

Improved Estimates of the Isotopic Correction Constants for the Triple Point of Water

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Abstract: In 2006, the CIPM clarified the definition of the kelvin by specifying the isotopic composition of the water to be used in the realisation of the triple point. At the same time, the Consultative Committee on Thermometry gave recommended values for the isotopic correction constants to be used for water departing from the specified composition. However, the uncertainties in the values for the correction constants were undesirably large due to unresolved differences between the data sets from which the values were determined. This paper derives improved values of the constants by considering additional data derived from isotopic fractionation measurements and the heats of fusion and freezing points of the relevant water isotopologues. Values of the corrections determined from the expanded data are $A_D = 671(10) \mu\text{K}$, $A_{18\text{O}} = 603(3) \mu\text{K}$, and $A_{17\text{O}} = 60(1) \mu\text{K}$. A typical correction made with these values lies just within the expanded uncertainty ($k = 2$) of the corrections made with the older values, but has about half the uncertainty.

Keywords: triple point, water, isotope, correction, temperature

1 Introduction

In 2006, the Comité International des Poids et Mesures (CIPM) clarified the definition of the kelvin by specifying the isotopic composition of the water used in the realisation of the triple point to be that of V-SMOW [1]. V-SMOW is a standard reference material representing standard mean ocean water and is distributed by the International Atomic Energy Agency for the calibration of mass spectrometers used in hydrogen- and oxygen-isotope analysis. The clarification in the definition of the kelvin followed research demonstrating the magnitude of isotopic effects on the water-triple-point temperature [2], and an international comparison of triple-point-of-water cells in which the larger than expected dispersion of results could be attributed, in part, to unaccounted variations in the isotopic composition of the water [3]. The CIPM's Consultative Committee on Thermometry (CCT) accompanied the CIPM's definitional clarification, with a set of recommended values for the isotopic correction constants to be used for water departing from the specified composition [4]. The values of the correction constants were based largely on the cryoscopic measurements of Kiyosawa [5], with supporting evidence from White *et al* [2] and the historical measurements of LaMer and Baker [6]. Unfortunately, the estimation of the uncertainties in the correction constants was difficult. Firstly, there were no estimates of the uncertainties in Kiyosawa's cryoscopic measurements, nor were there measured values for the isotopic composition of the D₂O and H₂¹⁸O waters used in the experiments, other than the supplier's specification. This situation was further complicated by more recent work of Kiyosawa [7] suggesting the possibility that Kiyosawa's water samples were contaminated by other isotopologues [8]. Secondly, the waters used by White *et al* [2] did not span a sufficient range of both D and ¹⁸O isotopic compositions to enable correction constants to be determined with a low uncertainty. Finally, the much earlier measurements of LaMer and

Baker were of a time when estimates of uncertainties were not routinely reported. The CCT task group investigating the isotopic influences on the triple point concluded that Kiyosawa's measurements were the most precise and assigned the values derived from Kiyosawa's data to the correction constants. The recommended correction equation is

$$\Delta T_{\text{iso}} = -A_{\text{D}}\delta\text{D} - A_{18\text{O}}\delta^{18}\text{O} - A_{17\text{O}}\delta^{17}\text{O}, \quad (1)$$

where δD , $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ are the measured isotopic departures from V-SMOW expressed as delta values, and $A_{\text{D}} = 628 \pm 20 \mu\text{K}$, $A^{18}\text{O} = 641 \pm 50 \mu\text{K}$ and $A^{17}\text{O} = 57 \pm 5 \mu\text{K}$ [4]. The assigned standard uncertainties are Type B assessments based on the degree of consistency amongst the various reported values, tempered with knowledge that some systematic effects had not been investigated.

The clarification of the definition and the application of corrections to water-triple-point measurements have contributed to significant improvements in the reproducibility of water-triple-point cells. The CCT-K7 comparison, which commenced before the clarification, included cells that realised temperatures spanning about 250 μK , with most of the variation caused by impurities, and between 70 μK and 110 μK of the variation probably due to isotopic effects. More recent, informal, comparisons of cells from different manufacturers indicate that the reproducibility amongst new cells corrected for isotopic composition is about 30 μK , with the uncertainty in the isotopic corrections probably contributing less than 5 μK [e.g., 9]. Although the clarification and corrections have reduced the uncertainty to practically negligible levels, there remains a need for improved confidence, preferably accompanied by reduced uncertainty, in the values assigned to the correction constants.

This paper infers values of the isotopic correction constants using additional information from the values of the solid-liquid isotopic fractionation factors as measured by Lehmann and Siegenthaler [10], with supporting data from the known thermophysical properties of the water isotopologues. Section 2 below explains and applies the relationship between the freezing-point elevation and isotopic fractionation as given by Van't Hoff's relation. Section 3 then discusses the results and compares the inferred values with the historical data.

2. Van't Hoff's relation and the inferred values for the isotopic corrections

The isotopic influence on the triple-point temperature arises from equilibrium quantum-mechanical effects [11]. Because the electronic structure of atoms is the same for all isotopes of a particular element, the heavier mass atoms tend to form bonds with lower vibrational frequencies, and hence occupy slightly lower energy states. This leads to a variety of thermophysical effects that include a raised freezing-point temperature with heavy isotopes and a weak solid-liquid fractionation effect favouring the heavy isotopes in the solid phase. By treating the dilute isotope as a dilute impurity, these two effects can be related by Van't Hoff's relation [12]:

$$\Delta T = \frac{RT_f^2}{\Delta H_f} X_i (\alpha_{\text{S-L}} - 1) \quad (2)$$

where ΔT is the rise in freezing-point temperature due to the mole fraction X_i of the dilute heavy isotope (or isotopologue), $\alpha_{\text{S-L}}$ is the solid-liquid fractionation factor for the isotope, T_f is the freezing-point temperature, R is the gas constant, and ΔH_f is the enthalpy of fusion. For the triple point of water, the cryoscopic constant $RT_f^2 / \Delta H_f$ is 103.28 K.

The definition of the kelvin requires the water to have the isotopic composition of V-SMOW with $R_D = 0.000\,155\,76$ mol ^2H per mol ^1H , $R_{17\text{O}} = 0.000\,379\,9$ mol ^{17}O per mol ^{16}O , and $R_{18\text{O}} = 0.0020052$ mol ^{18}O per mol ^{16}O . This corresponds to mole fractions, $X_D = 0.00015574$, $X_{17\text{O}} = 0.00037900$, and $X_{18\text{O}} = 0.00200043$.

The isotopic correction constant for ^{18}O is, from (1)

$$A_{18\text{O}} = \frac{RT_f^2}{\Delta H_f} X_{18\text{O},\text{VSMOW}} \left[\alpha_{\text{S-L}}(^{18}\text{O}/^{16}\text{O}) - 1 \right]. \quad (3)$$

The isotopic correction constant for the deuterium requires an additional factor of 2 to account for the fact that almost all of the deuterium is distributed in the water as HDO rather than D_2O , that is $X_{\text{HDO}} = 2 \times X_D$, and hence

$$A_D = \frac{RT_f^2}{\Delta H_f} 2X_{\text{D},\text{VSMOW}} \left[\alpha_{\text{S-L}}(\text{D}/\text{H}) - 1 \right]. \quad (4)$$

The isotopic correction constant for ^{17}O is inferred from the value of the ^{18}O constant by assuming that the fractionation factor scales according to the masses of the isotopes [11], i.e., proportional to $(M_2 - M_1)/M_1 M_2$, where M_1 and M_2 are the molecular masses of the isotopologues:

$$A_{17\text{O}} = \frac{RT_f^2}{\Delta H_f} X_{17\text{O},\text{VSMOW}} \left[\alpha_{\text{S-L}}^{0.526} (^{18}\text{O}/^{16}\text{O}) - 1 \right]. \quad (5)$$

Because ^{17}O occurs in very low concentrations, and ^{17}O fractionation is very weak, the value and uncertainty for $A_{17\text{O}}$ have little effect on the isotopic correction for typical triple-point-of-water cells.

The most recent values of the solid-liquid fractionation factors are those reported by Lehmann and Siegenthaler [10]: $\alpha_{\text{S-L}}(^{18}\text{O}/^{16}\text{O}) = 1.00291(3)$, and $\alpha_{\text{S-L}}(\text{D}/\text{H}) = 1.0212(4)$. The measurements were made by slow freezing of water at 0°C , measuring the fractionation as a function of the velocity of the freezing interface, and then extrapolating to zero interface velocity. The reported uncertainties are the Type A uncertainties in the parameter values determined from the least-squares fit. There are additional uncertainties associated with the isotope measurements, but only Type A uncertainties characterising the precision of the measurements are given: 0.03‰ for $^{18}\text{O}/^{16}\text{O}$, and 0.5‰ for D/H . Although no indication of the total uncertainty is given, such measurements are usually made by interpolating the isotopic measurements between those for standard reference materials SLAP (Standard light Antarctic precipitation) and V-SMOW, so that the absolute accuracy is comparable to the precision. The precision given is also very similar to the uncertainties offered by other stable-isotope laboratories. When the reported Type A uncertainties are used to calculate the correction constants using (2) to (4), the values $A_D = 682(13)\text{ }\mu\text{K}$, $A_{18\text{O}} = 601(7)\text{ }\mu\text{K}$, and $A_{17\text{O}} = 60(1)\text{ }\mu\text{K}$ are obtained.

3. Comparison with historical measurements

This section compares the values inferred from the fractionation factors with a variety of other historical measurements.

Kiyosawa measured the freezing point of water as a function of the fraction of the heavy isotopologues $D_2^{16}O$ and $H_2^{18}O$ [5]. The correction constants determined from his data are $A_D = 628.1(2.7) \mu K$, and $A_{18O} = 641.1(0.8) \mu K$, where the uncertainties are the Type A values determined from a least-squares fit of the temperature to the fraction of heavy isotope. As already noted, Kiyosawa reported only the manufacturer's specification for the composition of the water used in the measurements. Later measurements on $H_2^{17}O$ by Kiyosawa [7], following a similar procedure, seemed to show the effects of contamination by other heavy isotopologues [8]. If similar contamination occurred in the earlier measurements with $D_2^{16}O$ and $H_2^{18}O$, or the compositions were not exactly as specified by the manufacturer, then there may be significant systematic errors.

White et al

White *et al* measured the triple-point temperature realised by a total of five triple-point cells containing water of different isotopic compositions [2]. However the spread of compositions was limited with four cells close to the natural composition and only one significantly different being almost depleted of deuterium and about 35% depleted of ^{18}O . The measurements therefore placed a tight constraint on a combination of A_D and A_{18O} values but not on the individual values. The fit to the data yielded $A_D = 725(42) \mu K$ and $A_{18O} = 507(68) \mu K$. If the A_{18O} was assigned a value of $602 \mu K$ (inferred from linear interpolation between the freezing points), then the data indicated a value for $A_D = 668(12) \mu K$.

La Mer and Baker

La Mer and Baker [6] carried out measurements on D_2O and H_2O to test the equations produced by Seltz [13] for the composition of an ideal binary solution in solid and liquid phases. Their measurements of the temperature elevation of the freezing point versus mole fraction of deuterium oxide yielded data that fits well to

$$\Delta T = 4.212(9)X_D - 0.408(12)X_D^2, \quad (6)$$

so that the isotopic sensitivity, dT/dX_D , at very low concentrations is $4.212(9) K$, and the freezing point of pure D_2O ($X_D = 1$) is $3.804(4)$ degrees higher than for V-SMOW. LaMer and Baker concluded that the $D_2O - H_2O$ mixture showed significant departures from an ideal binary solution (the reasons are discussed in the next subsection). Nevertheless, the dT/dX_D value at $X_D = 0$ yields a useful estimate of $A_D = 656(2) \mu K$.

Thermophysical data

In an ideal binary solution, the two components are miscible, no heat is absorbed or liberated when the components are mixed, and the chemical potentials of the two components are the same. In a two-phase system (solid, S, and liquid, L) composed of components A and B, the two components are distributed in the two phases so as to satisfy [12]

$$\ln\left(\frac{X_A^L}{X_A^S}\right) = \frac{\Delta H_{f,A}}{R} \left(\frac{1}{T_A} - \frac{1}{T}\right), \quad (7)$$

and

$$\ln\left(\frac{X_B^L}{X_B^S}\right) = \frac{\Delta H_{f,B}}{R} \left(\frac{1}{T_B} - \frac{1}{T}\right), \quad (8)$$

These two equations are valid for all concentrations of A and B in an ideal solution. Equation (1) follows from (7) with the additional assumptions that B is dilute and $T - T_A$ is very small. Equation (1) is useful because it is observed that all binary solutions at sufficient dilution behave as ideal solutions [12]. Equations (7) and (8), when combined with the constraints $X_A^S + X_B^S = 1$, and $X_A^L + X_B^L = 1$, yield Seltz's equations for the solidus and liquidus [13]. The slope of liquidus near $X_B = 0$ and $T = T_A$ (i.e., B dilute), gives the isotopic sensitivity coefficient

$$\left. \frac{dT}{dX_B^L} \right|_{X_B^L=0} = \frac{T_A^2 R}{\Delta H_{f,A}} \left[\exp \left(\frac{\Delta H_{f,B}}{R} \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \right) - 1 \right]. \quad (9)$$

This is Van't Hoff's relation for dilute isotopes again, (1), but it now includes the functional form for the fractionation factor. That is, if the mixture of A and B is an ideal solution at high concentrations, the fractionation factor at low concentrations can be determined from the freezing-point temperature and enthalpy of fusion of the dilute isotopologue as

$$\alpha_{S-L}(B/A) = \exp \left(\frac{\Delta H_{f,B}}{R} \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \right). \quad (10)$$

Table 1 summarises the triple-point temperatures and enthalpies of fusion for the relevant water isotopologues.

Table 1: Literature values for the triple-point temperatures, enthalpies of fusion, relative temperature shift, and predicted solid-liquid fractionation factors for water isotopologues.

Isotopologue	T_f / K	ΔH_f / kJ.mol ⁻¹	$\Delta T_f / T_f$	α_{S-L}
H ₂ ¹⁶ O	273.1587 [2]	6.007(4) [14]	-	-
H ₂ ¹⁸ O	273.46(1) [15]	6.029(4) [15]	0.00110	1.0029(7)
D ₂ ¹⁶ O	276.97(2) [16]	6.315(11) [17]	0.01395	1.040(1)
HD ¹⁶ O	275.19(5) [18]	6.227(13) ¹ [18]	0.00744	1.0206(5)

When the fractionation factor is small, which is the case for all of the isotopes considered here, the liquidus (9) is nearly linear and the slope at low concentrations is approximated by

$$\left. \frac{dT}{dX_B^L} \right|_{X_B^L=0} = (T_B - T_A) \frac{T_A}{T_B} \frac{\Delta H_{f,B}}{\Delta H_{f,A}}. \quad (11)$$

¹Majoube [18] inferred values for the heat of vaporization at 0 °C from liquid phase HDO data (0 °C to 100 °C) and similarly for the heat of sublimation from the sublimation data (-30 °C to 0 °C) of [19]. The values were corrected to $T_f = 2.04$ °C and subtracted to obtain ΔH_f for HDO at the triple point.

Hence the relative uncertainty in the liquidus slope depends on the relative uncertainties in the temperature difference, the freezing-point temperatures, and the heats of fusion. Because the heat of fusion for ordinary water is known well [14] and its triple point temperature is defined, the uncertainty is dominated by the uncertainties in the properties of the dilute isotopologue. For example,

$$\frac{u^2(A_D)}{A_D^2} \approx \frac{u^2(T_{f,HDO})}{(T_{f,HDO} - T_{f,H_2O})^2} + \frac{u^2(\Delta H_{f,HDO})}{\Delta H_{f,HDO}^2}, \quad (12)$$

and similarly for A_{18O} .

First consider the case for $H_2^{18}O$, which is the simpler of the two calculations. Equation (10) is used directly with $A = H_2^{16}O$ and $B = H_2^{18}O$, the calculated fractionation coefficient is 1.00291(11), and the corresponding value of A_{18O} is 606(20). These values are very close to those determined from the Lehmann and Siegenthaler fractionation data, but have a higher uncertainty. Note too the high linearity of the $H_2^{18}O$ liquidus: the difference between the value calculated via (9) and the value obtained by linear interpolation (i.e. $T_B - T_A$) is less than 0.5%. This supports the use of linear interpolation by White *et al*, to constrain the value of A_{18O} . Table 2 summarises the various estimates of the correction constant A_{18O} .

Table 2: Summary of analysis for A_{18O}

Source of data	$A_{18O} / \mu K$	Comments
Lehman and Siegenthaler	601(7)	Type A only
Kiyosawa	641.1(0.8)	Type A only, with probable systematic effects
White <i>et al</i>	507(68)	Type A only
Calculated from Table 1	606(20)	Similar to linear interpolation (603)

For the case with $D_2^{16}O$ as a dilute impurity, the situation is more complicated. As noted above, the data of LaMer and Baker does not follow the equation for an ideal binary solution. This is because the D_2O isotopologue dissociates according to



so the mixture has three components and not two. At very low concentrations of D_2O , nearly all of the deuterium is present as HDO, and (10) must be applied with $A = H_2O$ and $B = HDO$. At high concentrations, nearly all of the deuterium is present as D_2O , so that (10) must be applied with $A = D_2O$ and $B = HDO$. The difference in the two cases explains the difference in liquidus slope at the two extremes of (6), i.e., at $X_D = 0$ and $X_D = 1$, and the unexpectedly strong quadratic term in (6). To employ (10) to calculate the fractionation factor for HDO, we require the enthalpy of fusion and triple-point temperature for HDO. Because the HDO can never be isolated as a pure substance, both of these quantities are conceptual. The value for the triple point temperature of HDO of 275.19 K, given in Table 1, is taken from Majoube [18] which is calculated from his data on fractionation in dilute (e.g., natural) water solutions and other similar data for ice solutions. The Majoube data can likewise be used to derive a value for the HDO enthalpy of fusion. When combined according to (10), these data give a fractionation factor of 1.0206(5), and a correction constant of 662(16) only 2.8% less than the value inferred from the Lehmann and Siegenthaler

fractionation data. Table 3 summarises the various estimates of the isotopic correction constant A_D .

Table 3: Summary of analysis for A_D

Source of data	$A_D / \mu\text{K}$	Comments
Lehman and Siegenthaler	682(13)	Type A only
Kiyosawa	628.1(2.7)	Type A only, with probable systematic effects
White <i>et al</i>	725(42)	Type A only
	668(12)	Type A only, assumes 602 μK for $A_{18\text{O}}$
LaMer and Baker	656(2)	Type A uncertainties only
Calculated from Table 1 data	662(16)	Uncertainties from Majoube [18]

4. Discussion and conclusions

The analysis above considers a broader collection of archival data and theory on the freezing of water isotopologue solutions than was previously included in the evaluation of isotopic correction factors by the CCT task group. One of the most reassuring aspects of the analysis is the degree of consistency between the results derived from experiments with different physical principles. In particular, results determined from the isotopic fractionation factors, the thermophysical data, and the direct temperature-difference measurements using isotopically dilute (e.g. \sim natural) waters are very similar. As result of this reanalysis, we recommend values for the isotopic correction constants for the triple point of water $A_D = 671(10) \mu\text{K}$, $A_{18\text{O}} = 603(3) \mu\text{K}$, and $A_{17\text{O}} = 60(1) \mu\text{K}$. The recommended uncertainties are based on the un-weighted mean of values derived from experiments employing different physical principles. The unweighted mean was used because there is insufficient information available on the total uncertainties to enable the use of a weighted mean.

The data for the influence of the H_2^{18}O isotopologue are the simplest to address because the mixture is an ideal binary solution. The close agreement between the result from fractionation data of Lehman Siegenthaler and that from theory and the thermophysical data, within a few microkelvin, is very reassuring. The mean of the two results is $603 \mu\text{K}$, which is also the value obtained by linear interpolation between the freezing points. As explained above, the data from White *et al* is too uncertain for H_2^{18}O to usefully contribute the determination. The comparatively large difference between the Kiyosawa result and the other two suggests that Kiyosawa's might be subject to a systematic error. For example, contamination from as little as 0.3% D_2O would explain the deviation. The uncertainty, based on the consistency of the two selected values, is $3 \mu\text{K}$.

The data for the influence of D_2O is more complicated because the isotopologue dissociates forming a ternary solution. At low concentration typical of natural waters, it can be treated as a binary solution with HDO as the dilute solute. In this case, the agreement between the Lehman and Siegenthaler result and the result based on thermophysical data is within 2.8 % in A_D . Additionally, the data from White, *et. al.* also are in good agreement with these A_D values providing that the linearly interpolated $A_{18\text{O}}$ value is added in as a constraint. The simple mean of these three values for A_D is $671 \mu\text{K}$. The Kiyosawa result lies about 6.5% below this value, for reasons unknown.

It is instructive to compare the isotope correction and uncertainty for a triple point of water cell using the two sets of values (Table 4). The values of δD , $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ given in

the table are for an MSL-manufactured cell with a moderately large isotopic correction. There are several points to note. Firstly, the increase in the value of the correction is just within the expanded uncertainty of the total uncertainty determined using the CCT values, so the new correction is not significantly different from that calculated with the CCT values. Secondly, the uncertainties associated with the corrections for the oxygen isotopes are now negligible. Finally, the uncertainty in the deuterium correction, now the dominant term, is now half of the previous value, so that the total uncertainty is also halved.

Table 4: Comparison of isotope corrections and uncertainties for an MSL-manufactured water-triple-point cell. The uncertainties exclude the uncertainty associated with the isotopic analysis. All temperature values are in μK .

	Term	$\delta D = 96.1 \text{ ‰}$	$\delta^{18}\text{O} = -14.7 \text{ ‰}$	$\delta^{17}\text{O} = -7.8 \text{ ‰}$	Total correction
CCT values	ΔT	60.35	9.42	0.44	70.2(2.1)
	$u(\Delta T)$	1.92	0.74	0.04	
This work	ΔT	64.48	8.86	0.47	73.8(1.0)
	$u(\Delta T)$	0.96	0.04	0.01	

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