TEMPERATURE DEPENDENCE OF THE INTERMOLECULAR ACTIVATION ENERGY FOR FLOW IN LIQUIDS AND SOLUTIONS

Part VII.—Investigation of Steps in the Activation Energy for Some Light Aliphatic Hydrocarbons (C=6 upto C=12)

TAYEB M. QURESHI AND S.A. BARI

Physics Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

AND

M.M. QURASHI

Defence Science Organization, Ministry of Defence, Government of Pakistan, Karachi

(Received April 2, 1965)

Further accurate measurements of activation energy E_η, of viscous flow have been made on several light hydrocarbons, namely n—Hexane, n-Octane, Iso-Octane, n-Decane and Kerosene oil (Molecular weight=165). With the only exception of Iso-Octane, these results show a regular step-wise structure in E_η at lower temperatures, and cyclic behaviour at fairly high temperatures.

A plot of temperature for this transition versus the number of Carbon atoms, n, gives a smooth curve with the maximum curvature at n=15. An approximately linear graph for log(n) against this transition temperature has been plotted, together with the freezing and boiling points. These graphs suggest the presence of a transition between two *differently ordered* states of the liquids.

The behaviour of iso-Octane is anamolous in that it shows a cyclic variation at the *lower* temperatures, going over into a constant value of E above the transition temperature.

Introduction

The work done in this laboratory so far, on the precise measurements of activation energy of viscous flow E_η, using small measuring intervals of 1° to 2°C., for different liquids such as water, ethylene glycol and benzene, and solutions like dilute aqueous ethyl alcohol, dilute NaCl, have shown a stepwise behaviour in some cases and cyclic variations in others. In the case of water[1] and dilute ethyl alcohol[2] definite step-like variations were found, which are a function of temperature and alcohol concentration, while in similar measurements carried out in B.O.C. "60" oil and high-speed diesel oil in the range of 8° to 150°C., reported in part IV of this series,[3] steps were observed at the lower temperatures and cyclic behaviour at higher temperatures. The results on light lubricating oil showed a step-like variation having a series of short and long steps with a mean interval of 8°C., and changing over to cyclic variation near a temperature of 136°∓3°C. with amplitude of ±0.1 unit of E/R and mean period of about 12°C. (The temperature of 133°C. reported earlier[3] corresponds to the end of the last step, while the first minimum is at 139°C., so that the transition could have occurred anywhere in this range; therefore, it is preferable to quote it as 136°C.∓3°C.). The high-speed diesel oil ($C_{15}H_{32}$) showed long, clear and sharp steps of similar magnitude, viz. 0.1 unit of E/R, with a very definite constancy over long temperature-ranges, finally going over at 120°C.∓2°C. to sinusoidal variations with peak-to-peak amplitude of 0.1 unit of E/R, and period of 12°C. The preliminary data in the range of 10° to 55°C. on n-Decane exhibited only a step-structure, and the jump of 0.08 units of (E/R)/1000 at 20°C. was quite clear. Accordingly, it was considered worthwhile to repeat the measurements on n-Decane to higher temperatures with more precision (by using viscometer No.'O' instead of No. '1') and to extend the observations to lighter hydrocarbons. The present communication describes these new experiments with improved technique on (1) n-Decane (2) n-Octane, together with its isomer 2:2:4 Trimethyl pentane (3) Hexane, and (4) Kerosene oil (Molecular weight=165).

Experimental Technique

The value of E_η is determined as before from the differential of the logarithm of the Andrade equation viz.

$$E/R = \Delta \ln\eta / \Delta(1/T) = -T^2 \Delta \ln\eta / \Delta T,$$

which is equivalent to the established procedure of taking the mean slope of the curve for $\ln\eta$ against 1/T in the range of T and T+ΔT. The equation (1) can be rearranged as follows:

$$E_\eta/R = -T^2\Delta\ln(\nu\times\rho)/\Delta T$$
$$= -T^2\ln\nu/\Delta T + T^2(\tfrac{1}{\rho}\Delta\rho/\Delta T)$$
$$= -E_\nu/R + T^2\beta,$$

where η is dynamic viscosity, ν the kinematic viscosity, β the coefficient of dilatation and $T^2\beta$ is a small slowly varying correction term, which is not applied in the actual data given in the tables, but its values are given for some temperatures.

The details of the experimental technique are essentially the same as for the previous experiments on water, long-chain hydrocarbons and aqueous alcohol containing 4 to 14 percent water,[4] including vapour equilibrium bottle containing some of the liquid under the test to compensate the evaporation by maintaining dynamic equilibrium. Viscometer No. 'O' (constant being 0.000,735) of British Standard Specification 188, was used, and the flow-times fall between 700 seconds to 1600 seconds, depending upon the temperature and liquid used. When the steady state of temperature had been maintained for nearly 20 minutes, four to six readings were taken for each temperature, and times of flow were measured with a calibrated stop watch graduated to 0.1 seconds, thus giving a reading accuracy of $\pm$0.02 seconds for each temperature. The actual temperature was read on an ordinary mercury thermometer graduated to 0.1°C., whereas the thermal interval ΔT was recorded with a carefully calibrated Beckmann differential thermometer of nearly six degree scale. The height of meniscus of the liquid over the fiducial mark (above the large viscometer bulb) was determined by a cathetometer, giving an estimate to the third place of decimal in mm., and an appropriate correction was applied to the flow times. All these factors ultimately give a reproducibility of $\pm$0.004 in E/R÷1000, which ranges from 0.8 to 1.2 units for all the different liquids studied here.

Experiments with n-Decane ($C_{10}H_{22}$)

The first set of measurements were carried out on n-Decane (BDH, Analar) in the range of 9° to 90°C. with a thermal interval ΔT of 1°C. Viscometer No. 'O' (constant=0.000,735) was used, fixed vertically in a Townson-Mercer Thermostat bath. The actual Beckmann readings and flow times, together with the value of (E/R)/1000 obtained from these during heating and cooling sequences are presented in Table 1, together with the overall means and r.m.s. deviations estimated from the group of five successive observations. These deviations are only 0.004 units as compared with 0.011 in the earlier experiment, and the mean values of (E/R)/1000 are plotted as hollow circles in the lower half of Fig. 1, where the vertical scale is enlarged 2½ times in the previous data shown as solid circles in Fig. 1(top). A comparison shows that, while these two graphs are in essential agreement, the new data provides considerably more detail.

While the old graph (solid circles) only shows jumps at 19-22°C. and 38°C., the new data (hollow circles) shows two steps replacing the previously observed one at 38°C.) and a whole series of regular steps at the average interval of 13°C., each step having a truly horizontal portion, very much like those previously observed with high-speed diesel oil.[3] The average depth of the jumps is of the order of 0.04 units of (E/R)/1000, which is ten times the present r.m.s. deviation. This type of step-like variation is seen to continue upto 73°C.∓2°C., beyond which the phenomenon undergoes a change, and (E/R)/1000 begins to oscillate with an average peak-to-peak amplitude of 0.06 units and average temperature period of 8°C. This period compares with those previously observed in light lubricating oil (B.O.C. "60") and H.S. diesel, where these variations occur above 133°C. and 118°C., respectively.

Experiments with n-Octane and iso-Octane

Next, the measurements were carried out in the range of 5°C. to 75°C. on n-Octane (C_8H_{18}), having freezing point of 56.8°C. and boiling point 125.6°C. Extra pure Octane from BDH was transferred to viscometer No. 'O' and flow time was measured to an accuracy of $\pm$0.02 seconds. Table 2(a) gives the values of (E/R)/1000 obtained during heating and cooling, and the overall mean (E/R)/1000, together with estimated values of r.m.s. deviation for the groups of five successive temperatures, which is seen to be of the order of $\pm$0.005 units.

Fig. 2(top) is the plot of the overall mean (E/R)/1000 values for n-Octane against temperature, the scale being the same as adopted in the case of n-decane. The curve drawn through the plotted hollow circles shows a clear horizontal straight line extending all the way from 5°C. upto 50°C. with no detectable change in E, which differs from the step-like behaviour observed in other hydrocarbons. However, above 52°C.∓2°C., the Energy E begins to oscillate with peak-to-peak amplitude of 0.05 units of (E/R)/1000 and an average cyclic period of 6.2°C.

TABLE 1.—BECKMANN READINGS, MEAN TEMPERATURES IN °C., FLOW TIMES AND CALCULATED VALUES OF (E/R) 1000 = $-T^2$ $(\Delta \ln \nu/\Delta T)/1000$ FOR n-DECANE IN TEMPERATURE RANGE OF 9°C. TO 90 °C., USING $\Delta T = 1$°C.

Heating sequence						Cooling sequence						
Temperature °C.	Beckmann reading	Time of flow corrected for level	Mean temperature °C.	E/R ÷ 1000		Temperature °C.	Beckmann reading	Time of flow corrected for level	Mean temperature °C.	E/R ÷ 1000		Mean E/R ÷ 1000
				Uncorrected	Corrected					Uncorrected	Corrected	
1	2	3	4	5	6	7	8	9	10	11	12	13
9.0	0.183±0.001	377.85±0.01				9.0	0.189±0.001	377.85±0.01				
			9.50	1.272	1.275±0.004				9.50	1.267	1.271±0.004	1.273±0.002
10.0	1.182±0.000	371.95±0.01				10.0	1.192±0.000	371.90±0.00				
			10.50	1.274	1.263±0.004				10.50	1.275	1.271±0.004	1.267±0.004
11.0	2.185±0.001	300.09±0.02				11.0	2.189±0.000	366.07±0.01				
			11.50	1.265	1.271±0.004				11.50	1.274	1.280±0.004	1.275±0.005
12.0	3.186±0.000	360.41±0.00				12.0	3.191±0.001	360.35±0.01				
			12.50	1.271	1.273±0.004				12.50	1.266	1.267±0.004	1.270±0.003
13.0	4.186±0.000	354.87±0.01				13.0	4.192±0.000	354.84±0.00				
13.0	0.008±0.000	354.74±0.00				13.0	0.006±0.001	354.78±0.01				
			13.50	1.272	1.274±0.004				13.50	1.272	1.274±0.004	1.274±0.000
14.0	1.005±0.001	349.31±0.01				14.0	1.008±0.000	349.32±0.00				
			14.50	1.270	1.273±0.004				14.50	1.275	1.279±0.004	1.276±0.003
15.0	2.007±0.000	343.98±0.00				15.0	2.003±0.001	344.02±0.02				
			15.50	1.266	1.268±0.004				15.50	1.267	1.271±0.004	1.270±0.002
16.0	3.000±0.001	338.83±0.01				16.0	3.001±0.000	338.84±0.01				
			16.50	1.271	1.277±0.004				16.50	1.272	1.278±0.004	1.278±0.001
17.0	4.001±0.001	333.73±0.01				17.0	4.007±0.001	333.71±0.01				
			17.50	1.270	1.265±0.004				17.50	1.277	1.272±0.004	1.268±0.004
18.0	4.999±0.000	328.76±0.00				18.0	5.000±0.000	328.74±0.01				
18.0	0.110±0.001	328.56±0.02				18.0	0.119±0.001	328.54±0.01				
			18.50	1.270	1.273±0.006				18.50	1.275	1.278±0.006	1.276±0.002
19.0	1.114±0.000	323.67±0.01				19.0	1.120±0.000	323.65±0.00				
			19.50	1.263	1.261±0.006				19.50	1.272	1.268±0.006	1.264±0.004
20.0	2.108±0.000	318.96±0.01				20.0	2.113±0.001	318.91±0.01				
			20.50	1.203	1.198±0.006				20.50	1.201	1.204±0.006	1.201±0.003
21.0	3.106±0.001	314.55±0.02				21.0	3.110±0.000	314.52±0.01				
			21.50	1.194	1.200±0.006				21.50	1.200	1.206±0.006	1.203±0.003
22.0	4.114±0.000	310.21±0.01				22.0	4.113±0.001	310.19±0. 2				
			22.50	1.207	1.206±0.006				22.50	1.213	1.212±0.006	1.209±0.003
23.0	5.110±0.001	305.97±0.01				23.0	5.112±0.000	305.92±0.01				
23.0	2.228±0.000	306.53±0.01				23.0	2.225±0.001	306.56±0.01				
			23.50	1.201	1.204±0.003				23.50	1.205	1.209±0.003	1.207±0.003
24.0	3.234±0.000	302.35±0.00				24.0	3.222±0.000	302.37±0.00				
			24.50	1.194	1.200±0.003				24.50	1.203	1.207±0.003	1.203±0.004
25.0	4.232±0.000	298.31±0.01				25.0	4.221±0.000	298.30±0.01				
25.0	0.009±0.001	299.02±0.01				25.0	0.100±0.001	299.05±0.01				
			25.50	1.206	1.210±0.005				25.50	1.202	1.206±0.005	1.208±0.002
26.0	1.008±0.001	294.98±0.02				26.0	1.008±0.000	295.01±0.00				

(*Continued*) :-

(Table 1 Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
			26.50	1.212	1.216±0.003				26.50	1.203	1.198±0.005	1.204±0.006
27.0	2.014±0.000	291.00±0.00				27.0	2.000±0.001	291.12±0.02				
			27.50	1.200	1.207±0.005				27.50	1.202	1.208±0.005	1.208±0.001
28.0	3.012±0.000	287.17±0.01				28.0	2.996±0.000	287.29±0.01				
			28.50	1.192	1.197±0.005				28.50	1.202	1.208±0.005	1.203±0.005
29.0	4.005±0.001	283.46±0.01				29.0	3.999±0.000	283.51±0.00				
			29.50	1.217	1.212±0.005				29.50	1.212	1.207±0.005	1.209±0.003
30.0	5.013±0.000	274.69±0.01				30.0	5.002±0.000	279.76±0.01				
30.0	0.092±0.001	1446.69±0.02				30.0	0.050±0.001	1447.70±0.02				
			30.50	1.212	1.200±0.004				30.50	1.207	1.193±0.004	1.196±0.004
31.0	1.100±0.000	1427.03±0.01				31.0	1.047±0.000	1428.94±0.01				
			31.50	1.203	1.218±0.004				31.50	1.196	1.209±0.004	1.213±0.004
32.0	2.110±0.000	1409.08±0.02				32.0	2.043±0.001	1410.77±0.03				
			32.50	1.215	1.190±0.004				32.50	1.206	1.186±0.004	1.188±0.002
33.0	3.085±0.001	1391.33±0.01				33.0	3.052±0.000	1392.52±0.01				
			33.50	1.178	1.178±0.004				33.50	1.160	1.170±0.004	1.174±0.004
34.0	4.091±0.001	1373.90±0.02				34.00	4.051±0.001	1375.41±0.02				
			34.50	1.180	1.175±0.004				34.50	1.175	1.170±0.004	1.172±0.003
35.0	5.072±0.001	1357.20±0.02				35.0	5.072±0.001	1358.10±0.02				
35.0	0.135±0.002	1356.95±0.04				35.0	0.069±0.001	1357.68±0.02				
			35.50	1.175	1.178±0.005				35.50	1.169	1.172±0.005	1.175±0.003
36.0	1.125±0.000	1340.50±0.00				36.0	1.078±0.002	1341.00±0.03				
			36.50	1.177	1.174±0.005				36.50	1.178	1.175±0.005	1.174±0.001
37.0	2.101±0.001	1324.51±0.02				37.0	2.078±0.000	1324.62±0.01				
			37.50	1.167	1.170±0.005				37.50	1.170	1.174±0.005	1.172±0.002
38.0	3.092±0.001	1308.73±0.02				38.0	3.082±0.001	1308.59±0.02				
			38.50	1.163	1.168±0.005				38.50	1.170	1.175±0.005	1.172±0.003
39.0	4.089±0.000	1293.20±0.01				39.0	4.084±0.000	1292.89±0.01				
			39.50	1.172	1.167±0.005				39.50	1.181	1.176±0.005	1.172±0.005
40.0	5.072±0.001	1278.05±0.02				40.0	5.082±0.001	1278.17±0.02				
40.0	0.083±0.001	1282.17±0.02				40.0	0.038±0.001	1282.99±0.01				
			40.50	1.174	1.178±0.004				40.50	1.168	1.171±0.004	1.175±0.004
41.0	1.093±0.000	1266.81±0.01				41.0	1.033±0.000	1267.92±0.01				
			41.50	1.171	1.170±0.004				41.50	1.181	1.180±0.004	1.175±0.005
42.0	2.076±0.001	1252.17±0.03				42.0	2.041±0.000	1252.81±0.02				
			42.50	1.168	1.165±0.004				42.50	1.170	1.173±0.004	1.169±0.004
43.0	3.065±0.001	1237.74±0.01				43.0	3.044±0.002	1238.14±0.03				
			43.50	1.170	1.177±0.004				43.50	1.168	1.172±0.004	1.175±0.003
44.0	4.062±0.000	1223.43±0.01				44.0	4.043±0.000	1223.82±0.01				
			44.50	1.175	1.170±0.004				44.50	1.181	1.177±0.004	1.173±0.004
45.0	5.042±0.001	1209.55±0.02				45.0	5.044±0.001	1209.51±0.002				
45.0	-0.140±0.000	1207.70±0.00				45.0	-0.138±0.001	1208.00±0.000				
			45.50	1.168	1.170±0.004				45.50	1.171	1.173±0.004	1.172±0.001
46.0	0.883±0.001	1193.58±0.02				46.0	0.851±0.000	1194.30±0.01				
			46.50	1.176	1.178±0.004				46.50	1.165	1.167±0.004	1.172±0.005
47.0	1.880±0.000	1179.96±0.02				47.0	1.843±0.001	1180.86±0.03				
			47.50	1.159	1.155±0.004				47.50	1.144	1.146±0.004	1.151±0.005
48.0	2.842±0.000	1167.31±0.01				48.0	2.832±0.000	1167.94±0.01				

(Continued) :—

Table 1 (Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
			48.50	1.140	1.148±0.004				48.50	1.149	1.157±0.004	1.152±0.005
49.0	3.383±0.001	1154.63±0.02				49.0	3.830±0.001	1155.14±0.02				
			49.50	1.152	1.147±0.004				49.50	1.156	1.151±0.004	1.149±0.002
50.0	4.816±0.000	1142±17±0.01				50.0	4.820±0.001	1143.57±0.01				
50.0	0.160±0.000	1141±82±0.02				50.0	0.142±0.001	1141.13±0.02				
			50.50	1.158	1.158±0.004				50.50	1.149	1.151±0.004	1.155±0.004
51.0	1.125±0.001	1129.69±0.02				51.0	1.124±0.000	1128.91±0.01				
			51.50	1.157	1.154±0.004				51.50	1.152	1.151±0.004	1.153±0.002
52.0	2.103±0.000	1117.65±0.01				52.0	2.105±0.001	1117.28±0.02				
			52.50	1.145	1.148±0.004				52.50	1.152	1.155±0.004	1.152±0.003
53.0	3.064±0.001	1106.13±0.02				53.0	3.096±0.000	1105.34±0.01				
			53.50	1.149	1.155±0.004				53.50	14.45	1.150±0.004	1.153±0.003
54.0	4.062±0.000	1094.26±0.02				54.0	4.073±0.001	1093.81±0.02				
			54.50	1.159	1.152±0.004				54.50	1.155	1.153±0.004	1.152±0.001
55.0	5.030±0.000	1082.88±0.01				55.0	5.030±0.000	1080.59±0.01				
55.0	−0.160±0.000	1083.86±0.01				55.0	−0.140±0.001	1083.39±0.02				
			55.50	1.157	1.156±0.005				55.50	1.145	1.144±0.005	1.150±0.006
56.0	0.842±0.002	1072.30±0.02				56.0	0.841±0.000	1072.18±0.02				
			56.50	1.153	1.156±0.005				56.50	1.144	1.150±0.005	1.153±0.003
57.0	1.822±0.000	1061.77±0.01				57.0	1.794±0.001	1061.48±0.03				
			57.50	1.146	1.149±0.005				57.50	1.156	1.158±0.005	1.154±0.005
58.0	2.818±0.001	1050.74±0.00				58.0	2.762±0.001	1050.63±0.02				
			58.50	1.123	1.130±0.005				58.50	1.115	1.122±0.005	1.126±0.004
59.0	3.759±0.000	1040.69±0.01				59.0	3.750±0.000	1040.16±0.00				
			59.50	1.105	1.100±0.005				59.50	1.109	1.105±0.005	1.103±0.002
60.50	5.247±0.001	1025.38±0.02				60.50	5.247±0.001	1024.80±0.02				
60.00	0.106±0.001	1029.44±0.02				60.0	0.112±0.001	1029.18±0.01				
			60.50	1.107	1.110±0.004				60.50	1.103	1.104±0.004	1.107±0.003
61.0	1.099±0.000	1019.32±0.01				61.0	1.080±0.000	1019.45±0.01				
			61.50	1.108	1.105±0.004				61.50	1.102	1.099±0.004	1.102±0.003
62.0	2.093±0.002	1009.33±0.02				62.0	2.079±0.001	1009.47±0.02				
			62.50	1.097	1.100±0.004				62.50	1.094	1.097±0.004	1.098±0.002
63.0	3.095±0.000	1000.50±0.01				63.0	3.087±0.001	1000.73±0.02				
			63.50	1.100	1.105±0.004				63.50	1.095	1.100±0.004	1.103±0.003
64.0	4.088±0.001	990.97±0.02				64.0	4.077±0.000	991.21±0.00				
			64.50	1.105	1.100±0.004				64.50	1.113	1.108±0.004	1.104±0.004
65.0	5.063±0.000	981.65±0.01				65.0	5.062±0.001	981.72±0.02				
65.0	−0.008±0.001	981.96±0.02				65.0	0.000±0.002	981.97±0.03				
			65.50	1.098	1.100±0.006				65.50	1.103	1.105±0.006	1.102±0.003
66.0	1.000±0.000	972.69±0.01				66.0	0.999±0.000	973.03±0.01				
			66.50	1.100	1.101±0.006				66.50	1.107	1.110±0.006	1.105±0.005
67.0	1.966±0.001	963.77±0.02				67.0	1.990±0.001	963.90±0.02				
			67.50	1.096	1.101±0.006				67.50	1.086	1.091±0.006	1.096±0.005
68.0	2.949±0.001	954.98±0.02				68.0	2.972±0.001	955.17±0.02				
			68.50	1.100	1.100±0.006				68.50	1.104	1.107±0.006	1.104±0.004

(Continued) :-

(Table 1 Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
69.0	3.942±0.000	946.05±0.02				69.0	3.950±0.002	946.30±0.03				
			69.50	1.109	1.105±0.006				69.50	1.104	1.100±0.006	1.102±0.003
70.0	4.917±0.002	937.39±0.03				70.0	4.952±0.000	937.44±0.01				
70.0	0.103±0.001	927.85±0.02				70.0	0.113±0.002	937.66±0.02				
			70.50	1.100	1.102±0.006				70.50	1.089	1.091±0.006	1.097±0.006
71.0	1.076±0.000	929.39±0.01				71.0	1.099±0.000	929.18±0.01				
			71.50	1.106	1.103±0.006				71.50	1.111	1.108±0.006	1.106±0.003
72.0	2.059±0.002	920.92±0.03				72.0	2.092±0.001	920.61±0.02				
			72.50	1.093	1.097±0.005				72.50	1.098	1.092±0.006	1.095±0.003
73.0	3.034±0.000	912.73±0.01				73.0	3.088±0.000	912.20±0.01				
			73.50	1.053	1.055±0.006				73.50	1.059	1.064±0.006	1.059±0.003
74.0	4.037±0.001	904.76±0.02				74.0	4.061±0.000	904.41±0.01				
			74.50	1.051	1.046±0.006				74.50	1.058	1.053±0.006	1.050±0.003
75.0	5.029±0.002	897.10±0.02				75.0	5.053±0.002	896.65±0.03				
75.0	0.008±0.001	897.10±0.02				75.0	0.006±0.001	897.05±0.02				
			75.50	1.027	1.032±0.007				75.50	1.032	1.037±0.007	1.035±0.002
76.0	1.086±0.000	889.72±0.01				76.0	0.979±0.002	889.67±0.04				
			76.50	1.051	1.049±0.007				76.50	1.057	1.055±0.007	1.052±0.003
77.0	2.049±0.001	882.37±0.02				77.0	1.941±0.001	882.32±0.02				
			77.50	1.049	1.053±0.007				77.50	1.056	1.060±0.007	1.057±0.004
78.0	3.050±0.000	874.87±0.01				78.0	2.940±0.001	874.78±0.01				
			78.50	1.073	1.078±0.007				78.50	1.078	1.083±0.007	1.080±0.003
79.0	4.005±0.001	867.65±0.02				79.0	3.940±0.000	867.18±0.01				
			79.50	1.108	1.103±0.007				79.50	1.103	1.098±0.007	1.101±0.003
80.0	5.004±0.002	859.94±0.03				80.0	4.905±0.001	859.77±0.03				
80.0	0.116±0.001	860.21±0.02				80.0	0.110±0.001	860.17±0.01				
			80.50	1.085	1.088±0.007				80.50	1.093	1.096±0.007	1.092±0.004
81.0	1.110±0.001	852.83±0.01				81.0	1.005±0.002	852.74±0.02				
			81.50	1.080	1.077±0.007				81.50	1.085	1.082±0.007	1.080±0.003
82.0	2.078±0.001	845.73±0.01				82.0	1.978±0.001	845.61±0.01				
			82.50	1.042	1.045±0.007				82.50	1.054	1.058±0.007	1.051±0.007
83.0	3.055±0.001	838.95±0.02				83.0	2.953±0.001	838.77±0.02				
			83.00	1.026	1.031±0.007				83.50	1.028	1.043±0.007	1.037±0.006
84.0	4.010±0.000	832.51±0.01				84.0	3.919±0.000	832.25±0.01				
			84.50	1.057	1.053±0.007				84.50	1.051	1.047±0.007	1.052±0.005
85.0	4.998±0.001	825.74±0.02				85.0	4.994±0.002	825.61±0.02				
85.0	0.008±0.001	826.17±0.01				85.0	0.103±0.001	826.23±0.01				
			85.50	1.054	1.050±0.006				85.50	1.069	1.055±0.006	1.052±0.003
86.0	0.996±0.002	819.51±0.02				86.0	1.076±0.000	819.64±0.00				
			86.50	1.072	1.069±0.006				86.50	1.072	1.068±0.006	1.069±0.001
87.0	1.962±0.001	812.98±0.02				87.0	2.064±0.002	812.96±0.02				
			87.50	1.087	1.092±0.006				87.50	1.096	1.110±0.006	1.096±0.005
88.0	2.967±0.000	806.16±0.00				88.0	3.019±0.000	806.44±0.01				
			88.50	1.097	1.099±0.006				88.50	1.084	1.087±0.006	1.092±0.005
89.0	3.966±0.002	799.43±0.02				89.0	4.009±0.001	799.85±0.01				
			89.50	1.085	1.080±0.006				89.50	1.096	1.091±0.006	1.086±0.005
90.0	4.932±0.001	793.12±0.01				90.0	4.987±0.002	793.34±0.02				

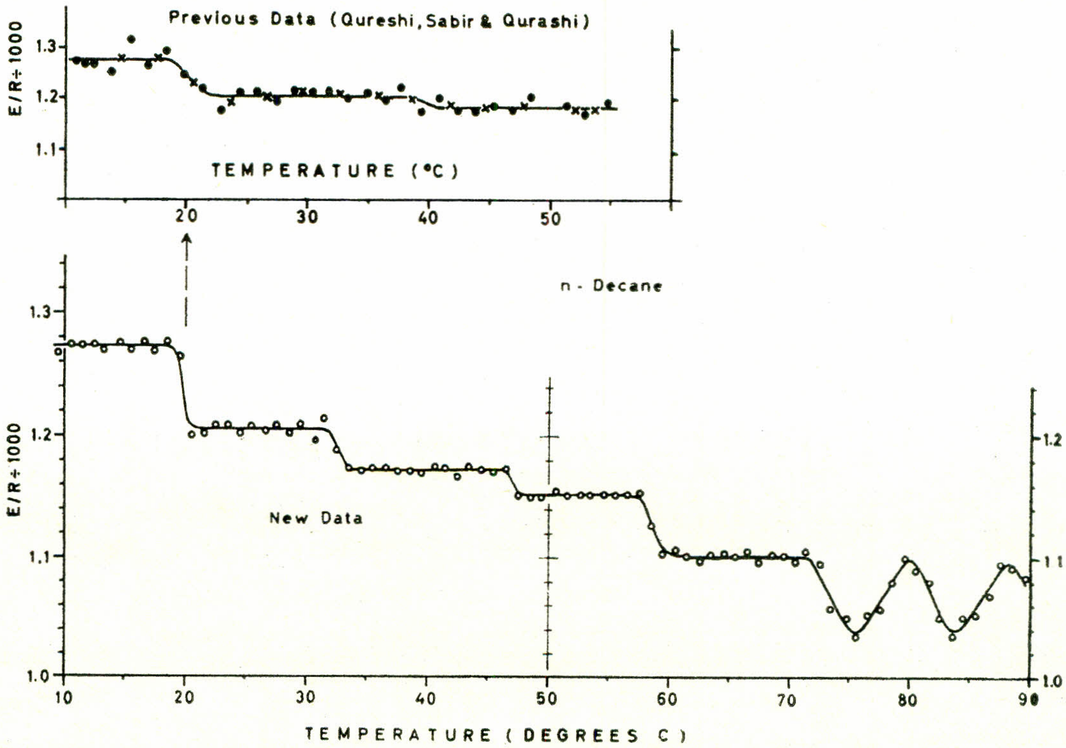

Fig. 1.—Graphs showing the variation of the activation energy of viscous flow E/R with temperature for n-decane; the upper graph (solid circles and crosses) is the previously reported data using the measuring interval of 2°C.

The lower graph (hollow circles) is the data obtained by using viscometer No. '0' and a measuring thermal interval of I°C. This graph provides more details, and shows a regular series of steps, followed by cyclic variation above 73∓2°C.

These results on n-octane are somewhat out of the run, so it was considered desirable to study one of its isomeric forms to determine whether this feature is characteristic of the eight aliphatic carbon atoms only, or also depends upon factors such as configuration. Iso-octane (2:2:4 trimethyl pentane, $(CH_3)C\text{-}CH_2\text{-}CH(CH_3)_2$) of special spectroscopic grade (BDH) was considered for this purpose; it has lower freezing point (−107.3°C.) and boiling point (99.2°C.) as compared to n-octane. The viscosity measurements were carried out with viscometer No 'O', exactly as for n-decane and n-octane, the time of flow ranging from 1100 seconds at lower temperatures to 600 seconds at higher temperatures. The measurements were carried out in the range of 5° to 73°C. at the interval of 1°C., and the values of (E/R)/1000 against temperature in °C. obtained during heating and cooling sequences are collected in Table 2(b), together with overall means and r.m.s. deviations (for the groups of measurements of 5) which comes out to be of the order of ± 0.004 units. The solid circles in Fig. 2(bottom) show these values plotted against temperature in °C., and a smooth curve is drawn through all these points. This curve is different from all the previous work so far reported, in so far as at lower temperatures it assumes a cyclic form, with peak-to-peak amplitude of the order of 0.04 units of E/R÷1000 and period 6°C., while above 53°C., it undergoes a sudden change and jumps upwards to a horizontal straight line going upto the last experimental point at 73°C., which is very near to its boiling point (99.2°C.). Secondly the E/R values are somewhat higher than n-octane by 0.05 units, and the mean values of E appears to go through an absolute minima in the neighbourhood of 30°C. It is also notable that the transition from sinusoidal variation to the horizontal straight line occurs at the same temperature of 54°C., where the transition in n-octane took place in reversed order.

Experiment with n-Hexane (C_6H_{14})

To study further these interesting phenomena in the activation energy E in the lighter hydrocarbons, experiments were carried out on n-hexane C_6H_{14}, (special for spectroscopy BDH) having freezing point-95°C. and boiling point 68.7°C. This is highly volatile and therefore

TABLE 2 (a).—MEASURED ACTIVATION ENERGIES (E/R)/1000 FOR n- OCTANE IN THE TEMPERATURE RANGE OF 5°C. TO 75°C. USING $\Delta T = 1°C$.

Mean temperature °C.	$(E/R)/1000 = -T^2 (\Delta \ln \upsilon/\Delta T)/1000$			Mean temperature °C.	$(E/R)/1000 = -T^2 (\Delta \ln \upsilon/\Delta T/T)/1000$		
	Heating sequence	Cooling sequence	Mean		Heating sequence	Cooling sequence	Mean
5.5	0.962±0.004	0.971±0.004	0.966±0.005	41.5	0.980±0.005	0.972±0.005	0.976±0.004
6.5	0.958±0.004	0.963±0.004	0.965±0.002	42.5	0.968±0.005	0.964±0.005	0.966±0.002
7.5	0.964±0.004	0.970±0.004	0.967±0.003	43.5	0.960±0.005	0.965±0.005	0.963±0.002
8.5	0.968±0.003	0.972±0.003	0.970±0.002	44.5	0.964±0.005	0.963±0.005	0.964±0.001
9.5	0.963±0.003	0.968±0.003	0.966±0.002	45.5	0.968±0.004	0.962±0.004	0.965±0.003
10.5	0.969±0.003	0.964±0.003	0.966±0.002	46.5	0.975±0.004	0.964±0.004	0.970±0.006
11.5	0.963±0.003	0.966±0.003	0.965±0.001	47.5	0.962±0.004	0.974±0.004	0.968±0.006
12.5	0.966±0.003	0.962±0.003	0.964±0.002	48.5	0.968±0.004	0.964±0.004	0.966±0.002
13.5	0.977±0.004	0.968±0.004	0.972±0.004	49.5	0.960±0.004	0.970±0.004	0.965±0.005
14.5	0.960±0.004	0.968±0.004	0.964±0.004	50.0	0.966±0.005	0.964±0.005	0.965±0.001
15.5	0.958±0.004	0.970±0.004	0.964±0.006	51.5	0.963±0.005	0.966±0.005	0.965±0.001
16.5	0.962±0.004	0.964±0.004	0.963±0.001	52.5	0.955±0.005	0.969±0.005	0.962±0.007
17.5	0.960±0.004	0.967±0.004	0.963±0.003	53.5	0.942±0.005	0.948±0.005	0.945±0.003
18.5	0.960±0.004	0.950±0.004	0.955±0.005	54.5	0.937±0.005	0.944±0.005	0.941±0.003
19.5	0.965±0.004	0.972±0.004	0.968±0.004	55.5	0.952±0.005	0.958±0.005	0.955±0.003
20.5	0.976±0.004	0.969±0.004	0.972±0.003	56.5	0.969±0.005	0.960±0.005	0.965±0.004
21.5	0.965±0.003	0.967±0.003	0.966±0.001	57.5	0.960±0.005	0.967±0.005	0.964±0.003
22.5	0.960±0.003	0.967±0.003	0.964±0.003	58.5	0.966±0.005	0.962±0.005	0.964±0.004
23.5	0.967±0.003	0.962±0.003	0.965±0.003	59.5	0.916±0.006	0.928±0.006	0.922±0.006
24.5	0.970±0.003	0.961±0.003	0.965±0.005	60.5	0.928±0.006	0.922±0.006	0.925±0.003
25.5	0.958±0.003	0.964±0.003	0.961±0.003	61.5	0.955±0.006	0.948±0.006	0.952±0.004
26.5	0.975±0.003	0.966±0.003	0.970±0.004	62.5	0.980±0.006	0.972±0.006	0.976±0.004
27.5	0.958±0.003	0.964±0.003	0.961±0.003	63.5	0.956±0.006	0.967±0.006	0.962±0.005
28.5	0.974±0.003	0.967±0.003	0.971±0.004	64.5	0.935±0.006	0.926±0.006	0.931±0.005
29.5	0.978±0.003	0.963±0.004	0.971±0.004	65.5	0.915±0.005	0.926±0.005	0.920±0.006
30.5	0.968±0.005	0.958±0.005	0.963±0.005	66.5	0.932±0.005	0.932±0.005	0.932±0.006
31.5	0.964±0.005	0.963±0.005	0.964±0.001	67.5	0.945±0.005	0.934±0.005	0.940±0.006
32.5	0.963±0.005	0.960±0.005	0.962±0.002	68.5	0.958±0.005	0.964±0.005	0.961±0.003
33.5	0.967±0.005	0.961±0.005	0.964±0.003	69.5	0.978±0.005	0.977±0.005	0.978±0.001
34.5	0.966±0.005	0.964±0.005	0.965±0.001	70.5	0.957±0.006	0.964±0.006	0.960±0.004
35.6	0.965±0.004	0.966±0.004	0.966±0.001	71.5	0.928±0.006	0.922±0.006	0.925±0.003
36.5	0.966±0.004	0.962±0.004	0.964±0.002	72.5	0.920±0.006	0.912±0.006	0.916±0.004
37.5	0.960±0.004	0.968±0.004	0.965±0.004	73.5	0.922±0.006	0.917±0.006	0.920±0.003
38.5	0.968±0.004	0.963±0.004	0.966±0.003	74.5	0.938±0.006	0.928±0.006	0.933±0.005
39.5	0.965±0.004	0.962±0.004	0.963±0.002				
40.0	0.972±0.005	0.969±0.005	0.971±0.002				

Note:—

Temperature °C.:	10	20	30	40	50	60	80
Correction $T^2\beta/1000$:	0.003	0.003	0.004	0.004	0.004	0.004	0.005

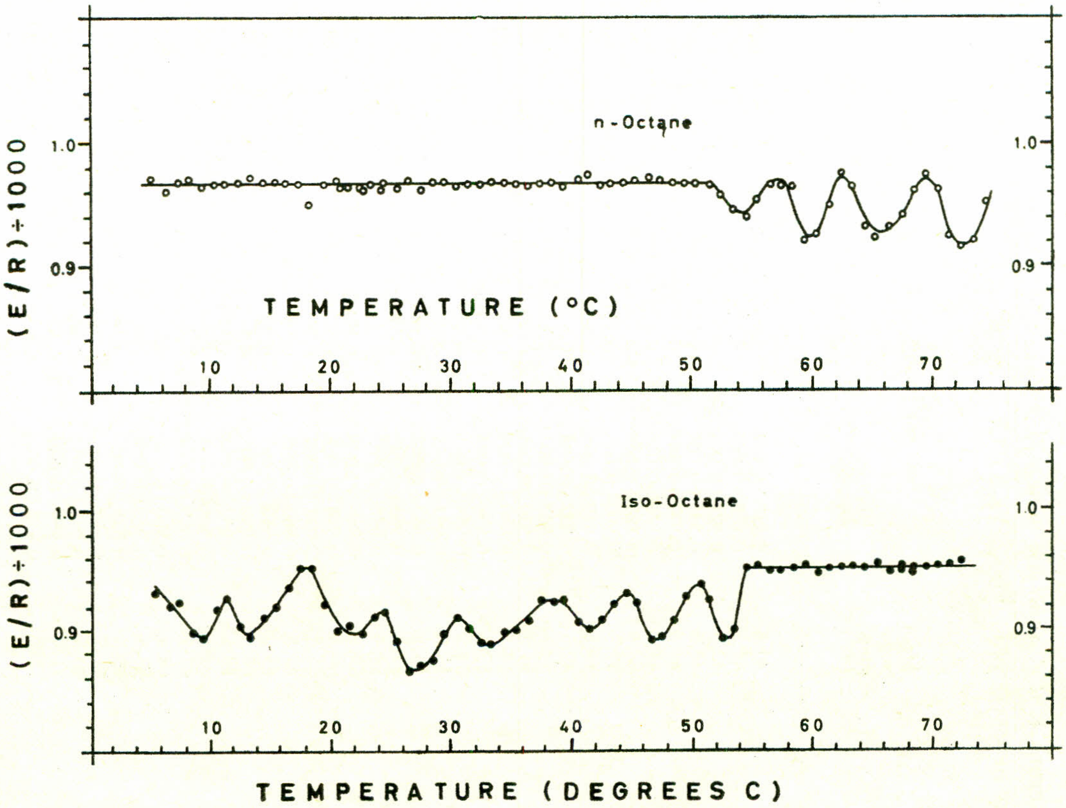

Fig. 2.—Plot of variation of (E/R)/1000 with temperature obtained with the improved technique at intervals of 1°C. for n-octane. Upper graph (hollow circles) is for n-octane from 5°C. to 75°C. A long flat extending over at least 45°C. changes over to cyclic variation at 52°C.∓2°C.

Lower graph (solid circles) is for iso-octane, showing anomalous behaviour, viz. cyclic variation of E/R at lower temperatures, going over to constant value of E/R at 54°C. This straight line goes to a considerable range, close to its boiling point (99.2°C.).

especial care had to be taken during viscosity measurements in the range of 4°C. to 50°C. at thermal interval of 1°C. Particular care was necessary in sucking the liquid up in the capillary limb bulb. The flow times in seconds (measured in viscometer No. 'O' and corrected for equilibrium level), the Beckmann readings, the mean temperature (°C.) and the calculated values of (E/R)/1000, together with r.m.s. deviations as estimated for the successive sets of five readings taken at a stretch (which is of the order of ±0.004 units of E/R÷1000) are given in Table 3 for both the heating and cooling sequences. Fig. 3, plotted to the same scale as for n-octane, etc., is the graphical representation of these (E/R)/1000 values (hollow circles), where the radii of these circles are approximately of the magnitude of r.m.s. deviations. This curve shows clear normal step-like variation upto 38°C.∓2°C., the average step-length being 15°C. The two sharp jumps at 24.5°C., which are of the magnitude of 0.05 and 0.04 units of(E/R)/1000 respectively, viz. twelve and ten times the r.m.s. error, are quite significant. Above this temperature of 38°C.∓2°C., the phenomena undergo the usual change in E, and the energy begins to oscillate with a cycle of 8.2°C. and peak-to-peak amplitude of 0.07 units of (E/R)/1000, which is seven times the r.m.s. deviations.

Results on Kerosene Oil and Discussion

Thus, it is evident that all the straight-chain, hydrocarbons so far investigated exhibit a step-like variation of a definite pattern at the lower temperatures, and undergo abrupt change to cyclic variation of definite amplitude and period at higher temperatures, well below the boiling point. This transition temperature is apparently a characteristic of various factors, among which

TABLE 2 (b).—MEASURED ACTIVATION ENERGIES E/R ÷ 1000 FOR ISO-OCTANE (2:2:4 TRIMETHYL PENTANE) IN THE RANGE OF 5° TO 73°C. USING $\Delta T = 1°C$.

Mean tempe-rature (°C.)	$(E/R)/1000 = -T^2(\Delta \ln \upsilon/\Delta T)/1000$			Mean tempe-rature (°C.)	$(E/R)/1000 = -T^2(\Delta \ln \upsilon/\Delta T)/1000$		
	Heating sequence	Cooling sequence	Mean		Heating sequence	Cooling sequence	Mean
5.5	0.930±0.003	0.935±0.003	0.932±0.003	40.5	0.910±0.004	0.904±0.004	0.907±0.003
6.5	0.917±0.003	0.924±0.003	0.920±0.004	41.5	0.898±0.004	0.904±0.004	0.901±0.003
7.5	0.920±0.003	0.928±0.003	0.924±0.004	42.5	0.924±0.004	0.914±0.004	0.919±0.005
8.5	0.905±0.003	0.894±0.003	0.899±0.005	43.5	0.925±0.004	0.920±0.004	0.923±0.003
9.5	0.896±0.003	0.990±0.003	0.893±0.003	44.5	0.932±0.004	0.927±0.004	0.930±0.003
10.5	0.920±0.004	0.916±0.004	0.918±0.002	45.5	0.920±0.005	0.925±0.005	0.922±0.003
11.5	0.922±0.004	0.932±0.004	0.927±0.004	46.5	0.887±0.005	0.896±0.005	0.892±0.004
12.5	0.900±0.004	0.908±0.004	0.904±0.004	47.5	0.900±0.005	0.891±0.005	0.895±0.004
13.5	0.900±0.004	0.893±0.004	0.896±0.003	48.5	0.912±0.005	0.903±0.005	0.907±0.005
14.5	0.905±0.004	0.917±0.004	0.911±0.004	49.5	0.932±0.005	0.924±0.005	0.928±0.004
15.5	0.918±0.003	0.923±0.003	0.920±0.002	50.5	0.933±0.003	0.944±0.003	0.938±0.006
16.5	0.942±0.003	0.952±0.003	0.947±0.004	51.5	0.930±0.003	0.918±0.003	0.924±0.006
17.5	0.956±0.003	0.949±0.003	0.953±0.004	52.5	0.890±0.003	0.897±0.003	0.893±0.004
18.5	0.960±0.003	0.945±0.003	0.952±0.007	53.5	0.900±0.003	0.901±0.003	0.901±0.001
19.5	0.925±0.003	0.922±0.003	0.923±0.002	54.5	0.955±0.003	0.947±0.003	0.951±0.005
20.5	0.895±0.005	0.905±0.005	0.900±0.005	55.5	0.953±0.003	0.954±0.003	0.954±0.001
21.5	0.910±0.005	0.901±0.005	0.905±0.005	56.5	0.953±0.003	0.943±0.003	0.948±0.005
22.5	0.898±0.005	0.898±0.005	0.898±0.000	57.5	0.953±0.003	0.945±0.003	0.949±0.004
23.5	0.918±0.005	0.908±0.005	0.913±0.005	58.5	0.956±0.003	0.946±0.003	0.951±0.005
24.5	0.919±0.005	0.911±0.005	0.915±0.004	59.5	0.958±0.003	0.950±0.003	0.954±0.004
25.5	0.895±0.004	0.887±0.004	0.891±0.004	60.5	0.944±0.005	0.950±0.005	0.947±0.003
26.5	0.868±0.004	0.862±0.004	0.865±0.003	61.5	0.948±0.005	0.955±0.005	0.951±0.004
27.5	0.864±0.004	0.878±0.004	0.871±0.007	62.5	0.960±0.005	0.942±0.005	0.951±0.009
28.5	0.875±0.004	0.877±0.004	0.876±0.001	63.5	0.952±0.005	0.952±0.005	0.952±0.000
29.5	0.902±0.004	0.894±0.004	0.898±0.004	64.5	0.956±0.005	0.950±0.005	0.953±0.003
30.5	0.914±0.003	0.907±0.003	0.911±0.004	65.5	0.952±0.004	0.959±0.004	0.955±0.004
31.5	0.907±0.003	0.900±0.003	0.903±0.003	66.5	0.946±0.004	0.950±0.004	0.948±0.002
32.5	0.886±0.003	0.894±0.003	0.890±0.006	67.5	0.957±0.004	0.953±0.004	0.955±0.002
33.5	0.886±0.003	0.893±0.003	0.889±0.004	68.5	0.950±0.004	0.945±0.004	0.948±0.003
34.5	0.896±0.003	0.900±0.003	0.898±0.002	67.5	0.955±0.004	0.948±0.004	0.951±0.003
35.5	0.906±0.004	0.895±0.004	0.901±0.004	68.5	0.958±0.005	0.943±0.005	0.951±0.008
36.5	0.912±0.004	0.907±0.004	0.909±0.002	69.5	0.953±0.005	0.950±0.005	0.951±0.001
37.5	0.925±0.004	0.922±0.004	0.923±0.003	70.5	0.950±0.005	0.956±0.005	0.953±0.003
38.5	0.930±0.004	0.921±0.004	0.925±0.004	71.5	0.959±0.005	0.950±0.005	0.954±0.005
				72.5	0.955±0.005	0.954±0.005	0.955±0.001

TABLE 3.—BECKMANN READINGS, MEAN TEMPERATURES IN °C., FLOW TIMES AND THE CALCULATED VALUES OF $(E/R)/1000 = -T^2 (\Delta \ln \upsilon / \Delta T)/1000$ FOR n-HEXANE FROM 5°C. TO 50°C. USING VISCOMETER NO '0' AND $\Delta T = 1$°C.

Heating sequence						Cooling sequence						
Temperature (°C.)	Beckmann reading	Time of flow (secs) corrected for level	Mean temperature (°C.)	E/R ÷ 1000 Uncorrected	E/R ÷ 1000 Corrected	Temperature (°C.)	Beckmann reading	Time of flow (secs.) corrected for level	Mean temperature (°C.)	E/R ÷ 1000 Uncorrected	E/R ÷ 1000 Corrected	Overall mean (E/R)/1000
1	2	3	4	5	6	7	8	9	10	11	12	13
4.0	1.356±0.001	761.87±0.02				4.0	1.360±0.000	761.88±0.02				
			4.50	0.848	0.851±0.004				4.50	0.758	0.861±0.004	0.856±0.005
5.0	2.352±0.000	753.57±0.02				5.0	2.362±0.001	753.43±0.03				
			5.50	0.847	0.843±0.004				5.50	0.839	0.835±0.004	0.839±0.004
6.0	3.358±0.001	745.38±0.03				6.0	3.360±0.000	745.35±0.00				
6.0	0.080±0.001	745.36±0.02				6.0	0.080±0.000	745.36±0.01				
			6.50	0.861	0.861±0.002				6.60	0.857	0.857±0.002	0.859±0.002
7.0	1.080±0.000	737.22±0.02				7.0	1.083±0.000	737.21±0.02				
			7.50	0.778	0.778±0.002				7.50	0.786	0.786±0.002	0.782±0.004
8.0	2.090±0.001	729.91±0.03				8.0	2.095±0.000	729.80±0.02				
			8.50	0.781	0.780±0.002				8.50	0.790	0.789±0.002	0.785±0.005
9.0	3.090±0.000	722.77±0.01				9.0	3.090±0.000	722.61±0.01				
			9.50	0.787	0.786±0.002				9.50	0.775	0.774±0.002	0.780±0.006
10.0	4.110±0.001	715.54±0.01				10.0	4.118±0.001	715.44±0.02				
			10.50	0.784	0.786±0.002				10.50	0.781	0.783±0.002	0.784±0.001
11.0	5.133±0.000	708.44±0.00				11.0	5.136±0.001	708.39±0.02				
11.0	0.008±0.000	711.24±0.01				11.0	0.010±0.001	711.27±0.02				
			11.50	0.785	0.782±0.003				11.50	0.785	0.782±0.003	0.782±0.000
12.0	0.980±0.001	704.47±0.03				12.0	0.983±0.002	704.46±0.00				
			12.50	0.780	0.780±0.003				12.50	0.790	0.790±0.003	0.785±0.005
13.0	1.960±0.000	697.90±0.01				13.0	1.960±0.000	697.83±0.02				
			13.50	0.788	0.784±0.003				13.50	0.792	0.788±0.003	0.786±0.002
14.0	2.981±0.001	691.10±0.02				14.0	2.986±0.000	690.96±0.01				
			14.50	0.786	0.790±0.003				14.50	0.780	0.784±0.003	0.787±0.003
15.0	3.971±0.000	684.63±0.02				15.0	3.967±0.000	684.60±0.02				
			15.60	0.780	0.783±0.003				15.50	0.776	0.779±0.003	0.781±0.002
16.0	4.989±0.001	678.14±0.03				16.0	4.993±0.000	678.09±0.01				
16.0	0.063±0.000	677.90±0.01				16.0	0.063±0.000	677.89±0.00				
			16.50	0.790	0.787±0.002				16.50	0.797	0.794±0.002	0.790±0.003
17.0	1.069±0.000	671.51±0.02				17.0	1.073±0.001	671.42±0.02				
			17.50	0.800	0.800±0.002				17.50	0.794	0.794±0.002	0.797±0.003
18.0	2.081±0.001	665.10±0.02				18.0	2.078±0.000	665.11±0.02				
			18.50	0.804	0.800±0.002				18.50	0.791	0.787±0.002	0.793±0.006
19.0	3.060±0.000	658.97±0.02				19.0	3.060±0.000	659.06±0.02				
18.0	2.085±0.000	666.49±0.02				18.0	2.085±0.000	666.56±0.00				

(Continued) :—

(Table 3 Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
			18.50	0.794	0.790±0.003				18.50	0.789	0.784±0.003	0.787±0.003
19.0	3.076±0.001	660.35±0.03				19.0	3.072±0.001	660.49±0.02				
			19.50	0.790	0.794±0.003				19.50	0.796	0.800±0.003	0.797±0.003
20.0	4.075±0.000	654.29±0.01				20.0	4.080±0.000	654.33±0.01				
			20.50	0.790	0.793±0.003				20.50	00.794	0.797±0.003	0.795±0.002
21.0	5.082±0.000	648.28±0.02				21.0	5.080±0.001	648.33±0.02				
21.0	0.363±0.001	648.06±0.02				21.0	0.365±0.000	648.15±0.02				
			21.50	0.796	0.801±0.004				21.50	0.781	0.786±0.004	0.793±0.007
22.0	1.355±0.000	642.19±0.01				22.0	1.362±0.000	642.37±0.01				
			22.50	0.800	0.795±0.004				22.50	0.803	0.798±0.004	0.796±0.002
23.0	2.402±0.001	636.06±0.01				23.0	2.406±0.001	636.26±0.02				
			23.50	0.787	0.785±0.004				23.50	0.800	0.798±0.004	0.791±0.007
24.0	3.410±0.000	630.35±0.02				24.0	3.408±0.000	630.49±0.02				
			24.50	0.744	0.750±0.004				24.50	0.752	0.758±0.004	0.754±0.004
25.0	4.442±0.000	624.92±0.01				25.0	4.440±0.001	624.99±0.01				
			25.50	0.737	0.732±0.004				25.50	0.732	0.727±0.004	0.730±0.002
26.0	5.410±0.001	619.94±0.02				26.0	5.410±0.000	620.04±0.01				
25.6	0.943±0.000	621.13±0.02				26.0	0.985±0.000	620.94±0.02				
			26.30	0.738	0.738±0.003				26.50	0.736	0.736±0.003	0.737±0.001
27.0	1.981±0.000	615.85±0.01				27.0	1.980±0.000	615.85±0.00				
			27.7	0.748	0.745±0.003				27.75	0.740	0.737±0.003	0.741±0.004
28.5	3.489±0.001	608.23±0.02				28.5	3.484±0.001	608.33±0.02				
			29.25	0.734	0.739±0.003				29.25	0.739	0.744±0.003	0.741±0.003
30.0	4.992±0.000	600.92±0.01				30.0	4.990±0.000	600.91±0.01				
30.0	0.091±0.001	600.92±0.02				30.0	0.090±0.000	600.91±0.01				
			30.50	0.725	0.728±0.003				30.50	0.737	0.740±0.003	0.734±0.006
31.0	1.100±0.000	596.17±0.01				31.0	1.100±0.001	596.78±0.03				
			31.50	0.750	0.748±0.003				31.50	0.743	0.741±0.003	0.744±0.004
32.0	2.122±0.000	591.27±0.02				32.0	2.120±0.000	591.23±0.01				
			32.50	0.751	0.747±0.003				32.50	0.747	0.743±0.003	0.745±0.002
33.0	3.100±0.000	586.64±0.01				33.0	3.105±0.000	586.59±0.01				
			33.50	0.737	0.741±0.003				33.50	0.745	0.749±0.003	0.745±0.004
34.0	4.092±0.001	582.09±0.02				34.0	4.096±0.000	582.01±0.02				
			34.50	0.735	0.737±0.003				34.50	0.740	0.742±0.003	0.739±0.002
35.0	5.083±0.000	577.63±0.02				35.0	5.085±0.000	577.53±0.02				
35.0	-0.128±0.000	576.60±0.01				35.0	-0.125±0.000	576.58±0.02				
			35.50	0.749	0.750±0.003				35.50	0.746	0.747±0.003	0.748±0.002
36.0	0.880±0.000	572.05±0.02				36.0	0.878±0.001	572.07±0.01				
			36.50	0.745	0.747±0.003				36.50	0.741	0.743±0.003	0.745±0.002
37.0	1.876±0.001	567.64±0.02				37.0	1.870±0.000	567.70±0.02				
			37.50	0.738	0.734±0.003				37.50	0.739	0.735±0.003	0.735±0.001
38.0	2.861±0.000	563.38±0.01				38.0	2.862±0.000	563.46±0.01				
			38.50	0.722	0.722±0.003				38.50	0.723	0.723±0.003	0.723±0.000

(Continued) :—

(*Table 3 Continued*)

1	2	3	4	5	6	7	8	9	10	11	12	13
39.0	3.855±0.000	559.23±0.02				39.0	3.855±0.001	559.31±0.02				
			39.50	0.704	0.702±0.003				39.50	0.706	0.704±0.003	0.703±0.001
40.0	4.832±0.001	555.31±0.01				40.0	4.832±0.000	555.38±0.02				
40.0	0.032±0.000	555.23±0.01				40.0	0.030±0.000	555.17±0.01				
			40.50	0.722	0.721±0.003				40.50	0.710	0.709±0.003	0.715±0.006
41.0	1.032±0.000	551.17±0.02				41.0	1.036±0.001	551.15±0.03				
			41.50	0.740	0.740 0.003				41.50	0.733	0.733 0.003	0.736 0.003
42.0	2.036±0.001	547.05±0.03				42.0	2.034±0.000	547.09±0.01				
			42.50	0.781	0.777±0.003				42.50	0.770	0.766±0.003	0.771±0.004
43.0	3.034±0.000	542.79±0.01				43.0	3.038±0.001	542.86±0.02				
			43.50	0.762	0.766±0.003				43.50	0.747	0.751±0.003	0.758±0.007
44.0	4.025±0.001	538.72±0.02				44.0	4.030±0.000	538.86±0.01				
			44.50	0.747	0.744±0.003				44.50	0.745	0.742±0.003	0.743±0.001
45.0	5.031±0.000	534.74±0.02				45.0	5.030±0.000	534.90±0.02				
45.0	0.113±0.001	532.08±0.02				45.0	0.110±0.000	532.07±0.02				
			45.50	0.722	0.725±0.003				45.50	0.712	0.715±0.003	0.720±0.005
46.0	1.110±0.000	528.32±0.02				46.0	1.110±0.000	528.35±0.01				
			46.50	0.724	0.721±0.003				46.50	0.721	0.718±0.003	0.720±0.002
47.0	2.123±0.000	524.54±0.01				47.0	2.125±0.000	524.58±0.01				
			47.50	0.704	0.700±0.003				47.50	0.701	0.697±0.003	0.699±0.002
48.0	3.053±0.000	521.11±0.01				48.0	3.053±0.000	521.27±0.00				
			48.50	0.706	0.710±0.003				48.50	0.710	0.714±0.003	0.712±0.002
49.0	4.058±0.001	517.55±0.02				49.0	4.060±0.000	517.68±0.01				
			49.50	0.713	0.716±0.003				49.50	0.715	0.718±0.003	0.717±0.001
50.0	5.060±0.000	514.01±0.01				50.0	5.060±0.000	514.14±0.02				

Note:—				
	Temperature:-	10	20	30
	Correction $T^2\beta/1000$:	0.004	0.004	0.004

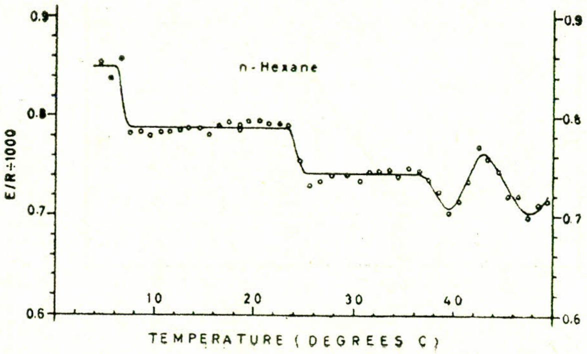

Fig. 3.—Graph showing the variation of E/R with temperature °C. for n-hexane in the region of 4°C. to 50°C. This again shows a regular series of sharp steps, followed by cyclic variation above 38°∓2°C.

the carbon chain length appears to be a major factor.

In order to examine this idea, the transition temperature collected on the few hydrocarbons,

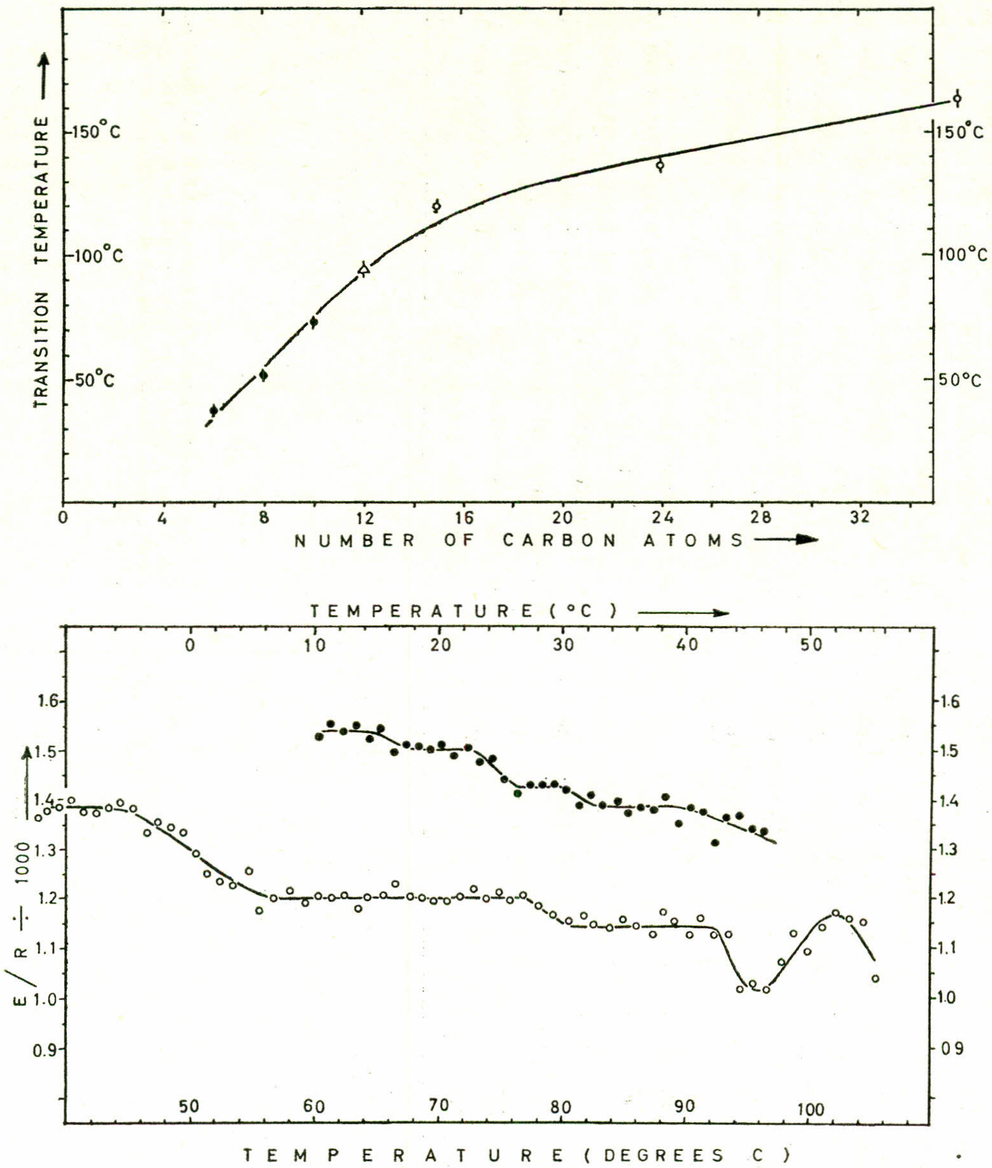

Fig. 4.—(Top) Plot of temperature for transition from stepwise structure to cyclic variation, versus n, the number of carbon atoms in the molecule. Solid circles are the points for pure normal hydrocarbons, and the hollow circles are for the mineral oils. This curve has minimum curvature near n=15. The triangle is an additional point for Kerosene oil.

Fig. 4.—(Bottom) Plot of (E/R)/1000 against temperature for Kerosene Oil (Mol. wt: 165) in the temperature range of 10° to 47°C. (solid circles) and 47°C. to 106°C. (hollow circles). This curve also shows a step-wise behaviour which undergoes to cyclic variation above 94∓2°C. like the other hydrocarbons.

are plotted as solid and hollow circles in Fig. 4(top) against the number 'n' of carbon atoms in the molecule. The circle can all be connected by a smooth curve as shown in the figure, but there is a rather large gap between decane and H.S. diesel oil with n = 15, where the curve exhibits maximum curvature. Accordingly, activation energy measurements were carried out on Kerosene oil of molecular weight 165, corresponding approximately to $C_{12}H_{26}$, and the results are shown in Fig. 4 (bottom). It is seen that here again there is a sequence of constant region of E/R

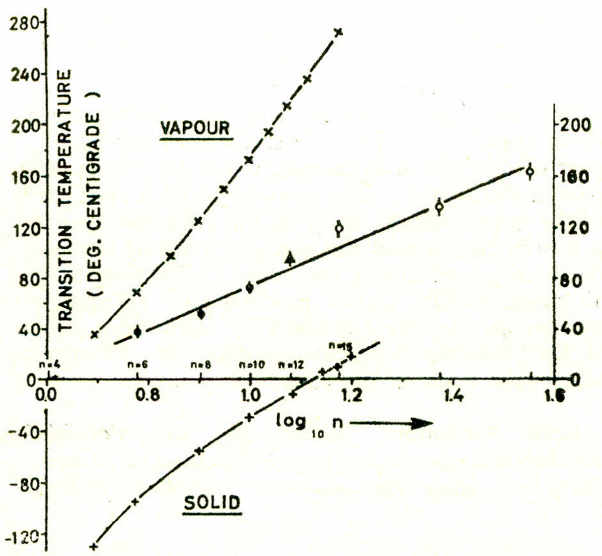

Fig. 5.—Plot of temperature of transition from step-wise behaviour to cyclic variation, against $\log_{10} n$ n is the number of carbon atoms in the molecule.

The solid circles are the points for pure normal hydrocarbons, hollow circles are for the mineral oils and the triangle is an additional point for Kerosene oil.

Inclined crosses are the boiling points and horizontal crosses are the freezing points for some of the hydrocarbons.

separated by sharp steps upto a temperature of $94° \mp 2°$C., after which the oscillatory behaviour sets in. This transition temperature is plotted as a triangle in Fig. 4 (top), and is seen to fall on the previously drawn curve.

With a view to further developing the relationship between this transition temperature and the number 'n' of carbon atoms in the chain, this graph is replotted against $\log_{10} n$ in Fig. 5. The points are now well-represented by a straight line through them, and for comparison, the upper and lower series of crosses show the succession of boiling and freezing points of the corresponding liquids and pure hydrocarbons.

It is now apparent that the straight line (or curve in Fig. 4 (a)) representing the transition temperatures divides the liquid range into two phases of some sort, with step-like transitions in E/R occurring below the line and cyclic variations above the line. Presumably this regular and consistent transition is connected with a type of order$\rightleftharpoons$disorder phenomenon occurring in all the hydrocarbons.

References

1. M.M. Qurashi and A.K.M. Ahsanullah, Brit. J. Appl. Phys., **12,** 65 (1961).
2. A.K.M. Ahsanullah, S. R. Ali, M.M. Qurashi, Pakistan J. Sci. Ind. Res., **5,** 133 (1962).
3. Tayeb M. Qureshi, M. Sabir and M.M. Qurashi, Proc. Pakistan Acad. Sci., **1,** 1 (1964).
4. Tayeb M. Qureshi, K. Hussain and M.M. Qurashi, Proc. Pakistan Acad, Sci., **2,** 21 (1965).