[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Preparation of Deuterium-Free Water. Deuterium Content of Ordinary Water and the Atomic Weight of Hydrogen. Electrolytic Separation of the Oxygen Isotopes[1]

BY HERRICK L. JOHNSTON

Both the value of the H/D ratio of hydrogen in ordinary water and the question of the existence or non-existence of electrolytic separation of the oxygen isotopes[2,3] have been subject to some doubt. Recently, in the course of preparing relatively large quantities of deuterium-free water for certain biological investigations, opportunity was afforded to obtain quantitative data of considerable accuracy bearing on both of these important questions.

Fifty liters of Columbus City water, made 0.5 *N* in potassium hydroxide,[4] were reduced by five successive stages of fractional electrolysis to a final light fraction of 45 cc. The electrolysis was carried out between iron electrodes which were known to give, at higher concentrations of deuterium, an electrolytic separation of 8 toward the isotopes of hydrogen. 25% of the electrolyte was decomposed in each stage of the electrolysis and the electrolytic gases, dried with calcium chloride and passed through an explosion trap containing fine sand, were burned at a Pyrex jet. This light 25%, from each stage, served for the preparation of the electrolyte in the subsequent stage.

Samples of the initial water and samples of the "light water" from each of the electrolytic stages were carefully purified[5] and densities determined with a precision of ±0.5 p. p. m. (equivalent to 0.002° in the "float temperature"), or better, by means of a totally submerged float. The results are given in Table I.

TABLE I

DENSITY LOSSES (IN TERMS OF EQUILIBRIUM TEMPERATURES FOR THE TOTALLY SUBMERGED FLOAT) IN THE RECOMBINED GASES FROM SUCCESSIVE STEPS IN ELECTROLYSIS

			Beckmann thermometer readings, °C.		Density loss in p. p. m.
Sample			I	II[6]	
Normal water			3.491	...	..
Light fraction from	1st	electrolysis	3.430	...	16.7
	2d	..	3.410	...	22.1
	3rd	..	3.403	3.404	23.9
	4th	..	...	3.398	25.4
	5th	..	...	3.392	27.0

A simple calculation indicates that, for any reasonable value of the H/D ratio in ordinary water, two electrolytic stages with a separation factor of 8 should reduce the deuterium content of the recovered gases to a value that would correspond to less than 1 p. p. m. in the density of water and that a third electrolysis should lower the deuterium concentration in the light fraction to a point below our ability to detect it. Density changes observed in later stages of electrolysis must, therefore, result from the electrolytic separation of the oxygen isotopes alone. Since we may anticipate that the percentages of O^{18} and of O^{17} in the oxygen will change but slightly in a

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[1] Presented before the Symposium on Deuterium, Joint Meeting of Sections B and C, American Association for the Advancement of Science, Pittsburgh. Penna., Dec. 28, 1934.

[2] (a) Lewis and Macdonald, *J. Chem. Phys.*, **1**, 341 (1933); (b) Lewis and Cornish, THIS JOURNAL, **55**, 2616 (1933); (c) Bleakney and Gould, *Phys. Rev.*, **44**, 265 (1933); (d) Ingold and Ingold, *Nature*, **134**, 661 (1934); for numerous earlier references, see Bleakney and Gould.

[3] (a) Washburn, Smith and Frandsen, *Bur. Standards J. Research*, **11**, 453 (1933); (b) Webb, *Ind. Eng. Chem., News Ed.*, **12**, 63 (1934).

[4] The deuterium introduced with this amount of potassium hydroxide is sufficient to raise the density of the electrolyte made with deuterium-free water by only 0.1 p. p. m. and will influence the density of the water produced by combustion of the electrolytic gases by less than 0.02 p. p. m.

[5] For details of the purification see Snow and Johnston, *Science*, **80**, 210 (1934). Specific gravities were measured with a Pyrex float at about 27°. Calibration against purified normal water was made every day that samples were analyzed in order to guard against calibration changes due to variations in the float. During the period of the determinations recorded in this paper this proved unnecessary since four independent calibrations gave the respective values: 3.491°, 3.491°, 3.492° and 3.491° (±0.001° in each calibration) for the temperature of floating equilibrium in normal water. Our method of procedure would also have corrected for effects due to variations in atmospheric pressure [*cf.* Gilfillan, THIS JOURNAL, **56**, 406 (1934); also *cf.* Lamb and Lee, *ibid.*, **35**, 1666 (1913), and Richards and Harris, *ibid.*, **38**, 1000 (1916)] had such effects existed. However, during approximately one year's experience with this same float, in almost daily use, we have observed no fluctuations such as can be ascribed to atmospheric pressure variations. Our experience in this respect coincides with that of Emeleus and co-workers [*J. Chem. Soc.*, 1207 (1934)] and with that of Richards and Harris (*loc. cit.*) for a float of borosilicate glass.

[6] The product resulting from re-electrolysis of the light fraction produced in the first step (by 25% decomposition of the original 50 liters) was accidentally contaminated by breakage of a cell during a fourth step in electrolysis. To complete the data a second light fraction (designated as II), equal in volume to the first, was electrolyzed from the original 37-liter residue. To make the readings under the two columns comparable for the later steps in electrolysis a small correction amounting to 0.002° (equivalent to 0.6 p. p. m. in density) was subtracted from the observed readings on II to correct for the slight O^{18} enrichment of the original 75% residue from which it was produced. The corrected readings are recorded in the table. Justification for this procedure is indicated by the good agreement of II after a third step in electrolysis, with I at the same state. This indicates that the excess deuterium initially in II, as well as that in I. was completely removed in three electrolyses.

single stage of the electrolysis, we would expect that the density losses which accompany successive electrolyses of deuterium-free water would be nearly linear with the numbers of successive electrolyses.

Figure 1, in which the precision of the individual density measurements is indicated by the dimensions of the circles, shows that the expectations expressed in the preceding paragraph are realized experimentally. Extrapolation of the linear portion of the curve back to the x-axis intercepts the latter at −0.070° relative to ordinary water and thus measures the density change which would accompany the complete removal of deuterium *alone* from ordinary water. This is equivalent to 19.1 p. p. m. in density (± about 1 p. p. m. for probable error in the slope of the line) and gives an H/D ratio,[7] for ordinary water, of 5750 ± 250.

This result confirms Bleakney and Gould's[2c] figure of 5000 ± 500, obtained with the mass spectrograph, and fails to agree with the recent results of Ingold and Ingold,[2d] who report a ratio of 9000 to 1.[8]

From the slope of the linear portion of the curve in Fig. 1, which proves to be 0.006° (equivalent to 1.6 p. p. m. in density) we obtain 1.008 ± 0.003 for the electrolytic separation factor of O^{18} from O^{16}. This factor is defined, in a manner similar to that for hydrogen, by the relationship[9]

$$d \log O^{16} = \alpha \, d \log O^{18} \qquad (1)$$

The factor 1.008 yields a value for O^{18} enrichment of the residue equivalent to 1.2 p. p. m. increase in density for each time that an aqueous solution is reduced to half volume by electrolysis. It also yields an O^{18} impoverishment in the first electrolytic oxygen from normal water which amounts to about 2 p. p. m. in density. Although these changes in density are readily measurable by precision methods and are significant in some experimental work relating to water of low deuterium content, they likewise show the futility of attempting the preparation of O^{18} or of O^{17} in high concentration, by electrolysis. Thus one may easily compute, from the factor 1.008, that a volume reduction sufficient to convert ordinary water to a residue 99% in D_2O will enrich the residue with O^{18} to the extent of only 20 p. p. m. in the density of the water. Yet more striking, as an illustration, is the computation that reduction of the entire ocean, by electrolysis, to a residual cubic millimeter would less than double the concentration of the heavy isotopes of oxygen.[10]

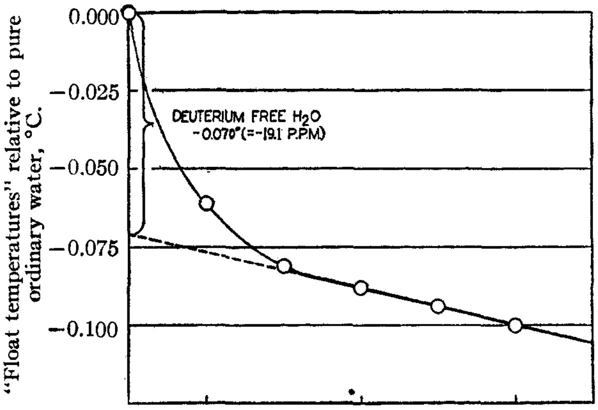

Fig. 1.—Density decrease of the light fractions of water as a function of the stages of electrolysis.

Other methods[11] of bringing about the separation appear more promising.

Using Aston's figure[12] of 1.00778 for the mass of the H atom, that of Bainbridge,[13] 2.01363 for the D mass number, and the figure 5750 ± 250 for the ratio H/D, we obtain 1.00795 for the atomic weight of normal hydrogen based on the scale O^{16} = 16.0000. Converting to the chemical scale, we obtain 1.00770 by the use of Manian, Bleakney and Gould's[9] value for the O^{18} abundance ratio, or 1.00775 by Mecke and Childs' value for the

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[7] Based on the figure 1.1079 for the specific gravity (25°) of pure D_2O.

[8] These authors state that they employed electrolysis, chemical separation and fractional distillation and obtained a maximum decrease in density, of 12 p. p. m., which they believe is characteristic of pure protium oxide. In our own work we obtained a considerably larger decrease than this in the first stage alone. Furthermore, we found this decrease to be highly reproducible. Thus the entry 3.430° in Table I represents the average of four independent electrolyses, each with about 12 liters of the original water, none of which deviated from the mean by more than 0.001°.

[9] Integration of (1), and rearrangement of terms, yields

$$(O_i^{18}/O_f^{18})^{\alpha-1} = (O_i^{16}/O_i^{18})/(O_f^{16}/O_f^{18}) \qquad (2)$$

as an exact integral, in which the subscripts refer to initial (i) and to final (f) quantities of the oxygen atoms in the electrolyte during a single stage in the electrolysis. In computing α by this equation we employed 514 [Manian, Urey and Bleakney, THIS JOURNAL, **56**, 2601 (1934)] for the ratio (O_i^{16}/O_i^{18}) and evaluated the other ratios in (2) with the aid of the slope taken from Fig. 1. It seems justifiable to disregard the influence of O^{17} enrichment in this calculation.

[10] There is, of course, the possibility of a more efficient separation of oxygen isotopes with other electrode materials or under other conditions of electrolysis but it seems hardly probable, in view of the high efficiency of our cells toward deuterium separation, that this would be true to such an extent as to modify greatly the above figures.

[11] (a) Lewis and Cornish, THIS JOURNAL, **55**, 2616 (1933); (b) Lewis and Luten, *ibid.*, **55**, 5062 (1933).

[12] Aston, *Proc. Roy. Soc.* (London), **A115**, 487 (1927).

[13] Bainbridge, *Phys. Rev.*, **44**, 57 (1933).

abundance ratio. The present accepted value on the chemical scale is slightly higher than this although it would appear that the chemical determinations should run low by from 0.00010 to 0.00015 unit due to isotopic separation in the preparation of the gas.

Summary

Deuterium free water (less than 1 D atom in 1,000,000 H atoms) has been prepared by the fractional electrolysis of 50 liters of normal water.

Density changes were determined for the light fraction in each step of the electrolysis, by means of the totally submerged float. Graphic treatment of the data yields 19.1 ± 1 p ,p. m. for the influence of deuterium on the density of ordinary water. This corresponds to an abundance ratio of 5750 ± 250 for H/D, which confirms Bleakney and Gould's figure of 5000 ± 500, obtained with the mass spectrograph.

The electrolytic separation factor for O^{16} relative to O^{18} proves to be 1.008 ± 0.003. This indicates the futility of attempting to prepare pure O^{18} or pure O^{17} by electrolysis.

From the H/D ratio of 5750 the atomic weight of normal hydrogen is computed to be 1.00795 on the O^{16} scale. It is 1.00770 or 1.00775 on the chemical scale, based on O^{18} abundance ratios of Manian, Bleakney and Urey or of Mecke and Childs, respectively.

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[Contribution from the Department of Chemistry, Cornell University]

The Properties of Thallium Triethyl[1]

By E. G. Rochow and L. M. Dennis

Thallium triethyl was first prepared by Groll[2] in 1930,[3] by the action of lithium ethyl upon diethyl thallic chloride in solution in petroleum ether, the apparatus being filled with nitrogen.

The authors first attempted to synthesize thallium trimethyl by the interaction of (a) mercury dimethyl and metallic thallium at elevated temperatures, (b) methyl iodide and an alloy of sodium and thallium, and (c) thallium-copper couple on methyl iodide. In each case no appreciable yield of a volatile compound of thallium was obtained.

To gain familiarity with the Groll synthesis of thallium triethyl with the view of ascertaining whether a modification of it might yield the methyl compound, his method was repeated, but the reactions were carried on in the vacuum apparatus developed in the Cornell laboratory which made possible the preparation, purification and study of the properties of thallium triethyl in the absence of air, moisture and foreign gases that might affect its behavior.

Experimental

Pulverized diethyl thallic chloride was placed in the tube H (Fig. 1), which was then evacuated and sealed. The end of the normal joint at G was closed by a curved drawn-out tip which could be broken off against a stationary indentation when H was rotated in the joint G. Granular metallic lithium was placed in the bulb C, the system attached to the vacuum apparatus by means of the joint A, and evacuated.

Purified petroleum ether and mercury diethyl were distilled into C and the stopcock B was closed. C was heated to 70° for four days, the arms being cooled to prevent loss of petroleum ether. The solution of lithium ethyl thus formed was poured into the bulb F by raising C until sufficiently tilted to allow decantation through the tube D. Some petroleum ether was distilled back into C to dissolve the remaining lithium ethyl, and again decanted. F was then sealed off at the constriction E. The bulb was cooled to −10° and the contents of the tube H added by breaking off its tip at G. The bulb was then shaken mechanically for five hours while the reaction proceeded.

The bulb was attached to the vacuum chain by means of the joint I and the volatile substances were distilled out. Petroleum ether was separated from the alkyl by fractionating *in vacuo*, leaving thallium triethyl as a bright yellow liquid.

The alkyl was analyzed by distilling a sample into a weighed bulb, condensing an excess of water in the bulb,

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] H. P. A. Groll, This Journal, **52**, 2998 (1930).

[3] We had planned to take up, in the Cornell laboratory, the study of the normal thallium alkyls as a continuation of our investigations of the alkyls of gallium [Dennis and Patnode, *ibid.*, **54**, 182 (1932); "Gallium Trimethyl," Thesis of P. L. Brandt, 1932] and indium [Dennis, Work and Rochow, *ibid.*, **56**, 1047 (1934)], but as Dr. Groll's article established his priority in the field, we deferred doing so until word was received from him that he did not intend to carry further his researches on thallium compounds of this type.