Adjustments to the NIST Realization of the ITS-90 from 5 K to 24.5561 K

W. L. Tew and C. W. Meyer
National Institute of Standards and Technology
Gaithersburg, MD 20899 USA

Abstract

Recent clarifications[1] issued by the Consultative Committee on Thermometry (CCT) for the definitions of the equilibrium hydrogen (e-H_2) triple point (TP) and vapor-pressure points (VPs) have resulted in adjustments to the NIST-disseminated ITS-90 (T_{90}) in the range of the interpolating constant volume gas thermometer (ICVGT) from 5 K to 24.56 K. The NIST-disseminated ITS-90 is derived from capsule standard platinum resistance thermometers (SPRTs) calibrated over their lowest-defined sub-range of 13.8 K to 273.16 K and from realization of the ICVGT from 5 K to 24.556 K[2] . The SPRT subrange-1 uses e-H_2 VPs and both definitions use the e-H_2 TP as a calibration points. These calibrations are traceable to NIST realizations of the e-H_2 TP and VPs which were performed using highly-depleted hydrogen gas. The revised CCT definitions for all e-H_2 fixed points now call for a less-depleted composition equivalent to that of Standard Light Antarctic Precipitation (SLAP). This has necessitated adjustments in both the ICVGT range and the SPRT subrange-1. One effect of this adjustment has been changes in the observed non-uniqueness in the overlap range from 13.8 K to 24.556 K. Another effect has been a larger difference between the ICVGT and NPL-75 temperatures in the region from ~ 10 K to 20 K. The differences T-T_{90} reported by Pitre *et. al*.[3] in the range of the ICVGT have likewise been adjusted.

Introduction

Recent clarifications[1] recommended by the Consultative Committee on Thermometry (CCT) regarding the isotopic composition for the definitions of the equilibrium hydrogen (e-H_2) triple point (TP) and vapor-pressure points (VPs) impact realizations of the International Temperature Scale of 1990 (ITS-90) for two defined sub-ranges. First, the range defined by the interpolating constant volume gas thermometer (ICVGT) from 5 K to 24.56 K has one of three calibration points determined by the e-H_2 TP. Second, the lowest (#1) sub-range for the Standard Platinum Resistance Thermometer (SPRT-1, 13.8033 K to 273.16 K) requires calibration at all three e-H_2 fixed points in addition to the five other fixed points. Adjustments to both of these ITS-90 sub-ranges become necessary when the H_2 isotopic composition used for these fixed-point realizations differs from that now specified by the CCT. Such adjustments will affect the results of key comparisons and thermodynamic determinations when data exists with respect to either of these two ITS-90 sub-ranges.

Implications of the "mise en pratique"[1] for ITS-90 Realizations at NIST

The ITS-90 now defines all e-H_2 fixed points for an isotopic composition equivalent to Standard Light Antarctic Precipitation (SLAP).[1] The isotopic composition expressed as a mole fraction is $x \equiv$ [D]/[H] and is commonly given in units of μmol D/mol H. The as-realized fixed point temperatures, T_{meas}, derived from hydrogen of a different composition will differ from the 'as-defined' temperatures, T_{90}, according to

$$T_{\mathrm{meas}} = T_{90}(e\text{-H}_2\ \mathrm{TP}) + k_{\mathrm{D}}(x\text{-}x_0)\ , \tag{1a}$$

and

$$T_{\mathrm{meas}} = T_{90}(e\text{-H}_2\ \mathrm{VP}j) + r_{\mathrm{D}j}(x\text{-}x_0)\ , \tag{1b}$$

where x_0 = 89 ppm D for SLAP and j=1,2. The fixed point temperatures for $x = x_0$ are: $T_{90}(e\text{-H}_2\ \mathrm{TP})\equiv 13.8033$ K ; $T_{90}(e\text{-H}_2\ \mathrm{VP1})\equiv 17.035$ K (p=33.3213 kPa); and $T_{90}(e\text{-H}_2\ \mathrm{VP2})\equiv 20.27$ K (p=101.292 kPa). The TP correction is now well known at k_{D}=5.42 μK·(μmol D·mol^{-1})$^{-1}$ [4]. The VP corrections used here of r_{D1}=2.5 μK·(μmol D·mol^{-1})$^{-1}$ and r_{D2}=2.9 μK·(μmol D·mol^{-1})$^{-1}$, however, are only estimates based on ideal solution models[5] near the bubble-point (vanishing vapor fraction). These correction functions are shown in Figure 1 along with the NIST reference hydrogen[6] composition of x=29 μmol D·mol^{-1}. The NIST e-H_2 fixed point realizations are colder than those derived from the mise-en-pratique prescriptions by the amounts: –0.325 mK at 13.803 K; –0.150 mK at 17.036 K; and –0.174 mK at 20.268 K.

There are further complications for those ITS-90 temperatures between these and adjacent fixed points as derived from either the ICVGT or SPRT-1 definitions. In order to discuss these complications, it is necessary to differentiate the various interpolated temperatures: a.) 'as-realized' with calibrations of thermometers traceable to uncorrected fixed-point temperatures T_{GT} and T_{SP1} for ICVGT or SPRT-1 realizations respectively; and b.) 'as-defined' via corrections applied to the interpolated temperatures yielding $T_{90\text{-GT}}$ and $T_{90\text{-SP1}}$. In the case of the ICVGT, rhodium-iron resistance thermometers (RIRTS) are calibrated via the as-realized temperatures, which creates an additional distinction, "as-maintained" temperatures, $T_{RI\text{-}GT}$, derived from the RIRT calibrations. Table 1 defines the notation used here for these temperatures.

Table 1. Notation used for fixed-point and interpolated temperatures.

Temperature Definition Type	As-Realized or As-Maintained	As-Defined (or Corrected)	Range / K
Hydrogen Fixed Points	T_{meas}	T_{90}	13.8, 17.0, 20.27
SPRT-1 / SPRTs	T_{SP1}	$T_{90\text{-}SP1}$	13.8 to 273.16
ICVGT	T_{GT}	$T_{90\text{-}GT}$	5 to 25.5561
ICVGT / RIRTs	$T_{RI\text{-}GT}$	$T_{90\text{-}GT}$	5 to 25.5561

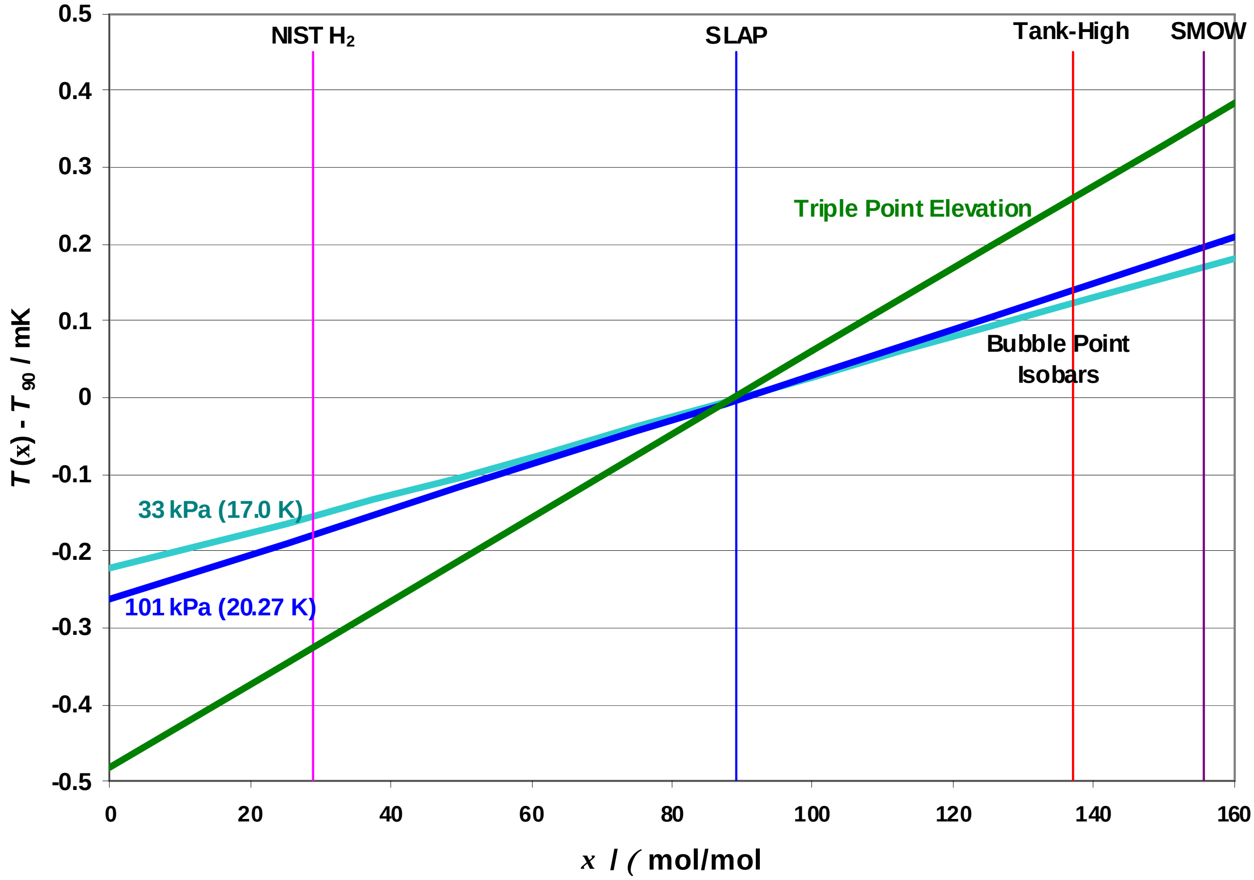

Figure 1. The temperature change due to isotopic composition of H_2 as realized by the e-H_2 triple point and the evaporation-limit ('bubble point') vapor pressure points. Standard Light Antarctic Precipitation (SLAP) is the composition defined by the ITS-90 technical annex [1] . NIST H_2 reference cells contain hydrogen which is depleted with respect to SLAP. The relative elevations associated with Vienna Standard Mean Ocean Water (VSMOW)-equivalent and the heaviest tank (commercial gas) hydrogen are shown for comparison.

Temperatures derived from the as-realized ICVGT are corrected by an amount ΔT_{GT} given by

$$\Delta T_{\mathrm{GT}} = T_{\mathrm{90GT}} - T_{\mathrm{GT}} . \quad (2)$$

Similarly, temperatures from the SPRT-1 sub-range are corrected by an amount ΔT_{SP1} given by

$$\Delta T_{\mathrm{SP1}} = T_{\mathrm{90SP1}} - T_{\mathrm{SP1}} . \quad (3)$$

As defined here, these corrections are negative over the interval $5\ \mathrm{K} \le T_{90} \le 24.5561\ \mathrm{K}$. For example, when calibrated via a ‘cold’ e-H_2 TP cell, the ICVGT is assigned an erroneous temperature T_{GT}=13.8033 K , while the correct temperature is actually lower, or $T_{90\text{-}GT}$=13.802975 K. Hence the correction ΔT_{GT} is negative. Similar arguments apply to the signs for ΔT_{SP1} at all three e-H_2 fixed points. For temperatures derived via the as-maintained ICVGT from calibrated RIRTs, the approximation $\Delta T_{RI\text{-}GT} \cong \Delta T_{GT}$ is sufficient, where only small differences exist due to imperfect interpolation of the RIRT fitting function.

The as-realized ICVGT temperatures are interpolated via a quadratic function in the pressure p,

$$T_{GT} = a + bp + cp^2 , \quad (4)$$

where the original coefficients a, b, and c, are derived by an exact solution to the system of three equations derived from three calibration points. For the NIST ICVGT realization [2] these points are assigned T_{GT}= 5.0 K, 13.8033 K, and 24.5561 K according to NIST fixed-point realizations. Applying the correction of ΔT_{GT} = –0.325 mK to T_{GT} at 13.8033 K generates all new coefficients: a', b', and c'. The resulting correction function is shown as a dark green parabolic curve in Figure 2. The correction as expressed in units of mK is approximated by the quadratic function,

$$\Delta T_{\mathrm{GT}} = A + BT_{90-\mathrm{GT}} + CT_{90-\mathrm{GT}}^2 \quad (5)$$

where A= + 0.4217163 mK ; B= – 0.1014592 mK·K^{-1} ; and C= + 0.003432441 mK·K^{-2}. It should be noted that these coefficients may also be obtained analytically from a, b, c, a', b', and c'. But the resulting expressions are cumbersome and of no practical advantage compared to the purely numerical approach used here.

In contrast, SPRT temperatures for subrange-1 are interpolated via a seven-parameter deviation function of the resistance ratio W ,

$$\Delta W_1(T_{90}) \equiv a_1[W(T_{90})-1] + b_1[W(T_{90})-1]^2 + \sum_{i=1}^{5} c_i \{\ln[W(T_{90})]\}^{i+2} . \quad (6)$$

where the coefficients a, b, and c_i, (i =1 to 5) are derived by an exact solution to the system of 7 equations. Applying corrections of ΔT_{SP1} = –0.325 mK for the e-H_2 TP, ΔT_{SP1} = –0.150 mK for the e-H_2 VP1 at 33 kPa, and ΔT_{SP1} = –0.174 mK for the VP2 at 101 kPa, generates a new set of deviation function coefficients. The resulting correction function as defined by equation 3 is shown as the dark red curve in Figure 2. This curve is the arithmetic sum of individual propagated error curves from these three fixed point temperatures.

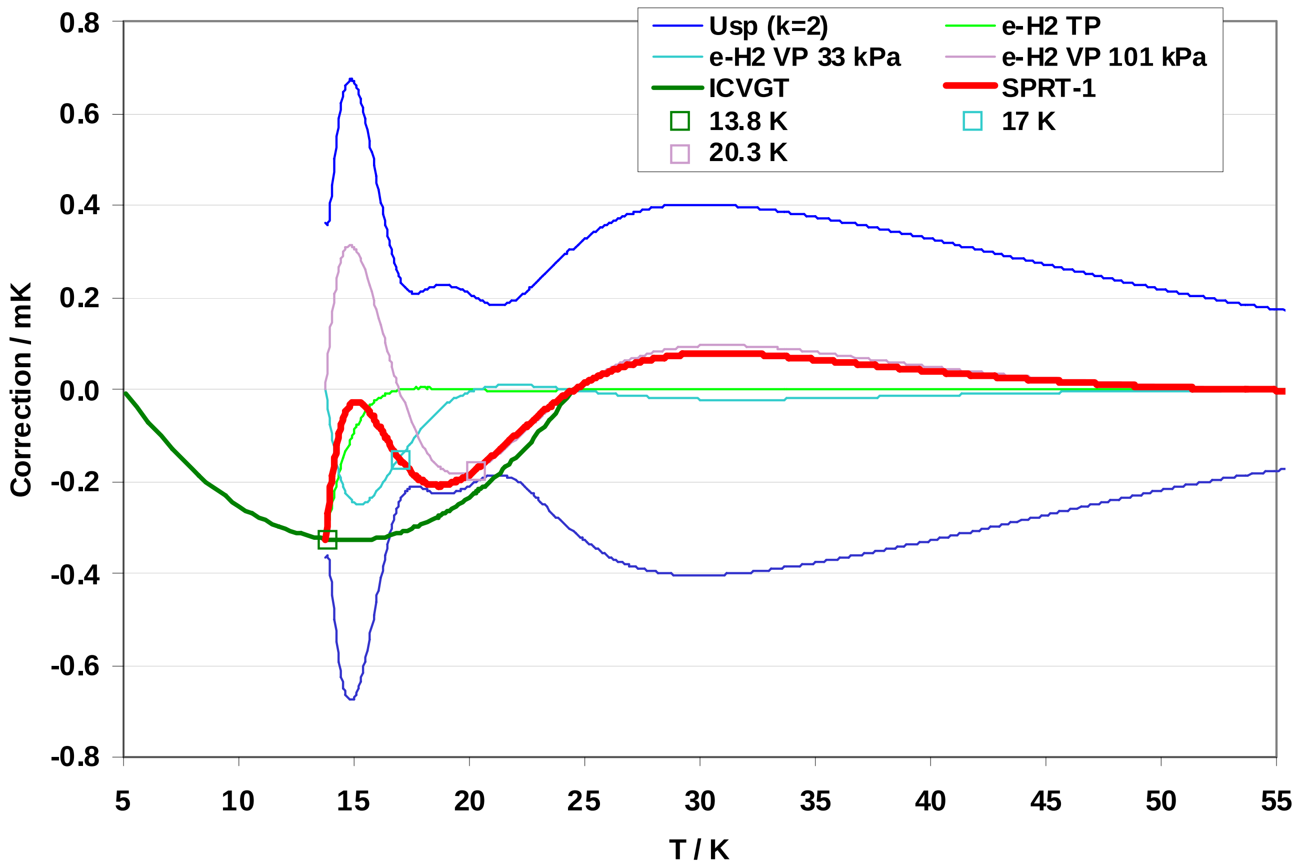

Figure 2. The correction function for the ICVGT (green) and SPRT-1 (red) definitions of the ITS-90 relevant to NIST realizations of the e-H_2 fixed points. The individual contributions to the correction for the SPRT-1 sub-range as propagated from the three individual hydrogen fixed points are shown along with the total expanded (k = 2) root-sum-square (RSS) uncertainty bounds U_{sp} (positive and negative) in blue.

The difference between the green and red correction curves of Figure 2 represents non-uniqueness in the ITS-90 in the overlapping interval of 13.8 K to 24.556 K of these two sub-ranges. The non-uniqueness shown here increases the non-uniqueness at 17 K from what we have already reported[7] in this range of overlap.

Comparisons with archival and new thermodynamic temperature determinations

The NPL-75 Gas Thermometer Scale[8] from 2.7 K to 27.1 K has been carried on RIRTs 229078 and 229079 at NIST since 1979. NIST thermometer calibrations in this range were based on these RIRTs from 1980 to 1990 on the EPT-76, and from 1990 to 1996 on an approximate conversion from EPT-76, "ITS-90W"[9]. The ITS-90W was an as-maintained "wire-scale" version of ITS-90 disseminated prior to the completion of low-temperature ITS-90 realizations at NIST in 1996. These NPL-75 calibrations of these RIRTs were recently compared directly against the NIST ICVGT scale. Results are shown in Figure 3 in terms of both uncorrected T_{GT} and corrected $T_{90\text{-}GT}$ ICVGT temperatures in their range of overlap from 5 K to 24.556 K.

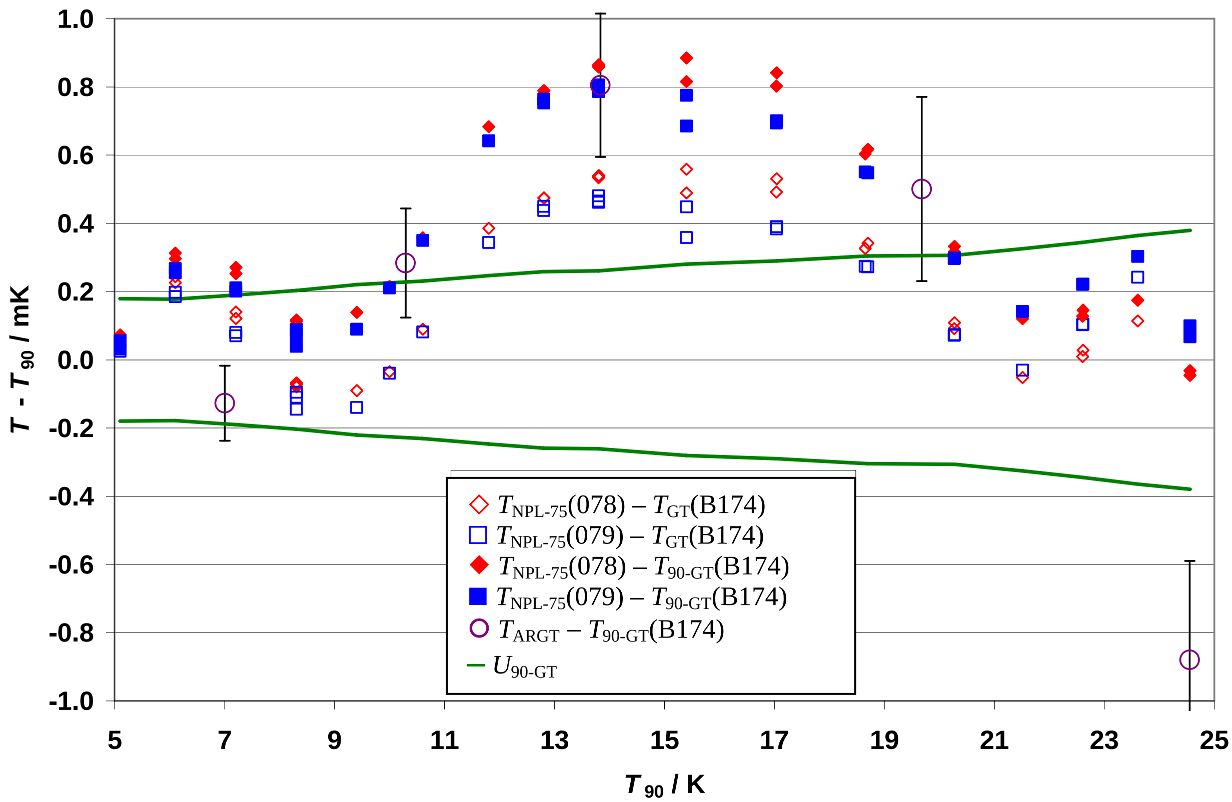

Figure 3. The comparison between NPL-75 temperatures ('T') as carried on NIST RIRTs 229078 ($T_{NPL\text{-}75}$(078), in red) and 229079 ($T_{NPL\text{-}75}$(079), in blue) versus the original ICVGT (T_{GT}, open symbols) and corrected ICVGT ($T_{90\text{-}GT}$, solid symbols) temperatures ('T_{90}') carried on RIRT B174. The Acoustic Resonance Gas Thermometer (ARGT) results ('T') from [3] are shown versus the adjusted ICVGT scale ($T_{90\text{-}GT}$). ICVGT expanded (k=2) uncertainties $U_{90\text{-}GT}$ are shown as upper and lower bounds in green.

Recent thermodynamic temperature determinations[3] using an acoustic resonance gas thermometer (ARGT) were made with respect to the NIST realization of the ICVGT as recorded on RIRT A129. The ITS-90 temperatures used in reference [3] were not corrected according to the prescribed adjustment described above. The corrected results at the five temperatures reported for the ARGT are plotted in Figure 3 with respect to RIRT B174 and are also tabulated in Table 2. The differences between the two RIRTs A129 and B174 are approximate only, are of no special significance, and are primarily due to non-unique interpolation errors in the statistical fits of the RIRT resistances $R(T_{90})$. The additional uncertainty in T_{90} from correcting the ICVGT is less than 0.02 mK and is generally negligible compared to other sources of uncertainty in the ICVGT range.

Table 2. Values of differences relevant to correcting the reported T-T_{90} data of Pitre, *et. al.* [3] in the range of the ICVGT for a SLAP-equivalent e-H_2 TP.

T_{90} [K]	$T_{90\text{-GT}}$–T_{GT} [mK]	T_{ARGT} –T_{GT}(A129)[3] [mK]	$T_{90\text{-GT}}$(A129) – $T_{90\text{-GT}}$(B174) [mK]	T_{ARGT} –T_{GT}(B174) [mK]	T_{ARGT} –$T_{90\text{-GT}}$(B174) [mK]
24.551	0.000	–0.83	–0.05	–0.88	–0.880
19.679	–0.246	0.24	0.015	0.255	0.501
13.837	–0.325	0.46	0.02	0.48	0.805
10.293	–0.259	–0.01	0.035	0.025	0.284
7.0055	–0.121	–0.31	0.062	–0.248	–0.127

Uncertainties

There are additional uncertainties $u_c(T)$ which correspond to these corrections, $u_{cGT}(T)$ for the ICVGT and $u_{cSP1}(T)$ for the SPRT-1 definition. Table 3 shows examples of these corrections, the correction uncertainties, and the total uncertainty $u_{Total}(T)$ at the three e-H_2 fixed point temperatures as applied to the ICVGT and SPRT-1 definitions. The total uncertainties are standard (k=1) values for RIRT calibrations in the case of the ICVGT and SPRT calibrations in the case of the SPRT-1 definition. These uncertainties will propagate to other temperatures in a manner similar to the green and red traces shown in Figure 2.

Table 3. Values of isotopic corrections, correction uncertainty, and total calibration uncertainty for the ICVGT SPRT-1 definitions. The uncertainties are standard (k=1) values.

	ICVGT definition (RIRTs)			SPRT sub-range 1 definition		
T_{90} [K]	$T_{90\text{-GT}}$–T_{GT} [mK]	u_{cGT} [mK]	$u_{Total\text{-}GT}$ [mK]	T_{90SP1}–T_{SP1} [mK]	u_{cSP1} [mK]	$u_{Total\text{-}SP1}$ [mK]
13.803	–0.325	0.019	0.133	–0.325	0.019	0.184
17.036	–0.311	0.018	0.147	–0.150	0.038	0.129
20.268	–0.226	0.013	0.154	–0.174	0.044	0.109

The uncertainty in the correction for the e-H_2 TP, u_c(13.8 K) , is derived by adding in quadrature the uncertainties due to the slope of the liquidus line (e.g. 0.31 in 5.42 mK·mol/μmol D) and the NIST gas composition [6] (e.g 0.3 in 29.1 μmol D/mol). The uncertainties in the e-H_2 VPs are primarily due to uncertainty in the ideal solution model prediction for the correction which we assume is 25 % of the correction. The uncertainties in $T_{ARGT} - T_{90}$ are essentially unchanged from those reported in reference [3].

Conclusions

The *Mise en pratique* for the definition of the kelvin[1] has clarified the isotopic composition of hydrogen for ITS-90 realization. These clarifications have forced a small adjustment in the NIST-disseminated version of the ITS-90 in the range of : a.) the ICVGT, 5 K to 24.556 K; and b.) the SPRT sub-range 1 from 13.8 K to 273.16 K. The magnitude of these adjustments are 0.33 mK at 13.8 K and smaller at other temperatures. The adjustments result in an increase in the ITS-90 non-uniqueness T_{90SP1}–$T_{90\text{-}GT}$ of +0.16 mK at 17 K beyond that previously reported[7] of +0.65 mK, yielding a net observed non-uniqueness of +0.81 mK. In contrast, the ITS-90 non-uniqueness at 20.27 K is decreased in magnitude, but by a much smaller 0.05 mK, resulting in a net observed non-uniquess at this temperature of –0.2 mK. These adjustments are comparable to or less than the expanded k=2 NIST uncertainties of these ITS-90 temperatures. Similar adjustments to those shown here may also be necessary for the ITS-90 as disseminated from other National Metrology Institutes.

The agreement, as measured at NIST, between the corrected version of the ICVGT and the NPL-75 (as copied onto two NIST RIRTs) is slightly worse between ~ 10 K and 20 K than that observed prior to the adjustment. Finally, the recent values of T-T_{90} derived from ARGT determinations [3] are adjusted here in the ICVGT range to reflect these T_{90} corrections. The good agreement between the ARGT results and the NPL-75 results for the 10.3 K, 13.8 K, and 19.7 K points is unchanged by these adjustments. Those results for the ARGT at 7 K are in good agreement with the adjusted ICVGT and in slight disagreement with the NPL-75. The ARGT –ICVGT difference of ~ (–0.83 to –0.88) mK at 24.56 K is unaffected by the adjustment. The difference of $T_{ARGT} - T_{90\text{-}GT}$(B174) =0.805 mK at 13.837 K is consistent with our previous estimate[3] of $T - T_{90}$ =0.8 mK for the e-H_2 TP as corrected to a SLAP composition.

References

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