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COMPARATIVE MEASUREMENTS OF THE TEMPERATURE DERIVATIVES OF VISCOSITY, DENSITY AND REFRACTIVE INDEX OF PURE LIQUIDS AND SOLUTIONS

Part I.—Some Dilatometric Measurements on Ethylene Glycol at Intervals of 1°C. to 2°C. in the Range of 20°C. to 80°C.

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Recent work on analysis of the temperature variations of coefficient of dilatation, α, and new measurements on refractive index of water[7] have shown good correlation with previously reported jumps in activation energy, E_η. In order to elucidate further the physical basis for such behaviour, similar measurements have been made on coefficient of dilatation($\alpha = \frac{1}{V_0}\frac{\Delta V}{\Delta T}$) of ethylene glycol in the range of 20°-80°C., with temperature intervals ΔT=1°-2° C. A large dilatometer with a calibrated capillary is used, in which a change of 1°C. produces a change of about 40 mm. in the level. With temperature control within 0.002 to 0.005°C., an accuracy of 1 in 400 in α is attainable.

The temperature variation of α shows a nicely undulating regular graph from 30°C. to 75°C., and the mean graph of two sets of measurements exhibits a peak-to-peak amplitude of about 1.2×10^{-5} with a period of 4° to 6°C. The majority of the minima in α correspond closely (within $\pm$1°C.) with sharp jumps in E_η/R for ethylene glycol. Some extra minima are also found at 42°, 56° and 67°C., each of which is in the middle of a long "flat" i.e. constant region of E_η/R. Further work on other liquids and solutions is planned.

1. Introduction

In a series of earlier papers [1-5] from this Laboratory, dealing with accurate measurements of the temperature variation of activation energy of viscous flow of pure liquids and solutions, the existence of (i) discrete jumps in this energy E_η for dihydroxylic liquids, and (ii) oscillatory phenomena in E_η for monohydroxylic liquids and simple hydrocarbons have been reported. In two more recent publications, an analysis of the temperature derivative of (i) coefficient of dilatation[6] and (ii) refractive index[7] has been made for water and found to show good correlation with the previously reported jumps in E_η for water.[2] However, due to the marginal accuracy of the coefficient of dilatation as deduced from data on density above 20°C., the interpretation was not as definite as could be desired.

The jumps in E_η had been observed relatively more clearly in the case of ethylene glycol,[3] and a large recognizable systematic fine-structure had previously been reported in the inter-molecular activation energy of flow,[3] and had moreover been separable into two sequences, slightly out of phase with each other. At the same time the coefficient of dilatation of glycol is about 60×10^{-5}, which is twice the mean figure for water in the range of 10°C. to 70°C. It could therefore be anticipated that possible variations might be more easily and definitely observed in this liquid. Accordingly, the present communication gives an account of some accurate dilatometric measurements carried out on several samples of ethylene glycol. Measurements of α have so far been made at intervals of 1°C. to 2°C. in the range of 20°C. to 80°C.

2. Experimental Details

Because ethylene glycol takes up moisture when exposed to the atmosphere, it was decided to use a dilatometer so that the experimental sample could be kept fully enclosed and out of contact with the atmospheric humidity. Accordingly, a large dilatometer was blown from hard glass with a bulb of about 70 ml. capacity and a long capillary tube of 1 mm. bore, 3 mm. wall thickness and about 100 cm. length. This was supported in a thermostatically controlled bath, as shown in

Fig. 1, with about 75 cm. of the capillary tube projecting outside the bath.

With this dilatometer, a 1 mm. change in level in the capillary corresponds to $\pm 0.000,01$ i.e. 1×10^{-5} in density, and a change of 1°C. in the

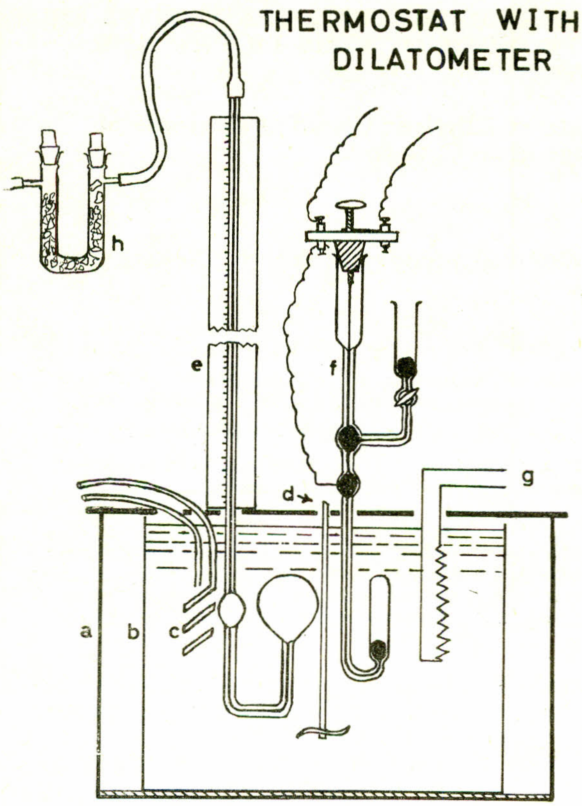

Fig. 1.—Sketch of thermostat with cooling and coil thermal control, showing dilatometer (with standard scale against capillary) and drying tube.

temperature produces a change of about 40 mm. in the level of the ethylene glycol, which can be readily measured to 0.1 mm. giving an attainable accuracy of 1 in 400 in the value of α. Of course, a corresponding degree of refinement in the control and measurement of the temperature is necessary. Thus, for working with temperature interval $\Delta T = 2$°C., the temperature measurements must be accurate to 0.01°C. at least. The values of α can be calculated from the measured rise Δl of the liquid in the capillary in the temperature interval T, T+ ΔT by means of the equation

$$\alpha = \frac{1}{V} \frac{\Delta V}{\Delta T} = \frac{\pi r^2}{V} \frac{\Delta l}{\Delta T} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where V is the volume of the dilatometer and r is the mean radius of its capillary. The value of V was determined by weighing the dilatometer when empty and filled with liquid, while values of r^2 were obtained from the weight of a column of mercury, the length of which was measured at different parts of the length of the capillary, which had index marks engraved on it, so as to obtain the calibration curve shown in Fig. 2. If m is the mass of the mercury column, ρ_{Hg} its density, and l_{Hg} its length corrected for the spherical ends, then

$$\pi r^2 \times \rho_{Hg} \times l_{Hg} = m$$

$$\text{Whence } \pi r^2 = \frac{m}{\rho_{Hg} \times l_{Hg}} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

substitution of which in equation (1) gives the formula

$$\alpha = \frac{m}{\rho_{Hg} \times V \times l_{Hg}} \times \frac{\Delta l}{\Delta T} \quad \ldots\ldots\ldots\ldots (3)$$

After calibration, the dilatometer was filled by connecting it to a bottle filled with pure dry ethylene glycol, and alternately evacuating air from the whole system and letting in dry air. The last 5 ml. or so of the dilatometer were filled by alternate heating and cooling 3 or 4 times. The filled dilatometer was placed vertically in position in the thermostat and the open end of the capillary was connected to two calcium chloride tubes in series. A standard (steel) mm. scale was fixed in position alongside the dilatometer capillary.

3. Preliminary Trial of Apparatus

The whole set up was tried out in the range of 80°C. to 125°C., by taking readings at every 1°C. to 2°C., care being taken to wait for half an hour at each temperature to allow the liquid in the dilatometer to attain thermal equilibrium. It was found that there were large fluctuations of the order of 0.5 to 1 mm. in the level of the meniscus, and this was rectified by improving the thermostatic control. Also, it was decided to repeat each set of readings over a 8° to 12°C. range with both heating and cooling sequences, so that errors due to departure from equilibrium are further compensated out.

The first set of measurements taken from 85°C. to 120°C. are shown in Fig. 3, right hand bottom corner, where the lower curve is the raw data for dl/dT and the upper curve is plotted after

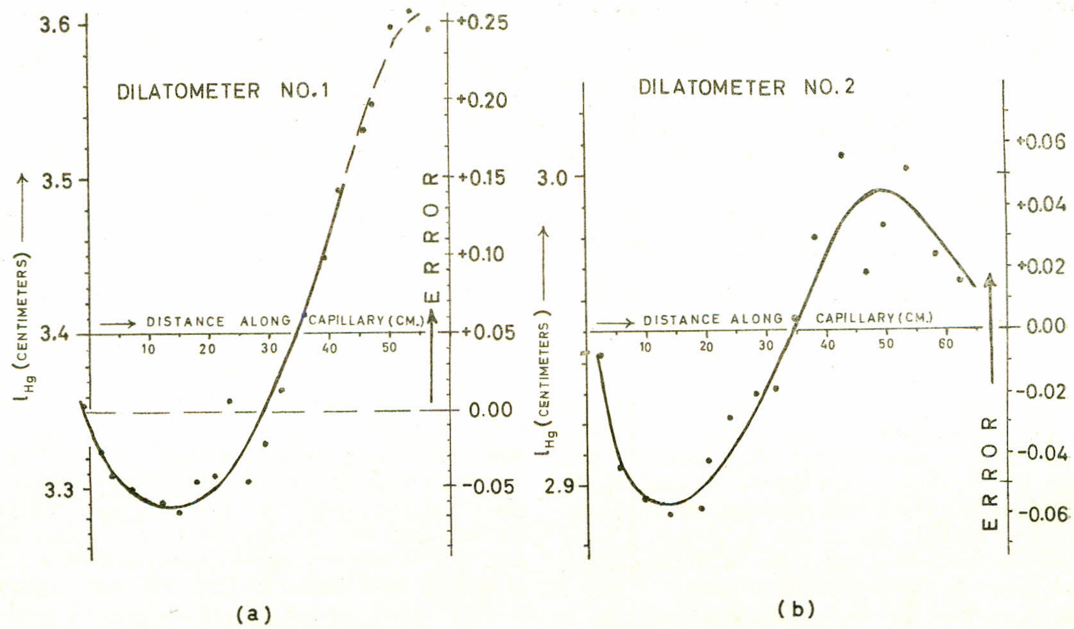

Fig. 2.—Calibration curves for dilatometer No. 1 and 2; the curve for No. 1 was utilized below 40 cm. before it goes up steeply. An accuracy of 1 in 500 is apparent.

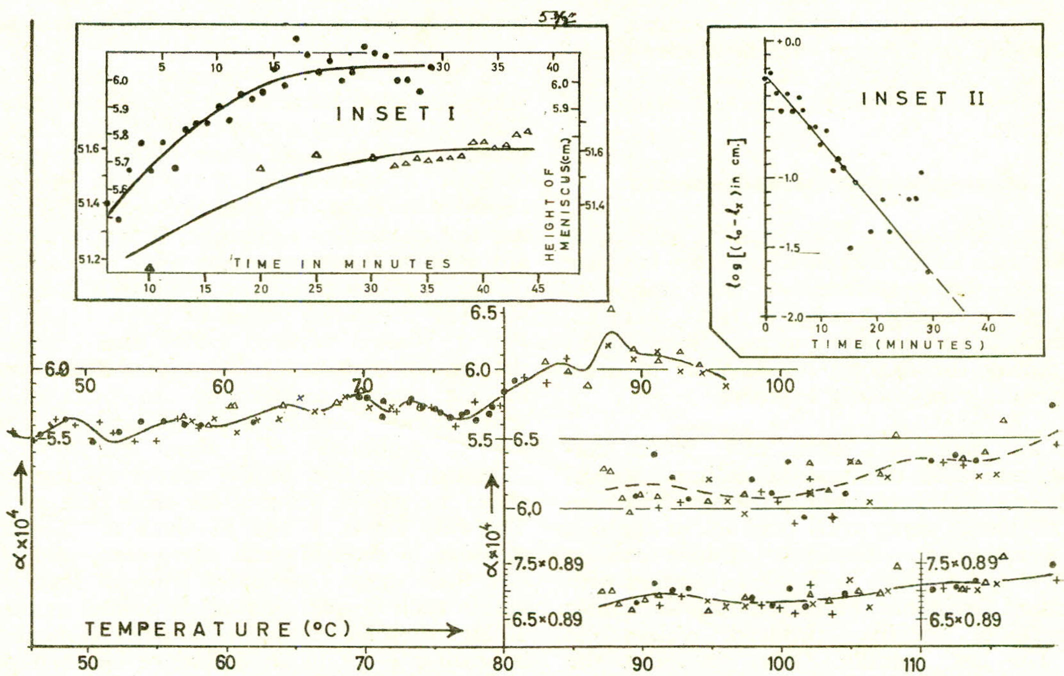

Fig. 3.—Preliminary measurements showing the measured coefficient of dilatation, α, of ethylene glycol, plotted as $0.89 \times \dfrac{\Delta l}{\Delta T}$ in the right-hand side lower graph, which shows uncorrected trial measurements. The right-hand side upper graph shows the corrected values.

The middle of the figure shows more accurate measurements (corrected); solid circles and triangles are for heating sequences, and the crosses for cooling sequences. Definite undulations with a period of 5° or so are to be found.

Inset I: height of meniscus plotted against time, showing the rate of attainment of thermal equilibrium.

Inset II: logarithmic plot of the upper graph in Inset I, where l_0 is height of meniscus at equilibrium and l_x that at a given instant. This graph shows that the lack of equilibrium is much less than 0.1 mm. after one hour.

applying the capillary calibration corrections, and with an enlarged vertical scale, which represents $\frac{dl}{dT} \times 0.89 = \alpha \times 10^4$. The solid circles and triangles correspond to measurement with the heating sequence while the crosses correspond to the cooling sequence. It is seen that even in this preliminary experiment, a reproducibility of nearly $\pm 0.15 \times 10^{-4}$ is attainable on the average in the values of α. Moreover, the mean curve drawn through all the experimental points does show evidence of a periodic variation of α with temperature.

Therefore efforts were made to examine and improve the experimental technique. For one thing, it was then noticed that the level continued to creep for as long as one hour, because of the slow attainment of thermal equilibrium as shown in the insets to Fig. 3. It can be deduced from these graphs that, after the lapse of an hour, the residual error in the level is less than 0.1 mm., and therefore this waiting period was adopted in all later experiments. In an effort to reduce the possibility of systematic residual error remaining after application of the calibration correction, successive groups of readings were arranged with a 5°C. to 6°C. overlap so that measurements of $\Delta l/\Delta T$ at corresponding temperatures were obtained from two entirely different sections of the capillary.

4. More Accurate Measurements

The new dilatometer was cleaned, calibrated and filled with a fresh sample of pure dry ethylene glycol, and the measurements were taken in groups, each covering a range of 12°C. to 14°C., after which it was necessary to expel some of the glycol during the heating sequence or to draw in some during the cooling sequence.

With the thermostat set at any given temperature, and after the lapse of an hour, several readings (5 to 10) were taken of the meniscus level in the capillary, along with readings of the 0.2 degree thermometer. The means of these readings for one group are given in Table 1, together with the standard deviations (estimated from the scatter of the readings) and the deduced values of $\Delta l/\Delta T$. The last column (No. 7) shows the values of $1.50 \times \Delta l/\Delta T$ which equal $\alpha \times 10^4$ in case of this dilatometer.

The results from 42°C. to 96°C. are plotted in the middle of Fig. 3, and the improved consistency of the measurements is apparent. The standard deviation about the mean graph drawn through all the points is of the order of 0.05×10^{-4} in α. At the same time, the graph now shows clear evidence of a periodic, roughly sinusoidal variation in α with a peak-to-peak amplitude of about 0.2×10^{-4}, and a period of the order of 6°C.

In order to further increase the accuracy, it was thought to use a Beckmann differential thermometer having a six-degree scale, graduated in hundredths of a degree, so that readings of ΔT can be taken to ± 0.002°C. with the help of a magnifying thermometer reader. The clean and dry dilatometer was refilled with a fresh, dry and pure sample of ethylene glycol in the usual way, and placed in the thermostatically controlled bath. Temperature control to ± 0.002°C. to ± 0.005°C. was maintained throughout the experiment. After attaining good thermal equilibrium by waiting for an hour or so, groups of readings were taken in ranges of 12°C. to 16°C. with repetitions for heating and cooling temperature sequences. For each subsequent set of measurements, a volume of glycol equivalent to the expansion for 12°C. to 16°C. was expelled during the heating sequences and drawn in during the cooling sequences so that only a slight overlap occurs between successive sets. These results are given in Table 2 and plotted in Fig. 4 (lower curve, labelled Expt. I.)

A second series of measurements was then taken, labelled Expt. II in Fig. 4 and given in Table 3, such that a particular group of readings taken in the lower half of the dilatometer capillary in Expt. I, correspond to the upper half of the capillary in Expt. II, and vice versa. By applying this particular technique, it was hoped that any residual error remaining after the calibration of the capillary would be completely taken care of. The measured values of Expt. I and II in Fig. 4, plotted as solid circles and triangle for the heating temperature sequences, and as crosses for the cooling temperature sequences, show a series of clear maxima and minima with a peak-to-peak amplitude of about 1.2×10^{-5}, the standard deviation of the scatter of the points about the graphs being of the order of 0.2×10^{-5}. The two Expts. I and II show a satisfactory measure of peak-by-peak agreement, and therefore their mean (calculated from all four points within each degree interval) is plotted at the top of Fig. 4 (solid circles) with short vertical lines indicating $\frac{1}{2}$ the mean difference between points of Expt. I and II. This mean graph is a considerable improvement on the individual graphs, and enables us to draw a nicely undulating regular graph from 30°C. to 75°C., in which the individual points show a r.m.s. scatter of a little over 0.1×10^{-5} about the graph, while the amplitude of the variation in α is the same as before, i.e. 1.2×10^{-5}, and the period is 4° to 6°C.

TABLE I.—PILOT EXPERIMENT WITH DILATOMETER NO. 2.

Heating sequence							Cooling sequence						
Temperature °C.	Height of the meniscus level cm.	Δl uncorr. cm.	Δl corr. cm.	Mean Temp. °C.	$\frac{\Delta l}{\Delta T}$	$1.50\frac{\Delta l}{\Delta T} \approx 10^4\times\alpha$	Temperature °C.	Height of the meniscus level cm.	Δl uncorr. cm.	Δl corr. cm.	Mean Temp. °C.	$\frac{\Delta l}{\Delta T}$	$1.50\frac{\Delta l}{\Delta T} \approx 10^4\times\alpha$
1	2	3	4	5	6	7	1	2	3	4	5	6	7
43.91±0.03	8.73±0.02						43.96±0.02	8.87±0.01					
		6.77±0.03	6.90	44.84	3.69	5.54			5.18±0.02	5.28	44.68	3.70	5.55
45.78±0.03	15.50±0.02						45.39±0.04	14.05±0.02					
		6.27±0.02	6.38	46.64	3.69	5.54			5.57±0.04	5.67	46.16	3.66	5.49
47.51±0.03	21.77±0.01						46.94±0.04	19.62±0.03					
		6.84±0.03	6.92	48.43	3.76	5.64			5.45±0.03	5.53	47.66	3.76	5.64
49.35±0.03	28.61±0.03						48.41±0.04	25.07±0.01					
		7.82±0.04	7.84	50.42	3.65	5.48			5.54±0.02	5.59	49.16	3.73	5.60
51.50±0.02	36.43±0.02						49.91±0.03	30.61±0.02					
		5.70±0.02	5.66	52.26	3.70	5.55			—	—	—	—	—
53.03±0.03	42.13±0.01						50.70±0.03	29.88±0.01					
		—	—	—	—	—			5.35±0.02	5.37	50.92	3.76	5.64
—							51.13±0.04	35.23±0.02					
									5.53±0.03	5.50	51.88	3.69	5.54
52.96±0.02	41.80±0.02						52.62±0.02	40.76±0.02					
		7.12±0.03	7.02	53.88	3.75	5.63			5.88±0.03	5.81	53.42	3.65	5.48
54.83±0.02	48.92±0.03						54.29±0.02	46.64±0.02					
		5.37±0.03	5.29	55.54	3.75	5.63			5.59±0.02	5.51	54.96	3.65	5.48
56.24±0.03	54.29±0.01						55.72±0.01	52.23±0.01					
		5.14±0.02	5.08	56.92	3.74	5.61			5.76±0.02	5.68	56.58	3.76	5.64
57.60±0.01	59.43±0.01						57.23±0.01	57.99±0.01					
		4.52±0.02	4.48	58.20	3.73	5.60			6.10±0.02	6.05	58.04	3.72	5.58
58.80±0.02	63.95±0.01						58.86±0.05	64.09±0.02					

TABLE 2.—PRELIMINARY MEASUREMENTS ON DILATATION OF ETHYLENE GLYCOL WITH A MEASURING INTERVAL OF TEMPERATURE $\Delta T = 1$ °C. IN THE RANGE 30°-81 °C. USING DILATOMETER NO. 2 (PLOTTED AS EXPERIMENT I IN FIG. 4).

Heating sequence							Cooling sequence						
Beckmann Temperature °C.	Height in the meniscus level cm.	Δl Uncorr. cm.	Δl Corr. cm.	Mean Temp. °C.	$\frac{\Delta l}{\Delta T}$	$1.50\frac{\Delta l}{\Delta T} \approx \alpha \times 10^4$	Beckmann Temperature °C.	Height in the meniscus level cm.	Δl Uncorr. cm.	Δl Corr. cm.	Mean Temp. °C.	$\frac{\Delta l}{\Delta T}$	$1.50\frac{\Delta l}{\Delta T} \approx \alpha \times 10^4$
1	2	3	4	5	6	7	1	2	3	4	5	6	7
1.512±0.003	28.94±0.01						1.275±0.005	28.09±0.01					
		3.31±0.01	3.33	30.65	3.63	5.45			3.68±0.02	3.70	30.46	3.61	5.42
2.430±0.003	32.25±0.00						2.300±0.001	31.77±0.01					
2.430±0.003	32.25±0.00						2.295±0.002	31.77±0.00					
		4.09±0.01	4.09	31.68	3.61	5.42			3.77±0.00	3.78	31.50	3.61	5.42
3.563±0.002	36.34±0.01						3.342±0.003	35.54±0.00					
		3.94±0.01	3.92	32.80	3.60	5.40			3.32±0.01	3.31	32.47	3.57	5.36
4.652±0.002	40.28±0.00						4.268±0.002	38.86±0.01					
							4.118±0.002	38.32±0.00					
									3.53±0.01	3.50	33.28	3.60	5.40
0.999±0.003	44.86±0.01						5.091±0.002	41.85±0.01					
		3.41±0.02	3.36	35.07	3.63	5.45			3.29±0.02	3.25	34.22	3.61	5.42
1.924±0.004	48.27±0.01						5.990±0.001	45.14±0.01					
		3.79±0.01	3.73	36.05	3.64	5.46							
2.948±0.001	52.06±0.00												
2.917±0.003	51.92±0.01						2.499±0.002	50.40±0.01					
		3.95±0.02	3.90	37.07	3.63	5.45			3.65±0.02	3.60	36.55	3.62	5.43
3.992±0.001	55.87±0.01						3.492±0.002	54.05±0.01					
3.926±0.004	55.61±0.01						3.492±0.002	54.05±0.01					
		3.84±0.01	3.80	38.06	3.62	5.43			3.50±0.01	3.46	37.59	3.59	5.38
4.977±0.003	59.45±0.00						4.456±0.004	57.55±0.00					
		3.62±0.01	3.59	39.07	3.64	5.46			3.78±0.01	3.74	38.59	3.64	5.46
5.964±0.005	63.07±0.01						5.484±0.004	61.33±0.01					
1.399±0.003	10.09±0.01						1.049±0.002	8.77±0.01					
		3.61±0.02	3.68	39.90	3.68	5.53			3.52±0.02	3.59	39.50	3.68	5.53
2.400±0.003	13.70±0.01						2.024±0.002	12.29±0.01					
		3.68±0.02	3.75	40.90	3.67	5.51			3.57±0.02	3.64	40.50	3.70	5.56
3.421±0.003	17.38±0.01						3.007±0.003	15.86±0.01					
3.421±0.003	17.38±0.01						2.966±0.004	15.68±0.01					
		3.53±0.02	3.59	41.90	3.64	5.46			3.62±0.02	3.69	41.46	3.67	5.51
4.407±0.004	20.91±0.01						3.971±0.002	19.30±0.01					
1.487±0.005	20.90±0.01						3.971±0.002	19.30±0.01					
		3.70±0.02	3.75	42.90	3.68	5.53			3.59±0.02	3.64	42.45	3.66	5.50
2.505±0.005	24.60±0.01						4.966±0.003	22.89±0.01					

1	2	3	4	5	6	7	1	2	3	4	5	6	7
2.588±0.004	24.90±0.01												
		3.63±0.02	3.67	43.96	3.71	5.57							
3.577±0.004	28.53±0.01												
		3.71±0.01	3.73	44.96	3.65	5.48							
4.599±0.005	32.24±0.00												
2.588±0.003	30.75±0.01						2.283±0.003	29.64±0.01					
		3.63±0.02	3.64	45.59	3.68	5.53			3.69±0.02	3.71	45.29	3.72	5.58
3.577±0.004	34.38±0.01						3.281±0.003	33.33±0.01					
		3.78±0.02	3.77	46.59	3.68	5.53			3.73±0.02	3.73	46.27	3.66	5.50
4.602±0.004	38.16±0.01						4.301±0.002	37.06±0.01					
4.716±0.004	38.55±0.01						4.332±0.003	37.14±0.01					
		3.87±0.02	3.84	47.70	3.75	5.62			3.73±0.02	3.70	47.29	3.69	5.54
5.741±0.004	42.42±0.01						5.334±0.004	40.87±0.01					
							3.067±0.004	38.97±0.01					
									3.68±0.02	3.65	47.69	3.69	5.54
							4.056±0.004	42.35±0.01					
									3.83±0.02	3.78	48.69	3.68	5.53
							5.083±0.004	46.18±0.01					
1.545±0.004	44.56±0.01						1.053±0.003	42.71±0.01					
		3.62±0.02	3.57	49.29	3.74	5.61			3.65±0.02	3.61	48.77	3.72	5.58
2.499±0.003	48.18±0.01						2.023±0.004	46.36±0.01					
		3.87±0.02	3.81	50.29	3.71	5.57			3.70±0.02	3.65	49.75	3.74	5.61
3.527±0.004	52.05±0.01						3.000±0.003	50.06±0.01					
		3.87±0.02	3.82	51.31	3.70	5.56			3.68±0.02	3.63	50.73	3.74	5.61
4.559±0.004	55.92±0.01						3.970±0.004	53.74±0.01					
		3.71±0.02	3.67	52.32	3.68	5.53			3.64±0.02	3.59	51.71	3.67	5.51
5.554±0.006	59.63±0.00						4.949±0.004	57.38±0.01					
1.081±0.003	3.01±0.01						4.949±0.004	57.38±0.01					
		3.68±0.02	3.73	53.30	3.76	5.64			3.57±0.02	3.53	52.70	3.68	5.53
2.071±0.006	6.69±0.01						5.907±0.005	60.95±0.01					
2.071±0.006	6.69±0.01						1.590±0.004	4.92±0.01					
		3.73±0.02	3.79	54.30	3.77	5.65			3.75±0.02	3.81	53.83	3.79	5.69
3.076±0.002	10.42±0.01						2.594±0.005	8.67±0.01					
		3.65±0.02	3.72	55.31	3.76	5.64			3.66±0.02	3.73	54.85	3.74	5.62
4.066±0.004	14.07±0.01						3.589±0.004	12.33±0.01					
		3.64±0.02	3.71	56.31	3.71	5.57			3.64±0.02	3.71	55.84	3.76	5.64
5.066±0.004	17.71±0.01						4.576±0.005	15.97±0.01					
1.024±0.005	17.22±0.01						4.576±0.005	15.97±0.01					
		3.80±0.02	3.86	57.15	3.80	5.70			3.59±0.02	3.65	56.82	3.74	5.61
2.041±0.004	21.02±0.01						5.553±0.004	19.56±0.01					
2.041±0.004	21.02±0.01						1.596±0.003	10.38±0.01					
		3.82±0.02	3.87	58.20	3.85	5.78			3.73±0.02	3.79	57.72	3.83	5.74
3.046±0.004	24.84±0.01						2.584±0.003	23.11±0.01					
3.050±0.003	24.83±0.01						2.584±0.003	23.11±0.01					

1	2	3	4	5	6	7
		3.67±0.02	3.71	59.21	3.76	5.64
4.038±0.005	28.50±0.01					
		3.87±0.02	3.88	60.21	3.85	5.78
5.046±0.004	32.37±0.01					
0.669±0.002	32.06±0.01					
		3.86±0.02	3.86	61.15	3.80	5.70
1.686±0.004	35.92±0.01					
		3.90±0.02	3.88	62.17	3.88	5.82
2.687±0.004	39.82±0.01					
0.063±0.004	47.80±0.01					
		3.68±0.02	3.62	62.18	3.83	5.75
1.007±0.004	51.48±0.01					
1.007±0.004	51.48±0.01					
		3.79±0.02	3.73	63.15	3.79	5.69
1.992±0.007	55.27±0.01					
0.514±0.005	40.70±0.01					
		3.89±0.01	3.85	64.01	3.91	5.87
1.498±0.005	44.59±0.00					
1.498±0.005	44.59±0.00					
		3.99±0.01	3.93	65.01	3.91	5.87
2.504±0.005	48.68±0.01					
		3.83±0.02	3.77	66.01	3.79	5.68
3.498±0.005	52.41±0.01					
		3.88±0.02	3.83	67.01	3.83	5.74
4.499±0.001	56.29±0.01					
0.388±0.006	4.31±0.01					
		3.80±0.02	3.86	67.50	3.82	5.73
1.398±0.004	8.11±0.01					
		3.89±0.02	3.96	68.50	3.92	5.88
2.407±0.005	12.00±0.01					
		3.81±0.02	3.88	69.50	3.89	5.84
3.405±0.007	15.81±0.01					
		3.79±0.02	3.86	70.50	3.88	5.82
4.401±0.006	19.60±0.01					
0.044±0.005	19.22±0.01					
		3.77±0.02	3.83	71.49	3.93	5.90
1.018±0.004	22.99±0.01					
1.018±0.004	22.99±0.01					
		3.81±0.02	3.86	72.40	3.93	5.90
2.000±0.003	26.80±0.01					
		3.94±0.02	3.97	73.43	4.03	6.04
2.987±0.004	30.74±0.01					
2.987±0.004	30.74±0.01					
		3.81±0.02	3.82	74.48	3.83	5.75

1	2	3	4	5	6	7
		3.69±0.01	3.73	58.74	3.77	5.65
3.572±0.005	26.80±0.00					
		3.62±0.01	3.65	59.72	3.80	5.70
4.532±0.004	30.42±0.01					
4.532±0.004	30.42±0.01					
		3.56±0.02	3.57	60.68	3.80	5.69
5.473±0.004	33.98±0.01					
0.056±0.003	29.89±0.01					
		3.78±0.01	3.80	60.53	3.82	5.73
1.051±0.002	33.67±0.00					
		3.75±0.01	3.74	61.54	3.80	5.70
2.034±0.002	37.42±0.01					
2.149±0.005	34.92±0.01					
		3.86±0.02	3.85	62.50	3.88	5.82
3.140±0.003	38.78±0.01					
3.140±0.003	38.78±0.01					
		4.01±0.02	3.98	63.53	3.79	5.68
4.189±0.004	42.79±0.01					
1.009±0.003	42.69±0.01					
		4.20±0.02	4.14	64.54	3.88	5.82
2.075±0.008	46.89±0.01					
		3.67±0.02	3.61	65.56	3.88	5.82
3.006±0.004	50.56±0.01					
		4.31±0.02	4.25	66.59	3.83	5.74
4.117±0.006	54.87±0.01					
4.025±0.006	54.46±0.01					
		3.71±0.02	3.66	67.53	3.96	5.94
4.949±0.005	58.17±0.01					
1.890±0.003	10.01±0.01					
		3.88±0.02	3.95	69.01	3.95	5.93
2.890±0.005	13.89±0.01					
		3.70±0.02	3.77	70.00	3.87	5.81
3.863±0.006	17.59±0.01					
3.863±0.006	17.59±0.01					
		3.90±0.02	3.97	71.01	3.92	5.88
4.876±0.004	21.49±0.01					
0.580±0.004	10.18±0.01					
		3.82±0.02	3.89	71.99	3.92	5.88
1.573±0.005	14.00±0.01					
		3.88±0.02	3.95	73.00	3.97	5.96
2.567±0.006	17.88±0.01					
2.588±0.005	17.90±0.01					
		4.00±0.02	4.07	74.04	3.97	5.96

1	2	3	4	5	6	7	1	2	3	4	5	6	7
3.984$\pm$0.009	34.55$\pm$0.01						3.614$\pm$0.005	21.90$\pm$0.01					
3.977$\pm$0.004	34.40$\pm$0.01	3.89$\pm$0.02	3.88	75.50	3.90	5.85	3.614$\pm$0.005	21.90$\pm$0.01	3.99$\pm$0.02	4.04	75.03	3.96	5.94
4.971$\pm$0.004	38.29$\pm$0.01						4.635$\pm$0.004	25.89$\pm$0.01					
0.655$\pm$0.004	26.83$\pm$0.01	3.86$\pm$0.02	3.89	76.50	3.96	5.94	0.221$\pm$0.007	25.11$\pm$0.01	3.79$\pm$0.02	3.83	75.96	3.93	3.90
1.638$\pm$0.005	30.69$\pm$0.01	3.91$\pm$0.02	3.92	77.51	3.96	5.94	1.196$\pm$0.005	28.90$\pm$0.01	3.86$\pm$0.02	3.88	76.99	4.01	6.02
2.628$\pm$0.004	34.60$\pm$0.00						2.164$\pm$0.007	32.76$\pm$0.01					
2.623$\pm$0.005	34.59$\pm$0.01	3.90$\pm$0.02	3.89	78.53	3.98	5.97	2.164$\pm$0.007	32.76$\pm$0.01	4.03$\pm$0.02	4.03	78.02	3.98	5.97
3.600$\pm$0.006	38.49$\pm$0.01						3.176$\pm$0.006	36.79$\pm$0.01					
3.600$\pm$0.006	38.49$\pm$0.01	3.97$\pm$0.02	3.93	79.55	3.93	5.90	3.021$\pm$0.004	36.20$\pm$0.01	3.92$\pm$0.02	3.90	78.96	3.92	5.88
4.601$\pm$0.005	42.46$\pm$0.01						4.016$\pm$0.008	40.12$\pm$0.01					
0.218$\pm$0.006	42.07$\pm$0.01	4.02$\pm$0.02	3.97	80.50	3.97	5.96	4.016$\pm$0.008	40.12$\pm$0.01	3.92$\pm$0.02	3.88	79.95	4.01	6.02
1.219$\pm$0.006	46.09$\pm$0.01						4.984$\pm$0.006	44.04$\pm$0.01					
							0.716$\pm$0.005	43.98$\pm$0.01	4.00$\pm$0.02	3.94	81.00	3.96	5.94
							1.710$\pm$0.004	47.98$\pm$0.01					

Table 3.—Preliminary Measurements on Dilatation of Ethylene Glycol with Measuring Interval of Temperature $\Delta T = 1°C.$ in the Range 17°-75°C. Using Dilatometer No. 2 (Experiment II).

Rising sequence							Falling sequence						
Beckmann Temp. °C.	Height of the meniscus level cm.	Δl Uncorr. cm.	Δl Corr. cm.	Mean Temp. °C.	$\frac{\Delta l}{\Delta T}$	$150\times\frac{\Delta l}{\Delta T} \approx \alpha\times 10^4$	Beckmann Temp. °C.	Height of the meniscus level cm.	Δl Uncorr cm.	Δl Corr. cm.	Mean Temp. °C.	$\frac{\Delta l}{\Delta T}$	$1.50\times\frac{\Delta l}{\Delta T} \approx \alpha\times 10^4$
1	2	3	4	5	6	7	1	2	3	4	5	6	7
0.483±0.003	2.37±0.01												
		3.80±0.02	3.84	17.55	3.54	5.32							
1.575±0.005	6.17±0.01												
3.212±0.002	4.65±0.01												
		3.42±0.02	3.47	17.98	3.56	5.34							
4.188±0.002	8.07±0.01												
1.575±0.005	6.17±0.01						3.699±0.003	6.35±0.00					
		2.65±0.02	2.69	18.47	3.54	5.32			3.63±0.01	3.69	18.48	3.53	5.30
2.334±0.009	8.82±0.01						4.746±0.004	9.98±0.01					
0.809±0.001	10.83±0.02						4.642±0.002	9.62±0.00					
		4.13±0.02	4.21	19.91	3.62	5.43			3.31±0.01	3.37	19.41	3.56	5.34
1.972±0.004	14.90±0.01						5.591±0.001	12.93±0.01					
							0.978±0.003	13.24±0.01					
									3.60±0.01	3.67	20.48	3.59	5.38
1.974±0.002	14.95±0.01						1.999±0.002	16.84±0.00					
		3.81±0.02	3.88	21.05	3.58	5.38			3.51±0.00	3.57	21.50	3.59	5.38
3.056±0.003	18.76±0.01						2.992±0.002	20.35±0.00					
		3.32±0.02	3.37	22.06	3.55	5.32			3.50±0.00	3.55	22.48	3.54	5.32
4.005±0.003	22.08±0.01						3.994±0.004	23.85±0.00					
		3.82±0.02	3.87	23.04	3.59	5.38			3.53±0.01	3.57	23.46	3.57	5.36
5.084±0.006	25.90±0.01						4.994±0.005	27.38±0.01					
0.958±0.002	24.98±0.01						4.016±0.003	23.92±0.00					
		3.49±0.02	3.52	23.82	3.59	5.38			3.43±0.00	3.47	23.48	3.55	5.32
1.938±0.002	28.47±0.01						4.994±0.002	27.35±0.00					
		3.51±0.02	3.53	24.80	3.60	5.40			3.20±0.01	3.22	24.40	3.55	5.32
2.918±0.002	31.98±0.01						5.900±0.004	30.55±0.01					
2.918±0.002	31.98±0.01						1.153±0.004	29.95±0.01					
		3.46±0.01	3.46	25.77	3.57	5.36			3.11±0.02	3.12	25.14	3.60	5.40
3.887±0.001	35.44±0.00						2.020±0.002	33.06±0.01					
		3.31±0.00	3.30	26.70	3.55	5.32			3.77±0.02	3.77	26.10	3.60	5.40
4.816±0.002	38.75±0.00						3.067±0.002	36.83±0.01					
1.146±0.003	38.64±0.01						3.067±0.002	36.83±0.01					
		3.13±0.02	3.10	27.58	3.59	5.38			3.85±0.02	3.84	27.13	3.58	5.38
2.008±0.002	41.77±0.01						4.142±0.003	40.68±0.01					
									3.07±0.02	3.03	28.09	3.57	5.36
2.136±0.004	42.34±0.01						4.991±0.002	43.75±0.01					
		3.50±0.02	3.46	28.56	3.52	5.28			3.26±0.02	3.22	28.97	3.56	5.34

1	2	3	4	5	6	7
3.119±0.002	45.84±0.01					
		3.75±0.02	3.69	29.62	3.55	5.32
4.158±0.003	49.59±0.01					
		3.72±0.02	3.66	30.64	3.61	5.42
5.172±0.002	53.31±0.01					
1.586±0.006	16.32±0.01					
		3.72±0.01	3.79	34.82	3.65	5.48
2.624±0.005	20.04±0.00					
		3.41±0.01	3.46	35.83	3.64	5.46
3.575±0.007	23.45±0.01					
3.575±0.007	23.45±0.01					
		3.47±0.02	3.51	36.78	3.63	5.45
4.542±0.003	26.92±0.01					
4.638±0.002	27.28±0.01					
		3.28±0.02	3.30	37.78	3.60	5.40
5.554±0.004	30.56±0.01					
3.317±0.003	30.38±0.01					
		3.57±0.01	3.58	38.70	3.62	5.43
4.305±0.004	33.95±0.00					
		4.02±0.01	4.01	39.75	3.62	5.43
5.414±0.004	37.97±0.01					
1.501±0.002	34.87±0.01					
		3.80±0.02	3.79	40.00	3.71	5.57
2.523±0.005	38.67±0.01					
		3.67±0.02	3.62	41.00	3.65	5.48
3.515±0.004	42.34±0.01					
1.008±0.001	42.77±0.00					
		3.67±0.00	3.62	42.10	3.66	5.50
1.996±0.005	46.44±0.00					
1.996±0.005	46.44±0.00					
		3.58±0.01	3.53	43.08	3.69	5.54
2.953±0.004	50.02±0.01					
2.953±0.004	50.02±0.01					
		3.55±0.02	3.50	44.04	3.63	5.45
3.918±0.002	53.57±0.01					
		3.78±0.02	3.73	45.01	3.65	5.48
4.940±0.003	57.35±0.01					

1	2	3	4	5	6	7
5.896±0.001	47.01±0.01					
1.265±0.001	47.78±0.01					
		3.53±0.02	3.48	30.10	3.60	5.40
2.231±0.001	51.31±0.01					
		3.96±0.01	3.90	31.13	3.60	5.40
3.314±0.001	55.27±0.00					
		3.60±0.01	3.53	32.26	3.53	5.30
4.318±0.001	58.87±0.01					
		3.95±0.01	3.92	33.22	3.61	5.42
5.404±0.001	62.82±0.00					
2.268±0.002	18.77±0.01					
		3.61±0.01	3.67	35.51	3.63	5.45
3.278±0.003	22.38±0.00					
2.018±0.002	22.56±0.01					
		3.50±0.02	3.54	36.52	3.65	5.48
2.986±0.002	26.06±0.01					
2.986±0.002	26.06±0.01					
		3.43±0.02	3.46	37.48	3.62	5.43
3.942±0.002	29.49±0.01					
3.982±0.003	29.61±0.01					
		3.76±0.02	3.78	38.52	3.65	5.48
5.017±0.003	33.37±0.01					
		3.38±0.02	3.38	39.50	3.62	5.43
5.951±0.004	36.75±0.01					
2.030±0.001	36.80±0.01					
		3.81±0.02	3.79	40.50	3.67	5.51
3.061±0.002	40.61±0.01					
		3.74±0.01	3.70	41.50	3.64	5.46
4.077±0.003	44.35±0.00					
		3.69±0.00	3.64	42.50	3.64	5.46
5.077±0.002	48.04±0.00					
2.416±0.004	48.00±0.01					
		3.87±0.01	3.81	42.50	3.64	5.46
1.369±0.002	44.13±0.00					
2.576±0.002	47.93±0.01					
		3.68±0.01	3.63	42.50	3.65	5.48
1.581±0.001	44.25±0.00					
2.702±0.004	48.34±0.01					
		3.77±0.01	3.71	43.63	3.69	5.54
3.708±0.002	52.11±0.00					
		3.80±0.01	3.75	44.64	3.65	5.48
4.735±0.004	55.91±0.01					

1	2	3	4	5	6	7	1	2	3	4	5	6	7
		3.72±0.02	3.68	46.00	3.66	5.50			3.73±0.01	3.69	45.60	3.65	5.48
5.945±0.004	61.07±0.01						5.747±0.003	59.64±0.00					
0.779±0.003	8.50±0.01												
		3.72±0.01	3.79	47.04	3.70	5.56							
1.805±0.005	12.22±0.00						1.308±0.002	10.40±0.01					
		3.69±0.01	3.76	48.05	3.72	5.58			3.49±0.02	3.56	47.51	3.71	5.57
2.815±0.005	15.91±0.01						2.267±0.005	13.89±0.01					
		3.67±0.02	3.74	49.06	3.69	5.54			3.45±0.02	3.51	48.46	3.72	5.58
3.830±0.005	19.58±0.01						3.209±0.004	17.34±0.01					
3.830±0.005	19.58±0.01						3.226±0.005	17.39±0.00					
		3.77±0.02	3.83	50.08	3.70	5.56			3.79±0.01	3.85	49.49	3.71	5.57
4.866±0.004	23.35±0.01						4.264±0.005	21.18±0.01					
		3.65±0.01	3.69	51.10	3.73	5.60			3.52±0.02	3.57	50.49	3.70	5.56
5.855±0.004	27.00±0.00						5.228±0.005	24.70±0.01					
0.893±0.003	24.25±0.01												
		3.79±0.02	3.83	51.25	3.74	5.61							
1.916±0.004	28.04±0.01						1.493±0.003	26.44±0.01					
		3.84±0.02	3.86	52.40	3.74	5.61			3.53±0.02	3.56	51.93	3.67	5.51
2.947±0.004	31.88±0.01						2.465±0.005	30.07±0.01					
		3.63±0.02	3.64	53.41	3.67	5.51			4.02±0.02	4.04	52.98	3.37	5.60
3.938±0.005	35.51±0.01						3.548±0.006	34.09±0.01					
3.806±0.005	35.01±0.01						3.514±0.005	33.93±0.01					
		3.63±0.02	3.62	54.29	3.76	5.64			3.77±0.02	3.76	54.04	3.74	5.61
4.768±0.004	38.64±0.01						4.520±0.002	37.70±0.01					
		3.74±0.02	3.71	55.28	3.74	5.61			3.79±0.02	3.76	55.04	3.72	5.58
5.760±0.002	42.38±0.01						5.530±0.005	41.49±0.01					
4.414±0.004	42.49±0.01						3.935±0.004	40.66±0.01					
		3.75±0.02	3.70	56.29	3.70	5.56			3.91±0.02	3.86	55.83	3.75	5.62
5.415±0.004	46.24±0.01						4.965±0.003	44.57±0.01					
1.899±0.002	46.32±0.01						4.965±0.003	44.57±0.01					
		3.84±0.02	3.78	57.36	3.82	5.73			3.71±0.02	3.66	56.84	3.70	5.56
2.887±0.003	50.16±0.01						5.953±0.004	48.28±0.01					
2.887±0.003	50.16±0.01						2.380±0.005	48.29±0.01					
		3.84±0.01	3.78	58.39	3.73	5.60			3.87±0.02	3.80	57.87	3.79	5.69
3.900±0.003	54.00±0.00						3.383±0.006	52.16±0.01					
3.900±0.003	54.00±0.00						3.396±0.003	52.12±0.01					
		3.79±0.01	3.74	59.40	3.75	5.62			3.88±0.01	3.83	58.89	3.79	5.69
4.896±0.004	57.79±0.01						4.407±0.005	56.00±0.00					
1.004±0.006	59.61±0.01						4.407±0.005	56.00±0.00					
		3.73±0.01	3.70	60.80	3.67	5.51			3.78±0.00	3.74	59.90	3.70	5.56
2.011±0.007	63.44±0.01						5.418±0.004	59.78±0.00					
0.164±0.003	4.13±0.01						1.935±0.005	3.37±0.01					
		4.08±0.02	4.14	60.88	3.82	5.73			3.83±0.02	3.88	60.63	3.86	5.79
1.247±0.004	8.21±0.01						2.941±0.005	7.20±0.01					

1	2	3	4	5	6	7
		3.84±0.02	3.91	61.92	3.91	5.86
2.248±0.004	12.05±0.01					
2.248±0.004	12.05±0.01					
		3.94±0.02	4.01	62.94	3.85	5.78
3.289±0.003	15.99±0.01					
3.289±0.003	15.99±0.01					
		3.72±0.02	3.79	63.96	3.76	5.64
4.297±0.004	19.71±0.01					
1.079±0.004	17.99±0.01					
		3.97±0.02	4.03	64.25	3.84	5.76
2.127±0.003	21.96±0.01					
		3.99±0.02	4.04	65.40	3.82	5.73
3.183±0.003	25.95±0.01					
		3.96±0.02	3.99	66.49	3.81	5.72
4.231±0.004	29.91±0.01					
0.536±0.002	26.74±0.01					
		4.23±0.02	4.26	66.79	3.88	5.82
1.633±0.007	30.97±0.01					
		3.85±0.02	3.86	67.91	3.87	5.80
2.630±0.003	34.82±0.01					
		4.29±0.02	4.28	68.95	3.94	5.91
3.715±0.003	39.11±0.01					
0.922±0.003	39.92±0.01					
		4.02±0.02	3.98	70.51	3.88	5.82
1.948±0.005	43.94±0.01					
3.906±0.004	51.72±0.01					
		3.83±0.02	3.78	73.54	3.90	5.85
4.874±0.004	55.55±0.01					
0.430±0.006	51.88±0.01					
		3.89±0.02	3.84	73.51	3.89	5.84
1.417±0.004	55.77±0.01					
1.417±0.004	55.77±0.01					
		3.90±0.02	3.86	74.54	3.92	5.88
2.403±0.003	59.67±0.01					
		3.89±0.02	3.86	75.59	3.91	5.87
3.390±0.002	63.56±0.01					

1	2	3	4	5	6	7
		3.86±0.02	3.93	61.64	3.83	5.74
3.967±0.004	11.06±0.01					
1.879±0.005	10.67±0.01					
		3.74±0.02	3.81	62.53	3.88	5.82
2.859±0.003	14.41±0.01					
2.830±0.003	14.26±0.01					
		3.74±0.02	3.81	63.51	3.82	5.73
3.827±0.004	18.00±0.00					
		3.89±0.02	3.95	64.54	3.87	5.81
4.847±0.002	21.89±0.02					
0.604±0.004	16.17±0.01					
		3.85±0.02	3.92	63.84	3.83	5.74
1.627±0.004	20.02±0.01					
		3.97±0.02	4.03	64.97	3.91	5.86
2.657±0.004	23.99±0.01					
		3.77±0.02	3.81	66.02	3.80	5.70
3.661±0.009	27.76±0.01					
2.441±0.008	27.52±0.01					
		3.96±0.02	3.99	67.04	3.85	5.78
3.477±0.003	31.48±0.01					
		4.00±0.02	4.01	68.09	3.86	5.79
4.515±0.009	35.48±0.01					
1.707±0.007	37.79±0.01					
		4.02±0.02	3.99	70.00	3.95	5.93
2.716±0.004	41.81±0.01					
2.664±0.004	41.63±0.01					
		4.04±0.02	3.99	70.99	3.93	5.90
3.679±0.004	45.67±0.01					
0.008±0.004	45.67±0.01					
		3.94±0.02	3.88	72.01	3.88	5.82
1.008±0.005	49.61±0.01					
		3.95±0.02	3.89	73.03	3.87	5.81
2.014±0.003	53.56±0.01					
1.947±0.003	53.22±0.01					
		3.96±0.02	3.91	73.98	4.07	6.11
2.907±0.005	57.18±0.01					
0.737±0.005	52.92±0.01					
		3.90±0.02	3.85	73.88	3.95	5.93
1.712±0.005	56.82±0.01					
		4.06±0.02	4.02	74.89	4.05	6.08
2.704±0.005	60.88±0.01					
		3.81±0.02	3.79	75.90	3.90	5.85
3.676±0.005	64.69±0.01					

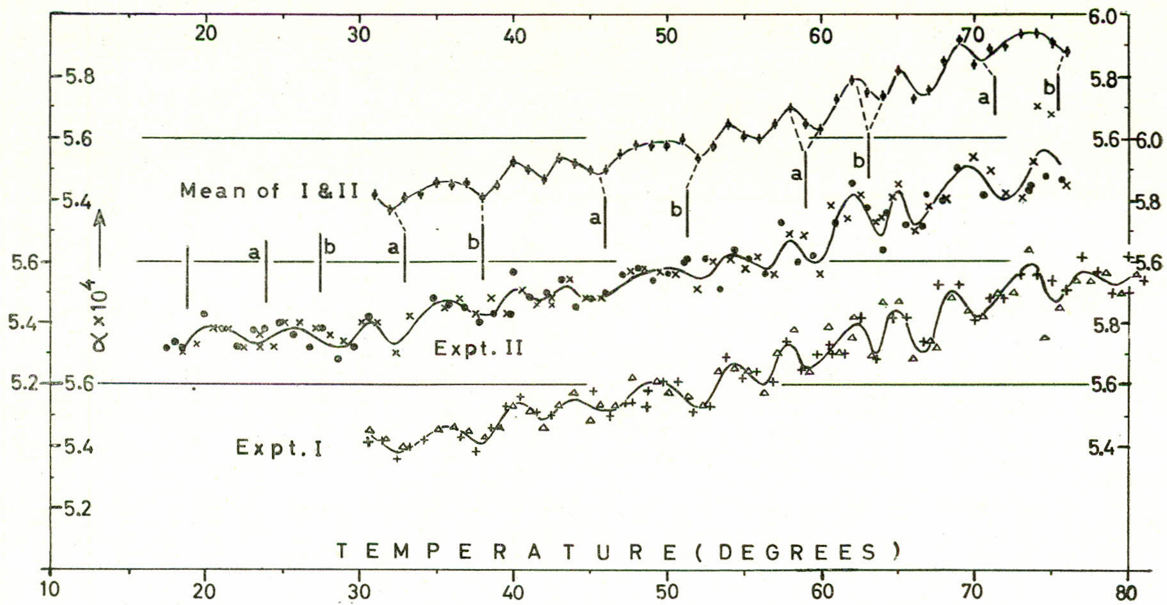

Fig. 4.—Plots of coefficient of dilatation, α, against temperature of ethylene glycol in new careful measurements. Solid circles and triangles are for heating sequences, and crosses for cooling sequences. The top graph is the mean of the two sets of measurements, calculated from all four points within each degree interval. The standard error of the means is indicated by the short vertical lines drawn through the points. It is seen that the minima in the top-most curve agree well with the temperatures at the jumps in the $E\eta/R$ graph denoted by 'a' and 'b' vertical lines in Fig. 4.

5. Discussion

At this stage, we can compare the mean graph of Expt. I and Expt. II with those of the previously reported accurate measurement of $E\eta/R$ on ethylene glycol,[3] wherein a series of sharp jumps in E/R were observed. It is found that the majority of minima in α correspond very closely with these sharp jumps in $E\eta/R$ for flow, which are indicated by the thick vertical lines (marked "a" and "b") below the top graph of Fig. 4. The two jumps at 59°C. and 63°C. could either correspond to the minima at 60°C. and 64°C. or to the maxima at 58°C. and 62°C., respectively. Although the general correspondence noted above provides some comparison with that previously noted in case of pure water, there are some extra minima to be found at temperatures 42°C., 56°C. and 67°C., each of which is in the middle of a long "flat" i.e. constant region of E/R. It is quite possible that two or more types of intermolecular rearrangements are involved in the various jumps, and also that some of the jumps and the changes in α are incorrectly located due to marginal accuracy. It is proposed to improve the accuracy of the apparatus used, and further measurements on liquids like benzene and other systems such as dilute alcohol are planned for a better understanding of these phenomena.

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References

1. (a) M. Naseem, and M.M. Qurashi, Pakistan, J. Sci. Ind. Res., **1**, 197 (1958).
   (b) A. Rauf, and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **2**, 30 (1959).
2. M.M. Qurashi, and A.K.M. Ahsanullah, Brit. J. Appl. Phys., **12**, 65 (1961).
3. A.K.M. Ahsanullah and M.M. Qurashi, Brit. J. Appl. Phys., **13**, 334 (1962).
4. A. Momin Chowdhry, Hameed Ahmad, and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **3**, 101 (1960).
5. M. Tayeb Qureshi, M. Sabir, and M.M. Qurashi, Proc. Pakistan Acad. Sci., **1**, (1964) (in Press).
6. M.M. Qurashi, Pakistan J. Sci. Ind. Res., **6**, 213 (1963).
7. A.K.M. Ahsanullah and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **6**, 243 (1963).