CHANGE OF INDEX OF REFRACTION OF WATER WITH CHANGE OF TEMPERATURE.

BY FREDERICK A. OSBORN.

INTRODUCTION.

THE change of the index of refraction of water with change of temperature has been studied by a number of investigators, among whom the following may be mentioned:

Jamin[1] made observations on the change of the index of refraction of water between 0° and 30°. He used an interference method, but apparently did not publish any values. He contented himself with a general statement of the change and gave the empirical formula

$$K_t = K_0 - (0.0000125731t) - (0.0000019291t^2)$$

as expressing his results.

Gladstone and Dale,[2] soon after the work of Jamin, studied the same problem, making use of a hollow prism and the method of minimum deviation. They worked between the temperatures of 0° and 40° and remark "our determinations were performed repeatedly and most carefully on water near the freezing point." They call attention to the fact that the change of index between 0° and 5° is much less than that between 5° and 10°, finding from their work that the change is .0001 and .0002 respectively. Their method enabled them to express the change of index to the fourth decimal place.

Ruhlman,[3] by a method similar to that of Gladstone and Dale, obtained the index of refraction of water between 0° and 100° for the lithium, sodium and thallium lines. His values are given to five decimal places.

Lorenz[4] used an interference method and worked between 0° and 34°. $d\mu/dt$ was found from the shift of the fringes with change of the temperature and an accuracy of 3 units in the seventh decimal place was claimed. No experimental data were given but his results are expressed by the equation

[1] Comptes Rendus, 43, p. 1191, 1856.
[2] Phil. Trans., p. 887, 1885.
[3] Pogg. Ann., 132, p. 1177, 1867.
[4] Wied. Ann., 11, p. 70, 1880.

$$\frac{d\mu}{dt} = - 10^{-6}(0.076 - 5.606t + 0.06403t^2) \text{ for the Na line,}$$

$$= - 10^{-6}(0.952 - 5.586t + 0.06402t^2) \text{ for the Li line.}$$

Dufet[1] used two different methods. In the prism method, the prisms filled with water at a given temperature, were adjusted to minimum deviation. The water was then exchanged for water at a higher temperature, and the displacement of the lines was observed as the temperature fell. From this shift of the lines, and the other measurable quantities, he computed $d\mu/dt$. In the interference method he used Talbot's fringes, and observed the passage of about 180 fringes between 0° and 50°. In part of this work a quartz plate was immersed in the water, and for part a crown glass plate was substituted. The values for $d\mu/dt$ obtained by his different methods sometimes differ from each other by as much as 45×10^{-7}. Dufet expresses his results by the equation

$$\frac{d\mu}{dt} = - 10^{-7}(125.46 + 41.285t - 0.01304t^2 - 0.0046t^3).$$

Values for $d\mu/dt$ obtained from this equation occasionally differ from his mean experimental values by as much as 7×10^{-7}.

Kettler[2] repeated Ruhlman's work for temperatures above 20° using a total reflection refractometer.

Walter,[3] using the minimum deviation method, has done some careful work for the range 0° to 30°. His results are given to the fifth decimal place.

Conray,[4] by the same method, but with a spectrometer graduated to 10″, has made a study of the change of index between 0° and 10°. He claims an accuracy in the sixth decimal place, although greater differences between successive determinations for the same temperature range are found.

Bender,[5] with the Pulfrich refractometer, has studied the change of the index of refraction of water between 0° and 40° using the H_a, H_β, H_γ lines. His values are expressed to five decimal places.

More recently Gifford,[6] using a new prism method, has determined the index at 15° for a large number of wave-lengths. The values obtained are considered correct to within two units in the fifth decimal place. A

[1] J. de Phy., p. 401, 1885.
[2] Wied. Ann., 33, p. 353, 506, 1888.
[3] Wied. Ann., 46, p. 422, 1892.
[4] Proc. Royal Soc., 58, p. 228–234, 1895.
[5] Ann. d. Phy., p. 343, 1899.
[6] Roy. Soc. Proc., 70, p. 329, 1902; 78, p. 406, 1906-7.

still later determination by Baxter, Burgess, and Daudt[1] gives the value of the index for Na light at the temperatures 20°, 25°, and 30°. These investigators used the prism method also and consider their results correct to three units in the fifth decimal place.

While the change of the index of refraction of water with change of temperature has been studied by these and many others, the methods used and the results obtained are such as to make it seem desirable to repeat the work.

It was thought that the Abbe-Pulfrich interferometer could be made to give more accurate results than those thus far obtained and the present paper has for its object the application of the interferometer to the determination of the change of the index of refraction of water with change of temperature.

Method.

The method used in this piece of work is that first used by Reimerdes[2] in his work on the change of the index of refraction of quartz. The change in the index of the liquid is determined by the shift of interference fringes in a fused quartz system.
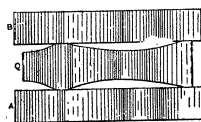

Fig. 1.

The arrangement of the system is shown in Fig. 1. A bed plate *A*, of fused quartz, 38.4 mm. in diameter and 10 mm. thick, with its upper face plane polished, is placed on a horizontal surface. Upon the quartz surface is placed a fused quartz ring *Q* of 31.8 mm. in external diameter, 24.4 mm. internal diameter, and approximately 9.9 mm. high. The cover plate *B* of fused quartz, is approximately 36 mm. in diameter and 8 mm. thick. Its surfaces are plane polished and inclined to each other at an angle of about 20″, so as to deflect from the field the light reflected from its upper surface.

The quartz ring was cut from a plate of quartz whose surfaces were plane polished and slightly inclined to each other. The ends of this ring were ground away in such a manner as to leave on each end three equidistant feet, whose surfaces are portions of the original plane polished surfaces of the plate from which the ring was cut. The inclination of the faces of this plate to one another was such that when the ring is placed, as in the figure, between the bed and cover plates the opposite reflecting surfaces, *i. e.*, the upper surfaces of the bed plate and the lower surface of the cover plate, are properly inclined to produce suitable interference fringes.

[1] Am. Chem. Soc. Jour., 33, p. 893, 1911.
[2] Inaugural Dissertation, Jena, 1896.

The cover plate B has on its lower surface at the center, a small circle which serves in the field of view as the reference point from which the measurements are made.

When the apparatus is in adjustment and the field illuminated by monochromatic light, the field is seen to be crossed by parallel interference fringes. Each dark band represents a definite thickness of the air between A and B. If λ be the wave-length of the light used, then the difference in the thickness of the air layer for any two adjacent dark bands is $\lambda/2$. If the space between A and B be filled with a liquid, the effect is to increase the optical thickness between A and B from d to μd and the distance between any two fringes, the band width, is less than the distance between these same fringes in air.

When the fused quartz system and the liquid are heated, the fringes move across the field toward the thick edge of the wedge. The index of refraction of the water decreases with rise of temperature, hence the wave-length in the water becomes longer. There will be fewer wave-lengths between any two opposite points of the wedge. But a given fringe is due to the retardation of a definite number of wave-lengths of the light reflected from the upper surface of the bed plate over that reflected from the lower surface of the cover plate, so if the wave-lengths become longer, a thicker part of the wedge is needed to give the same number of wave-lengths retardation. Therefore, the bands move toward the thick edge of the wedge and the number passing the reference circle indicates the decrease in the number of waves between the surfaces at that point due to the lengthening of λ.

The expansion of the quartz ring increases the distance between the plates and decreases the number of fringes that would otherwise cross the reference circle toward the thick edge of the wedge, or increases the number of wave-lengths under the reference circle, which would cause a shift of the fringes toward the thin edge of the wedge. The resultant shift of fringes is the difference of these two effects and, owing to the small expansion of the fused quartz, is toward the thick edge of the wedge.

The change in the index of refraction for a given temperature change is given by the formula

$$\frac{d\mu}{dt} = -\frac{N\frac{\lambda}{2}}{L_1(t_2 - t_1)} - \alpha\mu_1.$$

That this is so appears from the following considerations.

Let n be the number of fringes shifted for the temperature interval $(t_2 - t_1)$.

L_1 and L_2 be the thicknesses of the liquid (length of ring) at t_1 and t_2.

t_1 and t_2 be the lower and higher temperatures.

μ_1 and μ_2 be the indices of refraction of the liquid at t_1 and t_2.

λ be wave-length in air of the light used.

λ_1 and λ_2 be corresponding wave-lengths in the liquid at t_1 and t_2.

α be the mean coefficient of expansion of the fused quartz ring for the given temperature interval $(t_2 - t_1)$.

$$\mu_1 = \frac{\lambda}{\lambda_1} \text{ and } \mu_2 = \frac{\lambda}{\lambda_2}, \quad \lambda_1 = \frac{\lambda}{\mu_1} \text{ and } \lambda_2 = \frac{\lambda}{\mu_2},$$

$$n = \frac{2L_1}{\lambda_1} - \frac{2L_2}{\lambda_2} = \frac{2L_1}{\dfrac{\lambda}{\mu_1}} - \frac{2L_2}{\dfrac{\lambda}{\mu_2}} = \frac{2L_1}{\dfrac{\lambda}{\mu_1}} - \frac{2L_1[1 + \alpha(t_2 - t_1)]}{\dfrac{\lambda}{\mu_2}}$$

$$= 2L_1 \frac{(\mu_1 - \mu_2)}{\lambda} - \frac{2L_1}{\lambda} \mu_2 \alpha(t_2 - t_1),$$

$$\mu_2 - \mu_1 = -\frac{n\dfrac{\lambda}{2}}{L_1} - \mu_2 \alpha(t_2 - t_1),$$

$$\frac{d\mu}{dt} = \frac{\mu_2 - \mu_1}{t_2 - t_1} = -\frac{n\lambda}{2L_1(t_2 - t_1)} - \mu_2 \alpha$$

$$= -\frac{n\lambda}{2L_1(t_2 - t_1)} - \mu_1 \alpha,$$

as the difference between μ_1 and μ_2 is not sufficiently large to affect the value of the corrections.

APPARATUS.

The instrument used was an Abbe-Pulfrich interferometer such as described in detail by Pulfrich[1] and also by Randall.[2] The source of the light was a small mercury arc lamp, giving a very brilliant light in which the line in the green was especially prominent.

The quartz system was set up in a glass cell, 7 cm. in diameter and 4 cm. deep, which was placed in the double walled galvanized iron tank, T. The cover, G, closed the tank and made it water-tight by means of mercury between the double walls. The small opening in G at the top, 3 cm. in diameter, was closed by a glass plate. A Beckmann thermometer, B, and a stirrer, S, were introduced into the cell through the cover as shown in Fig. 2. The tank with its optical system was rigidly supported by the arm L, which was clamped to the stone pier on which the interferometer rested.

[1] Zeitschr. fur Instrumentenkunde, 1898, p. 261.

[2] PHYS. REV., 20, 1905.

The heating was obtained by means of two coils of No. 28 iron wire wound on the insulated vessel *V*, which was 18 cm. in diameter and 25 cm. deep. The coils, shown by the small circles, were wound separately, the turns about 5 mm. apart, so that the coils could be used alone, in series, or in parallel. The coils were covered with a layer of asbestos and then with wool felt. This vessel was made to fit closely into another iron vessel which was set inside a larger tank 35 cm. in diameter and 40 cm. high. The space between the two could be filled with water or with ice.
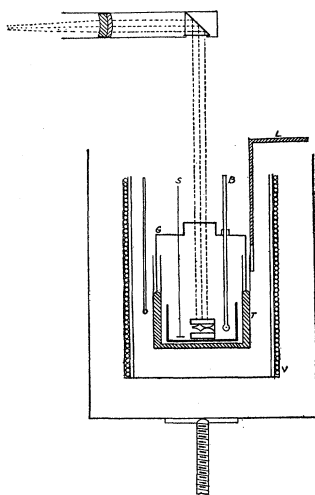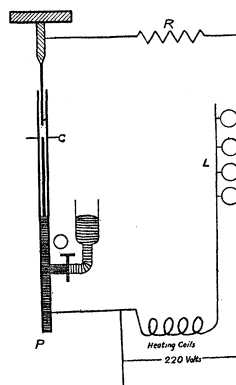
Fig. 2.   Fig. 3.

The thermostat used was a slight modification of a form which has already been described by the writer.[1] Around the inside of *V* was a liquid thermometer of 180 c.c. volume. This thermometer consisted of a ring of glass tubing, 17 cm. in diameter with six thin-walled vertical glass tubes, 20 cm. long, fused into it and hanging downward, all filled with toluol, except one which was filled with mercury and connected with the regulator at *P*, Fig. 3.

Fig. 3 shows the regulator and the electrical connections. The heating current was regulated by a lamp bank, *L*, not more than six 16 c.p. 220-volt lamps being required for the highest temperature. The thermostat was adjusted for a given temperature, by making the resistance in the rheostat, *R*, of such value that the current in the heating coils was insufficient to raise the temperature of the bath; the latter, cooling slightly, caused the mercury in the capillary, *C*, to fall, thus cutting out the rheostat circuit, and allowing more current to go through the heating

[1] Jour. Phys. Chem., 9, 1905, p. 297.

coils.   When the temperature of the bath rose, the mercury rose also in the capillary, cutting in the rheostat.

Since the large volume of the liquid thermometer made it more sensitive than the thermometer in V, the bath was easily held at a temperature, constant to within 2 or 3 thousandths of a degree for half a day or more. The consequent variation of the temperature in the cell was not more than .002° in the same ime.

Stirrers in T and V kept the water thoroughly agitated.

ADJUSTMENT OF APPARATUS.

The preliminary adjustments of the instrument and the optical system for work with the fringes has been described by Pulfrich.[1]

When the system was in good adjustment, the liquid whose index of refraction was to be studied was poured into the glass cell, until, when the cover plate B was put on the quartz ring, the liquid came within a mm. of the top of B.   The cover G was then put on and the entire bath raised by means of a screw until the water around the tank T came within a cm. of the glass top on G.   The temperature of the bath was then raised to the desired point and the thermostat set in operation by closing the stop cock O and adjusting the platinum point in the capillary tube.

The temperature in the cell would gradually rise for two or three hours, after which the Beckmann thermometer showed no change of temperature greater than .002°.   When the temperature had been constant for two hours longer, the position of the bands was read and also the temperature. One hour later both were read again.   If no change in either was found, the temperature of the liquid was assumed to have become constant.

The temperature was then slowly raised 5° and the displacement of the fringes was counted.   This displacement was, after the first 10 minutes, very uniform, until the temperature of the cell was within 0.5° of that of the surrounding water bath when the displacement became slow.   The entire time for this displacement of the fringes was usually about two hours.   But, as in getting the initial position of the bands, the final reading was not taken until the thermometer had been constant to within .002° for three hours.   The number of whole bands shifted being known by actual count, the total shift was then given by the formula.

$$N = M + d_2 - d_1,$$

where M = number of whole bands counted, d_2 and d_1 the fractions of a band at the higher and lower temperatures respectively.   These fractions were found from the readings of the micrometer with which the interferometer was provided.

[1] Zeitsch. fur Instrumentenkunde, 13, Oct., Nov., Dec., 1893.

THERMOMETERS.

Two thermometers were used: For the water bath, thermometer No. 2,107, range − 10° to 50° by 1/10°, recently calibrated at the National Bureau of Standards; for the liquid in the cell a Beckmann thermometer, compared with No. 2,107, and, for the 5° interval, compared with one made by Haak, reading to .01° which had been calibrated at the Reichsanstalt.

The mean temperature of the water in the cell was obtained in each case by translating the readings of the Beckmann thermometer into degrees centigrade.

SPHEROMETER.

A Geneva Society spherometer was used to measure the quartz ring, and the readings could be made to .001 mm. A mean of thirty readings gave for the length of the ring 9.901 mm.

DEGREE OF ACCURACY.

From the formula

$$\frac{d\mu}{dt} = - \frac{n\lambda}{2L_1(t_2 - t_1)} - \alpha\mu_1$$

it is evident that the value of $d\mu/dt$ depends upon the three measurable quantities, n, L, and t.

In finding n from the formula

$$n = M + d_2 - d_1,$$

the d's can be found with an error affecting n by ± .02 of a fringe. The resulting error in $d\mu/dt$ is 10×10^{-8}. The difference in temperature could be determined with an error of ± .002. The error in $d\mu/dt$ from this source is 4×10^{-8}. The length of L could be found to ± .001 mm., resulting in an error in $d\mu/dt$ of 1×10^{-8}.

The total error in the final result due to these errors is

$$E = 10^{-8}\sqrt{10^2 + 4^2 + 1^2} = 10.8 \times 10^{-8},$$

or 1 unit in the seventh decimal place.

Scheel has found the length of a fused quartz ring similar to the one used here to be well represented by the expression

$$l_t = l_0(1 + 0.322 \times 10^{-6}t + 0.00147 \times 10^{-6}t^2).$$

The mean value of α computed from the above formula for each temperature range was used; and μ_1, as found by the prism method, using a Zeise spectrometer, is 1.3342. μ_1 need not be known with the greatest accuracy as an error of .001 is negligible as affecting the factor $\alpha\mu_1$.
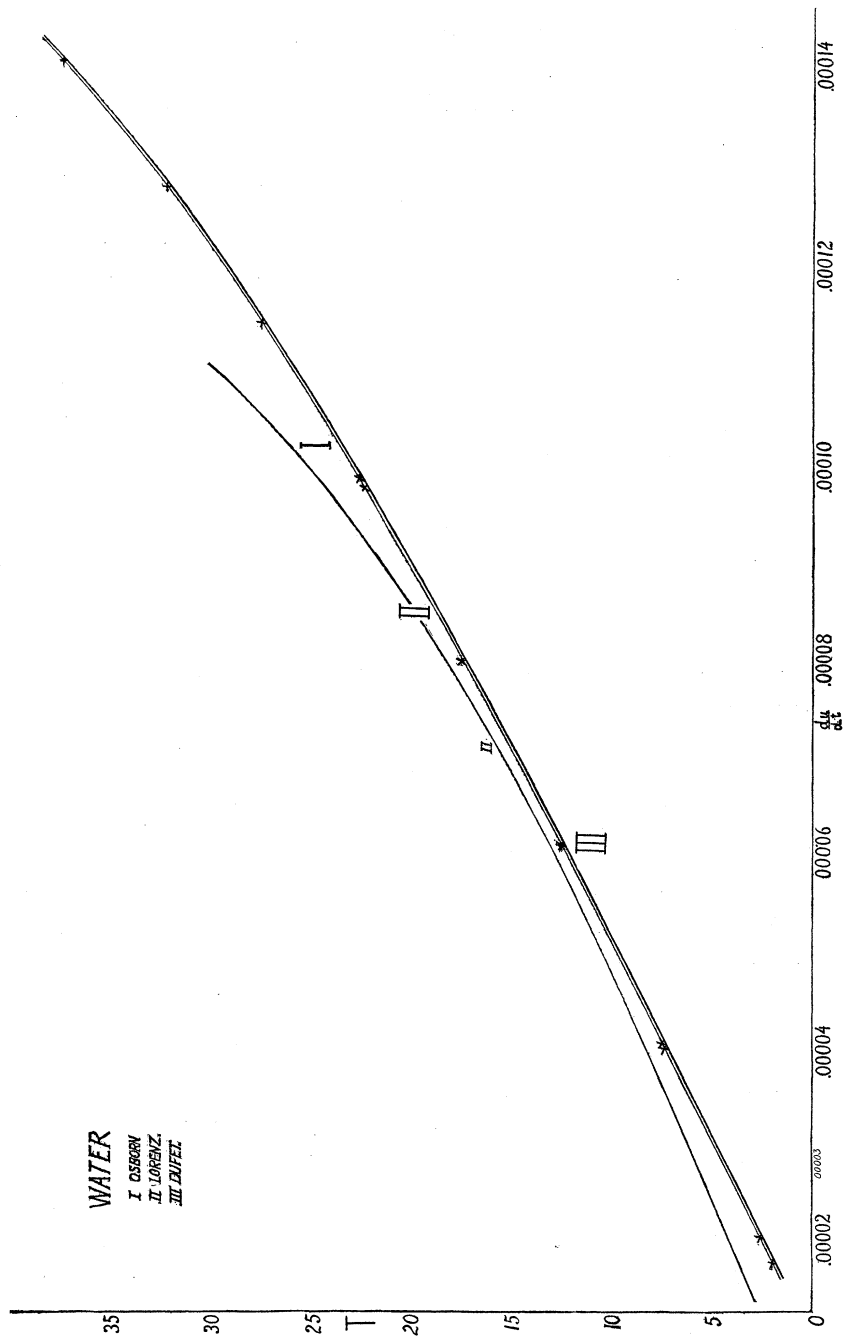
Fig. 4.

EXAMPLE OF A COMPLETE DETERMINATION.

Length of fused quartz ring.............................9.901 mm.
Thickness of water layer.................................9.901 mm.
Conductivity of water used (free from dissolved air).........1.7×10^{-6}

Time.	Temperature of Bath.	Temperature of Water in the Cell, Beckmann Thermometer.	Temperature of Emergent Column of Beckmann.	Shift of Fringes.	d's from Micrometer Readings.
9:30A.M.	25.00° C.	1.150			12 noon
1:00		.170	23.5	0	
2:00		.190			$d_1 = .190$
1:00		.190			1:30 P. M.
1:30		.190			$d_2 = .186$
					Mean .188
1:45	25.5			1	
50		1.900		1	
54				1	
58				1	
2:02				1	
06				1	
10				1	
14				1	5:00 P. M.
18				1	
22				1	
26				1	$d_2 = - .047$
29				1	
33				1	
37				1	
40				1	6:30 P. M.
44				1	
48				1	$d_2 = - .043$
54				1	
59				1	
3:16	29.98			1	Mean − .045
4:00		6.120	25.5	1	
5:00		.130		$\overline{21}$	
30		.130			
6:30		.130			

$$N = M + d_2 - d_1 = 21 + (- 0.045) - 0.188 = 20.767,$$

$$t_2 - t_1 = 6.130 - 1.190 = 4.940°,$$

$t_2 - t_1$ corrected for emergent stem and mercury out of bulb = 4.999°,

$$\frac{d\mu}{dt} = - \frac{20.767 \times .0005460}{2 \times 9.901 \times 4.999} - .00000048 = - .0001150$$

at 27.49°.

TABLE I.

Water.

Conductivity of water, 1.7 × 10⁻⁶ (air-free).
L = 9.901 mm.
λ = .0005460 mm.

Date.	Series.	Temp. Range.	Temp. Diff. $t_2 - t_1$	Total Shift of Fringe.	$\dfrac{d\mu}{dt}$	At
March 23	1	20–25	5.014	17.95	.0000992	22.58°
25	1	20–25	4.992	17.90	983	22.33
26	2	25–30	4.999	20.767	1150	27.49
27	2	30–25	4.981	20.684	1150	27.51
28	2	30–35	4.952	22.978	1284	32.25
28	2	35–30	4.860	22.540	1284	32.23
April 2	2	35–40	5.015	25.541	1409	37.50
3	2	40–35	5.013	25.528	1409	37.50
5	3	15–20	4.934	14.393	809	17.37
6	3	20–15	4.860	14.156	808	17.38
6	3	15–10	4.965	11.170	625	12.49
8	3	10–5	4.990	7.617	424	7.49
8	3	5–0	4.714	3.805	227	2.61
11	4	10–15	5.009	11.284	624	12.50
11	4	15–20	5.007	14.607	809	17.37
12	4	20–25	4.961	17.786	993	22.53
12	4	25–30	4.893	20.331	1150	27.46
13	4	30–35	5.052	23.429	1284	32.27
13	4	35–40	4.910	25.017	1410	37.48
14	4	5–10	4.730	7.271	420	7.34
14	4	5–0	4.495	3.632	227	2.59

Table I. gives the complete set of experimental data. Each series represents a new set-up of the apparatus and a new supply of water taken from a common source.

Fig. 4, Curve I., expresses the results graphically, and they may also be given by the equation

$$\frac{d\mu}{dt} = - \ 10^{-7} \times (118.73 + 41.4184t - 0.02376t^2 - .0043757t^3).$$

This equation expresses correctly the experimental results to approximately one unit in the seventh decimal place.

CONCLUSION.

The results contained in Table I. show that the method here employed gives more concordant results than any method previously used and that in the determination of $d\mu/dt$ an accuracy of one unit in the seventh decimal place has very approximately been attained. This result has been achieved principally through the accuracy with which the shift of the

TABLE II.

Comparison of Results.[1]

Temp.	Lorenz.	Dufet.	Osborn.	Temp.	Lorenz.	Dufet.	Osborn.
38°		.0001423	.0001418	19°	.0000833	.0000874	.0000867
37		1402	1398	18	801	838	831
36		1380	1375	17	767	801	794
35		1357	1352	16	732	764	757
34		1333	1327	15	696	726	720
33		1308	1301	14	659	688	682
32		1282	1276	13	620	650	644
31		1256	1249	12	580	611	605
30	.0001105	1228	1221	11	538	572	565
29	1087	1200	1194	10	496	532	526
28	1067	1170	1163	9	452	493	486
27	1045	1140	1134	8	407	453	447
26	1024	1109	1103	7	360	412	406
25	1001	1078	1072	6	313	372	365
24	976	1045	1039	5	264	331	325
23	950	1012	1006	4	213	290	284
22	923	978	972	3	162	249	243
21	894	944	938	2	109	208	201
20	864	909	903	1	55	167	160

interference bands could be measured by the Abbe-Pulfrich interferometer and also by the extremely exact control and measurement of the temperature.

In comparing the results here obtained with those of other observers, it will be noticed from the results tabulated in Table II. and also from the Curves I. and III. that a constant difference exists between the results of Dufet and those of the writer. This difference is six or seven units in the seventh decimal place. The experiments of Lorenz furnish data for estimating the variation of $d\mu/dt$ with respect to λ. The change in $d\mu/dt$ to be expected for a change from the Na line, λ 5,893, used by Dufet to the Hg line, λ 5,460, used by the writer, is, according to Lorenz, 6.8 units in the seventh decimal place in the temperature region 10°–30°. The results of the two investigations appear therefore to be in complete accord. This is somewhat remarkable when one considers that each of Dufet's final results is the mean of four different determinations which often differ from one another by several units in the sixth decimal place.

The empirical equation here given expresses the experimental results to one unit in the seventh decimal place. It is given in preference to adopting the Dufet equation with a suitable alteration of its constant term as it agrees more closely with the experimental data.

[1] Computed from the empirical equations.

Gifford's data on the change of the temperature refractive coefficients with wave-length are not sufficiently explicit to warrant an estimate of the difference which should exist between the values here presented and those of Dufet.

The changes in the index for the temperature interval 20° to 25° and 20° to 30° as computed by the formulæ of Dufet and the writer, the later values being corrected for wave-length, *i. e.*, to Na 5,893, agree with the recently measured changes according to Baxter, Burgess, Doudt, as the following table shows.

	B., B. & D. Observed.	Dufet Comp.	Osborn Comp.
20°–25°	.00051	.0004973	.0004975
20°–30°	.00109	.0010745	.0010748

The differences all lie within the estimated errors of observation.

To Professor Reed, under whose direction this work was done, the writer wishes to express his thanks.

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