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THE ISOTOPIC FRACTIONATION OF WATER

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ABSTRACT

When water is subjected to electrolysis an isotopic fractionation takes place, the evolved hydrogen being richer in the H^1 isotope and the evolved oxygen richer in the O^{16} isotope than is the water from which they are evolved. If the gases resulting from the electrolysis of water are recombined, the water produced has a lower density than the water from which they were evolved. The residual water grows progressively more dense as the elctrolysis proceeds, owing to the increasing concentration of the H^2 isotope of hydrogen and, to a less extent, also of the O^{18} isotope of oxygen. Curves illustrating the efficiency of the fractionation process are given. Substantially pure H^2, pure H^1, and pure O^{16} can be obtained by this fractionation process. The heavy water obtained by the process has a higher freezing point, a higher boiling point, and a lower refractive index than normal water. Isotopic fractionation of water by distillation and by adsorption has also been accomplished. A differential pycnometer method for measuring specific gravity, accurate to 1 part in a million, is described.

CONTENTS

I. INTRODUCTION

On December 9, 1931, an experiment was started at the Bureau of Standards for the purpose of attempting to produce an isotopic fractionation of water by electrolysis. In this experiment, normal water was acidified with sulphuric acid and electrolyzed between platinum electrodes.

The evolved gases were passed through a condenser for the purpose of condensing out the water vapor and collecting the spray and returning them to the system. The experiment was continued until 98 percent of the original water had been decomposed. The density of the residual water was then determined and found to be higher than that of normal water by 164 parts in a million. Before the completion of this experiment, samples of water were obtained from commercial electrolytic cells and examined spectroscopically and found to have a higher concentration of the H^2 isotope than normal water, thus proving that an isotopic fractionation of hydrogen takes place during electrolysis. This discovery was published [1] and it was stated

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[1] Washburn, E. W., and Urey, Harold C., Proc. Nat. Acad. Sci., vol. 18, p. 496, July 1932. The density of one sample of the water which was examined spectroscopically was greater than that of normal water by 52 parts per million.

that the electrolysis was being continued for the purpose of determining the physical properties of the new kind of water and also of ascertaining whether an isotopic fractionation of oxygen was also taking place. The purpose of the present paper is to present the results thus far obtained. The experimental work here recorded is to be regarded as exploratory in nature and should be repeated at some future time with greater accuracy and with more attention to detail and to the effects of various factors which could not be studied in the initial experiments.

II. THE PREPARATION OF WATER OF LOW DENSITY

A solution of sodium sulphate in normal water was caused to flow continuously through an electrolytic cell at such a rate that 10 percent of it was decomposed by the electrolysis. The oxygen from this electrolysis was combined with commercial hydrogen, and the density of the resulting water measured and found to be less by 11 parts per million (two determinations, -10.6 and -11.0) than that of the water produced by burning in air hydrogen from the same tank, this latter water having the same density as normal water (one determination, -1 part per million). The hydrogen from the above electrolysis was also burned to water, the density of which was only slightly ($\ngtr$ 5 parts per million) less than that of normal water.

The above experiment was then repeated with a larger amount of normal water which was decomposed only to the extent of 4 percent. The gases from this electrolysis were recombined and produced water having a density lower than that of normal water by 12 parts per million (two determinations, -12 and -13). This water was then re-electrolyzed in the same manner with 15 percent decomposition and the gases recombined. They produced water with a density lower than that of normal water by 19 parts per million (two determinations, -19.7 and, after redistillation, -18.8). This sample was tested for ammonia with Nessler's reagent with a negative result. A parallel experiment with water containing 0.2 part NH_3 per million gave a strong positive test.

The only plausible explanation of the above results appears to be the occurrence of an isotopic fractionation of oxygen, electrolytic oxygen being richer in the O^{16} isotope than the water from which it is generated. By a systematic continuation of experiments of the above character, it should be possible to prepare water of the formula $H_2^1O^{16}$ and consequently H^1 hydrogen and O^{16} oxygen. With these pure gases available in quantity, it will be possible to prepare water composed of H^1 hydrogen combined with normal oxygen and water composed of O^{16} oxygen combined with normal hydrogen. On electrolysis, the first of these will fractionate only with respect to oxygen and the second only with respect to hydrogen.

III. THE PREPARATION OF WATER OF HIGH DENSITY AND THE VARIATION OF DENSITY WITH CONTINUED ELECTROLYSIS

Fifteen liters of water having an initial specific gravity of 1.000034 was obtained from a commercial electrolytic cell.[2] This water was made 0.01 *N* with sulphuric acid and was then subjected to electrolysis

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[2] We are indebted to the Southern Oxygen Company of South Washington, Va., for this water.

with a current of 21 amperes between an anode of bright platinum and a gold-plated copper cathode covered with platinum black.

From time to time the electrolysis was interrupted and the specific gravity of the residual water determined. During the first part of the electrolysis, the excess of specific gravity (that is, the excess over that of normal water taken as unity) was doubled each time the volume of the water was reduced one half. The complete specific gravity curve is shown in figures 1 and 2.

When the volume of the residual water had been reduced to 4 liters, it was temporarily transferred to an electrolytic apparatus so designed as to permit the collection of the two gases separately. The oxygen evolved from this water was combined with normal hydrogen to produce 300 ml of water which was found to have normal density. The hydrogen was combined with normal oxygen and the specific gravity of the resulting water was measured and is represented on figure 1 by point *A*. Again, when the volume of the residual water had reached 300 ml ($D=1.000674$), the evolved gases were recombined to produce 100 ml of water whose specific gravity (1.000161) is represented on figure 1 by point *B*. The locus of the curve through points A and B when compared with the density curve of the residual

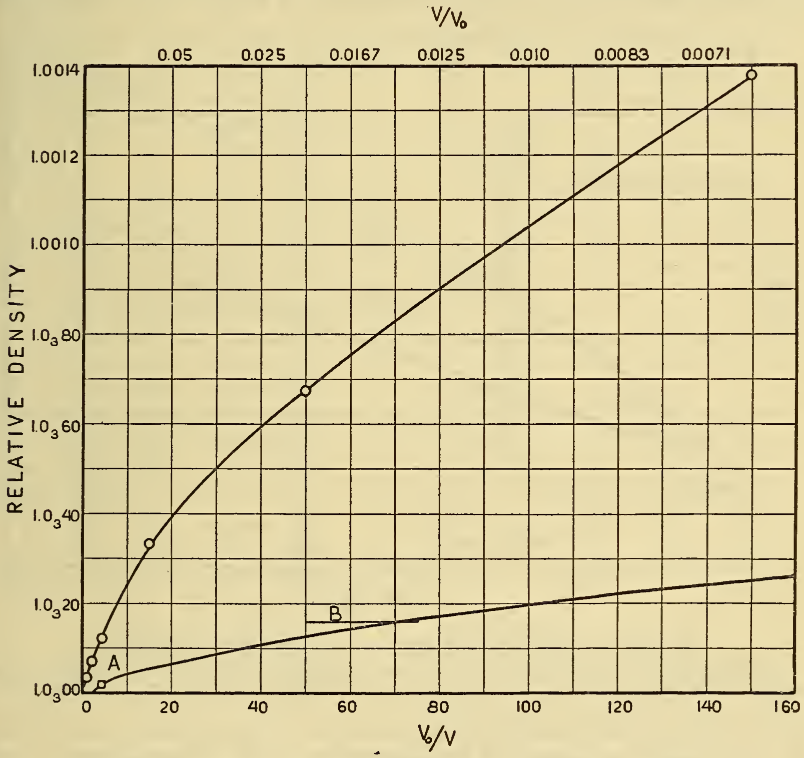

FIGURE 1.—*Variation of density with continued electrolysis.*

The ordinates are values of the specific gravity, the abscissae values of the ratio of the initial volume of the water to its volume at the time the current was interrupted in order to determine the density. The upper curve represents the density of the residual water, the lower curve that of the water formed by recombining the evolved gases.

water shows that a high efficiency of fractionation was being maintained as the electrolysis proceeded.

When the specific gravity of the residual water had reached 1.001376, the electrolysis was interrupted in order to measure some of the physical properties of this heavy water. These are reported below.

When electrolysis was resumed the water was made conducting with dehydrated barium hydroxide [3] and electrolyzed between platinum electrodes until its volume had been reduced to 18 ml. During this stage of the electrolysis, the oxygen and hydrogen evolved were dried and separately combined with normal hydrogen and normal oxygen respectively, to yield two samples of water, one of which contained only an increased concentration of O^{18} and possibly of O^{17} and the other only an increased concentration of H^2. The density of the first of these lots of water was measured and found to be about 18 parts per million higher than that of normal water. This increased density is further evidence of an isotopic fractionation of oxygen[4] but, as would be expected, the efficiency of the oxygen fractionation is much less than that of the hydrogen.

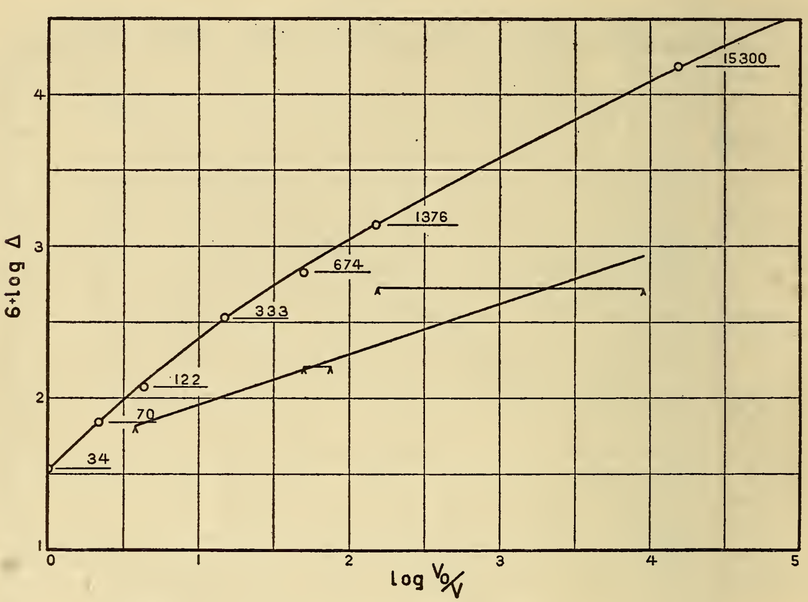

FIGURE 2.—*Variation of density with continued electrolysis.*

Logarithmic graph. The two curves have the same significance as in figure 1. The numerical values shown on the upper curve are the values of Δ, the increase in specific gravity, in parts per million.

The specific gravity of the water produced by burning the hydrogen was also measured and found to be 1.000539. The locus of this value is shown on figure 2.

The electrolysis was continued until a final sample of water 2.1 ml in volume was obtained. This water had a specific gravity of 1.0153. During this part of the electrolysis, the hydrogen evolved was col-

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[3] The addition of barium oxide for the purpose of giving a conducting solution has the advantage that a constant concentration of electrolyte can be maintained during the electrolysis owing to the limited solubility of $Ba(OH)_2 \cdot 8H_2O$, and the water held by this compound is readily recovered by ignition or by treating the solution with carbon dioxide and filtering off the barium carbonate formed. By this procedure none of the hydrogen is retained by the electrolyte.

[4] See p. 454.

lected and, after purification, its atomic weight was determined by reduction of CuO and found to be 1.012.

IV. THE DENSITY MEASUREMENTS

Since the course and extent of the isotopic fractionation are most readily measured by the change in the density of the water, it was necessary to have available an accurate method for measuring small density differences. The following method was devised for this purpose.

The density measurements were made with twin pycnometers of fused silica provided with 1 mm capillary necks (see figure 3). The volume of the capillary neck per unit length was determined by careful calibration with a mercury thread and the volume (V_1 and V_2) of each pycnometer up to a reference mark on the neck was determined by weighing the pycnometer filled with water.

The procedure for determining the density of a sample of water is the following: Pycnometer 1 is filled with the reference liquid, normal water, until the meniscus stands at some convenient point in the neck. The filling is accomplished by sucking the water into the pycnometer through a capillary silver tube.

Pycnometer 2 is then similarly filled with the liquid whose density is to be determined. Both pycnometers are placed side by side in a constant temperature bath provided with a plate glass window. As soon as equilibrium is attained, as shown by a stationary meniscus, the distance of each meniscus above the reference mark is read with the aid of a cathetometer.[5] Knowing the volume of the capillary per unit length, the difference $\Delta C = \mu_1 - \mu_2$, in the masses of the water above the reference marks in the two pycnometers, 1 and 2, can be computed.

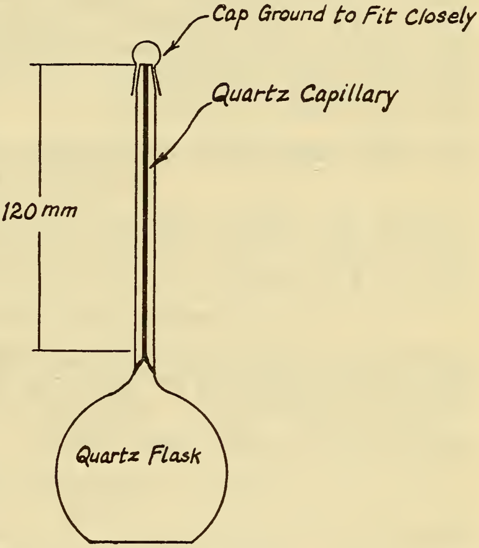

FIGURE 3.—*Fused-silica pycnometer*

The caps are now placed on the pycnometers and these are dried, placed on opposite pans of a balance and the difference, $\Delta m = m_1 - m_2$, in their masses determined to the nearest 0.03 mg. The above series of operations is now repeated with the reference liquid in pycnometer 2 and the other liquid in pycnometer 1, giving respectively $\Delta C'$ and $\Delta m'$.

The relative densities of the two liquids are then calculated from the relation

$$D = \frac{d}{d_N} = 1 + \frac{\Delta m - \Delta m' - \Delta C + \Delta C'}{d_N(V_1 + V_2)} = 1 + \Delta \tag{1}$$

where d_N is the density of the reference liquid, in this instance water.

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[5] Or, with some sacrifice of accuracy, by means of graduations on the neck of the pycnometer.

Obviously, it is not necessary to make any corrections for reduction to vacuo in any case where this method would be used, that is, where d is approximately equal to d_N. The method is essentially a differential one and with 60 ml pycnometers the results are reproducible to about 1 part in a million.

V. PURIFICATION OF THE WATER FOR DENSITY MEASUREMENTS

All of the density measurements reported in this paper were made on samples of carefully purified water. The method of purification followed was essentially that employed in preparing high-grade conductivity water. It consisted in the following series of distillations in the order named with rejection in each case of a small initial distillate and a small final residue: (1) Simple distillation; (2) distillation from alkaline permanganate solution; (3) distillation from dilute phosphoric acid solution; and (4) simple distillation, usually after the first density measurement.

VI. THE RELATION BETWEEN DENSITY AND ISOTOPIC COMPOSITION

Using the atomic weights,[6] $H^1=1.00778$, $H^2=2.01363$, $O^{16}=16$, $O^{17}=17$, and $O^{18}=18$, the absolute density of a sample of water is given by the relation

$$d=2(1.0058P_2+P_{18}+0.5P_{17}+9.00778)/V \tag{2}$$

in which P_2 is the atomic fraction of H^2 in the hydrogen, P_{18} and P_{17} the atomic fractions of O^{18} and O^{17} in the oxygen and V the effective average molal volume. Referred to normal water as unity the specific gravity of the water will be

$$D=\frac{d}{d_N}=1+\Delta. \tag{3}$$

Hence

$$\Delta=\frac{2(1.0058P_2+P_{18}+0.5P_{17}+9.00778)-Vd_N}{Vd_N}. \tag{4}$$

For normal water, if we put

$$P_2=(3\pm2)\times10^{-5} \tag{5}$$

$$P_{18}=(159\pm3)\times10^{-5} \tag{6}$$

$$P_{17}=\text{negligible} \tag{7}$$

we have

$$Vd_N=2(1.0058P_2+P_{18}+9.00778) \tag{8}$$

$$=18.0188\pm0.0001. \tag{9}$$

Hence, if V is independent of the isotopic composition,

$$\Delta=\frac{2.0116P_2+2P_{18}+P_{17}-(0.0032\pm0.0001)}{18.0188\pm0.0001}. \tag{10}$$

If in the given sample of water, the oxygen is normal oxygen, equation (10) gives

$$P_2=8.957\Delta+0.00003\pm0.00008. \tag{11}$$

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[6] Bainbridge, Kenneth T., Phys. Rev., vol. 44, p. 57; 1933.

If the hydrogen is normal hydrogen, equation (10) gives

$$P_{18}+0.5P_{17}=9.0094\Delta+0.0016\pm0.00007. \qquad (12)$$

The calculation of P_2 or of $P_{18}+0.5P_{17}$ by the above equations is rendered uncertain to the extent indicated by the ± signs, owing to our present lack of exact knowledge of the isotopic compositions of normal hydrogen and normal oxygen. When pure H^1 and pure O^{16} become available (and their preparation appears to offer no particular difficulty) it will be possible to obtain exact equations for P_2 and for $P_{18}+0.5P_{17}$ in terms of Δ, provided the molal volume V can be shown to be independent of the isotopic composition.

From the data obtained in our first experiment, described in section 1 above, it is obviously possible to compute a value for the atomic fraction of H^2 in the hydrogen of normal water by neglecting the oxygen fractionation and assuming that the electrolysis is 100 percent efficient with respect to the hydrogen fractionation. The value thus obtained is 3×10^{-5}. This is probably a minimum value.

VII. SOME PHYSICAL PROPERTIES OF THE HEAVY WATER

The refractive index, freezing point, boiling point, and thermal expansion of the heavy water were measured. The results of some of these measurements have already been published.[7] The methods used are described below. A sample of water with specific gravity 1.001376 was used in all of the measurements.[8]

The refractive index.—This was determined by the Optics Division of this Bureau. At 25° C, the refractive index of the heavy water for $\lambda=5876$ A was found to be less than that of normal water by $(59\pm1)\times10^{-6}$.

The freezing point.—Using 60 ml of water, the time-temperature cooling curve was determined through the freezing range with a platinum resistance thermometer sensitive to better than 0.001° C. The first experiment was made with normal water. This was followed by two runs with the heavy water and these by a second run with normal water. The results are shown in figure 4. The flatness of the curves in the freezing range indicates that during crystallization isotopic fractionation does not occur to an appreciable extent for the volume of water used in these experiments.

The boiling point.—Twin vacuum-jacketed boilers of the Cottrell[9] type provided with internal coil heaters of platinum were connected by a 10-junction thermel of copper-constantan. The difference in temperature of the two junctions was measured with a Brooks-Spinks[10] potentiometer and a sensitivity of better than 0.001° was attained. In the first experiment, normal water was placed in both boilers and the zero of the apparatus determined. The normal water in one boiler was then replaced by the heavy water and the difference in boiling temperatures directly measured. The two kinds of water were then interchanged in the two boilers and the experiment repeated. The above set of experiments was then repeated with a White poten-

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[7] Washburn, Edward W., Smith, Edgar R., and Frandsen, Mikkel, J. Chem. Physics, vol. 1, p. 288, 1933.

[8] Later measurements with a sample of water of specific gravity 1.1 have recently been reported by G. N. Lewis, J. Am. Chem. Soc., vol. 55, p. 3057, 1933.

[9] Cottrell, F. G., J. Am. Chem. Soc., vol. 41, p. 721, and figure 1, p. 730, 1919.

[10] Brooks, H. B., and Spinks, A. W., Bur. Standards Jour. Research, vol. 9, p. 781, 1932.

tiometer. All four results agreed and showed that the boiling point of the heavy water was higher than that of normal water by 0.02 ± 0.002° C.

The temperature of maximum density.—The twin silica-glass pycnometers were filled, one with normal water and the other with the heavy water, and placed side by side in the regulated bath. The bath was held at a series of constant temperatures between 2.5 and 4.9° C. and when equilibrium was attained the volume of each sample of water was measured by determining with a cathetometer the position of the meniscus in the capillary. The relation between temperature and volume is displayed graphically in figure 5. The peculiar effect observed in the neighborhood of 3.75° is apparently real but discussion of this phenomenon will be postponed until further measurements can be made.

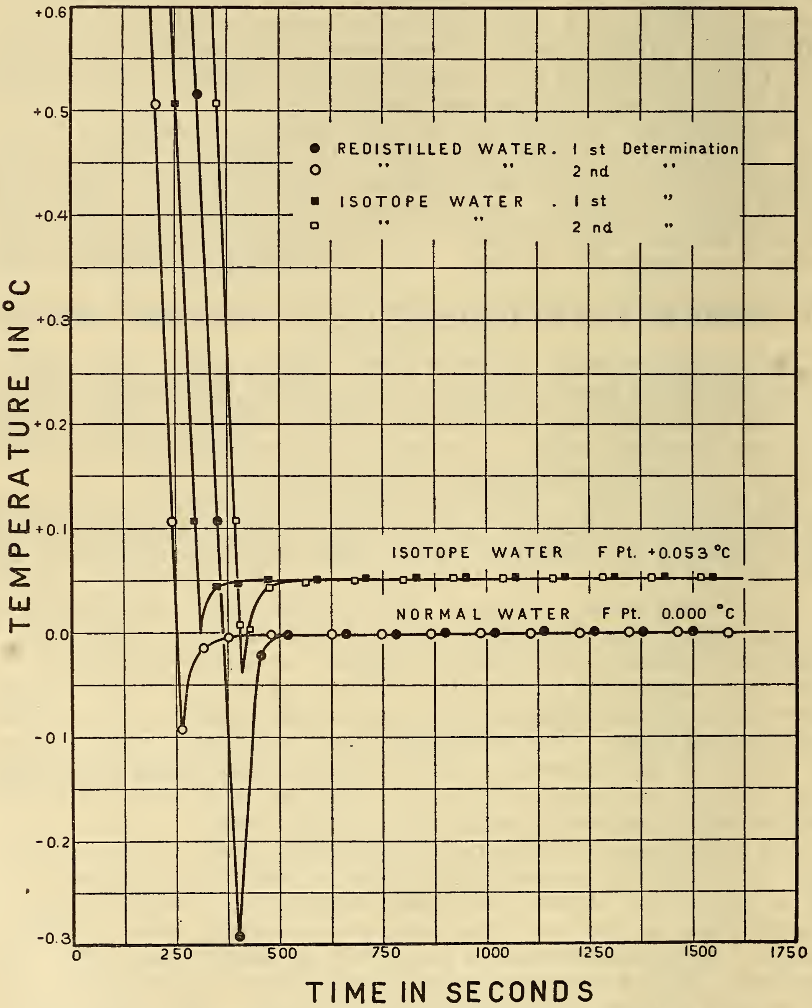

FIGURE 4.—*Time-temperature cooling curves through the freezing point.*

The "isotope water" employed had a specific gravity of 1.001376.

VIII. ISOTOPIC FRACTIONATION OF WATER BY DISTILLATION AND BY ADSORPTION[11]

By distilling with the 35-foot packed-column still described in a previous publication,[12] two fractionations were made with the results shown in table 1.

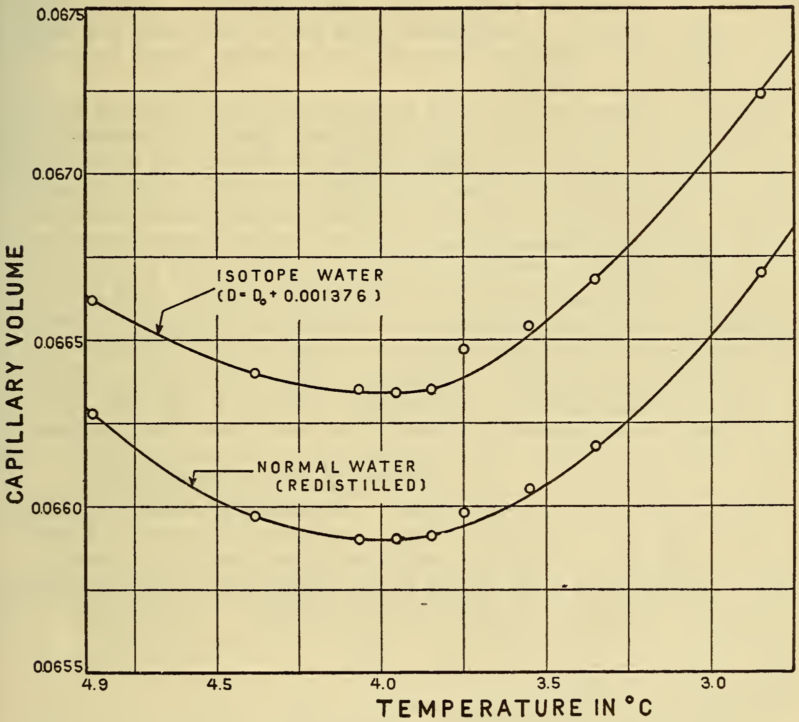

Figure 5.—*Thermal expansion of water in the neighborhood of 4° C.*

Table 1

[ppm=parts per million]

Water used	Volume distilled	Date of distillation	Density increase		Density difference directly determined. Residue-distillate
			Still residue	Initial distillate	
	l		*ppm*	*ppm*	*ppm*
Normal Δ=0	1.5	December 1931	32	−14	41
Heavy Δ=53.3 ppm	10	April 1933	53.3	−13.2	64.9

These results demonstrate that isotopic fractionation by distillation is entirely feasible and this process should find application as a supplement to fractionation by electrolysis. Further investigation is needed in order to determine how distillation operates with respect to the fractionation of oxygen and of hydrogen, since it depends

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[11] The results of these experiments were briefly reported in a previous publication. Washburn, Edward W., and Smith, Edgar R., J. Chem. Phys., vol. 1, p. 426, 1933.

[12] Bruun, Johannes H., and Schicktanz, Sylvester T., Bur. Stands. J. Res., vol. 7, fig. 17, p. 872, 1931.

upon a different principle and may be more efficient, for example in the fractionation of the oxygen isotopes, than is the process of electrolysis.

Ordinary conductivity water as prepared in the laboratory is the result of several distillations and different lots of such water may be expected to show small differences in density. Owing to the inefficient stills used in preparing such water, the differences should be less than 1 ppm, however. Differences of a few tenths part per million in the density of different lots of conductivity water have been reported by Lamb and Lee.[13]

Isotopic fractionation of water by adsorption on charcoal has also been found to occur. In one experiment, 300 g of charcoal was heated in high vacuum to a temperature of 350° C. The bulb containing the charcoal was then immersed in liquid air and oxygen admitted. The oxygen was then pumped out, after which the charcoal was gradually heated again to 350°. After the bulb had cooled to room temperature, 500 ml of heavy water ($\Delta = 53$ ppm) was admitted to the bulb and allowed to stand for 5 weeks. 176 ml of the supernatant water was distilled off and set aside, after which the distillation was continued and the last 123 ml which distilled off was also collected and set aside. The last of the water came off when the charcoal had attained a temperature of 620° C. in high vacuum.

The densities of these two end fractions were then compared directly with each other and separately with the original water used in the experiment. The following results were obtained:

Density difference, adsorbed water − supernatant water, 12.4 ppm.
Density difference, original water − supernatant water, 6.5 ppm.
Density difference, adsorbed water − original water, 6.5 ppm.

These results show that water can be isotopically fractionated by adsorption. Further investigation in this field is necessary, however, to determine the practical possibilities of the method.

WASHINGTON, August 2, 1933.

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[13] Lamb, Arthur B., and Lee, R. Edwin, Am. Chem. Soc., vol. 35, p. 1681, 1913.