

Notizen

Thermal Expansion of Heavy Water between 7 and 26 °C

J. Brulmans, J. Verdonck, and H. L. Eschbach

Central Bureau for Nuclear Measurements, Geel/Belgium

(Z. Naturforsch. **30 a**, 107–108 [1975];
received November 9, 1974)

Using six carefully calibrated quartz floats the thermal expansion of water with a D₂O content of 99.74 mole % has been measured between 7 and 26 °C. The extrapolation to 100% D₂O with natural oxygen isotopic composition is made.

The isotopic composition of a mixture of D₂O and H₂O is often determined by methods based on density measurements. It can be shown (Shatenstein¹, Rowland²) that the accuracy of such measurements depends on the reliability of the densities of pure normal and pure heavy water. Furthermore for many application it is very useful to know the thermal expansion of D₂O at or below room temperature with high accuracy. It was the aim of these experiments to establish the temperature dependence of 100% D₂O in the temperature range between 7 and 26 °C. (It should be noted that in the following all values given refer to water with a natural isotope composition of oxygen.)

All densities were determined by the float method^{1,3,4}. This method is based essentially on the measurement of the temperature at which a calibrated float is in equilibrium with the sample to be measured. The floats are made of fused silica and have a total volume of about 20 cm³.

The temperature dependence of the heavy water was determined in two steps. First six floats were adjusted to the expected densities of D₂O. An attempt was made to distribute the equilibrium temperatures at equal intervals in the temperature range. The exact calibration of the floats was carried out by hydrostatic weighing in H₂O at their equilibrium temperature for heavy water. By doing so effects due to thermal expansion were avoided. The error on these calibrations is $2 \cdot 10^{-6} \text{ g cm}^{-3}$. The density of light water at the calibration temperatures was calculated using a formula given by Tilton and Taylor⁵. With these six floats the temperature dependence of 99.74 mole% D₂O was measured.

In the second step of the measurement the density of very highly enriched water (99.95 mole%) of which only a small quantity was available was

measured at an equilibrium temperature near 25 °C. This sample (D 223 *) was obtained from the CEA, France. For the density measurement a well-aged float (V 26) was recalibrated together with two high precision density standards made out of silicon monocrystals **. The density of this heavy water (D 223) at the equilibrium temperature of $24.9704 \text{ °C} \pm 5 \cdot 10^{-4} \text{ K}$ was $d = 1.104438_0 \pm 2 \cdot 10^{-6} \text{ g cm}^{-3}$. From this a corrected value for the density of pure D₂O at 25 °C was derived: $d^{25} = 1.104481_0 \text{ g cm}^{-3}$. Further details on these measurements will be published elsewhere⁶.

The extrapolation from the measurements reported to a temperature-density curve for 100% D₂O is based on two assumptions.

In the first place it is assumed that mixtures of deuterium oxide and ordinary water form ideal solutions. Secondly it is assumed that the shape of the curve for 99.74 mole% D₂O is within the limits of error identical with that for 100% D₂O.

That the first assumption can be made has been shown by Longworth⁷ who found that within the range of error for his density measurements ($1 \cdot 10^{-5}$) the mixture of D₂O and H₂O behaves indeed as an ideal one and its volume is equivalent to the total volumes of the components. We confirmed this for high D₂O concentrations with a smaller error. In the region <99 mole% D₂O it was found with an uncertainty of $2 \cdot 10^{-6} \text{ g cm}^{-3}$

Table 1. Equilibrium temperatures of pure heavy water and corresponding densities.

Float nr.	Equilibrium temperature t (°C)	Density d (g cm ⁻³)
1	$25.6179 \pm 5 \cdot 10^{-4}$	$1.104344_0 \pm 5 \cdot 10^{-6}$
2	$23.5194 \pm 5 \cdot 10^{-4}$	$1.104785_1 \pm 5 \cdot 10^{-6}$
3	$20.8436 \pm 5 \cdot 10^{-4}$	$1.105262_3 \pm 5 \cdot 10^{-6}$
4	$17.6499 \pm 5 \cdot 10^{-4}$	$1.105689_6 \pm 5 \cdot 10^{-6}$
5	$14.7797 \pm 5 \cdot 10^{-4}$	$1.105933_7 \pm 5 \cdot 10^{-6}$
6	$12.4678 \pm 5 \cdot 10^{-4}$	$1.106039_2 \pm 5 \cdot 10^{-6}$
6	$10.1286 \pm 5 \cdot 10^{-4}$	$1.106047_2 \pm 5 \cdot 10^{-6}$
5	$7.9332 \pm 5 \cdot 10^{-4}$	$1.105948_4 \pm 5 \cdot 10^{-6}$

* The isotopic composition of this water was measured by T. Babeliowsky (see Babeliowsky and Brulmans⁶).

** One of these standards (BCMN 1) has been sent to the BIPM and the other (BCMN 2) to the NBS for an intercomparison. In an earlier check the density measurements with BCMN 2 carried out at the NBS and the CBNM differed only by $2 \cdot 10^{-6} \text{ g cm}^{-3}$.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

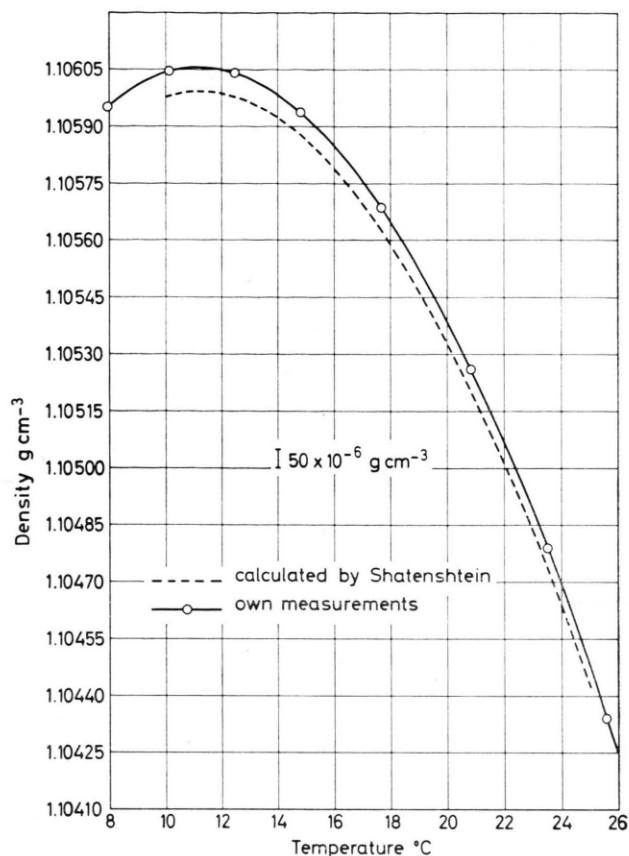


Fig. 1.

that a decrease of the deuterium oxide concentration of 0.1 mole% lowered the density of the water linearly by $1.099 \cdot 10^{-4} \text{ g cm}^{-3}$ (see also Babeliowsky and Brulmans⁶).

The second assumption is corroborated by (Shatenstein¹) who reported a curve based on his own measurements as well as on an evaluation of data found in literature.

If now the measurements with the six floats are extrapolated to pure deuterium oxide the values in Table 1 result.

A fourth degree polynomial can be fitted to the experimental points in such a way that $\Delta d = 2.06 \cdot 10^{-6} \text{ g cm}^{-3}$ (see solid curve in Figure 1). It should be noted that between 10 and 25 °C the relative values taken from Shatenstein's curve (dashed curve Fig. 1) agree within $1 \cdot 10^{-5} \text{ g cm}^{-3}$.

We wish to thank Dr. R. Batchelor for his useful comments on the manuscript.

¹ A. I. Shatenstein, E. A. Yakovleva, E. N. Zyyagintseva, Ya. M. Varshavskii, E. A. Izrailevich, and N. M. Dykhno, Isotopic Water Analysis AEC-tr 4136 [1960].

² P. R. Rowland, AEEW-M 745 (1967).

³ J. Spaepen, Mededelingen van de Koninklijke Vlaamse Academie voor Wetenschappen XIX (1957), Nr. 5.

⁴ I. Kirshenbaum, Physical Properties and Analyses of Heavy Water, McGraw-Hill, New York 1951.

⁵ L. W. Tilton and J. K. Taylor, J. Res. NBS **18**, 205 [1937].

⁶ T. Babeliowsky and J. Brulmans, to be published.

⁷ L. Gl. Longworth, J. Am. Chem. Soc. **59**, 1483 [1937].