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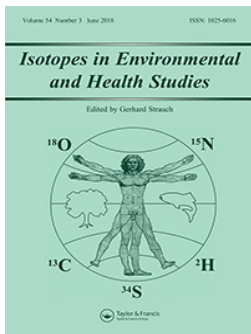
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# Ice–liquid isotope fractionation factors for $^{18}\text{O}$ and $^2\text{H}$ deduced from the isotopic correction constants for the triple point of water

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## ABSTRACT

The stable isotopes of water are extensively used as tracers in many fields of research. For this use, it is essential to know the isotope fractionation factors connected to various processes, the most important of which being phase changes. Many experimental studies have been performed on phase change fractionation over the last decades. Whereas liquid–vapour fractionation measurements are relatively straightforward, vapour–solid and liquid–solid fractionation measurements are more complicated, as maintaining equilibrium conditions when a solid is involved is difficult. In this work, we determine the ice–liquid isotope fractionation factors in an indirect way, by applying the Van't Hoff equation. This equation describes the relationship of the fractionation factors with isotope-dependent temperature changes. We apply it to the recently experimentally determined isotope dependences of the triple point temperature of water [Faghihi V, Peruzzi A, Aerts-Bijma AT, et al. Accurate experimental determination of the isotope effects on the triple point temperature of water. I. Dependence on the  $^2\text{H}$  abundance. *Metrologia*. 2015;52:819–826; Faghihi V, Kozicki M, Aerts-Bijma AT, et al. Accurate experimental determination of the isotope effects on the triple point temperature of water. II. Combined dependence on the  $^{18}\text{O}$  and  $^{17}\text{O}$  abundances. *Metrologia*. 2015;52:827–834]. This results in new values for the  $^2\text{H}$  (deuterium) and  $^{18}\text{O}$  fractionation factors for the liquid–solid phase change of water, which agree well with existing, direct experimental data [Lehmann M, Siegenthaler U. Equilibrium oxygen- and hydrogen-isotope fractionation between ice and water. *J Glaciol*. 1991;37:23–26]. For  $^2\text{H}$ , the uncertainty is improved by a factor of 3, whereas for  $^{18}\text{O}$  the uncertainty is similar. Our final results are  $\alpha_{\text{S-L}}(^2\text{H}/^1\text{H}) = 1.02093(13)$ , and  $\alpha_{\text{S-L}}(^{18}\text{O}/^{16}\text{O}) = 1.002909(25)$ , where the latter is the weighted average of the previous experimental study and this work.

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## 1. Introduction

Stable isotopes play a profound role as natural tracers in a multitude of research fields, such as hydrology, paleoclimatology and biology and biomedicine [1–8]. That they are

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so useful is to a large extent thanks to the fact that well-characterized changes in the abundance of isotopologues occur when a substance undergoes a chemical or physical change, for example a phase change. This phenomenon is called isotope fractionation, and is characterized by its isotope fractionation factor  $\alpha$ , the ratio between the abundance ratios for the rare and abundant isotopes in both materials or phases [9]. To make full use of the power of stable isotopes as tracer, quantitative knowledge of the isotope fractionation factors involved is a necessity.

Perhaps the best example of a field where such quantitative knowledge is crucial is the global water cycle, which is dominated by phase transitions [1–3]. Therefore it is only logical that water isotope fractionation of the isotopologues of water during a phase transition has attracted much attention ever since isotopes got recognized as potential tracers (that is the last 60+ years).

Isotope fractionation arises from both equilibrium and kinetic effects, in which kinetic fractionation occurs in irreversible processes that are circumstance-specific and therefore difficult to measure in general [2,9]. Water equilibrium fractionation processes have been studied by many researchers, and fractionation factor data were derived from both theoretical calculations, laboratory experiments and other, indirect ways [10–21]. Investigations of the water liquid–vapour equilibrium fractionation factors, both for  $^{18}\text{O}$  and  $^2\text{H}$ , are numerous. Horita and Wesolowski have summarized experimental results for the hydrogen and oxygen isotope liquid–vapour equilibrium fractionation factors for the 0–350 °C temperature range [11]. There are also, although fewer, studies that focus on equilibrium hydrogen and oxygen isotope fractionation factors between ice and liquid, and ice and vapour [12–14,16–19,22]. Among them, the work on ice–liquid by Lehmann and Siegenthaler [10] stands out thanks to its carefulness and reliability. They determined the fractionation factors to be 1.00291(3) and 1.0212(4) for  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$ , respectively, through measurements at 0 °C. These results are used widely [2].

A use of these data probably never foreseen by the original researchers is in thermometry. The definition of the Kelvin is based on the triple point of water (TPW), the single point at which the three phases of water coexist (0.01 °C, 273.16 K). As the exact triple point temperature is dependent on the isotopic composition of the water used, the definition prescribes the use of the international isotopic water calibration material Vienna Mean Ocean Water (VSMOW). Of course, actual triple point cells are never filled with VSMOW, but rather made from continental surface water, which is depleted in heavy isotopes to a varying extent. Furthermore, the extensive purification steps of the water, which involve distillation and vacuum extraction of impurities, influence the isotopic composition as well. Therefore, the triple point temperature realized with such cells needs to be corrected for the isotopic difference between the actual water in the cell and VSMOW. The Consultative Committee for Thermometry (CCT) has prescribed the correction to be used [23]:

$$\Delta T = T_{\text{meas}} - T_{\text{VSMOW}} = A_{2\text{H}}\delta^2\text{H} + A_{18\text{O}}\delta^{18}\text{O} + A_{17\text{O}}\delta^{17}\text{O}, \quad (1)$$

$A_{2\text{H}}$ ,  $A_{18\text{O}}$  and  $A_{17\text{O}}$  are the isotopic correction coefficients;  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{17}\text{O}$  are the isotopic deviations from VSMOW expressed as delta values, defined in the usual way (not multiplied by 1000) as  $\delta = R_{\text{sample}}/R_{\text{VSMOW}} - 1$ , where  $R$  is the isotopic abundance ratio. Until recently, the best values for the  $A$  coefficients were based on a compendium of

several, rather unsystematic temperature and isotope measurements with real triple point cells [24], and in addition on a clever use of the ice–liquid water fractionation factor reported by Lehmann and Siegenthaler [10]. White and Tew derived the isotopic dependences of the triple point temperature from the isotope fractionation factors between ice and liquid by using the Van't Hoff's relation [24]. The values they obtained in that way corresponded well with the directly derived results (and are more accurate), and the mean values presented in their work are recommended for use with the International Temperature Scale of 1990 (ITS-90) [25].

Recently, in a collaborative project of Centre for Isotope Research (CIO) of the University of Groningen with the Van Swinden Laboratory (VSL) of the Dutch Metrology Institute, more accurate and reliable values for the  $A$  coefficients have been obtained by direct experimental assessment [26,27]. These researchers prepared two times five triple point cells with isotopically accurately known waters over a wide range of  $\delta$  values by using gravimetric mixing of well-characterized parent waters, and then measured the triple point temperatures of the cells with well-established thermometric procedures. The new values for the  $A$  coefficients, not significantly different from the former ones but more precise, are now in the process of becoming the prescribed ones by the CCT.

Now that these coefficients have been established through direct measurements, it is tempting to follow the relation between these coefficients and the isotope fractionation between ice and liquid in the same way White and Tew [24] did, but backwards, and deduce independent, and possibly more accurate values for the ice–liquid isotope fractionation factors. That is the subject of this paper. Section 2 gives the explanation on how to use Van't Hoff's equation in this case, as well as the detailed calculation that results in the  $\alpha_{S-L}$  ( $^{18}\text{O}/^{16}\text{O}$ ) and  $\alpha_{S-L}$  ( $^2\text{H}/^1\text{H}$ ), along with their uncertainties. In section 3, we compare the new fractionation factors with the data of Lehmann and Siegenthaler [10], both their values and their uncertainties.

## 2. Calculation of the isotope fractionation factors for ice vs liquid

### 2.1. The Van't Hoff relation and isotope fractionation

The Van't Hoff relation, or equation, was introduced by Jacobus Henricus Van't Hoff for dynamic chemistry [28]. It has since then very successfully been applied in exploring the changes in state functions in thermodynamic systems. The Van't Hoff relation can relate the change of an equilibrium constant  $K$  of a phase change to the change in temperature by assuming the enthalpy of the reaction  $\Delta H$  is constant over a small temperature range [29]. In its basic (integral) form, the equation is:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right), \quad (2)$$

where  $K_1$ ,  $K_2$  are the equilibrium reaction constants for the process under study at temperatures  $T_1$  and  $T_2$ , respectively.  $R$  is the universal gas constant ( $8.3144598(48) \text{ J mol}^{-1} \text{ K}^{-1}$ ) [30], and  $\Delta H$  is the enthalpy change for the process. For the ice–liquid transition of water, its value is  $6.0068(36) \text{ kJ mol}^{-1}$  (at  $273.153 \text{ K}$ ,  $101.325 \text{ kPa}$ ) [31,32].

The Van't Hoff equation can be used to relate isotope-specific equilibrium constants (and thus isotope fractionation) to temperature changes in phase changes. In the

following, we will restrict ourselves to water and the liquid–solid phase change. Isotopologues with higher mass will have lower mobility than light ones, which will result in a lower diffusion velocity and a smaller chemical reactivity. Moreover, due to the bigger atomic diameter, water molecules containing heavier oxygen or hydrogen isotopes have lower vibrational frequencies and a higher binding energy. Therefore, heavier isotopologues have a higher freezing point temperature. Furthermore, in a mixture of the liquid and solid phase, the heavier molecules show a slight preference for the solid phase, and this preference is expressed as the solid–liquid fractionation factor  $\alpha$ , being the ratio of ratios of the heavy to light isotopologues in both phases:  $R_{\text{solid}}/R_{\text{liquid}}$  [9,33]. These two effects are coupled through the Van't Hoff equation. Two waters, with different isotopic composition, exhibit different average reaction constants  $K_1$  and  $K_2$  for freezing. That treatment is allowed because the abundances of the heavier isotopologues are low, and they can be treated as impurities. These average reaction constants are composed of the reaction constants for the different isotopologues in the waters, in general  $K_A$  for the abundant isotope, and  $K_R$  for (one of the) heavier ones. The relation  $K_R/K_A$  is equal to  $R_{\text{solid}}/R_{\text{liquid}}$ , being the fractionation factor  $\alpha$ . The two waters will have slightly different freezing temperatures  $T_1$  and  $T_2$ , according to Equation (2). In this way, the Van't Hoff equation builds the relation between isotope fractionation and shifts of freezing temperature.

White and Tew [24] have used this relation, along with isotope fractionation measurements [10], to deduce the isotopic effect on the temperature shift. However, this was not for the freezing point, but for the TPW: the state at which three phases (gas, liquid, and solid) of water coexist in a thermodynamic equilibrium state. However, as the TPW is only 0.01 K higher than the freezing point, using the isotope fractionation for the freezing point is fully justified. Independent measurements of TPW temperature shifts due to isotopic composition have become available by now [26,27]. Hence, we will follow the opposite path.

## 2.2. Isotope fractionation factor calculation based on Van't Hoff relation

Let  $K_1$ ,  $K_2$  be the equilibrium reaction constants between the solid and liquid phase, respectively, for VSMOW and isotopically different water used to make triple point water cells.  $T_1$ ,  $T_2$  are the measured triple point temperatures for two waters, and  $\Delta H$  is the enthalpy of fusion, slightly altered due to the 0.01 K higher temperature, and the much lower pressure (611 Pa) of the triple point: 6.007 (10) kJ mol<sup>-1</sup> [31].

Both equilibrium reaction constants  $K$  are composed of  $K_A$  for the abundant isotopologue and  $K_R$  for the rare isotope, where  $K_R = \alpha K_A$ , with the solid–liquid fractionation factor  $\alpha$ . With mole fractions of the heavy isotopologue  $X_1$  in VSMOW [34] and  $X_2$  in the other water,  $K_1$ ,  $K_2$  can be expressed as

$$K_1 = K_A(1 - X_1) + K_R X_1, \quad (3)$$

$$K_2 = K_A(1 - X_2) + K_R X_2. \quad (4)$$

For their ratio, we find:

$$\ln\left(\frac{K_2}{K_1}\right) = \ln\left(\frac{(\alpha - 1)X_2 + 1}{(\alpha - 1)X_1 + 1}\right) = \frac{\Delta H \Delta T}{RT_f^2}, \quad (5)$$

where we have also used the approximation:

$$\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \approx \frac{-\Delta T}{T_f^2}. \quad (6)$$

The latter approximation is fully justified, given the fact that the temperature differences are below 1 mK.  $T_f$  is the TPW temperature, defined to be 273.16 K.  $\Delta T$  is the difference in the triple point temperature caused by the isotope effects, and this difference is directly related to the coefficients in Equation (1).

To simplify the expressions, we define:

$$B = \exp\left(\frac{\Delta H \Delta T}{RT_f^2}\right). \quad (7)$$

The TPW isotope correction constants  $A$  are defined such that they express the isotopic influence on the triple point temperature as the temperature change for a doubling of the isotope abundance ratios  $R$ . Therefore, we can replace  $\Delta T$  in Equation (7) by the appropriate  $A$  coefficient, if we choose:

$$R_2 = \frac{X_2}{1 - X_2} = 2R_1 = \frac{2X_1}{1 - X_1}, \quad (8)$$

and thus

$$X_2 = \frac{2X_1}{1 + X_1}. \quad (9)$$

At natural abundance, almost all of the deuterium is distributed in water as  $\text{H}^2\text{HO}$  rather than as  $^2\text{H}_2\text{O}$ , therefore  $X_{\text{H}^2\text{HO}}$  is a very good approximation equal to  $2X_{2\text{H}}$ .

Now from Equations (5) and (7), the ice–liquid hydrogen fractionation factor can be expressed by

$$B_{2\text{H}} = \exp\left(\frac{\Delta H A_{2\text{H}}}{RT_f^2}\right), \quad (10)$$

$$\alpha_{\text{S-L}}(^2\text{H}/^1\text{H}) = 1 + \frac{B_{2\text{H}} - 1}{2X_{2,2\text{H}} - 2X_{1,2\text{H}}B_{2\text{H}}}, \quad (11)$$

Here  $A_{2\text{H}}$  is based on the study by Faghihi et al. [26].  $X_{1,2\text{H}}$  is the  $^2\text{H}$  abundance of VSMOW and  $X_{2,2\text{H}}$  is coupled to  $X_{1,2\text{H}}$  through Equation (9). The two '2's' in the denominator of Equation (11) occur since the water molecule contains two hydrogen atoms:  $X_{\text{H}^2\text{HO}} = 2X_{2\text{H}}$  for natural abundances, in which the abundance of  $^2\text{H}_2\text{O}$  can be neglected. Table 1 shows the numerical values and their uncertainties.

In a second paper, Faghihi et al. [27] also present results for the influence of the oxygen isotopes on the TPW temperature. However, they combined the  $^{17}\text{O}$  and  $^{18}\text{O}$  isotope

**Table 1.** Summary of analyses for  $\alpha_{\text{S-L}}(^2\text{H}/^1\text{H})$ .

Term	Value	Standard uncertainty $u$ ( $k = 1$ )
$X_{1,2\text{H}}$	$1.5574 \times 10^{-4}$	$8.0 \times 10^{-8}$ [34]
$A_{2\text{H}}$ (K)	$6.73 \times 10^{-4}$	$4.0 \times 10^{-6}$ [26]
$\alpha_{\text{S-L}}(^2\text{H}/^1\text{H})$	1.02093	$1.3 \times 10^{-4}$

effects on the triple point temperature to an integrated correction  $A_0$  and recommended a new correction equation.

$$\Delta T = T_{\text{meas}} - T_{\text{VSMOW}} = A_{2\text{H}}\delta^2\text{H} + A_0\delta^{18}\text{O}. \quad (12)$$

The combination is based on the fact that triple cells are usually filled with natural isotopic abundances following the Meijer–Li equation:

$$\delta^{17}\text{O} = (1 + \delta^{18}\text{O})^\lambda, \quad (13)$$

$$A_0 = A_{180} + \lambda A_{170}, \quad (14)$$

with  $\lambda = 0.5281$  (1) [27,35,36]. Moreover, in comparison with  $A_{180}$  and  $A_{2\text{H}}$ ,  $A_{170}$  has little effect on  $\Delta T$  because of the low abundance and the weak fractionation effects of  $^{17}\text{O}$ . For our purpose, we need the  $A_{180}$  value, so we use the  $A_{170}$  value from White and Tew [24] ( $A_{170} = 60(1) \mu\text{K}$ ), which was actually deduced from a previous  $A_{180}$  value using Equation (13) to find  $A_{180}$ . Now the ice-liquid water fractionation factor for  $^{18}\text{O}$  can be expressed by:

$$B_{180} = \exp\left(\frac{\Delta H A_{180}}{RT_f^2}\right), \quad (15)$$

$$\alpha_{\text{S-L}}(^{18}\text{O}/^{16}\text{O}) = 1 + \frac{B_{180} - 1}{X_{2,180} - X_{1,180}B_{180}}, \quad (16)$$

where once again  $X_{2,180}$  is related to  $X_{1,180}$  through Equation (9). Table 2 gives the numerical results.

The uncertainty in  $\alpha$  values is dominated by the uncertainties of the  $A_{2\text{H}}$  and  $A_{180}$  coefficients. We used the NIST Uncertainty Machine [38] to double check the uncertainty values.

### 3. Discussion, conclusions and outlook

The present work is motivated by the results of a recent accurate empirical investigation of the  $^2\text{H}$ ,  $^{18}\text{O}$  and  $^{17}\text{O}$  isotope dependence of the TPW temperature conducted in a collaborative project of VSL and CIO [26,27]. The results of that work agree very well with previously recommended values, but especially for  $^2\text{H}$  with improved total uncertainty. As the previously determined coefficients were largely based upon a combination of ice-liquid isotope fractionation measurements [10], our hope was that following the calculations backward with the new TPW dependences would result in fractionation factors with improved uncertainties.

For  $^2\text{H}$ , this is indeed what our result shows. The value of  $\alpha_{\text{S-L}}(^2\text{H}/^1\text{H})$  in this work is 1.02093 (13) ( $k = 1$ ), which is in good agreement with the result 1.0212 (4) of Lehmann and Siegenthaler's study [10], while the uncertainty has improved by a factor of 3.

For  $^{18}\text{O}$ , our new value 1.00291 (5) also agrees well with the data from [10], 1.00291(3), but its uncertainty is slightly higher. The uncertainty in both our values is almost entirely

**Table 2.** Summary of analyses for  $\alpha_{\text{S-L}}(^{18}\text{O}/^{16}\text{O})$ .

Term	Value	Standard uncertainty $u$ ( $k = 1$ )
$X_{1,180}$	$2.0011 \times 10^{-3}$	$4.5 \times 10^{-7}$ [37]
$A_0$ (K)	$6.30 \times 10^{-4}$	$1.0 \times 10^{-5}$ [27]
$A_{180}$ (K)	$5.98 \times 10^{-4}$	$1.0 \times 10^{-5}$ [27]
$\alpha_{\text{S-L}}(^{18}\text{O}/^{16}\text{O})$	1.002907	$4.9 \times 10^{-5}$



determined by the uncertainty in the two  $A$ -coefficients; all other values needed in Equation (16) have a much smaller relative uncertainty.

The excellent agreement between our present results and those by [10] gives confidence in the correctness of these fractionation factors. Since these new results have been determined in a fully independent way, a weighted average of the results is justified. A weighted average of the values for  $^{18}\text{O}$  yields 1.002909 (25) (for which we deduced the next decimal (5) in the result of [10] by carefully reading the graph in the paper). For  $^2\text{H}$ , our present results 'outweighs' the one by Lehmann and Siegenthaler [10] such that the final averaged result is virtually the same as our result:  $\alpha_{S-L} (^2\text{H}/^1\text{H}) = 1.02093$  (13).

For the triple point work, determination of an independent  $^{17}\text{O}$ -dependence was not necessary. From a point of view from the present work, a newly, directly determined  $A^{17}\text{O}$  with sufficient precision would have been extremely useful, the more so in the light of the expanding use of  $\delta^{17}\text{O}$  and its related ' $^{17}\text{O}$  excess'  $\Delta^{17}\text{O}$ . Therefore, we encourage the research groups of [26,27] to perform such work.

Finally, it is important to realize that the same principle, namely utilizing the Van't Hoff equation to deduce isotope fractionation factors from isotope-dependent temperature shifts, can be used for other phase changes as well.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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