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The Discontinuity in the First Derivative of the ITS-90 at the Triple Point of Water

R. L. Rusby

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Abstract This paper investigates the discontinuity in the derivative $[\mathrm{d}W/\mathrm{d}T_{90}]_{\mathrm{TPW}}$ of the ITS-90 at the triple point of water, using data for over 40 calibrated standard platinum resistance thermometers (SPRTs). It finds that the discontinuity is in most cases somewhere between 0 and −6 parts in 10^5, in relative terms, but that the higher numerical values are obtained for 'less ideal' SPRTs (those with lower temperature coefficients of resistance), and also for sub-ranges not extending beyond the indium point. These results are investigated vis-à-vis the long-standing observation that the ITS-90 reference values $W_{\mathrm{r}}(\mathrm{Ga})$ and $W_{\mathrm{r}}(\mathrm{Hg})$ are not completely consistent with data for $W(\mathrm{Ga})$ and $W(\mathrm{Hg})$ for real SPRTs. It discusses what may be done in a future scale to ensure continuity in the first derivative, and it concludes with a comment about the acceptance criteria for SPRTs in the scale.

Keywords ITS-90 · SPRT · Water triple-point

1 Introduction

It is important for good practical thermometry that the temperature scale should be continuous in value and in at least the first derivative, as well as being a close approximation to the ideal of thermodynamic temperature. The ITS-90 reference and deviation functions for representing the calibrations of standard platinum resistance thermometers (SPRTs) are analytic and continuous, except at the junction between the two main ranges at the triple point of water (T_{TPW}, 273.16 K), and also at the freezing point of aluminum, 660.323 °C. At T_{TPW} the reference functions are forced to be continuous as far as the second derivative [1,2], but the mathematics do not include any constraints

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R. L. Rusby (✉)
Engineering Measurements Division, National Physical Laboratory, Teddington TW11 0LW, UK
e-mail: richard.rusby@npl.co.uk

on even the first derivative of the deviation functions at that point. At 660.323 °C the first derivative is continuous, but the second is not. A discontinuity would, in principle, manifest itself in any application where an SPRT is used to measure a thermal property, and in thermodynamic investigations of the ITS-90 itself, specifically as a discontinuity in the quantity $[\mathrm{d}(T - T_{90})/\mathrm{d}T]_{\mathrm{TPW}}$.

2 Mercury–Gallium Inconsistency

In the process of formulating the ITS-90, SPRT calibration data were investigated with the object of ensuring, if possible, that the allowed sub-ranges are mutually consistent within about 0.5 mK, and that the discontinuity in $[\mathrm{d}W/\mathrm{d}T_{90}]_{\mathrm{TPW}}$ is no greater than 10^{-5} in relative terms (i.e., 10 ppm). The process was an iterative one, continuing into the 1989 meeting of the CCT which finalized the scale, and is discussed by Crovini et al. [2]. In particular, an adjustment of −0.4 mK (a minor amount in the context of the thermodynamic uncertainty) was made to the assigned temperature of the triple point of mercury to ensure that the sub-range to the argon point is consistent with sub-ranges extending to lower temperatures. Figure 1.7 of the Supplementary Information for the ITS-90 [3], shows that an inconsistency or error in the mercury point exerts considerable leverage at temperatures down to 84 K. Similar consistency tests were carried out for SPRT sub-ranges above T_{TPW}, and minor adjustments were made to some of the assigned temperatures [2].

Although the sub-range consistency below T_{TPW} broadly meets the 0.5 mK criterion [4], there is nevertheless a small mismatch between the reference functions in ranges not far from T_{TPW}. Specifically, in investigating correlations between SPRT fixed-point ratios, various authors [5–7] have noted that the reference resistance ratios $W_{\mathrm{r}}(\mathrm{Hg})$ and $W_{\mathrm{r}}(\mathrm{Ga})$, where $W(T) = R(T)/R(T_{\mathrm{TPW}})$, lie the equivalent of 1 mK to 1.5 mK away from the line correlating (W(Hg), W(Ga)) data for real SPRTs. This is shown in Fig. 1 for 17 capsule-type SPRTs, and implies that the discontinuity in $[\mathrm{d}W/\mathrm{d}T_{90}]_{\mathrm{TPW}}$ is significantly larger than 10 ppm. The offset cannot be removed by adjusting the assigned W-values (or temperatures) without upsetting the sub-range consistency, and a solution would therefore require changes to be made to one or both of the reference functions.

Also shown in Fig. 1 are some data for calibrations of long-stem SPRTs from the argon point to the zinc point or aluminum point. Values of W(Ga) were not measured, so *interpolated* values are plotted instead. The data lie somewhat above the correlation line for the capsule SPRTs. Note, in particular, that W(Ga) values interpolated from the Ar–Zn data are well correlated with the reference values, the fitted line (fortuitously) passing within 0.1 mK of ($W_{\mathrm{r}}(\mathrm{Hg})$, $W_{\mathrm{r}}(\mathrm{Ga})$). Similar effects are discussed in the next section.

3 Discontinuity in $[\mathrm{d}W/\mathrm{d}T_{90}]$ at the Triple Point of Water

While the Hg–Ga inconsistency is an anomaly with little practical impact on the implementation of the ITS-90 or the calibration of SPRTs, it is notable that it has been detected in measurements of thermodynamic temperature using spherical acoustic resonators. Figure 2 of Pitre et al. [8] shows that data from four sources suggest that

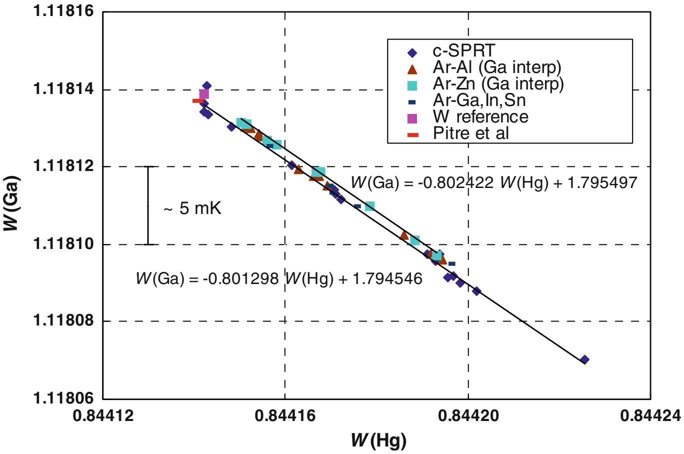

Fig. 1 Correlation between W(Ga) and W(Hg) for 17 capsule-type SPRTs measured at NPL, including a linear fit. Also shown are the points given by the ITS-90 reference values W_r(Ga) and W_r(Hg), and for the capsule-SPRT used by Pitre et al. [8]. Data for long-stem SPRTs calibrated up to the indium, tin, zinc, or aluminum points are included, using *interpolated* values of W(Ga), and a linear fit is drawn through the data for the SPRTs calibrated up to the zinc point

the derivative $\mathrm{d}T/\mathrm{d}T_{90}$ has a discontinuity of approximately 4×10^{-5}, when the data are taken over the range from 200 K to 375 K (or from 234 K to 302 K). It became an issue in the analysis by CCT WG4 [9] of the differences $(T - T_{90})$, when it was proposed to represent the differences by analytical expressions, to ask what the discontinuity in $[\mathrm{d}(T - T_{90})/\mathrm{d}T]_{\mathrm{TPW}}$ should be.

Since T is perfectly continuous, the problem is entirely with T_{90}, and hence it is not necessary to use thermodynamic methods to detect it: one need only look at SPRT calibration data. Moreover, since the ITS-90 reference functions are continuous in first and second derivatives at T_{TPW} (whatever the Hg–Ga mismatch may be), the discontinuity lies in the deviation functions. Inspection of these show that the derivative $\mathrm{d}\Delta W/\mathrm{d}W$ is simply given by the first coefficient a (exceptionally, for the sub-range to the neon point it is given by $a + c_1$). Therefore, the discontinuity can simply be deduced from the difference $(a^{+} - a^{-})$, where a^{+} and a^{-} are the coefficients derived from sub-ranges above and below T_{TPW}, respectively.

Two factors conspire to give multiple values rather than a single result. The first is, of course, that the experimental data are imperfect and will show some scatter (as also in Fig. 1). The second is the existence of non-uniqueness in the ITS-90. Each SPRT will give a different result, and the result may also be affected by the particular sub-ranges chosen. This is investigated here using calibration data which have been obtained in a 20-year period, for the same 43 SPRTs of various kinds as were considered in Fig. 1.

Figure 2 shows $(a^{+} - a^{-})$ plotted against W(Hg) for capsule-type SPRTs calibrated from the argon point to the gallium point, and long-stem SPRTs calibrated from the argon point to various upper temperatures from the gallium point to the aluminum point. All the differences $(a^{+} - a^{-})$, except one presumed outlier are within the range 0 to -6×10^{-5}, but there are some interesting features.

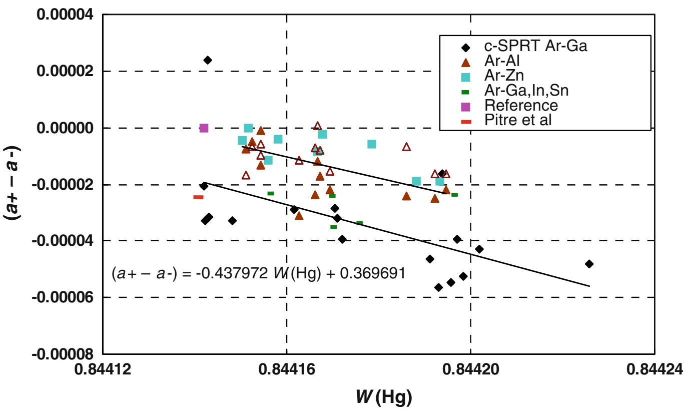

Fig. 2 Differences between the ITS-90 *a*-coefficients, a^+ and a^-, derived from sub-ranges above and below T_{TPW}, respectively, representing the discontinuity in the first derivative $[\mathrm{d}W/\mathrm{d}T_{90}]_{\text{TPW}}$ for the SPRTs as in Fig. 1. The *lower line* is a fit to the data for capsule-type SPRTs calibrated up to the gallium point; *the upper line* is a linear fit to long-stem SPRTs extending to the zinc or aluminum points. Data shown by *open triangles* are for the Ar–Al calibrations recalculated as Ar–Zn. One division in the ordinate is equivalent to a discontinuity of 20 μK/K. A shift of this magnitude would be produced by an error or change of ~0.6 mK in the gallium point or ~0.8 mK in the mercury point

First, there is a tendency for the discontinuity to become larger for larger values of W(Hg), i.e., as the platinum becomes less ideal and the deviations (a values) themselves become larger. (Equivalent graphs can be plotted with W(Ga), a^+, or a^- as the horizontal axis.) It is not clear why this should be, although it is presumably related to increasing deviations from Matthiessen's rule, which lead to the sub-range inconsistencies, as is discussed in Sect. 4 of White and Strouse [10].

Second, there seems to be a small but clear separation between calibrations extending up to the indium point, and those extending beyond this. The two lines in the figure are linear fits to the two groups, and they are separated by approximately 2×10^{-5}. Within the upper group, it is notable that calibrations up to the aluminum point are mostly below the fitted line and calibrations up to the zinc point are mostly above it, but if the Ar–Al data are re-calculated only up to the zinc point (shown by the open triangles), they become more nearly consistent with the Ar–Zn data.

Third, we note that the upper line tends towards zero difference at the reference value of W_{r}(Hg). It may be that the SPRTs investigated in the formulation of the ITS-90 were close to this condition and thereby encouraged the conclusion that discontinuities would be less than 10^{-5}. The separation of the two lines in both Figs. 1 and 2 suggests that there are inconsistencies between sub-ranges which include the gallium or indium point, and those extending to the zinc and aluminum points, which do not.

It would be interesting to compare the results for these thermometers with SPRT calibration data in other NMIs, which by now exist in large numbers but are rarely published. Unfortunately, the HTSPRTs used in defining the ITS-90 reference function above T_{TPW} appear not to have been calibrated at the mercury or gallium points, so they cannot be plotted in Figs. 1 and 2, but one SPRT for which we have deduced data is the capsule thermometer used by Pitre et al. [8]. From their Tables 1 and 2 we find that $(a^+ - a^-) = -2.5 \times 10^{-5}$. This result is plotted in Fig. 2 and it is seen to lie close to the line for the NPL capsule SPRTs. The discontinuity at T_{TPW} is comparable with, though slightly smaller than, the 4×10^{-5} deduced by the authors for the combined acoustic data over a significant range (see above). The sign difference is just a matter of the way the differences are taken.

Finally, we note that the NPL capsule SPRTs had been calibrated down to the triple point of hydrogen, and for each thermometer the values of a^- (or $a^- + \mathrm{c}_1$ for the sub-range to the neon point) are very consistent for all four sub-ranges, generally within 3×10^{-6}. For the ranges above T_{TPW}, we do not have a complete set of data at all the fixed points, so it is not possible to test the sub-range consistency. However, as mentioned above, when the Ar–Al data are re-calculated only up to the zinc point, they become more compatible with the Ar–Zn data.

4 Removing the Discontinuity

We now consider how it might be possible to remove the discontinuity in a future scale by changing the mathematical formulation. The first option would be simply to set $a^- = a^+$, i.e., to use the data above T_{TPW} to define the derivative at T_{TPW} for the range below this (or vice versa). In that case, the mercury point becomes redundant (remembering that it was introduced in place of the measurement above T_{TPW} in the IPTS-68). The disadvantage of this is that the potential for non-uniqueness would be increased, as in the IPTS-68, and it would be necessary to check the effect thoroughly. The second option would be to fit the deviations by a single continuous function over the complete calibration range, whatever it may be; for example, from the triple point of argon to the freezing point of zinc or aluminum, or (with a different function) from the triple point of hydrogen to the melting point of gallium. This is an extension of the concept used in the ITS-90 for the short-range interpolation between the mercury and gallium points, spanning the triple point of water.

It might also be desirable to introduce least-squares interpolation or a choice in the points measured. This is another step on the road to greater flexibility in the scale, and the number of possible combinations (of ranges, fixed points, and orders of fit) would be significantly increased. Again it would be necessary to check the consequences (and the mutual consistency of the reference functions) thoroughly, to ensure that it does not introduce excessive non-uniqueness of various kinds. In the case of a least-squares solution, the further choice exists as to whether or not to force $W = 1$ at T_{TPW} or to treat this as just another data point in the fit.

If options such as these are not acceptable, some discontinuity seems unavoidable, but with improved design of the scale they could still be small enough to be tolerated. A further option to reduce them may be to restrict the criteria for acceptance of SPRTs in ITS realizations.

5 Acceptance Criteria for the ITS

The values of W(Ga) and W(Hg) are special in being the alternatives used for determining whether a particular SPRT is of acceptable quality for use within the ITS-90 formulation. Of course, the formulation is widely used even with industrial PRTs (though it is unnecessarily complicated for this purpose), but where neither criterion is met there is an obligation to use additional temperatures to check the accuracy of the interpolation.

Two acceptance criteria were given so that the ranges above and below T_{TPW} would be independent, but the values specified are not exactly equivalent: it is somewhat easier to qualify at the mercury point than at the gallium point. It has been suggested [10] that a single criterion for the value of $S = (W - 1)/(W_{\mathrm{r}} - 1)$ could be adopted regardless of temperature, but in this case a marginal thermometer could still qualify at a lower temperature, but fail at a higher temperature. The value of the a coefficient could equally be used, though the criterion could then only be applied *after* the complete calibration has been carried out.

The real problem with the acceptance criteria is that they are absolute cut-offs, whereas in fact a thermometer that just fails is unlikely to be significantly worse than one that just passes. In view of the tendency to larger discontinuities (and non-uniqueness in general) with increasing $W(\mathrm{Hg})$, as indicated in Fig. 2, and given that carefully made thermometers can qualify without difficulty, the present criteria could be tightened up for calibrations with best uncertainties. A second tier of uncertainty might then be permitted for non-compliant SPRTs.

6 Conclusions

The discontinuity in the derivative $[\mathrm{d}W/\mathrm{d}T_{90}]_{\mathrm{TPW}}$ has been investigated using data for 43 SPRTs calibrated above and below T_{TPW} . It is found in general to be larger than was foreseen during the formulation of the scale, and to be dependent on the quality of the thermometer and also on the upper temperature of the calibration. For many of the long-stem SPRTs investigated in the work (especially those with the higher temperature coefficients) the discontinuity is within the criterion set, but there are suggestions of sub-range dependence above T_{TPW}.

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