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Proposal of amendement of the ITS-90 definition concerning the triple point of equilibrium hydrogen

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Introduction

The phase equilibria of spin-equilibrated molecular hydrogen (e-H_2) from 13.8 K to approximately 20.3 K have been used to define the International Temperature Scale (ITS) since the advent of the IPTS-68. The text of the ITS-90 specifies only that the “natural isotopic composition” is to be used.[1] The supplementary information [2] goes further to state that the “normal isotopic composition of hydrogen” is 150 μmol of D per mole of ^{1}H.

However, it has been recently recognised [3] that hydrogen isotope fractionation occurs by a variety of mechanisms both in the natural terrestrial environment and in the synthesis of commercial gas leading to wide variations in the isotopic content. This fact is long since known in the scientific community of geochemists. The isotope ratio, $R_D \equiv [D]/[^1H]$, of molecular hydrogen found in the terrestrial environment varies between approximately 25 μmol/mol and 184 μmol/mol.[4] The variations in commercial H_2 tank gas, which similarly depend on the method of synthesis, are slightly less than this range[5]. Archival and theoretical considerations for isotopic dependence in the e-H_2 fixed points are fully given in Ref.6. Until recently, only a single paper [7] reported so far in the literature the dependence of T_{tp} on R_D, but on the full composition range, with no specific regards to the initial slope (dilute solutions): the best guess gives a dependence of about +5.6 μK/(μmol D/mol H), leading to a possible error in the T_{tp} determination due to this single source of more than 0.5 mK. On the contrary, the state of the art is today aiming at an uncertainty budget of ± 0.1 mK in total, requiring the purity/isotopic component uncertainty being kept within about ± 30 μK.

The problem affects also the two ITS-90 fixed points based on e-H_2 vapour pressure near 17 K and 20 K but will not be further addressed in this document, as, at present, the problem has prompted new studies on the effect on the triple point temperature only. [8-10] The preliminary results are qualitatively coherent with the literature data and confirm the strong dependence of T_{tp} on R_D. These studies are additionally complicated by the observed interaction of the catalyst, used for spin equilibration, and the condensed substance. These studies required, contrarily to the past, the use of gases of certified R_D values: these values were found in the whole expected range of R_D variability in commercial samples, confirming the actual occurrence of errors of more than 0.5 mK in different realisations of this defining fixed point.

The ambiguity in the ITS-90 present definition for T_{tp}(e-H_2)

Each ITS-90 fixed point is defined: a) for a specific physical state of a substance; b) for an ideally pure substance; c) for the “natural isotopic composition”. This allows independent realisation of the scale.

However, with the decrease of the state-of-the-art uncertainty in fixed point realisations, while the purity of the best commercial gases today generally fits the purpose, the expression “natural isotopic composition” is becoming ambiguous, at least for hydrogen (but possibly also for other substances, e.g., neon and water).

There are no other more accurate formal definitions to refer to, issued by an international authority recognised for this purpose. The IUPAC Committee on Atomic Weights and Abundances is reviewing the matter on a regular basis [4] but issues only recommendations (similar to the CCT WG2 list of temperature values for the secondary fixed points). The CCQM has recently been informed of the problem but has not yet decided if and how to handle it.

For hydrogen, the IAEA in Wien has, for the purpose of geochemistry, long since defined two isotopic reference materials: Standard Mean Ocean Water (SMOW)[11] or its practical equivalent, Vienna SMOW (VSMOW)[12], and Standard Light Antarctic Precipitation (SLAP). The absolute isotopic ratios of these standard reference waters have been determined to be R_D = 156 µmol/mol and 89 µmol/mol respectively. These are standard reference materials supplied as water, but valid also for hydrogen in the gaseous form when a standard practice to obtain the gas from the water is used.

Part of the problem concerning the ITS-90 definition – The indication that the pure substance must have the "natural isotopic composition" should be replaced, for hydrogen, with a new, sufficiently accurate, definition not relaxing the principle that the physical substance is referred to.

For non-isotopic purity, the certification of the producer, that the substance has a maximum impurity content, allows for an estimate of the uncertainty arising at least from the estimate of the worst-case departure from the ideal substance.

For the isotopic impurity, the definition of (ideal) substance is itself affected, not generally being an isotopically pure one, but that of the "naturally occuring" isotopic mixture. As it already happened in the field of geochemistry, an empirical reference isotopic composition is now needed also in thermometry for hydrogen.

There are mainly two possible categories about the ways in which the $T_{tp}(e\text{-H}_2)$ could be re-defined in the ITS-90 in order to remove the ambiguity:

A) definitions specifying a fixed isotopic composition to be used for all the realizations and requiring the use of certified gas of that composition;

B) definitions specifying an ideal composition to which all variable composition gas samples would be corrected by their measured mass values on the basis of a defined T vs HD content function.

The fixed or ideal isotopic composition could be: isotopically pure light hydrogen ($^1H_2$), VSMOW composition hydrogen; SLAP composition hydrogen; or any other nominal composition, better if defined by a recognized international authority (including CCT itself). Of these choices, both pure light and VSMOW hydrogen have the disadvantage that such compositions are beyond the range readily available and would require special preparations to produce samples. In general, the uncertainty attributed to the applied correction will increase for gases in proportion to their difference in composition from any isotopically defined gas. In this context, a value close to SLAP definition for the e-H_2 fixed-points under option B seems be a reasonable choice as it is roughly midway in the range of typical H_2 tank gas isotopic compositions, thereby minimising the error propagation as well (see Fig.1: note that the uncertainty of the preliminary data presently available is about 8 %).

In the proposed ITS-90 amendment text the type B) definition is proposed, as it seems more simple to implement. The proposed text concerns H_2 in general, thus implying the definition of all fixed points using H_2. This does not seem to be a problem: when also data concerning the isotopic effect on vapour pressure will be available they will simply be applied for getting the best accuracy.

Part of the problem concerning the Supplementary Information – It seems more appropriate not to include in the new ITS-90 definition a stipulated value for the correction, but to leave it –as has been done, e.g., for the hydrostatic-head correction, though not being exactly the same case– to the Supplementary Information: its value could slighly change with improving measurement techniques.

In addition, it is suggested to WG1 that the Supplementary Information indicate that the correction is relevant only to realisations aiming at a total uncertainty better than about ± 1 mK.

Finally, the Supplementary Information should also give some advises about certification, since its uncertainty enters into the error budget as well. In fact, both alternatives A) and B) will require measurement and or certification of the deuterium content of the sample gas.

Proposal for an amendment of the ITS-90

The formal text is reported in Appendix A to this Document.

It is proposed for the CCT approval in its 2001 Meeting and, if approved, for subsequent transmission to the CIPM that has to take the formal decision, together with a summary of the present document justifying its need.

It is also suggested that, in the transmission letter to the CIPM, the CCT stresses the fact that in one field of Metrology, temperature, the current expression "natural isotopic composition" is not accurate anymore to allow state-of-the-art realisations of some standards and, consequently, that a CIPM decision is called for about who should address the problem to submit a more precise definition.

Stressing also the need for a closer collaboration with Chemical Metrology about gas certification and its traceability could be useful.

Proposal for a CCT Recommendation

As said before, much work has already been done to obtain the correction function, but still more work remains to be done, expected to be finalised in 1-2 year time, probably more when effects on the vapour pressure and included, and certainly more when the effect on other substances is considered. As usual, the impetus depends also on the financial resources and they, in turn, depend on the importance attached to the activity. It is therefore important that CCT stresses, in a Recommendation, the importance and urgency of continuing the activities in this field. A proposed text is reported in Appendix B.

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APPENDIX A

Proposed amendment 2001 to the text of the ITS-90

Specification of the substance required for the realisation of the fixed points of *e*-H_2

Table 1, note a, is changed to the following:

"All substances except ^{3}He are of natural isotopic composition. The temperature values in the Table for H_2 are given for the equilibrium concentration of the ortho- and para-molecular forms and for the isotopic ratio D/H = 10^{-4} exactly."

APPENDIX B

Recommendation N. …

The Comité Consultatif de Thermométrie recommends that urgent research work is continued for the determination, at an uncertainty level of 30 μK, of the relationship between the temperature value of ITS-90 fixed points based on hydrogen and the isotopic composition of gaseous hydrogen naturally occurring or produced with a variety of methods, and of the effect on the same temperature values of the catalysts used to ensure spin equilibrium.

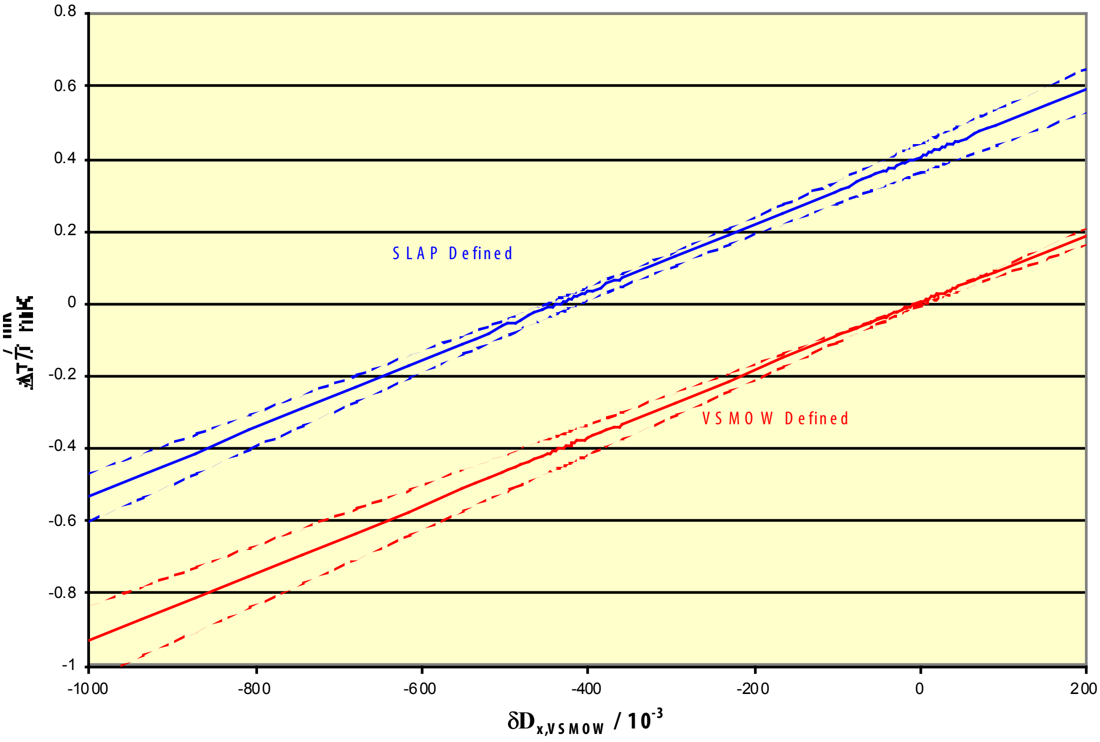

Figure 1. The theoretical corrections (solid lines) and standard uncertainties (dashed lines) for a SLAP defined and a VSMOW defined *e*-H_2 triple point as a function of δD value of the sample with respect to VSMOW. The correction factor itself is assumed to be established to within a standard uncertainty of 5 %. [6]