature derived in Ref. [1]. Equation (7) also requires B_0 at the reference temperature T_0, which was between 273.14 K and 273.15 K for each point. This was obtained with sufficient accuracy by a small extrapolation based on the values given in Ref. [11] for 273.15 K (11.92814 cm^3/mol) and 273.16 K (11.92811 cm^3/mol). Note that a simple plot like Figure 1 cannot be drawn for this correction, because (see equation (7)) it depends not only on the temperature but also on the pressure.

4. Results

Our results are collected in Table 1, which presents the data points in the same order as Table 1 of Ref. [1]. The first two columns are taken from the 1989 paper of Edsinger and Schooley [1], with the first column converted to kelvins. In the third column, we report values of B calculated from the pair potential of Czachorowski *et al.* [11]. The next two columns report the correction for nonideality, ΔT_{vir}, computed from equation (7). The subscript 89 indicates calculation with the $B(T)$ correlation used in Refs. [1] and [2], while the subscript 23 indicates use of the more accurate $B(T)$ calculated in the present work. $\Delta T_{\mathrm{vir,89}}$ is the same as column 8 in Ref. [1], but with one more digit printed to make the small differences from $\Delta T_{\mathrm{vir,23}}$ more evident. The correction for Schooley's improved thermal expansion values, calculated from equation (5), is denoted by $\Delta T_{\mathrm{expan}}$. The overall correction relative to the values reported in Ref. [1], due to

Table 1. Corrections to the CVGT results reported in Ref. [1]. Subscripts 89 and 23 represent quantities calculated in Ref. [1] and the present work, respectively. ΔT_{expan} is the temperature correction due to a refined thermal expansion calculated by equation (5). $\Delta T_{\text{corr},23}$ is the net correction derived in this work.

T_{68} (K)	$(T - T_{68})_{89}$[a] (mK)	$B(T^*)$[b] (cm^3/mol)	$\Delta T_{\text{vir},89}$ (mK)	$\Delta T_{\text{vir},23}$ (mK)	ΔT_{expan} (mK)	$\Delta T_{\text{corr},23}$[c] (mK)	$(T - T_{68})_{23}$ (mK)
933.6641	−122.6	9.70498	12.94	12.39	0.79	0.24	−122.4
730.1240	−48.5	10.24338	7.60	7.34	3.14	2.89	−45.6
853.1255	−95.4	9.90528	10.73	10.30	1.74	1.31	−94.1
730.1223	−50.5	10.24339	7.60	7.34	3.14	2.89	−47.6
933.6625	−116.8	9.70497	12.94	12.39	0.79	0.24	−116.6
853.1046	−81.8	9.90530	10.73	10.30	1.74	1.31	−80.5
903.8929	−103.2	9.77723	12.11	11.60	1.06	0.55	−102.6
793.1500	−67.9	10.06489	9.16	8.82	2.57	2.22	−65.7
730.1070	−49.6	10.24344	7.60	7.34	3.14	2.89	−46.7
933.6379	−103.9	9.70500	12.94	12.39	0.79	0.24	−103.7
933.6072	−109.5	9.70509	12.94	12.39	0.79	0.24	−109.3
903.8921	−97.7	9.77722	12.06	11.56	1.06	0.55	−97.1
793.1575	−70.6	10.06488	9.16	8.82	2.57	2.22	−68.4
730.1488	−45.1	10.24330	5.70	5.51	3.14	2.95	−42.1
933.6078	−124.3	9.70512	9.70	9.29	0.79	0.37	−123.9
933.6047	−117.1	9.70511	6.47	6.19	0.79	0.51	−116.6
853.3270	−88.1	9.90474	5.37	5.15	1.74	1.53	−86.6
933.6073	−114.0	9.70510	3.23	3.10	0.79	0.65	−113.3
505.1172	−33.2	10.98831	2.90	2.83	1.82	1.75	−31.4
618.1498	−30.6	10.59132	5.07	4.93	3.05	2.92	−27.7
730.1652	−49.5	10.24326	7.60	7.34	3.14	2.89	−46.6
618.1500	−34.7	10.59133	5.07	4.93	3.05	2.92	−31.8
505.1219	−33.5	10.98829	2.90	2.83	1.82	1.75	−31.7
730.1805	−47.7	10.24322	7.60	7.34	3.14	2.89	−44.8
618.1416	−32.2	10.59135	5.06	4.93	3.05	2.92	−29.3
505.1106	−35.1	10.98834	2.90	2.83	1.82	1.75	−33.3

[a] From column 10 in Table 1 of Ref. [1].
[b] From Ref. [12]. $T^* = T_{68} + (T - T_{68})_{89}$.
[c] $\Delta T_{\text{corr},23} = \Delta T_{\text{expan}} + (\Delta T_{\text{vir},23} - \Delta T_{\text{vir},89})$

both the adjustment to the thermal expansion and the improved values of B, is labeled as $\Delta T_{\text{corr},23}$. The final column gives our corrected values for $(T - T_{68})$, which should replace the values given in column 10 of Table 1 of Ref. [1].

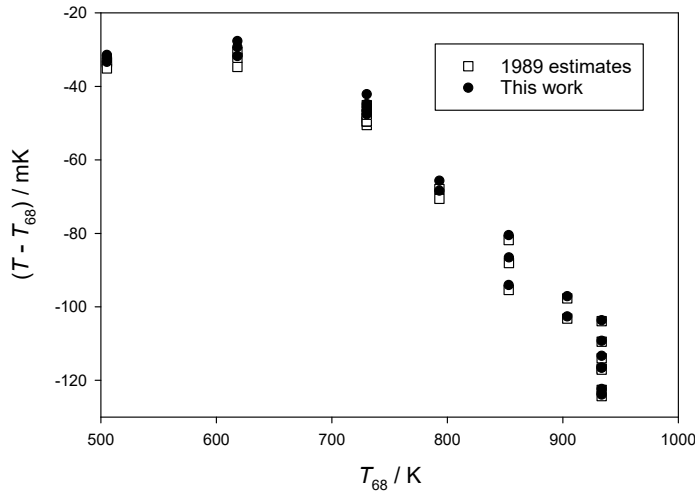The final values of $(T - T_{68})$ derived here are shown in Figure 2, along with the

Figure 2. Values of $(T - T_{68})$ derived in this work (Table 1) compared to values originally reported in Ref. [1].

values originally reported in Ref. [1]. The adjustments are quite small compared to the magnitude of $(T - T_{68})$, and somewhat small compared to the scatter in the reported values at near-identical temperatures. In all cases, $(T - T_{68})$ becomes slightly less negative, so that the resulting thermodynamic temperatures are slightly higher.

5. Discussion

We have calculated two small corrections to the CVGT data that were reported by Edsinger and Schooley in 1989 [1]. The first correction implements a refined expression that was presented by Schooley [9] for the linear thermal expansion of the bulb material; it increases the calculated thermodynamic temperature by amounts ranging from 0.8 mK to just over 3 mK (see Figure 1). The second correction results from greatly improved knowledge of the second virial coefficient of helium; it reduces the calculated thermodynamic temperature by amounts on the order of 0.1 mK to 0.5 mK. The net effect of these corrections is to increase the values of $(T - T_{68})$ compared to the values reported in Ref. [1]; the $(T - T_{68})$ are still negative but with a slightly reduced magnitude.

The magnitude of the correction derived in this work ranges from near zero at temperatures near 933 K, to roughly 3 mK at intermediate temperatures (near 700 K), to roughly 2 mK near 505 K. To put this in perspective, in its 2011 recommendation [6], the CCT estimated a standard uncertainty in its consensus $(T - T_{90})$ of 1.3 mK at 505 K and values near 6 mK to 8 mK from 600 K to 933 K. The 2011 recommendation was based in part on the data from Ref. [1] in this temperature range. The corrections recommended here are not negligible compared to those uncertainties.

Edsinger and Schooley [1] did not perform a complete uncertainty analysis by

modern standards, but if one adds in quadrature the different estimated uncertainty components in their Table 3 the resulting uncertainty in $(T - T_{68})$ is roughly 5 mK at 505 K and 11 mK at 933 K. The present adjustments therefore result in data that remain well within the uncertainties estimated in 1989.

We note that the 1989 uncertainty budget can be modified, because B is now known with such accuracy that the "virial correction" component of the uncertainty is nearly zero. This was not the largest contribution to the uncertainty, but it was not completely negligible, especially at high temperatures (the uncertainty component due to the virial correction was estimated as 4 mK at 933 K). Eliminating the virial component of the uncertainty budget of Ref. [1] reduces the estimated uncertainty at 933 K from approximately 11 mK to 10 mK.

Despite our inclusion of a refined estimate for the thermal expansion of the bulb material, we cannot recommend any reduction of the uncertainty components from Ref. [1] related to thermal expansion. Inherent to the experiment are systematic errors from applying a uniform linear thermal expansion to a cylinder made by welding together sheets of platinum–rhodium alloy, and these are likely larger than the uncertainty from knowledge of the alloy's linear expansion.

Because of the sensitivity to thermal expansion, it is unlikely that future CVGT experiments similar to those of Ref. [1] could achieve significantly smaller uncertainties. However, it has been noted [7] that a modern implementation of CVGT could bypass the thermal expansion problems by using microwave resonances (probably in a quasi-spherical or quasi-cylindrical vessel) to measure the volume of the bulb *in situ* during the experiments. The feasibility of such volume measurements has been demonstrated [14]. Modern CVGT could also operate at somewhat higher pressures while keeping the uncertainty due to gas nonideality small; this is possible due to the availability of highly accurate first-principles calculations for the second [11] and third [15] virial coefficients of helium.

We report our results as $(T - T_{68})$ to maintain a direct connection to the previous work [1]. Any future use of these values to develop recommendations of $(T - T_{90})$ can use procedures previously employed by the CCT for converting between IPTS-68 and ITS-90 [6, 16, 17].

While efforts are being made to extend other approaches for measuring thermodynamic temperature, such as acoustic gas thermometry, to higher temperatures [18, 19], there are still very few data available above 550 K. The CVGT data of Ref. [1], now corrected, are therefore likely to be valuable for future recommendations of $(T - T_{90})$ at these temperatures and/or for any revision of the International Temperature Scale that might be considered.

Acknowledgments

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