# Establishment and Corroboration of a Thermodynamically Consistent Helium-3 Vapour-Pressure Scale

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The helium-3 vapour-pressure scale (VPS) of the ITS-90 (Equation (6a)  $T_{90}(p)$  in the text, with  $T_{90}$  being the ITS-90 temperature value and p the vapour pressure) deviates systematically from thermodynamic temperature T below about 1.2 K. The difference  $T_{90}$  - T increases with decreasing temperature up to about 1 mK at 0.65 K. This fact has been demonstrated in three different ways by two independent groups in each case. The results obtained were the basis for establishing and corroborating a new, thermodynamically consistent helium-3 VPS, called PTB-2006.

## (I) Primary thermometry below 2 K

Both at PTB [Schuster and Hechtfischer 1992] and at NIST [Fogle *et al.* 1992], a combination of absolute and relative primary thermometry was used to obtain thermodynamic temperature values below 1.2 K. Relative primary thermometry was performed with magnetic thermometers (PTB: single-crystal cerous magnesium nitrate (CMN), NIST: approximation with powdered CMN) calibrated above 1.2 K against copies of the NPL scale  $T_{X1}$  [Rusby and Swenson 1980], which in turn is a magnetic extrapolation of the constant-volume gas-thermometry scale NPL-75 [Berry 1979]. (The scale  $T_{X1}$  is the thermodynamic basis of both the provisional 0.5 K to 30 K temperature scale EPT-76 [Durieux *et al.* 1979 *Metrologia* **15** 57-63, BIPM 1979 *Metrologia* **15** 65-68] and the ITS-90 [Preston-Thomas 1990] from 0.65 K to 2.6 K [Durieux and Rusby 1983, Rusby and Durieux 1984, Rusby *et al.* 1991]. The text of the EPT-76 does not contain a formula for the temperature dependence of the helium-3 vapour pressure, but only values of the deviation from older scales at fifteen temperatures from 0.5 K to 3.2 K.) The two magnetic extrapolations were checked below 1 K independently by absolute primary thermometry.

Both at PTB and at NIST, the deviation of the NPL scale  $T_{X1}$ , and thus in good approximation of ITS-90, from the obtained thermodynamic temperature data was determined. (The two groups compared their magnetic thermometers with different rhodium-iron resistance thermometers (RIRTs) calibrated nominally on the EPT-76, but in reality, these resistance thermometers carried copies of the NPL scale  $T_{X1}$ .) The results are shown in Figures 1 and 2. (For all figures of this document, the figure captions correspond as far as possible to those in the original papers. The temperature differences  $\Delta T = (T_{X1}-T_{CMN})$  between RIRT wire scales  $(T_{X1})$  and the CMN thermometer  $(T_{CMN})$  measured at PTB are shown in three plots. In Figure 1,  $\Delta T$  is shown with straight lines between the measured data points for individual RIRTs. In Figure 3, all  $\Delta T$  values are given as vertical dashes. In Figure 2, a solid line goes through mean values of the differences measured with different RIRTs.)



**Figure 1** (on the left): Figure 2 in [Schuster and Hechtfischer 1992]: Temperature deviation of different rhodium-iron resistors (readings  $T_R$ ), which carry EPT-76 (in reality  $T_{X1}$ ), from a single crystal cerous magnesium nitrate (CMN) thermometer (reading  $T_C$ ) that was calibrated between 1.2 K and 1.8 K using the same resistors. The symbol "+" denotes results obtained with superconductive reference points.

**Figure 2** (on the right): Figure 4 in [Fogle *et al.* 1992]: Temperature differences between  $T_{76}$  (EPT-76 (in reality  $T_{X1}$ )) and  $T_{CMN}$  (powdered CMN thermometer) versus temperature for the two RIRTs Nos. 232321 and B189. Included for comparison are the results of Schuster and Hechtfischer [Schuster and Hechtfischer 1992] who approximated the EPT-76 using three RIRTs (from KOL, NPL and PRMI; the vertical bars represent typical variations in approximating the EPT-96 via calibrations from these three laboratories) and superconductive reference points (standard reference material device SRM 767 from NIST).

Using the results obtained, the helium-3 melting-pressure scale PTB-96 has been established at PTB, the relative thermodynamic standard uncertainty  $u_{r,T96}$  of which has been estimated to be approximated by the relation  $\ln(u_{r,T96}) = -7.6-0.43 \times \ln(T_{96}/\text{K})$  [Fellmuth *et al.* 2003]. It ranges from 0.06% at 0.65 K to 0.04% at 1 K. Apart from a small pressure adjustment, the PTB-96

melting-pressure-versus-temperature relation is used for establishing the PLTS-2000 from the minimum of the helium-3 melting pressure at about 0.3 K to 1 K [Rusby *et al.* 2002]. Its thermodynamic standard uncertainty has been estimated to be 0.5 mK down to 500 mK, which corresponds to a decrease of  $u_{r,T2000}$  from 0.08% at 0.65 K to 0.05% at 1 K. The uncertainty estimates for PLTS-2000 are slightly larger than those for PTB-96 because they also consider the small differences between the results obtained at PTB and NIST, respectively.

#### (II) Thermodynamic calculations below 2 K

For the vapour pressure of the light helium isotope helium-3, calculations applying the thermodynamic vapour-pressure equation (TVPE) were performed by Fellmuth and Schuster [Metrologia 1992] and Reesink and Durieux [Metrologia 1996], respectively. In both cases, the calculations were based on a careful evaluation of the pressure-volume-temperature (pVT) data available in literature for the liquid and vapour phases. Unfortunately, the uncertainty of this input data was too large for absolute calculations. But it was possible to check the internal consistency of the helium-3 VPS of the ITS-90. For this purpose, the TVPE was extended by appropriate correction functions, which contain additional parameters. These parameters must be determined by calibration using sufficiently accurate pressure-temperature data. For internal consistency checks, this means to use the helium-3 VPS of the ITS-90 at temperatures, at which this VPS has been verified to be thermodynamically sufficiently accurate, namely at and above 1.5 K. By this means, three different calculations with the TVPE have been compared in [Metrologia 1992] based on reasonable choices of the data for the second and third virial coefficients of the vapour, and for the heat capacity of the liquid. The results obtained with two onepoint calibrations (OPC, calibration temperatures 1.5 K and 2.0 K, respectively) are compared with those obtained with a two-point calibration (TPC, 1.5 K and 2.0 K), see Figure 3. Applying a slightly different method of calculation and choosing, within the uncertainty, above 0.9 K other liquid-entropy data, Reesink and Durieux [Metrologia 1996] got results, which are in excellent agreement with those of Fellmuth and Schuster [Metrologia 1992], see Figure 4.



**Figure 3** (on the left): Figure 4 in [Metrologia 1992]: Experimental values  $\Delta T = (T_{X1}-T_{CMN})$ , as shown in Figure 1 as curves, in comparison with  $\Delta T = (T_{76}-T_{VPS})$  versus temperature for the thermodynamic VPS obtained with the TVPE with calibration at two points (TPC (1.5 K, 2.0 K)) and the accompanying VPS with one-point calibration at 1.5 K (OPC (1.5 K)) and 2.0 K (OPC (2.0 K)), respectively, based on reasonable choices of the data for the second and third virial coefficients of the vapour, and for the heat capacity of the liquid of helium-3. **Figure 4** (on the right): Figure 12 in [Metrologia 1996]: Differences  $T_{76}(^{3}\text{He}) - T_{calc}$  for a TVPE

calculation with carefully selected *pVT* data.

## (III) Comparison of ITS-90 and PLTS-2000 below 1 K

The deviation of the helium-3 VPS of the ITS-90 from thermodynamic temperature below 1 K has been directly verified by comparison with the PLTS-2000 in two laboratories: PTB [Engert *et al.* 2007] and LNE-CNAM [Pan *et al.* 2021]. At PTB [Engert *et al.* 2007], the comparison was performed using RIRTs as transfer standards. First, in the range from 0.65 K to 1 K, the RIRTs were calibrated against the PLTS-2000 in a commercial dilution refrigerator using a home-made melting-pressure sensor [Schuster and Wolber 1986, Schuster and Hoffmann 1997, Schuster *et al.* PTB-ThEx-21 2001]. The standard calibration uncertainty ranged from 62  $\mu$ K at 0.65 K to 86  $\mu$ K at 1 K. Then, comparison measurements with the helium-3 vapour pressure were performed in another special dilution refrigerator having pressure-sensing tubes with extremely large inner diameters to ensure that the uncertainty component caused by the thermonolecular pressure difference, being the dominant uncertainty component at the low-temperature end of the VPS, was negligible. The vapour pressure was measured applying capacitive diaphragm gauges, calibrated traceably to the national standard. The resulting standard uncertainty of the transfer of the RIRT calibration to the helium-3 vapour pressure increased from 174  $\mu$ K at 0.65 K to 234  $\mu$ K at 1 K. To cover the temperature range from 0.65 K to 3.2 K,

calculations with the TVPE yielded a second data set for the range from 1 K to 2 K, in which reliable thermodynamic data was not available, and above 2 K, the ITS-90 was accepted to be sufficiently correct, i.e. the third data set was deduced directly from the ITS-90. Combining all three data sets, a new helium-3 vapour-pressure scale, called PTB-2006, was established. It has been estimated that the standard uncertainty of the PTB-2006 with respect to thermodynamic temperature has its maximum at 1 K (0.56 mK), with lower values at the ends of the scale 0.65 K (0.43 mK) and 3.2 K (0.5 mK). The deviation of the ITS-90 helium-3 VPS from the three sets of input data for the PTB-2006 is shown in Figure 5.

Pan *et al.* [Metrologia 2021] have directly compared the helium-3 vapour and melting pressure scales. For this purpose, the vapour-pressure cell and the melting-pressure sensing element were installed on the same copper platform within the vacuum chamber of a commercial dilution refrigerator. Similar to the equipment used in [Engert *et al.* 2007], specially designed pressure-sensing tubes reduced the uncertainty components for the vapour-pressure measurement. The melting-pressure sensing element was made and tested at PTB [Schuster and Hoffmann 1997, Schuster *et al.* PTB-ThEx-21 2001]. The standard uncertainty estimates for the weighted-mean results for the difference  $T_{90} - T_{2000}$  obtained in two low-temperature runs as shown in Figure 6 are between 94  $\mu$ K and 0.17 mK with a maximum around 0.9 K.



**Figure 5** (on the left): Figure 3 in [Metrologia 2007]: Differences between the helium-3 vapourpressure equation of the ITS-90 and the input data set  $T_{\text{VPnew}}$  for the new helium-3 vapourpressure scale PTB-2006 as a function of temperature. The three subgroup data sets for the new scale are market by different symbols (VP stands for vapour pressure). For details see [Metrologia 2007].

**Figure 6** (on the right): Figure 13 in [Metrologia 2021]: Values of  $T_{90} - T_{2000}$  from 0.65 K to 1 K from [Metrologia 2021] (two low-temperature runs in 2019 and 2020, respectively) in

comparison with the results obtained in [Metrologia 2007]. The dashed lines correspond to the combined standard uncertainty of PTB-2006

All results shown in Figures 1 to 6 coincide within their combined standard uncertainty estimates. This clearly supports the thermodynamic basis of the new helium-3 VPS PTB-2006, which agrees with the PLTS-2000. If measurements are to be made both below and above 1 K, the two scales PLTS-2000 and PTB-2006 should be applied together. The use of PTB-2006 between 0.65 K and 2 K has been recommended by a working group of the Consultative Committee for Thermometry [Fischer *et al.* 2011].

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