

A PRELIMINARY EXAMINATION OF THE TEMPERATURE VARIATION OF REFRACTIVE INDEX OF WATER AND ITS FIRST DERIVATIVE

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In previous work, the activation energy E_η of viscous flow and the first derivative of the coefficient of dilatation, $\delta\alpha/\delta T$ have been found to exhibit sharp jumps at corresponding temperatures. In an effort to establish these phenomena on a firmer footing, the first derivative of the refractive index $\delta n/\delta T$ has been measured for pure water at 1°C . intervals from 15°C . upto 50°C .

The values obtained at 20°C . with both the red and blue cadmium lines agree with that quoted in the literature, but the complete graph of $\delta n/\delta T$ against temperature shows a series of well-defined cyclic variations with a mean period of about 4°C . and an amplitude of 20-50% of the mean value. This feature is confirmed by more accurate measurements made with the strong green line, and by comparison with the graph of α for water. A comparison of the temperatures at the maxima and minima is made with those for the jumps in E_η and $\delta\alpha/\delta T$, and it appears that there is general agreement within about 1°C . Further work on aqueous solutions and pure liquids is in progress.

1. Introduction

In the course of a series of experimental investigations of the intermolecular activation energy ϵ in various pure liquids^{1,2} as well as in solutions,³ it had been found that this energy exhibits a definite level structure with fairly sharp discontinuities or jumps between successive levels. The measurements were based on the first derivative of the viscosity, and the energy ϵ was obtained as :

$$\epsilon/k = E_\eta/R = -T^2 \Delta \ln \eta / \Delta T \quad (1)$$

where k is Boltzmann's constant and ΔT is the small measuring interval of 1° to 2°C . Some of the larger jumps were shown to be observable even in the older standard viscosity data available in International Critical and Landolt Bornstein Tables,⁴ thus confirming the essential repeatability of these discontinuities.

In an effort to establish this type of phenomena on a firmer footing and to throw further light on their physical basis, it was considered desirable to reinvestigate more accurately some other simple physical properties, like refractive index and dilatation, using a smaller temperature interval than what has been employed before, so as to determine the first derivatives of these properties at various temperatures. Some results calculated from standard data on dilatation of water have separately been reported,⁵ and good correspondence with the jumps from viscosity data was observed. The present communication gives the results obtained in a reinvestigation of the refractive index of water, using a standard research laboratory refractometer, and a thermal interval of 2 degrees C.

2. Experimental Technique

In the absence of any definite information about the magnitude of the effect being looked for, it

was thought desirable to use a fairly sensitive instrument, such as the Bellingham and Stanley (Pulfrich type) critical-angle refractometer, which is ordinarily guaranteed to give an accuracy of nearly 0.000,02 in the measurement of refractive index for a liquid. It also has the advantage of a very effective thermostatic chamber for the sample liquid under test, in which a thermometer graduated in 0.2 degree C. can be fitted, so that temperatures can be read to 0.02 $^\circ\text{C}$.

The fine setting of the cross-hairs on the particular spectral line used is effected by means of a tangent screw operated by a drum, one revolution of which corresponds to 15 minutes of arc, and this drum is subdivided in units of 10 seconds so that a reading can be recorded to ± 2 secs. of arc. The refractive index 'n' (relative to air) of the liquid in the cell is calculated as

$$n = N \sin(A - i) = \sin A \sqrt{N^2 - \sin^2 B} - \cos A \sin B \quad (2)$$

where A is the angle of the glass prism, N is its refractive index, i is the angle of incidence onto the second face of the prism, and B is the angle of emergence from the prism into the air (Fig. 1 inset). It is readily seen by differentiation that

$$- \frac{dn}{dB} = \cos B \left\{ \frac{\sin A \sin B}{\sqrt{N^2 - \sin^2 B}} + \cos A \right\}$$

$= 0.950 (0.5 + 0.154) = 0.619$
for $N = 1.74$, $A = 60^\circ$ and $B \approx 18^\circ$. It follows that
 $-10^4 \Delta n / \Delta T = 0.619 \times 10^4 \times \Delta B / \Delta T$
 $= +1.80 \times \Delta \theta' / \Delta T \quad (3)$

when $\Delta \theta'$ is the change in angle measured in minutes of arc on the drum, and for water,

$$\frac{10^4}{1-n} \frac{\Delta n}{\Delta T} = \frac{1.80}{0.33} \frac{\Delta \theta'}{\Delta T} = 5.5 \frac{\Delta \theta'}{\Delta T} \quad (4)$$

Since dn/dT is of the order of 10^{-4} for most liquids, it follows that for $\Delta T = 2^\circ\text{C}$., $\Delta \theta'$ will be of the order of 1 minute of arc, which should be measu-

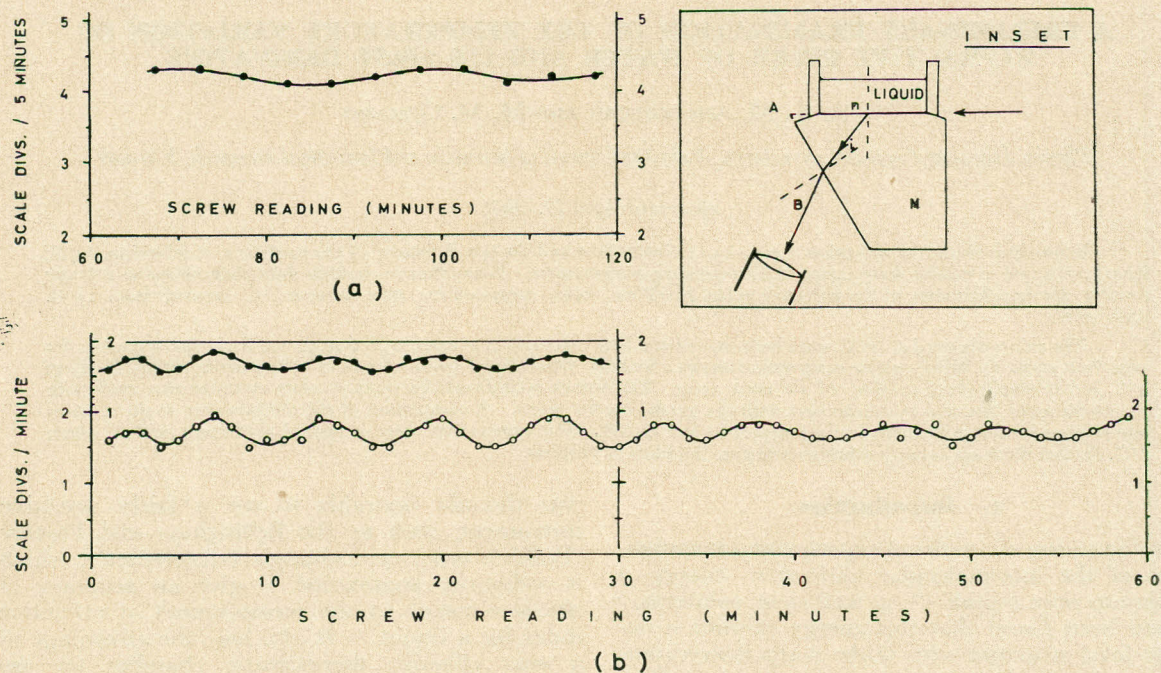


Fig. 1.—(a) Differential calibration curve showing number of scale divisions on lamp and scale corresponding to successive movements of 5 minutes of arc on the drum of the tangent screw. (b) Similar differential calibration curve (hollow circles) for intervals of 1 minute of arc. The solid circles show the means of points separated by a range of 30 minutes. (Inset: Sketch of the prism, liquid chamber and path of the light in the refractometer.

rable to ± 3 seconds of arc, yielding an accuracy of the order of 5% in $\Delta n/\Delta T$. For the same accuracy in ΔT , temperature control to $\pm 0.05^\circ\text{C}$. is ample, and this was easily obtained by circulating water from an ordinary controlled bath through the chamber inside and round the liquid cell.

Although the tangent screw and drum graduations were expected to be quite uniform on this particular instrument, nevertheless it was thought desirable to make a preliminary calibration of the drum by an optical method. A small plane mirror was mounted rigidly on the telescope arm of the refractometer with its plane parallel to the horizontal axis of the refractometer, and a lamp and vertical scale was set up to indicate the rotation of the telescope. Readings on the scale were first recorded corresponding to a series of drum settings covering four revolutions of the drum at intervals of 5 minutes (going from 1° to 2°) and the results are plotted in Fig. 1 (a) as a differential calibration curve showing the number of vertical scale divisions corresponding to this particular constant interval on the drum. It is seen that the curve exhibits a periodic variation of only $\pm 3\%$ (i. e. 9 secs. of arc) about the mean the period being very nearly 30 minutes of arc. A finer calibration at closer intervals of 1 minute of arc was next carried out (with a two-times sensitive

scale arrangement), and Fig. 1 (b) shows the corresponding differential curve (hollow circles) plotted from 0 through 30 minutes to 60 minutes, together with the mean of two sets of repeating measurements (solid circles) over successive range of 30 minutes of arc, i. e. two drum revolutions, which again appears to be the major repetition period. The measured scale readings corresponding to successive movements of one minute of arc on the drum are seen to show a further short cyclic variation with a mean period of about 6 minutes, and an amplitude of at most ± 0.12 scale division about the mean value of 1.68 divisions/minute. This corresponds to a *root-mean square* variation of $\pm 5\%$ in the value of the 1-minute divisions of the drum, i. e. to ± 3 seconds of arc, which would lead to a change of only 0.1×10^{-4} in the refractive index 'n'. This is only twice as great as the actual reading accuracy of the drum graduations, and should not therefore give rise to any significant spurious variations of $d\theta'/dT$ and therefore of dn/dT .

3. Preliminary Measurements of n at Various Temperatures

The first measurements of dn/dT were carried out by filling the thermostatted liquid cell with double-distilled conductivity water, and measur-

ing the absolute value of n for the cadmium red line ($\lambda = 6438.5 \text{ \AA}$) at a series of temperatures from 18°C. to 34°C. differing by 1°C. The mean of three readings was taken at each temperature, and the observed data are given together with the r.m.s. deviations in Table I, the last column of which shows the values of $104 \times \frac{\Delta n}{1-n} / \Delta T$ calculated with $\Delta T = 2^\circ\text{C.}$

These values are plotted as large hollow circles against the mean temperature in the lower half of Figure 2 (a), with the short vertical lines representing the standard deviation estimated in Table I from the variation between repeated readings. The best graph through the plotted points shows two definite maxima at 22°C. and 32°C. with a poorly defined one in between. The differences between the peaks and troughs for the well-defined maxima are about three times the estimated standard deviation of the experimental points.

sirable to dispense with the repeated measurement of the position of the normal to the emergent face of the prism and the angle B, but to measure instead *only the small changes* in the angle B by permanently *locking the drum to the telescope* and scale, and taking the readings θ from the drum only. This has the advantage of eliminating the error (up to $10''$ of arc) involved in setting the glass scale graduations against the fiducial marks each time, and therefore the accuracy of the changes $\Delta B = + \Delta \theta$ can be improved considerably. A further device was to take observations at the even degrees of temperature during heating and at the odd degrees during cooling, thus effectively doubling the density of observations. The repeated drum readings taken at each temperature as well as their means are given in Table 2, together with the r.m.s. deviations, and column 4 shows the values of the change $\Delta \theta'$ in minutes of arc for $\Delta T = 2^\circ\text{C.}$ calculated from these. The standard deviation for $\Delta \theta'$ is seen to be much less than before and indicates an accuracy of the order of 3% i. e. ± 2 sec. of arc on the average.

TABLE I.—PRELIMINARY MEASUREMENTS OF n AT VARIOUS TEMPERATURES FOR THE RED CADMIUM LINE. (THE STANDARD DEVIATION FOR n IS GIVEN IN THE 5TH PLACE).

Temperature ($^\circ\text{C.}$)	Angle (B- 17°)	Refractive index= n	$-\Delta n \times 10^4$ for 2°C.	$104 \cdot \frac{\Delta n}{1-n} / \Delta T$
18.0	$55'-58'' \pm 2''$	$1.331,76 \pm 5$	—	—
19.0	—	—	1.5 ± 0.7	2.2 ± 1.0
20.0	$56'-53'' \pm 20''$	$1.331,61 \pm 5$	—	—
21.0	$57'-15'' \pm 5''$	$1.331,54 \pm 5$	3.3 ± 0.7	4.9 ± 1.0
22.0	$58'-24'' \pm 30''$	$1.331,28 \pm 5$	3.5 ± 0.7	5.2 ± 1.0
23.0	$59'-00'' \pm 0''$	$1.331,19 \pm 5$	2.3 ± 0.7	3.6 ± 1.0
23.9	$59'-45'' \pm 20''$	$1.331,05 \pm 5$	1.8 ± 0.7	2.7 ± 1.0
25.0	$1^\circ-0'-00'' \pm 15''$	$1.331,01 \pm 5$	1.1 ± 0.7	1.5 ± 1.0
26.0	$1^\circ-0'-25'' \pm 25''$	$1.330,94 \pm 5$	1.5 ± 0.7	2.2 ± 1.0
27.0	$1^\circ-0'-55'' \pm 10''$	$1.330,86 \pm 5$	2.2 ± 0.7	3.3 ± 1.0
28.0	$1^\circ-1'-48'' \pm 3''$	$1.330,72 \pm 5$	2.3 ± 0.7	3.4 ± 1.0
29.0	$1^\circ-2'-10'' \pm 15''$	$1.330,63 \pm 5$	1.6 ± 0.7	2.4 ± 1.0
30.0	$1^\circ-2'-28'' \pm 18''$	$1.330,56 \pm 5$	1.0 ± 0.7	1.5 ± 1.0
31.0	$1^\circ-2'-42'' \pm 12''$	$1.330,53 \pm 5$	2.6 ± 0.7	3.9 ± 1.0
32.0	$1^\circ-4'-5'' \pm 5''$	$1.330,30 \pm 5$	2.8 ± 0.7	4.2 ± 1.0
33.0	$1^\circ-4'-30'' \pm 5''$	$1.330,25 \pm 5$	1.2 ± 0.7	1.8 ± 1.0
34.0	$1^\circ-5'-18'' \pm 18''$	$1.330,18 \pm 5$	—	—
R.M.S. deviation = $\pm 15''$		R.M.S. deviation = $\pm 5 \times 10^{-5}$		

4. Differential Measurements for the Cadmium Red and Blue Lines

In an effort to improve the accuracy of the experimental values of $\Delta n / \Delta T$, it was thought de-

A plot of the results is shown in the upper half of Figure 2 (a), where the solid circles refer to the heating sequence and the hollow circles to the cooling sequence. Since the calibration of Figure 1 indicated a r.m.s. fluctuation of 3 seconds of

arc in the value of 1 minute on the drum, the circles in Fig. 2 are drawn with radius equal to this. The best graph drawn through these solid and hollow circles shows a succession of maxima and minima with a peak-to-peak amplitude of 20 to 40 seconds of arc, i. e. 6 to 12 times the r. m. s. errors possible. We find clear maxima at 23°C. and 32°C. in agreement with the indications of the preliminary experiment. The small maximum 'A' at 41°C. marked by a small arrow could be a fortuitous one, because the broken line also gives an acceptable curve through the points in this region.

These measurements were next carried out with the blue line ($\lambda = 4800\text{\AA}$), the visibility of

which is rather poor and therefore the same accuracy could not be obtained in setting the refractometer telescope. The drum locking with respect to the glass scale was changed by 1 minute so as to remove the consistent errors due to the screw, and the results, as plotted in the lowest curve of Figure 2 (b) against "Expt. 1", show that the graph is very similar to that for the red line, although the scatter of the point is much greater than before. A repetition of the measurements with the drum tangent screw locked in a different position on the scale gave the graph marked "Expt. 11". The topmost curve shows a plot of the means of Expt. 1 and 11, the undulations in which indeed follow the graph for the red line closely although with a somewhat smaller amplitude.

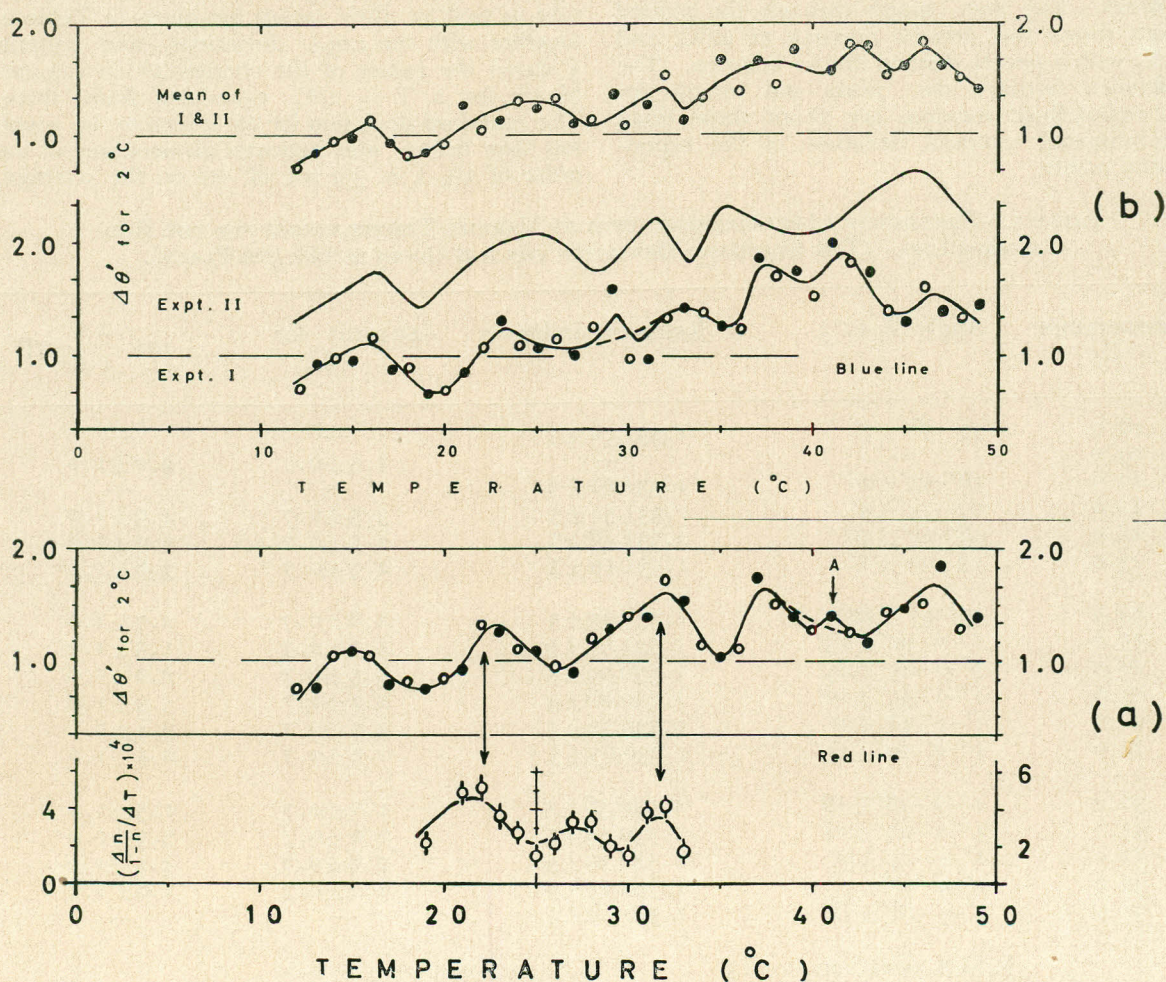


Fig. 2.—(a) The lowest curve (large hollow circles) shows a plot of the preliminary measurements of $\frac{\Delta n}{1-n} / \Delta T$ in Table 1 for the cadmium red line, the short vertical lines representing the estimated standard deviation. The upper curve is a plot of the values of $\Delta\theta'$ (in minutes) for every 2°C., obtained from differential measurements (cf. Table 2), the solid circles being for the heating sequence and the hollow circles for cooling. The small peak at 'A' could be a spurious one. (b) Similar differential measurements of $\Delta\theta'$ for every 2°C., with the cadmium blue line, the topmost curve being a plot of means of corresponding points for Expt. I and II. This mean plot is in satisfactory agreement with the previous graph for the red line.

TABLE 2.—TEMPERATURE READINGS OF DRUM θ , CALCULATED VALUES OF $\Delta\theta'$ (IN MINUTES) FOR 2°C. FOR WATER IN THE RANGE 10°C.—50°C. USING THE CADMIUM RED LINE.

Heating sequence				Cooling sequence			
Temp. (°C.)	Drum readings	Mean — θ	+ $\Delta\theta'$ for 2°C. (in minutes)	Temp. (°C.)	Drum readings	Mean — θ	+ $\Delta\theta'$ for 2°C. (in minutes)
1	2	3	4	5	6	7	8
				11.00	2° 1' 50" 2° 1' 48"	2° 1' 49" ± 1"	
12.00	2° 1' 15" 2° 1' 15"	2° 1' 15" ± 0"	0'—44"=0'.73	13.00	2° 1' 5" 2° 1' 2"	2° 1' 4" ± 1"	0'—45"=0.75
14.00	2° 0' 32" 2° 0' 30"	2° 0' 31" ± 1"	1'—05"=1'.08	15.00	2° 0' 0" 2° 0' 4"	2° 0' 2" ± 2"	1'—02"=1'.03
16.00	1° 59' 28" 1° 59' 24"	1° 59' 26" ± 2"	0'—47"=0'.78	17.00	1° 59' 0" 1° 58' 58"	1° 58' 59" ± 1"	1'—03"=1.05
18.00	1° 58' 40" 1° 58' 38"	1° 58' 39" ± 1"	0'—45"=0'.75	19.00	1° 58' 10" 1° 58' 10"	1° 58' 10" ± 0"	0'—49"=0'.82
20.00	1° 57' 52" 1° 57' 55"	1° 57' 54" ± 1"	0'—55"=0'.92	21.00	1° 57' 18" 1° 57' 20"	1° 57' 19" ± 1"	0'—51"=0'.85
22.00	1° 57' 0" 1° 56' 58"	1° 56' 59" ± 1"	1'—15"=1'.25	23.00	1° 56' 0" 1° 56' 0"	1° 56' 0" ± 0"	1'—19"=1'.32
24.00	1° 55' 45" 1° 55' 42"	1° 55' 44" ± 1"	1'—02"=1'.03	25.00	1° 54' 52" 1° 54' 55"	1° 54' 54" ± 1"	1'—06"=1'.10
26.00	1° 54' 42" 1° 54' 42"	1° 54' 42" ± 0"	0'—54"=0'.90	27.00	1° 53' 58" 1° 53' 56"	1° 53' 57" ± 1"	0'—57"=0'.95
28.00	1° 53' 48" 1° 53' 48"	1° 53' 48" ± 0"	1°—17"=1'.28	29.00	1° 52' 45" 1° 52' 45"	1° 52' 45" ± 0"	1'—12"=1'.20
30.00	1° 52' 30" 1° 52' 32"	1° 52' 31" ± 1"	1'—23"=1'.38	31.00	1° 51' 20" 1° 51' 22"	1° 51' 21" ± 1"	1'—24"=1'.40
32.00	1° 51' 7" 1° 51' 10"	1° 51' 8" ± 2"	1'—32"=1'.53	33.00	1° 49' 40" 1° 49' 34"	1° 49' 37" ± 3"	1'—44"=1'.73
34.00	1° 49' 35" 1° 49' 38"	1° 49' 36" ± 1"	1'—02"=1'.03	35.00	1° 48' 25" 1° 48' 30"	1° 48' 28" ± 2"	1'—09"=1'.15
36.00	1° 48' 35" 1° 48' 32"	1° 48' 34" ± 1"	1'—46"=1'.76	37.00	1° 47' 20" 1° 47' 25"	1° 47' 22" ± 2"	1'—06"=1'.10
38.00	1° 46' 48" 1° 46' 48"	1° 46' 48" ± 0"	1'—24"=1'.40	39.00	1° 45' 52" 1° 45' 50"	1° 45' 51" ± 1"	1'—31"=1'.52
40.00	1° 45' 25" 1° 45' 22"	1° 45' 24" ± 1"	1'—24"=1'.40	41.00	1° 44' 34" 1° 44' 34"	1° 44' 34" ± 0"	1'—17"=1'.28
42.00	1° 44' 0" 1° 44' 0"	1° 44' 0" ± 0"	1'—09"=1'.15	43.00	1° 43' 18" 1° 43' 20"	1° 43' 19" ± 1"	1'—15"=1'.25
44.00	1° 42' 52" 1° 42' 50"	1° 42' 51" ± 1"					1'—27"=1'.45

(Contd. on page 248)

(TABLE 2 *Contd.*)

1	2	3	4	5	6	7	8
			1'-28"=1'.46	45.00	1° 41' 55" 1° 41' 50"	1° 41' 52" ±2"	
46.00	1° 41' 25" 1° 41' 21"	1° 41' 23" ±2"					1'-31"=1'.52
			1'-51"=1'.85	47.00	1° 40' 20" 1° 40' 22"	1° 40' 21" ±1"	
48.00	1° 39' 35" 1° 39' 30"	1° 39' 32" ±2"					1'-17"=1'.28
			1'-23"=1'.38	49.00	1° 39' 5" 1° 39' 3"	1° 39' 4" ±1"	
50.00	1° 38' 10" 1° 38' 8"	1° 38' 9" ±1"					—
r.m.s. deviation=±1.2"		r.m.s. deviation=±1.7"=±0.03'		r.m.s. deviation=1".2		r.m.s. deviation=±1.7"=±0.03'	

For comparison with measurements of other workers on water, it may be noted that $dn/dT \times 104$ at 20°C. is given ⁶ as -0.8, which is in good agreement with our values at the second minimum in Fig. 2 (a) and Fig. 2 (b) for both the red and the blue lines. Of course it must be noted that our measurements require correction for the effect of temperature on the refractometer prism. This may be estimated at $\frac{1}{2} dn/dT$, i. e. 0.09×10^{-4} , and is negligible.

5. Differential Measurements for the Cadmium Green Line

The above experiment was finally repeated using the cadmium green line ($\lambda = 5086\text{Å}$), which has a relatively high intensity, and therefore it was expected that more precise settings

of the refractometer telescope cross-hair could be made with it. The mean values of the drum settings for the various temperatures are shown in Table 3 for the heating and cooling sequences together with the r.m.s. deviations, which are seen to be a little greater than 1 second of arc. The values of $\Delta\theta'$ for $\Delta T = 2^\circ\text{C}$. are also shown and in the fourth column are the calculated values

$$-104 \Delta \left\{ \ln \frac{n^2 - 1}{n^2 + 2} \right\} / \Delta T$$

$$= 104 \times 0.905 \frac{\Delta n}{1 - n} / \Delta T = 5.0 \frac{\Delta\theta'}{\Delta T} \quad (5)$$

on the basis of equation (3). These values are plotted in the upper half of Fig. 3, the solid circles being for the heating and the hollow circles for the cooling sequence.

TABLE 3.—TEMPERATURE, MEAN READING OF ANGLE θ AND CALCULATED VALUES OF $\Delta\theta'$ FOR 2°C. AND $5\Delta\theta'/\Delta T$ FOR WATER, USING THE CADMIUM GREEN LINE IN THE RANGE OF 21°—50°C.

Heating sequence				Cooling sequence			
Temp. (°C.)	Mean reading of angle 'θ'	$\Delta\theta'$ for 2°C.	$5\Delta\theta'/\Delta T$	Temp. (°C.)	Mean reading of angle 'θ'	$\Delta\theta'$ for 2°C.	$5\Delta\theta'/\Delta T$
		—	—	21.00	1°-2'-28"±2"		
22.00	1°-2'-28"±0"			23.00	1°-1'-34"±1"	0.90	2.25
24.00	1°-1'-14"±1"	1.23	3.08	25.00	1°-0'-14"±2"	1.33	3.32
26.00	0°-59'-54"±1"	1.33	3.33	27.00	0°-58'-45"±3"	1.48	3.70
28.00	0°-58'-46"±1"	1.13	2.83	29.00	0°-57'-41"±1"	1.06	2.65
30.00	0°-57'-35"±0"	1.18	2.96	31.00	0°-56'-24"±2"	1.28	3.20
32.00	0°-56'-12"±0"	1.38	3.46	33.00	0°-55'-0"±0"	1.40	3.50
34.00	0°-55'-1"±1"	1.18	2.96	35.00	0°-53'-51"±1"	1.15	2.88
36.00	0°-53'-46"±1"	1.25	3.12	37.00	0°-52'-15"±0"	1.60	3.58
38.00	0°-52'-1"±1"	1.75	4.38	39.00	0°-50'-29"±1"	1.76	4.40
40.00	0°-50'-21"±1"	1.66	4.16	41.00	0°-49'-1"±1"	1.46	3.65
42.00	0°-48'-40"±0"	1.68	4.20	43.00	0°-47'-24"±2"	1.62	4.05
44.00	0°-47'-13"±1"	1.48	3.62	45.00	0°-45'-51"±1"	1.55	3.88
46.00	0°-45'-36"±1"	1.62	4.05	47.00	0°-44'-1"±1"	1.83	4.58
48.00	0°-44'-4"±1"	1.53	3.82	49.00	0°-42'-10"±0"	1.85	4.62
50.00	0°-42'-46"±4"	1.40	3.50			—	—

The smooth graph drawn through the plotted points is seen to be a very regular one, with an r. m. s. scatter in the experimental values of about 0.1, i.e. 3%. For comparison, the lower half of the Fig. 3 shows a plot of the corresponding mean values obtained for the red and blue cadmium lines, and the two graphs show excellent agreement from 25° to 50°C. and even the doubtful maximum at 41°C. is brought out more clearly by the new data. Below 25°C. there appears to be a discrepancy of about 1.5° to 2°C. in the positions of the maxima and minima, the reason for which is not clear, although it may simply be a result of cumulative experimental errors.

On theoretical grounds the molar refraction, $[(n^2-1)/(n^2+2)] \times M/d$, is expected to be constant,

and therefore

$$(n^2-1)/(n^2+2) \propto d/M \quad \text{whence}$$

$$-\Delta \ln \left(\frac{n^2-1}{n^2+2} \right) / \Delta T = - \left(\Delta d / \Delta T \right) / d = \alpha, \quad (6)$$

where α is the coefficient of dilatation of the liquid. Accordingly, the thin line curve in the top half of Fig. 3 shows the values of $\alpha \times 10^4$ as calculated from the standard data for the density of pure water.⁷ It is at once seen that the graph for α does approximately pass through the mean of the undulatory graph based on the refractive index, thus indicating the approximate validity of equation (6) on the average. However, the undulations are as much as 30-50% of the mean value, and therefore indicate the existence of

TABLE 4.—COMPARISON OF THE MEAN TEMPERATURES FOR JUMPS IN $E\eta$ AND $\delta\alpha/\delta T$ WITH MAXIMA AND MINIMA IN THE $(\Delta\theta'/\Delta T)$ GRAPHS (CF. FIG. 3.)

No. of discontinuity	3	4	5	6	7	8	9	10	11
Weighted mean temp. from $E\eta$ and $\delta\alpha/\delta T$	11.7	15.7	17.6	21.9	27.8	33.8	36.9	41.8	49.0
	± 0.1	± 0.1	∓ 0.1	∓ 0.3	± 0.5	± 0.1	± 0.0		
Weighted mean temp. from $\Delta\theta'/\Delta T$ graphs of Fig. 3.		Maxima	16.8	(24.4)	(31.5)		37.1	41.5	47.3
			± 0.6	± 0.6	∓ 0.2		± 0.3	∓ 0.3	± 0.4
	Minima ~ 14			20.3	27.7	34.2	(40.0)	(43.4)	
				± 0.7	± 0.3	∓ 0.4	± 0.0	± 0.4	
Difference:			-0.8	-1.6	-0.1	+0.4	+0.2	-0.3	-1.7

Note:—Overall mean difference = $-0.6 \pm 0.6^\circ\text{C}$.

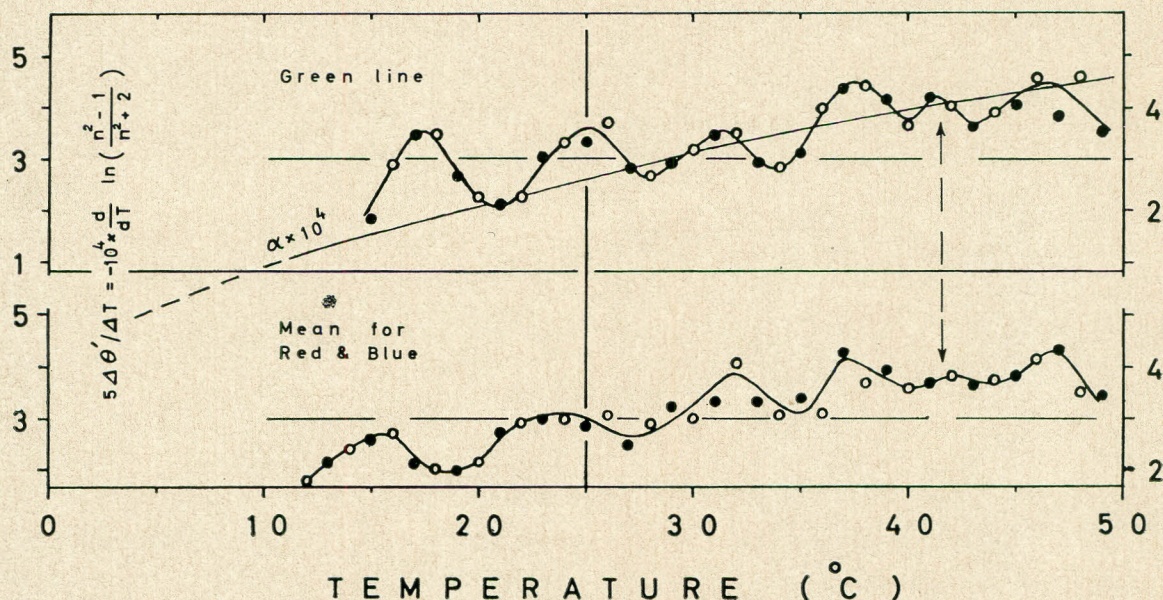


Fig. 3.—(Top): Plot of $5\Delta\theta'/\Delta T = 10^4 \times \frac{d}{dT} \ln \left[\frac{n^2-1}{n^2+2} \right]$ for water measured with the cadmium green line; solid circles for rising temperature and hollow circles with falling temperature. The thin continuous line shows $10^4 \times \alpha$ the coefficient of dilatation. (Bottom): The corresponding plot of $5\Delta\theta'/\Delta T$ from the mean of data for the red and blue lines.

another physical effect, especially below 27°C., where the values from the refractive index are all equal to or greater than α . In this connection, it is significant that equation (6) is very closely satisfied in the neighbourhood of 20°C., where dn/dT had previously been determined, and this perhaps accounts for the lack of further study of dn/dT .

6. Conclusion

In view of these findings, it is instructive to compare these measurements of dn/dT with those of other properties of water, namely viscosity and dilatation, jumps in the derivatives of which have recently been found to show a one-to-one correspondence.⁵ Table 4 shows the mean temperature for the jumps based on viscosity and dilatation compared with the weighted mean (2:1 for the upper and lower curves in Fig. 3) temperatures at the maxima and minima in the values of $\Delta \ln [(n^2-1)/(n^2+2)]/\Delta T$, and it is at once seen that of the eight jumps in this temperature range, four agree in position with the maxima, while the other four fit the minima. The agreement is in all cases satisfactory, the average discrepancy being $-0.6^\circ\text{C.} \pm 0.6^\circ\text{C.}$ as seen in Table 4. This agreement suggests a

further study of $\delta^2 n/\delta T^2$ as fully corresponding to E_η and $\delta\alpha/\delta T$ and opens up the field for more detailed correlation of the above three properties; further studies are planned on a series of pure liquids and solutions.

References

1. M. M. Qurashi and A. K. M. Ahsanullah, *British J. Appl. Phys.*, **12**, 65 (1961).
2. A. K. M. Ahsanullah and M. M. Qurashi, *ibid.*, **13**, 334 (1962).
3. A. K. M. Ahsanullah, S. R. Ali and M. M. Qurashi, *Pakistan J. Sci. Ind. Research*, **5**, 133 (1962).
4. (a) *International Critical Tables* (McGraw Hill Book Co., Inc., New York & London, 1929), Vol. V, p. 22.
(b) Landolt Bornstein, *Physikalisch-Chemische Tabellen* (Julius Springer, Berlin, 1927), I. Erg.-Bd., p. 84.
5. M.M. Qurashi, *Pakistan J. Sci. Ind. Research*, **6**, 213 (1963).
6. G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants* (Longmans, Green & Co., London, 1959), 12th edition, p. 82.
7. *Ibid.*, p. 31.