

The Refractive Index of $\text{H}^2\text{H}^2\text{O}$; The Refractive Index and Density of Solutions of $\text{H}^2\text{H}^2\text{O}$ in $\text{H}^1\text{H}^1\text{O}$

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A determination has been made of the refractive index of nearly pure H_2^2O and of a 50 percent solution of H_2^2O in H_2^1O over a range of temperatures and wave-lengths. In both cases temperatures of maximum refractive index have been found. The differences between these temperatures and the temperature of maximum refractive index for ordinary water are in accord with the differences in those physical properties of the two kinds of water which have already been investigated. The dispersion of H_2^2O

is lower than that of H_2^1O . The densities and refractive indices of solutions of different concentrations of H_2^2O in H_2^1O have been determined. It is found that these solutions do not obey the laws of the ideal solution to the extent that the partial molal volumes are functions of the concentration of the isotopic water. This deviation from ideality is not found in the refractive indices of these solutions.

WHEN the first water containing a high concentration of the hydrogen isotope was obtained in this laboratory, I found the refractive index to be appreciably smaller than that of ordinary water; this was mentioned by Professor Lewis¹ in his first communication on the hydrogen isotope. In these early experiments there was no way of determining the exact isotopic composition of the water and even after the specific gravity of pure H_2^2O had been ascertained with fair accuracy, it was still uncertain whether water containing varying amounts of the heavy isotope would obey the simple laws of mixing. Hence it seemed necessary to sacrifice a certain amount of nearly pure H_2^2O in order to find by actual dilution with ordinary water the exact relation between isotopic composition, specific gravity and refractive index.

DENSITY AND CONCENTRATION

The H_2^2O was prepared by Lewis and Macdonald according to the method described by them.² The experimental procedure was as follows: The specific gravity of a sample of water, which was about 98 percent H_2^2O , was determined with a pycnometer of about 0.35 cc capacity. Following this the refractive index was

determined, after which the specific gravity was again ascertained. A weighed portion of the sample was then mixed with a known weight of ordinary water. Again specific gravity was ascertained before and after the determination of the refractive index; subsequent dilutions and specific gravity determinations were made in the same manner. The concentrations were thus obtained in terms of the concentration of the original sample independently (except as noted below) of any specific gravity determinations. All specific gravity determinations were made at 25.0°C. In the solutions where the concentration of H_2^2O was high, it was found that a certain amount of dilution (as evidenced by a change in density) had taken place in the course of the manipulations necessary for the determination of the refractive index. This was a consequence of the unavoidable exposure of the solution to the air. The dilution was small in amount and appeared to be consistent with obvious predictions: it was roughly dependent upon the time of exposure and upon the concentration of the solution. Accordingly, the concentrations obtained from the weight dilutions were corrected to take into account the dilution during handling. These corrections were small enough so that there should be no errors in concentrations greater than 0.2 percent. The probable error in the specific gravity determinations should be slightly less than 0.0001.

¹ G. N. Lewis, *J. Am. Chem. Soc.* **55**, 1297 (1933).

² Lewis and Macdonald, *J. Chem. Phys.* **1**, 341 (1933).

On the assumption that the equation,³

$$s = 1.0000 + 0.1056 N_2 + \alpha N_1 N_2, \quad (1)$$

is the best solution for the data, the best values for the mol fraction of the initial sample and for the constant α have been obtained. s is the specific gravity of the isotopic solution and N_1 and N_2 are the mol fractions of H_2^{16}O and H_2^{18}O (and also the atom fractions of H^1 and H^2), respectively. The agreement between the calculated and observed values is sufficient evidence of the satisfactoriness of this solution. In Table I the

TABLE I. *Specific gravities and molecular volumes of H_2^{18}O solutions in H_2^{16}O .*

N_2	Spec. gr. (obs.)	Spec. gr. (calc.)	Mol. vol. (obs.)	Deviation from linearity
1.0000	(1.1056)	(1.1056)	(18.114)	0.000
0.970	1.1024	1.10241	18.112	.001
.817	1.0863	1.08613	18.097	.001
.617	1.0649	1.06489	18.083	.007
.460	1.0482	1.04827	18.069	.009
.340	1.0356	1.03561	18.055	.007
.164	1.0171	1.01718	18.036	.006
.000	(1.0000)	(1.0000)	18.014	.000

values observed and calculated for specific gravities and those observed for molecular volumes are given. In column 5 are given the differences between the observed molecular volumes and the molecular volumes calculated on the assumption that that quantity is a linear function of the mol fraction. The molecular volumes are based on specific gravities; the molecular weights used are 18.014 and 20.027.

Now if this were a perfect solution, the specific volume would be a linear function of the weight fraction (1), the molecular volume (of the solution as a whole) a linear function of the mol fraction (2); the density would not be a linear function of the weight fraction (3), nor of the mol fraction (4) (i.e., the constant α in Eq. (1) would not be zero even for a perfect solution). But from the fact that the last two functions are

not linear it may be deduced that the solution is not perfect.

Any of the four functions above may be approximated satisfactorily to a function of the form of Eq. (1). Eq. (1) itself becomes, on supplying the constant α ,

$$s = 1.0000 + 0.1056 N_2 - 0.0012 N_1 N_2. \quad (2)$$

Eq. (2) is of practical importance only in determining concentrations from densities.⁴ Also of interest is the relation between molecular volume and mol fraction:

$$V_m = 18.014 + 0.100 N_2 + 0.031 N_1 N_2, \quad (3)$$

where V_m is the molecular volume of the solution. From Eq. (3) the partial molal volumes may be obtained. At $N_2 = 0.5$ the partial molal volume of H_2^{18}O is 0.05 percent higher and at $N_2 = 0$ it is 0.2 percent higher than at $N_2 = 1$.

REFRACTIVE INDEX AND CONCENTRATION

The refractive index was determined for all solutions interferometrically. For the most concentrated solution, and also for the solution of mol fraction 0.459, it was also determined with a Pulfrich refractometer.

In all the determinations with the Pulfrich refractometer the zero setting of the micrometer screw was left unchanged. Under these conditions the refractive index of ordinary water was also determined at 20°C. To all values obtained, both for ordinary water and for the isotopic solutions, a correction was added (0.00007) such that the results for ordinary water should show least deviation from the values given by the *International Critical Tables*. All refractive indices are referred to air.

The interferometric determinations of the differences between the refractive index of ordinary water and of the isotopic solutions depend upon the well-known equation,

$$\Delta n = M\lambda/2L, \quad (4)$$

where M is the displacement of the fringe system in terms of the number of fringes and L is the length of the chamber used (the light passes through it twice). The quantity M was obtained

³ Lewis and Macdonald (J. Am. Chem. Soc. **55**, 3057 (1933)) have given the provisional value of 1.1056 for the specific gravity of pure H_2^{18}O at 25°C. In the light of later determinations this value seems a little low but we shall retain it until we can be much more certain of the true value.

⁴ Cf. Lewis and Luten, J. Am. Chem. Soc. **55**, 5061 (1933).

as the quotient of the shift in the fringe system in terms of micrometer readings and the fringe width in terms of micrometer readings,⁵

$$M = (r' - r_0)/w. \quad (5)$$

The initial determination with the Pulfrich refractometer eliminated any uncertainty in the location of the central fringe. For the Rayleigh-Zeiss interferometer used, the apparent shift for pure H₂O with white light is 22.0 fringes when the actual shift is only 15.8 fringes. Finally, since the chamber used was only 1 mm long, there may have been a constant error as great as 1 percent in the direct determination of its length and, as a consequence, in all the results obtained from the interferometer. Since the results obtained with the Pulfrich refractometer are more reliable a small correction was made to bring the interferometric results into agreement with those obtained with the Pulfrich.

The refractive index shows no deviation from linearity with mol fraction. In Table II the dif-

TABLE II. $n_1 - n$ at 25.0°C.

Mol fraction	5461 Hg	5461 calc.	5800 white light	5800 calc.	5893 Na _D	5893 calc.
1.000		.00461		.00449		.00445
0.977	.00451	.00451	.00439	.00438	.00436	.00435
.967	.00444	.00446	.00433	.00434	.00430	.00431
.816	.00378	.00376	.00367	.00366	.00365	.00364
.616	.00285	.00284	.00278	.00276	.00275	.00274
.459	.00212	.00212	.00205	.00206	.00203	.00204
.340	.00155	.00157	.00152	.00153	.00150	.00152
.164	.00076	.00076	.00073	.00074	.00074	.00073

ferences between ordinary water and the solutions in question are given for three wave-lengths at 25.0°. The values calculated by the equation

$$n_1 - n = N_2(n_1 - n_2) \quad (6)$$

where n_1 , n_2 and n are the refractive indices of H₂O, H₂O and the solution, are given in columns 3, 5, and 7.

⁵ Cf. L. H. Adams, J. Am. Chem. Soc. **37**, 1181 (1915); J. Wash. Acad. Sci. **5**, 267 (1915) on the question of interferometer calibration.

REFRACTIVE INDEX AND TEMPERATURE

There is a temperature of maximum refractive index for ordinary water as has been shown by Pulfrich. The maximum lies between -1 and -2°C. I have found maxima also in the refractive indices of 97.7 and 45.9 mol percent solutions. For the former the maximum is close to +6°C and for the latter close to +3°C. For ordinary water the point of maximum refractive index lies between five and six degrees below the point of maximum density; the same is true of H₂O.⁶ Aside from the displacement in both coordinates there is little difference in the curves of the three solutions of mol fractions 0.0 (light), 0.459 (medium) and 0.977 (heavy), shown in Fig. 1. (In Fig. 1 the scale is the same for each of the

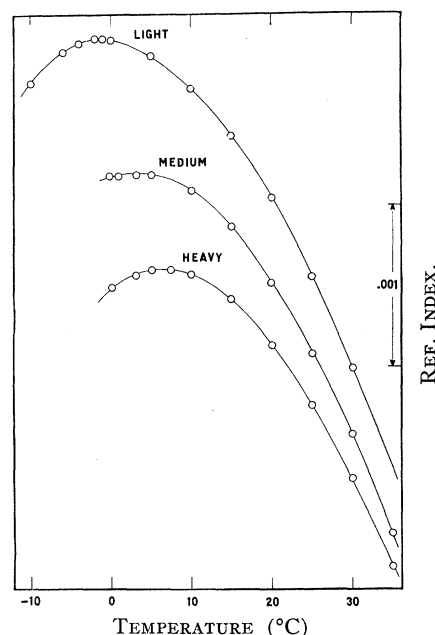


FIG. 1.

curves but is displaced vertically to bring the curves closer together.) The temperature coefficients are practically independent of wave-length over the range studied. The maxima for all five wave-lengths fall within a few tenths of a degree of the values given above. Table III gives the experimental results over the whole range of temperature and wave-length.

⁶ Lewis and Macdonald (J. Am. Chem. Soc. **55**, 3057 (1933)) give +11.6° as the point of maximum density for H₂O.

TABLE III. *Refractive indices.*

$T(^{\circ}\text{C})$	6563 H α	5893 Na D	5461 Hg	4861 H β	4358 Hg
<i>Ordinary water from I.C.T.</i>					
20.0	1.33115	1.33300	1.33447	1.33714	1.34030
<i>Observed for ordinary water</i>					
20.0	1.33118	1.33300	1.33449	1.33712	1.34025
<i>Mol fraction H$_2^2$O = 0.459</i>					
35.0	1.32764	1.32936	1.33075	1.33330	1.33630
30.0	1.32825	1.32998	1.33137	1.33391	1.33693
25.1	1.32875	1.33048	1.33186	1.33443	1.33743
20.0	1.32920	1.33092	1.33232	1.33490	1.33789
15.1	1.32953	1.33127	1.33265	1.33523	1.33824
10.1	1.32976	1.33150	1.33290	1.33546	1.33848
5.1	1.32987	1.33160	1.33301	1.33557	1.33858
3.2	1.32988	1.33160	1.33302	1.33558	1.33859
0.9	1.32987	1.33159	1.33301	1.33558	1.33858
-0.2	1.32986	1.33159	1.33301	1.33556	1.33857
<i>Mol fraction H$_2^2$O = 0.977</i>					
35.0	1.32552	1.32715	1.32844	1.33089	1.33376
30.05	1.32608	1.32770	1.32900	1.33144	1.33436
25.0	1.32654	1.32816	1.32947	1.33192	1.33482
20.1	1.32692	1.32853	1.32986	1.33231	1.33520
15.0	1.32720	1.32882	1.33013	1.33259	1.33550
10.0	1.32734	1.32897	1.33028	1.33274	1.33564
7.5	1.32737	1.32900	1.33030	1.33278	1.33567
5.2	1.32738	1.32900	1.33031	1.33277	1.33567
3.1	1.32736	1.32897	1.33028	1.33276	1.33565
0.1	1.32727	1.32889	1.33021	1.33265	1.33556

TABLE IV. *Refractive index of pure H $_2^2$ O.*

$T(^{\circ}\text{C})$	λ	6563	5893	5461	4861	4358
n_2	20.0	1.32683	1.32844	1.32976	1.33221	1.33509
$n_1 - n_2$	20.0	0.00435	0.00456	0.00473	0.00491	0.00516
$T(^{\circ}\text{C})$	0	5	10	15	20	
$n_2 D$	1.32877	1.32888	1.32886	1.32871	1.32844	
$T(^{\circ}\text{C})$	25	30	35			
$n_2 D$	1.32806	1.32760	1.32705			

TABLE V. *Dispersion of H $_2^2$ O.*

	$n_{4358} - n_{4861}$	$n_{4861} - n_{5461}$	$n_{5461} - n_{5893}$	$n_{5893} - n_{6563}$	$n_{4358} - n_{6563}$
H $_2^2$ O	0.00313	0.00263	0.00149	0.00182	0.00907
H $_2^1$ O	0.00288	0.00245	0.00132	0.00161	0.00826

The refractive index for pure H $_2^2$ O is given in Table IV. The molecular refraction of ordinary water at 20° for the sodium *D*-line is 3.7121; for pure H $_2^2$ O the corresponding value is 3.687.

DISPERSION

In Table V it is seen that the dispersion of pure H $_2^2$ O is definitely less than that of ordinary

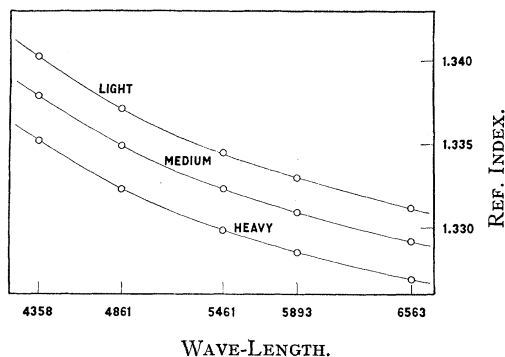


FIG. 2.

water. Fig. 2 gives the dispersion for ordinary water, for 45.9 and 97.9 mol percent H $_2^2$ O, at 20°.

We have seen that the molecular refraction of H $_2^2$ O is lower, which is to say that the refractive index is even lower than can be accounted for by the difference in molecular volumes. This abnormality and the lower dispersion, taken together, indicate that the effective position of the absorbing region in the ultraviolet, which is chiefly responsible for the refractive index of H $_2^2$ O in the visible, is further removed from the visible than is the corresponding region for H $_2^1$ O.

CONCLUSION

Within the last year two papers have appeared which deal, in part, with the refractive index of heavy water. In the first, Washburn, Smith and Frandsen⁷ have given for the difference between the refractive indices of ordinary water and water of specific gravity 1.0014 for the sodium *D*-line at 25° the value $(60 \pm 2) \times 10^{-6}$. If this be extrapolated to pure H $_2^2$ O the difference is 0.00447 ± 0.00015 . The corresponding value given above is 0.00445. In the second paper Selwood and Frost⁸ give results for the refractive index of pure H $_2^2$ O which must be corrected slightly in the light of the relations, described herein, between concentration and density. The values obtained from their experimental data are given together with the corresponding results obtained in this investigation (see Table VI). There is the possibility that the difference may be due partially to the presence of O¹⁸ in the water used in this

⁷ Washburn, Smith and Frandsen, *J. Chem. Phys.* **1**, 288 (1933).

⁸ Selwood and Frost, *J. Am. Chem. Soc.* **55**, 4335 (1933).

TABLE VI.

	Selwood and Frost	This investi- gation
$(n_D 20)_1 - (n_D 20)_2$	0.00473	0.00456
$(n_C 20)_1 - (n_C 20)_2$	0.00429	0.00435

investigation, though there is no other reason to suspect its presence. O^{18} , if present in small amounts, can not affect the relations between density and concentration; it will, however, depress the values for $n_1 - n_2$.

If it should be found that there are errors due to the facts that (1) the value 1.1056 for the specific gravity of $H_2^{18}O$ at 25° is too small or (2)

O^{18} is present, then the experimental results may easily be corrected in the light of such findings.

Finally, it is deserving to note, in view of recent misuse, that the value 1.1056 given by Lewis and Macdonald is for the *specific gravity* of $H_2^{18}O$ at $25^\circ C$. Since the temperature coefficients of the two kinds of water are different they must be taken into account in work at other temperatures. The same caution applies even more pointedly to the use of the refractive indices, for there the difference in temperature coefficients is large.

It is a pleasure to acknowledge my indebtedness to Professor Lewis, who suggested and directed this work.