Comment on ‘Freezing Point Mixtures of $\text{H}_2^{16}\text{O}$ with $\text{H}_2^{17}\text{O}$ and Those of Aqueous $\text{CD}_3\text{CH}_2\text{OH}$ and $\text{CH}_3^{13}\text{CH}_2\text{OH}$ Solutions’

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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 $^{17}\text{O}$ enriched water show an unexpectedly large linear dependence on the concentration of $\text{H}_2^{17}\text{O}$. Surprisingly, the constant of proportionality to $\text{H}_2^{17}\text{O}$ concentration is nearly five times larger than that of $\text{H}_2^{18}\text{O}$ found in earlier studies by Kiyosawa $^2$ (Kiyosawa 1991). We show that the $\text{H}_2^{17}\text{O}$ 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 $\text{H}_2^{18}\text{O}$ and $\text{D}_2\text{O}$ results from Kiyosawa 1991$^4$ but not consistent with the $\text{H}_2^{17}\text{O}$ 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 $\text{H}_2^{17}\text{O}$ proportionality from Kiyosawa 2004 is about ten times larger than similarly predicted. One possible explanation is that the original $^{17}\text{O}$ enriched water sample contained a small amount of $\text{D}_2\text{O}$, 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 $\chi(\text{H}_2^y\text{O})$ for an isotopic solute $\text{H}_2^y\text{O}$ where $y = 17$ or 18 via $\chi(\text{H}_2^y\text{O}) = 0.018m/(1+0.018m)$. 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 $R(\text{O})_s$ of the sample ‘s’ and $R(\text{O})_{\text{SMOW}}$ of the IRM with respect to $^{16}\text{O}$ are used to calculate the relative depletion or enrichment according to

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

and the conversion to mole fraction is given by
\[ X(H_2^{17}O)_s = \frac{R^{(17)O}_{s}}{1 + R^{(17)O}_{s} + R^{(18)O}} \approx R^{(17)O}_{SMOW}(\delta^{17}O + 1), \tag{2} \]

where terms of order \( R^2 \) or greater have been neglected (\( R<<1 \) in all natural waters). The value \( R^{(17)O}_{SMOW} = 0.0003799 \) \[^6\] is used for calculations presented here. An analogous set of relations also apply in the case of \(^{18}O \) where \( R^{(18)O}_{SMOW} = 0.002\ 005\ 20(45), \) \[^7\].

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 \( H_2^{17}O/ H_2^{16}O \) system which is incommensurate with the relatively small deviations from ideality observed in either the \( H_2^{18}O/ H_2^{16}O \) 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 I).

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 \( H_2^{17}O + H_2^{16}O \) solutions are similar to the \( H_2^{18}O + H_2^{16}O \) solutions, then the \( H_2^{17}O \) solution melting data should be about 7 % above the ideal solution boundary, or approximately \( \Delta T = 0.16X(H_2^{17}O) \), 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 isotomers 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 \cite{12} performed vapor pressure ratio measurements on a variety of heavy-oxygen water samples, including one 55\% $\text{H}_2^{17}\text{O}$ enriched sample, and derived expressions for the relative isotopic fractionation constant $\alpha_{17}$ 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 \cite{13} to the $\text{H}_2^{16}\text{O}$ and $\text{H}_2^{18}\text{O}$ vapor pressures over that range.

The theory of VPIE as originated by Bigeleisen \cite{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 $\Delta T_{\text{tp}}$ between the triple-point temperatures $T_{\text{tp}}$ 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 $\Delta T_{\text{tp}} \ll T_{\text{tp}}$. An estimate for the $\text{H}_2^{17}\text{O}$ triple point based on the rule of the geometric mean using the Nagano, \textit{et. al.} $\text{H}_2^{18}\text{O}$ 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 \cite{15}. These estimates are considerably less accurate than the direct measurements of $T_{\text{tp}}(\text{H}_2^{18}\text{O})$, in part because the uncertainty in the calculation from the poorly known difference of $dP/dT$ between solid and liquid phases \cite{15}. Other semi-empirical estimates of the $T_{\text{tp}}$ of the isotopomers are possible by similar simultaneous solution of the empirical vapor pressure equations \cite{11}. However, in the case of $\text{H}_2^{17}\text{O}$, 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, \textit{et. al.}, \cite{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

$$T_{\text{mix}} = T_{\text{VSMOW}} + A_0 \delta \text{D} + A_{17}\delta^{17}\text{O} + A_{18}\delta^{18}\text{O}, \tag{3.}$$

where $T_{\text{mix}}$ is the observed freezing point of the isotopic mixture assuming a linear dependence on the relative isotopic variations. The additional term proportional to $\delta^{17}\text{O}$ was included in the treatment with an \textit{a priori} assigned depression constant $A_{17} = 57 \mu\text{K}$. This value was derived by assuming a value for the triple point of pure $\text{H}_2^{17}\text{O}$ of 273.16 K (the geometric mean of 273.16 K and the $\text{H}_2^{18}\text{O}$ $T_{\text{tp}}$ given in reference \cite{18}). The depression constant $A_{17}$ is then related to the triple point temperatures of the isotopomers according to

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

Based on these assumptions and the temperature difference measurements provided by three different national standards laboratories the authors found depression constants of \( A_D = (725 \pm 42) \mu K \) and \( A_{18O} = (507 \pm 68) \mu K \). 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 \( \delta D / \delta^{18O} \) parameterization: \( A'_D = 628 \mu K \) and \( A'_{18O} = 642 \mu K \) 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 \( A'_{17O} = 596 \mu K \) or ten times the value assumed by White, et. al. If the value 596 \( \mu K \) for \( A_{17O} \) is incorporated \textit{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 \((\delta^{17O} = -0.358)\) in \(^{17O}\) with respect to SMOW, should be some 190 \( \mu K \) 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 \(^{17O}\) enriched water sample used in Kiyosawa 2004. The author states:

“The \( \text{H}_2^{17O} \) sample was obtained as a mixture containing 10 atom-% \( \text{H}_2^{17O} \) in ordinary water with small undetermined amounts of \( \text{H}_2^{18O} \), \( \text{D}_2 \), etc.”

If we suppose the \(^{17O}\) enriched water sample was contaminated with only 3.5 mole-% of \( \text{D}_2^{16O} \), 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 \( \text{D}_2^{16O} \) melting points which indicates a constant proportionality of approximately 4 \( K \) per mole fraction \( \text{D}_2^{16O} \) \((i.e. \{3.5/10\} \times 4 \text{\ K} = 1.4 \text{\ K} \approx 0.9 \times 1.57 \text{\ K})\). Most of the remaining effect, 0.17 \( K \) per mole fraction, could then be explained by the known \(^{17O}\) 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 \( \text{H}_2^{17O} \) 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 \(^{17O}\) enriched water sample.
Table I: Literature values for melting- or triple-point-transition temperature differences between heavy-oxygen water isotopomers and light water.

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

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