

Dependence of the triple-point temperature of diluted mixtures of deuterium (as HD)¹ in protium on the deuterium content

B. Fellmuth, L. Wolber (PTB); Y. Hermier (BNM-INM/CNAM); F. Pavese, P.P.M. Steur, I. Peroni (IMGC); A. Szmyrka-Grzebyk, L. Lipinski (INTiBS-PAN); W.L. Tew (NIST); T. Nakano, H. Sakurai, O. Tamura (NMIJ/AIST); D. Head (NPL); K.D. Hill, A.G. Steele (NRC)

In view of the state-of-the-art level of accuracy of low-temperature measurements, it is necessary to realise the triple point of equilibrium hydrogen as a defining fixed-point of the ITS-90 with an uncertainty approaching 100 μK . This level of uncertainty is presently unachievable due primarily to an ambiguity of definition. The text of the ITS-90 specifies only that hydrogen of “natural isotopic composition” be used to realise the fixed point. As first pointed out by Pavese et al. [1, 2], variations of the deuterium content (relative to hydrogen) occur in both the natural terrestrial environment and in the synthesis of commercial gas to such an extent that the desired uncertainty is exceeded by an order of magnitude. Ways to remove the ambiguity regarding the definition of the hydrogen triple point are discussed in Pavese et al. [2, 3] and in the accompanying working document “Proposal of a provisional integration of the ITS-90 definition concerning the temperature of the triple point of equilibrium hydrogen” by Pavese et al. One simple way could be to specify an ideal composition to which all variable-composition hydrogen fixed-point samples may be corrected based on their measured deuterium content and a specified value for the slope of the dependence of the triple-point temperature on the HD content. Until recently, only a single paper [4] has reported this dependence, though over the full composition range and with no specific regard to the initial slope (dilute mixtures). To determine the dependence for diluted mixtures as accurately as necessary, an international collaboration took place that included all metrological institutes realising the hydrogen triple point as a temperature fixed point. Preliminary results have already been published [5-11]. A comprehensive description of the final results is being prepared. This document gives a short overview.

To investigate the thermodynamic properties of the mixtures and to discern the different effects influencing the melting temperature, 27 sealed fixed-point cells have been filled and measured, and some have been compared with an open-cell system. Mixtures in the deuterium content range from 27 $\mu\text{mol D/mol H}$ to 155 $\mu\text{mol D/mol H}$ were studied, using cells containing different types of spin-conversion catalyst (5 different types of catalyst), different catalyst-to-liquid volume ratios (a few per cent to more than 100 per cent), and different designs. The range of deuterium content covers nearly its variation in both the natural terrestrial environment and in commercial gas. It corresponds to a range of the triple-point temperature slightly larger than 0.7 mK. The inclusion of different cell designs is especially influential in determining the cell thermal behaviour and, thus, the temperature-measurement errors. The cells have been measured at eight institutes in accordance with a detailed protocol, which facilitates a direct comparison of the results. By this comparison, significant inter-institute deviations due to different measurement facilities and methods have been ruled out both concerning the melting temperatures and the thermal parameters of the cells. The uncertainty estimates for the determination of the deuterium content have been checked by including analysis results of 4 different sources. From the melting temperatures of those sample portions not in direct contact with the catalysts, an improved preliminary value of 5.3 $\mu\text{K per } \mu\text{mol D/mol H}$ has been obtained for the initial slope of the dependence of the

¹ For diluted mixtures, the probability for deuterium to form D_2 is so small that only HD is present: the mixtures are actually H_2 -HD.

triple-point temperature of hydrogen isotopic mixtures on the deuterium content. The standard uncertainty of this value is $0.4 \mu\text{K}$ per $\mu\text{mol D/mol H}$. It is close to the literature value of $5.6 \mu\text{K}$ per $\mu\text{mol D/mol H}$ for larger concentration solutions [4].

Figure 1 shows the dependence of the equilibrium melting temperature T_e of those sample portions, which are not in direct contact with the spin-conversion catalysts, on the deuterium content. The T_e values are drawn relative to that of the reference cell $\text{H}_2\text{-1}$, T_{Ref} . Cell $\text{H}_2\text{-1}$ was measured frequently during the whole investigation period, and most of the other cells have been directly compared with it at PTB. The results of the other measuring institutes are considered by adding their measured differences between melting temperatures of several cells to the melting-temperature value obtained at PTB for one of these cells. In the legend, the cell manufacturer and, after the slash, the measuring institute are given. The straight line in Figure 1 results from a linear fit to the data taking into account errors in both variables in a simple way. The final slope will be determined soon, after the final evaluation of the data, by applying a total least squares method.

Considering the relevant range of the triple-point temperature of about 0.7 mK , the achieved uncertainty of the slope would allow the correction of all variable-composition hydrogen fixed-point samples to a specified isotopic composition with an uncertainty well below $100 \mu\text{K}$. The obtained results represent, therefore, a reliable experimental basis for re-defining the triple point of equilibrium hydrogen as a defining fixed point of the ITS-90 in a manner that decreases the uncertainty of the fixed-point realisation by nearly one order of magnitude. A proposal for a re-definition (or other recommendations for solving the problem) must be urgently prepared by Working Group 1 for consideration by the CCT, taking into account the discussions in [2, 3] and in the accompanying working document “Proposal of a provisional integration of the ITS-90 definition concerning the temperature of the triple point of equilibrium hydrogen” by Pavese et al.

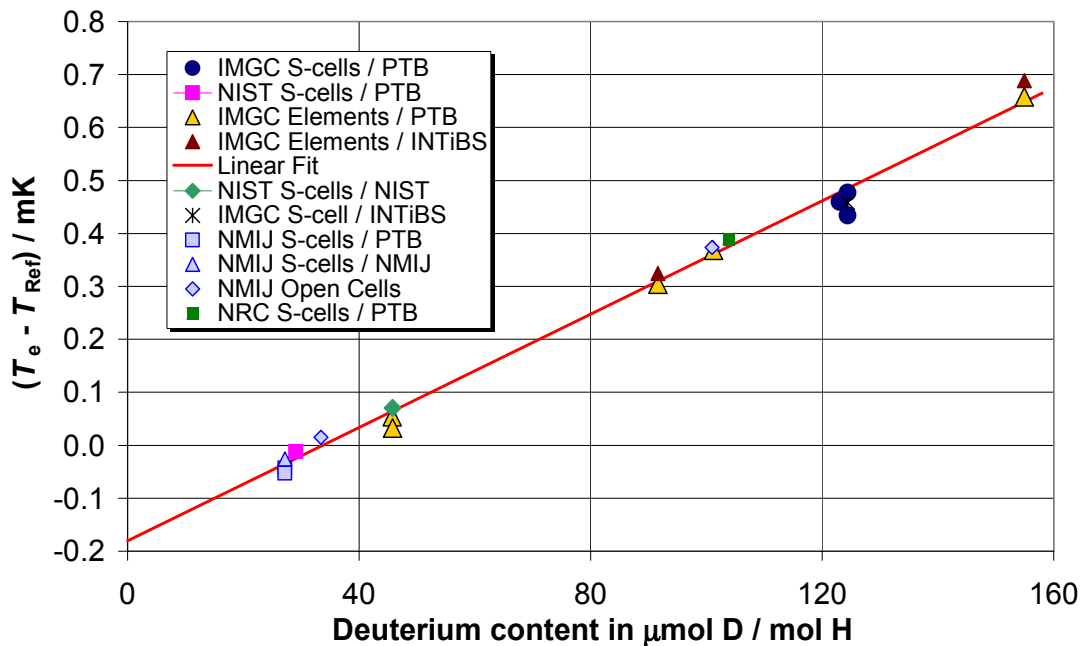


Figure 1: Dependence of the equilibrium temperature T_e on the deuterium content. The temperature values for different cells are drawn relative to the equilibrium temperature T_{Ref} of the reference cell $\text{H}_2\text{-1}$.

References

1. F. Pavese and W.L. Tew, On the isotopic composition of commercial hydrogen vs “natural composition” and the problems for the ITS-90 definition, BIPM Com. Cons. Thermométrie 20, 2000, Document CCT/2000-19.
2. F. Pavese, W.L. Tew, and A.G. Steele, Archival and theoretical considerations for isotopic dependence in the e-H₂ fixed points, *Proceedings of TEMPMEKO 2001, 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, edited by B. Fellmuth, J. Seidel, G. Scholz, VDE Verlag GmbH, ISBN 3-8007-2676-9, Berlin, 2002, pp. 429-434.
3. F. Pavese, B. Fellmuth, D. Head, Y. Hermier, H. Sakurai, A.G. Steele, A. Szmyrka-Grzebyk, W.L. Tew, Proposal of amendment of the ITS-90 definition concerning the triple point of equilibrium hydrogen. BIPM Com. Cons. Thermométrie 21, 2001, Document CCT/01-07.
4. N.G. Bereznyak, I.V. Bogoyavlenskii, L.V. Karnatsevich, V.S. Logan, Melting diagram of the pH₂ – oD₂, pH₂ – HD, and oD₂ – HD systems, *Soviet Physics JETP*, 30 (6), pp. 1048-1049, 1970
5. B. Fellmuth, D. Berger, and L. Wolber, An international star intercomparison of low-temperature fixed points using sealed triple-point cells, *Proceedings of TEMPMEKO '99, 7th International Symposium on Temperature and Thermal Measurements in Industry and Science*, edited by J.F. Dubbeldam et al., IMEKO / NMi-VSL, Delft, 1999, pp. 233-238.
6. B. Fellmuth, D. Head, F. Pavese, A. Szmyrka-Grzebyk, and W.L. Tew, Special Problems When Realising the Triple Point of Hydrogen as a Defining Fixed Point of the ITS-90, *Proceedings of TEMPMEKO 2001, 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, edited by B. Fellmuth, J. Seidel, G. Scholz, VDE Verlag GmbH, ISBN 3-8007-2676-9, Berlin, 2002, pp. 403-410.
7. B. Fellmuth, D. Berger, L. Wolber, M. de Groot, D. Head, Y. Hermier, Y.Z. Mao, T. Nakano, F. Pavese, V. Shkraba, A.G. Steele, P.P.M. Steur, A. Szmyrka-Grzebyk, W.L. Tew, L. Wang, and D.R. White, An International Star Intercomparison Of Low-Temperature Fixed Points Using Sealed Triple-Point Cells, *Temperature: Its Measurement and Control in Science and Industry*, Vol. 7, edited by D.C. Ripple et al., AIP Conference Proceedings, Melville, New York, 2003, to be published.
8. H. Sakurai, Precise realization of the triple points of equilibrium hydrogen and argon using a closed cycle refrigerator, *Proceedings of TEMPMEKO '99, 7th International Symposium on Temperature and Thermal Measurements in Industry and Science*, edited by J.F. Dubbeldam et al., IMEKO / NMi-VSL, Delft, 1999, pp. 124-128.
9. H. Sakurai, Calorimetric study of the triple point of equilibrium hydrogen, *Proceedings of TEMPMEKO 2001, 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, edited by B. Fellmuth, J. Seidel, G. Scholz, VDE Verlag GmbH, ISBN 3-8007-2676-9, Berlin, 2002, pp. 411-416.
10. T. Nakano, O. Tamura, and H. Sakurai, New sealed cells for the realization of cryogenic fixed points at NMIJ/AIST, *Temperature: Its Measurement and Control in Science and Industry*, Vol. 7, edited by D.C. Ripple et al., AIP Conference Proceedings, Melville, New York, 2003, to be published.
11. A.G. Steele, Revisiting the triple point of spin-equilibrated hydrogen at the National Research Council of Canada, *Proceedings of TEMPMEKO 2001, 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, edited by B. Fellmuth, J. Seidel, G. Scholz, VDE Verlag GmbH, ISBN 3-8007-2676-9, Berlin, 2002, pp. 417-422.