The results of this investigation indicate that this general equation without any modification may be valid in non-aqueous solutions. It may at least be said that the Harned and Embree equation is able to reproduce the experimental results in solutions covering a wide range of dielectric constant, extending from 80 in aqueous solutions to 15.4 in a solvent containing 70% dioxane by weight at 50°.

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A Redetermination of the Protium–Deuterium Ratio in Water[1]

BY NORRIS F. HALL AND THOMAS O. JONES

Since Bleakney and Gould[2] gave 5000 as the H/D ratio in rain water, several attempts[3] have been made to check this value by preparing water free from deuterium and comparing its density with that of ordinary water. Most of these fall roughly into two groups, resulting in values either near 5500 or near 9000.

Lewis in 1933[4] calculated the value 6500 on the basis of his first electrolytic fractionations. Recently Applebey and Ogden[5] have suggested an upper limit of 7000 on the basis of electrolyses and the assumption of "reasonable" values of the electrolytic separation factor. The opinion has been expressed[6] that Applebey's results definitely discredit values of the H/D ratio in the neighborhood of 9000. By most workers[7] Johnston's recent value (−18.3 γ in density, equivalent to a ratio of 5800) appears to be accepted as the most probable. We have now redetermined this ratio by a method which involves no extrapolation, and in which the final value is approached from both the light and heavy side.

Plan of Work

We prepared nearly deuterium-free water electrolytically by two methods. The first involved the recombination of the electrolytic gases according to the method used by Taylor, Eyring and Frost.[8] We shall refer to this method as "mixed recovery."

In one experiment 55 liters of Lake Mendota water was electrolyzed in potassium hydroxide solution with iron cathodes to about 70% of the original volume, and the 16 liters of water collected was reëlectrolyzed. This procedure was repeated five times until the volume of the last condensate was 150 ml. The amount collected at each stage was about 30% of the preceding volume. In a later experiment this process was independently repeated through four stages of electrolysis.

In the second method, called "separation recovery," we collected the hydrogen separately and burned it in ordinary air. Calculations of the equilibrium constant at high temperatures indicated that exchange effects in the flame could not introduce density differences in the burned water as great as 1 γ, and at the time this work was undertaken the results of Dole, Titani and Greene[9] were not available to us, so that we assumed that air oxygen and surface water oxygen had the same isotopic composition.

By this method two runs were made. In one run (III) through four stages using bell type cells, 30 liters of water was reduced to 150 ml. In the second (run IV), V-type cells (Fig. 1) with a loose plug of glass wool as a diaphragm were used. The initial and final volumes were 24 liters and 400 ml., respectively, and the electrolysis was carried again through four stages.

Because the results of the two types of electrolysis described did not agree, and because we expected on the basis of Johnston's work[3] a displacement of the oxygen isotope ratio during mixed recovery electrolysis, we decided to normalize the oxygen isotope content of some of our samples by equilibration against the standard

(1) Presented at the Kansas City meeting of the American Chemical Society, April 15, 1936.

(2) Bleakney and Gould, *Phys. Rev.*, **44**, 265 (1933) (5000).

(3) Urey and Teal, *Rev. Modern Phys.*, **7**, 40 (1935) (5000); H. L. Johnston, THIS JOURNAL, **57**, 484, 2737 (1935) (5800); Ingold, Ingold, Whitaker and Whitlaw-Gray, *Nature*, **134**, 661 (1934) (9000); Tronstad, Nordhagen and Brun, *ibid.*, **136**, 515 (1935) (5500); Morita and Titani, *Bull. Chem. Soc. Japan*, **10**, 257 (1935) (5500); Christiansen, Crabtree and Laby, *Nature*, **135**, 870 (1935) (8400).

(4) Lewis and Macdonald, *J. Chem. Phys.*, **1**, 823 (1933).

(5) M. P. Applebey and G. Ogden, *J. Chem. Soc.*, 163 (1936).

(6) S. Glasstone, *Ann. Rep. Chem. Soc.*, **32**, 42 (1935).

(7) Cf. E. H. Riesenfeld and T. L. Chang, *Ber.*, **69A**, 1305, 1307, 1308 (1936).

(8) Taylor, Eyring and Frost, *J. Chem. Phys.*, **1**, 823 (1933).

(9) M. Dole, THIS JOURNAL, **57**, 2731 (1935); *J. Chem. Phys.*, **4**, 268 (1936); Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 36 (1936); C. H. Greene and R. J. Voskuyl, THIS JOURNAL, **58**, 693 (1936).

water through the medium of carbon dioxide gas. This was done as described below. As a valuable check on the density measurements, the index of refraction of many of the samples was determined.
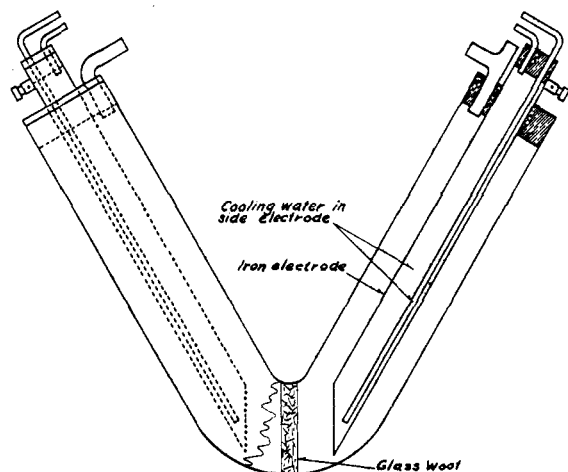

Fig. 1.—Electrolytic cell for separation recovery.

Experimental

1. Purification of Samples.—Each sample of water was distilled three times, once from alkaline permanganate in an all-glass still with a very short (1.27 cm.) Hempel column to trap spray, once from a drop of phosphoric acid through a 10-cm. Widmer column, and finally through a simple quartz still directly into the density apparatus or the interferometer cell. Small equal head and tail fractions were discarded. All the samples and the standard water were treated in exactly the same manner.

2. Density Measurements.—A magnetically controlled buoyancy apparatus (Fig. 2) was used, similar in principle to that described by Lamb and Lee.[10] The totally submerged quartz float was about 13 cm. long and had a volume of 8.2383 cc. at 25°. A cobalt–steel permanent magnet was sealed in the bottom of the float and held permanently in place with wax. The sample tube had a volume of about 60 cc. and had a bottom ground flat inside to which the magnetic float was attracted by the field of the coil beneath the sample tube. It was found that the float centered itself automatically and reproducibly in the field of the coil. The tube and connections were of Pyrex with metal parts of brass. The coil was held rigidly fixed below the tube by a brass and wax collar. By slowly reducing the current through the coil the exact voltage was found which just prevented the float from rising. The apparatus was calibrated by successively adding weighed platinum rings to the top of the float and measuring the e. m. f. required to hold the float against the bottom of the vessel. From the weight differences, the e. m. f. differences and the volume of the float and rings, it was found that one millivolt corresponded to a density change of 9.22 γ. This factor was found to be constant over the total density range studied (some 150 γ). The apparent precision of a single reading was 0.1 γ, and the measurement could be

repeated at different times on the same samples to 0.2 or 0.3 γ. The apparatus was submerged in a thermostat which was constant to ±0.005°. The fluctuations in the apparent density of a given sample as it stood in the bath were hardly detectable, but measurements were always made at the crests of the bath temperature fluctuations.

Each sample was evacuated to remove dissolved air, opened to the atmosphere, closed, brought to temperature in the thermostat, opened and closed once more. This procedure removed the bulk of the dissolved air, but permitted small amounts to redissolve. No effect on the density from this source could be detected. Preliminary measurements showed that increases of barometric pressure produced an apparent density increase of 0.1 γ per cm. Since control measurements on the standard water were always made within a few hours of the measurements of an unknown sample, corrections from this source were always within the precision of the measurements themselves and were not applied.
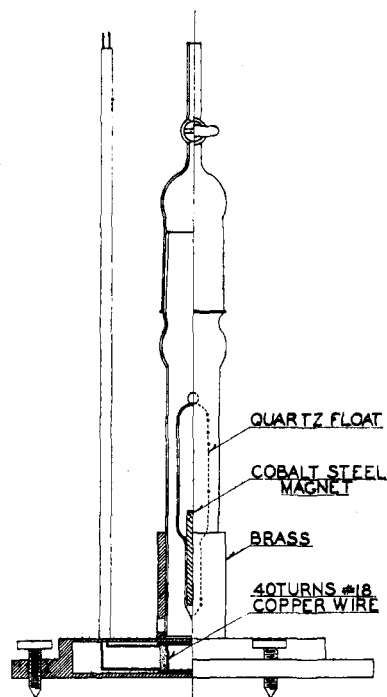

Fig. 2.—Density apparatus.

3. Carbon Dioxide Equilibration.—Saturating towers of a type described by Kraus[11] were used and filled with glass pearls. The gas current acting as an air lift circulated the water over the pearls and gave very efficient scrubbing. The gas was first scrubbed with a large quantity of the standard water which was frequently renewed. It was next thoroughly dried and then saturated by long and repeated contact with the unknown sample. As it left the sample the gas passed through reflux condensers and freezing traps to recover any water carried out, and this was united with the main sample. The density of the standard water was not affected by carbon dioxide treatment in this way.

(10) A. B. Lamb and R. E. Lee, THIS JOURNAL, **35**, 1666 (1913).

(11) C. A. Kraus, and H. C. Parker, *ibid.*, **44**, 2429 (1922).

4. Index of Refraction Measurements.—We fortunately were able to secure the loan for a time from the U. S. Forest Products Laboratory of a Rayleigh gas interferometer, through the courtesy of Dr. Alfred J. Stamm whose assistance is gratefully acknowledged. For this instrument a liquid cell-pair was constructed of Pyrex consisting of a 90-cm. long tube 3 cm. wide within which a 1-cm. tube was sealed by means of side inner seals (Fig. 3). Plate glass windows were cemented on the parallel ground ends. The standard water was placed in the larger tube and the sample in the smaller one. The whole cell was immersed in a water thermostat. Readings could be repeated to three or four scale divisions, so that the instrument was sensitive to refractive index differences of about 2×10^{-8}.

Table I

Removal of Deuterium from Water

I. Mixed Recovery

(1) Electrolysis stage	(2) $-\Delta d \times 10^6$	(3) $-\Delta d \times 10^6$ after CO$_2$ treatment	(4) $\Delta n \times 10^7$	(5) $-\Delta'd$ calcd. from $\Delta n \times 10^6$
Ia	14.0		*a*	
	13.8			
Ib	21.2		6.05	15.8
	21.4		6.3	
Ic	23.3		5.85	
	23.5		6.05	15.5
	23.7			
	24.6			
Id	24.0		*a*	
	24.1			
	25.5			
Ie	25.4		6.05	
	24.8		6.3	16.3
	24.6			
IIa	17.1	15.0	6.05	15.2
	17.2		7.0	
IIb	20.3	16.0	6.6	15.7
	20.3		6.8	
IIc	22.1	16.6	6.8	15.9
IId	25.4	16.5	6.7	15.9
			6.9	

II. Hydrogen Burned in Air

IIIa	6.8			
	6.5			
IIIb	8.3			
	8.2			
IIIc	10.4			
	10.6			
	11.8			
IIId	12.0			
	11.9			
IVa	7.6	13.6		
IVb	8.1	16.3		
IVc	8.9	16.4		
IVd	8.9	16.7		

a In runs Ia, Id the amount of water available was too small for a determination of Δn.

Results

The columns of Table I show (1) the run (Roman numeral) and stage of electrolysis (small letter) referred to; (2) the difference in d_{25}^{26} between the purified electrolyzed sample and the
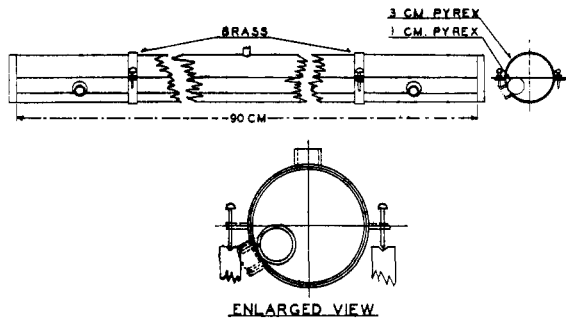

Fig. 3.—Interferometer cell.

purified standard water; (3) the same difference after the sample had been equilibrated with carbon dioxide and repurified; (4) the difference in index of refraction between the purified sample and the purified standard water (in run II these measurements were made on the samples which had been treated with carbon dioxide); (5) the specific gravity difference calculated from the measurement of n. In columns 2, 3 and 4 of Table I, each figure represents an individual determination. In calculating the values in column 5, the mean of the corresponding experimental values was used in each case. These results are also exhibited in Fig. 4, in which, however, only the mean values appear. The two upper curves represent the density differences obtained in runs III and IV by separation recovery. The lower two curves are the results of runs I and II by mixed recovery. The small circles and crosses on the middle curve show the values for all samples treated with carbon dioxide. The large circles give the values calculated from the index of refraction measurements.

For comparison with the water of Lake Mendota, we also made some density determinations on water from Lake Michigan, on the artesian well water of the Madison City supply, and on two samples of sea water taken from the Atlantic near the S. E. corner of Martha's Vineyard island.

Table II

Sample		$\Delta\gamma$	
Lake Michigan	+0.3	+0.4	+0.2
Madison City Water	−0.2	−0.3	
Atlantic Ocean I	+1.4	+1.8	
Atlantic Ocean II	+1.4	+1.6	

Table II gives the density differences of these samples from Lake Mendota water.
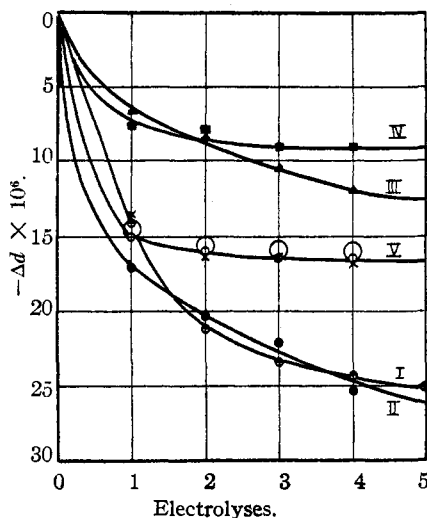

Fig. 4.—Removal of deuterium from water: ●, II knallgas water; ◑, I knallgas water; ○, V knallgas water; after carbon dioxide treatment; ◉, calcd. from interferometer; ▲, III hydrogen burned in air; ■, IV hydrogen burned in air; ✕, air water after carbon dioxide treatment.

Discussion of Results

(a) **Mixed Recovery.**—Runs I and II are in substantial agreement with the results of Johnston[3] in that they seem to show composite density decrements due to (1) the progressive removal of all the deuterium, (2) a more or less steady but incomplete removal of O^{18}. Our results differ from his in that the decrement due to O^{18} removal does not seem to be constant and reproducible from stage to stage and run to run. Since the electrode surface and other conditions may be expected to vary with time, a completely constant fractionation factor for oxygen seems hardly to be expected. If our results are treated by Johnston's method of extrapolation to stage zero to correct for O^{18} removal, the residual density difference depends on the method of extrapolation. For these and other reasons, we have preferred to rely on the carbon dioxide method of restoring the original O^{18}/O^{16} ratio, rather than on correcting for its displacement by the electrolysis. Our average density decrease per stage due to oxygen in run II is 2.0 γ compared to the value 1.6 γ given by Johnston. (There is, of course, no reason why the gross separation factor in the two cases should be identical.)

(b) **Carbon Dioxide Equilibration.**—When samples from the mixed recovery electrolysis (run II) were treated with equilibrated carbon dioxide for several days, they showed in every case an *increase* in density (*i. e.*, an approach to the density of the original water). After removal from the apparatus, purification and density determination, the samples were returned to the apparatus and treated with carbon dioxide for several days more. The treatment was continued in every case until there was no further measurable change in density. The final values obtained (run II, column 3, Table I) point clearly to 16.5 ±0.5 γ as the best value for the density decrement of deuterium-free water.

(c) **Separation Recovery.**—In two runs by this method density decreases of only about 12 and 9 γ, respectively, were obtained in four stages of electrolysis and burning. Since nearly all the deuterium (accounting for a density decrease of 10–15 γ) must have been removed in the first stage, the only way of accounting for this large excess density is to assume either that the nearly pure protium becomes reënriched in deuterium at each stage, or else that the oxygen isotope ratio has been significantly altered. To test the latter hypothesis, the samples from run IV were equilibrated with carbon dioxide against the standard water, and all showed further *decreases* in density (*cf.* columns 2 and 3, Table I). These decreases, which average 7.4 γ for the four stages, are in the direction, are of the order of magnitude to be expected from the work of Dole and others, since the oxygen of the original water had been replaced by (heavier) air oxygen in the burned water. The value found (7.4 γ) lies between those given by Dole and by Morita and Titani.[9] The indicated value for the density decrease of deuterium-free water is here again 16.5 ± 0.5 γ in complete agreement with the "mixed recovery" value.

(d) **Interferometry.**—Index of refraction measurements furnish independent evidence of the removal of deuterium from water, since unlike the density the value of n is relatively independent of changes in the amount of O^{18}.

It may be inferred from earlier work[3,12] that if $-\Delta d$ is the difference in density at 25° between two samples of water low in deuterium and normal as to oxygen isotope ratio, then $-10^6 \Delta d$

(12) D. B. Luten. Jr., *Phys. Rev.*, **45**, 161 (1934); L. W. Tilton and J. K. Taylor. *Bur. Standards J. Research*. **13**, 207 (1934).

should equal about (1062/453) × $10^7 \Delta n$ where Δn is measured with white light at the same temperature. Applying this factor 2.34 to the measured index of refraction differences in run II, column 4, we obtain the calculated density differences in column 5, which are somewhat lower than the measured values (col. 3). This suggests that the factor 2.34 may be a little low. Best agreement would be secured by using the value 2.39. The extra handling and purification of the samples with the attendant dangers of fractionation or contamination may be responsible for the slight lack of agreement found, or the error may reside in the density and index of refraction work of others on which the calculation is based. In any event, the total discrepancy is less than 1 part per million in the density, and is probably within the error of the refractive index determinations.

Run I was made before we had begun to use the equilibration method, and therefore the index of refraction measurements were made on samples of which the O^{18} content had been lowered by electrolysis. This should have caused a decrease in the observed Δn, so that a positive correction should be applied to the Δn figures in Table I, run I, column 4. Subtracting from the observed value of $- \Delta d$ for stage Ib the hypothetical value 16.0 γ and correspondingly subtracting 16.5 from the observed value in stages Ic and Ie, we get the values 5.3, 7.0, and 8.6 as the decreases due to O^{18} removal. Multiplying these by the factor 0.073 to convert $10^6 \Delta d$ into $10^7 \Delta n$, we have as O^{18} corrections +0.4, +0.5 and +0.6. Adding these to the observed $10^7 \Delta n$ values and multiplying by the conversion factor 2.39 we arrive at the values 15.8, 15.5 (and 16.3) which may be compared with the directly measured values 16.0 and 16.6 in run II and 16.3 and 16.4 in run IV. We thus have two fully independent and two partly independent series of values, obtained in two different ways, all of which are consistent with the value 16.5 ± 0.5 γ for the decrease in specific gravity of water due to complete removal of deuterium without disturbance of the oxygen isotope ratio. If this result is accepted, and the value 1.1074 is correct for the specific gravity of pure deuterium oxide (oxygen normalized) at 25°, the protium-deuterium ratio in Lake Mendota water becomes 6400

± 200. (This computation takes account of the non-additivity of volumes found by Luten[12] as does the calculation of Δn just given.)

Since the measurements reported in Table II indicate in connection with many published results of others that Lake Mendota water has about the same density as surface fresh water everywhere, the value 6400 may perhaps be taken as the correct value for such water in general.

Using this ratio, Aston's recent redetermination of the physical atomic weights of the hydrogens and the Mecke–Childs conversion factor, the physical atomic weight of ordinary hydrogen becomes 1.0083 and the chemical value 1.0081.

Summary

1. Surface water from Lake Mendota (Madison, Wis.) was freed from deuterium by repeated electrolysis with recombination of the electrolytic gases. When the *deficiency* in O^{18} thus caused had been restored by carbon dioxide equilibration against the original water, the density loss due to deuterium alone was 16.5 γ.

2. The same water was electrolyzed in stages and the electrolytic hydrogen burned in air. The *excess* of O^{18} thus introduced was removed in the same way, and the density loss was again 16.5 γ.

3. Index of refraction measurements on the equilibrated water indicated that the entire decrease was due to deuterium.

4. Index of refraction measurements on electrolyzed but not equilibrated water gave values consistent with the postulated displacement of the oxygen isotope ratio.

5. The protium–deuterium ratio in surface fresh water inferred from these results is 6400 ± 200, confirming Lewis' early estimate.

6. Both the lower and the higher values of this ratio reported in the literature may possibly be due to actual differences in the water studied, but it is believed that many of them rest upon inadequate correction for alteration in the oxygen isotope ratio.