

Evaluation of the depression constants for D and ^{18}O isotopes for the triple-point temperature of water

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1. Introduction

In a recent paper presented to the Chicago symposium on *Temperature, its Measurement and Control in Science and Industry*, the authors reported an assessment of the depression constants for D and ^{18}O isotopes on the triple-point temperature of water [1]. The paper compared estimates of the isotopic depression constants from three sources: values interpolated from reported freezing-point or triple-point temperatures of the nearly pure isotopomers H_2^{16}O , D_2^{16}O and H_2^{18}O , values obtained from a set of measurements of 5 triple-point-of-water cells with varying levels of isotope depletion, and the results of a reanalysis of Kiyosawa's [2] measurements of freezing-point elevation with isotopically enriched waters. The paper recommended the values of constants determined from a reanalysis of Kiyosawa's data. Unfortunately, because of the page restriction, not all of the analysis or issues could be addressed in detail. The purpose of this paper is to elaborate on aspects of the paper that might be of interest to those involved with the definition of the temperature scale. Specifically we describe the derivation of Equation 5 of [1], report the reanalysis of Kiyosawa's data in detail, note some unresolved issues relating to uncertainties in Kiyosawa's results, and include the results of measurements of LaMer and Baker [3].

2. Derivation of Equation (5)

Conventionally the isotopic composition of natural waters is described in terms of the departure of the isotope concentrations from that of Vienna-SMOW, a standard reference material of known isotopic composition representing Standard Mean Ocean Water. The deviations are reported as delta-values:

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

and similarly for δD and $\delta^{17}\text{O}$. The best measured values of the ratios of the isotopes in V-SMOW are

$$(\text{D}/^1\text{H})_{\text{V-SMOW}} = 0.000\,155\,76(5),$$

$$(^{18}\text{O}/^{16}\text{O})_{\text{V-SMOW}} = 0.002\,005\,20(45), \text{ and}$$

$$(^{17}\text{O}/^{16}\text{O})_{\text{V-SMOW}} = 0.000\,379\,9(8).$$

If it is assumed that the heavy isotopes are dilute, so that the isotopic effects are linear and there is no interaction between the different isotopes, the influence of variations in the concentrations on the triple-point temperature can be described by:

$$T_{\text{meas}} = T_{\text{V-SMOW}} + A_{\text{D}}\delta\text{D} + A_{^{17}\text{O}}\delta^{17}\text{O} + A_{^{18}\text{O}}\delta^{18}\text{O} .$$

where $T_{\text{V-SMOW}} = 273.16$ K by definition. The A_i coefficients can be determined by additionally assuming the triple-point temperature is proportional to the mole fraction of the various species. Thus, the effect of deuterium is modelled as

$$T = T(\text{H}_2\text{O}) \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{O}] + [\text{D}_2\text{O}]} + T(\text{D}_2\text{O}) \frac{[\text{D}_2\text{O}]}{[\text{H}_2\text{O}] + [\text{D}_2\text{O}]} .$$

This can be expressed also in terms of the ratio of deuterium to hydrogen:

$$T = T(\text{H}_2\text{O}) \frac{1}{1 + [\text{D}]/[\text{H}]} + T(\text{D}_2\text{O}) \frac{[\text{D}]/[\text{H}]}{1 + [\text{D}]/[\text{H}]}$$

This can be applied to V-SMOW, for which the ratio $[\text{D}]/[\text{H}]$ is known and equal to $(\text{D}/\text{H})_{\text{V-SMOW}}$ as given above. That is

$$T_{\text{V-SMOW}} = T(\text{H}_2\text{O}) \frac{1}{1 + (\text{D}/\text{H})_{\text{V-SMOW}}} + T(\text{D}_2\text{O}) \frac{(\text{D}/\text{H})_{\text{V-SMOW}}}{1 + (\text{D}/\text{H})_{\text{V-SMOW}}}$$

and hence the triple-point temperature of water is

$$T = T_{\text{V-SMOW}} + T(\text{H}_2\text{O}) \left(\frac{1}{1 + [\text{D}]/[\text{H}]} - \frac{1}{1 + (\text{D}/\text{H})_{\text{V-SMOW}}} \right) + T(\text{D}_2\text{O}) \left(\frac{[\text{D}]/[\text{H}]}{1 + [\text{D}]/[\text{H}]} - \frac{(\text{D}/\text{H})_{\text{V-SMOW}}}{1 + (\text{D}/\text{H})_{\text{V-SMOW}}} \right)$$

The term in $[\text{D}]/[\text{H}]$ can be substituted using the definition of δD :

$$\delta\text{D} = \left[\frac{(\text{D}/\text{H}) - (\text{D}/\text{H})_{\text{V-SMOW}}}{(\text{D}/\text{H})_{\text{V-SMOW}}} \right] \quad \text{or} \quad (\text{D}/\text{H}) = (1 + \delta\text{D})(\text{D}/\text{H})_{\text{V-SMOW}}$$

Hence

$$T = T_{\text{V-SMOW}} + \delta\text{D}(T(\text{D}_2\text{O}) - T(\text{H}_2\text{O})) \left[\frac{(\text{D}/\text{H})_{\text{V-SMOW}}}{(1 + (1 + \delta\text{D})(\text{D}/\text{H})_{\text{V-SMOW}})(1 + (\text{D}/\text{H})_{\text{V-SMOW}})} \right]$$

Note that the temperature difference is a weak non-linear function of δD because of the term in δD in the denominator. For the cases when $|\delta\text{D}| < 1$ the non-linearity is within 0.02% (0.2% for the ^{18}O case). Therefore, for delta values close to zero, i.e. waters close to SMOW, the equation is well approximated by:

$$T = T_{\text{V-SMOW}} + \delta\text{D}(T(\text{D}_2\text{O}) - T(\text{H}_2\text{O})) \left[\frac{(\text{D}/\text{H})_{\text{V-SMOW}}}{(1 + (\text{D}/\text{H})_{\text{V-SMOW}})^2} \right]$$

This is Equation (5) in [1]. Analogous equations apply for the ^{17}O and ^{18}O isotopes.

3. Analysis of Kiyosawa's data

Kiyosawa reported the results of two experiments to determine the freezing-point dependence of water on the molal concentration of the heavy isotopes D and ^{18}O . A plot of the composition of Kiyosawa's solutions together those used in [1] is shown Figure 1. The following two sub-sections summarise the reanalysis of the data reported in [1].

3.1 Deuterium

Columns 1 and 3 of Table 1 summarise the results of Kiyosawa for mixtures of deuterium-enriched waters. The mole fraction (Column 2), X , is derived from the molality, m , according to the formula

$$X = \frac{18.01m}{1000 + 18.01m}$$

A fit of the observed temperature difference to the equation $\Delta T = kX$ yields

$$k = \frac{\sum \Delta T_i X_i}{\sum X_i^2} = 4.0336 \text{ K}$$

Molality D (mol/kg)	Mole fraction	ΔT observed /K	ΔT fitted /K	Residuals /K
0.099955	0.001797	0.00679	0.007248	0.00046
0.10093	0.001815	0.00675	0.007319	0.00057
0.19929	0.003576	0.0142	0.014426	0.00023
0.20183	0.003622	0.0138	0.014609	0.00081
0.29979	0.005370	0.0215	0.021662	0.00016
0.30213	0.005412	0.0217	0.021830	0.00013
0.40017	0.007156	0.0292	0.028863	-0.00034
0.40023	0.007157	0.0288	0.028868	0.00007
0.49666	0.008866	0.0358	0.035761	-0.00004
0.49794	0.008888	0.0363	0.035853	-0.00045
0.59768	0.010650	0.0426	0.042957	0.00036
0.60192	0.010725	0.0437	0.043259	-0.00044

Table 1: A summary of the analysis of the results of Kiyosawa's measurements of freezing-point temperature versus molality of the enriched deuterium solutions.

Predicted values of ΔT are given in Column 4 of Table 1, and the residuals in the fit (observed – fitted values) are given in Column 5. The standard deviation, s , of the residuals is 0.42 mK, hence the uncertainty in k is

$$s_k = \frac{s}{(\sum X_i^2)^{1/2}} = 0.017 \text{ K.}$$

Since $\Delta T = kX$, ΔT for the two pure isotopomers can be estimated by setting $X=1$, and the term $T(\text{D}_2\text{O}) - T(\text{H}_2\text{O})$ in Equation (5) can be replaced by k . Hence, the depression coefficient when the deuterium concentration is expressed in term of delta values is 628.1(2.7) μK . With 11 degrees of freedom, the expanded uncertainty for a 95% level of confidence is approximately 6 μK , based on a coverage factor of 2.2.

3.2 Oxygen, ^{18}O

Table 2 summarises Kiyosawa's results and the reanalysis of the results for ^{18}O .

Molality (mol/kg)	Mole fraction	ΔT observed /K	ΔT fitted /K	Residuals /K
0.5034	0.00899	0.00249	0.002884	0.00039
0.7124	0.01267	0.00422	0.004067	-0.00015
1.5000	0.02631	0.00867	0.008444	-0.00023
2.0130	0.03499	0.01140	0.011231	-0.00017
2.8570	0.04894	0.01550	0.015709	0.00021

Table 2: A summary of the analysis of the results of Kiyosawa's measurements of freezing-point temperature versus molality of the enriched ^{18}O solutions.

In this case $k = 0.321(4) \text{ K}$, so the depression constant is estimated as 641(8) μK , with a corresponding expanded uncertainty of 23 μK with a coverage factor of 2.78.

3.3 Uncertainties in Kiyosawa's data

Unfortunately Kiyosawa provides no information about the uncertainties in his measurements. Indeed the description of the experiments is very brief:

“D₂¹⁶O (99.8%) and H₂¹⁸O (99%) were purchased from Stohler and Prochem, respectively. The H₂¹⁶O used was distilled from deionised water. The molal concentrations m of D₂¹⁶O and H₂¹⁸O were calculated from the purity of the purchased specimens, with isotope waters other than D₂¹⁶O and H₂¹⁸O being regarded as H₂¹⁶O.

The freezing point depression or elevation was measured with an osmometer (Advanced Instruments, Type 3W), which had been calibrated with standard aqueous NaCl solutions. ⁽²⁷⁾ The osmometer was equipped with a thermistor to detect the freezing point of the aqueous solution to be examined and a cooling bath in which a glass tube containing the aqueous solution could be cooled slowly.

The freezing points were measured thrice at one molal and the deviation of each measured value from the mean was within ± 0.00037 °C. The measured freezing-point depressions were expressed in terms of θ/m and the change in the freezing point ΔT from 0 °C.”

From the description of the experiment there are several possible sources of uncertainty, in addition to the Type A uncertainty determined from the results above:

- Calibration of the osmometer. The specifications for the 3W could not be located but other osmometers manufactured by Advanced instruments have linearities of about 1% and repeatabilities of between 0.5% and 1.0% depending on the instrument model. The Type A uncertainties calculated above are consistent with an instrument of 1% accuracy.
- Uncertainties in the supplier’s measurements of isotopic composition of the supplied waters.
- Assumption that, for example, only the [D] is varying during the experiments on D. In particular, a small difference between the D/H ratios in the H₂¹⁸O and H₂¹⁶O waters would bias the results of the ¹⁸O measurements.
- Measurements of freezing-point temperatures within a capillary instead of triple-point temperatures in full-sized cells.
- Kiyosawa assumed his solvent water to be pure H₂¹⁶O, when in reality this was probably distilled tapwater taken from fresh continental surface water in Japan. Therefore, it is reasonable to assume that the isotopic composition of this water was slightly depleted with respect to SMOW, and close to the GMWL. In this sense, the mole fraction, X , shown here is not absolute but an “excess” mole fraction relative to the solvent water. The uncertainty due to the true composition of the solvent introduces some uncertainty in the meaning of $X=0$ and hence also in the k values as the least-square fits are forced to $\Delta T=0$ at $X=0$.

Thus there remain several potentially significant sources of uncertainty in the measurements. Certainly the expanded uncertainties reported in [1], based only on the Type A components, will be optimistic.

4. Comparison with other data

Table 3 summarises various measurements of the deuterium depression constant.

Source	dT/dX_D /K	Standard uncertainty /K
Interpolation between t.p. values [1]	3.811	0.01
Kiyosawa [2]	4.034	0.017 ($\nu = 11$)
White <i>et al</i> [1]	4.14	0.09 ($\nu = 3$)
LaMer and Baker [3]	4.212	0.009 ($\nu = 6$)

Table 3: Summary of various estimates of the deuterium depression constant.

The interpolated value of dT/dX_D given in the first row of Table 3 is provided for comparison only. It is known from theory and experiment that the dependence of the temperature on mole fraction is not linear so the interpolated value is expected to be low. As described above, the value of Kiyosawa is derived from measured freezing-point depressions of dilute solutions. The value from White *et al* is based on the measurements of triple-point cells made with depleted water. These measurements are corrected for ¹⁸O composition using Kiyosawa’s value for the ¹⁸O depression constant. The last value is that of LaMer and Baker, dates from 1934, and is based on a quadratic fit of the freezing points of strong solutions of D₂O in H₂O. As with Kiyosawa’s data, LaMer and Baker’s data was taken using osmometry and the uncertainty

is a Type A value determined from the least squares fit to the data and subject to similar uncertainty concerns as described above for Kiyosawa's data. Figure 2 shows the observed freezing points as a function of deuterium concentration from the results of both LaMer and Baker and Kiyosawa.

It is notable that the results of Kiyosawa and LaMer and Baker are not quite consistent, there being about a 4.5% difference between the two while the combined standard uncertainty accounts for about 0.5%. However, as discussed above, the total uncertainty is certainly low because only the Type A components have been accounted for.

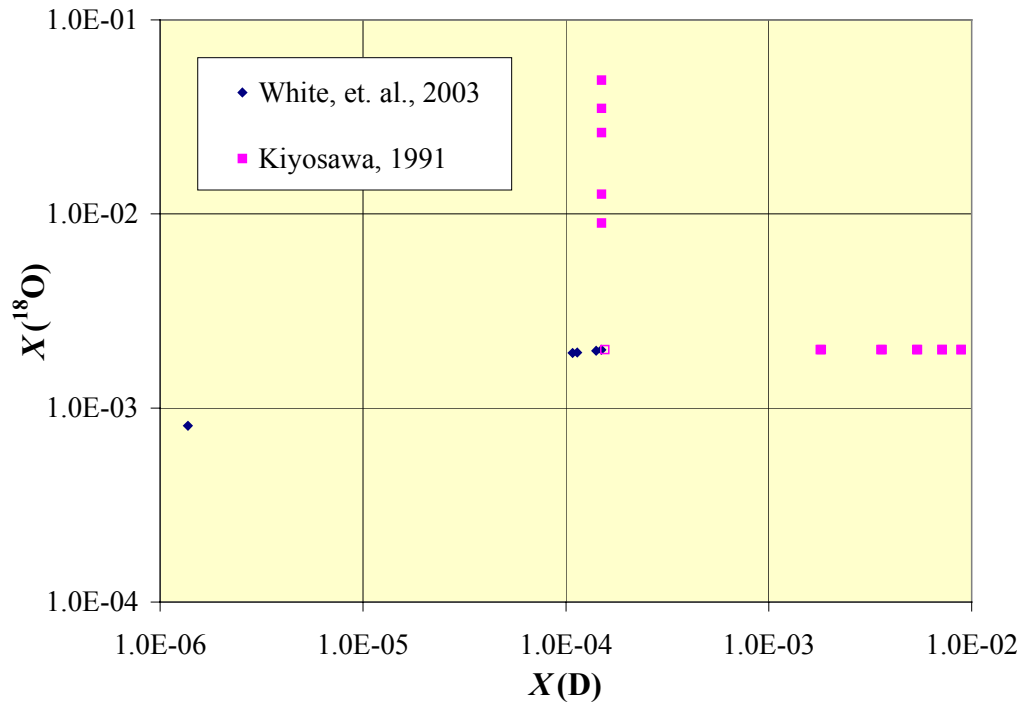


Figure 1. The absolute mole fractions in deuterium $X(D)$ and ^{18}O , $X(^{18}O)$, for the isotopic water solutions used by Kiyosawa and by White, *et. al.* The assumption being made is that Kiyosawa's solvent water (open square) was only slightly depleted with respect to SMOW.

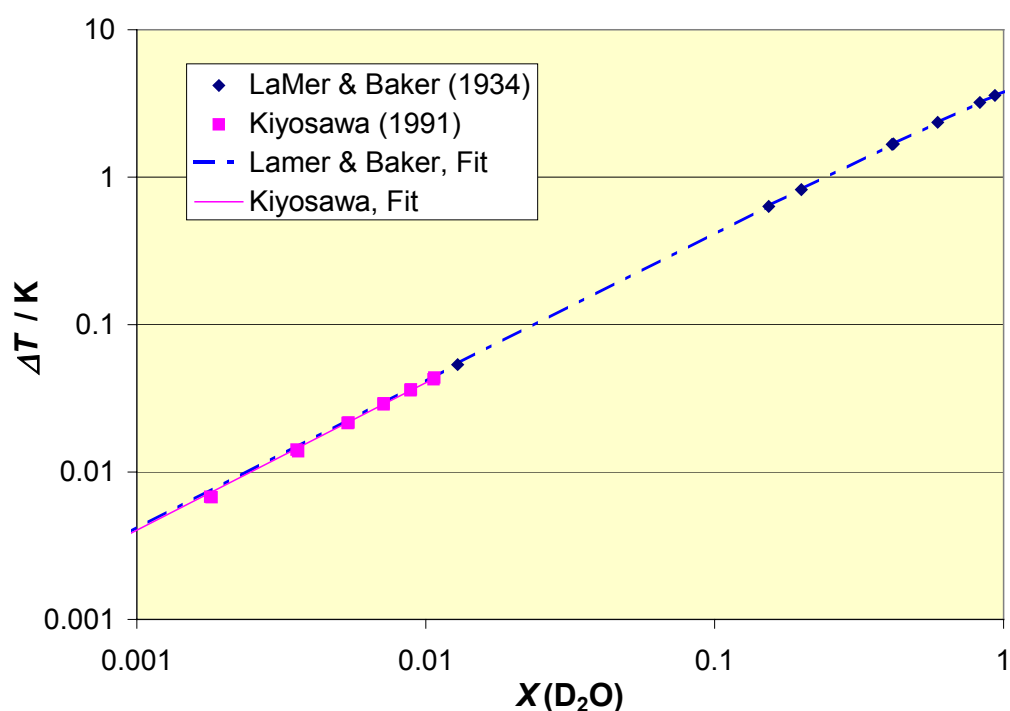


Figure 2. The freezing-point depression data for H₂O – D₂O solutions as reported by LaMer and Baker, 1934 and Kiyosawa, 1991.

5. Discussion

The magnitude of isotope corrections for the temperature of triple-point cells is sufficiently small (< 80 μK) that the uncertainty in the corrections is currently negligible. If the Type A uncertainties are indicative of the total uncertainty in Kiyosawa's measurements then the expanded uncertainty in typical corrections is less than 1 μK. A five-fold-higher value due to other factors would still be a minor contribution to the total given the other sources of uncertainties in realisations of the triple point. However, should the depression constant be required with a greater accuracy and confidence then the values should be redetermined with an improved experiment.

Given the limited variation in the isotopic composition of natural waters, the strong correlations between the D and ¹⁸O concentrations in natural waters, and the limited accuracy of temperature difference measurements, any future determinations of the isotopic depression constants should be determined using triple-point cells manufactured from enriched waters with delta values greater than 1. Also the composition of the cells should be determined by measurement and not inferred from the manufacturer's specification of the waters.

References

- [1] White D R, Dransfield T D, Strouse G F, Tew W L, Rusby R L, and Gray J, Effects of Heavy Hydrogen and Oxygen on the Triple-Point Temperature of Water, In *Temperature, Its measurement and Control in Science and Industry*, Vol 7 (In Press).
- [2] Kiyosawa, K. J., Freezing-point of mixtures of H₂¹⁶O and H₂¹⁸O, *Soln. Chem.* **20**, 583-588 (1991).
- [3] LaMer, V. and Baker, W., *J. Am. Chem. Soc.* **56**, 2641-2643 (1934).