

THE RELATIONSHIP BETWEEN VISCOSITY AND MOLECULAR STRUCTURE

Part III.—Accurate Measurements of the Temperature Dependence of the Activation Energy of Viscous Flow in Ethylene Glycol*

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1. Introduction

The nature of the connection between the viscosity of hydroxylic and other associated liquids and the molecular structure existing within these liquids has been the subject of detailed investigation in the Central Laboratories.¹⁻⁴ In previous communications,^{3,4} some preliminary results were presented on the temperature variation of the viscosities of mineral oils and of glycerol and ethylene glycol, and graphs showing the activation energy of viscous flow as a function of temperature were obtained. These graphs for glycerol and glycol are reproduced in Fig. 1, and they indicate that in each case the variation of the energy E , occurs in a series of approximately equal step-like segments, the width and depth of which appear to be characteristic of each liquid. Moreover, the corresponding curves for $\ln 1/A$, where A is the concentration factor in the Andrade equation $\eta = A \exp(E/RT)$, show steps whose depths may conceivably be interpreted as whole numbers (2 and 4) governing the size of the molecular aggregates, as appears from Eyring's interpretation of A as $h/(\text{volume of one unit of flow})$. However, the measurements with ethylene glycol were handicapped by the fact that the experimental error was sometimes as much as a quarter of the magnitude of the above effects. It was therefore considered desirable (a) to decrease this experimental error as much as possible, and (b) to take measurements with a smaller temperature interval ΔT between successive readings, so as to examine the variation of E within each segment, which extends over nearly 13°C . in the case of ethylene glycol. As pointed out at the end of Part II of this series of papers,⁴ both these desiderata can be achieved by using a Beckmann differential thermometer and a good stop-watch capable of being read to a fiftieth of a second. The activation energy, E , can then be measured over intervals of 2.5°C ., with an accuracy approaching 0.2%. In the present communication, results obtained with this improved technique are presented for the case of ethylene glycol between the temperatures of 40°C . and 120°C . A connec-

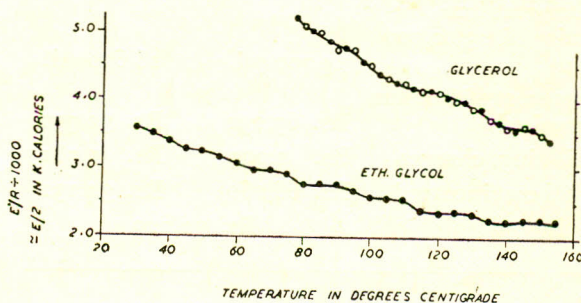


Fig. 1.—Preliminary measurements showing the temperature dependence of activation energy of viscous flow for glycerol and ethylene glycol (from Part II, Figs. 4 and 5).

tion between the variations of E and $\ln 1/A$ is also derived.

2. Experimental Details and Estimation of Corrections

(a) The usual type of Beckmann thermometer has a six-degree scale, graduated in hundredths of a degree, so that readings can be taken to 0.001°C . with the help of a magnifying thermometer reader. It was found preferable not to use the last half-degree at each end, and to work with two 2.5°C . intervals from 0.5 to 3.0 and 3.0 to 5.5 scale degrees. This arrangement gives us 5 to 6 experimental points for each of the segments, and has the added advantage that the calibration corrections to the Beckmann scale are equal and opposite for successive intervals, so that the means of successive points in the graph for energy against temperature will be independent of this calibration error. With the particular thermometer used in the present experiments, this error was found to be $\pm 0.001,5^\circ\text{C}$. for the two intervals of 2.5°C ., which can be ignored, since the individual temperatures are read to 0.001°C . and the probable observational error in ΔT is therefore $0.001,4^\circ\text{C}$. However, a small residual correction for the value of the mean Beckmann degree remains outstanding, and is found from the expansion of mercury to be as follows:

Temperature ($^\circ\text{C}$.)	0	50	100	150
Size of Beckmann degree ($^\circ\text{C}$.)	0.996	0.998	1.000	1.002

*This communication is based on a thesis presented by Abdul Rauf for the degree of M.Sc. to the University of Karachi.

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(b) There is now the problem of attaining an equivalent percentage accuracy in the measurement of $\Delta \ln v \simeq \Delta \ln t$.

If $\bar{t} = 1/2 (t_1 + t_2)$, and $\Delta t = t_2 - t_1$, then

$$\begin{aligned} \Delta \ln t &= \ln t_2 - \ln t_1 = \ln \frac{t_2}{\bar{t}} - \ln \frac{t_1}{\bar{t}} \\ &= \ln \left(1 + \frac{\Delta t}{2\bar{t}} \right) - \ln \left(1 - \frac{\Delta t}{2\bar{t}} \right) \\ &= 2 \left(\frac{\Delta t}{2\bar{t}} + \frac{1}{3} \left(\frac{\Delta t}{2\bar{t}} \right)^3 + \dots \right) \\ &= \frac{\Delta t}{\bar{t}} \left(1 + \frac{1}{12} \left(\frac{\Delta t}{\bar{t}} \right)^2 + \dots \right), \quad (1) \end{aligned}$$

which shows that the percentage accuracy of $\Delta \ln t$ is equal to that of Δt . The result (1) is especially useful in our calculations for $\Delta \ln v / \Delta T$ because the term $1/12 (\Delta t / \bar{t})^2$ is always very small and often negligible as $\Delta t / \bar{t}$ is of the order of 0.1 in the experiments described here, e.g. from $E/R \sim -T^2 \Delta \ln v / \Delta T$, we get $\Delta t / \bar{t} = 0.08$ for $T = 350^\circ \text{K}$, $(E/R)/1000 = 4$, and $\Delta T = 2.5^\circ \text{C}$.

It is now clear from equation (1) that, in order to attain an accuracy of 0.2% in $\Delta \ln t$, i.e. $(t_2 - t_1) / \bar{t}$, we must measure t_1 and t_2 to an accuracy of $1/\sqrt{2} \times 0.08 \times 0.2\%$, i.e. 1 part in 8,000, for which a good stop-watch, readable to 0.02 second, must be used because the times of flow will be of the order of 100 seconds. Further, the mean of several measurements of flow time should be taken in order to eliminate the effect of personal error, which may amount to 0.05 second in a single measurement. It will also be necessary to make corrections for the kinetic energy of flow and for the variation of liquid level in the viscometer. In Part I (Appendix II) the following equation was developed³

$$\begin{aligned} -\frac{\Delta \ln v}{\Delta T} &= - \left(\frac{\ln t_2 - \ln t_1}{T_2 - T_1} \right) \left(1 + 2 \frac{B/A}{\bar{t}^2} \right) \\ &+ \frac{\alpha}{100} \frac{x_2 - x_1}{T_2 - T_1} \quad (2) \end{aligned}$$

where t_1 and t_2 are the times of flow at temperatures T_1 and T_2 , respectively, and x_1 and x_2 are the corresponding heights of the liquid level above the fiducial mark of the large viscometer bulb. A and B are the constants in the equation $v = At - B/t$, while α is the percent increase in flow time for $x = 1$ cm., and is usually a little less than unity for the British standard pattern of

U-tube viscometer. Thus if $T_2 - T_1 = 2.5^\circ \text{C}$., and an accuracy of 0.2% is aimed at in $\Delta \ln v / \Delta T$ (~ 0.03), the measurement of x_1 and x_2 should be accurate to $0.03 \times \frac{2.5}{\sqrt{2}} \times 0.2$ cm., i.e. 0.1 mm.

The correction for the changing level varies very slowly with temperature, and it is sufficient to measure the rise in level produced during a 20°C . rise in temperature and thence to estimate the correction for a 2.5°C . temperature difference. A mean value of 0.08 cm. rise for $\Delta T = 2.5^\circ \text{C}$. was obtained with the viscometers used in the present set of experiments.

In equation (2), the term $\Delta \ln t / \Delta T \times 2 \frac{B/A}{\bar{t}^2}$, which corresponds to the kinetic energy correction, is very small, its magnitude being of the order of 0.0003 ± 0.0001 for the readings taken with viscometer No. 2, and about 0.00005 for those taken with viscometer No. 1, which amount to somewhat less than 1% and 0.3% respectively of the measured quantity, $-\Delta \ln v / \Delta T$, and have a very small variation with temperature. Since most of the measurements described in this communication were made with viscometer No. 1, the kinetic energy correction can be neglected.

(c) The correction to be made for measuring v in place of η was also derived in Part I (Appendix II)³ as

$$E/R = -T^2 \Delta \ln \eta / \Delta T = -T^2 \Delta \ln v / \Delta T + T^2 \beta, \quad (3)$$

where $\beta = -(d\rho/dT)/\rho$, and can be determined from the coefficient of dilatation of the experimental liquid. For ethylene glycol, the International Critical Tables give the standard formula,

$$\rho_t = 1.1257 - 0.5713 \times 10^{-3} t - 2.766 \times 10^{-6} t^2 + 10.9 \times 10^{-9} t^3 \dots \quad (4)$$

which is correct to within 0.001 in the range 0°C . to 136°C . Differentiation gives

$$-10^3 d\rho/dt = 0.5713 + 2 \times 2.766 \times 10^{-3} t - 3 \times 10.9 \times 10^{-6} t^2, \quad (5)$$

whence β is readily calculated. Table I gives the values of ρ , β , and $T^2 \beta$, calculated at intervals

TABLE I.—CORRECTION FOR DILATATION OF GLYCOL.

Temperature (C.)	20	40	60	80	100	120
Density ρ g./ml.	1.113	1.099	1.084	1.068	1.052	1.036
$1000 \times \beta$	0.601	0.673	0.724	0.753	0.758	0.739
$T^2 \beta / 1000$	0.052	0.066	0.080	0.094	0.105	0.114

of 20°C. from 20°C. upto 120°C. from which the correction $T^2\beta/1000$ appears to be quite significant at the higher temperatures.

(d) A special precaution for all experimental work with ethylene glycol is the use of water-free material and the prevention of subsequent moisture absorption. Pure ethylene glycol (supplied by Griffin and Tatlock) was first redistilled under a pressure of 25 mm. of mercury, only the fraction coming over at 108°C. to 109°C., being accepted, after which the distillate was dried in vacuum over sulphuric acid and stored in a vacuum desiccator. For transferring the glycol into the viscometer with a minimum uptake of moisture from the atmosphere, the special pipette shown in Fig. 2(a) was constructed, having a stop-cock and drying tube attached to its upper end. The pipette was first flushed with dry air by gently pumping air into it through the drying tube and then glycol

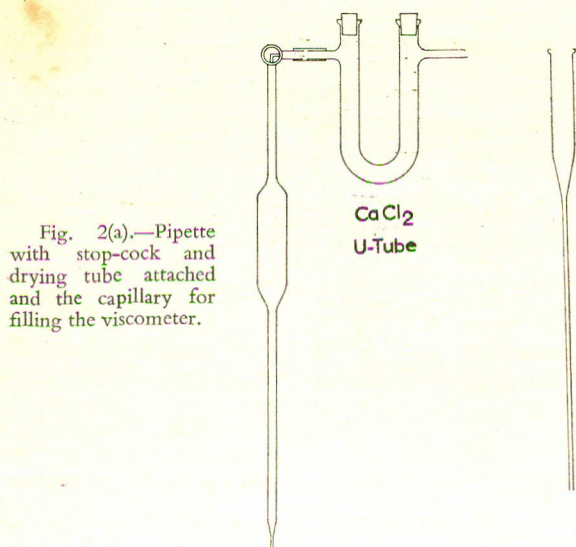


Fig. 2(a).—Pipette with stop-cock and drying tube attached and the capillary for filling the viscometer.

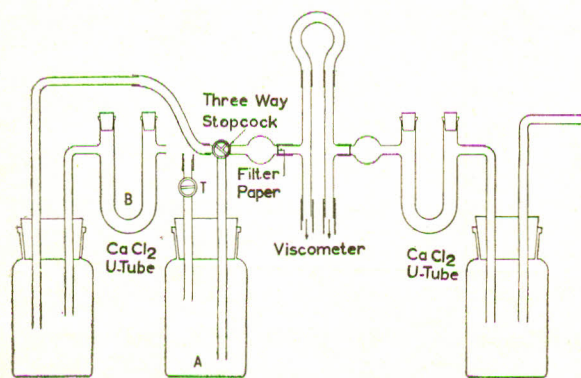


Fig. 2(b).—System of drying tubes, cocks, and ballast bottle for operating the viscometer without the entry of moist air.

was sucked into the pipette. The required volume of glycol was run into the viscometer, which had drying tubes, stop-cocks, and a ballast bottle A attached to it as shown in Fig. 2(b). The ballast bottle and the cocks are used to control the sucking up of the liquid in the capillary limb of the viscometer, as described⁴ in Part II of this paper, the three-way stop-cock serving to connect this capillary limb either with A, the ballast bottle (in which a slight vacuum is previously created by suction, after which the cock T on the bottle is closed), or with B, the drying tube, whose other end is open to the atmosphere.

3. The First Series of Measurements

The viscometer was supported vertically inside an electrically heated glycerine bath³ (Part I, Fig. 2) whose temperature could be controlled to within 0.002°C. by means of an automatic glycerine-filled control thermometer, provided that large fluctuations of mains voltage were compensated manually. The temperature range from 40°C. to 120°C. was covered in two stages of about 40°C. each, with an overlap of a few degrees near 80°C. In this first set of measurements, a British standard U-tube viscometer No. 2 (constant = 0.056) was used for the range of 40°C. to 80°C. and viscometer No. 1 for the higher temperature range in order to obtain sufficiently long times of flow. The viscometer was carefully filled (by means of a tube drawn into a capillary, Fig. 2(a), so as to avoid wetting the viscometer tube above the main bulb) and the volume of glycol was adjusted so that at the starting temperature (42.5°C. in the first set) the level was about 3 mm. below the fiducial mark on the tube immediately above the bulb, in order to allow for expansion of the glycol with rise of temperature.

The glycol having been completely enclosed in the viscometer with its system of drying tubes, the temperature of the bath was adjusted manually to within a few tenths of a degree, and then the Beckmann thermometer was adjusted to read nearly 5.5 degrees (minus) when placed in the bath. The automatic temperature control was then set to maintain the Beckmann reading steady at some value within 0.02 of 5.50° when the temperature had remained steady for nearly twenty minutes, five successive readings of the time of flow were taken with a calibrated stop-watch, the Beckmann reading being noted at regular intervals of 20 seconds during the flow. The means of the flow times as well as of the Beckmann readings were recorded, together with their respective standard deviations. The temperature was then raised until the Beckmann reading corresponded to 3.00, and the foregoing set of

measurements were repeated at this temperature, and then in the same way flow times were recorded for a reading of 0.50. The left-hand half of Table 2(a) shows these readings for a mean Beckmann reading of 3.012, while the right-hand half shows the corresponding measurements taken during the cooling of the bath as described below. The bath temperature was raised about 0.5°C. (so that the Beckmann reading was nearly 0.00), maintained at this value for a few minutes, and then lowered successively to 0.50, 3.00 and 5.50 at each of which temperatures, the flow times and Beckmann readings were recorded as before.

It is seen from Table 2(a) that (i) the temperature fluctuation is of the order of $\pm 0.003^\circ\text{C}$., (ii) the mean temperature during any one flow period, being obtained from seven readings, should be accurate to better than 0.001°C ., and (iii) the standard error of the mean time of flow for five observations is of the order of 0.03 seconds, which corresponds to an accuracy of 1 part in 4000. This is slightly short of the accuracy aimed at, and therefore this viscometer (No. 2) was used for the lower temperature range in the first set of experiments only, while viscometer No. 1 (which gives flow times ten times as long) was used for all succeeding measurements. Table 2(b) gives the overall mean values of the flow times and the Beckmann readings over the first 5 degree interval together with the calculated values of $-T^2(\Delta \ln t / \Delta T) / 1000 = (E'/R) / 1000$. The table shows satisfactory agreement between the values of this quantity obtained during the heating and cooling of the bath, the standard deviations of the final means being about ± 0.012 , which corresponds to an accuracy of 0.3%.

The results obtained from the first series of experiments are shown in Table 3, the range from 76°C . to 120°C . having been covered with fresh sample of glycol in viscometer No. 1. Two facts about the values calculated for $(E'/R) / 1000$ are noteworthy: (1) the standard deviation of the means obtained from the measurements with rising and falling temperatures in the lower temperature range is nearly 0.015, and (2) there is a systematic tendency at temperatures above 75°C . for the value under the heading "temperature rising" to be higher than the corresponding value under the heading "temperature falling", the magnitude of the difference rising from 0.02 for 75°C . upto 0.16 for 110°C . (inset to Fig. 3). This difference is attributable to the gradual loss of glycol by evaporation, but, due to the symmetrical mode of taking observations with rising and falling temperatures, the means of corresponding values in the two columns will be substantially independent of the error due to

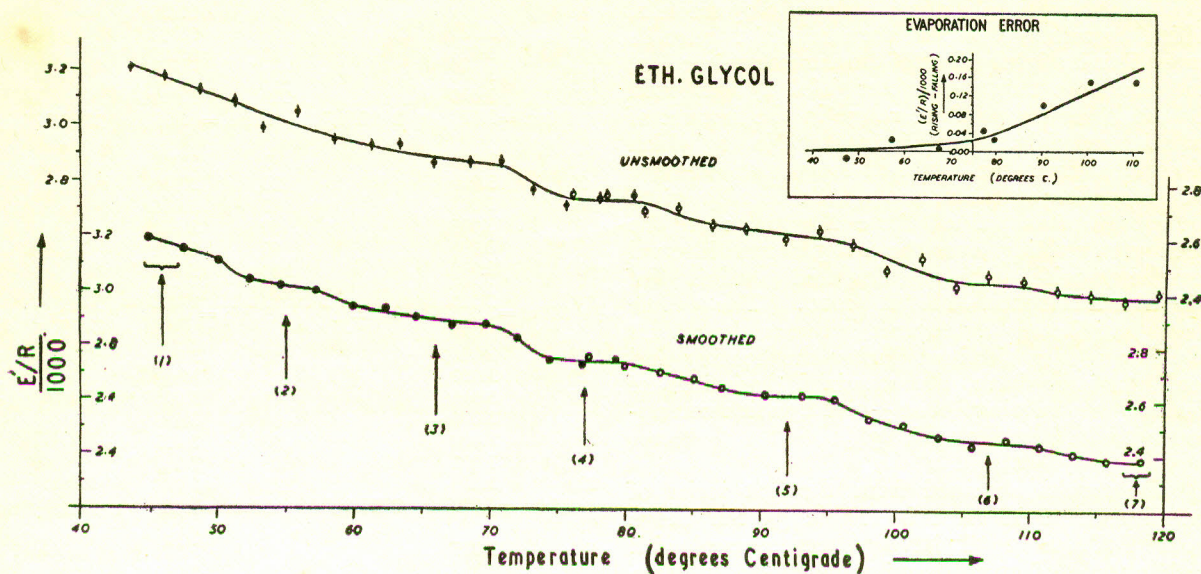
this cause. These mean values are plotted against temperature as the upper graph in Fig. 3, and they confirm the presence of step-like segments previously observed in the preliminary measurements shown in Fig. 1. The scatter of the points is nearly ± 0.02 , which is in reasonable agreement with

TABLE 2(a).—TYPICAL SET OF MEASUREMENTS WITH VISCOMETER NO. 2 AT 44.85°C .

Temperature rising			Temperature falling		
Time elapsed since commencement (secs.)	Reading on Beckmann thermometer	Time of flow	Time elapsed since commencement (secs.)	Reading on Beckman thermometer	Time of flow
0	3.014		0	3.003	
20	3.019		20	3.001	
40	3.021		40	3.006	
60	3.023		60	3.010	
80	3.020		80	3.005	
100	3.020		100	3.005	
120	3.020		120	3.004	
Mean = 3.020		2' 12.94"	Mean = 3.005		2' 12.94"
0	3.010		0	3.005	
20	3.000		20	3.010	
40	3.003		40	3.016	
60	3.005		60	3.020	
80	2.998		80	3.021	
100	2.999		100	3.022	
120	2.992		120	3.026	
Mean = 3.001		2' 12.80"	Mean = 3.017		2' 12.90"
0	3.020		0	3.010	
20	3.020		20	3.012	
40	3.013		40	3.020	
60	3.004		60	3.023	
80	3.002		80	3.025	
100	3.001		100	3.027	
120	3.000		120	3.024	
Mean = 3.009		2' 13.06"	Mean = 3.020		2' 12.90"
0	3.015		0	3.021	
20	3.017		20	3.030	
40	3.020		40	3.030	
60	3.014		60	3.029	
80	3.014		80	3.027	
100	3.012		100	3.015	
120	3.012		120	3.007	
Mean = 3.015		2' 12.92"	Mean = 3.023		2' 12.86"
0	3.017		0	3.004	
20	3.017		20	3.006	
40	3.018		40	3.012	
60	3.018		60	3.020	
80	3.013		80	3.026	
100	3.016		100	3.010	
120	3.014		120	3.010	
Mean = 3.106		2' 12.98"	Mean = 3.013		2' 12.90"
Overall means	3.012	2' 12.94"	Overall means	3.016	2' 12.90"
	± 0.003	± 0.04 "		± 0.003	± 0.01 "
Temperature of bath = 44.85°C .			Temperature of bath = 44.85°C .		

TABLE 2(b).—CALCULATIONS FOR THE VALUES OF $\left(-\frac{T^2}{1000} \frac{\Delta \ln t}{\Delta T}\right)$ AT 43.6°C. AND 46.1°C.

	Mean Beckmann reading	Mean time of flow (secs.)	$T_1 - T_2 = \Delta T$	$t_1 - t_2 = -\Delta t$	$-\frac{\Delta \ln t}{\Delta T} \times 100$	Mean temperature °C.	$-\frac{T^2}{1000} \frac{\Delta \ln t}{\Delta T}$	Mean of values for heating and cooling sequences
Heating sequence	5.499 ± 0.002	143.98 ± 0.04	2.487	11.04 ± 0.06	$3.206 \pm .017$	43.6 ₁	$3.214 \pm .018$	3.208 ± 0.008
	3.012 ± 0.003	132.94 ± 0.04		2.488	9.88 ± 0.06	$3.104 \pm .018$	46.1 ₀	
	0.524 ± 0.001	123.06 ± 0.05						
Cooling sequence	5.510 ± 0.002	143.93 ± 0.04	2.494	11.03 ± 0.04	$3.196 \pm .012$	43.6 ₀	$3.203 \pm .012$	3.182 ± 0.016
	3.016 ± 0.003	132.90 ± 0.01		2.502	10.06 ± 0.04	$3.146 \pm .012$	46.1 ₀	
	0.514 ± 0.002	122.84 ± 0.04						

Fig. 3.—First series of results for the temperature variation of $(E'/R)/1000$ for ethylene glycol: upper graph; unsmoothed; lower graph, smoothed; inset, dependence of evaporation error on temperature.

the estimates of random error obtained from Table 3 and the inset to Fig. 3. In order to decrease the scatter still further, smoothed values of $\frac{E'/R}{1000} = -\frac{T^2}{1000} \frac{\Delta \ln t}{\Delta T}$ have been calculated in Table 3 by taking the means of experimental values at successive temperatures, and these smoothed values are plotted in the lower graph of Fig. 3, which brings out the regular recurrence of the steps more clearly than does the upper graph. However, the process of smoothing obscures the detail present in intervals of less than 5°C., and therefore it was considered preferable to increase the accuracy by repeating the whole series of

measurements over the range 40°C. to 120°C. Such a repetition would also serve as a check on the reproducibility of the steps observed in the curve.

4. Second Series of Measurements

Fresh samples of redistilled ethylene glycol were used, and the values of $(E'/R)/1000$ obtained from this second set of measurements are given in Table 4(a) alongside of the corresponding values from the first series. The standard deviations for the second set were found to be about two-thirds

TABLE 3.—VALUES OF $(E'/R)/1000$ OBTAINED FROM THE FIRST SERIES OF MEASUREMENTS.

Mean temperature (°C)	$\frac{T^2}{1000} \frac{\Delta \ln t}{\Delta T} = \frac{E'}{R} / 1000$			Smoothed $\frac{E'}{R} / 1000$	Mean temperature (°C)	$-\frac{T^2}{1000} \frac{\Delta \ln t}{\Delta T} = \frac{E'}{R} / 1000$			Smoothed $\frac{E'}{R} / 1000$
	temperature rising	temperature falling	Mean			Tempera- ture rising	Temperature falling	Mean	
43.60	3.214	3.203	3.208±8		76.10	2.776	2.760	2.768±8	
46.10	3.160	3.203	3.182±16	3.195	78.55	2.773	2.756	2.764±10	2.766
48.73	3.136	3.125	3.130±9	3.156	81.33	2.762	2.656	2.709±15	2.736
51.20	3.071	3.115	3.093±17	3.112	83.83	2.754	2.680	2.717±7	2.713
				3.044					2.686
53.30	3.024	2.966	2.995±21		86.40	2.721	2.592	2.656±16	
55.75	3.081	3.018	3.050±22	3.022	88.90	2.669	2.619	2.644±8	2.650
58.53	2.965	2.936	2.951±13	3.000	91.86	2.661	2.546	2.604±10	2.624
61.15	2.919	2.956	2.938±14	2.944	94.36	2.689	2.585	2.637±7	2.620
				2.942					2.610
63.33	2.987	2.903	2.945±25		96.82	2.643	2.525	2.584±8	
65.83	2.883	2.865	2.874±10	2.910	99.33	2.571	2.415	2.493±14	2.538
68.47	2.895	2.874	2.884±10	2.879	101.98	2.640	2.434	2.537±22	2.515
70.85	2.888	2.882	2.885±15	2.884	104.51	2.492	2.370	2.431±10	2.484
				2.834					2.452
73.13	2.835	2.734	2.784±30		106.93	2.562	2.381	2.472±11	
75.57	2.690	2.760	2.725±35	2.754	109.51	2.519	2.386	2.452±12	2.462
78.00	2.797	2.713	2.755±26	2.740	111.95	2.545	2.301	2.423±19	2.438
80.55	2.807	2.722	2.764±25	2.760	114.45	2.532	2.268	2.400±21	2.412
									2.387
					116.97	2.455	2.293	2.374±14	
					119.50	2.498	2.312	2.405±15	2.390

NOTE.—The standard deviations have been obtained as the means of two estimates, namely the errors in time and temperature measurements and the differences between measurements made with rising and falling temperature sequences (with allowance for evaporation error in the higher temperature range).

of those for the first set, which is partly due to the use of viscometer No. 1 throughout, and partly to an improvement in technique consequent upon practice. The degree of agreement between the results of the two sequences of measurements is consistent with their separate standard errors, when account is taken of the systematic defect of 0.02 to 0.04 due to the larger kinetic energy correction for viscometer No. 2, which was used in the lower temperature range for the first series. The data obtained from the second series of measure-

ments are plotted in Fig. 4, the smoothed graph in which is seen to agree remarkably well with the corresponding (smoothed) graph in Fig. 3. A comparison of the temperatures at the middle of the flat parts of the successive steps is made in Table 4(b) for the two series of measurements, and shows agreement to within 1.5°C., thus providing an excellent confirmation of the reproducibility of the experimental data. The mean interval between successive steps is found to be $11.2^\circ \pm 0.7^\circ\text{C}$.

TABLE 4(a).—COMPARATIVE TABLE OF VALUES OF $(E'/R)/1000$ OBTAINED FROM THE TWO SERIES OF MEASUREMENTS.

Second series		First series		Overall mean		Total correction	Second series		First series		Overall mean		Total correction
Temp.	$\frac{E'/R}{1000}$	Temp.	$\frac{E'/R}{1000}$	Temp.	$\frac{E'/R}{1000}$		Temp.	$\frac{E'/R}{1000}$	Temp.	$\frac{E'/R}{1000}$	Temp.	$\frac{E'/R}{1000}$	
40.45	3.264			40.45	(3.264)	0.090	78.02	2.776	76.10	2.768	77.05	2.772	0.095
42.95	3.252	43.60	3.208	43.3	3.230		80.42	2.758	78.55	2.764	79.5	2.761	
46.01	3.199	46.10	3.182	46.05	3.190				81.33	2.709	80.9	2.734	
48.51	3.186	48.73	3.130	48.6	3.158		83.67	2.717	83.83	2.717	83.75	2.717	
50.80	3.158	51.20	3.093	51.0	3.126	0.095	86.18	2.694	86.40	2.656	86.3	2.675	0.095
53.40	3.052	53.30	2.995	53.35	3.024		88.96	2.641	88.90	2.644	88.95	2.642	
56.04	3.051	55.75	3.050	55.9	3.050		91.45	2.671	91.86	2.604	91.65	2.638	
58.54	3.102	58.53	2.951	58.55	3.026		94.34	2.601	94.36	2.637	94.35	2.619	
61.16	2.973	61.15	2.938	61.15	2.956	0.100	96.87	2.609	96.82	2.584	96.85	2.596	0.100
63.65	2.865	63.33	2.945	63.5	2.905		99.66	2.524	99.33	2.493	99.5	2.508	
66.37	2.959	65.83	2.874	65.6	2.916		102.1	*	101.98	2.537	100.7	2.515	
68.88	2.898	68.47	2.884	68.7	2.891		104.66	2.540	104.51	2.431	103.2	2.484	
71.38	2.853	70.85	2.885	71.1	2.874	0.105				104.6	2.486		
73.87	2.834	73.13	2.784	73.5	2.809		107.21	2.464	106.93	2.472	107.05	2.468	0.105
76.25	2.771	75.57	2.725	75.9	2.748		110.36	2.471	109.51	2.452	109.95	2.462	
78.75	2.735	78.00	2.755	78.4	2.745		112.90	2.473	111.95	2.423	112.4	2.448	
—	—	80.55	2.764	80.55	(2.764)	0.110	116.10	*	114.45	2.400	115.7	2.387	0.110
							118.67	*	116.97	2.374	118.25	2.390	
									119.50	2.405			

*The measurements at 102°C. was accidentally missed out, while those at 116.1°C. and 118.7°C. were rejected because a particle had found its way into the liquid in the viscometer.

TABLE 4 (b).—COMPARISON OF TEMPERATURES AT MIDDLE OF FLAT PART OF STEPS IN THE TWO SERIES OF MEASUREMENTS.

Ordinal No. of step ..	I	2	3	4	5	6
Temperature from 1st series (°C.)	47.5	56	66.5	79.5	93	104
Temperature from 2nd series (°C.)	47.5	57	66.5	80	91.5	102.5
Mean (°C.)	47.5	56.5	66.5	79.8	92.2	103.2
First Differences (°C.) ..		9.0	10.0	13.3	12.4	11.0

TABLE 5.—MEAN VALUES OF $\frac{E'/R}{1000}$ AND TEMPERATURE AT THE MIDDLE OF THE FLAT PORTIONS OF THE STEPS.

Ordinal No. of flat	1	2	3	4	5	6	7
$\frac{E'/R}{1000}$ for flat ..	3.19	3.040	2.900	2.752	2.632	2.468	2.375
Correction ..	0.090	0.095	0.100	0.100	0.100	0.105	0.110
T_m = Temperature at middle of flat (°C.)	46.0	55.5	66.5	78.5	92.0	106.5	~ 119

The mean value of $(E'/R)/1000$ at corresponding temperatures in the two series of measurements can now be taken. These means are also given in Table 4(a) and are plotted in the upper curve of Fig. 5, in which the hollow circles are for the high

temperature range, and the four crosses correspond to points taken from the smoothed values of Table 3, due to the accidental non-availability of the corresponding observations in the second series of measurements. The mean graph brings out the

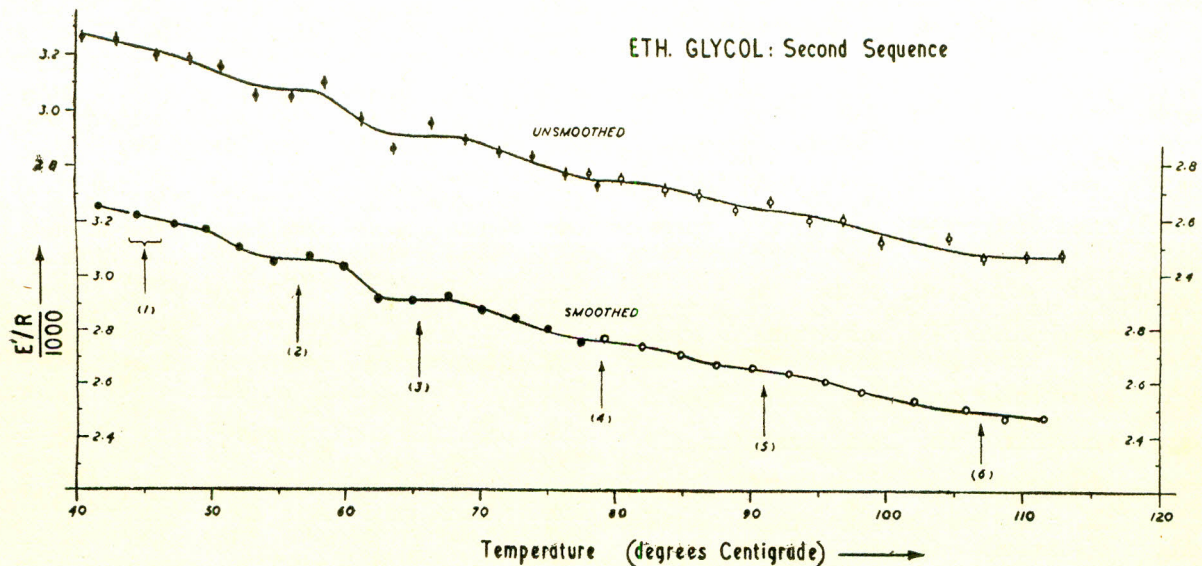


Fig. 4.—Graphs of second sequence of measurements of $(E'/R)/1000$ for ethylene glycol: upper graph; unsmoothed; lower graph smoothed.

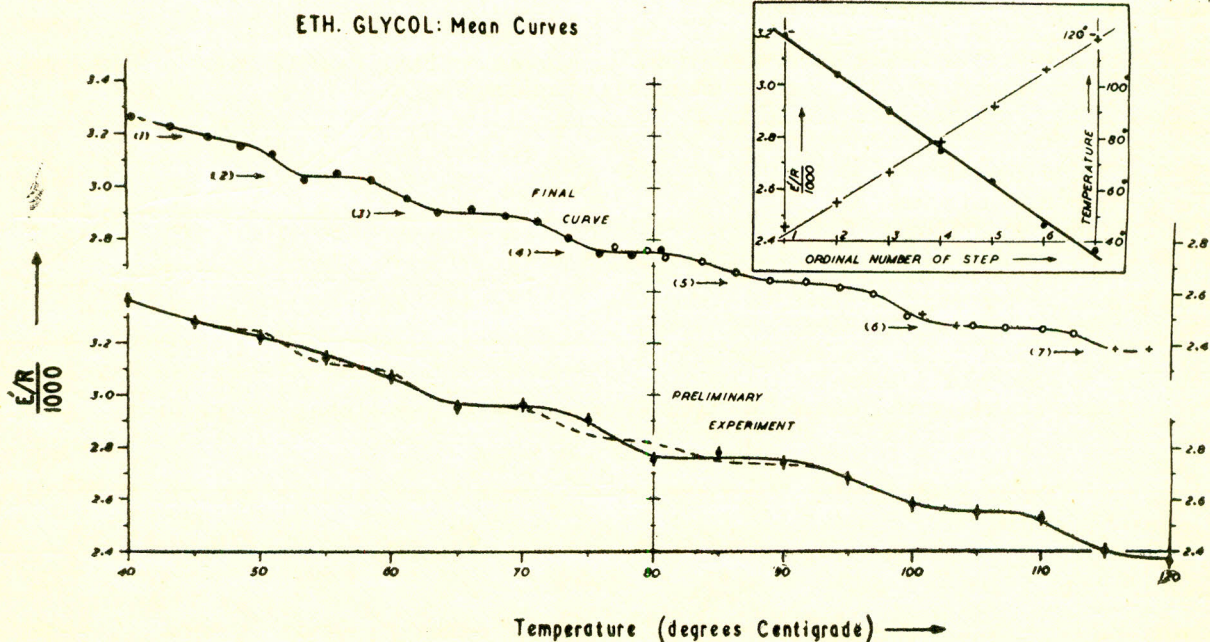


Fig. 5.—Mean curve for $(E'/R)/1000$ (upper graph) compared with the preliminary data of Fig. 1 (lower graph), the standard errors being indicated by the radii of the circles in the upper graph and by the short vertical lines in the lower graph. The inset shows plots of $(E'/R)/1000$ and of temperature at the middle of the flats against the ordinal number of the step.

regularity of the steps very well, the r.m.s. scatter of the points about the graph being only 0.014, while the average height of the steps is nearly 0.14 units of $(E/R)/1000$, i.e. ten times as great. Detailed comparison of the steps with the corresponding portion of the graph obtained from the preliminary data of Fig. 1 (re-plotted in the lower part of Fig. 5, the short vertical lines representing the estimated standard deviations) shows discrepancies only in the neighbourhood of 57°C. and 77°C. Both of these can, however, be removed by drawing the preliminary curve as indicated by the broken line, which is still consistent with the known standard error of ± 0.025 unit in the plotted points. It is clear that the upper graph represents a considerable improvement in two different ways: (a) the standard deviation has been decreased by a factor of two, and (b) twice as many experimental points have been obtained with half the previous measuring interval of temperature.

5. Discussion of the Characteristics of the Steps

In Table 5 are collected the data on the flat portions of the steps as obtained from the upper graph of Fig. 5. These data are plotted in the inset to Fig. 5, and they provide evidence for the constancy of the interval between successive steps with regard to both energy and temperature. The mean corrected energy interval $\Delta E/R$ is found to be $0.138 - 0.004 \pm 0.009$, and the mean temperature interval is $12.1 \pm 0.7^\circ\text{C}$. (cf. the value of $11.2 \pm 0.7^\circ\text{C}$. obtained from Table 4(b)). The exact constancy of both these quantities cannot however be regarded as proved unless the data are extended down to the freezing point, which it is hoped to do in a further set of experiments.

It is also important to determine accurately the shape of the curve over any one step, which can best be done by averaging the variation observed over a range of about 17°C. in each of the six steps for which data can be obtained from Fig. 5. For this purpose we plot each step starting with the origin at the relevant coordinates of $(E/R)/1000$ and temperature given in Table 5, and then obtain

the means of the corresponding sets of points for each value of $\Delta T = (T - T_m)$. This process yields the mean values given in Table 6 and plotted in Fig. 6. The flat part of the step is seen to extend over about 4°C., i.e. one-third of the temperature interval between steps, while the oblique portion extends over the remaining two-thirds. Since the size of the measuring intervals is 2.5°C. and the averaging of the six segments obscures some of the detail over another $\pm 1^\circ\text{C}$., it appears that, even for an infinitely small measuring interval, the flat region of the experimental curve of Fig. 6 will be increased by at most 2°C. on either side. The extent of the horizontal portion is therefore definitely less than 8°C. its most probable value being $6.0 \pm 1.0^\circ\text{C}$. It follows that the extent of the oblique portion is $12.1^\circ - (6.0 \pm 1.0^\circ)$, i.e. $6.1^\circ \pm 1.0^\circ\text{C}$. Thus the transition from one step to the next appears to be spread over a range of nearly 6°C., and should therefore be of the second order, like the magnetic (ferromagnetic \rightleftharpoons paramagnetic) transformation and the order \rightleftharpoons disorder transition in alloys, etc. The energy jump at each step is equal to $0.135 \times 0.086 \text{ e.v.} = 0.012 \text{ e.v.}$, which corresponds to energies in the far infra-red region of molecular rotations. It must

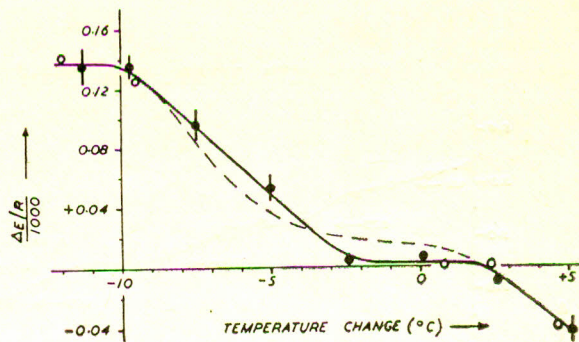


Fig. 6.—The full line shows the mean variation of $(E/R)/1000$ over one step, the standard errors of the plotted points being indicated by the short vertical lines. The broken line is drawn for a truly sinusoidal variation. The hollow circles have been plotted by shifting the solid circles through 12.0°C . and 0.135 units of $(E/R)/1000$.

TABLE 6.—AVERAGED VARIATION OF $\frac{\Delta E/R}{1000}$ OVER ONE COMPLETE SEGMENT.

$T = T - T_m (^\circ\text{C})$	-11.3	-9.7	-7.5	-5.0	-2.4	+0.1	+2.6	+5.1
$\left(\frac{\Delta E/R}{1000}\right)_{\text{corr.}}$	0.133 ± 0.012	0.134 ± 0.008	0.094 ± 0.010	0.054 ± 0.008	0.005 ± 0.004	0.007 ± 0.003	-0.009 ± 0.002	-0.041 ± 0.008

however be noted that the standard deviations of the mean values of Table 6 and Fig. 6 are considerable, amounting to as much as 10% of the value of the energy step, and are about twice what had been expected from the accuracy of the experimental data. This leaves room for the possible presence of some steps or other variation with a smaller temperature interval than 12°C., for the further investigation of which it is desirable to obtain experimentally the complete equation of the transition curves between steps, from more precise measurements using a smaller measuring interval of 1°C. It may, nevertheless, be pointed out that the experimental curve is not sinusoidal, cf. the very significant departure from the sinusoidal curve depicted by the broken line in Fig. 6.

6. The Variation of the Factor A

Finally, it is to be noted that the variation of $\ln 1/A$, where A is the concentration factor in the Andrade equation, $\eta = A \exp\left(\frac{E}{RT}\right)$, (6)

runs parallel to that of E/R. This result was noted in previous papers, and can be shown to be generally true, because we have

$$\frac{E}{R} = -T^2 d \ln \eta / dT, \text{ which yields}$$

$$-d \ln \eta = \frac{E}{R} \frac{dT}{T^2},$$

$$\text{i.e. } - \left| \ln \eta \right|_1^2 = \int_1^2 \frac{E}{R} \frac{dT}{T^2} = - \left| \frac{E}{RT} \right|_1^2$$

$$+ \int_1^2 \frac{d}{dT} \left(\frac{E}{R} \right) \frac{dT}{T}$$

after integration by parts, and therefore

$$\left| \frac{E}{RT} \right|_1^2 - \left| \ln \eta \right|_1^2 = \int_1^2 \frac{d(E/R)}{T}. \quad (7)$$

From equation (6) we get $-\ln A = \frac{E}{RT} - \ln \eta$, whence we obtain with the help of equation (7),

$$\Delta \ln (1/A) = - \left| \ln A \right|_1^2 = \left| \frac{E}{RT} \right|_1^2 - \left| \ln \eta \right|_1^2$$

$$= \int_1^2 \frac{d(E/R)}{T} = (\overline{1/T}) \int_1^2 d(E/R)$$

$$= \overline{1/T} \Delta \left(\frac{E}{R} \right), \quad (8)$$

where $(\overline{1/T})$ is the mean value of $1/T$ in the range of temperatures considered. This result shows that the variation of $\ln(1/A)$ in any small temperature range is $(\overline{1/T})$ times the corresponding variation to E/R, and indicates that the variations of $\ln 1/A$ and those of E/R are both brought about by one and the same characteristic property of the molecules. Equation 8 enables us to estimate $\Delta \ln 1/A$ over any one segment such as in Fig. 6. If we take the mean temperature as 80°C., then $T=353^\circ$, and $(\overline{1/T}) = 2.83 \times 10^{-3}$, so that $\Delta (\ln 1/A)$ for one step is equal to $2.83 \times 10^{-3} \times (0.135 \pm 0.009) \times 1000 = 0.382 \pm 0.025$

This makes the ratio A_1/A_2 of the two concentration factors equal to 1.46 ± 0.04 , which is definitely not an integer, but may approximate either to $3/2$ or to $\sqrt{2}$.

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