WORKING GROUP 4 REPORT TO CCT

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Terms of reference : thermodynamic temperature determinations and extension of the ITS-90 to lower temperatures

1. Introduction

The 9th International Symposium on Temperature and Thermal Measurements in Industry and Science, *Tempmeko 2004*, in Cavtat (June 2004) included several papers of relevance to Working Group 4. It provided the opportunity for six members of the group to meet to review developments and make provisional plans for future activities.

Also of note, in January 2005 a 1-day workshop on '*Methods for new determinations of the Boltzmann constant*' was held at PTB.

Following our established practice, the present report gives brief information on current projects to determine thermodynamic temperatures, and refers to developments at ultra-low temperatures. In a departure from previous practice, it also considers the implications of a possible redefinition of the SI unit of temperature, the kelvin, in the light of the PTB workshop (see Document CCT/05-02 and www.ptb.de: select '*structure*' and '*temperature*' twice, then '*actual scientific news*').

In Section 4 we make a specific request to publish our '*Supplementary Information for the PLTS-2000*' in the Journal of Low Temperature Physics, as well as in the BIPM pubication, to give it wider availability to those who need the information.

2. Thermodynamic temperature determinations

This section is a short resumé of work in progress and new values of thermodynamic temperature between 1 K and 1358 K (work related to the high-temperature eutectic fixed points is under review in WG5). It is grouped according to the technique used: gas thermometry, noise thermometry and radiometry. The proceedings of Tempmeko 2004 are not yet available, and references are to papers as submitted.

As in 2003, we are aware of no experiments in **constant-volume gas thermometry** other than as interpolations for realising the ITS-90 below 24.5561 K, at NMIJ, PTB and IMGC.

No papers on **acoustic gas thermometry** were presented at Tempmeko 2004, but both the NIST and IMGC/IEN groups gave presentations at the PTB workshop, see above. Moldover showed results obtained by Pitre (of BNM-INM) in collaboration with himself and Tew (of NIST) in a 0.5 litre quasi-spherical resonator, at about 12 temperatures in the range from 234 K down to 7 K. Measurements were made relative to an isotherm near 273.16 K, and microwave resonances were used to monitor changes in the resonator dimensions. These new measurements differ from previous primary acoustic thermometry in several significant respects:

1. the shape of the cavity resonator was that of a deliberately distorted sphere
2. the working gas was helium (except argon was used for the 149.62 K isotherm)
3. the cavity walls were copper : previous acoustic thermometers used steel.

In the range of overlap and within combined uncertainties, the current data agree with previous acoustic thermometry. This demonstrates the robustness of primary acoustic thermometry to changes in the shape of the cavity, the material forming the cavity, and to the thermometric gas.

Results were presented as $10^6(T - T_{90})/T_{90}$, which reaches, for example, about - 70 ppm (8 mK) at 120 K and - 90 ppm (0.6 mK) at 7 K, with smaller differences at intermediate temperatures. The point using argon is in close agreement with that using helium. Figure 1 illustrates the consistency of acoustic gas thermometry obtained by different groups working in different countries. The unweighted average of $(T - T_{90})$ at the gallium point is (3.95 ± 0.86) mK. (The uncertainty is one standard deviation.) The unweighted average of $(T - T_{90})$ at the mercury point is (-3.32 ± 0.69) mK.

Moldover also reported at the workshop that the consensus of acoustic thermometry results show a discontinuity in the slope $(\mathrm{d}T_{90}/\mathrm{d}T)$ above and below 273.16 K, of about 4×10^{-5}. Thus the inconsistency between the ITS-90 reference resistance values $W_r(T_{90})$ at the melting point of gallium and the triple point of mercury, as seen relative to W-values measured with platinum resistance thermometers, has been confirmed thermodynamically.

A paper on the NPL experiment in **Rayleigh-scattering gas thermometry** was presented at Tempmeko 2004 by de Podesta (NPL, Paper 63) In this technique the elastic scattering from a laser beam passing through a gas is observed and related to the gas density. Two gas cells have been assembled to allow simultaneous measurements at unknown and reference temperatures at equal pressures. Recent work has focused on reducing the extraneous scatter and improving the signal-to-noise. The experiment is planned to run with argon or xenon in the range 173 K to 300 K.

A new experiment in **dielectric constant gas thermometry** is being set up at PTB (Fellmuth *et al*, Tempmeko 2004, Paper 51). Initially it will be used together with the CVGT for interpolation in the range 3 K to 24.5561 K, but later it is planned to use it for primary gas thermometry between 84 K and 273 K. Meanwhile, the earlier PTB DCGT work has been re-analysed, using *ab initio* values for the polarisability of helium, so as to generate absolute thermodynamic data. The differences relative to the PTB copy of NPL-75, when normalised to the ITS-90 fixed point values, are plotted in Figure 2.

Tests have been undertaken of electromagnetic interference in the **noise thermometer** at MSL (White, Tempmeko paper 147), but no further progress has been made. The electronic system for the noise thermometer at NIM has been built, and a data-processing program is now being assembled, prior to testing. These two noise thermometers are designed for measurements at the freezing point of indium and up to 900 K, respectively.

No new data have been generated with the programmable ac Josephson quantised-voltage noise source (QVNS) at NIST. Temperatures measured in the range 273 K to 505 K will be used primarily for vetting the system, at Boulder, looking for consistency with the NIST acoustic gas thermometry. Measurements between 505 K and 933 K, at Gaithersburg, will use the tin point as a reference temperature.

New **spectral radiometric measurements** of the thermodynamic temperatures of the freezing points of silver and gold, using an absolute pyrometer AP1, were presented at Tempmeko 2004 by Yoon *et al* (NIST, Plenary Paper 4). The values of ($T - T_{90}$) were (0.026 ± 0.13) K and (0.014 ± 0.16) K, respectively, with uncertainties at $k = 2$. The largest uncertainty component was 0.15 % of radiance due to the measurement of the absolute responsivity of the detector.

Absolute radiometric determinations of the freezing point of copper were reported by Noorma *et al* of MIKES, Finland (Tempmeko 2004 Paper 22) using a two-aperture radiometer with small aperture areas. The results varied with wavelength, the differences ($T - T_{90}$) being -0.30, -0.04 and 0.03 K at 901, 800 and 594 nm, respectively. Uncertainties were 0.20, 0.17 and 0.20 K ($k = 1$), dominated by the calibration of the radiometer.

In an experiment at BNM-INM, Briaudeau and colleagues (Tempmeko 2004, Paper 263) have measured the freezing point of copper using a spectroradiometer calibrated against a monochromatic source, rather than a filter radiometer. The value reported was ($T - T_{90}$) = (-0.14 ± 0.14) K, the main source of uncertainty being that in the radiance of the laser source against which the blackbody radiance was compared. This can be reduced by calibration using a cryogenic radiometer, whereupon an uncertainty of about ± 0.05 K is expected to be achievable, limited by geometrical factors.

In a joint effort by BIPM and NMIJ, Goebel *et al* have reported measurement of the freezing point of copper using two lens-based filter radiometers calibrated absolutely using conventional spectro-radiometric methods (Tempmeko 2004, Paper 58). By linking the copper point at BNM-INM and the radiometers of BIPM by means of a transportable copper point furnace, the value of ($T - T_{90}$) was determined to be 0.148 K with an uncertainty of 0.077 K ($k = 1$).

In Tempmeko 2004 Paper 16, Ali (NIS, Egypt) reported a determination of the freezing point of copper relative to that of silver, by relative radiation thermometry. His result was 0.011 K above the ITS-90 value with an uncertainty of 0.015 K ($k = 1$).

The NPL Absolute Radiation Detector (ARD) has been rebuilt with an enlarged radiation trap designed to reduce the uncertainties arising from diffraction and scattering of radiation. For the same reasons, it is also necessary to replace the blackbody radiator with a more conventional design. The first objective of the experiment is a determination of the Stefan-Boltzmann constant, but temperature measurements are planned, from 234 K to 429 K. See Document CCT/05-02. Absolute spectral radiation thermometry is also in progress at NPL, and is expected to lead to new values for the freezing points of aluminium, silver and copper.

The possibility of carrying out Fourier Transform infrared thermometry in a sodium heat-pipe blackbody was further explored by Steele *et al* (NRC, Tempmeko Paper 81). The authors conclude that the principal assumptions of the method, namely that the spectral emissivity of the source is temperature independent and that the detector responsivity is linear, are not significantly violated and that it would be worth refining the apparatus to reduce the influence of ambient temperature variations and to improve the correction of spectrometer drift.

Triple and vapour pressure points of hydrogen

WG4 has been consulted by WG1 concerning the isotopic composition of the hydrogen on which the assigned triple-point and vapour-pressure temperatures in the ITS-90 were based. This was in the hope that a specific composition could be identified and recommended for improved reproducibility of realization.

Unfortunately the information appears not to have been recorded, although there was some recognition of the effect at the time: for example, Compton (TMCSI Vol. 4, pp195-209, 1972) notes that the (normal) boiling point of hydrogen could vary by 0.35 mK depending on the liquid/vapour ratio in the bulb. Possible significant variations in the composition of the supplied gas samples were discounted.

However, new information has been obtained at PTB using the recalculated DCGT data, see above, from which it is estimated that the thermodynamic temperature of the hydrogen cell H_2-1 is 13.80365 K, with a standard uncertainty of 0.0005 K. Since it is also estimated that the hydrogen in this cell contains only 35 micro-mol of deuterium, it is necessary to make a correction for the isotope depletion. On this basis the triple-point of Standard Light Antarctic Precipitation (SLAP) is calculated to be 13.8039 K. This is 0.0006 K higher than the ITS-90 value.

Using acoustic gas thermometry, Pitre, Moldover, and Tew (collaboration of BNM-INM and NIST) determined that the thermodynamic temperature of the triple point of 'SLAP'-corrected e-H_2 TP is (13.804 08 ± 0.000 25) K. This determination is based on the NIST realizations of the e-H_2 TP and an interpolating constant-volume gas thermometer (ICVGT) as carried on RIRT A129. At a later date, this collaboration will provide an improved assessment of this fixed-point temperature, independent of the ICVGT, and with a smaller uncertainty.

Discussion

A number of experiments are in progress, and there have been some notable new results since our last survey: the NIST/BNM-INM acoustic thermometry, the NIST, MIKES and BNM-INM absolute radiometry, the NIS relative radiometry and, at low temperatures, the PTB recalculated DCGT work.

Figure 3 is an up-dated version of our 2003 figure of differences $(T - T_{90})$/K, extended to 1358 K to allow data at the gold and copper points to be included. Additions are the NIST/BNM-INM acoustic thermometry, the radiometric data of Yoon *et al* (at the silver and gold points), and Fox *et al* (now including the gold point). The noise thermometry measurement of the copper point by Edler et al (TS8) is also included, but the MIKES and BNM-INM radiometry results have uncertainties which are too large to be accommodated. We have also included the $k = 1$ uncertainties in the thermodynamic temperatures of the ITS-90 fixed points, as estimated in Table 1.2 of the Supplementary Information. They are joined by dotted lines, on the assumption that the uncertainties in the ITS-90 vary linearly between the fixed points.

It remains the case that the most pressing need at high temperatures is for a new determination of the zinc point with an uncertainty comparable with what has recently been achieved at the tin point. This would finally resolve the long-standing discrepancies at that point, and it would also allow new values for the higher fixed points to be calculated from relative spectral radiation thermometry (Fischer and Jung, Metrologia, 1989, **26**, 245-252), with lower uncertainty than has so far been achieved in direct measurements.

Figure 4 is an expansion of Figure 3 over the range up to 505 K (the freezing point of tin). This plot shows more clearly the consistency between the four sets of acoustic data, and the discrepancies between these and earlier work (constant volume gas thermometry by Kemp *et al* and Astrov *et al*, and total radiation thermometry by Quinn *et al*, all pre-1990). The discrepancies are very marked in the region down to 100 K but, as indicated earlier, they are confirmed by the new results of Pitre, Moldover and Tew, which also provide further information down to 7 K.

The only other low temperature data to have been added to Figure 4 since 2003 are the DCGT data of Fellmuth *et al* (Figure 2) in the range 4.2 K to 27 K. WG4 proposes to review differences ($T - T_{90}$) in this range in more detail as a later activity.

In summary, it has become more clearly evident in the last few years that over much of the range the ITS-90, the scale which NMIs are disseminating to their customers, has larger thermodymanic errors than was predicted at the time of its adoption. We believe that efforts to confirm and extend knowledge of thermodynamic temperature should continue and be encouraged.

3. Definition of the kelvin

Closely allied to the subject of thermodynamic temperature determinations is the definition of the kelvin, the unit for such determinations. In the last two years there has been speculation as to whether it would be possible or desirable in the foreseeable future to change the definition. This is only incidentally related to the discussion arising from CCT-K7 about specifying the isotopic composition of the water to which the present definition should refer.

The alternative now being discussed is that the use of the 'quasi-artefact' water might be avoided altogether by specifying a value for the Boltzmann constant, k_B. The two main advantages of this are (see Fischer *et al*, Tempmeko 2004 Plenary Paper 3):

- that the unit would simply be related to a fundamental constant, much as has been done for some other units such as the metre, and
- that no particular temperature or measurement method would be favoured. For example, a radiometric determination of the gold point would stand on its own, without any link (actual or implied through an experimentally-determined value of k_B) to the triple point of water, or any other specified temperature.

This is very much in line with the ambitions which the CCU has for the SI, as witnessed by the recent paper by Mills *et al* (Metrologia, April 2005) proposing the redefinition of the kilogram by specifying a value for the Planck constant or the Avogadro constant. The question for us is whether the Boltzmann constant is known well enough to allow a redefinition of the kelvin to be recommended. We therefore need to assess the current, and likely future, uncertainty in k_B.

As a first step, a workshop on *Methods for new determinations of the Boltzmann constant* was held at PTB, with CCT and EUROMET sponsorship, in January 2005.

A report on the proceedings has been submitted by Fellmuth *et al* as CCT/05-02. Four approaches were identified: acoustic gas thermometry, thermal equation-of-state methods, radiation thermometry and methods based directly on statistics and quantisation. The present value, with an uncertainty of 1.7 ppm, comes from the NIST acoustic thermometry in 1988, and the conclusion at the workshop and in Document CCT/05-02 is that in the mid-term (5 to 10 years?) the acoustic method may give 1 ppm (at $k = 1$) and dielectric constant gas thermometry 2 ppm. Other techniques are thought likely to be limited to 5 – 10 ppm or more.

One consequence of fixing k_B at a defined time, for example, in 2010, is that the resources that NMIs now devote towards improving primary thermometry near the triple point of water might then be redirected towards improving primary thermometry at temperatures much farther from the triple point of water. Such a redirection might lead to a more nearly thermodynamic scale more quickly. Because the uncertainty of primary thermometry is on the order of 2 ppm near the triple point of water, a major effort would be needed to reduce this uncertainty. In contrast, the uncertainty in temperature measurement increases substantially at higher and lower temperatures, for example, to about 10 ppm at 150 K and 500 K, and larger amounts beyond. Thus, a smaller effort is required to significantly improve the scale away from the triple point of water.

Implications

It may be argued that the value of k_B should be of similar uncertainty to the uncertainty of the realization of the water triple point, before a redefinition can be recommended. This is not reasonable, however, because the realization of the triple point is a necessary part of any experiment to determine k_B, and it seems likely that the thermodynamic uncertainties will always considerably exceed this.

On the other hand, if the value of k_B is fixed with its present value, the uncertainty of 1.7 ppm would imply an uncertainty in the temperature of the triple point of water of almost 0.5 mK. Given that the current value of k_B is derived almost entirely from a single determination, we would want to have confirmation at least at this level of uncertainty before the unit is re-defined.

Even an uncertainty of 1 ppm, equivalent to 0.27 mK, is large compared with the *precision* of ‘ITS thermometry’ in this range. Therefore there is no immediate suggestion that a new definition of the unit would lead to thermodynamic methods replacing the ITS, which would continue the tradition of providing a convenient substitute for thermodynamic techniques. Exceptions may apply at very low and very high temperatures, where recourse to thermodynamic techniques may be advantageous.

If, at a later time, new experiments were to show that the adopted value of k_B was incorrect by 1 ppm, a future ITS might adopt a value of (say) 273.1603 K for the triple point. There is no difficulty about this, as the water triple point would no longer have a special status (just as the steam point became ‘unfixed’ in 1954). At the time of any scale revision, the conventionally-adopted temperature values always change in line with current thermodynamic knowledge, and much larger changes can be expected at all other points.

During the PTB workshop consideration was briefly given to the form of words which might be used in a new definition, before it was deemed to be an unproductive use of time. For the record, the wording proposed by Fischer was

The kelvin is the change of thermodynamic temperature that results in a change of thermal energy kT by 1.38065xx . 10^{-23} *joule.*

Nomenclature

In the above, we have used the symbol k_B for the Boltzmann constant, although ISO 31-8 specifies just *k*. However, this symbol is overworked and k_B avoided possible confusion with *k*, the uncertainty coverage factor. We believe it would be advantageous if k_B could be officially recognised as an acceptable alternative.

What do we mean by 'realization of the kelvin'?

In considering the revision of Appendix 2 of the SI brochure 'Practical realization of the definitions of some important units' M Stock wrote (7 January 2005): "*Does it make sense to talk about the 'realization of the kelvin'? Of course a WTP cell realizes a certain multiple of the kelvin, but does it "realize the kelvin"? If this phrase makes sense, is the realization just the operation of the WTP cell or does it include the primary thermometers necessary to measure any other temperature? The difference between the kelvin and the other base units is of course that temperature is an intensive quantity and that in addition to the definition of the unit something else, a primary thermometer, is needed to determine any other temperature.*"

Perhaps this section of the SI Brochure should open with a statement such as : 'It is in the nature of definition of the kelvin that a realisation is not of the unit itself but 273.16 units. Thereafter, other values of thermodynamic temperature can be determined using one of a number of so-called primary thermometers…', and continue from there.

Is it fundamentally important in this context that temperature is an intensive quantity? - all the base units have their pecularities. More widely, pressure and emf are also intensive, but one can add them in appropriate devices, or otherwise build up scales. In thermodynamic thermometry one must work with ratios, or link to the unit via the Boltzmann constant - it may be harder, but is it really an essential difference? (Of course, a discussion on this is not required for the SI Brochure.)

4. Extension of the ITS-90 to lower temperatures : developments below 1 K

No new experiments have been reported which might resolve the differences in the ^{3}He feature temperatures (0.9 mK to 2.4 mK) between the PTB-96 scale and the University of Florida scale. At temperatures between 0.65 K and 1 K, work is in progress at PTB to make direct comparisons between the ITS-90 (^{3}He vapour pressures) and the PLTS-2000 (^{3}He melting pressures).

The WG4 project to produce Supplementary Information for the realisation of the PLTS-2000 is at an advanced stage but work has been temporarily suspended. It will resume in time for its inclusion in the main CCT document.

It has been suggested to us that this part of the Supplementary Information should be given wider exposure, for example, by publication in the Journal of Low Temperature Physics, since potential users will read the journal, but not the CCT publication. Permission is therefore sought to submit it to this journal.

A number of papers at Tempmeko 2004 were concerned with developments in thermometry at temperatures below 1 K.

Paper 50 (Fellmuth *et al*) described the realisation of the International Temperature Scales in the cryogenic range at PTB. Of particular relevance is the discussion on the use of the ^{3}He melting-pressure thermometer for the realisation of the PLTS-2000, and the uncertainties following from the different calibration methods.

Two papers (Rusby *et al*, Paper 200, and Peruzzi *et al*, Paper 241) described the results of the EU-funded project on ‘ULT Dissemination’. The first was an overview, while the second concerned the evaluation of the new SRD1000 superconductive reference device.

Two further papers (Reesink *et al*, Paper 79, and Uuispaikka *et al*, Paper 250) described experiments with Coulomb blockade thermometers, which are potential primary thermometers for the range down to about 0.03 K, and can also be used as self-calibrating secondary devices. The operating principle is that the conductance of a series of N-I-N junctions dips at low bias voltage, and the half-width of the dip is well-related to temperature. The principle has been demonstrated experimentally, though the uncertainty of results to date has been limited to about 1 % of T.

A further paper (230, by Mitin *et al*) was concerned with Ge-GaAs resistance devices as secondary sensors for use at low temperatures and high magnetic fields.

References to work plotted in Figures 1-4.

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Pitre, Moldover, and Tew: 2005, to be published

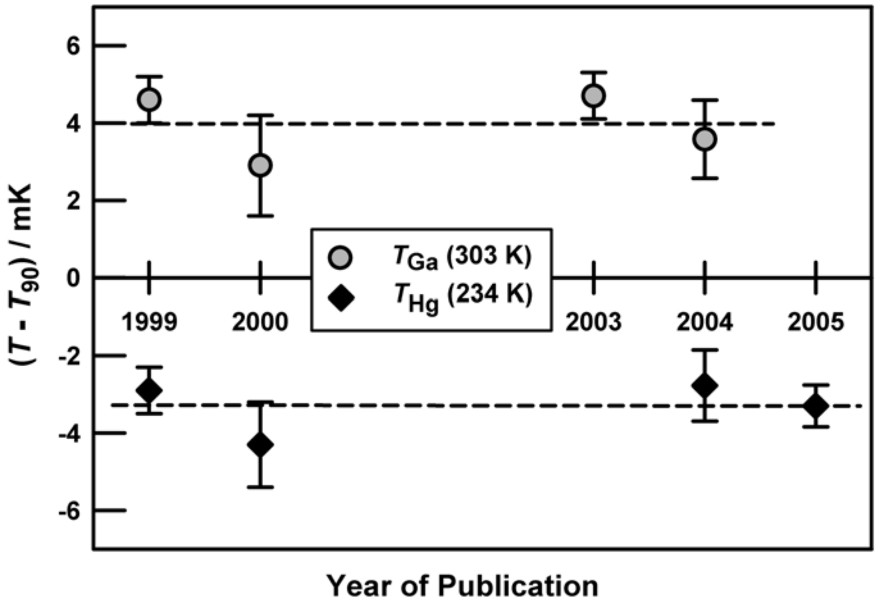
Figure captions

Figure 1: Recent acoustic determinations of $(T - T_{90})$ at the melting point of gallium and the triple point of mercury. The data sources by year are: 1999 (Moldover *et al*, 2000 (Ewing and Trusler), 2003 (Strouse *et al*), 2004 (Benedetto *et al*), 2005 (Pitre *et al*).

Figure 2: Deviation of the PTB DCGT scale from the ITS-90 (from Fellmuth *et al*, Tempmeko paper 50)

Figure 3 : Graph of differences between published thermodynamic temperature determinations and the ITS-90 up to 1358 K. Uncertainty bars are at $k = 1$. The $k = 1$ uncertainties in the thermodynamic temperatures of the ITS-90 fixed points, as estimated in Table 1.2 of the Supplementary Information, are included, joined by dotted lines on the assumption that the uncertainties in the ITS-90 varies linearly between the fixed points.

Figure 4 : Graph of differences between published thermodynamic temperature determinations and the ITS-90 up to 505 K. Uncertainty bars are at $k = 1$. The $k = 1$ uncertainties in the thermodynamic temperatures of the ITS-90 fixed points, as estimated in Table 1.2 of the Supplementary Information, are included, joined by dotted lines on the assumption that the uncertainties in the ITS-90 varies linearly between the fixed points.



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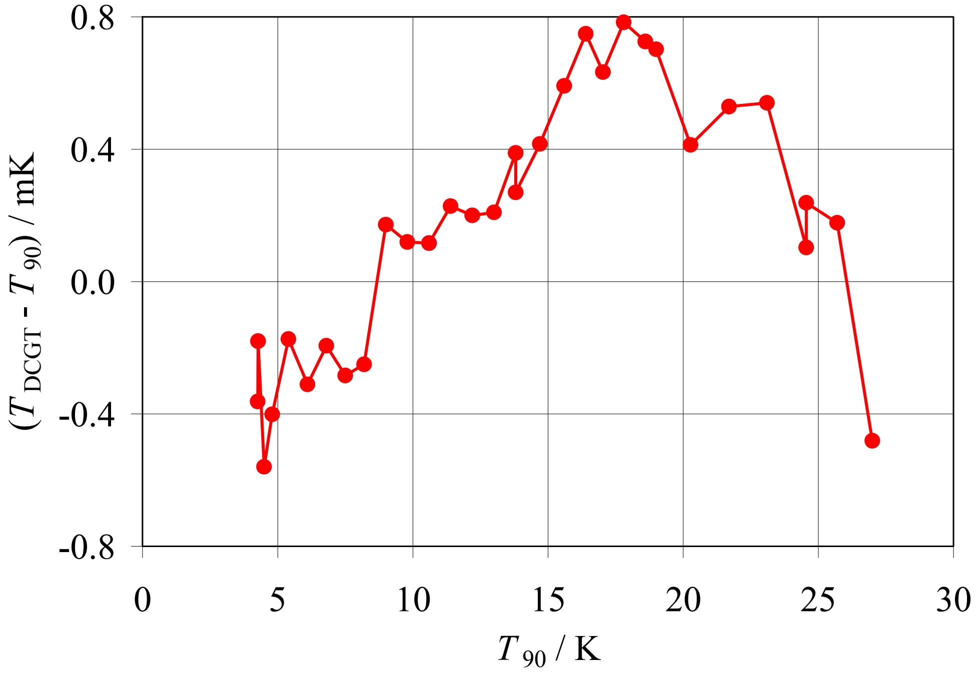

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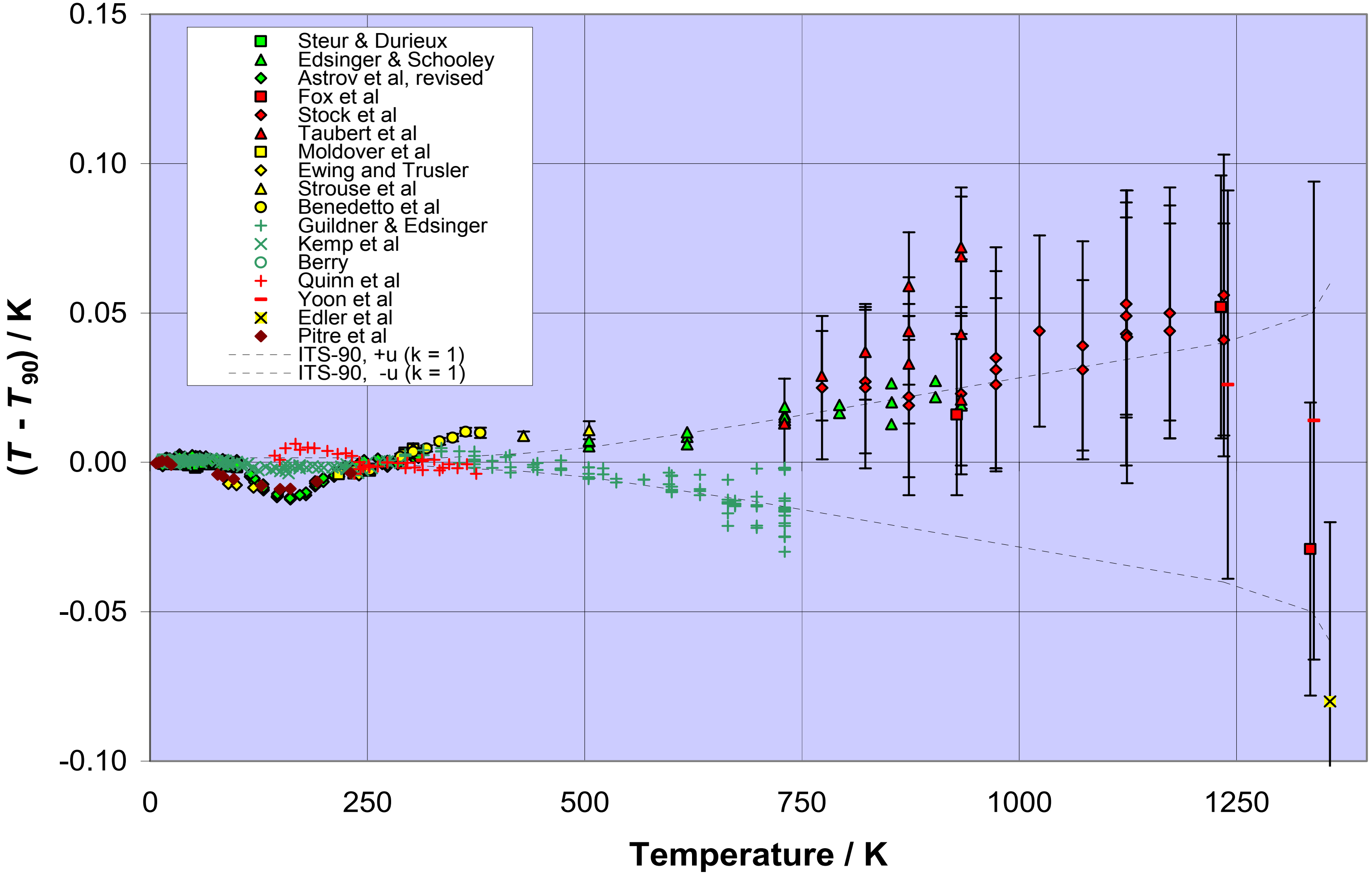

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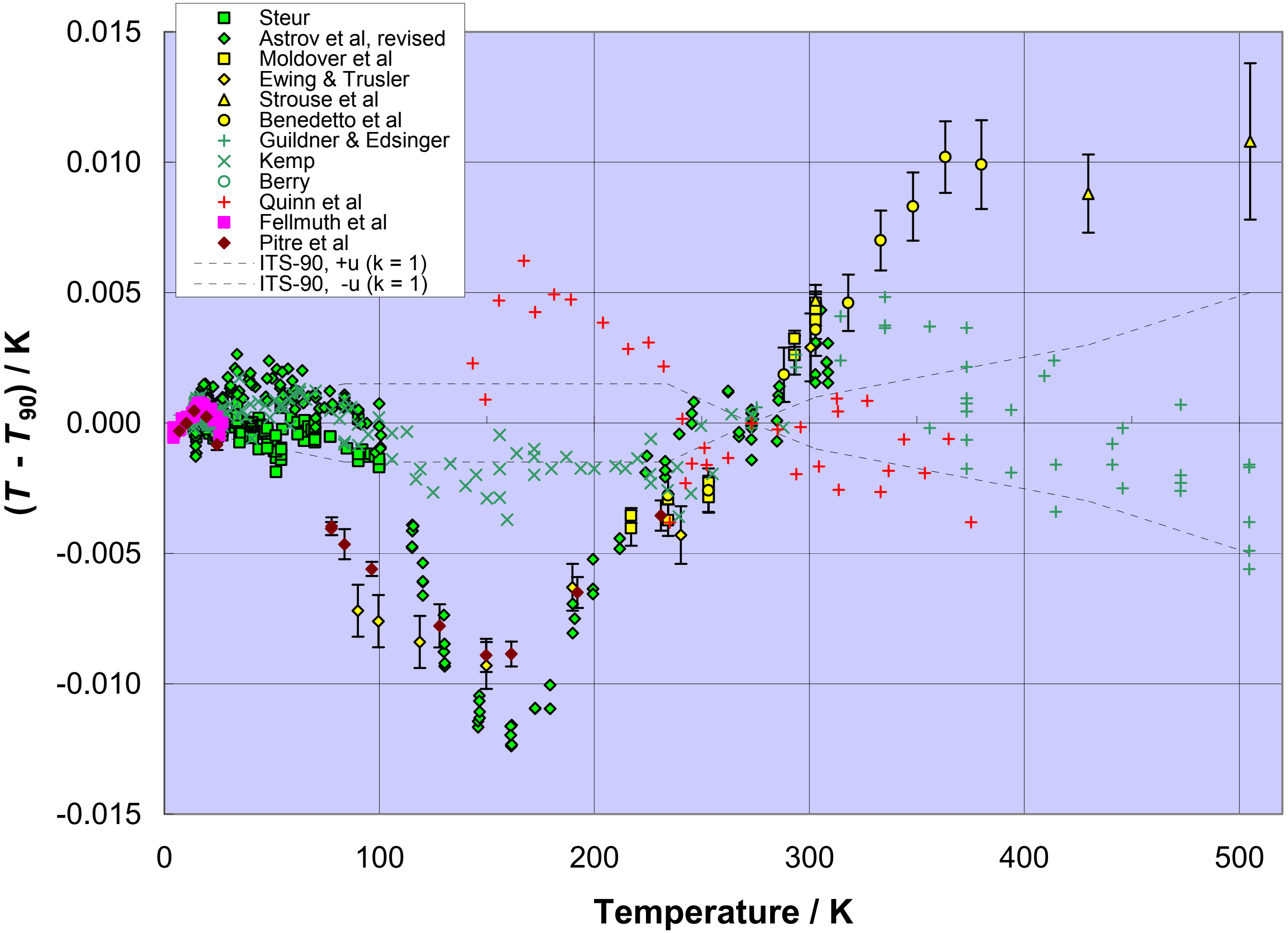

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