# STUDIES IN THE RELATIONSHIP BETWEEN VISCOSITY AND MOLECULAR STRUCTURE

Part V.—Preliminary Investigation of Periodicity in the Temperature Variation of the Activation Energy in Aqueous Ethyl Alcohol in the Temperature Range of 5°C. to 55°C.

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As a sequel to the discovery of well-defined steps in the temperature variation of inter-molecular activation energy of viscous flow in poly-hydroxylic liquids like glycerol, ethylene glycol and water, the investigations have been extended to the case of ethyl alcohol, which has one hydroxyl group. Preliminary results obtained with a 2°C. measuring interval are reported here, and they show the presence of a fairly regular sinusoidal variation with a period of 10.4°C. and a peak-to-peak amplitude of about 0.102 units of  $(\varepsilon/k)/1000$  for redistilled rectified spirits (ethyl alcohol containing 6.5% water). Similar experiments on ethyl alcohol containing 12.3% water indicate a much smaller variation of peakto-peak amplitude nearly 0.02 units with a period of about 8.8°C. These results are generally compatible with the extensive measurements already existing on the water-ethyl alcohol system, but the standard data is not accurate enough to indicate the small variations described in the present communication.

#### Introduction

The existence of a temperature periodicity in the intermolecular activation energy of viscous flow has been investigated in this laboratory for several poly-hydroxylic liquids, namely glycerol, ethylene glycol and water, and described in previous communications<sup>1-3</sup> of this series. It was found that in all cases the experiments showed the existence of regularly recurring ranges of temperature, within which the activation energy is exactly constant. The drop from one step to the next is not, however, equally sharp for all cases. Since the liquids examined so far have two or three hydroxyl groups in the molecule, it was considered worthwhile to carry out similar investigations with some mono-hydroxylic liquids. In the present communication, the status of the existing standard data on ethyl alcohol is examined, and a preliminary account is given of more accurate results obtained with aqueous ethyl alcohol in the relatively easily accessible temperature range of  $5^{\circ}$ C. to  $55^{\circ}$ C. The experiments with absolute alcohol will be reported separately.

### 1. Consideration of Earlier Standard Data

Standard data on the viscosity of ethyl alcohol at several temperatures are available in Kaye and Laby's *Tables of Physical and Chemical Constants*<sup>4</sup> and in *Physico-Chemical Constants of Pure Organic Compounds*<sup>5</sup> (data of Titani (1927) and others). These data, which are compiled from the work of several authors, are believed to be accurate to somewhere around  $\pm$  0.001 centipoise. The data from Kaye and Laby are shown in the second row of Table 1, while the third row gives the calculated values of  $\Delta \ln \eta/\Delta T$  and the

fourth row shows the corresponding values of the quantity  $(\varepsilon/k)/1000$  calculated by using the well known logarithmic derivative of the Andrade equation, viz.

$$-\frac{\Delta \ln \eta}{\Delta T} = \frac{\varepsilon}{k}/T^2, \qquad (1)$$

where 'z' is the activation energy of viscous flow for the liquid and 'k' is Boltzmann's constant. In the present case,  $\Delta T$  is limited to being 10°C., and accordingly for intermediate temperatures the interpolated values of (\$\varepsilon k)/1000 at 10°C., 20°C., etc. are given in parentheses. On the basis of an accuracy of  $\pm$  0.001 centipoise in the values of viscosity, the average uncertainty in the calculated values of  $(\epsilon/k)/1000$  works out to be of the order of  $\pm$  0.02. The above values of  $\varepsilon/k$  are plotted as hollow circles in Fig. 1(a) (top), while the corresponding values calculated from the set of standard data in Physico-Chemical Constants Pure Organic Compounds are plotted as of crosses in Fig. 1(a) (top), and the smoothed values from the graph are given in the fifth row of Table 1. Although both graphs show a prominent maximum followed by a minimum, the discrepancies between the two sets of values are very considerable, especially in the region of 20°C. to 35°C., and the crosses are, on the average. higher by about 0.05 units.

In the next row of Table 1 are given the means of the two sets of values, together with their standard errors, the sign  $\pm$  indicating that the value in the second set is higher than that in the first set. The average standard error of the means comes out to be  $\pm$  (0.022  $\pm$  0.046), indicating that the truly random standard error is 0.046, while there is a consistent discrepancy of 2  $\times$  0.022  $\pm$  0.044 between the two sets of values. The mean values of ( $\epsilon/k$ )/1000 are plotted in Fig. 1(b) (bottom) as solid circles with the short vertical lines corresponding to the standard error of 0.046 units estimated above. The straight line shown in the graph fits the plotted points satisfactorily, the maximum deviation being 2.2 times the standard error. There is thus little justification for drawing the dotted curved line through them, which would show a periodicity of about  $35^{\circ}$ C., with a maximum in the neighbourhood of  $32^{\circ}$ C. Similar considerations apply to the values of  $\epsilon/k$  for alcohol containing 5% and 10% water obtained from the *International Critical Tables*, 6 Vol. V, shown in the last two rows of Table I, and plotted (squares and triangles) in Fig. 1(b).

102

It must be noted here for comparison that the heights of the steps observed in previous experiments on ethylene glycol<sup>1</sup>,<sup>2</sup> and water<sup>3</sup> are of the order of 0.1 unit of  $(\epsilon/k)/1000$ , and it thus follows from the above analysis that the standard data plotted in Fig. 1 are quite inadequate for discovering any effect of this order in the case of ethyl alcohol. Therefore the preliminary experiments described herein were undertaken, in which the values of  $(\epsilon/k)/1000$  were directly measured in the range of 5°C. to 55°C., aiming at an accuracy of  $\pm$  0.01 units of  $(\epsilon/k)/1000$ . These experiments were first carried out on redistilled

rectified spirits with a water-content of about 6%, and were then repeated with alcohol containing 11% water.



Fig. 1.—(a). Plots of  $(\varepsilon/k)/1000$  for ethyl alcohol, as calculated from two sets of standard data (i) Titani and others, crosses and (ii) International Kaye and Laby Tables, hollow circles. (b). Plots of  $(\varepsilon/k)/1000$  as calculated from the standard data for the water ethyl alcohol system: (i) solid circles, mean for pure ethyl alcohol, with vertical lines indicating estimated standard deviation, (ii) squares, for alcohol containing 5% water, (iii) triangles, for alcohol with 10% water.

TABLE I.—INTER-MOLECULAR ACTIVATION ENERGY & FOR ETHYL ALCOHOL, CALCULATED FROM THE STANDARD PUBLISHED VISCOSITY DATA.

					and the second second										
Temperature (°C)	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70
η (cP) Kaye & Laby 1.7	67 -		1.447	_	1.197	-	1.000	_	0.830	_	0.700	-	0.594	-	0.502
- 100(Δlnη/ΔT) -	- 2.	00 <b>0</b>	-	1.896	-	1.80 <b>0</b>	-	1.862	-	1.696	-	1.642	-	1.684	
$\frac{\epsilon/k}{1000} = \frac{T^2}{1000} - \frac{\tau}{\chi} (\Delta \ln \eta / \Delta T)$	- 1.	.54 <b>6</b>	(1.56 <b>0</b> )	1.575	(1.588)	1.602	(1.685)	1.76 <b>8</b>	(1.744)	1.72 <b>o</b>	(1.745)	1.77 <b>o</b>	(1.851)	1.93 <b>2</b>	
ε/k → Calculated from "Physico- 1000 Chemical Constants of Organ Compounds."	1. ic	.624	1.59 <sub>1</sub>	1.60 <b>8</b>	1.688	1.84o	1.94 <b>5</b>	1.80 <b>2</b>	1.69 <b>0</b>	1.642	1.712	1.818	1.86 <b>0</b>	1.84 <b>0</b>	
€/k	1.5	585	1.576	1.592	1.638	1.72 <sub>I</sub>	1.815	1.785	1.717	1.68 <sub>1</sub>	1.728	1.794	1.856	1.886	
Mean 1000	÷	039	.016	±.016	±.050	±.119	±.130 ;	±.017	±.027 :	±.039	±.016	±.024	<b>±</b> .004	±.046	
ε/k with 5% water 1000 (Int. Crit. Tables)	1.	.838	1	1.836	-	1.905	-	1.94 <b>0</b>	-	1.916	-	1.882	-	1.845	
ε/k 1000 (Int. Crit. Tables)	2.	120	-	2.04 <b>2</b>	-	2.058	-	2.06 <b>2</b>	-	2.045	Ι	1.978	-	1.90 <b>2</b>	

### 2. Details of Experimental Procedure

The apparatus was essentially the same as that used previously for the investigations on water,<sup>3</sup> including the ballast bottle device for controlling the evaporation of the experimental liquid from the viscometer. The measurement of the level of the liquid with reference to the fiducial mark above the large lower bulb of the U-tube viscometer was however carried out by mounting a vertical transparent millimetre scale immediately behind the viscometer, both the scale and the fiducial mark being observed simultaneously through a cathetometer telescope placed about eight feet away. Readings of level could thus be taken to 0.1 mm. or a little better, which suffices to give an accuracy of 0.01% in the corrected flow times.

U-tube Viscometer No. 1 (B. S. S.) with a constant of 0.004,25 was used in these preliminary experiments, and it gave flow times ranging from 350 secs. at 10°C., to 150 secs. at 55°C. Since three to five measurements are taken at each temperature, an accuracy of 0.02 secs. is attainable in the flow time, which, for a measuring interval  $\Delta$  T of 2°C., leads to a reliability of about $\pm 0.4\%$  in the value of the energy  $\epsilon$  calculated by means of the formula (1), which can be put as

$$\varepsilon/\mathbf{k} = -\mathbf{T}^{2} \Delta \ln \eta / \Delta \mathbf{T}$$

$$= -\mathbf{T}^{2} \Delta \ln \nu / \Delta \mathbf{T} - \frac{\mathbf{T}^{2}}{\rho} \Delta \rho / \Delta \mathbf{T}$$

$$= \varepsilon' / \mathbf{k} - \frac{\mathbf{T}^{2}}{\rho} \Delta \rho / \Delta \mathbf{T}, \qquad (2)$$

where the second term constitutes a small slowvarying correction. This estimate of 0.4% corresponds to an error of  $\pm 0.008$  in the calculated quantity  $\frac{\epsilon'/k}{1000}$ , which itself is of the order of 2 in the range of temperatures studied here.

The ethyl alcohol used for the experiments was purified by repeated distillation, the rectified spirits thus collected containing about 5% water. The water content of the samples prepared for the measurement of activation energy was estimated in two different ways, (i) by density measurements before and after each experiment, and (ii) from the absolute value of viscosity measured at a standard temperature during the experiment itself. The two sets of estimates were in essential agreement with each other.

The experiments were split into two parts, the first from room temperature (which was  $25^{\circ}$ C. to  $30^{\circ}$ C.) down to  $5^{\circ}$ C., and then the second from room temperature up to  $55^{\circ}$ C. The visco-

sity measurements were made at intervals of  $2^{\circ}$ C., and the temperature for each reading was maintained by electrical relays to within  $\pm 0.005^{\circ}$ C.

The temperature measurements were made with an accuracy of  $\pm 0.005^{\circ}$ C., using a calibrated fifth degree thermometer with a magnifying thermometer reader. In this way, an accuracy of about 0.5% could be obtained in the measurements of the two-degree temperature intervals  $\Delta$  T. This would correspond to an error of  $\pm 0.010$ in the experimental values of  $(\epsilon/k)/1000$ .

# 3. Experimental Results with Rectified Spirits (containing 6% water)

The results of the first series of experiments with redistilled rectified spirits, extending from 16°C. to 54°C. and corrected for level variation, are given in the first two columns of Table 2, and are plotted in the lowest curve (solid triangles) of Fig. 2, where the short vertical lines indicate the averaged standard deviations estimated experimentally from the differences between the readings obtained with rising and falling temperature sequences. Although these deviations are considerably larger than the expected value of about 0.015, a satisfactory curve can nevertheless be drawn through the experimental points. This curve shows four pairs of alternate maxima and minima with a complete cycle extending over 10° to 12°C. The peak-to-peak amplitude appears to be somewhat variable, and lies between 0.08 and 0.16 units of  $(\epsilon/k)/1000$ , but it is probable that part of this variation is due to the rather large standard deviation (about 0.03) of the individual points. (Although it is not easy to fix wholly the precise cause of this large standard



Fig. 2.—(Lower half) Plots of experimental values of  $(\varepsilon/k)/1000$  for alcohol having 6.1% water. The short verticallines indicate the estimated standard deviations of the plotted points for the two separate experiments, while the radii of the solid circles show the standard deviations of the mean values. (Top half) Corrected mean curve for  $(\varepsilon/k)/1000$  (full line), compared with the graphs based on earlier standard data for alcohol with 5% water (broken line) and 10% water (chain-dotted line).

deviation, it may be noted for comparison that an average value of  $\pm$  0.026 was obtained in the comparable preliminary measurements with ethylene glycol reported in Part II of the present series of communications).<sup>1</sup> The water content of the alcohol, as estimated from its density and value of its viscosity, was found to vary from 5.9% at the beginning of the experiment to 6. 5% at the end, giving a mean of  $6.2\% \pm 0.3\%$ .

104

from 5.6% to 6.4%), and, in addition to the temperature range previously covered, the measurements were taken down to 5°C., which is the lowest temperature easily attainable by circulating icecold water. This enables us to cover an additional complete cycle of variation of the energy  $\varepsilon$ in the low temperature region. The measurements in the region were taken twice so that the means would be comparable in accuracy with the means of the two series of experiments above 16°C. The results of this second series are given in the third and fourth columns of Table 2, and are

A second series of experiments was now carried out with a fresh sample of alcohol (water content

TABLE 2.—PRELIMINARY MEASUREMENTS OF ACTIVATION ENERGY OF VISCOUS FLOW  $\varepsilon$  for Rectified Spirits from 5°C. to 55°C.

Correction	n of I and II	Mea	riment II	Expe	Experiment I	
$T^{2}\beta/1000$ +Residua thermo- metric correction	$\frac{\varepsilon'/k}{1000} = -T^2 \Delta \ln \nu / \Delta T$ ÷ 1000	Temper- ature (°C.)	$\frac{\varepsilon'/k}{1000} = -T^2 \Delta \ln \nu / \Delta T$ ÷ 1000	Temper- ature (°C.)	Temper- ature (°C.) $-T^2 \Delta \ln \nu / \Delta T$ $\div 1000$	
	1.017 + .010	6.0	$1.017 \pm .010$	6.0		
	$1.065 \pm .020$	8.0	$1.965 \pm .020$	8.0	· · · · · · · · · · · · · · · · · · ·	
( 0.083	$1.854 \pm .016$	10.0	1.854 + .016	10.0	_	
-0.03	$1.776 \pm .011$	12.0	1.776 + .011	12.0	and the second second	
(	1.859± .001	14.0	1.859 ±.001	14.0	- pro-	-
	1.912± .038	16.0	1.875	16.0	1.950	16.0
	$1.908 \pm .042$	18.0	1.865	18.0	1.950	18.0
f 0.091	1.8107.008	20.0	1.818	20.0	1.801	20.0
1-0.03	$1.844 \pm .005$	22.0	1.939	22.0	1.848	22.0
	1.8407 .016	24.0	1.856	24.0	1.824	24.0
	1.864± .018	26.0	1.847	26.0	1.882	26.0
	1.896± .019	28.0	1.877	28.0	1.915	28.0
∫ 0.101	$1.814 \pm .007$	29.8	1.807	29.5	1.821	30.0
1-0.03	$1.833 \mp .018$	31.5	1.851	31.0	1.815	32.0
	$1.846 \pm .026$	$33 \cdot 5$	1.820	33.0	1.972	34.0
	1.905± .015	35.5	1.890	35.0	1.920	36.0
	1.880± .000	37.5	1.880	37.0	1.881	38.0
∫ 0.112	$1.920 \mp .035$	39.5	1.954	39.0	1.886	40.0
1-0.03	$1.832 \pm .003$	41.5	1.829	41.0	1.834	42.0
	$1.841 \pm .009$	43.5	1.832	43.0	1.850	44'.0
	1.908± .003	45.5	1.905	45.0	1.910	46.0
	1.918± .036	47.5	1.882	47.0	1.955	48.0
0.121	1.9027.002	49.5	1.904	49.0	1.899	50.0
1-0.03	$1.864 \pm .015$	51.5	1.849	51.0	1.878	52.0
	1.8547 .018	53.5	1.872	53.0	1.836	54.0
	1.88	55.0	1.876	55.0	-	

plotted as hollow circles in Fig. 2 (solid circles below 16°C.). It is seen, after allowing for random errors of the order of 0.03 units of  $(\varepsilon/k)/1000$ , as previously estimated, that the two graphs are in essential agreement, both as regards the temperatures at which the various maxima and minima occur and as regards the mean amplitude.

### 4. Discussion of Results with Rectified Spirits

The means of the two series of measurements are shown in the next two columns of Table 2 together with their deviations, where  $\mp$  indicates that the values from experiment II are higher. An analysis yields an overall standard deviation of  $\pm$  0.017 for the means as shown in the end of Table 2. These means are plotted as solid circles in Fig. 2, and it is to be noted that the minimum and maximum values of the peakto-peak amplitude in this mean graph are 0.070 and 0.150, respectively. The average value of the peak-to-peak amplitude for the two complete waves above  $30^{\circ}$ C. comes out to be 0.088  $\pm$  0.005, while that for the two waves below this temperature is 0.115  $\pm$  0.015. Although the difference between these two figures may be indicative of a progressive increase of amplitude with falling temperature, they can be considered equal within the present limits of experimental error, and we may take the mean peak-to-peak amplitude from  $5^{\circ}$  to  $55^{\circ}$ C. to be 0.102  $\pm$  0.012.

In order to examine the degree of uniformity of the temperature interval per cycle, it is convenient to determine the temperature corresponding to the midpoints between each maximum and the neighbouring minimum. These temperatures are arranged in Table 2(a), together with their first differences. The differences range from 4.8° to 5.7°C., thus showing that the temperature interval for each half cycle is reasonably constant. The overall mean value is  $5.18^{\circ} \pm 0.12^{\circ}$ C., whence we obtain the mean period of one complete cycle to be twice this, i.e. 10.4°  $\pm$  0.2°C.

For comparison with the broken line graph of Fig. 1(b), based on earlier standard data for alcohol containing 5% water , it is necessary to add the small correction term,  $T^2\beta/1000 = -T^2/\rho(\Delta \rho/\Delta T)$ 

 $\div$  1000. Values of this, together with a residual thermometric correction amounting to 0.030, are given in Table 2 (last column). This correction varies slowly, from 0.05 to 0.10, over the whole range of temperatures, and its incorporation will not significantly affect the foregoing quantitative conclusions ragarding the cyclic variation observed in the activation energy. The corrected curve is shown by the full line graph at the top of Fig. 2, while the broken line and the chain dotted line show for comparison the corresponding graphs for alcohol containing 5% and 10% water, respectively, based on the previous standard data as given in Table 1 and Fig. 1(b).

The full line curve (at the top of Fig. 2) lies between the broken and chain dotted lines, and, in the region below 40°C., it would be evenly placed about the previous standard data for ethyl alcohol containing 6.5% water, in satisfactory agreement with the known mean water content of  $6.1\% \pm 0.4\%$  for our experimental samples of rectified spirits. Above 40°C., the curve obtained from the present experiments is higher by about 0.05 units than the previous standard data for alcohol with 6.5% water. This dis-crepancy may be significant, but is nevertheless within the limits of error for the previous standard data, cf. Table 1 and Fig. 1. It can thus be concluded that the present measurements are consistent with earlier standard data, but indicate. in addition, the presence of a cyclic variation with a period of  $10.4^{\circ} \pm 0.2^{\circ}$ C., and a peak-to- peak amplitude of  $0.102 \pm 0.012$  units of  $(\epsilon/k) \div 1000$ . It is to be noted here that, as shown (both experimentally and theoretically) in earlier papers, 1,2 there will be an exactly corresponding cyclic variation in ln 1/A, with a peak-to-peak amplitude of  $(I/T) \times 0.102 \times 1000 = 0.33$ , which yields a ratio of 1.4 for Amax/Amin.

# 5. Experimental Results with Alcohol containing 12% Water

In order to form some idea of the possible changes with water percentage to be expected in the above characteristics of the curves for  $\epsilon/k$ against temperature in the alcohol-water system, another series of experiments was performed with alcohol containing about 12% water. This series

TABLE	2	a	)
	-	100	/ .

Temperature at midpoint of max. and min. (°C.)	9.2 14	2 19.0	24.4 29	).2 34.2	39.8 44.9	50.6
First differences (°C.)	5.0	4.8 5	4 4.8	5.0 5.6	5 5.1 5.7	

is of particular interest because the graphs of Fig. 2 and Fig. 1(b) suggest that some concentration between 6% and 12% water will give an almost constant value of  $\varepsilon/k$  over the whole temperature range from 0°C. to 70°C. The experimental samples were prepared by adding calculated amounts of double-distilled water to the previously dstilled rectified spirits, and the total water content was estimated by the two methods, as before.

A synopsis of the final results obtained from experiments with three samples of this aqueous alcohol is given in Table 3, which shows the mean of three series of experiments, each with a newly blended sample of the aqueous alcohol, the water contents of the three samples being  $12.5 \pm 0.7\%$ ,  $12.2 \pm 0.2\%$ , and  $12.3 \pm 0.8\%$  with an overall mean of  $12.3 \pm 0.5\%$ .

Two facts are immediately noticeable in Table 3. First, that the values of  $(\varepsilon'/k) \div 1000$  show an



Fig. 3.—(Lower half) Plot of values of  $(\varepsilon/k)/1000$  for alcohol containing 12.3% water, obtained as the mean of three separate experiments; the radii of the circles indicate the estimated standard deviation. (Top half) The corrected values of  $(\varepsilon/k)/1000$  compared with the graphs based on previous standard data for alcohol containing 10% water (full line) and 12.5% water (broken line).

overall decrease of just about 0.1 in the 44 degree interval from 10°C. to 54°C., and second, that the cyclic variation with a period of about 10°C., so clearly observed in the samples with 6% water has apparently disappeard. On plotting the data of Table 3 (on an expanded scale for  $\varepsilon'/k$ ), we get Fig. 3, which shows graphs for  $\varepsilon'/k \div 1000$  and for the corrected values, together with the graphs based on previous standard data for alcohol with 10% and 12.5% H2O. It is seen (Fig. 3, lower half) that a small periodic variation with a peakto-peak amplitude of 0.02 units of  $(\varepsilon'/k) \div 1000$ can be traced, even though this amplitude is only twice as great as the standard error of the individual values of Table 3. An estimate of the period of this variation can also be made, and is found to be nearly 8.8°C., as against 10.2°C. observed for the samples containing 6% water.

### 6. Conclusions

These observations suggest that this period changes smoothly from the already known value of 6.2°C. for water<sup>3</sup> to a value somewhat greater than 10°C., perhaps  $2 \times 6.2^{\circ} = 12.4^{\circ}$ C., for pure anhydrous ethyl alcohol. On this hypothesis of a gradual transition, the sinusoidal behaviour observed in ethyl alcohol should, with increasing water-content, gradually give place to the stepwise behaviour observed in the case of pure water, and the corrected graph of Fig. 3 (upper half) suggests that this particular blend (i.e. 12.3%  $H_2O$ ) represents approximately the situation where both these types of behaviour are about equally balanced, resulting in an almost constant value of  $\varepsilon/k \div 1000$  over the whole temperature range examined. For the further elaboration of these ideas, it is necessary

 (a) to extend the experiments to the region of lower as well as higher water-content so as to get a complete picture of these interesting phenomena, and

Table 3.—Mean Results of Measurements of  $\varepsilon'/k \div 1000$  on Alcohol Containing 12.3 $\pm 0.5\%$  Water.

Temperature (°C.)	10.1	12.0	14.0	16.0	18.0	20.0	22.0	24.0	26.0	28.0	30.0	32.0
ε'/k ÷ 1000	2.080 ±.020	2.060 ±.010	2.080 ±.016	2.093 ±.019	2.055 ±.004	2.066 ±.007	2.059 ±.005	2.064 ±.016	2.054 ±.006	2.028 $\pm .012$	2.046 ±.005	$52.0575 \pm .009$
Temperature (°C.)	34.0	36.0	38.0	40.0	42.0	44.0	46.0	48.0	50.0	5 <b>2</b> .0	54.0	-
ε′/k÷ 1000	$2.058 \pm .001$	2.036 ±.009	2.028 ±.007	$2.039 \pm .015$	$2.025 \pm .014$	2.008 ±.013	$2.015 \pm .009$	$\frac{1.991}{\pm .002}$	$2.032 \pm .020$	2.016 ±.020	1.963 ±.010	) —

NOTE:—R. M. S. Standard Deviation for the whole temperature range =  $\pm 0.012$ 

(b) to improve the accuracy of the foregoing measurements by a factor of five to ten, if possible.

Experiments along these lines are in hand, and their results will be reported in later communications.

# References

- M. Naseem and M. M. Qurashi, Pakistan J. Sci. Ind. Research, 1, 197 (1958).
- 2. A. Rauf and M. M. Qurashi, ibid., 2, 30(1959).

- 3. M. M. Qurashi and A. K. M. Ahsanullah, British J. Appl. Phys., in press. Also Pakistan J. Sci. Ind. Research, **3**, 93 (1960).
- Pakistan J. Sci. Ind. Research, 3, 93 (1960).
  G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants* (Longman, Green & Co., London, 12th edition, 1959) p. 36.
- 5. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds* (Elsevier Publishing Co., Inc., London, 1950), p. 311.
- 6. International Critical Tables (McGraw-Hill Book Co., Inc., New York and London, 1929), Vol. V, p. 22.