

Section 2. Technical annex for the International Temperature Scale of 1990 (ITS-90)

Adopted by the CCT on 10 June 2005

This Technical Annex includes specifications beyond the definitions in the text of the International Temperature Scale of 1990 (ITS-90) that are deemed essential for the unambiguous realization of the ITS-90. Specifications within the Technical Annex are considered mandatory extensions of the text of the ITS-90.

For material taken directly from the text of the ITS-90, the *mise en pratique* refers to “defined” or “assigned” values or procedures. Where additional material other than the ITS-90 text has been deemed essential for inclusion in the Technical Annex, the *mise en pratique* of the definition of the kelvin refers to “specified” values or procedures.

A. Isotopic composition and corrections for the triple point of water

The effects of isotopic composition on the triple point of water are discussed in detail in [1].

The international science community, through the International Atomic Energy Agency, uses a defined Standard Mean Ocean Water (SMOW) as a point of reference for studies in the isotopic composition of waters. In practice, measurements of isotopic composition are made with respect to V-SMOW (Vienna-SMOW) and SLAP (Standard Light Antarctic Precipitation) [2, 3], two widely distributed standard reference water samples that span the isotopic range of naturally occurring samples. The IUPAC in “Atomic Weights of the Elements: Review 2000” recommended the following isotopic amount-of-substance ratios for V-SMOW, based on the best measurements available [4]:

$$\begin{aligned}({}^2\text{H}/{}^1\text{H})_{\text{V-SMOW}} &= 0.000\,155\,76\,(5), \\({}^{18}\text{O}/{}^{16}\text{O})_{\text{V-SMOW}} &= 0.002\,005\,2\,(5), \\({}^{17}\text{O}/{}^{16}\text{O})_{\text{V-SMOW}} &= 0.000\,379\,9\,(9).\end{aligned}$$

For the purposes of thermometry, it is convenient to specify these absolute values for the isotopic composition of the water in an ideal triple-point-of-water cell. Thus, the triple point of water is defined as the equilibrium temperature of vapour, liquid and solid water with the liquid water having the isotopic composition defined by the following amount-of-substance ratios: 0.000 155 76 mole ${}^2\text{H}$ per mole ${}^1\text{H}$, 0.000 379 9 mole ${}^{17}\text{O}$ per mole ${}^{16}\text{O}$ and 0.002 005 2 mole ${}^{18}\text{O}$ per mole ${}^{16}\text{O}$. The triple point of water is assigned the temperature $T_{90}(\text{TPW}) = 273.16\text{ K}$ on the ITS-90. Isotopic deviations of V-SMOW from SMOW are negligible when expressed as an equivalent change in the water triple-point temperature.

Variations in isotopic amount-of-substance ratios are conventionally reported as deviations from V-SMOW; for example:

$$\delta^{18}\text{O} = \left[\frac{({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}} - ({}^{18}\text{O}/{}^{16}\text{O})_{\text{V-SMOW}}}{({}^{18}\text{O}/{}^{16}\text{O})_{\text{V-SMOW}}} \right],$$

and similarly for δD (where symbol D designates ${}^2\text{H}$, and symbol H will subsequently designate ${}^1\text{H}$) and $\delta^{17}\text{O}$. Usually the results are in the parts-per-thousand range, so are expressed in permil (per thousand, ‰).

The isotopic composition of all naturally occurring surface water is sufficiently close to that of V-SMOW that the effect of the isotopes on the triple-point temperature can be specified by a linear function of the delta values:

$$T_{\text{meas}} = T_{90}(\text{TPW}) + A(\text{D})\delta\text{D} + A(^{17}\text{O})\delta^{17}\text{O} + A(^{18}\text{O})\delta^{18}\text{O}.$$

The most precise set of isotopic depression constants presently available, and those specified for use with the ITS-90, are by Kiyosawa [5] who measured the melting-point elevation of samples of water enriched with D and ^{18}O . The depression constants were found from Kiyosawa's data to be: $A(\text{D}) = 628 \mu\text{K}$ and $A(^{18}\text{O}) = 641 \mu\text{K}$. The value of $A(^{17}\text{O})$ is inferred as $57 \mu\text{K}$.

B. Isotopic composition and corrections for the triple point of equilibrium hydrogen

The effects of isotopic composition on the triple point of equilibrium hydrogen and uncertainties related to these effects are discussed in detail in [6].

The isotopic composition of commercially available hydrogen varies from an amount-of-substance ratio of about 27 micromoles D per mole H to about 150 micromoles D per mole H. It has been established [7, 8] that the discrepancies previously found at the triple point are mainly due to the variable deuterium content in the hydrogen used for its realization.

It is therefore specified that the ITS-90 temperature assigned to the triple point of equilibrium hydrogen, $T_{90}(\text{e-H}_2 \text{ TP}) = 13.803 \text{ 3 K}$, is taken to refer to an isotopic amount-of-substance ratio of 0.000 089 02 mole D per mole H. This is the isotopic ratio determined for SLAP [2].

To correct to the isotopic reference ratio, the following function is specified:

$$T_{\text{meas}} = T_{90}(\text{e-H}_2 \text{ TP}) + k_{\text{D}}(x - x_0),$$

where x denotes the isotopic amount-of-substance ratio of the sample in micromoles D per mole H, $x_0 = 89.02 \mu\text{mol/mol}$ the reference ratio specified above, and k_{D} the slope of the triple-point temperature dependence on deuterium ratio. The current best value for k_{D} , and the value specified for the ITS-90, is given by Fellmuth *et al.* [9] as $5.42 \mu\text{K}/(\mu\text{mol/mol})$.

C. Isotopic composition for the vapor-pressure points of equilibrium hydrogen

The effects of isotopic composition on the vapor-pressure points of equilibrium hydrogen and the uncertainties related to these effects are discussed in detail in [6].

Isotopic fractionation manifests itself as a difference of as much as 0.4 mK between the dewpoint (vanishingly small liquid fraction) and the bubble point (vanishingly small vapor fraction) [8].

To reduce the effect of isotopic fractionation while maintaining coherence over the whole of the vapor pressure range (i.e., including the triple point), it is therefore specified that the ITS-90 relations for the vapor pressure of equilibrium hydrogen are referenced to an isotopic amount-of-substance ratio of 0.000 089 02 mole D per mole H, the isotopic ratio determined for SLAP.

D. References

- [1] Ripple D.C., Gam K.S., Hermier Y., Hill K.D., Rusby R.L., Steele A.G., Steur P.P.M., Stock M., Strouse G.F., White D.R., Summary of Facts Relating to Isotopic Effects and the Triple Point of Water: Report of the *ad hoc* Task Group on the Triple Point of Water, Comité Consultatif de Thermométrie, Working Document CCT/05-07 (2005).
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