The Natural Separation of the Isotopes of Hydrogen. I. The Concentration of Deuterium in Benzene, Kerosene and Honey

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Waters obtained in the combustion of benzene, kerosene and honey have been analyzed for their deuterium content by density measurements. In all cases the concentration of deuterium is greater in these substances than it is in distilled water from Lake Michigan.

THE interesting discoveries of Lewis[1] and of Taylor, Swingle, Eyring and Frost[2] of the inability of living organisms to live or to grow in nearly pure deuterium oxide suggested the possibility of a natural selection of protium in preference to deuterium in the animal and vegetable kingdoms. In order to ascertain if any separation of the isotopes of hydrogen takes place in the organic world I began last December to analyze naturally occurring substances for their deuterium content. Meanwhile Washburn and Smith[3] in an investigation begun in August, 1932, were examining the sap and the dry wood of a willow tree for their deuterium content. A preliminary notice of this investigation states that water obtained from the sap is 2.8 parts per million heavier than ordinary water while water obtained from the combustion of the dry wood was 5.4 parts per million heavier than ordinary water. They also proved that this increase of density was due to an increase in percentage of deuterium in the water.

I have examined honey, kerosene and benzene and find, similarly to Washburn and Smith, that water obtained from the combustion of these substances is in all cases *heavier* than ordinary water. These results were not expected on the basis of the physiological experiments carried out in pure deuterium oxide since if the deuterium had been rejected instead of utilized in the synthesis of cellulose, honey, benzene and kerosene the water resulting from the combustion of these substances would have been *lighter* than ordinary water. However, experiments[4] of Barnes, of Meyer and of Richards on the physiological behavior of *Spirogyra sp.*, *Aspergillus sp.* and *Saccharomyces cerevisiae* indicate that dilute solutions of deuterium oxide have a decided effect in accelerating or modifying the growth and development of these substances. If this is the case, one might expect that deuterium would be selected preferentially, thereby increasing the atomic weight of hydrogen in organic compounds and causing the density of water obtained by combustion to be greater than that of ordinary water. In this way it is possible to explain qualitatively the increase in the atomic weight of hydrogen reported by Washburn and Smith and by this paper.

EXPERIMENTAL

(a) Honey

Honey of an unknown origin was dropped at the rate of one drop every twenty seconds onto dull red hot copper oxide in a Pyrex tube through which a stream of dried tank oxygen was passed. The details of this burner are shown in Fig. 1 where A is the reservoir for the liquid honey, B is the tip from which the honey dropped onto the copper oxide D, E is a side tube to allow the tip B to be freed of tar or carbon by a blast of air, and C and D are inlets for oxygen. The copper oxide was electrically heated and the combustion

[1] G. N. Lewis, J. Am. Chem. Soc. **55**, 3503 (1933).

[2] H. S. Taylor, W. W. Swingle, Henry Eyring and A. A. Frost, J. Chem. Phys. **1**, 751 (1933).

[3] E. W. Washburn and E. R. Smith, Science **79**, 2043 (1934).

[4] T. C. Barnes, J. Am. Chem. Soc. **55**, 4332 (1933); Am. J. Bot. **20**, 681 (1933); S. L. Meyer, Science **79**, 210 (1934); O. W. Richards, Am. J. Bot. **20**, 679 (1933).
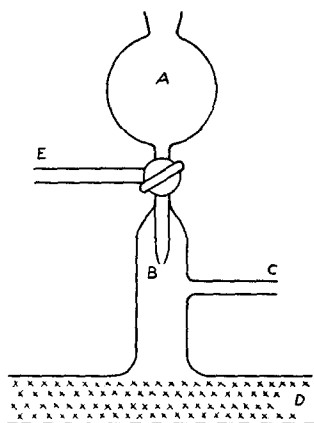
FIG. 1. Burner for honey.

FIG. 2. Burner for kerosene and benzene.

was allowed to run continuously for seventy-two hours until 570 cc of water had been condensed. The formation of tar and carbon at B or on the inside walls of the upright tube was prevented by passing oxygen in at C in addition to at D and by keeping the copper oxide hot enough so that the honey burst into a little flame as each drop fell on the copper oxide. The condensed water contained appreciable quantities of organic matter judging from its color and odor. It was first distilled in such a way that the vapors were mixed with dried oxygen and then passed through a 55 cm column of dull red hot copper oxide. From this point on the purification consisted of ten distillations from alkaline potassium permanganate, a distillation in vacuum followed by distillations from alkaline potassium permanganate and a dilute solution of phosphoric acid. No change in density could be detected between the distillation in vacuum and the subsequent distillation from phosphoric acid.

(b) Kerosene

Kerosene from the Oklahoma oil fields was burnt at the surface of a sintered glass wick in an apparatus, the details of which are shown in Fig. 2 where A is the inlet for kerosene, B and C are air inlets, W is the sintered glass wick made of ground Pyrex glass and A represents a packing of string to prevent a too rapid flow of kerosene into the burner. The burner was inserted into the combustion apparatus and held in place by a rubber connection at E. Air was admitted into the apparatus at B and C, the speed of flow
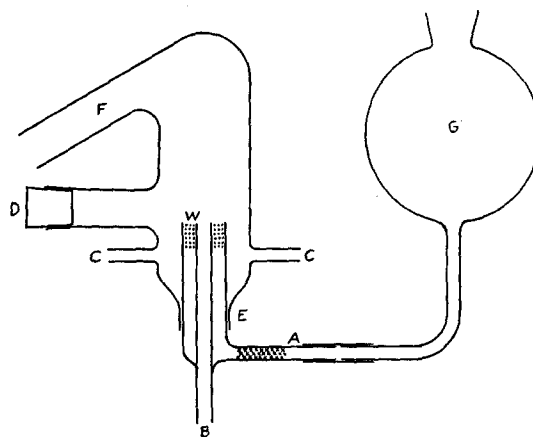
through B could be controlled independently. The cork stopper at D could be removed to light the flame. The vapors were led to an efficient condenser by means of the tube F. It was impossible to obtain a satisfactory combustion of kerosene in an atmosphere of pure oxygen due to the deposition of carbon in tree-like growths on the surface of the wick. The level of the kerosene in the reservoir, G was maintained at a height three inches above the top of the wick in order to provide the necessary pressure to force the kerosene up onto the sintered glass wick. About 600 cc of kerosene were burnt over a period of 72 hours and about 500 cc of water were obtained. The water was purified in the same way that the honey water was purified except that no distillation in vacuum was carried out and only seven redistillations were considered necessary.

(c) Benzene

Mallinckrodt thiophene free benzene obtained as a by-product in the distillation of coal was burnt in the apparatus illustrated in Fig. 2. Due to the relatively high percent of carbon in benzene the combustion was more difficult, required more air and gave rise to considerably more soot than did the combustion of kerosene. In order to prevent the large amount of uncondensable gases such as carbon dioxide and nitrogen from carrying off too much of the desired water vapor, the gases were not passed through the water collecting flask but were by-passed over it. The water was first filtered to remove as

much carbon as possible, then distilled twice from alkaline permanganate and its density measured. Two more redistillations from alkaline permanganate did not measurably alter the density.

(d) Tests of the purity of the water

Since the measurement of the relative density of water may be carried out with an error of less than a part per million (*vide infra*), the only uncertainty in the results reported in this paper is the question of the purity of the water. The density of the benzene water after the second and fourth distillations was 7.9 parts per million heavier than ordinary water. In order to see if this difference in density was caused by impurities, about 250 cc of this benzene water were electrolyzed at a current of nine amperes between a lead anode and a nickel cathode. The mixed hydrogen and oxygen gases were next washed in three tall towers containing, respectively, distilled water, ten percent potassium hydroxide solution and concentrated sulfuric acid. Finally the gases were converted back to water over a copper catalyst. The density of this water after a distillation from alkaline permanganate was still greater than that of ordinary water treated in the same way to the extent of 3.6 parts per million. Thus, 250 cc of ordinary water electrolyzed until 3.5 cc remained in the electrolysis cell decreased in density 7.7 parts per million while the benzene water electrolyzed until 4.0 cc remained in the electrolysis cell decreased in density 12.0 parts per million. It is difficult to decide how much of this decrease is due to a separation of isotopes and how much to elimination of impurities.[5] The point of interest is that the benzene water was still heavier than ordinary water similarly treated.

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[5] The difference between a decrease in density of 7.7 and 12.0 parts per million seems large. However, if the decrease in density is due entirely to a separation of the isotopes of hydrogen, and if ordinary water is 20 parts per million and benzene water 27.9 parts per million heavier than pure protium oxide then a decrease of 7.7 parts in 20 parts is a decrease of 39 percent while a decrease of 12.0 parts in 27.9 parts is a decrease of 43 percent. From this standpoint the greater decrease in density of the benzene water on electrolysis does not indicate that the benzene water was more impure than the ordinary water, but merely that it contained more deuterium. In other words the

Another method of testing the effectiveness of the methods outlined above for purifying water is to contaminate some ordinary water deliberately and then to study the rapidity with which it can be made pure again. To 500 cc of ordinary distilled water about 1 cc of the following chemicals was added, acetic acid, ethyl alcohol, benzoic acid, formaldehyde, acetaldehyde, benzene, ammonium nitrate, sodium nitrate and sodium nitrite. To the solution enough potassium permanganate was added to give a permanent purple color and a considerable quantity of barium hydroxide was added. Distillation from this mixture was difficult due to the presence of a large amount of manganese dioxide. After a second distillation from alkaline permanganate, the water was four parts per million heavier than pure water, after a third distillation the difference in density was only one part per million while after a fourth distillation from alkaline permanganate the density of the previously contaminated water was equal to that of pure water within the experimental uncertainty. Apparently four redistillations from alkaline permanganate are sufficient to free water from considerable amounts of impurities.

(e) Density measurements

The density was measured by the totally immersed float method; the density of the water being adjusted to that of the float by altering the temperature of the water according to the method first used by Richards and Shipley.[6] A 14 cc Pyrex float weighted with mercury was used. The float was aged by heating at 110° in an electric oven for twenty-four hours and was steamed out before use. No appreciable change in the temperature at which the float and water had the same density could be detected over a period of three months, nor could any definite relation between the barometric pressure and the equilibrium temperature be discovered. (See Table I.) Any possible errors due to a change in the barometric pressure or to a change in the density of the float were eliminated by always

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benzene water and ordinary water lost nearly the same percentage of their deuterium content on electrolysis.

[6] T. W. Richards and J. W. Shipley, J. Am. Chem. Soc. **34**, 599 (1912).

TABLE I. *Buoyancy float data for ordinary water.*

Exp. No.	Date	Barometer	No. of redistillations	Temperature 2.700° Beckmann = 23.412°C
1	1/5	742	one	2.705
2	1/12	742	one	2.703
3	1/13	736	one	2.735 (?)
4	1/15	751	one	2.693
5	1/17	757	one	2.695
6	1/19	751	one	2.697
7	1/26	746	eight	2.697
8	2/8	759	one	2.694
9	2/8	759	two	2.697
10	2/14	742	three	2.703
11	2/17	752	four	2.700
12	2/17	752	five	2.736 (?)
13	2/19	753	six	2.693
14	2/19	753	seven	2.697
15	3/7	752	one	2.704
16	3/9	755	one	2.702
17	3/14	759	one	2.702
18	3/17	738	one	2.713
19	3/21	742	one	2.714

redetermining the equilibrium temperature for pure water immediately before making a density measurement of the various waters under investigation. The float cylinder was surrounded by two water baths according to the method of Lamb and Lee.[7] In agreement with them it was found necessary to eliminate all vibrations by stopping the stirring motor before observing the motion of the float. During the observation period no temperature control was possible, but tests proved that the temperature of the water in the float cylinder changed only 0.002° in twenty minutes under unusually adverse conditions. The time necessary for the observation of the float was five to ten minutes. After immersing the float in the water, the cylinder was exhausted (at room temperature) until the water boiled vigorously. The float was never allowed to come to the surface of the water after this boiling out, because it was found that tiny air bubbles might adhere to the top of the float when the float was pushed below the surface of the water.

The reproducibility of the measurements for laboratory distilled water are indicated in Table I where the first column gives the number of the experiment, column two the date, column three the barometric pressure, column four the number of redistillations of the laboratory distilled water

previous to the measurement, and column five the equilibrium temperatures as read on the Beckmann thermometer. In an actual measurement the temperature was changed in increments of 0.005° and the equilibrium temperature was estimated to 0.001°. The high data for experiments 3 and 12 may be due to small air bubbles adhering to the top of the float. It was after the twelfth experiment that the float was always kept totally immersed. Variations greater than 0.005° are probably due to changes in the barometric pressure. The increase in the temperature between experiments 14 and 15 may be due to a slight change in the density of the float.

The values for the rise in temperature necessary to bring the density of the water obtained in the combustion of honey, kerosene and benzene to the density of ordinary water are given in Table II. For purposes of comparison data obtained with water deliberately contaminated as related above are also given.

TABLE II. *Buoyancy float data for various types of water.*

Exp. No.	Date	Redistillations	$\Delta t°$	Exp. No.	Date	Redistillations	$\Delta t°$
Water from Kerosene				*Water from Honey*			
1	2/14	3	0.030	1	1/13	3	0.055
2	2/17	4	.028	2	1/15	5	.044
3	2/17	5	.027	3	1/19	8	.023
4	2/19	6	.025	4	1/20	9	.024
5	2/19	7	.025	5	1/26	10	.028
Accepted value = 0.025				6	2/8	12	.016
Density increment = 6.2 parts per million				7	2/19	14	.018
				Accepted value = 0.017			
				Density increment = 4.1 parts per million			
Water from Benzene				*Contaminated ordinary water*			
1	3/7	2	0.031	1	3/16	1	0.14
2	3/9	4	.031	2	3/16	2	.019
Accepted value = 0.031				3	3/17	3	.006
Density increment = 7.9 parts per million				4	3/21	4	−.003

CONCLUSIONS

The data indicate a definite increase in the atomic weight of hydrogen due to a natural isotopic separation. Bleakney and Gould[8] estimate the concentration of deuterium in rain water to be one part in five thousand parts of hydrogen. If the water of Lake Michigan con-

[7] A. B. Lamb and R. E. Lee, J. Am. Chem. Soc. 35, 1666 (1913).

[8] W. Bleakney and A. J. Gould, Phys. Rev. 44, 265 (1933).

tains this concentration of deuterium, it is possible to calculate the concentration of deuterium in kerosene, benzene and honey by means of the equation

$$\Delta s = 0.1056x \qquad (1)$$

given by Lewis and Luten.[9] In Eq. (1) Δs is the density increment between the water under consideration and pure protium oxide, and x is the mole fraction of deuterium oxide or the atom fraction of deuterium. Calculations for kerosene water yield for Δs 26 parts per million and for x

[9] G. N. Lewis and D. B. Luten, Jr., J. Am. Chem. Soc. **55**, 5062 (1933).

1.3 parts in 5000. Thus there is roughly 30 percent more deuterium in Oklahoma kerosene than there is in ordinary water. Similar calculations yield for the concentration of deuterium in benzene 1.4 and in honey 1.2 parts of deuterium per 5000 parts of hydrogen. In the case of water from honey we are assuming that the increase in density is due entirely to an increase in the concentration of deuterium. The work of Washburn and Smith indicates that this assumption is probably correct.

Further experiments are planned. It is hoped that the results of this paper and additional results will shed light on the origin of petroleum.