

The Relative Atomic Weight of Oxygen in Water and in Air II. A Note on the Relative Atomic Weight of Oxygen in Fresh Water, Salt Water and Atmospheric Water Vapor

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Citation: [The Journal of Chemical Physics](#) **4**, 778 (1936); doi: 10.1063/1.1749791

View online: <http://dx.doi.org/10.1063/1.1749791>

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is of the same order of magnitude as that of an ordinary OH. In formic acid Pauling and Brockway found, however, that the distance between two oxygen atoms bound by a hydrogen bond was about 2.67Å, which agrees well with previous crystal structure values, and with distances calculated by Errera and Mollet from known angles and distances alone. If, then, the H atom remains at approximately the normal distance of 0.96Å from the oxygen to which it was originally bonded it will be 1.71Å from the other. It is known that interatomic forces decrease very rapidly with distance so the vibration in this case would be essentially H against one O and the energy consideration given above would indicate that the frequency would be almost unchanged. Since this is obviously not so, let us turn to the perhaps more reasonable case of the hydrogen atom midway between the two oxygens, with the force so distributed that each OH bond is the same. Assuming that the force constant varies with distance in the inverse cube fashion suggested by Badger²⁴ it is possible to calculate the OH vibration frequency for this case. Assuming further

²⁴ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934).

that the oxygen atoms are stationary and that the equilibrium O—H distance is 1.33Å we find, that the 3400 cm⁻¹ frequency shifts to nearer 2400. However, it is not necessary that the H lie on the O—O line and the O—H separation may be larger than that used above. Below are given frequency values corresponding to several O—H separations, taking the O—O distance constant at 2.67Å.

r	1.33	1.40	1.50	1.60	1.70
$\bar{\nu}$	2390	2050	1680	1390	1170.

In a recent paper Gillette and Sherman²⁵ seem to favor a structure for the formic acid dimer in which the hydrogen atom, while located on the line of centers of the oxygen atoms, is neither in the center nor at the normal O—H distance from one. This would lead to a vibration frequency between the above 2400 and 3400 cm⁻¹. It would appear from this that almost any value of the OH frequency in compounds of this type would be reasonable, and it is unfortunate that as yet no spectrum has been analyzed carefully enough to permit of its identification.

²⁵ R. H. Gillette and A. Sherman, *J. Am. Chem. Soc.* **58**, 1135 (1936).

The Relative Atomic Weight of Oxygen in Water and in Air

II. A Note on the Relative Atomic Weight of Oxygen in Fresh Water, Salt Water and Atmospheric Water Vapor

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(Received September 12, 1936)

Purified Lake Michigan water appears to be nearly exactly intermediate in density between purified Atlantic Ocean water and water condensed from the atmosphere. Within the experimental error the entire difference in density between fresh and salt water appears to be due to differences in the oxygen isotopic ratios. The bearing of these results on theories explaining the relatively large concentration of O¹⁸ in the atmosphere is discussed.

IN applying¹ the isotopic exchange theory of Urey and Greiff² to the interpretation of the relatively large concentration of O¹⁸ in the atmosphere, the author estimated that of the difference in density between purified salt water and fresh water amounting to 1.9 p.p.m. ap-

proximately 1.6 p.p.m. was due to a difference in the isotopic ratio of oxygen. Greene and Voskuyl³ state, "yet it is improbable that more than 1 p.p.m. . . . is due to the oxygen isotopes." There is also the possibility that fresh water might have the same isotopic composition as atmospheric water vapor. In order to answer these questions

¹ M. Dole, *J. Chem. Phys.* **4**, 268 (1936).

² H. C. Urey and L. J. Greiff, *J. Am. Chem. Soc.* **57**, 321 (1935).

³ C. H. Greene and R. J. Voskuyl, *J. Am. Chem. Soc.* **58**, 693 (1936).

TABLE I. *Density data for purified Atlantic Ocean water and water condensed from the atmosphere.*

Source of Water	Δt	γ
Atlantic Ocean	+0.006 (P)	+1.5
	+0.005 (Q)	+1.5
Atmosphere		
Sample I	-0.0045 (P)	-1.3
	-0.005 (P)	-1.4
Sample II	-0.007 (Q)	-2.1
	-0.010 (Q)	-3.0
Average of atmosphere water	-0.0066	-1.95

(P) signifies measurement made with a Pyrex float at 29.0°; (Q) signifies a quartz float used at 29.9°; γ is the difference in density between these waters and normal (purified Lake Michigan) water expressed in parts per million.

it was decided to measure the differences in density between these three sources of water and to determine the roles of the oxygen and hydrogen isotopes in producing these differences.

In the author's application of the Urey and Greiff theory the fractionation factor 1.014 for the separation of the oxygen isotopes when water evaporates from a large body of water was also used, but here again this was only a reasonable estimate since this factor depends upon the temperature⁴ and it is not known at what temperature water vapor is in equilibrium with water of the (which?) ocean. If the relative atomic weight of oxygen between atmospheric water vapor and fresh water is known, then it would be unnecessary to apply the fractionation factor 1.014 and the Urey and Greiff theory could be applied directly without introducing this uncertainty.

EXPERIMENTAL

The ocean water was kindly obtained for us by the U. S. Coast Guard 45 miles east of Cape Ann.⁵ Laboratory distilled water which originally comes from Lake Michigan served as the fresh water and water vapor was frozen out of the air by passing air obtained outside of the chemical laboratory through a dry-ice acetone trap at the rate of two to three liters a minute. The air was first passed through a water condenser which cooled the air and in which some water would condense on very humid days. The completeness of the removal of the water vapor from the air was tested by allowing the dried air to pass through a weighed phosphorus pentoxide tube

⁴ M. H. Wahl and H. C. Urey, J. Chem. Phys. **3**, 411 (1935).

⁵ We are indebted to Edward Page, Esq., for arranging with the Coast Guard to get this water.

TABLE II. *Density data for waters made from the oxygen (after electrolysis) of Atlantic Ocean water, Lake Michigan water and water vapor and from tank hydrogen.*

Source of Oxygen in Water	Δt	γ
Lake Michigan I	-0.040	
	-0.042	
	-0.0426	
II	-0.040	
	-0.039	
Average	-0.0407	-12.2
Atlantic Ocean	-0.034	
	-0.0335	
	-0.038	
Average	-0.0352	-10.6
Water vapor	-0.046	
	-0.0455	
	-0.0455	
Average	-0.0457	-13.7

for 17 hours. While 17.8 cc of water were frozen out in the dry-ice trap, the phosphorus pentoxide tube gained only 0.027 gram in weight. The freezing out of the water vapor was carried on continuously from April 27 to May 25, the first 300 cc of water condensed (to May 12) was taken as the first sample and the water obtained (330 cc) from May 12 to May 25 constituted the second sample. We have no assurance that the water frozen out represents a true sample from the isotopic point of view of the water contained in the earth's atmosphere, but since the chemical composition of the atmosphere (when dry) is known to be remarkably constant, we can assume that the isotopic composition of the water vapor in the air is also constant.

The purification of the water and the density measurement technique have been repeatedly described in previous papers. The results of the density measurements are given in Table I.

In order to separate these density differences into those due to variations in the oxygen isotope ratios and to variations in the D/H ratio, these waters were electrolyzed along with normal water, the oxygen collected, purified and recombined with tank hydrogen according to the method previously described.⁶ The two samples of water collected from the atmosphere were mixed before the electrolysis was carried out. Values of γ after electrolysis are given in Table II. All measurements were made using the quartz float.

⁶ M. Dole, J. Am. Chem. Soc. **58**, 580 (1936).

DISCUSSION

From Table I it is seen that purified Atlantic Ocean water is 1.5 p.p.m. heavier than Lake Michigan water. Greene and Voskuyl⁷ found a difference of 1.8 p.p.m. between ocean water and Cambridge, Massachusetts tap water and a difference of 0.4 p.p.m. between Lake Michigan water and Cambridge tap water. Subtracting 0.4 from 1.8 we obtain 1.4 p.p.m. for the excess density of Atlantic Ocean water over Lake Michigan water as given by the work of Greene and Voskuyl. This is in excellent agreement with our result of 1.5 p.p.m. A similar calculation using Gilfillan's datum⁸ and the figure 0.4 p.p.m. given by Greene and Voskuyl yields 1.9 p.p.m., not in quite such good agreement. The water condensed from the atmosphere is definitely lighter than Lake Michigan water, in fact, just about as much lighter as the ocean water is heavier than Lake Michigan water. We are not certain whether the different results for samples I and II of the water condensed from the atmosphere represent a real variation or are simply experimental errors.

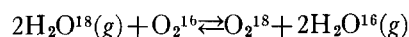
We are particularly interested in the data of Table II which demonstrate that practically all of the density differences of Table I are due to variations in the oxygen isotope ratios. From Table II it is also evident that the oxygen of Lake Michigan is nearly exactly intermediate in isotopic composition between the oxygen of the Atlantic Ocean and oxygen of atmospheric water vapor. From Table II it can also be calculated that the oxygen isotope fractionation factor for the equilibrium between water vapor and the Atlantic Ocean is 1.014, or exactly the value given by Wahl and Urey⁴ for 11.2° (52°F). This is a reasonable result.

We should expect part of the differences in density given in Table I to be due to the hydrogen isotopes; perhaps the difference in density between Lake Michigan water and water from the atmosphere which is not accounted for by the oxygen isotope ratio differences, 0.4 p.p.m., is caused by variations in the D/H ratio, but our work does not appear to be accurate enough to settle the question of the hydrogen isotopes in this case.

⁷ C. H. Greene and R. J. Voskuyl, *J. Am. Chem. Soc.* **56**, 1650 (1934).

⁸ E. S. Gilfillan, Jr., *J. Am. Chem. Soc.* **56**, 406 (1934). This water came from the ocean near Bermuda.

We can now proceed to recalculate the difference in density between water made from atmospheric oxygen and the oxygen of Lake Michigan water expected on the basis of the Urey and Greiff theory. At 223°A the enrichment factor for the equilibrium



is 1.0338,¹ which is equivalent to 7.5 p.p.m. difference in water density. Subtracting 1.5 p.p.m. the difference in the density of water condensed from the atmosphere and Lake Michigan water due to the oxygen isotopes as given in Table II we obtain 6.0 p.p.m. as the theoretical difference in density between water made of atmospheric oxygen and the oxygen of Lake Michigan water, the hydrogen in the two waters being identical in isotopic composition. This agrees exactly with our measured difference, and lends strength to the application of the¹ Urey and Greiff theory.

Greene and Voskuyl³ have recently presented an interesting theory to account for our observed value of 6.0 p.p.m. They assume that carbon dioxide of the atmosphere is in equilibrium with the water of the atmosphere at 0°C. This carbon dioxide is then absorbed by plants where it gives up its two oxygen atoms which become uniformly mixed with one atom in the water molecule of the plant which the carbon dioxide unites with. Two atoms of oxygen are then liberated by the plant and should have the average isotopic composition of the oxygen in the carbon dioxide and the water of the plant. They calculate an expected density difference of 6.8 p.p.m. However, if they had assumed the carbon dioxide water equilibrium to be established at 25°C, they would have obtained 5.7 p.p.m. from their calculations instead of 6.8 p.p.m. The chief difficulty with the theory of Greene and Voskuyl aside from ignorance concerning the isotopic composition of the oxygen in carbon dioxide of the atmosphere is that practically nothing is known concerning the photosynthetic reaction in plants. However, their theory is an entirely plausible one and it may be that both the effect calculated by the author and that suggested by Greene and Voskuyl are operative.

Grateful appreciation is expressed to Mr. B. Z. Wiener for experimental assistance.