

Comment on ‘Freezing Point Mixtures of H₂¹⁶O with H₂¹⁷O and Those of Aqueous CD₃CH₂OH and CH₃¹³CH₂OH Solutions’

W. L. Tew¹ and D. R. White²,

¹ National Institute of Standards and Technology,
Gaithersburg, MD 20899-8363, USA

² Measurement Standards Laboratory,
PO Box 31310, Lower Hutt, New Zealand

Abstract

In a recent article in *Journal of Solution Chemistry*, Kiyosawa^[1] (Kiyosawa 2004) reports that the freezing points of isotopic mixtures of ordinary water and ¹⁷O enriched water show an unexpectedly large linear dependence on the concentration of H₂¹⁷O. Surprisingly, the constant of proportionality to H₂¹⁷O concentration is nearly five times larger than that of H₂¹⁸O found in earlier studies by Kiyosawa^[2] (Kiyosawa 1991). We show that the H₂¹⁷O result is not consistent with other data or models. For example, a recent determination of the triple-point temperature dependence on isotopic composition in naturally and artificially depleted waters^[3], is consistent with the H₂¹⁸O and D₂O results from Kiyosawa 1991^[4] but not consistent with the H₂¹⁷O results from Kiyosawa 2004. Additionally, the results from Kiyosawa 1991 are close to what would be found in ideal solutions for those isotopic forms, while the H₂¹⁷O proportionality from Kiyosawa 2004 is about ten times larger than similarly predicted. One possible explanation is that the original ¹⁷O enriched water sample contained a small amount of D₂O, and the sample, if available, should be subject to isotopic analysis to help resolve these inconsistencies.

Keywords: Freezing Point, Triple Point, Oxygen Isotopes, Heavy Oxygen Water, Isotopic Mixtures, Temperature Fixed Points,

The data in both Kiyosawa 1991 and Kiyosawa 2004 are presented in terms of the molality of the isotopomer solutes. The data are most readily compared with the literature when isotopic concentrations expressed in molality m are converted to mole fractions $X(\text{H}_2^y\text{O})$ for an isotopic solute H₂^yO where $y = 17$ or 18 via $X(\text{H}_2^y\text{O}) = 0.018m/(1+0.018m)$. Similarly, when treating terrestrial waters, the isotopic concentration is often expressed in terms of the relative depletion parameters $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, which expresses the isotopic content relative to that of an Isotope Reference Material (IRM) such as Standard Mean Ocean Water (SMOW) or a practical equivalent Vienna-SMOW^[5]. The isotope ratios $R(^y\text{O})_s$ of the sample ‘s’ and $R(^y\text{O})_{\text{SMOW}}$ of the IRM with respect to ¹⁶O are used to calculate the relative depletion or enrichment according to

$$\delta^{17}\text{O}_{s,\text{SMOW}} = \left(\frac{R(^{17}\text{O})_s}{R(^{17}\text{O})_{\text{SMOW}}} - 1 \right), \quad (1.)$$

and the conversion to mole fraction is given by

$$X(\text{H}_2^{17}\text{O})_s = \frac{R(^{17}\text{O})_s}{1 + R(^{17}\text{O})_s + R(^{18}\text{O})_s} \cong R(^{17}\text{O})_{\text{SMOW}} (\delta^{17}\text{O} + 1), \quad (2.)$$

where terms of order R^2 or greater have been neglected ($R \ll 1$ in all natural waters). The value $R(^{17}\text{O})_{\text{SMOW}} = 0.0003799$ ^[6] is used for calculations presented here. An analogous set of relations also apply in the case of ^{18}O where $R(^{18}\text{O})_{\text{SMOW}} = 0.00200520(45)$, ^[7].

For the purposes of this discussion, we make a few simplifying approximations. First, we assume that the temperature difference between the triple point and the normal melting point is always 0.01 K for all the water isotopomers. This is equivalent to saying that the difference in the normal melting point between two isotopomers will be the same as the difference in their triple points. Secondly, we ignore the difference between the triple point temperature of SMOW (assumed to be exactly 273.16 K) and that of the pure light isotopomer H_2^{16}O , which is estimated^[3] to be 273.1587 K.

In Kiyosawa 1991, the freezing point results for the solutions of both D_2O and H_2^{18}O showed a linear dependence on concentration (see Figure 1). A linear extrapolation from these data to an isotopically pure water of H_2^{18}O predicts a temperature difference $\Delta T = 0.32$ °C between the melting points of H_2^{16}O and H_2^{18}O . This is only 7 % higher than the difference derived from direct determinations of T_{tp} for H_2^{18}O ^[8] (see Table I). It is also consistent with an ideal-solution model in which the excess free energy in the isotopic mixtures is relatively small ^[9].

In contrast, the freezing point results for the solutions of H_2^{17}O in Kiyosawa 2004 showed a much larger linear dependence than observed in the H_2^{18}O mixtures. This implies a large excess free energy in the $\text{H}_2^{17}\text{O}/\text{H}_2^{16}\text{O}$ system which is incommensurate with the relatively small deviations from ideality observed in either the $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ system or the HOH/HOD/DOD system ^[9]. In fact, when extrapolated to pure H_2^{17}O , the result implies a $\Delta T = 1.57$ °C between the melting points of the pure isotopomers H_2^{17}O and H_2^{16}O , much larger than any prediction of which we are aware (see Table 1).

Figure 1 summarizes Kiyosawa's results and the ideal solution predictions plotted against mole fraction. The results for both H_2^{18}O from Kiyosawa 1991 and H_2^{17}O from Kiyosawa 2004 are shown with least-square linear fits. The ideal solution phase boundaries are calculated based on the perfect solid-solution treatment by Seltz^[10] assuming the values for the T_{tp} and heat of fusion given by Nagano, *et. al.* ^[8] in the case of H_2^{18}O and the mean of those values with those of H_2^{16}O in the case of the H_2^{17}O . If the $\text{H}_2^{17}\text{O} + \text{H}_2^{16}\text{O}$ solutions are similar to the $\text{H}_2^{18}\text{O} + \text{H}_2^{16}\text{O}$ solutions, then the H_2^{17}O solution melting data should be about 7 % above the ideal solution boundary, or approximately $\Delta T = 0.16X(\text{H}_2^{17}\text{O})$, which is almost ten times smaller than reported in Kiyosawa 2004.

The Kiyosawa 2004 result also conflicts with archival data on both vapor pressure isotope effects (VPIE) and melting of the pure isotopomers of water. The older data are summarized in the review by Jancso and Van Hook ^[11]. More recently, the triple point of the pure isotopomer H_2^{18}O has been directly measured by Nagano, *et. al.* ^[8] (see Table I). To our knowledge, no similar measurements have been performed on a comparably isotopically pure sample of H_2^{17}O .

However, Szapiro and Steckel^[12] performed vapor pressure ratio measurements on a variety of heavy-oxygen water samples, including one 55% H₂¹⁷O enriched sample, and derived expressions for the relative isotopic fractionation constant α_{17} in terms of temperature over the range 40 °C to 90 °C. This result was found to be only 11 % greater than what would be predicted by applying the rule of the geometric mean^[13] to the H₂¹⁶O and H₂¹⁸O vapor pressures over that range.

The theory of VPIE as originated by Bigeleisen^[14] concerns the role of molecular structure in the calculation of the temperature dependence of the relative vapor pressures between pure isotopomers. In addition, these results can be used to predict difference relations ΔT_{tp} between the triple-point temperatures T_{tp} within a series of isotopomers. One consequence of the theory is that for a given isotopic series the rule of the geometric mean for triple point transitions should be obeyed in the limit that quantum effects are small and $\Delta T_{tp} \ll T_{tp}$. An estimate for the H₂¹⁷O triple point based on the rule of the geometric mean using the Nagano, *et. al.* H₂¹⁸O triple point value is shown in Table I.

Some theoretical calculations of the triple points of the pure water isotopomers can be made based on a detailed application of the Bigeleisen theory and simultaneous solution of the resulting analytical equations for the vapor pressure isotope ratios for solid and liquid phases^[15]. These estimates are considerably less accurate than the direct measurements of $T_{tp}(\text{H}_2^{18}\text{O})$, in part because the uncertainty in the calculation from the poorly known difference of dP/dT between solid and liquid phases^[15]. Other semi-empirical estimates of the T_{tp} of the isotopomers are possible by similar simultaneous solution of the empirical vapor pressure equations^[11]. However, in the case of H₂¹⁷O, there is no solid-phase vapor pressure data available and theoretical calculations based on molecular models must be substituted. These published estimates are shown in Table I and indicate the range of values based on the analytical and semi-empirical treatments.

In the recent experimental study by White, *et. al.*,^[3] the differences between the triple point temperatures of several samples of isotopically depleted water were determined with uncertainties as low as 0.02 mK. The data were used in a two-parameter least-squares treatment of the equation

$$T_{mix} = T_{VSMOW} + A_D \delta D + A_{17O} \delta^{17}O + A_{18O} \delta^{18}O \quad , \quad (3.)$$

where T_{mix} is the observed freezing point of the isotopic mixture assuming a linear dependence on the relative isotopic variations. The additional term proportional to $\delta^{17}O$ was included in the treatment with an *a priori* assigned depression constant $A_{17O} = 57 \mu\text{K}$. This value was derived by assuming a value for the triple point of pure H₂¹⁷O of 273.31 K (the geometric mean of 273.16 K and the H₂¹⁸O T_{tp} given in reference^[8]). The depression constant A_{17O} is then related to the triple point temperatures of the isotopomers according to

$$A_{17O} = \frac{R(^{17}\text{O})_{\text{SMOW}}}{[1 + R(^{17}\text{O})_{\text{SMOW}}]^2} [T(\text{H}_2^{17}\text{O}) - T(\text{H}_2^{16}\text{O})] \quad , \quad (4.)$$

together with analogous equations for A_D and A_{18O} . This approximation is derived in reference 4 and is applicable to depleted waters only where $\delta^{17}O < 1$.

Based on these assumptions and the temperature difference measurements provided by three different national standards laboratories the authors found depression constants of $A_D = (725 \pm 42) \mu\text{K}$ and $A_{18O} = (507 \pm 68) \mu\text{K}$. These values may be compared to those derived from a similar least-squares treatment^[4] of the Kiyosawa 1991 data expressed in mole fractions and then converted to the $\delta D / \delta^{18}O$ parameterization: $A'_D = 628 \mu\text{K}$ and $A'_{18O} = 642 \mu\text{K}$ which are discrepant by 13 % and 26 % respectively. These discrepancies are within experimental error at the 95% confidence level providing that a nominal 5 % uncertainty is assigned to the Kiyosawa 1991 data. Thus, the two data sets are considered consistent within the experimental uncertainties.

In contrast, the depression constant A_{17O} computed from the Kiyosawa 2004 data is $A'_{17O} = 596 \mu\text{K}$ or ten times the value assumed by White, *et. al.* If the value $596 \mu\text{K}$ for A_{17O} is incorporated *a priori* in the analysis of the triple point data from White, *et. al.*, serious inconsistencies become apparent. In particular, the observed triple point temperature differences for one particular triple point cell ('98/1'), which was 35.8 % depleted ($\delta^{17}O = -0.358$) in ^{17}O with respect to SMOW, should be some $190 \mu\text{K}$ greater than was observed on average. Such a temperature difference is about 10 times the measurement resolution of the three laboratories, so it should have been easily observed. We therefore conclude that the results of Kiyosawa 2004 are inconsistent with those of White, *et. al.*

Finally, we wish to point out the lack of a complete quantitative isotopic analysis of the ^{17}O enriched water sample used in Kiyosawa 2004. The author states:

“The H_2^{17}O sample was obtained as a mixture containing 10 atom-% H_2^{17}O in ordinary water with small undetermined amounts of H_2^{18}O , D_2O , *etc.*”

If we suppose the ^{17}O enriched water sample was contaminated with only 3.5 mole-% of D_2^{16}O , then this would be sufficient to produce 90 % of the observed effect on the melting points. This is based on the Kiyosawa 1991 data for D_2^{16}O melting points which indicates a constant proportionality of approximately 4 K per mole fraction D_2^{16}O (*i.e.* $\{3.5/10\} \times 4 \text{ K} = 1.4 \text{ K} \approx 0.9 \times 1.57 \text{ K}$). Most of the remaining effect, 0.17 K per mole fraction, could then be explained by the known ^{17}O enrichment at a magnitude consistent with other data and predictions.

In summary we find that the results of Kiyosawa 2004 on isotopically enriched solutions of H_2^{17}O are inconsistent with other data on depleted waters and inconsistent with theoretical predictions. We are unaware of any other isotopic system in which the substitution of one isotope of intermediate mass has such an incommensurate effect compared to that of the adjacent isotopes. We recommend that further isotopic analysis be performed on Kiyosawa's ^{17}O enriched water sample.

Table I: Literature values for melting- or triple-point-transition temperature differences between heavy-oxygen water isotopomers and light water.

$T(\text{H}_2^{17}\text{O})-T(\text{H}_2^{16}\text{O})$	$T(\text{H}_2^{18}\text{O})-T(\text{H}_2^{16}\text{O})$	Reference	Comments
	0.28 ± 0.02 °C	[16]	Observed melting point
	0.30 ± 0.01 °C	[8]	Observed triple point
0.28 °C	0.53 °C	[15]	Analytical calculation from VPIE
0.21 ± 0.05 °C	0.38 ± 0.05 °C	[11]	Semi-empirical calc. from VPIE
0.15 ± 0.01 °C		[3]	Calc. mean w/ H_2^{18}O T_{tp} from [8]
1.57 °C	0.32 °C	[2,1]	Extrapolated values from Kiyosawa

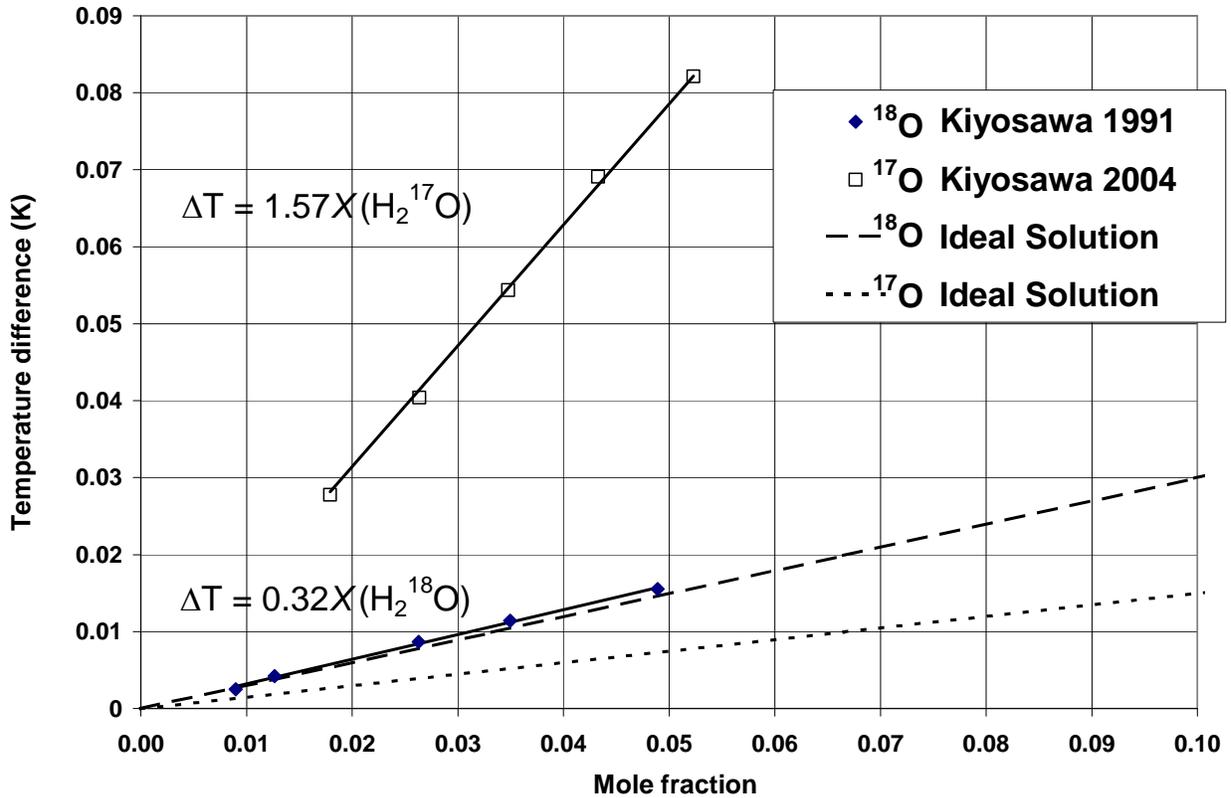


Figure 1: Kiyosawa H_2^{18}O data from 1991 and H_2^{17}O data from 2004. The equations are least-square fits to the data. The 'Ideal Solution' lines represent calculated phase boundaries of an ideal binary solid solution with $\Delta T=0.3$ K and 0.15 K between the isotopically pure forms of H_2^{18}O and H_2^{17}O respectively. The liquidus and solidus boundaries are practically linear and nearly coincident.

References

1. Kiyosawa, K., *J. Soln. Chem.* **33**, 323-326, (2004).
2. Kiyosawa, K., *J. Soln. Chem.* **20**, 583-588, (1991).
3. White, D. R., Dransfield, T. D., Strouse, G. F., Tew, W. L., Rusby, R. L., and Gray, J. In: *Temperature, Its Measurement and Control in Science and Industry*, **Vol 7**, D. C. Ripple, Ed., AIP CP 684, 221-226, (2003).
4. White, D. R., and Tew, W. L., In: *Report of the 22nd Meeting of the Consultative Committee for Thermometry*, Document CCT/03-21, BIPM, Sevres, France, (2003).
5. Gonfiantini, R., *Nature* **Vol. 271**, pp. 534-536, (1978).
6. Li, W., Jin, D., and Chang, T. L., *Kexue Tinbao* **33**, 1610-1613, (1988).
7. Baertschi, P., *Earth Plan. Sci. Lett.*, **31**, 341-344, (1976).
8. Nagano, Y., Miyazaki, Y., Matsuo, T., and Suga, H., *J. Phys. Chem.* **97**, 6897, (1993).
9. Jancso, G., Rebelo, L. P. N. and VanHook, W. A., *Chem. Rev.* **93**, 2645, (1993).
10. Seltz, H. *J. Amer. Chem. Soc.* **56**, 307, (1934).
11. Jancso, G. and Van Hook, W. A., *Chem. Rev.* **74**, 689, (1974).
12. Szapiro, S. and Steckel, F., *Trans. Faraday Soc.* **63**, 883-894, (1967).
13. Hopfner, A., *Angew. Chem. Internat. Edit.* **8**, 689, (1969).
14. Bigeleisen, J., *J. Chem. Phys.* **34**, 1485, (1961).
15. Van Hook, W. A., *J. Phys. Chem* **72**, 1234, (1968).
16. Steckel, F. and Szapiro, S., *Trans. Faraday Soc.* **59**, 331-343, (1963).