THE DENSITY OF HEAVY WATER BETWEEN 25° AND 100°C.

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ABSTRACT

The density of heavy water has been determined between 25° and 100°C. Using the known data below 25°, we are able to construct a density table for heavy water between its freezing and boiling points with an accuracy of five units in the fifth decimal place. Figures are given to show the density difference between heavy water and ordinary water and also their density ratio, which tends to pass over a maximum at a temperature not far above the boiling point.

INTRODUCTION

Apart from the earlier determinations of the density of heavy water with errors in the fourth decimal place, Tronstad and his collaborators[1] were the first to carry out a very accurate determination in the temperature range between 10° and 27° with an error of one unit in the fifth decimal place, while Johnston's value[2] at 27° and Swift's value[3] at 5° are somewhat less accurate.

The density measurement was first extended to 50° in this laboratory[4] and later by Wirtz[5]. Above 50°, the only data known in the literature are Bridgman's values[6] at 60° and 80°, which are believed to have an error of a few units in the fourth decimal place.

MATERIAL

Two ampules of heavy water of different concentrations used in this experiment were prepared by the Norsk Hydro-Elektrisk Kvaelstofaktieselskab, Oslo. This commercial heavy water is known[7] to contain 0.32

1. K. Stokland, E. Ronaess and L. Tronstad, *Trans. Faraday Soc.* **35** (1939), 312.
2. H.L. Johnston, *J. Am. Chem. Soc.* **61** (1939). 878.
3. E. Swift, Jr., *ibid.* **61** (1939), 198.
4. T. L. Chang and J.Y. Chien, *ibid.* **63** (1941), 1709.
5. K. Wirtz, *Naturwiss.* **30** (1942), 330; *Physik.* Z. **43** (1942), 465.
6. P. W. Bridgman, *J. Chem. Phys.* **3** (1935), 547.
7. L. Tronstad and J. Brun, *Trans. Faraday Soc.* **34** (1938), 766.

weight per cent of D_2O^{18}, while the normal concentration of O^{18} corresponds to 0.21 weight per cent. A distilling apparatus of pyrex glass is specially made for the purpose of vacuum distillation. It consists of a 25-milliliter bulb with a neck and an upper extension, which ends with a ground-joint connection leading to the side-arm of a receiver. The ground-joint connection can be sealed with mercury during distillation. The receiver is a bulb of 100-milliliter capacity and can be closed with a rubber stopper, which carries a glass tubing leading to a three-way stopcock and a glass rod, to whose lower end can be fastened with nickel wire the quartz pycnometer (*vide infra*) in the inverted position so that its mouth is dipped into the distillate.

A Cenco high-vac oil pump is used for evacuation. Between the pump and the stopcock is inserted a tube containing active charcoal fitted with cotton plugs at both sides. After the heavy water has been delivered into the distilling flask, the latter is chilled with an ice-water bath and the system is evacuated. Then the stopcock is closed and the receiver chilled with the same bath, while the distilling flask is warmed with a bath of warm water. The heavy water distils quietly into the receiver. After almost all the liquid has distilled over, air dried through calcium chloride is admitted through the three-way stopcock into the system, so that the distillate is pressed into the pycnometer leaving a tiny bubble at the top. The pycnometer is then taken out by removing the rubber stopper and immediately closed up with the cap, in order to avoid the contamination by atmospheric moisture.

PYCNOMETRY

A pycnometer of vitreous quartz made by Geyer, Berlin, shown in Fig. 1, has a capacity of 16 milliliters, and the capillary of the neck has a radius of 0.24mm. It is provided with a ground-joint cap. During the observation, the cap is removed and a pyrex-glass tube is fitted on the neck by means of a rubber stopper, as shown in the figure. The upper end of the tube is closed by another rubber stopper. The whole is so immersed in the thermostat that the mouth of the pycnometer is well below the liquid surface of the bath.

When the pycnometer is warmed up, the heavy water expands through the capillary and forms an hemispherical water cap, which may partly evaporate off, but is finally wiped dry with a small piece of filter paper fitted on the end of a glass rod, which is inserted into the tube by momentary removal of the upper rubber stopper. Then the cap is immediately put upon the capillary by means of another glass rod fitted with a piece of rubber tubing, which holds loosely the cap. Next the pycnometer is quickly brought to room temperature by immersing into another small thermostat. After the pycnometer has been cleaned with alcohol and carefully dried with linen, it is ready to be weighed.

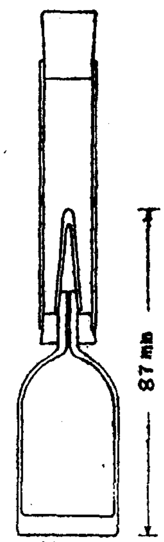

Fig. 1. The quartz pycnometer

THERMOSTAT

A pyrex-glass beaker of 3-liter capacity is fitted with a cloth jacket filled with cotton. The bath liquid is distilled water covered with a layer of paraffin oil to prevent evaporation. The use of distilled water is necessary since tap water leaves troublesome deposits on the pycnometer at high temperatures. The usual technique of maintaining constancy in temperature is employed. Heating at various temperatures is done with two to four 135-watt heaters controlled with rheostats to secure temperatures slightly below the desired ones. The fine adjustment of temperature is performed by a 5-watt heater, operated by a relay and a toluene-mercury regulator. The bath-liquid is efficiently stirred by a small motor stirrer. Throughout the investigated range between 25° and 100° a temperature constancy of 0.01° is obtained.

A mercury thermometer with a normal-glass bulb and graduated to a tenth of a degree allows 0.01° to be estimated. This thermometer has recently been compared with one certified by the Bureau of Standards, U.S.A., kept at the Institute of Chemistry, Academia Sinica, Shanghai. As the mercury thread above the bath surface is very long at temperatures near 100°, the temperature of the emergent thread is estimated by inserting another thermometer at different heights. In such cases the temperature correction amounts to about one degree and herein lies the chief error of temperature estimation.

A duration of about 20 minutes is required for the pycnometer to assume the bath temperature.

MEASUREMENT

We first determine the density of ordinary water which has been purified by distillation over alkaline permanganate and in vacuum as in the case of heavy water described above. In the temperature range between 50° and 100°, our density values agree with those of Thiesen[8] within three units in the fifth decimal place. All weighings are correct to 0.1 mg. and are reduced to vacuum in the customary manner. At different temperatures the volume of the pycnometer is corrected by using the known coefficient of thermal expansion of vitreous quartz.[9]

In each series of measurements on the density of heavy water, we always start with the temperature 25°. The density ratio of heavy water and ordinary water, denoted by d_{25}^{25}, serves to calculate the mole percentage of D_2O of the sample observed. In this connection the formula due to Swift[5] is regarded to possess an accuracy of 0.01 mol% in the estimation of the concentration. We have carried out altogether three series of measurements. The density of each sample of heavy water is determined at temperature intervals of five degrees. At the end of each series of measurements the density ratio is checked. As a small portion of the water has extruded from the pycnometer during the observation at higher temperatures, the loss is compensated by adding heavy water of known concentration. In the first and third series of measurements we have not detected any decrease in concentration more than 0.01 mol%, which corresponds to one unit in the fifth decimal place of the density value and is within our experimental error. But in the second series the concentration drops by 0.05 mol%, and correction has been made in the final extrapolation of the observed values to 100% D_2O.

8. Landolt-Börnstein, "Physikalisch-Chemische Tabellen". 5. Aufl., Hw. I (1923). 74.
9. "International Critical Tables". IV (1928). 21.

RESULTS

The results of our three series of measurements are shown in Table I. The density of the sample at 25°, as stated above, is used to calculate

TABLE I

Measurement on the density of D_2O samples

Series	Mol% D_2O	Temp. °C	Density of D_2O sample g./ml.	Density difference between 100% D_2O and ordinary water g./ml.
I	99.87	25.00	1.10426	0.10733
		50.35	09534	757
		55.36	9289	747
		60.27	9027	731
		65.35	8734	708
		70.29	8439	689
		75.66	8093	658
		80.67	7761	633
		85.82	7395	597
		90.89	7030	569
		95.98	6647	538
		99.44	6370	508
II	99.84	25.00	1.10423	0.10733
		45.33	09758	764
		50.38	9527	756
		55.38	9281	743
		60.33	9020	731
		66.38	8675	709
		70.38	8429	688
		75.68	8088	659
		85.84	7392	600
		90.96	7022	572
		96.08	6633	537
	99.81	99.49	6357	505
III	99.81	25.00	1.10420	0.10733
		30.10	10295	752
		35.10	10144	762
		40.17	09966	768
		45.31	9758	767

the mole percentage. For the sake of simplicity, we have included the density increment due to the presence of excess O^{18} in the D concentration.

For instance, the so-called "99.87 mol% D_2O" (column 2) indicates actually a sample of water which contains 99.77 mol% D_2O and 0.10 mol% O^{18} water. Such an assumption is justified in the subsequent calculation of the density of 100% D_2O with normal content of O^{18} *(vide infra)*.

The density of the sample observed is given in the fourth column of the table corresponding to the temperature given in the third column. We record here the observed densities only in six significant figures. As a 16-milliliter sample weighs about 18 grams and a difference of 0.02mg. can be estimated with the balance used, we can actually obtain seven figures for the density value. For instance, the density of the sample containing 99.87 mol% D_2O at 50.35° is estimated to be 1.095 344 g./ml. But in the table we have rounded off the seventh figure, because the sixth figure has already an error of a few units.

From the experimental density value with six decimal places we subtract the known density value of ordinary water in six decimal places[10] at the corresponding temperature. The result is linearly extrapolated to 100% D_2O, and given with five decimal places in the last column of Table I. As has been mentioned, in the extrapolation to 100% D_2O with normal isotopic composition of O^{18}, the excess of the O^{18} water is included in the D_2O content. The error so introduced may be estimated as follows.

Let us suppose the density ratio d_{25}^{25} of H_2O^{18}, which is unknown, equals 20.02/18.02, or 1.111, while d_{25}^{25} of D_2O is 1.10764. Therefore the difference is about 0.003 for 100% H_2O^{18} and D_2O. Now, if we mistake 0.1 mol% H_2O^{18} for D_2O, an error of 0.000 003 is introduced into the density value. It is clear that the fifth decimal place will scarcely be affected.

Again, the minute amount of dissolved air may cause an error of a few units in the seventh decimal place in the neighborhood of room temperature; the error is still smaller at higher temperatures. Nor does the deviation from the normal atmospheric pressure, which is within ±10mm. Hg during our experiment, affect the sixth decimal place.

The density differences between 100% D_2O and ordinary water so

10. A. Stähler, "Handbuch der Arbeitsmethoden in der anorganischen Chemie", **III/I** 9 (113), 51.

obtained at the observed temperatures as listed in the last column of Table I are plotted and smoothed as shown in Fig. 2. The experimental points have an average deviation corresponding to 0.000 02 g./ml. from the smoothed curve.

THE DENSITY TABLE

From the smoothed curve of Fig. 2, we can read the density differences between heavy water and ordinary water in the temperature range

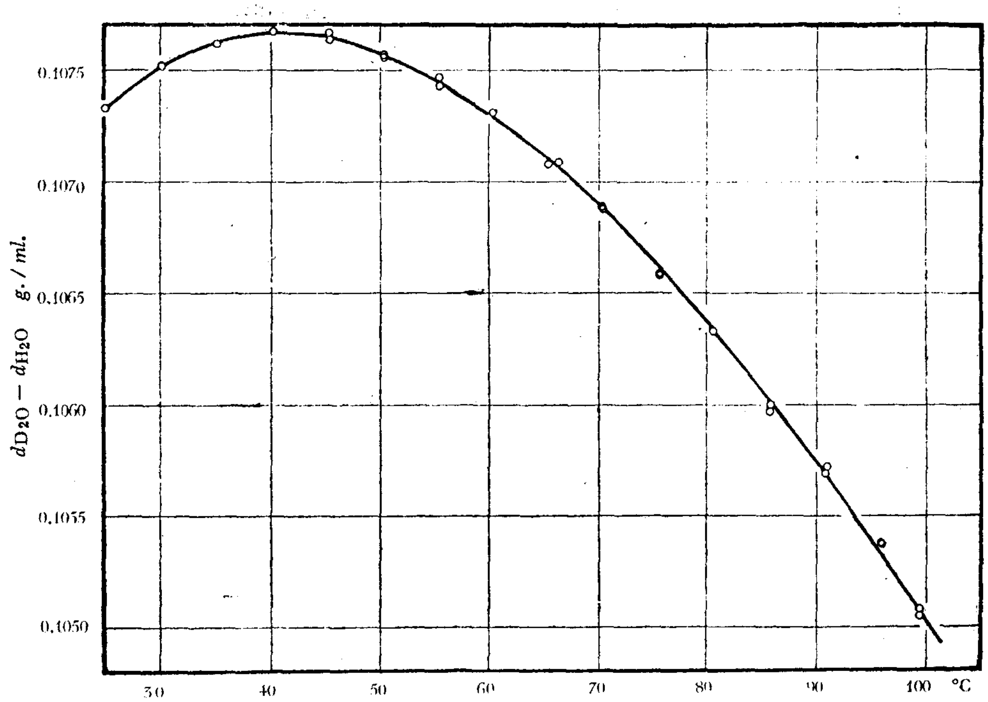

Fig. 2. Density difference between heavy and ordinary water.

between 25° and 100°. With the known data below 25°, we are able to construct a density table for heavy water in the liquid state under one atmosphere pressure in the complete temperature range between its freezing and boiling points. Our data between 25° and 50° stand between those of our earlier measurements and those given by Wirtz. Our earlier values are on the average three units in the fifth decimal place too high, while Wirtz's values about seven units in the same decimal place too low.

Tronstad's values between 10° and 27° are regarded to possess a high accuracy[5]. Our earlier determinations in this temperature range, as a part of an investigation to locate the maximum difference between the densities of ordinary and heavy water, are several units in the fifth decimal place too low. Therefore Tronstad's data are employed in our density table for this temperature range. Again, we use Swift's value at 5° for the same reason.

Bridgman's data[6] at 60° and 80° are about three units in the fourth decimal place too high. Besides, his data at 40° and 50° are about six units in the fourth decimal place too high, while his value at 20° is two units in the fourth decimal place too low in comparison with the accepted value of Tronstad.

Table II[11] gives the density value of heavy water with normal isotopic composition of oxygen, at temperatures of 5-degree intervals between its freezing point[12] 3.80° and its boiling point[13] 101.40°. We include also a value at the temperature of its density maximum[1, 14], that is 11.2°. The densities of ordinary water, which contains 0.018 mol% D_2O and oxygen in normal isotopic ratio, are listed side by side for the purpose of comparison. Those values at temperatures below 40° are the mean of the values of Thiesen and Chapius, while those above 40° are due to Thiesen[15].

We believe that our density values of heavy water above 30°, by considering all sources of error, have an accuracy of about 5 units in the fifth decimal place.

DISCUSSION

In the fourth column of the table are recorded the density differences, which possess a maximum value of 0.107 67 g./ml. at 40°. This

11. This density table has been sent to "*Nature*" as a preliminary report.
12. V.K. LaMer and W.N. Baker, *J. Am. Chem. Soc.* **56** (1934), 2641.
13. F.T. Miles and A.W.C. Menzies, *ibid.* **58** (1936), 1067.
14. T. L. Chang and J.Y. Chien, *J. Chinese Chem. Soc.* **8** (1941), 74.
15. "International Critical Tables", **III** (1928), 24.

value is more probable than that given in our earlier paper[4], which is three units in the fifth decimal place too high.

The density ratio between heavy and ordinary water is given in the last column of the table. It increases by diminishing amount with in-

TABLE II.

Density table of heavy water.

Temperature °C	d_{H_2O} g./ml.	d_{D_2O} g./ml.	$d_{D_2O} - d_{H_2O}$ g./ml.	$\frac{d_{D_2O}}{d_{H_2O}}$
3.8	1.00000	1.10538	0.10538	1.10538
5	0.99999	10555	556	556
10	9973	10595	622	625
11.2	9961	10596	635	639
15	9913	10583	670	678
20	9823	10530	707	726
25	9707	10440	733	764
30	9568	10319	751	798
35	9406	10169	763	827
40	9225	09992	767	851
45	9024	9790	766	871
50	8807	9565	758	888
55	8573	9319	746	902
60	8324	9054	730	913
65	8059	8771	712	924
70	7781	8471	690	933
75	7489	8154	665	940
80	7183	7821	638	946
85	6865	7472	607	950
90	6534	7109	575	954
95	6192	6732	540	957
100	5838	6342	504	960
101.4	5736	6229	493	960

creasing temperature. As predicted in our earlier paper, the density ratio necessarily passes through a maximum, since the ratio will become unity[16] at 370°. The density ratios at different temperatures are plotted in Fig. 3, from which one can clearly see the general trend of the curve, and one can roughly estimate that the temperature at which a maximum occurs lies not far above the boiling point.

16. E.H. Riesenfeld and T.L. Chang, Z. *physik. Chem.* **B33** (1936), 120.

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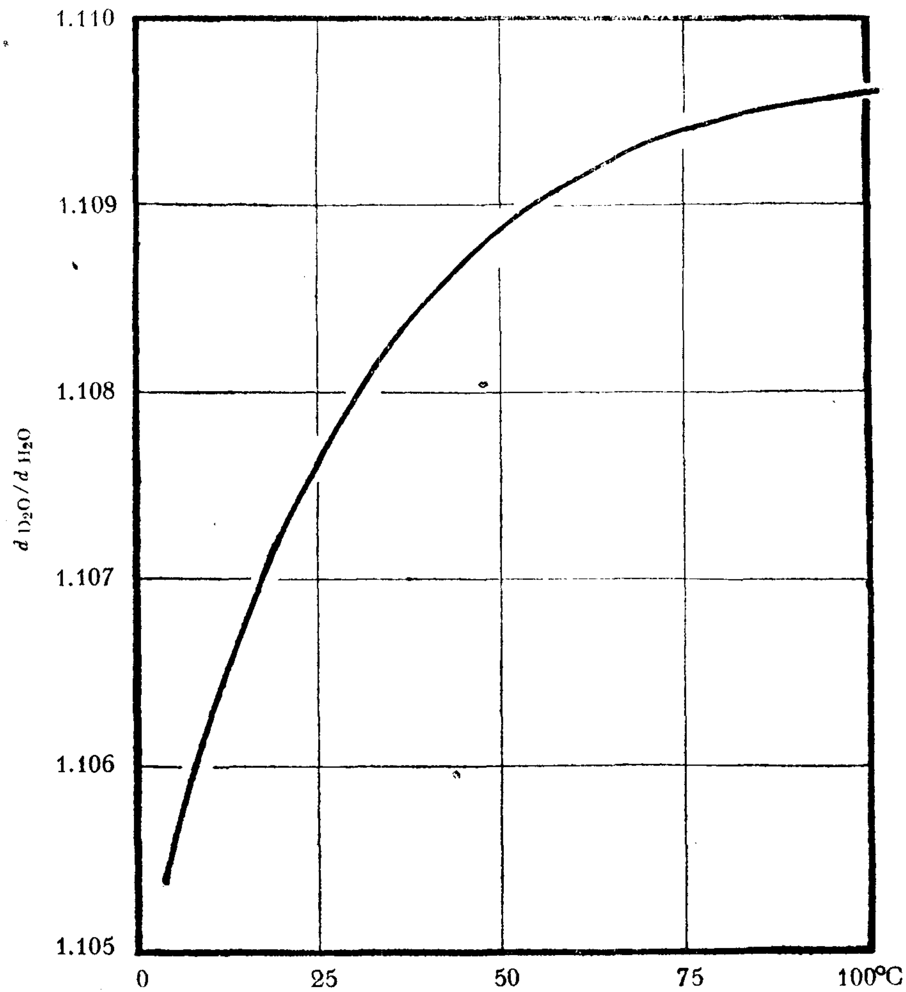

Fig. 3. Density ratio between heavy and ordinary water.

same substance; to Mr. T.C. Chu, assistant research fellow of the same institute, for comparing our thermometer with one having a certificate; to Prof. W. Brüll, head of the Chemistry Department of the Catholic

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中 文 提 要

重水在攝氏 25° 至 100° 間之密度

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重水在 50° 以上，迄今尚無較爲準確之測量。作者用一具 16 ml 容量之水晶比重瓶，在 25° 至 100°C 間，測得重水之密度。兹引用 25° 以下已知之數值，製成一重水密度表，自其冰點迄沸點，每隔 5 度，列示其密度之數值。此等數值之準確度，約爲十萬分之五。