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Thermal Expansion of Heavy Water between 7 and 26 °C

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Using six carefully calibrated quartz floats the thermal expansion of water with a D_2O content of 99.74 mole % has been measured between 7 and 26 °C. The extrapolation to 100% D_2O with natural oxygen isotopic composition is made.

The isotopic composition of a mixture of D_2O and H_2O is often determined by methods based on density measurements. It can be shown (Shatenstein[1], Rowland[2]) 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 D_2O at or below room temperature with high accuracy. It was the aim of these experiments to establish the temperature dependence of 100% D_2O 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 D_2O. 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 H_2O at their equilibrium temperature for heavy water. By doing so effects due to thermal expansion were avoided. The error on these calibrations is $2 \cdot 10^{-6}$ g cm^{-3}. The density of light water at the calibration temperatures was calculated using a formula given by Tilton and Taylor[5]. With these six floats the temperature dependence of 99.74 mole% D_2O 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 °C $\pm 5 \cdot 10^{-4}$ K was $d = 1.104\,438_0 \pm 2 \cdot 10^{-6}$ g cm^{-3}. From this a corrected value for the density of pure D_2O at 25 °C was derived: $d^{25} = 1.104\,481_0$ g cm^{-3}. Further details on these measurements will be published elsewhere[6].

The extrapolation from the measurements reported to a temperature-density curve for 100% D_2O 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% D_2O is within the limits of error identical with that for 100% D_2O.

That the first assumption can be made has been shown by Longsworth[7] who found that within the range of error for his density measurements $(1 \cdot 10^{-5})$ the mixture of D_2O and H_2O behaves indeed as an ideal one and its volume is equivalent to the total volumes of the components. We confirmed this for high D_2O concentrations with a smaller error. In the region <99 mole% D_2O it was found with an uncertainty of $2 \cdot 10^{-6}$ 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	$25.617\,9 \pm 5 \cdot 10^{-4}$	$1.104\,344_0 \pm 5 \cdot 10^{-6}$
2	$23.519\,4 \pm 5 \cdot 10^{-4}$	$1.104\,785_1 \pm 5 \cdot 10^{-6}$
3	$20.843\,6 \pm 5 \cdot 10^{-4}$	$1.105\,262_3 \pm 5 \cdot 10^{-6}$
4	$17.649\,9 \pm 5 \cdot 10^{-4}$	$1.105\,689_6 \pm 5 \cdot 10^{-6}$
5	$14.779\,7 \pm 5 \cdot 10^{-4}$	$1.105\,933_7 \pm 5 \cdot 10^{-6}$
6	$12.467\,8 \pm 5 \cdot 10^{-4}$	$1.106\,039_2 \pm 5 \cdot 10^{-6}$
6	$10.128\,6 \pm 5 \cdot 10^{-4}$	$1.106\,047_2 \pm 5 \cdot 10^{-6}$
5	$7.933\,2 \pm 5 \cdot 10^{-4}$	$1.105\,948_4 \pm 5 \cdot 10^{-6}$

[*] The isotopic composition of this water was measured by T. Babeliowsky (see Babeliowsky and Brulmans[6]).

[**] 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 $2 \cdot 10^{-6}$ g cm^{-3}.

that a decrease of the deuterium oxide concentration of 0.1 mole% lowered the density of the water linearly by $1.099 \cdot 10^{-4}$ g cm^{-3} (see also Babeliowsky and Brulmans [6]).

The second assumption is corroborated by (Shatenstein [1]) 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 $\overline{\Delta d} = 2.06 \cdot 10^{-6}$ 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 $1 \cdot 10^{-5}$ g cm^{-3}

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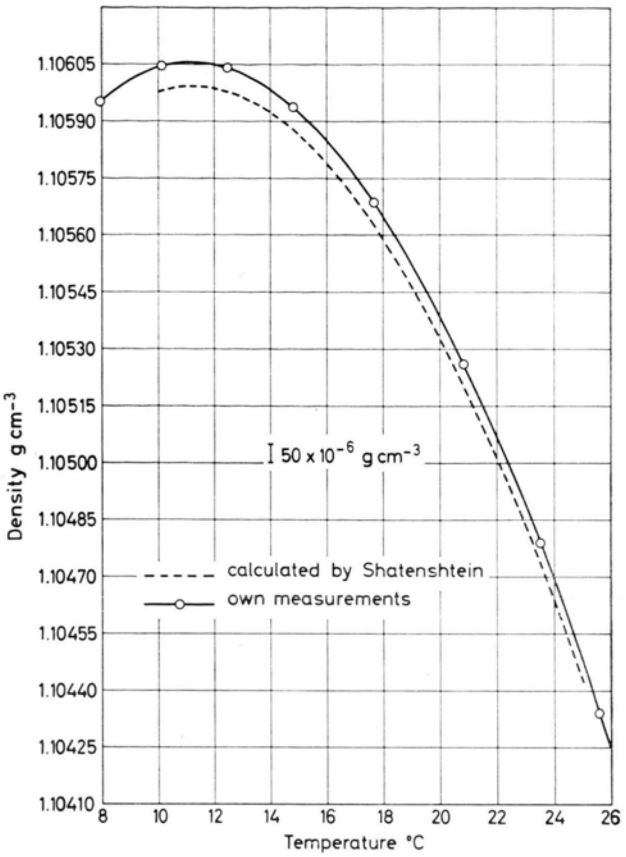

Fig. 1.

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