SPEED OF SOUND, ISOCHORIC HEAT CAPACITY, AND COEFFICIENT OF ISOTHERMAL COMPRESSION OF HEAVY WATER AT ATMOSPHERIC PRESSURE

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Experimental values of the speed of sound in heavy water at atmospheric pressure are presented for temperatures to 100°C. Values of isochoric heat capacity and the coefficient of isothermal compression are calculated for heavy water at atmospheric pressure over the temperature range indicated.

The isochoric heat capacity and isothermal compressibility of liquids may be calculated from data on acoustical properties. However, for heavy water at temperatures to 100°C and atmospheric pressure such calculations cannot be performed with sufficient accuracy, since the divergence of the few available experimental values of the speed of sound reaches 16-17 m/sec, greater than 1%. A new measurement of the speed of sound was performed by the frequency-pulse method, using the apparatus described in [1]. The error of the experimental values obtained, presented in Table 1, in accordance with [1] comprises 0.008% with consideration of errors in temperature-referencing and composition of the heavy water used. A comparison of the new results with the most reliable previous data [2] is shown in Fig. 1. The deviations at the endpoints are evidently caused by the fact that extrapolated values [2] were used in this case. For the comparison the speeds were recalculated for a 100% heavy-water concentration, using the additive property of the square of the speed of sound in the mixture components [3]. All further calculations were performed for 100% heavy water.

The speed of sound values obtained were approximated by an equation with coefficients calculated by the method of least squares on a BÉSM-4 computer:

$$w = \sum_{i=0}^{4} a_i (T/100)^i , \tag{1}$$

where $a_0 = -11930.27$; $a_1 = 13144.04$; $a_2 = -4894.21$; $a_3 = 827.469$; and $a_4 = -54.22109$. The values of Eq. (1) deviate from the original values by not more than 0.003%.

The temperature dependence of the speed of sound in heavy water, as in normal water, has an anomolous character, with the maximum speed located at 75.5°C in contrast to 74.31°C for normal water. The speed-of-sound values in heavy water are approximately 100 m/sec lower than corresponding values for normal water.

To calculate the isochoric heat capacity and coefficient of isothermal compressibility the well-known relationships

$$c_v = \frac{c_p}{1 + \dfrac{w^2 T \alpha^2}{c_p}} \tag{2}$$

and

$$\beta_t = \frac{v}{w^2\left(1 + \dfrac{w^2 T \alpha^2}{c_p}\right)} \tag{3}$$

were used, with v and α calculated with an equation from [4], while a separate equation was obtained for isobaric heat capacity. The initial data for the latter were the experimental results of Ferguson at temperatures of 4-52.8°C presented in [5] and the same study's data on the ratio of heat capacities of heavy and normal water for the range 60-120°C found by Rivkin and Egorov, together with heat-capacity values of normal water from [6].

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TABLE 1. Experimental Values of the Speed of Sound in Heavy Water; w, m/sec

t, °C	Concentration, %			t, °C	Concentration, %		
	99,73	99,3	100		99,73	99,3	100
4	1321,69	—	1321,41	65	—	1459,39	1458,71
6	1330,82	—	1330,54	70	—	1461,01	1460,37
8	1339,55	—	1339,27	75	—	1461,69	1461,01
10	1347,83	—	1347,55	80	—	1461,30	1460,62
12	1355,79	—	1355,51	85	—	1460,00	1459,32
20	1384,06	—	1383,78	90	—	1457,78	1457,11
30	1411,94	1412,35	1411,67	100	—	1450,96	1450,29
50	1447,13	1447,53	1446,86				

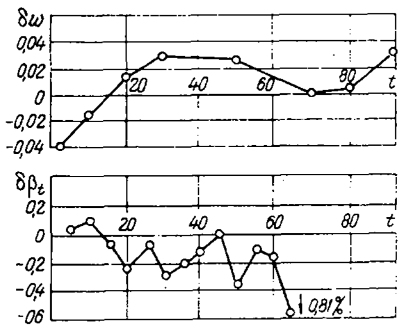

Fig. 1

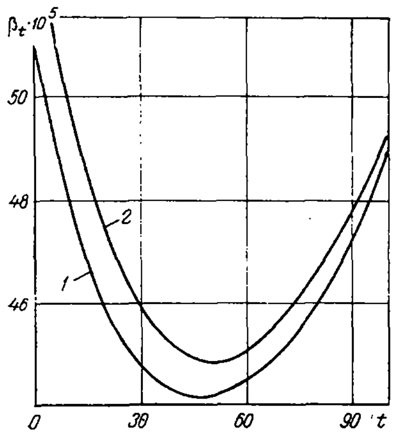

Fig. 2

Fig. 1. Comparison of experimental speed of sound values and calculated isothermal compressibility coefficient data with data of other authors: $\delta w = \{(w[2] - w[\text{MEI, i.e., present study}])/w[\text{MEI}]\} \cdot 100\%$, $\delta\beta_t = (\beta_t[7] - \beta_t[\text{MEI}])/\beta_t[\text{MEI}]\} \cdot 100\%$.

Fig. 2. Isothermal-compressibility coefficient of normal and heavy water versus temperature at atmospheric pressure: 1) H_2O according to data of [8]; 2) D_2O (present study).

TABLE 2. Calculated Values

t, °C	c_p, $\frac{kJ}{kg \cdot °C}$	c_v, $\frac{kJ}{kg \cdot °C}$	$\beta_t \cdot 10^5$, $\frac{1}{MPa}$	w, m/sec
4	4,2287	4,2199	51,911	1321,42
5	4,2280	4,2216	51,515	1326,04
10	4,2242	4,2239	49,790	1347,60
15	4,2200	4,2180	48,427	1366,79
20	4,2157	4,2063	47,353	1383,77
25	4,2115	4,1902	46,517	1398,69
30	4,2077	4,1710	45,883	1411,68
35	4,2042	4,1495	45,423	1422,88
40	4,2013	4,1263	45,114	1432,40
45	4,1990	4,1018	44,939	1440,38
50	4,1973	4,0766	44,885	1446,90
55	4,1964	4,0507	44,940	1452,08
60	4,1961	4,0245	45,096	1456,00
65	4,1965	3,9982	45,344	1458,74
70	4,1975	3,9718	45,680	1460,39
75	4,1989	3,9454	46,098	1461,00
80	4,2007	3,9190	46,595	1460,63
85	4,2027	3,8927	47,169	1459,34
90	4,2047	3,8663	47,817	1457,17
95	4,2065	3,8397	48,539	1454,15
100	4,2078	3,8129	49,335	1450,30
101	4,2080	3,8075	49,503	1449,44

Using the method of least squares, from these data the equation

$$c_p = \sum_{i=0}^{4} a_i (T/100)^i \tag{4}$$

was obtained with the BÉSM-4 computer, where $a_0 = -16.5786$; $a_1 = 26.5926$; $a_2 = -12.5871$; $a_3 = 2.61575$; $a_4 = -0.2016118$. The values of Eq. (4) diverge from the initial data by not more than 0.2%.

The values of speed of sound, isobaric and isochoric heat capacity, and coefficient of isothermal compression for heavy water, calculated with Eqs. (1)-(4), are presented in Table 2. The experimental and calculated values in the table refer to temperature values taken by MPTSh-68.

A comparison of the calculated β_t values with the experimental values of [7] is shown in Fig. 1. The divergence does not exceed 0.4%, with the exception of 65°C, where it reaches 0.81%.

The character of the temperature dependence of β_t in heavy water (Fig. 2) is anomalous, like that of normal water, with the difference that for heavy water the minimum is located at 50°C instead of 46°C for normal water [8]. The numerical values of β_t for heavy water are somewhat larger than for normal water: by 4.5% at 5°C and by 0.6% at t=100°C.

The temperature dependence of isochoric heat capacity in heavy water is also similar to the same function for normal water. Heat capacity decreases with growth in temperature, without reaching a minimum. The calculated values can be compared with others only at the two experimental points presented in [9]. The divergence at 21.14°C comprises 0.15%, while at 96.91°C it is 9%, with the experimental value higher. Such divergence can probably be explained by inaccuracy of the experimental value, since the c_v values obtained in [9] at 21.14 and 96.91°C are practically equal. At the same time it is known that isochoric heat capacity of normal water decreases with increase in temperature on the isobars in the liquid region [8, 10], and similar behavior may be assumed in heavy water on the basis of thermodynamic similarity.

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