calcium nitrate glasses were readily formed, and these showed no signs of further crystallization at room temperature even in the presence of large crystals of calcium nitrate. Cooling curves on melts of composition near that of the ternary eutectic showed a eutectic halt at 117.4°. No halt due to the inversion of potassium nitrate (128° in the pure substance[5]) was observed. This inversion of potassium nitrate should produce a slight break in the liquidus surface near the eutectic point.

The melting points of the ternary mixtures are given in Table II. The regions in which the three solid phases form (neglecting $4KNO_3 \cdot Ca(NO_3)_2$ and the low temperature form of potassium nitrate) and the eutectic points are shown in Fig. 2, the binary eutectics used being those of Rostkovsky[1f] and Carveth.[1a]

Summary

1. The liquidus curve of the binary system lithium nitrate–calcium nitrate has been determined. The eutectic temperature is 235.2°, the eutectic composition is at about 70% lithium nitrate.

2. The liquidus surface of the ternary system calcium, lithium and potassium nitrates has been explored partially. The ternary eutectic temperature is 117.4°, the eutectic composition is 15% calcium, 62% potassium and 23% lithium nitrates.

NEW YORK, N. Y. RECEIVED OCTOBER 15, 1936

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(5) F. C. Kracek, *J. Phys. Chem.*, **34**, 225 (1930).

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Redetermination of the Deuterium–Protium Ratio in Normal Water

BY J. L. GABBARD AND MALCOLM DOLE

In the course of preparing some deuterium-free hydrogen for use in one of the researches on the isotopes of oxygen in progress in this Laboratory, it became possible to redetermine, by means of a method involving a knowledge of the oxygen isotope ratios in water and air, the deuterium–protium ratio in normal water. Limitations of space forbid a detailed discussion of the many previous measurements of this ratio; the reader is referred to the recent papers of Morita and Titani[1] and of Hall and Jones[2] for references and comments on earlier work. At present there seem to be three apparently accurate determinations of the deuterium–protium ratio in which the difficulties due to oxygen isotope fractionation on electrolysis were recognized and avoided, namely, those of Johnston ($-18.3\,\gamma$),[3] Morita and Titani ($-18.9\,\gamma$) and Hall and Jones ($-16.5\,\gamma$). The symbol γ represents in p. p. m. the density of deuterium-free water less the density of normal water; from the γ values the deuterium–protium ratio is calculated easily. The maximum difference in the above results ($2.4\,\gamma$) is greater than the experimental errors of density measurement and is due, we believe, to the different methods used by the above authors in bringing to normal or correcting for the oxygen isotope ratios in the waters under investigation.

Since the relative atomic weight of oxygen in air and in water has been determined recently[4] it is possible to solve the oxygen isotope problem by combining the deuterium-free hydrogen with oxygen of the air and after measuring the density of resulting water, the proper correction for the difference in the atomic weight of air and water oxygen can be applied, yielding what should be the correct density of water made of isotopically pure protium and the oxygen of normal water. From this latter value the D/H ratio in normal water is calculated readily.

Experimental

The electrolysis apparatus was very kindly constructed for us by Dr. P. W. Selwood who was able to give us frequently valuable advice and suggestions from his great store of electrolytic experience. The lengthy first and second fractionations were carried out by Mr. Stanley Cristol working under an NYA grant from the government. In the case of all electrolyses after the first two, sodium peroxide instead of sodium hydroxide was added to the water to make it conducting; sodium peroxide was used because it contains no deuterium, the excess oxygen was eliminated by boiling. Data for the preparation of deuterium-free water are given in Table I where the letters after the numbers are labels serving to distinguish and identify the various waters in order to clarify the table. All the different waters mentioned in this paper will be marked in this way so that the previous history of the water can be found readily by the reader (N signifies normal, or Lake Michigan, water).

Part of the water obtained from each electrolysis was decomposed electrolytically, the hydrogen passed over hot

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

(2) N. F. Hall and T. O. Jones, THIS JOURNAL, **58**, 1915 (1936).

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

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

copper; it was next dried and then combined with dried atmospheric oxygen over a hot copper catalyst with the hydrogen always slightly in excess to prevent fractionation of the oxygen isotopes. The resulting water was condensed in a water condenser; in one experiment the water condenser was supplemented by a dry ice–acetone condenser, but no difference in the density of the water due to the introduction of the dry ice condenser could be detected. Data for the preparation of this water are given in Table II.

TABLE I

DATA OBTAINED IN THE PREPARATION OF DEUTERIUM-FREE WATER

Fractionation	Water taken, cc.	Water collected, cc.	% collected	Residue, cc.	Lost, cc.	cc. retained for hydrogen analyis
1	72,000 (N)	23,600 (A)	32.79	47,000	1400	
2	23,600 (A)	9,440 (B)	40.00			800 (B)
3	8,640 (B)	4,579 (C)	52.99	3,782 (D)	739	590 (C)
4	3,989 (C)	1,865 (E)	46.50	1,495 (F)	629	565 (E)
5	1,300 (E)	690 (F)	53.07	530 (G)	80	690 (F)

TABLE II

DATA OBTAINED IN THE PREPARATION OF WATER MADE FROM DEUTERIUM-FREE HYDROGEN AND ATMOSPHERIC OXYGEN

Fractionation	Water taken, cc.	Product, cc.	Residue, cc.	Water lost, cc.
2	800 (B)	300 (H)	200 (I)	300
3	590 (C)	285 (J)	50	265
4	500 (E)	255 (K)	50	195
5	675 (F)	440 (L)	50	185

The purification of the various waters and the method of measuring the density were essentially the same as previously described.[5]

In order to prevent the "light" water from being contaminated with normal water, some wash water for use in rinsing the various glass receptacles, thermometers, floats, etc., was prepared by electrolyzing approximately half of the residue from the second fraction in the hydrogen separation cells and combining the liberated hydrogen with atmospheric oxygen. Two liters of wash water having a density only slightly greater than the lightest fractions (J, K, L) were obtained.

The ordinary laboratory distilled water which comes originally from Lake Michigan was the standard water chosen. The hydrogen and oxygen of this water were assumed to be normal in their isotopic composition.

The density data are collected in Table III.

After the density of the various fractions had been measured, waters H, J, K, L, were mixed, the density of the mixture taken and then a very careful electrolytic fractionation carried out by decomposing 60% of the mixture. In this final step the air supplying the atmospheric oxygen was passed through a drying tower of solid potassium hydroxide and then through concentrated sulfuric acid.

The water resulting from the combustion of the electrolytic hydrogen and the atmospheric oxygen was completely recovered in a dry ice–acetone trap. These extra precautions did not lower the density of the "light" water below -9.0γ.

TABLE III

DATA FOR THE DENSITY OF THE VARIOUS WATERS

Fraction no.	Label	Δt,°C	γ
3	(J)	−0.029	− 8.7
		− .029	− 8.7
4	(K)	− .029	− 8.7
		− .032	− 9.6
5	(L)	− .030	− 9.0
		− .030	− 9.0
Accepted value:		− .030	− 9.0
2, 3, 4, 5 (Waters H, J, K, L, mixed):		− .029	− 8.7
2, 3, 4, 5 Mixed and further fractionated:		− .030	− 9.0
Water G		− .062	−18.6
Water M		− .041	−12.6

The density of water G was measured in order to see whether the electrodes of the cells had fractionated the oxygen isotopes during all the electrolyses. This water is probably equivalent to Johnston's light fraction from his second or third electrolysis since it represents the residue after decomposing 53% of water E from the fourth fractionation. The ability of the electrodes of the cells to fractionate the hydrogen isotopes was tested at the conclusion of the experiments; 1200 cc. of normal distilled water was placed in the cells and electrolyzed, and 490 cc. of first fraction water resulted. This water, water M, had a γ value of -12.6, which proved that the electrodes had not lost their activity for hydrogen isotope separation.

We conclude from our measurements that the density of deuterium-free water containing atmospheric oxygen is 9.0 p. p. m. lighter than purified Lake Michigan water.

The close agreement between the densities of waters J, K and L, indicates that the hydrogen must have been brought to a constant isotopic composition which we assume is practically pure protium.

Discussion of the Data and Comparison with Previous Results

In order to calculate from our value of $-9.0\ \gamma$ the density of D-free water containing normal oxygen, it is necessary to know the exact value for the difference in density of waters made of normal oxygen and atmospheric oxygen. This value has been determined carefully by a number of workers using an electrolytic method with rather excellent agreement considering the different techniques involved and the geographical location of the standard waters. In Table IV we have summarized recently published results.

Accepting $6.4\ \gamma$ as the excess density of water containing atmospheric oxygen, we can subtract this number from our datum of $-9.0\ \gamma$ to obtain $-15.4\ \gamma$ as the difference in density between deuterium-free water and normal water, the oxygen of both waters being isotopically identical. In Table V we have summarized all published re-

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[5] M. Dole, THIS JOURNAL, **58**, 580 (1936); *J. Chem. Phys.*, **2**, 337 (1934).

TABLE IV

DIFFERENCE IN DENSITY OF WATER CONTAINING NORMAL OXYGEN AND ATMOSPHERIC OXYGEN. (THE HYDROGEN HAVING THE SAME ISOTOPIC COMPOSITION IN EACH CASE)

Investigator	γ
Dole[4]	6.0
Greene and Voskuyl[a]	6.0
Hall and Johnston[b]	6.6
Morita and Titani[c]	7.0
Average	6.4

[a] C. H. Greene and R. J. Voskuyl, THIS JOURNAL, **58**, 693 (1936). [b] W. Heinlen Hall and H. L. Johnston, *ibid.*, **58**, 1920 (1936). [c] Ref. 1, p. 414.

sults for the γ-value of D-free water, and we have included also values of the D/H ratio (denominators rounded off to the nearest 100), calculated by the method of Morita and Titani,[1] using the accurate specific gravity value for heavy water given by Selwood, Taylor, Hipple and Bleakney.[6]

There is considerable discrepancy between these values for the D/H ratio. Christiansen, Crabtree and Laby,[7] Ingold, Ingold, Whitaker and Whytlaw-Gray,[8] and Tronstad, Nordhagen and Brun[9] do not state in their short "Letters to the Editor" whether or not they corrected for the electrolytic fractionation of the oxygen isotopes in their experiments. We are doubtful whether the D-free water prepared by Christiansen, Crabtree and Laby contained atmospheric oxygen as suggested by Morita and Titani,[1] inasmuch as the Australian workers stated that they burned the gases evolved. The data in Table V due to Edwards, Bell and Wolfenden,[10] and to Lewis and Macdonald[11] were obtained by measuring the rate at which deuterium concentrates on electrolysis. Knowing the fractionation factor for the cells, the D/H ratio in normal water can be calculated. Lewis and Macdonald made no attempt to correct for oxygen isotope fractionation. This method does not seem to be as accurate, however, as the method of measuring the density of D-free water.

TABLE V

DENSITY DIFFERENCES BETWEEN DEUTERIUM-FREE WATER AND NORMAL WATER FROM DIFFERENT INVESTIGATIONS

Investigation	Source of water	γ	D/H Ratio
This investigation	Lake Michigan	−15.4	1:6900
Christiansen, Crabtree and Laby	Melbourne rain water	−12.7	1:8400
Edwards, Bell and Wolfenden	Oxford, England		1:6200
Hall and Jones	Lake Mendota	−16.5	1:6500
Ingold, Ingold, Whitaker and Whytlaw-Gray	London, England	−12.0	1:8900
Johnston	Columbus, Ohio	−18.3	1:5800
Lewis and Macdonald	Berkeley, Calif.		1:6500
Morita and Titani	Osaka, Japan	−18.9	1:5600
Tronstad, Nordhagen and Brun	Rjukan, Norway	−18.5	1:5800

Johnston[3] assumes in his work that the oxygen isotope fractionation factor is independent of the kind of hydrogen isotope present in the water. This assumption was also tacitly made by one of us in obtaining the data of Table IV. Selwood, Taylor, Hipple and Bleakney[6] have calculated with the aid of the theory given by Eyring and Sherman[12] that the separation ratio for the bonds D-O^{18}, D-O^{16} is slightly higher than that for the bonds H-O^{18}, H-O^{16}, but they state that even when the concentration of deuterium had reached the high percentage of 90%, the effect was too small to be detected experimentally. Unless there are some unknown influences at work in the region of low deuterium concentration, it would appear that the assumption of independence for the oxygen isotope fractionation factor is entirely justified. Probably a greater source of uncertainty in Johnston's work is the difficulty regarding the extrapolation. We have reëxtrapolated his data, drawing our straight line through all of his circles, but purposely sloping the line to yield an extrapolated value as near our datum of −15.4 γ as possible. The result of this extrapolation was −15.9 γ, which indicates that Johnston's results are not entirely inconsistent with the work of this paper. We are not insisting, however, that our extrapolation is as reliable or more reliable than his.

It is more difficult to explain the discrepancy between the result of this investigation and that of Morita and Titani, which seems to have been carried out very carefully.[1] It is possible, of course, that Japanese water may contain more deuterium than the water of Lake Michigan, but it seems hardly likely that the difference will be great enough to cause a difference of 3 p. p. m. in the density, particularly since one of us has re-

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(6) P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr., and W. Bleakney, THIS JOURNAL, **57**, 642 (1935).

(7) W. N. Christiansen, R. W. Crabtree and T. H. Laby, *Nature*, **135**, 870 (1935).

(8) E. H. Ingold, C. K. Ingold, H. Whitaker and R. Whytlaw-Gray, *ibid.*, **134**, 661 (1934).

(9) L. Tronstad, J. Nordhagen and J. Brun, *ibid.*, **136**, 515 (1935).

(10) A. J. Edwards, R. P. Bell and J. H. Wolfenden, *ibid.*, **135**, 793 (1935).

(11) G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.*, **1**, 341 (1933). These authors also used the method of measuring the density of D-free water in estimating their D/H ratio.

(12) H. Eyring and A. Sherman, *ibid.*, **1**, 345 (1933).

cently found no measurable difference in the deuterium content of fresh and salt water.[13]

Hall and Jones' datum of $-16.5\ \gamma$, which differs from ours by 1.1 p. p. m., was obtained in two ways although both methods involved the normalization of the oxygen in the water by equilibration with carbon dioxide gas which had been equilibrated previously with normal water. Since carbon dioxide comes so slowly to equilibrium with water and since the equilibrium constant is a function of temperature, it would seem that this method is undesirable and difficult of application. The assumption is also made that the oxygen isotope equilibrium between carbon dioxide and water is the same irrespective of the deuterium content of the water. We examine this assumption below. Hall and Jones in a second series of experiments burned their cell hydrogen with atmospheric oxygen obtaining results which varied considerably, although their last measurements ($-8.9\ \gamma$) agreed almost exactly with ours ($-9.0\ \gamma$). However, on equilibration with carbon dioxide this water which was apparently exactly like ours, changed in density to $-16.5\ \gamma$, whereas our calculated result is $-15.4\ \gamma$. Thus the discrepancy between the work of Hall and Jones and our own is seen to be due to the two different ways in correcting for the oxygen isotope ratio. We believe that our method which consists essentially in measuring the oxygen isotope ratio in atmospheric oxygen gives a more reliable result than the method of Hall and Jones based on the carbon dioxide equilibration.

Calculation of Some Isotopic Exchange Equilibrium Constants.—Among the equilibrium constants of isotopic exchange reactions which Urey and Greiff[14] have calculated from spectroscopic data and statistical theory constants involving D_2O^{16} and D_2O^{18} are missing, because, undoubtedly, the supply of heavy water is so limited that no practical importance is attached to these constants, but in order to answer certain theoretical questions which have arisen we decided to calculate the equilibrium constants of the oxygen isotope reactions between carbon dioxide, oxygen and heavy water. If the distribution function ratio[15] $f_{D_2O^{18}}/f_{D_2O^{16}}$ is known, then the desired equilibrium constants can be calculated easily, making use of other distribution function ratios tabulated by Urey and Greiff. Frequencies for the D_2O^{16} and D_2O^{18} molecules were calculated using the equations of Van Vleck and Cross[16] after their force constants k_1, k_{12} and k_3 had been adjusted to give agreement between the calculated frequencies of the D_2O^{16} molecule (2666.0, 2785.0, 1176.6) and those (2666, 2784, 1179) observed by Barker and Sleator.[17] The results of the calculation are collected in Table VI.[18]

TABLE VI

MOLECULAR CONSTANTS

Molecule	ω_1	ω_2	ω_3	A_2/A_1	B_2/B_1
D_2O^{16}	2666.0	2785.0	1176.6	1.0083	1.0229
D_2O^{18}	2646.8	2770.3	1169.5		

DISTRIBUTION FUNCTION RATIOS

	273.1°A.	298.1°A.	600°A.
$\frac{f_{D_2O^{18}}}{f_{D_2O^{16}}}$	1.3043	1.2926	1.2316

EQUILIBRIUM CONSTANTS AND ENRICHMENT FACTORS

Reaction	$K_{298.1°}$	Enrichment factor
$CO_2^{16} + 2D_2O^{18}(g) \rightleftharpoons CO_2^{18} + 2D_2O^{16}(g)$	1.065	1.032
$O_2^{16} + 2D_2O^{18}(g) \rightleftharpoons O_2^{18} + 2D_2O^{16}(g)$	0.9990	0.9995

The distribution function ratio, $f_{D_2O^{18}}/f_{D_2O^{16}}$, is about 3% greater than the ratio $f_{H_2O^{18}}/f_{H_2O^{16}}$; hence the equilibrium constants of the reactions listed in Table VI are about 6% smaller than the constants for the normal water equilibria. Thus O^{18} tends to concentrate less in the gas phase and more in the aqueous phase; in the case of the oxygen–water equilibrium the new calculations show that the equilibrium concentrations of the reaction are shifted far enough so that O^{18} concentrates in the heavy water rather than in the gas. However, the difference in behavior between the carbon dioxide–water equilibrium and the carbon dioxide–heavy water equilibrium is not great enough to invalidate the equilibration method of Hall and Jones. In regard to the relative rate at which the carbon dioxide comes into equilibrium with the two kinds of water, nothing is known at the present time.

Summary

Deuterium-free hydrogen has been prepared and combined with atmospheric oxygen yielding

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(13) M. Dole, *J. Chem. Phys.*, December, 1936.

(14) H. C. Urey and L. Greiff, THIS JOURNAL, **57**, 321 (1935).

(15) Urey and Greiff's nomenclature is used throughout this discussion.

(16) J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.*, **1**, 350, 357 (1933).

(17) E. F. Barker and W. W. Sleator, *ibid.*, **3**, 660 (1935).

(18) At the suggestion of the referee of this paper we give the values of the force constants calculated by us by arbitrarily setting the value of k_{12} at 0.05×10^5, and by solving simultaneously three independent equations, for k_1, k_{12} and k_3. These three equations were obtained by substituting known values for the a_{ij} constants into the three equations for λ_1^2, λ_2^2 and λ_3^2. These last three quantities were also known from the experimental data. The new values of the force constants for the D_2O^{16} molecule are k_1, 7.796×10^5; k_{12}, 0.4976×10^5; k_3, 0.3598×10^5; and k_{12} 0.05×10^5.

water lighter by 9 p. p. m. than Lake Michigan water. When 6.4 p. p. m. are added to 9 p. p. m. to correct for the difference in atomic weight of atmospheric oxygen and aqueous oxygen, the density of D-free water containing normal oxygen is 15.4 p. p. m. lighter than normal water. From this the ratio of deuterium atoms to hydrogen atoms in Lake Michigan water is calculated to be 1:6900. Our density value of $-15.4\ \gamma$ agrees within 1.1 p. p. m. with that of Hall and Jones, $-16.5\ \gamma$, and confirms their belief that the commonly accepted value for the D/H ratio is too high and should be revised downward. Our result indicates, however, that the downward revision should be somewhat more than that recommended by Hall and Jones.

Isotopic exchange equilibrium constants involving D_2O^{16} and D_2O^{18} have been calculated and tabulated.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 21, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Solubilities of Potassium Chloride in Deuterium Water and in Ordinary Water from 0 to 180°

BY R. W. SHEARMAN AND ALAN W. C. MENZIES

Published measurements of solubility of salts in deuterium water[1] hitherto have been limited to a few determinations near room temperature. The present work is one of a series of studies over a wide temperature range undertaken in the hope of gaining insight into portions of the general subject of aqueous solubility.

Method and Materials.—For all our experiments with deuterium water, and for most of those with ordinary water, the method used was that described by Menzies.[2] A few experiments requiring much ordinary water in relation to the quantity of solute were carried out by the older synthetic method, where each experiment demands a separate sealed tube. Our method of securing and measuring steady temperatures has already been described;[2] and it may be added that about one-half of the measurements were carried out in the jacketed air-oven referred to in the earlier publication.

The deuterium water was similar to that described elsewhere,[3] with a content of 98.2% D_2O. The relative density of this water compared to ordinary water at 25° was taken as 1.1059 for the purposes of conversion of measured volumes to masses. In order to apply the small correction for the weight of water vapor present in the gas phase, values of the vapor pressure of saturated solutions of potassium chloride were derived, by extrapolation when necessary, from the work of Leopold and Johnston;[4] and these pressure values could, with adequate approximation, be adapted to suit the case of deuterium water solutions from a knowledge of solubility and of the vapor pressures of deuterium water relative to that of ordinary water.[3]

Potassium chloride is easily obtained of highest purity, and we estimate the impurity of our sample, other than water, as less than five parts per 10,000. Water was removed by slow heating to incipient fusion.[5]

Manner of Stating Solubility.—The solubility of potassium chloride in common water is reported in moles of solute per 1000 g. of water (55.51 moles H_2O), conformably to the practice of "International Critical Tables." To secure a comparable statement of solubility in deuterium water, we state the number of moles of solute per 1111.7 g. of solvent, which is 55.51 moles of D_2O. To arrive at this value from experiments made with 98.2% D_2O, we first computed, from the weights of solvent and solute used, the molal solubility in 1109.7 g. of our sample, which is the weight containing 55.51 moles of mixed D_2O and H_2O. By comparing the value so found with the molal solubility in ordinary water, we were able, by a short linear extrapolation, to arrive at the solubility per 55.51 moles of pure D_2O.

Experimental Results.—For all but the lower temperature experiments the identical solute material, 0.4086 g. of potassium chloride, was employed with both solvents. The total weight of 98.2% deuterium water employed was 1.39 g., and this was completely recovered in its original purity. In the case of deuterium water, the ratio of mass of solute to solvent was reduced for a few of the lower temperature experiments by using a smaller weight of solute in the apparatus described; and, in the case of ordinary water, by increasing the amount of solvent in separate sealed-tube experiments.

Table I records the results observed in ordinary water in the first two columns and in deuterium water in the third and fourth columns.

These observations were graphed in the manner described previously,[2] and solubility values read off for round values of temperature, as recorded in Table II, where, in the fourth column a comparison is made with the solubility values found in "International Critical Tables."

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(1) *Cf.* Taylor, Caley and Eyring, THIS JOURNAL, **55**, 4334 (1933).

(2) Menzies, *ibid.*, **58**, 934 (1936).

(3) Miles and Menzies, *ibid.*, **58**, 1067 (1936).

(4) Leopold and Johnston, *ibid.*, **49**, 1974 (1927).

(5) *Cf.* Cohen and Blekkingh, *Proc. Acad. Sci. Amsterdam*, **38**, 843 (1935).