The Deuterium–Protium Ratio. I. The Densities of Natural Waters from Various Sources

BY CHARLES H. GREENE[1] AND ROGER J. VOSKUYL[2]

One of the many interesting questions which arose when deuterium was discovered concerned the abundance and distribution of the new form of hydrogen. Since the numerous measurements which have been made of the abundance of deuterium have been summarized recently by several authors[3] it is unnecessary to enter into a detailed discussion of them here. It suffices to say that there is still an appreciable uncertainty in the deuterium–protium ratio in normal water.

One source of this uncertainty is the difficulty in adequately purifying water without altering its isotopic composition. We have found it necessary to employ a specially designed still and to control the distillations made to purify our samples with great care in order to avoid serious errors through the fractionation of the isotopes of hydrogen and oxygen in the distillation.

Another possible source of confusion is the fact that previous investigators have selected water from the most convenient tap as "normal" water. It seemed essential, therefore, in a study of the deuterium–protium ratio, to compare these various standards with our own Cambridge tap water. While we did not attempt to secure samples of the standard waters of all previous investigators, samples from enough representative locations were obtained to show that the differences between the results of different investigators cannot be explained by differences in their standard waters.

We were very fortunate in the hearty coöperation of all the scientists from whom we requested samples. We wish to thank particularly: Professor Toshizo Titani of the Imperial University at Osaka, Japan, for samples of Osaka tap water; Professor H. V. A. Briscoe of the Imperial College, London, England, for London tap water; Professor L. Tronstad and the Norsk Hydro-electrisch Kvaelstofaktieselskab, Rjukan, Norway, for the carefully purified distilled water used as standard in their work; Professor Herrick L. Johnston of Ohio State University for tap water

from Columbus, Ohio; Dr. E. R. Smith of the United States Bureau of Standards for Washington tap water and distilled water; Dr. A. Voskuil for Lake Michigan water; and Dr. Howard A. Voskuil for water from Lake Mendota, Madison, Wisconsin.

Professor Titani and Dr. Morita have also compared the densities of Osaka and Cambridge tap waters in their laboratory.[4] In this investigation they took particular care to avoid errors arising from the fractionation of isotopes during the purification of the samples of water. Their result, as will be seen below, is in entire accord with our own.

Through the kindness of Admiral R. R. Waesche, Commandant, and Commander G. W. Mac-Lane of the United States Coast Guard we obtained samples of water from the North Atlantic and from an iceberg. Our thanks are also due to Mr. L. H. Porter, Director of Operations, and to the Officers of the S. S. Southern Cross of the Munson Steamship Line for a sample of water from the surface of the Atlantic at the equator. We include our results with these samples in this report to illustrate extremes of density to be met with in natural waters.

In this paper, we describe a method of purifying water with suitable correction for the isotopic fractionation involved and a method of comparing the densities of different samples of water. This method of purifying samples of water and comparing their densities is applied to a survey of the densities of "normal" waters as well as to a few interesting samples from the ocean. In subsequent papers we plan to consider first the preparation of deuterium-free water of normal composition with respect to the oxygen isotopes and the comparison of its density with that of any of the "normal" waters and finally the calculation of the proportion of deuterium present in such normal waters.

Apparatus.—In order to compare the densities of different samples of water we have employed a method suggested by Lamb and Lee,[5] which consists in measuring the pressure at which a float remains exactly balanced in the

(1) Present address: Corning Glass Works, Corning, N. Y.
(2) Present address: Wheaton College, Wheaton, Ill.
(3) (a) N. F. Hall and T. F. Jones, THIS JOURNAL, 58, 1915 (1936); (b) J. L. Gabbard and M. Dole, ibid., 59, 181 (1937); (c) N. Morita and T. Titani, Bull. Chem. Soc. Japan, 11, 406 (1936); (d) ibid., 13, 424 (1938).

(4) T. Titani and N. Morita, Bull. Chem. Soc. Japan, 13, 409 (1938).
(5) A. B. Lamb and R. E. Lee, THIS JOURNAL, 35, 1666 (1913).

water. Our heavy-walled, stream-lined float, Fig. 2, was made of Pyrex brand chemical glass and weighted with mercury. It had a volume of 14.5 ml. and its density was adjusted to equal that of water at 4.58°. At this temperature the thermal expansion of water is equal to that of Pyrex brand chemical glass so that small variations in temperature produce no appreciable change in the relative densities of the float and water.

The float was permanently sealed in a chamber of similar shape (Fig. 1) having a volume of about 63 ml. so that a sample of 48.5 ml. of water was required for a determination of density. Capillary tubes for the introduction and removal of water samples were sealed to the top and bottom of the chamber. These tubes were sufficiently long so that there was no danger of the density of the water in the float chamber being changed by solution of the air admitted to the system when the pressure balance was made. The balancing pressure was corrected for any variation in the height of water in these tubes. The chamber was provided with pushed in points of glass which served to center the float and define its position when it rested at the bottom of the chamber.

The float chamber was permanently mounted in a well-stirred glass thermostat which was maintained at 4.58° by a stream of water which had passed through a coil of copper tubing in an ice reservoir. The flow of water was controlled by a magnetic valve which was operated by a thyratron regulator system. Since the pulsating current transmitted by a thyratron tube is not suitable for keeping a solenoid valve shut, the circuit was arranged so that the thyratron tube shorted the magnetic valve and caused it to open when the tube was conducting. A series resistance was necessary to prevent the tube being damaged by too heavy a plate current. With this system the temperature was kept constant to ±0.002°.

The motion of the float was observed by means of a wide field tube microscope with a scale in the ocular. The pressure was adjusted by admitting filtered air at 6 (Fig. 1) or removing it by an aspirator connected at 5. The balancing pressure was measured by means of an open arm manometer constructed of 12-mm. tubing and mounted in front of a mirror scale. The barometric pressure was recorded at the same time. Balancing pressures could be duplicated upon the same sample to 0.5 mm., which corresponds to 0.02 γ in density. (We use the symbol γ to denote one part per million.) About two hours was required for a sample to come to thermal equilibrium when it was stirred frequently by moving the float up and down.

Calibration of the Float.—The float was calibrated by determining the change in balancing pressure occasioned by hanging a small glass ring on its tip. The rings were weighed on a microbalance by substitution with the same set of standardized weights employed in weighing the float. A ring was sealed with the float in the cell which was provided with only a single inlet tube at the top during the calibration experiments. A sample of conductivity water was introduced by means of a capillary funnel and the cell was put in the thermostat and connected to the pressure system. The balancing pressure was determined as usual.

The cell was then removed from the thermostat and the ring slipped over the tip of the float without any change in the sample of water. To do this required a certain amount of manual dexterity. Several experiments failed at this point when the fragile ring was crushed between the float and the wall of the chamber. However, practice improved our skill in solving this three dimensional cat-in-the-corner puzzle, so that we were able to complete eight calibrations with five different rings.
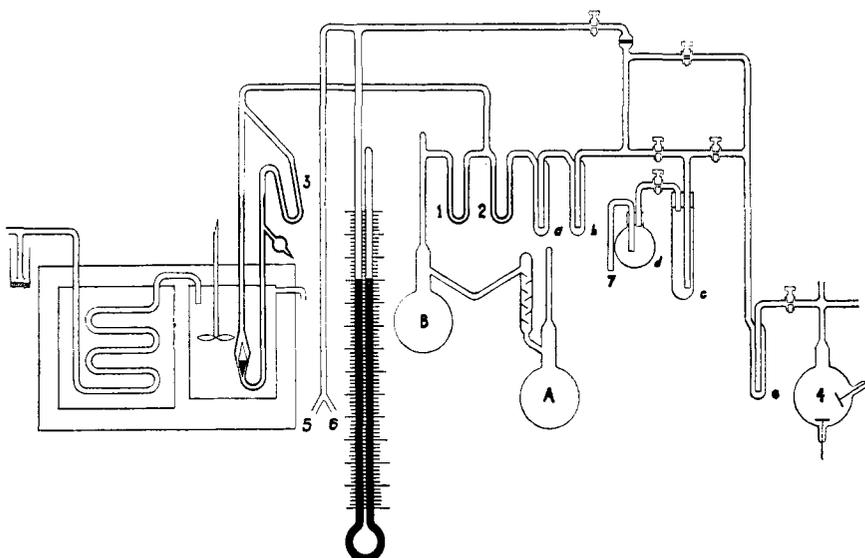

Fig. 1.—Vacuum distillation system and float chamber.

With the ring on the tip of the float, the cell was returned to the thermostat and the new balancing pressure determined. Finally the ring was slipped from the tip of the float and the original balancing pressure checked.

In a typical calibration experiment a ring weighing 0.001215 g. caused a change of 130.51 cm. in the balancing pressure of the float. Taking the density of Pyrex brand chemical glass as 2.23 g. per ml. one may calculate that the volume of the ring was 0.000545 ml. and hence that its effective weight under water was 0.000670 g. The weight of the float was 14.5060 g. Consequently, adding the ring changed the effective density of the float by $0.000670/14.506 = 46.19\ \gamma$. The effective change in density per centimeter of pressure was thus $46.19/130.51 = 0.3539\ \gamma/cm.$

It is rather interesting to observe that the sensitivity would have been 0.68 γ/cm. had the float been entirely incompressible. It appears then that our float was slightly less than half as compressible as water.

In Table I is given a summary of the eight successful calibration experiments.

TABLE I

SUMMARY OF FLOAT CALIBRATIONS

Mass of ring, mg.	Pressure difference, cm.	Calibration factor, γ/cm.
0.529	56.57	0.3556
.593	63.34	.3555
.593	63.29	.3557
.792	85.10	.3539
1.215	130.51	.3539
1.215	130.62	.3536
1.254	134.79	.3539
1.254	134.56	.3545
	Mean	.3546

Purification of Water.—For the purification of our samples we have employed five successive distillations, three of these being at atmospheric pressure and two in an evacuated all-glass system. Before the first distillation the sample (200 g.) was digested with 0.3 g. of potassium permanganate and 0.1 g. of sodium hydroxide for half an hour. For the second distillation 0.1 g. of permanganate and 0.1 g. of sodium hydroxide were added and for the final distillation at atmospheric pressure a very small drop of sulfuric acid.

These distillations at atmospheric pressure were carried out in special stills (Fig. 2) designed to prevent contamination of the distillate by entrained spray and yet minimize fractionation by refluxing. The spray trap b was packed with broken glass and was kept warm by a ring burner adjusted so that the glass remained wet to trap spray but did not condense enough vapor to drip back into the still. The rate of distillation was 1.5 to 2.0 ml. per minute. In each distillation exactly 5% of the water was rejected as a light fraction. At the end of each distilla-
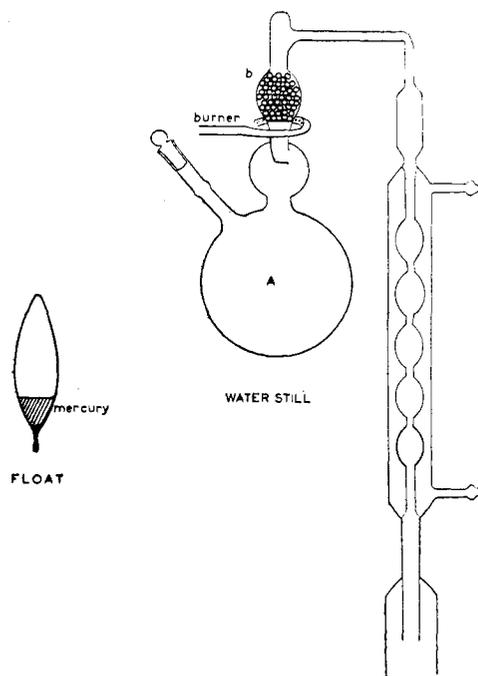

FLOAT

WATER STILL

Fig. 2.—Float and special still.

tion from 10–14% of the water was allowed to remain as a heavy fraction in the still. All fractions were weighed carefully to permit estimation of the correction to be applied to the final density for separation of isotopes in these distillations.

With these stills we obtained the separation of isotopes to be expected from a single theoretical plate. After this had been demonstrated by experiment, we were able to base our corrections upon the known vapor pressures of the various isotopic forms of water as will be explained below. Preliminary experiments with stills having columns of bulbs or indented tubes for spray traps showed more separation of isotopes than would be expected from a simple distillation. Furthermore, the amount of separation depended upon the rate of distillation.

The distillations under reduced pressure were made in the all glass system shown in Fig. 1. A 70-g. sample was weighed into flask A which contained 0.05 g. of barium hydroxide to remove any carbon dioxide dissolved in the sample. The barium hydroxide was renewed after three experiments since a slight but noticeable increase in density was apparent in some early experiments in which this precaution was not taken. The results of these experiments were discarded. Great care was taken in sealing off the tube through which the sample was put into flask A in order to avoid the entrance of flame gases into the system.

A water-bath was placed around flask A and heated to 38° while air was removed from the system at 7. Trap a was cooled with ice and traps b and c with dry ice and alcohol. Dissolved air was thus removed from the sample and a light fraction of about 5 g. collected in traps a, b and c. A weighed bulb d containing phosphorus pentoxide ensured against the loss of any water escaping condensation in the traps.

The capillary U tubes 1, 2, and 3 served as valves in the part of the system through which the purified water was distilled. They were closed by freezing a plug of ice in them with a dry-ice–alcohol bath and opened by melting the ice. After a sufficient light fraction had been collected, valves 1 and 2 were frozen and the sample distilled from flask A through a small spray trap into flask B. Meanwhile the light fraction and the water in trap 2 were distilled into c and weighed.

The system (except for flasks A and B) was then evacuated by a mercury vapor pump through the charcoal tube e. Tubes a, b and e were cooled in dry-ice-baths during this pumping, which reduced the pressure to 0.002 mm. or less. Trap 1 was then melted, the pumps shut off after pumping from A and B for a minute or two, and another small light fraction removed as before. The discharge tube 4 proved very convenient as a supplement to the McLeod gage for obtaining a quick indication of the approximate pressure in the system. This procedure of pumping and distilling out small light fractions was very effective in removing dissolved air from the water since there was no difficulty in distilling the sample from flask B into the cell in the thermostat through the long connecting tube and capillaries.

For this distillation trap 2 was frozen and flask B immersed in a water-bath at 60°. The cell was kept at 0° by ice in the thermostat. The distillation into the cell

required about seventy minutes and took place without any boiling or spattering. Nichrome windings and small gas flames prevented water from condensing elsewhere than in the cell. Finally the heavy fraction in flask B was removed and weighed in tube c.

The original sample of water was thus separated into three parts: (1) a light fraction consisting of the head fraction removed from flask A, plugs frozen in traps 1 and 2, the head fraction from flask B, and the second plug frozen in trap 2. (This last water was necessarily removed and weighed as part of the heavy fraction. Correction was made, however, by measuring its volume in trap 2 which was calibrated for this purpose.); (2) a middle fraction, the contents of the cell chamber which always had the same volume; (3) a heavy fraction left in flask B.

All of these quantities were weighed and in most cases 99.7% of the water introduced was accounted for. Water in the charcoal tube e was recovered by heating the tube and condensing the water in tube c.

Correction for Isotopic Fractionation during Low Pressure Distillation.

—Although the separation of the isotopic forms of water upon distillation is well known, previous investigators do not appear to have taken adequate precautions to avoid error from this source in the most precise density determinations. The precaution often mentioned of rejecting small equal head and tail fractions is not adequate unless the rejected fractions are so small as to imperil the efficiency of the distillation as a purification process. It should be remembered that a number of successive distillations are usually made in the purification of samples of water so that although the change in density caused by a single distillation is small, the total change occasioned by the purification may be significant. The fact that this change in the case of deuterium-free water is different from and less than the change with ordinary water must also be taken account of in determinations of the deuterium–protium ratio by the method of densities.

Although the distillations at atmospheric pressure gave results agreeing well with those to be expected from vapor pressures, the vacuum distillations resulted in a greater separation than would be expected. This is probably the result of a diffusion separation in the long tube through which the sample was distilled into the cell. Corrections for this separation were made upon an empirical basis by combining samples removed from the cell and determining the change in balancing pressure caused by a second set of vacuum distillations carried out on the combined sample. Since the size of the sample introduced into the system and the size of the middle fraction con-

tained by the cell chamber were constant, there was only one independent variable in the distillations. In Table II this variable is represented by the percentage of heavy fraction in column 1.

TABLE II
DISTILLATION EXPERIMENTS IN THE EVACUATED SYSTEM

% of heavy fraction	Balancing pressure, cm.	Original balancing pressure, cm.	Change, cm.
	A. Normal Water		
8.81	81.07	80.58	0.49
9.25	83.54	83.35	0.19
11.46	82.31	81.31	1.00
13.11	85.90	84.92	0.98
13.74	85.32	84.21	1.11
15.71	86.88	85.12	1.76
17.21	87.39	85.62	1.77
	B. Deuterium-Free Water		
9.42	124.65	124.66	−0.01
11.22	126.22	125.73	.49
12.05	128.65	128.21	.44
15.50	129.50	128.37	1.13
15.73	128.53	128.10	0.43[a]
16.98	124.99	123.55	1.44

[a] Omitted in finding least squares line.

The original balancing pressure in column 3 was obtained by averaging the balancing pressures of the two cell contents used in making up each sample. It is evident from the increases in balancing pressure recorded in column 4 that the vacuum distillations diminish the density of the water and that the change is greater, the greater the size of the heavy fraction rejected.

Similar experiments were carried out with deuterium-free water and are recorded in part B of Table II. Here the change caused by vacuum distillation is smaller as is to be expected since only the oxygen isotopes are fractionated.

In Fig. 3 these experimental points have been plotted, circles for ordinary water and triangles for deuterium-free water. The two straight lines were fitted to the points by least squares. One of the experiments with deuterium-free water was omitted in determining the constants of the line because of its large deviation from the line indicated by the other experiments. These lines have been used to determine the corrections to be subtracted from all measured balancing pressures to allow for the separation of isotopes occasioned by the purification in the vacuum system.

The precision of these corrections depended upon the exact control of the conditions of distillation and the exact measurement of the light, middle and heavy fractions into which the sample
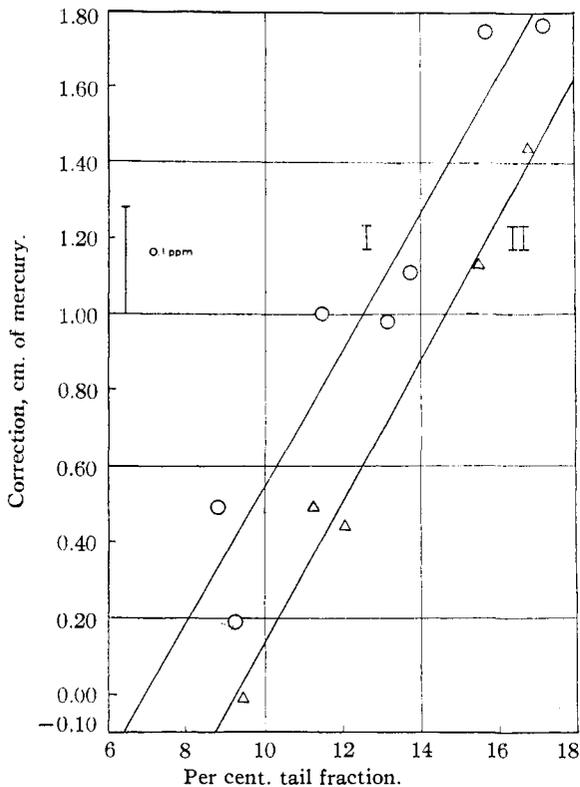
Fig. 3.—Corrections for vacuum distillations.

appears that the balancing pressure tended to increase with time. In the course of two years the density of the float increased by about 2 γ. This trend was not as regular as might be desired. There were times when the float would suddenly drop back to a balancing pressure observed some time previously and then slowly creep up again.

These irregularities were small; thus in the period from February 26, 1937, to June 8, 1937, the maximum variation in fifteen standardizing experiments was 0.8 cm. or 0.3 γ. However, in order to allow for this irregularity of the float, the points representing standardizing experiments were broken up into groups as shown in Fig. 4. Through each group the best straight line was drawn by least squares and this line was used to interpolate the best value for the balancing pressure of a stock sample upon any particular date. The few experiments with unknown water samples which happened to be performed in the intervals between the groups of points in Fig. 4 were rejected.

This gradual increase in the density of the float is probably to be ascribed to the same sort of thermal hysteresis of glass which causes the creep in the zero point of thermometers. Other authors have observed similar behavior in glass floats.[6] We found it advisable to keep the float at 0° during the intervals between a series of measurements. When it had been kept for some days
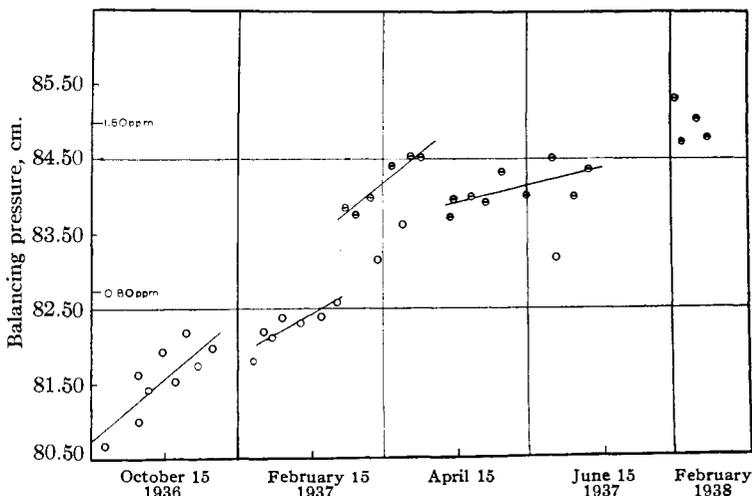
of water was separated. Calculations based on the change in the relative vapor pressures of the various isotopic forms of water with temperature indicate that an error of one degree in fixing the bath temperature for flask B would produce a change of only 0.02 γ in the density of the distillate in the cell. An error of 0.3 ml. in measuring the heavy fraction would change the correction by 0.02 γ also. These limits represent the error to be expected from this source.

Constancy of the Float.—For convenience in standardizing the distillations in the vacuum system and detecting any changes in the float, large stock samples of conductivity water were prepared and used as temporary standards with which to compare unknown samples of tap water, etc., after the distillations at atmospheric pressure. In Fig. 4, balancing pressures obtained with these stock solutions are plotted against time. Stock solutions A and B were used up in preliminary experiments necessary to develop our density apparatus. It

Fig. 4.—Change of balancing pressure with time: O, stock C; ⊖, stock D.

at room temperature the balancing pressures observed upon first cooling to 4.58° indicated a

(6) T. W. Richards and J. W. Shipley, THIS JOURNAL, **34**, 599 (1912); E. S. Gilfillan, Jr., *ibid.*, **56**, 406 (1934).

float density 0.2 or 0.3 γ less than that observed after twenty hours or more at ice temperatures.

Corrections for Distillations at Atmospheric Pressure.—Corrections for the three distillations at atmospheric pressure by which all samples of water were purified before being put into the vacuum system were based upon the vapor pressures of the various isotopic forms of water which have been measured by a number of investigators. These theoretical corrections were checked by experiments in which samples of a stock of known balancing pressure were distilled in the special stills at atmospheric pressure. In Table III are collected the vapor pressure data upon which we have based these corrections.

TABLE III

VAPOR PRESSURE RATIOS FOR THE ISOTOPIC SPECIES OF WATER AT 100°

Observers	$P_{H_2O}-$ P_{D_2O}, mm.	P_{HDO}/P_{H_2O} Calcd.	P_{HDO}/P_{H_2O} Exp.	$P_{H_2O^{18}}/$ $P_{H_2O^{16}}$
Lewis and Macdonald[7]	38.4	0.9742		
Miles and Menzies[8]	37.7	.9749		
Riesenfeld and Chang[9]	37.8	.9749	0.9737	0.9955
Wahl and Urey[10]			.9747[a]	.9970[a]
Lewis and Cornish[11]				.995
Selected value		.9742		.9955

[a] These values were obtained by the extrapolation of observations at lower temperatures.

Since Topley and Eyring[12] have shown theoretically that the vapor pressure of HDO is probably very close to the geometric mean of the vapor pressures of D_2O and H_2O, we have computed the ratios of vapor pressures in the third column on this basis. The value which we have selected for this ratio (0.9742) is amply precise for our purpose since the use of even the most divergent value in Table III makes a difference of less than 0.01 γ in the computed corrections for any of our distillations.

Assuming that the ratio O^{17} to O^{18} is 1:5 and that the vapor pressure of H_2O^{17} is the geometric mean of the vapor pressures of H_2O^{18} and H_2O^{16}, we find that the maximum correction to be applied for the fractionation of H_2O^{17} is less than 0.02 γ. Consequently we have neglected this isotopic form of water in making our corrections.

For these calculations we have assumed that ordinary water is heavier than pure protium oxide by 16 γ because of the presence of deuterium and

(7) THIS JOURNAL, **55**, 3057 (1933).
(8) Ibid., **58**, 1068 (1936).
(9) Z. physik. Chem., **B33**, 127 (1936).
(10) J. Chem. Phys., **3**, 411 (1935).
(11) THIS JOURNAL, **55**, 2616 (1933).
(12) B. Topley and H. Eyring, J. Chem. Phys., **2**, 217 (1934).

heavier than water containing only O^{16} by 216 γ because of the presence of O^{18}.[13]

Using the Rayleigh distillation formula we found that the rejection of 5% of each sample of water in a volatile fraction increased the density of the residue by 0.022 γ because of the increased concentration of deuterium and by 0.050 γ because of the increased concentration of O^{18}. In the same way we computed the changes in density occasioned by distilling the 95% left in the still. This was done for a number of ratios of final residue to main distillate since it was not convenient to make the final residue always the same fraction of the original sample. From the density of the final residue it was easy to calculate the density of the main fraction of the distillate and hence the change in density caused by the distillation.

These changes have been plotted against the size of the final residue expressed in per cent. of the original sample in Fig. 5. The density changes
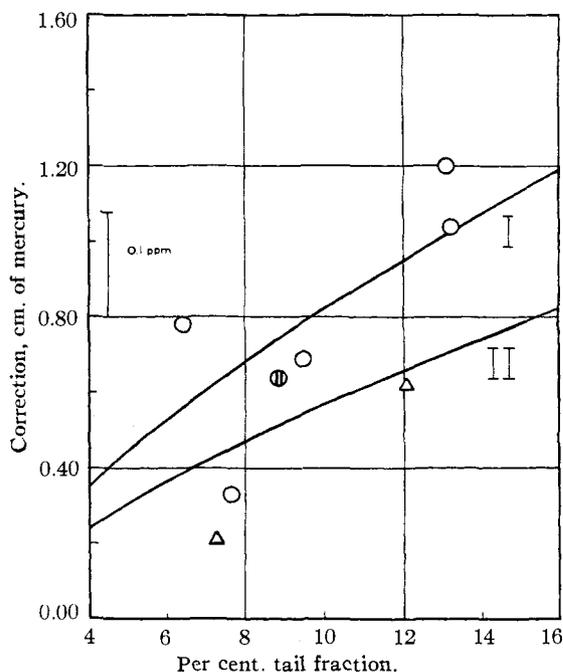

Fig. 5.—Corrections for distillations at atmospheric pressure.

have been expressed in centimeters of mercury by use of the calibration factor for our float. Curve II represents the change due to the fractionation of the oxygen isotopes only and is consequently applicable to samples of deuterium-free water while curve I represents the changes due to both oxygen and hydrogen isotopes in ordinary water.

(13) S. Manian, H. C. Urey and W. Bleakney, THIS JOURNAL, **56**, 2601 (1934).

The circles indicate the results of experiments with the stock samples of conductivity water while the triangles represent experiments with carefully purified deuterium-free water. The barred circle gives the result of an experiment in which the stock sample was twice distilled with the addition of the usual amounts of sodium hydroxide, potassium permanganate and sulfuric acid. The total change in density caused by the two distillations was, of course, halved in plotting the point. It is evident that the curves are consistent with the points within our experimental error. We have used these curves in making corrections for isotopic fractionation in all the distillations at atmospheric pressure used to purify various samples of water.

The Comparison of Various Samples of Water.—In Table IV are given the results obtained in comparing Cambridge tap water with stock D.

TABLE IV

THE COMPARISON OF CAMBRIDGE TAP WATER WITH STOCK
D

Balancing pressures in centimeters

Date	Obsd.	Distillation correction Atm.	Vacuum	Corr.	Stock D	Dif.
3/ 5/37	84.18	1.84	1.10	81.24	83.96	2.72
3/10/37	84.58	1.86	0.96	81.76	84.09	2.33
4/13/37	85.33	1.92	1.08	82.23	84.60[a]	2.37
5/27/37	84.90	1.99	1.10	81.81	84.23	2.42

Mean 2.46 ± 0.13

[a] The experiment on April 13, 1937, is subject to some uncertainty since it came in the period of the break in the thermal hysteresis curve of the float (Fig. 4). It has been arbitrarily referred to the preceding part of the curve since this results in better agreement with the other three experiments. Referring it to the following part of the curve would result in a discrepancy of 0.3 γ.

Table V gives the results of our comparisons of other samples of water with stock D and through it with Cambridge tap water.

The uncertainties indicated for the numbers in column 3 are the mean deviations from the mean. In all the cases in which we made more than one comparison of the density of a given sample of water with stock D the average deviation of the individual determinations from their means was 0.27 cm. or 0.10 γ. We estimate the uncertainty in the comparison of two of these samples as 0.14 γ. It is unfortunate that time did not permit us to carry out more determinations so that a satisfactory statistical treatment of the results would be possible. However, we feel that differences

TABLE V

THE DENSITIES OF NATURAL WATERS FROM VARIOUS
SOURCES

Source	No. of expts.	Stock D, cm.	Difference from Cambridge tap, cm.	γ
Cambridge tap	4	2.46 ±0.13	..	..
Osaka tap	3	2.71 ±0.19	0.25	0.09
London tap	1	2.83	.37	.13
Columbus tap	1	2.51	.05	.02
Washington tap	1	2.05	− .41	− .15
Average tap water				.02
Lake Mendota	3	4.63 ±0.54	2.17	.77
Lake Michigan	2	4.17 ±0.40	1.71	.61
Washington dist.	1	2.58	0.12	.04
Rjukan dist.	1	−6.36	−8.82	−3.12
Atlantic Ocean[a]	1	8.90	6.44	2.28
Atlantic Ocean[b]	2	10.79 ±0.14	8.33	2.95
Iceberg	1	−4.21	−6.67	−2.37

[a] Lat. 45°13′ N Long. 49° W.   [b] Lat. 00°00′.

greater than twice our uncertainty, *i. e.*, greater than 0.3 γ are almost certainly significant even though based on a single measurement while differences less than this may possibly be due to the random action of sources of error still beyond our control.

An earlier comparison of Lake Michigan water with Cambridge tap water made before our present type of still for distillations at atmospheric pressure was perfected indicated that Lake Michigan water is heavier than Cambridge tap water by 0.64 γ with an uncertainty of 0.23 γ. This is in excellent agreement with our present result.

It is apparent from Table V that the samples of tap water which we have measured have the same density within our experimental error. This implies that they are of the same isotopic composition, for it is rather unlikely that the isotopic ratios would be so compensated as to result in the same densities for waters of different isotopic compositions. We conclude that composite samples of water, like these tap waters, collected in the temperate zone and not subjected to evaporation may be expected to have the same density within a few parts in ten million.

Both of the samples from fresh water lakes are distinctly heavier than these tap waters although the difference is small (0.7 γ). This may be due to evaporation from the lakes which has slightly increased the concentrations of heavier isotopes in the lake waters. In order to compare our results with those of Hall and Jones[14] we may assume that Cambridge tap water and Madison City water are identical. On this basis, Hall and Jones' result for Lake Michigan water is identical with our own. They find, however, that Lake

(14) N. F. Hall and T. F. Jones, THIS JOURNAL, **58**, 1917 (1936).

Mendota water is 0.3 γ lighter than Lake Michigan water while we find that it is 0.1 heavier. The discrepancy is probably not greater than experimental errors in the density determinations.

The measurements upon the two samples of distilled water show clearly the necessity for care to avoid or correct for fractionation of isotopes in the purification of samples of water for exact density comparisons. In this connection it is interesting to note that all of our stock samples, which were prepared by two distillations of tap water, were lighter than tap water by approximately 1 γ. The first distillation was made in an ordinary gas-heated laboratory still and the second distillation from alkaline permanganate in a special conductivity water still, with care to reject equal light and heavy fractions.

The samples of water from the ocean are definitely heavier than fresh water. Our results are in better accord with those of Gilfillan[15] and Newman and Tohmfor[16] than with those of Wirth, Thompson and Utterback.[17]

It is interesting to note that water from the equator is heavier than water from the North Atlantic. This is probably due to the greater amount of evaporation in the tropics.

The sample for which we reported previously[18] a density 1.8 γ greater than tap water was collected a mile off shore at Gloucester, Mass. Although our distillation technique had not been perfected at that time, we believe that the difference between that sample and the sample collected in mid-Atlantic is significant. We attribute it chiefly to an admixture of polar water brought down by the Labrador current although fresh water from the coast may have played a part in diminishing its density.

The iceberg water represents the light fraction of atmospheric water condensed in the far north and contains an unusually large proportion of the light isotopes of hydrogen and oxygen. This is in accord with the results of other investigators[19] who have studied the densities of waters from glaciers and snow.

It appears from Table V that there is a difference of 5.3 γ between two of the samples of natural water measured in this research. This is considerably greater than the difference which would be produced by a single evaporation but, of course, is easily understandable as a result of fractional condensation. One might think of the earth as a huge fractionating column with an efficiency of about two theoretical plates. The heavy fraction of water from an isotopic standpoint collects in the tropics while the light fractions condense in the polar regions. We believe that a more extensive survey of the densities of natural waters would yield results of great interest to meteorologists and oceanographers.

Summary

1. Samples of tap waters which have been selected by various investigators as standards for the determination of the abundance of deuterium in natural water have been shown to have the same density with a precision of 0.1 γ.

2. The importance of careful control of the isotopic fractionation incidental to the purification of samples of water has been emphasized.

3. The role of evaporation and fractional condensation in determining the distribution of isotopes in the waters of the earth has been pointed out.

(15) E. S. Gilfillan, Jr., This Journal, **56**, 406 (1934).

(16) K. Newman and G. Tohmfor, *Z. physik. Chem.*, **A176**, 226 (1936).

(17) H. E. Wirth, T. G. Thompson and C. L. Utterback, This Journal, **57**, 400 (1935).

(18) C. H. Greene and R. J. Voskuyl, *ibid.*, **56**, 1649 (1934).

(19) (a) Riesenfeld and Chang, *Ber.*, **69B**, 1305 (1936); (b) Harada and Titani, *Bull. Chem. Soc. Japan*, **10**, 206 (1935); (c) Baroni and Fink, *Monatsh.*, 131 (1935); (d) Alexander and Munro, *Can. J. Research*, **14**, 1346 (1935).