The Density at 25 °C of D_2O with Natural Oxygen Isotopic Composition

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In measuring the influence of oxygen isotopic composition and of hydrogen content on the density of heavy water an extrapolation was made to 100% D_2O with natural oxygen isotopic composition, starting with the density of a highly enriched heavy water (99.95% D_2O, about natural oxygen isotopic composition).

A value of 1104.481 kg/m^3 at 25 °C was obtained.

1. Introduction

The composition of a mixture of D_2O and H_2O is very often determined by a method based on the measurement of the density of the mixture. Such methods have the advantage of being simple, both in conception and in the apparatus required, and can give a high degree of accuracy. Clearly they are based on an accurate knowledge of the density dependence on isotopic composition.

We report here a remeasurement of the density of pure D_2O with natural (i. e. as in air) oxygen isotopic composition and at a temperature of 25 °C. Since a sample of this nature was not available measurements were made on two sets of samples, one with differing heavy water contents in the range of 99.60 to 99.95% D_2O and almost the same oxygen isotopic composition, and one with differing ^{18}O contents (0.20 to 0.38%). From these measurements the required density was found by extrapolation.

Mass spectrometric methods were used to measure the isotopic composition of the samples both for hydrogen and oxygen.

2. Samples

A first group of samples was obtained by starting with a quantity of heavy water with a D_2O content of about 99.8 mole % and an ^{18}O content of 0.38 atom %. This water was partly normalized in oxygen isotopic composition by means of exchange with CO_2. The normalized water was then mixed in 3 mixing ratios 1:1, 3:1 and 1:3 with original water giving 4 samples with differing ^{18}O contents ranging from 0.26 to 0.38 atom %.

A second group of samples was obtained by mixing two waters with about natural oxygen isotopic composition with differing amounts of light water. In this way a series of 7 waters was obtained with ^{18}O content of either 0.203 or 0.212 atom % and D_2O content ranging from 99.61 to 99.95 mole %.

A final sample on which all measurements were done with the utmost care had a D_2O content of 99.95% and an ^{18}O content of 0.205 atom %. From this sample the extrapolation was made to 100% D_2O.

3. Density Measurements

A carefully fabricated and well aged float (V 26) with a volume of 20.7 cm^3 was calibrated in H_2O by hydrostatic weighing together with two silicon density standards CBNM 1 and CBNM 2. The density of H_2O was derived from [5]:

$$\varrho_{\mathrm{w}} = \left[1 - \frac{(t_{\mathrm{w}} - 3.9863)^2}{508929.2} \cdot \frac{t_{\mathrm{w}} + 288.9414}{t_{\mathrm{w}} + 68.12963}\right] \cdot [0.999973] \cdot \left[\frac{1}{1 - C\left(\frac{B}{760} + \frac{D}{1033} - 1\right)}\right].$$

The right side of this formula is composed of three terms separated by square brackets. The first term is the Tilton-Taylor formula [6] for ϱ_{w} as function of temperature t_{w} in g/ml. The second term reduces these values to g cm^{-3}. The third term finally is a correction for pressure, where C denotes the compressibility of water ($C = 47.7$ ppm/atm), B the barometric pressure in mm Hg and D the depth of immersion in cm. The values measured for float V 26 are listed in Table 1.

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Table 1. Mass, volume and density of float V 26 at 25 °C.

Mass	$22.85857 \pm 1 \cdot 10^{-5}$ g
Volume	$20.69702 \pm 2 \cdot 10^{-5}$ cm³
Density	$1.104438 \pm 1.6 \cdot 10^{-6}$ g cm⁻³

Temperature variations in the test tube during the density measurements on heavy water were smaller than ± 0.0003 K. The temperature was measured by a resistance thermometer of 25.5 Ohm and a Müller bridge type G 2 Leeds & Northrup. A water triple point cel was used as base for the temperature measurement. The D_2O to be measured was directly distilled under vacuum in the tube containing the float. After the determination of the density, part of heavy water was used for the measurement of the isotopic composition.

The density of the heavy water at 25 °C was evaluated using the curve for thermal expansion of D_2O as established in earlier measurements (Brulmans et alias [7]).

The equilibrium temperature of the float V 26 in the density measurement of the D 223 sample (cfr. 5.3) was 24.9704 °C, so the correction to reduce to 25 °C is small.

4. Determination of Isotopic Composition

4.1. Oxygen Isotopic Content

The method used was to bring a certain amount of natural CO_2 into contact with a $3-4$ cm³ heavy water sample and establish isotopic equilibrium, a catalyst not being required. The equilibrated CO_2 is transferred to the mass spectrometer where the intensity ratio of ions with mass 44 and mass 46 is measured. Mass 46 ions are $^{16}C\,^{16}O\,^{18}O^+$, $^{13}C\,^{16}O\,^{17}O^+$ and $^{12}C\,^{17}O\,^{17}O^+$, mass 44 ions only $^{12}C\,^{16}O\,^{16}O^+$. The mass spectrometer is not calibrated but samples are measured relative to natural CO_2, for which an oxygen isotopic composition is assumed as determined by Nier [3] for air oxygen: $^{17}O = 0.0375$ atom %; $^{18}O = 0.2039$ atom %.

The ^{17}O concentration could not be measured with sufficient accuracy since it is necessary to obtain it from the 45/44 isotope ratio which depends more strongly on the ^{13}C content. However, the ^{17}O concentration is about a factor of 5 to 6 smaller than the ^{18}O concentration and therefore is about 10 times less important in determining the density of the heavy water.

For our purpose we calculated the ^{17}O content by assuming that the enrichment in ^{17}O is half that of ^{18}O.

The oxygen isotopic composition of the water can be calculated from these measurements and assumptions if the separation factor of the oxygen isotopes between CO_2 and D_2O is introduced. This separation factor has been derived from a publication by Staschewski [4]:

$$\frac{(^{18}O/^{16}O)\,CO_2}{(^{18}O/^{16}O)\,D_2O,\,\text{liq.}}\;(25\ ^\circ C) = 1.026 \pm 0.001\,.$$

4.2. Deuterium Content

For the determination of the deuterium content of an unknown sample of heavy water the following procedure was developed [1]: In a dry box a conditioned PtO_2 catalyst is added to a sample of $3-4$ cm³ of the heavy water. After thorough degassing of the sample a measured quantity of about 8 cm³ NTP hydrogen gas with a high deuterium content is added which under the influence of the PtO_2 catalyst comes into isotopic equilibrium with the heavy water. The bulb with water, gas and catalyst is shaken in a thermostat bath at 25 °C for some hours.

The deuterium gas is then transferred to a sample inlet volume of the mass spectrometer passing two liquid nitrogen traps for drying.

The isotopic ratio (ratio of ion intensities) HD^+/D_2^+ is determined for this equilibrated deuterium sample alternatively with determination of the isotope ratio of a deuterium sample equilibrated with a reference heavy water sample, which had been previously calibrated by a method described in Reference [1].

In this way the absolute D_2O content of the unknown heavy water sample is measured with an accuracy of 0.001 mole % D_2O. This is equivalent with an uncertainty in the density of 1×10^{-6} g/cm³.

5. Experimental Results

5.1. Influence of the Oxygen Isotopic Composition on the Density of Heavy Water

Density and isotopic composition have been measured for 4 water samples with a ^{18}O concentration ranging from 0.256 to 0.378 atom % and a D_2O content ranging from 99.73 to 99.82 mole %.

After converting the measured densities to the values corresponding to 100% D_2O the results of Table 2 are obtained:

Table 2. Extrapolated density at 25 °C and oxygen isotopic content of 4 water samples.

Water	d^{25} (100% D) g/cm^3	^{17}O-fraction	^{18}O-fraction
D 32	1.104657	0.000 456	0.003 036
D 33	1.104742	527	3 779
D 35	1.104600	419	2 560
D 36	1.104716	508	3 553

Least squares fitting of a straight line through the points correlating extrapolated density and the quantity (1/2 ^{17}O-fraction + ^{18}O-fraction) gives as result:

$$\frac{\Delta d^{25}}{\Delta(\frac{1}{2}\,{}^{17}\mathrm{O}+{}^{18}\mathrm{O})} = 0.1113\ \mathrm{g/cm^3}\ \text{at}\ 25\ {}^\circ\mathrm{C} \pm 0.008\,.$$

5.2. *The Influence of the Hydrogen Isotopic Composition on the Density of Heavy Water*

Density and isotopic composition have been measured for 7 samples with a ^{18}O concentration close to that of air oxygen (ranging from 0.202 to 0.212 atom %). After reducing the measured densities to the values corresponding with a ^{18}O content of 0.204 atom % the results of Table 3 were obtained. The corrections are so small that the error on these is below 10^{-7} g/cm^3.

Calculating the coefficients of a linear correlation between density and D_2O content by a least square method we arrive at a density effect of $1.099 \times 10^{-3} \pm 0.014$ g/cm^3 mole % at 25 °C

Table 3. Extrapolated density at 25 °C and D_2O content of 7 heavy water samples.

Water	d^{25} (air oxygen composition) g/cm^3	D_2O (mole %)
D 216	1.104 0492	99.6145
D 200	2018	7519
D 201	2586	7955
D 213	3076	8587
D 217	3096	8513
D 215	4140	9464
D 198	4241	9535

5.3. *Extrapolating the Density of a Highly Enriched Heavy Water to 100% D_2O with Air Oxygen Isotopic Composition*

The isotopic composition and the density measured for the sample D 223 are given in Table 4.

Table 4. Density at 25 °C and isotopic content of a highly enriched heavy water sample.

Water	d^{25} g/cm^3	^{17}O-concentration	^{18}O-concentration	D_2O (mole %)
D 223	1.104431_6 ± 0.000002	0.0376 atom % ± 0.0001	0.2051 atom % ± 0.0001	99.9538 ± 0.0010

The correction on the density to reduce to an oxygen isotopic composition of 0.0375% ^{17}O and 0.2039% ^{18}O amounts to $-0.113 \times 0.0000125 = (-1.4 \pm 0.2) \times 10^{-6}$ g/cm^3. The uncertainty of this correction is due to an error in (1/2 ^{17}O + ^{18}O)-fraction of 0.000002. The extrapolation to 100% D_2O gives a change in the density of $1.099 \times 10^{-3} \times 0.0462 = (5.08 \pm 0.17) \times 10^{-5}$ g/cm^3. The error given is the combined statistical error in both factors. We therefore arrive at a final density value for 100% D_2O with natural air oxygen isotopic composition of

$$d^{25} = 1.104481 \pm 0.000003\ \mathrm{g/cm^3}\,.$$

The given uncertainty is a combined effect of statistical errors in the measured density and the two applied corrections.

6. Comparison with Literature Values

In Table 5 the results of measurements of the D_2O density of Kirshenbaum (1945), Voskuyl (1945), Shatenstein (1950), Wladimirski (1950–53), Steckel and Szapiro (1963) are reduced to the same experimental conditions.

For the common oxygen isotopic composition that of natural air is taken.

In some cases where the oxygen isotopic composition is given as that of natural mean river water this implies a correction on the density of about $+7 \cdot 10^{-6}$ g/cm^3. Chemical purity and dissolved gas content are supposed to have been of no significant density effect.

The first six entries of the table are reproduced from the book of Shatenstein [13], but reduced to air

Table 5. Density at 25 °C of D_2O (g/cm^3) with air oxygen isotopic composition.

Kirshenbaum et al. [8]	1.10449
Voskuyl, Barash [9]	1.10448_0
Shatenstein et al. [10]	1.10442_9
Wladimirski et al. [11]	1.10444
	1.10446
	1.10448
Steckel, Szapiro [12]	1.10444
This work	1.104481

oxygen composition where this was not already the case.

Steckel and Szapiro published results about the physical properties of heavy oxygen water, from which a value for the density of D_2O (with natural O abundance) was deduced.

7. Conclusion

The density value obtained in this work is in fair agreement with previously determined values as is shown in Table 5. However, as the detection limit of D_2O concentration variations is well below 0.001 mole % and density variations below 10^{-6} g/cm^3 can be detected the discrepancies between the density values cannot be ascribed to random spread in the measurement results, but must be due to some systematic effect in the procedure or calibration of some of the determinations used in obtaining final numerical values.

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