

Conclusions

The compositions of the cobaltic pentammine and hexammine salts of 12-molybdophosphoric acid have been determined. The divalent acid cations do not directly form salts with this acid but react with water forming a trivalent ion which then reacts with the molybdophosphate.

The compositions of the cobaltic hexammine molybdophosphate and the cobaltic aquapentammine molybdophosphate are quite similar.

Suggestions have been made concerning the use of hexammine cobaltic chloride as a reagent in the quantitative determination of phosphates.

BROOKLYN, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Protium-Deuterium Ratio and the Atomic Weight of Hydrogen

BY JOHN A. SWARTOUT AND MALCOLM DOLE

On the basis of a protium-deuterium ratio in normal water¹ of 5000, the International Committee on Atomic Weights² recently changed the accepted atomic weight of hydrogen from 1.0078 to 1.0081; no reference to the source of this ratio, 5000, was given and the Committee apparently overlooked the work of Gabbard and Dole³ who found 6900 and of Hall and Jones⁴ who found 6500. It is the purpose of this paper to demonstrate by a new exchange reaction method the validity of the Gabbard-Dole ratio of 6900, and to point out that the chemical atomic weight of hydrogen is probably closer to 1.0080 than to 1.0081. At the same time we shall also reinvestigate the density of water made from atmospheric oxygen as compared to normal water inasmuch as the published data in the literature vary from 6.0 to 8.6 γ ⁵ for this important constant of nature. We use methods presumably free of isotopic errors, or uncertainties inherent in electrolytic separation, in combustion, in dubious extrapolations or corrections to the data and in isotopic exchange equilibria which are functions of temperature. Furthermore, a modified float method of measuring densities sensitive to $\pm 0.1 \gamma$ or better and improved techniques throughout increase the reliability of the final observations.

In principle the new method consists in the continued elimination of all the heavy hydrogen from normal water through repeated exchange reactions $H_2 + HOD \rightleftharpoons HD + HOH$, without af-

fecting the isotopic composition of the oxygen, until the density of the water has been reduced to a constant minimum value. From the γ -value of this water the protium-deuterium ratio in normal water can be calculated. By burning deuterium-free hydrogen in excess with oxygen of the air, the relative atomic weight of atmospheric oxygen can be calculated from the appropriate combination of the above data.

We have also measured the protium-deuterium ratio in Atlantic Ocean water in order to investigate the influence of the source of the water on this ratio.

Experimental

Preparation of Deuterium-free Water Containing Atmospheric Oxygen.—The deuterium-free water which served as a source of D-free hydrogen was prepared by the fractional electrolysis of water using the cells of Gabbard and Dole.³ The complete elimination of deuterium was proved by combining the hydrogen from each successive electrolysis with atmospheric oxygen, the hydrogen always being in excess, and by measuring the density of the resulting water. When a minimum value of the density had been attained, the water was assumed to be D-free. Data obtained in this work are given in Table I and plotted in Fig. 1, where the rapidity with which deuterium is eliminated by electrolytic fractionation (factor equal to 5.2) is readily seen. In this plot the diameter of the circles is twice as great as the experimental error.

TABLE I
DATA FOR DENSITIES OF WATER MADE FROM HYDROGEN ON SUCCESSIVE ELECTROLYTIC FRACTIONATION AND ATMOSPHERIC OXYGEN

No. electrolytic fractionations	γ
1	-5.9
2	-7.5
3	-8.9
4	-8.9 \pm 0.1
5 (Gabbard and Dole ³)	-9.0 \pm 0.3
4 (Hall and Jones ⁴)	-8.9 \pm 0.3

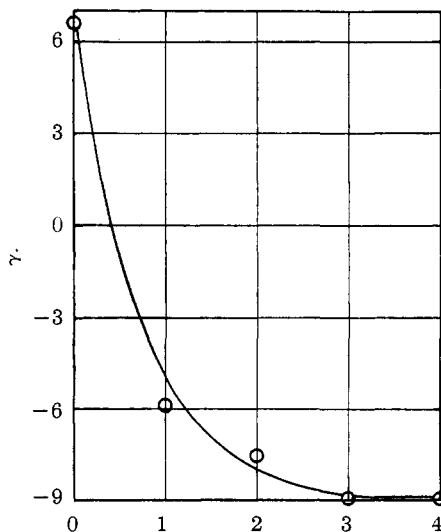
(1) We define the term "normal water" in this paper as signifying purified Lake Michigan water.

(2) G. P. Baxter, O. Hönlischmid and P. LeBeau, *THIS JOURNAL*, **60**, 737 (1938).

(3) J. L. Gabbard and M. Dole, *ibid.*, **59**, 181 (1937). For references to earlier results see this paper.

(4) N. F. Hall and T. O. Jones, *ibid.*, **58**, 1915 (1936).

(5) γ is defined as the excess density of the water in question over that of normal water in parts per million. A negative sign for γ means that the water is lighter than normal.



Number of electrolytic fractionations.

Fig. 1.—Density of water produced from the combustion of hydrogen from successive electrolyses with air oxygen.

Considering the excellent agreement between these independent measurements of the γ -value of D-free water containing atmospheric oxygen, there seems to be little reason to doubt the reliability of our final value of -8.9 .

Preparation of Deuterium-free Water Containing Normal Oxygen.—In order to prepare water containing normal Lake Michigan oxygen and D-free hydrogen, the D-free hydrogen produced by five electrolytic cells operating at ten amperes current was first purified by passing over hot copper to remove all oxygen, dried over calcium chloride, then bubbled through a sample of Lake Michigan water at 85° . The mixture of water vapor and hydrogen in a ratio of 1:2 was passed through a tube, 60×2.8 cm., containing platinized asbestos as a catalyst, and heated to 450° . Following the isotopic exchange, the water vapor was condensed in a water condenser, followed by a carbon dioxide-acetone trap. The exchanged hydrogen was conserved by burning with air over a copper catalyst.

Since equilibrium was reached during the passage of the vapors over the platinum, it was necessary to make a number of runs with each sample in order to reduce the deuterium concentration to a negligible value. The number of repetitions necessary for this was estimated from the equilibrium constant for the reaction at 450° 0.825, which was obtained by extrapolation of the data of Jones and Sherman.⁶ According to this calculation, the density of the sample should be within 0.1 p. p. m. of D-free water after seven runs.

In order to test this experimentally, an exploratory set of experiments was made, in which the density of the sample was measured after each equilibration. In these and all following experiments the D-free hydrogen was conserved by using hydrogen from the second electrolysis in the first three runs, that from the third electrolysis in the fourth and fifth runs, and that from the fourth electrolysis in all succeeding runs. The final result of this exploratory

set can be given no weight because, first, a portion of the sample was lost during the density measurements; second, the temperature measurements at which floating equilibrium occurred were made with a Beckmann instead of a

TABLE II

DATA FOR THE DENSITIES OF THE WATER OBTAINED IN THE EXPLORATORY TEST OF THE EXCHANGE FRACTIONATION

Equilibration no.	Δt , $^\circ\text{C}$.	γ
1	-0.024	-6.2
2	-0.036	-9.2
3	-0.047	-12.0
4	-0.054	-13.8
5	-0.057	-14.5
6	-0.057	-14.5

platinum thermometer; third, no extreme precautions were made in the purification of the samples, being distilled only from alkaline permanganate in Pyrex apparatus; and, fourth, the hydrogen in the final runs may not have been D-free, since no check was made upon it. A 150-ml. sample of normal Lake Michigan water was taken and six runs made. The data for the densities as measured after each equilibration are collected in Table II and plotted in Fig. 2.

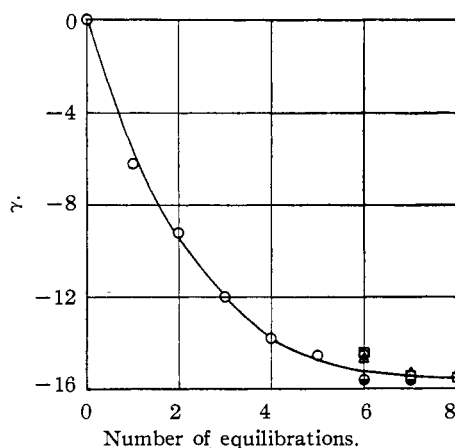


Fig. 2.—Decrease in density for each run through equilibrator: ○, exploratory expt.; □, sample 1; △, sample 2; ●, sample 3.

Following this work three new sets of experiments were made to determine the concentration of deuterium in three samples of Lake Michigan water. One sample of 300 ml. was taken directly from Lake Michigan while one of 300 ml. and one of 100 ml. were taken from the laboratory distilled water supply. Measurements showed that the laboratory distilled water has the same density as that in the Lake within ± 0.1 γ . Six equilibrations were made on each sample under the same conditions as in the exploratory sample. The original sample and the condensate after each run were weighed to determine any loss of water which might have occurred. In no case was the loss greater than 0.6%. After the sixth equilibration the water was purified and the density determined by the improved method. Repeated exchange equilibrations were then made until the density of the resulting water had been reduced to a minimum value (within the experimental error).

(6) T. Jones and A. Sherman, *J. Chem. Phys.*, **5**, 375 (1937).

TABLE III
DENSITY OF WATERS AFTER EQUILIBRATION WITH D-FREE

Equilibration no.	HYDROGEN	γ
	Sample 1	
1-6		-14.4
7		-15.4
8		-15.5
	Sample 2	
1-6		-14.6
7		-15.2
8		-15.4
	Sample 3	
1-6		-15.6
7		-15.6

A blank was run using nitrogen instead of hydrogen in order to make certain that no factor other than the removal of deuterium such as a possible change in the oxygen isotopic ratio caused the decrease in density. Nitrogen was passed through the apparatus in exactly the same way as was the hydrogen. Two evaporations and condensations of normal water were made, then the density was compared to that of the original water. No difference in density could be detected.

A 100-ml. sample of water taken from the Atlantic Ocean 45 miles east of Cape Ann, Massachusetts, was subjected to the same number of equilibrations as was the Lake Michigan water. Table IV gives the results of density measurements made upon this sample.

TABLE IV
DATA FOR THE DENSITY OF DEUTERIUM-FREE ATLANTIC OCEAN WATER

Equilibrations	γ
1-6	-13.6
7	-14.0
Normal ocean water	+ 1.7

From the last value of γ given in Table IV it is evident that normal ocean water is 1.7 p. p. m. heavier than normal Lake Michigan water, and that ocean water from which all deuterium has been removed is 14.0 p. p. m. lighter than normal lake water. This indicates that the difference between normal ocean water and ocean water with no deuterium is equal to: $14.0 + 1.7 = 15.7$ p. p. m. Another equilibration might have been made on the ocean water, since the difference between the density of the water after equilibrations six and seven is slightly outside the experimental error, but by analogy to the other experiments seven equilibrations should have been sufficient to remove all the deuterium.

The difference in concentration of the oxygen isotopes in air can be calculated from the difference between the densities of water containing air oxygen and no deuterium (Table I) and water containing normal Lake Michigan oxygen and no deuterium (Table III). The density difference of these two waters is $-15.5 - (-8.9) = -6.6 \gamma$.

Purification of Water Samples and Density Measurements.—The modified density measuring apparatus employing a platinum resistance thermometer and the new purification techniques were built and worked out by Mr. R. L. Slobod in a study of the isotopic composition of

oxygen in carbonate rocks. This work will be submitted shortly for publication. It is sufficient to state here that every attempt was made to reduce all errors in the relative density measurements to less than 0.1γ ; since repeated determinations usually agreed with each other within this range, we believe that our results are reliable, at least as far as the density measurements are concerned, to this small error.

Discussion

The Protium-Deuterium Ratio.—The average value for the difference between the densities of normal Lake Michigan water and water having the same oxygen isotopic content and no deuterium is given by the average of the data of Table III, or $-15.5 \pm 0.1 \gamma$. From this value the H/D ratio in normal water was found making use of the recent value for the density of pure deuterium oxide recently published by Stokland, Tronstad and Ronaess,⁷ 1.10764, and still more recently by Johnston,⁸ 1.10763. The mole fraction of deuterium oxide was calculated with aid of the equation published by Swift⁹

$$N_{D_2O} = \frac{9.257 \times 10^{-6} \gamma}{1 - 3.3 \times 10^{-8} \gamma}$$

Since the H/D ratio is given by the ratio N_{H_2O}/N_{D_2O} (here H_2O refers to pure protium oxide) our final result is 6970/1 or in round numbers 7000 \pm for the H/D ratio.

In Table V we have collected for purposes of comparison previous estimates of this ratio.

TABLE V
DENSITY DIFFERENCES BETWEEN DEUTERIUM-FREE WATER AND NORMAL WATER FROM VARIOUS INVESTIGATORS

	Source of water	γ	H/D ratio
This investigation	Lake Michigan	-15.5	6970
	Atlantic Ocean	-15.7	6880
Gabbard and Dole ⁵	Lake Michigan	-15.4	7020
	Lake Mendota	-16.5	6750
Johnston ¹⁰	Columbus, Ohio	-18.3	5900
Morita and Titani ¹¹	Osaka, Japan	-17.1	6320
Tronstad, Nordhagen, ¹² and Brun	Rjukan, Norway	-18.5	5840
	Tronstad and Brun ¹³	Rjukan, Norway	-20.0

From a study of this table it is evident that our results for both Atlantic Ocean and Lake Michigan water give a smaller amount of deuterium in water than any of the other results. Indeed our

(7) K. Stokland, E. Ronaess and L. Tronstad, *Trans. Faraday Soc.*, **35**, 312 (1939).

(8) H. L. Johnston, *THIS JOURNAL*, **61**, 878 (1939).

(9) E. Swift, *ibid.*, **61**, 198 (1939).

(10) H. L. Johnston, *ibid.*, **57**, 484, 2737 (1935).

(11) N. Morita and T. Titani, *Bull. Chem. Soc. Japan*, **13**, 419 (1938).

(12) L. Tronstad, J. Nordhagen and J. Brun, *Nature*, **136**, 515 (1935).

(13) L. Tronstad and L. Brun, *Trans. Faraday Soc.*, **34**, 766 (1938).

method of analysis of the water is such that it should give such a minimum value; that is, we know that there is at least as much heavy hydrogen in water as we find because our chief sources of error all tend to make the H/D ratio larger. Thus if we have not eliminated all the deuterium in our preparation of D-free water by either method, if any oxygen of the air leaked into our exchange apparatus, if our D-free water became contaminated in any way with ordinary water, the density of the D-free water would be greater than it should be and the amount of deuterium found correspondingly too small. But the reduction of the density of normal water to a constant minimum value, and the fact that no water was gained or lost in the exchange experiments, seem to rule out the first two possibilities. Five cc. of ordinary water mixed with 100 cc. of our water of γ value equal to -15.5 would produce an error of 1 p. p. m., but we estimate that the amount of ordinary water gained by the light water in the course of a density determination was 0.1 cc. or less since the distilling flask, condenser, receiver, and density measurement tube were always dried out before introducing the light water. The Pyrex float was the only object covered with a film of ordinary water that came into contact with the sample under investigation.

We believe that our method, eliminating as it does all uncertainty in regard to the isotopic composition of the oxygen, yields a reliable result. Furthermore since no great difference was found by us for the H/D ratio in Lake Michigan and Atlantic Ocean water, we disagree with the conclusion of Tronstad and Brun¹³ that the varying results of the different investigators indicate varying concentrations of deuterium in waters of different localities. As pointed out before by one of us¹⁴ slight differences in density of water from various natural sources are due primarily to variations in the oxygen isotope ratios. A further indication of the reliability of our H/D ratio is given in the following paragraph.

The Relative Atomic Weight of Atmospheric and Water Oxygen.—From the data of Tables I and III it is evident that the difference in density between normal water and water made from oxygen of the air is 6.6γ , the latter water being the heavier. In Table VI this value is given along with previous determinations by other investigators.

(14) M. Dole, *J. Chem. Phys.*, **4**, 778 (1936).

TABLE VI
DIFFERENCES IN DENSITY BETWEEN NORMAL WATER AND WATER MADE FROM ATMOSPHERIC OXYGEN AND NORMAL HYDROGEN

	γ
This investigation	6.6
Dole ¹⁵	6.0
Greene and Voskuyl ¹⁶	6.0
Hall and Johnston ¹⁷	6.6
Jones and Hall ¹⁸	6.1
Morita and Titani ¹⁹	7.0
Smith and Matheson ²⁰	8.6

With the exception of Smith and Matheson's result of 8.6γ , all the data of Table VI, although obtained by several methods, are in satisfactory agreement. The average of all the data of Table VI excluding the Smith and Matheson figure is 6.4γ , which when added to 8.9γ (from Table I) gives 15.3γ for the difference in density between normal water and deuterium-free water, a value in close agreement with our experimental data of Table III. Thus the data of Table III are consistent with the data of Tables I and VI; this is an important criterion of the accuracy of the γ values from which the H/D ratio is calculated.

The atomic weight of oxygen in the air is 0.000119 atomic weight units greater than the atomic weight of oxygen in water.

The Chemical Atomic Weight of Hydrogen.—Using our new value for the H/D ratio for normal water in calculating the chemical atomic weight of hydrogen by the same method as that of the International Committee on Atomic Weights² we obtain 1.0080 instead of the present accepted value of 1.0081.

Note Added to Proof.—Although we had intended to reserve the detailed discussion of the experimental techniques of water purification for the forthcoming publication with Mr. R. L. Slobod, the appearance of the paper by Greene and Voskuyl [*THIS JOURNAL*, **61**, 1342 (1939)] prompts us to state that possibly the data of Tables I, II, III, and IV may be as much as 0.25γ too positive because of the fact that in our distilling apparatus there may have been a greater fractionation and decrease in density of our normal water than of our D-free water. We were unsuccessful in an attempt to demonstrate this difference in the distilling properties of the two types of water, probably because the slight difference expected is about equal to our experimental error. Additional

(15) M. Dole, *ibid.*, **4**, 268 (1936).

(16) C. H. Greene and R. J. Voskuyl, *THIS JOURNAL*, **58**, 693 (1936).

(17) W. H. Hall and H. L. Johnston, *ibid.*, **58**, 1920 (1936).

(18) T. O. Jones and N. F. Hall, *ibid.*, **59**, 259 (1937).

(19) N. Morita and T. Titani, *Bull. Chem. Soc. Japan*, **11**, 403 (1936).

(20) E. R. Smith and H. Matheson, *J. Research Natl. Bur. Standards*, **17**, 625 (1936).

discussion of the work of Greene and Voskuyl, which overlaps ours to a certain extent, will be given later.

Acknowledgments.—We wish to acknowledge gratefully a grant from the Alexander Dallas Bache Fund of the National Academy of Sciences which made possible the use of the platinum resistance thermometer for measuring temperature. We are also indebted to Mr. R. L. Slobod and Mr. J. L. Gabbard for experimental cooperation.

Summary

1. Water containing normal Lake Michigan oxygen and pure protium has been prepared by an exchange reaction in the gas phase: $H_2 + HOD = HD + HOH$. The density of this water has been found to be 15.5 ± 0.1 p. p. m. lighter than normal Lake Michigan water. From this the ratio of hydrogen atoms to deuterium atoms was calculated to be 6970.

2. Water containing normal Atlantic Ocean

oxygen and pure protium was prepared by the same method. The difference in density between this and normal Atlantic Ocean water was found to be 15.7 ± 0.2 p. p. m., corresponding to a H/D ratio of 6900.

3. Deuterium-free hydrogen was burned with atmospheric oxygen and the density of the water produced was compared with that of water containing normal Lake Michigan oxygen and pure protium. The atmospheric oxygen water was found to be 6.6 p. p. m. heavier, which corresponds to a greater atomic weight of oxygen in air of 0.000119 ± 0.000002 atomic weight units.

4. The chemical atomic weight of hydrogen as calculated from our new H/D ratio is 1.0080 instead of the value of 1.0081 recently adopted by the International Committee on Atomic Weights.

EVANSTON, ILLINOIS

RECEIVED MAY 4, 1939

[CONTRIBUTION NO. 155 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

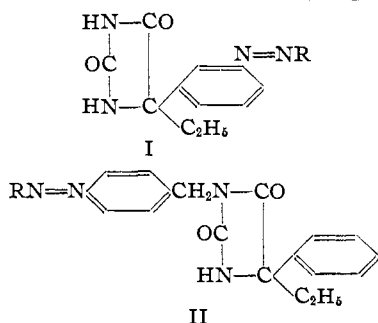
The Synthesis of Colored Derivatives of Nirvanol. II. N-Benzyl Azo Compounds¹

BY SHIRLEY POWELL LINGO² WITH HENRY R. HENZE

Last year there was reported³ an attempt to convert the soporific called Nirvanol into colored derivatives (I) possessing dyestuff properties. Since it is generally believed that the activity of soporifics is related, at least in part, to the alkyl or aryl groups present in a molecule, it follows that attachment of an azo linkage might so affect the influence of the phenyl group in Nirvanol as to reduce or completely alter its activity. Therefore it was decided to leave intact the phenyl and

ethyl groups at the 5-position of the hydantoin nucleus, and to introduce the azo grouping through attachment to a benzyl group linked to the amidic nitrogen of the heterocycle (II).

In this investigation the sodium salt of Nirvanol was condensed with *p*-nitrobenzyl chloride and the product reduced catalytically to form 3-*p*-aminobenzyl-5-ethyl-5-phenylhydantoin. The latter was diazotized and coupled, in turn, with dimethylaniline, β -naphthylamine, phenol, salicylic acid, α - and β -naphthol, and 1,5-dihydroxynaphthalene, respectively, to form colored azo derivatives. From alkaline solution the dyes derived from phenol, α -naphthol and salicylic acid impart a yellow or orange color, and the 1,5-dihydroxynaphthalene derivative a purple color, to silk or wool. The β -naphthol azo compound is too insoluble in dilute alkali to serve as a dyestuff for these fibers. Likewise, the β -naphthylamine derivative is too little soluble even in concentrated hydrochloric acid to impart color, whereas the azo dyestuff derived from dimethylaniline dyes silk or wool from an acid bath a light purple which is changed to yellow by contact with alkali.



(1) Presented before the Division of Medicinal Chemistry at the 97th meeting of the American Chemical Society, April 3-7, 1939, at Baltimore, Md.

(2) From the Ph.D. thesis of S. P. Lingo in June, 1939.

(3) Spurlock with Henze, THIS JOURNAL, 60, 3005 (1938).