THE VARIATION OF THE INDEX OF REFRACTION OF WATER, ETHYL ALCOHOL, AND CARBON BISULPHIDE, WITH THE TEMPERATURE.

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Synopsis.

Index of Refraction of Pure Water for Sodium Light from 15° to 100° C.—Very few observations had previously been made for temperatures above 50° C. A precision spectrometer was used. The brass prism with optical glass windows was gold plated inside to prevent contamination of the pure gas-free water tested, and means were provided for keeping the temperature within 0.1° C. Many readings were taken and the average values are probably accurate to within about 0.00002. When reduced to vacuum they are well represented by the empirical formula: $n = 1.33401 - 10^{-7}(66t + 26.2t^2 - 0.1817t^3 + 0.000755t^4)$. The *temperature coefficient* dn/dt changes from $-8(10)^{-5}$ at 15° to $-30(10)^{-5}$ at 100°.

Index of Refraction of Commercially Pure Ethyl Alcohol and Carbon Bisulphide for Sodium Light from 15° up to the Boiling Points.—While Kahlbaum's ethyl alcohol, 99.8 per cent. absolute, and Baker's C.P. CS_2 were used, the absolute values obtained differ somewhat from those given by others for pure samples. Nevertheless the *temperature coefficients* are probably not affected by the slight amount of impurity present and are of interest because very few results are available for liquids at temperatures above 40° C. The results correspond to the empirical equations: dn/dt(ethyl alcohol, 15 to 70°) $= -10^{-6}[404 + 0.44(t - 15) + 0.0075(t - 15)^2]$; dn/dt(CS_2, 15 to 45°) $= -10^{-6}[766 + 5.12(t - 15) - 0.105(t - 15)^2]$.

Introduction.—Historically the study of the change in the index of refraction of liquids with change in temperature dates from the work of Jamin in 1856.[1] Most of the investigations made have been at temperatures not differing greatly from room temperature. In the case of water all the investigations, with two exceptions, are within the temperature range of 0° to 50° C. The two exceptions mentioned are the work of Ruhlman[2] and Kettler,[3] whose investigations included temperatures in the range 50 to 100° C. A partial bibliography for the three liquids mentioned in the title may be found in Landolt-Bornstein Tabellen. A brief incomplete historical summary for the case of water is given by Osborn.[4] Osborn's work is concerned only with the change in the index of refraction of water with the temperature, the absolute value of the index not being determined. For the range 1° to 38° C. he determined this change to approximately one unit in the seventh decimal place.

[1] Comptes Rendus, 43, 1191, 1856.
[2] Pogg. Ann., 132, 177, 1867.
[3] Ann. d. Phys., 33, 353 and 506, 1888.
[4] Phys. Rev., 2d series, 1, 198, 1913.

This work, together with the value of the index as found in such investigations as those of Walter,[1] Gifford[2] and Baxter, Burgess, and Daudt,[3] constitutes a very complete study for the range below 40° C. The data for the range above 40° seem to be somewhat uncertain, the work of Ruhlman and Kettler not being always in good agreement. It therefore seemed justifiable to the writers to study anew the index of refraction of water, especially in the region between 40° and 100° but making a sufficient number of determinations below 40° to enable a comparison to be made with other recent determinations. Determinations of the index of refraction of ethyl alcohol and carbon bisulphide from 15° C. to their boiling points are also included.

Apparatus and Method.—After preliminary trials of different methods, the spectrometer method was adopted. There was available a new precision spectrometer, designed by one of the writers, and built in the shop of the department of physics. The weight of the heavy telescope, counterpoise, and table was supported in part by ball bearings, the design thus permitting of a fairly heavy load on the spectrometer table. The instrument was provided with all needed slow motions, clamping devices and adjustments. The ten-inch circle, divided into one twelfth degrees, was cut on the automatic circular dividing engine which was also built in the shop of the department of physics.[4] By the use of two microscopes with travelling eyepieces, 180° apart, the scale could be read to one half seconds if desired. The circle was cut soon after the calibration of the dividing engine, and the engine and circle showed errors not exceeding eight seconds. It was found that errors of setting were slightly greater than errors of graduation. With the first prism described below readings were made for each temperature on different parts of the scale, attempting thereby to eliminate errors of graduation by using different parts of the scale. Errors in setting were cared for by taking the mean of a large number of settings. With the second prism described below a calibrated part of the scale was used.

Two different prisms and heating devices were used. In the first of these, used for water only, the prism had a refracting angle of approximately 75°. It was constructed of heavy brass, with optical glass plates clamped on the sides. These plates were carefully tested. The faces of the brass prism were first milled as true as possible and then ground down and polished with abrasive powder and rouge. The glass plates were placed directly against the polished brass. The cubical

[1] Ann. d. Phys., 46, 423, 1892.

[2] Roy. Soc. Proc., 78, 406, 1906.

[3] Am. Chem. Soc. Jr., 33, 1, 893, 1911.

[4] PHYS. REV., XXX., 492, 1910.

contents of the prism were 70 c.c. The water was kept well stirred by an electrically driven stirrer. The stirrer and the interior of the brass prism were heavily gold plated. It was found that enough brass would dissolve in the water in the course of a few hours to change the index of refraction by approximately two units in the fourth decimal place. The prism was placed inside a double-walled, jacketed and well-insulated, electrical heating device. This jacketed heater, which measured 17 cm. in diameter by 12 cm. high, was placed on the spectrometer table from which it was well insulated. The jacket was provided with sliding shutters over the windows of the prism, these shutters being kept closed except when a reading was being made. It was found that the temperature could be brought readily to any desired point and held there ndefinitely to within one tenth of a degree. The temperature was measured with a calibrated Baudin mercury thermometer placed close to the line of vision. As a check, and also to determine the uniformity of the temperature distribution within the water, two thermocouples were inserted, the galvanometer used being sensitive enough to detect changes of 0.1°.

In the second form of apparatus the prism, again of brass, gold plated, with optical glass sides, had an angle of approximately 60° and was surrounded, except over the windows, by an oil-bath heater. The oil was heated electrically in a forty-gallon tank and by a rotary pump made to circulate vigorously about the prism. The heaters within the tank were operated by a thermostat and the temperature control rendered automatic. The main advantage in this form of heater was in the time saved through the automatic control. The temperature remained constant to within one twentieth of a degree during the time of making a set of readings at any temperature. In this case the thermometer was nearly totally immersed, thus obviating the necessity of stem corrections. The cubical contents of this prism were about 1500 c.c. The prism angle was of course redetermined for each prism every time the prism was cleaned, and the value checked to be sure that it did not change with change in temperature during a set of measurements.

Purity of the Water.—Since very small amounts of impurities were found materially to change the index of refraction special care was taken to obtain chemically pure water. This was furnished by the chemistry department and was redistilled in block tin and condensed directly into "Resistenz" bottles. In this way it was kept practically free from gases and no impurities could be detected. The conductivity was not taken. The usual method of heating to the boiling point was used to keep the liquid gas-free during a set of readings. After gold plating the interior of the prism contamination during use was practically eliminated. At a given temperature the water was often poured out, the prism washed and refilled and brought to the temperature under investigation with no change in the results.

Accuracy.—The index was calculated from the common minimum deviation formula. In determining the angle of minimum deviation the double angle was usually measured, that is, the prism was reversed and readings to the right and left of the zero setting taken. Six or seven readings were taken for each setting and with the first type of prism used these were repeated for different parts of the scale with the water held at a particular temperature. Readings taken throughout the temperature range were repeated during a period of several months and hence the values given represent the mean of a large number of readings. In determining the angle of the prism and the angle of minimum deviation the individual readings rarely differed from the mean by more than ten seconds and in most cases by much less than this amount. An error of ten seconds in the angle of minimum deviation introduced an error of approximately 3 units in the fifth decimal place with the 75° prism and 4 units in the fifth place with the 60° prism. An error of ten seconds in determining the angle of the prism introduced an error of approximately 2 units in the fifth place. It is believed that the final values for water relative to air given in Table II. are correct to within 2 units in the fifth place throughout the lower temperature range and to within 3 units in the fifth place for the higher temperature range. In Table IV. the values are reduced to the absolute index of refraction in order to compare them with the results of Kettler. In reducing the values observed in air to absolute values the question of distribution of the temperature gradient in the air outside the prism enters. Baxter, Burgess, and Daudt,[1] and others, have multiplied the value obtained in air by the index of refraction of air at the temperature of the water. Where the prism method is used this virtually assumes that the surfaces of equal temperature in the air outside the prism are normal to the direction of the incident and the emergent light. It is believed by the writers that with the prism used by them the more reasonable assumption is that the surfaces of equal temperature outside the prism are parallel to the faces of the prism, in which case it is the index of refraction of the air at room temperature which enters, irrespective of the temperature of the water in the prism. Hence in reducing the values to the absolute index the value obtained in air was, in each case, multiplied by 1.000272, the index of refraction of air at 20° C., which was approximately the room temperature throughout

[1] Loc. cit.

the investigation. At the highest temperature used the difference in the absolute index obtained by using the index of air at the room temperature and by using the index of air at the temperature of the water amounts to 8 units in the fifth place. Close to the prism faces the assumption made by the writers is doubtless nearest the truth; as one recedes from the prism faces, especially beyond the insulating jacket, the first assumption named more nearly represents the truth. The correct value therefore lies somewhere between the two. Of the two assumptions, if the one made by the writers be given the greater weight, then the error introduced by the uncertainty of the distribution of the temperature gradient in the air outside the prism cannot exceed 4 units in the fifth place at the highest temperature used. Hence the values of the index of refraction of water relative to vacuum are believed to be correct to within 2 units in the fifth place at approximately room temperatures, the possible error increasing with rise of temperature to perhaps three times this value at 100°. Changes in the index of refraction of air due to barometric changes affected the results by less than one unit in the fifth decimal place and were disregarded.

Results for Water.—In computing the observations for water where the actual temperatures differed by only a few tenths of a degree from integral values, the results were reduced to those for integral temperatures by interpolation. With this modification Table I. gives the experimental values obtained for the index of refraction of pure water relative to air for sodium light.

Table I.

The Index of Refraction of Pure, Gas-free Water, Relative to Air, for Sodium Light.

Temperature.	Index.	Temperature.	Index.	Temperature.	Index.	Temperature.	Index.
16° C....	1.33333	30° C...	1.33190	60° C...	1.32716	85° C...	1.32172
17......	1.33325	40......	1.33049	62......	1.32678	87......	1.32123
18......	1.33317	44......	1.32992	65......	1.32616	90......	1.32042
19......	1.33308	48......	1.32928	70......	1.32510	93......	1.31973
20......	1.33298	50......	1.32894	73......	1.32444	95......	1.31922
22......	1.33284	52......	1.32858	77......	1.32354	97......	1.31878
24......	1.33262	55......	1.32807	80......	1.32284	98.4....	1.31828
26......	1.33241	56......	1.32799	81......	1.32259		
28......	1.33220	58......	1.32758	82.5....	1.32218		

A large scale plot was made of the above values from which the values given in Tables II. and III. are taken.

In Tables III. and IV. the writers' values are compared with those of other observers. Table IV. is obtained from Table II. by multiplying

TABLE II.

The Index of Refraction of Pure Water, Relative to Air, for Sodium Light, obtained by Plotting the Results Given in Table I.

Temperature.	Index.	Temperature.	Index.	Temperature.	Index.	Temperature.	Index.
15° C....	1.33341	38° C...	1.33079	62° C...	1.32678	86° C..	1.32148
16......	1.33333	40......	1.33051	64......	1.32636	88.....	1.32100
18......	1.33317	42......	1.33023	66......	1.32596	90.....	1.32050
20......	1.33299	44......	1.32992	68......	1.32555	92.....	1.32000
22......	1.33281	46......	1.32959	70......	1.32511	94.....	1.31949
24......	1.33262	48......	1.32927	72......	1.32466	96.....	1.31897
26......	1.33241	50......	1.32894	74......	1.32421	98.....	1.31842
28......	1.33219	52......	1.32860	76......	1.32376	99.....	1.31813
30......	1.33192	54......	1.32827	78......	1.32332	100.....	1.31783
32......	1.33164	56......	1.32792	80......	1.32287		
34......	1.33136	58......	1.32755	82......	1.32241		
36......	1.33107	60......	1.32718	84......	1.32195		

by 1.000272, the refractive index of air. A column giving the variation of the index of refraction with the temperature is included in Table IV.

TABLE III.

Index of Refraction of Water, Relative to Air, Sodium Light.

Temperature.	Hall-Payne.	Walter.	Baxter-Burgess-Daudt.	Gifford.
15° C.........	1.33341	1.33339		1.33343
16...........	1.33333	1.33331		
18...........	1.33316	1.33316		
20...........	1.33299	1.33299	1.33299	
22...........	1.33281	1.33281		
24...........	1.33262	1.33261		
25...........	1.33251	1.33251	1.33248	
26...........	1.33241	1.33240		
28...........	1.33219	1.33218		
30...........	1.33192	1.33194	1.33190	

TABLE IV.

Absolute Index of Refraction of Water, Sodium Light.

Temp.	Kettler.	Hall-Payne.	*dn/dt.*	Temp.	Kettler.	Hall-Payne.	*dn/dt.*
15° C....	1.33365	1.33377	−0.00008	60° C..	1.32753	1.32754	− .00019
20......	1.33327	1.33335	− .00009	65.....	1.32655	1.32652	− .00020
25......	1.33281	1.33287	− .00011	70.....	1.32551	1.32547	−0.00021
30......	1.33226	1.33228	− .00013	75.....	1.32442	1.32434	−0.00022
35......	1.33164	1.33157	− .00014	80.....	1.32330	1.32323	−0.00023
40......	1.33093	1.33087	− .00015	85.....	1.32215	1.32208	−0.00024
45......	1.33017	1.33011	− .00016	90.....	1.32096	1.32086	−0.00025
50......	1.32934	1.32930	− .00017	95.....	1.31971	1.31959	−0.00026
55......	1.32847	1.32846	− .00018	100.....	1.31843	1.31819	−0.00030

Kettler made observations for sodium light at nine different temperatures ranging from 20.9° to 95.17° C. inclusive. From these nine observations by extrapolation and interpolation he gives a table of values from − 10° to 200° C., from which table the values given above are taken. We now know that extrapolation from the range he used to the zero point is not justifiable owing to the rapidly decreasing numerical value of dn/dt as the freezing point is approached. Extrapolation is also not justifiable near the boiling point because of the rapidly increasing numerical value of dn/dt. This rapid increase in the numerical value of dn/dt as the boiling point is approached is probably due to the increasing quantities of water vapor in the water.

Empirical Formulas.—Numerous empirical formulas have been proposed connecting the index of refraction of water with the temperature. Dufet [1] proposes

$$n = n_0 - 10^{-7}(125.5t + 20.642t^2 - 0.00435t^3 - 0.00115t^4),$$

where n represents the refractive index at the temperature $t°$ C., and n_0 the refractive index at 0° C. This formula was arrived at by setting up an empirical equation for dn/dt, from the best data available at that time in the range below 50°, and integrating. As tested by the writers the equation is not applicable to temperatures above 50° C. Walter's formula,

$$n = n_0 - 10^{-6}(12t + 2.05t^2 - 0.005t^3),$$

a modification of Dufet's formula, holds well over the range studied by Walter, that is, from 0° to 30° C. It does not hold for higher ranges. Owing to the relatively low values of dn/dt near the freezing point and the relatively high values near the boiling point a single simple equation covering the entire range from 0° to 100° cannot be expected to have a high accuracy over the entire range. The writers propose

$$n = 1.33401 - 10^{-7}(66t + 26.2t^2 - 0.1817t^3 + 0.000755t^4).$$

Walter's value for n_0, viz., 1.33401, is used. This equation was obtained by substituting in the general form, $n_0 - n = at + bt^2 + ct^3 + dt^4$, the values of n and t for four different temperatures and solving the four simultaneous equations for a, b, c, and d. This was done for four sets of equations, using different temperatures in the different sets and taking a mean of the values thus obtained. Some slight adjustments were then made by inspection and trial. The equation was tested at every five-

[1] Jour. de Physique, 4, 389, 1885.

degree point between 0° and 100°, and the maximum error was found to be at 75° where the deviation from the observed value is + 7 units in the fifth decimal place.

Osborn (loc. cit.) has given an empirical relation for the value of dn/dt which agrees very closely with experiment for the range 0° to 40° C. It is, however, not applicable above 50° C.

A number of empirical relations connecting the refractive index of a liquid with the density of the liquid have been proposed. Of these only two will be mentioned. Gladstone and Dale[1] have proposed the relation $(n - 1)/d = R$, where n is the index of refraction, d the density, and R a constant. Lorenz[2] proposed

$$\frac{n^2 - 1}{n^2 + 1} \cdot \frac{1}{d} = P, \text{ a constant.}$$

Table V. gives the values of R and P for water, the densities being taken from the sixth edition of the Smithsonian Tables.

TABLE V.

t.	R.	P.	t.	R.	P.	t.	R.	P.
15°...	0.33370	0.28030	50°..	0.33291	0.28030	90°.	0.33201	0.28079
20....	.33357	.28026	60...	.33276	.28043	95..	.33187	.28087
30....	.33336	.28023	70...	.33249	.28051	100..	.33163	.28088
40....	.33309	.28019	80...	.33221	.28063			

Getman and Wilson[3] give a few values between 15° and 40° C. for the refractive index and for R for water. Their values for the range studied are higher for the refractive index and R, and lower for dn/dt than those obtained by other observers, including the writers.

Ethyl Alcohol and Carbon Bisulphide.—A large number of determinations of the index of refraction of ethyl alcohol and carbon bisulphide have been made, but so far as the writers are aware no determinations have been made in the temperature ranges approaching the boiling points of either liquid. In connection with these liquids the second form of prism only, with automatic temperature control, was used. The same general procedure was followed and the same degree of accuracy reached as in the case of water. Here, however, the materials were not specially purified. Kahlbaum's ethyl alcohol, 99.8 per cent. absolute, and J. T. Baker and Co.'s carbon bisulphide were used. The analysis furnished by the makers for the carbon bisulphide was sp. gr. 1.27, N.V.M. 0.001 per cent., SO_2, H_2S, SO_3 none.

[1] Phil. Trans., 1858, p. 887.

[2] Wied. Ann., 11, 77, 1880.

[3] Amer. Chem. Jr., 40, 468, 1908.

Determinations were made of the index of refraction of ethyl alcohol for fifty different temperatures between the limits of 15° and 75° C. These represent a number of runs each taken throughout the temperature range, the observations extending over several months. The values obtained were plotted on a large scale from which plot the results given in Table VI. were taken.

Table VI.

Index of Refraction, Relative to Air, of Kahlbaum's Ethyl Alcohol, 99.8 Per Cent. Absolute, for Sodium Light.

t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
14° C....	1.36290	30° C...	1.35639	46° C...	1.34969	62° C...	1.34279
16......	1 36210	32......	1.35557	48......	1.34885	64......	1.34189
18......	1.36129	34......	1.35474	50......	1.34800	66......	1.34096
20.......	1.36048	36......	1.35390	52......	1.34715	68......	1.34004
22......	1.35967	38......	1.35306	54......	1.34629	70......	1.33912
24......	1.35885	40......	1.35222	56......	1.34543	72......	1.33820
26......	1.35803	42......	1.35138	58......	1.34456	74......	1.33728
28......	1.35721	44......	1.35054	60......	1.34368	76......	1.33626

Determinations were made of the index of refraction of carbon bisulphide at forty-three different temperatures between the limits of 15.95° and 44.7° C. These determinations represent many runs taken throughout the temperature range. These results were plotted and Table VII. made.

Table VII.

The Index of Refraction of Carbon Bisulphide, Relative to Air, for Sodium Light.

t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
15° C....	1.62935	24° C...	1.62226	34° C...	1.61413	44° C...	1.60582
16......	1.62858	26......	1.62064	36......	1.61247	45......	1.60499
18......	1.62704	28......	1.61902	38......	1.61080		
20......	1.62546	30......	1.61740	40......	1.60914		
22......	1.62387	32......	1.61577	42......	1.60748		

Table VIII.

Values of dn/dt for Ethyl Alcohol and Carbon Bisulphide.

Temperature.	Ethyl Alcohol.	Carbon Bisulphide.
15° C....................	−0.00040	−0.00077
25......................	− .00041	− .00081
35......................	− .00042	− .00082
45......................	− .00042	− .00083
55......................	− .00043	
65......................	− .00045	
75......................	− .00046	

If n represents the index of refraction at any temperature $t°$ C., and n' the index of refraction at 15° C., then as an empirical equation we may write

$$n = n' - 10^{-6}[a(t - 15) + b(t - 15)^2 + c(t - 15)^3].$$

For ethyl alcohol for the range 15° to 70° $n' = 1.36250$, $a = 404$, $b = 0.22$, $c = 0.0025$.

For carbon bisulphide for the range 15° to 45° $n' = 1.62935$, $a = 766$, $b = 2.56$, $c = -0.035$.

Andrews[1] has made determinations on the index of refraction of ethyl alcohol, giving great care to the purity of the alcohol. His value, which he believes correct to one unit in the fifth place, at 25° C., for sodium light is 1.359408. The writers' value at this temperature is 1.35844. The writers believe this difference in observed value of the index is due to the difference in purity. For carbon bisulphide at 20° C. and for sodium light Landolt-Bornstein Tabellen give 1.62772 as the mean of the values obtained by four observers. The writers' value is 1.62546. Again the only explanation that can be offered is the difference in purity of the material. While slight impurities will change the value of the index of refraction, it is hardly to be expected that they would produce a large change in the value of dn/dt and it is the change in the refractive index with the temperature, rather than the value of the index for pure material that is emphasized in the case of alcohol and carbon bisulphide.

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[1] Amer. Chem. Soc. Jr., 30, 353, 1908.