

### 439. *The Configuration of Flexible Polymethylene Molecules in the Gas Phase.*

By J. C. McCoubrey, J. N. McCREA, and A. R. UBBELOHDE.

Published data on the viscosities of gaseous hydrocarbons in the range 20—200° have been supplemented by new determinations, at various temperatures, for *isopentane*, *cyclopentane*, *n*-hexane, benzene, hex-1-ene, *methylcyclopentane*, *n*-, *iso*-, and *cyclo*-octane. Molecular volumes of the liquids at their boiling points have also been determined. By a survey of all the data and of entropies of vaporisation of the liquids at their boiling points, the conclusion reached is that the average molecular configuration of the flexible  $n\text{-C}_5\text{—C}_8$ -hydrocarbons in the vapour phase is quite highly coiled.

WHEN sufficiently large potential barriers oppose a change of shape, as in certain *cyclohexane* derivatives, or in unsaturated *cis-trans*-isomers, experiments on molecular configurations can be carried out by actual segregation of the different species, by using the standard techniques available for investigation of isomerism.

However, for problems of reaction mechanism, and for other problems of chemical physics, a knowledge of the average configuration of a molecule is required even in cases where the change of shape occurs too rapidly for any separation of the different configurations to be feasible. As a rough distinction for experimental convenience, molecular configurations with a half life of the order of one hour or less under the conditions of experiment may be termed "flexible." Normally these must be investigated from averaged properties of a mixture of molecules of different configurations.

Much theoretical and experimental work has been published recently on the average configuration in solutions of flexible molecules of high polymers. But statistical methods which are successful when the number of flexible units in a chain molecule is large do not offer the same scope when there are comparatively few units in the molecule. Information on the shorter polymethylene chains is relevant, for example, in problems of the influence of structure on the reactivity of such molecules in the gas phase (Ubbelohde, *Rev. Inst. Franç. du Pétrole et Ann. Combust. liq.*, 1949, 4, 488; McCoubrey and Ubbelohde, *Faraday Soc. Discuss.*, 1951). A convenient nomenclature is to describe the flexible molecules in their fully stretched zig-zag configuration as *trans*. As each C—C bond is rotated to the *cis*-position the coiling of a polymethylene molecule increases progressively.

The present paper records experimental results which yield information about the average configuration of polymethylene molecules in the range  $\text{C}_4\text{—C}_8$ . Earlier, rather scattered determinations of the viscosities, at various temperatures, of the vapours of *n*- and *iso*-butane, *n*-pentane, benzene, *n*- and *cyclo*-hexane, *n*-heptane, and *n*-octane have been supplemented by redeterminations in the case of benzene, *n*-hexane, and *n*-octane. New results have also been obtained for *iso*- and *cyclo*-pentane, hex-1-ene, *methylcyclopentane*, and *iso*- and *cyclo*-octane, in order to permit comparisons between structurally related compounds.

As discussed below, no fully worked out kinetic theory of momentum transfer is yet available for such flexible molecules. However, a comparison of calculated kinetic parameters within a series of structurally related compounds shows that polymethylene hydrocarbons up to  $\text{C}_8$  behave, in homomolecular collisions, predominantly as coiled molecules. This conclusion is compared with inferences based on parameters of the molecules not directly dependent on collisions, by use of new measurements of the molecular volumes of the liquids at their boiling points.

These measurements, and data on the entropies of vaporisation, confirm that on average the external aspect of molecules of *n*-paraffins in the gas phase is much the same as that of fully

branched isomers, so that the *n*-paraffins behave as if they were quite highly coiled in the gas phase, *i.e.*, as if many of the C-C bonds were on average far from the *trans*-configuration.

## EXPERIMENTAL.

*Materials* (cf. Table I).—Samples were purified where necessary by carefully controlled fractionation in a 12" column packed with glass helices (10–12 plates). The redistilled liquids were then carefully dried by bubbling dry oxygen-free nitrogen through them near the b. p.s. Final purification was by distillation within the apparatus. Before such a distillation the liquid was frozen repeatedly in liquid air and allowed to melt *in vacuo*, to expel permanent gases; this precaution appears to be particularly important when capillary methods are used in viscosimetry.

TABLE I.  
*Characteristics of materials used.*

Hydrocarbon.	Ref.	Boiling range, $\pm 0.1^\circ$ .	$n_{20}^D$ , *	<i>d.</i>	Mol. vol. at b. p., ml.	Mol. entropy of vaporisation at b. p., e.u. (ref. 2).
<i>n</i> -Butane .....	2	—	—	—	—	19.63
<i>iso</i> Butane .....	2	—	—	—	—	19.47
<i>n</i> -Pentane .....	1	37.0°	1.3575	0.610 $\pm$ 0.001	118.2	19.92
<i>iso</i> Pentane .....	1	28.0	1.3536	0.612	117.8	19.41
<i>cyclo</i> Pentane .....	1	49.2	1.4056	0.713	101.1	20.26
<i>n</i> -Hexane .....	1	68.3	1.3743	0.615	140.0	20.17
Hex-1-ene .....	1	63.5	1.3866	0.643	133.9	—
<i>cyclo</i> Hexane .....	1	80.7	1.4263	0.719	116.9	20.30
Methylcyclopentane .....	1	71.5	1.4095	0.699	120.3	20.30
Benzene .....	1	80.1	1.5008	0.814	95.0	20.81
<i>n</i> -Heptane .....	1	98.2	1.3875	0.615	162.6	20.36
2 : 2-Dimethylpentane .....	2	—	—	—	—	19.54
<i>n</i> -Octane .....	1	125.5	1.3974	0.616	185.3	20.96
2 : 2 : 4-Trimethylpentane ...	1	99.0	1.3912	0.625 $\pm$ 0.002	182.6	19.90
<i>cyclo</i> Octane .....	1	147.5	1.4588	0.744 $\pm$ 0.002	150.7	—

<sup>1</sup> Present experiments. <sup>2</sup> Bur. Stand. Amer. Petroleum Res. Project 44.

\* Determined on a Hilger-Abbé refractometer.

Thanks are offered to the Anglo-Iranian Oil Company for gifts of *n*-, *cyclo*-, and *iso*-pentane, *n*-hexane, and 2 : 2 : 4-trimethylpentane (*isooctane*), to Distillers Company Ltd. for gifts of *cyclopentane* and methylcyclopentane, and to the British Oxygen Company for a gift of *cyclooctane*. Hex-1-ene was obtained from Messrs. Light's, and *n*-octane (synthetic) from B.D.H. The benzene used was as purified for freezing-point measurements (Thompson and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 349).

*The Molecular Volume at the Boiling Point.*—To determine the density of the liquid hydrocarbon, a 0.5-ml. Pyrex pycnometer was calibrated with water. This pycnometer was then filled with a hydrocarbon and was suspended in the vapour at the b. p. The mass of liquid was found by then cooling and weighing the pycnometer. The method was checked by a number of experimental determinations with benzene. Standard precautions (cf. Burroughs, *Bur. Stand. J. Res.*, 1923, **1**, 635) were taken to ensure that the pycnometer was at the temperature of liquid-vapour equilibrium, and generally three determinations were made with each liquid. Results are recorded in Table I. Where comparisons could be made, the values agreed within 0.001 g./ml. with extrapolated I.C.T. values, further verifying the purity of the samples.

*Viscosities.*—The capillary viscometer used was basically similar to that described by Rankine (*Proc. Roy. Soc.*, 1913, **88**, 575) and Nasini (*ibid.*, 1929, **123**, 686); only major additions and improvements are described in Fig. 1. These included direct and continuous pressure measurement on both sides of the capillary by means of two Pyrex-spiral pressure gauges fitted with optical levers. The pressures of air required to bring the spirals back to the null point were read on a mercury manometer to 0.1 mm. Special experiments on the vapour pressure above the liquid in the tube during a run showed that the effective driving pressures were always less than the equilibrium vapour pressures at the bath-temperatures. By inserting a silver wire upwards through the column of liquid into the vapour much closer approximation of driving pressures to equilibrium vapour pressures could be obtained. Extremely vigorous stirring (using a magnetic plunger operated by a permanent magnet outside the tube) produced considerable splashing of the liquid and also gave good agreement between the driving pressures and the equilibrium vapour pressures. Actual behaviour in the absence of these precautions corresponded with a drop in temperature of about 1.5° at 50 mm. pressure on passage from the body of the liquid to the surface. Neither of the above methods was convenient for use in systematic measurements on the rate of transfer of mass through the capillary, so that continuous readings were taken of the actual driving pressure. The bath-temperature around the graduated tube was controlled to  $\pm 0.025^\circ$ . The portion of this tube (a 1-c.c. Pyrex pipette) which was used in the runs had a constant radius of 0.1085 cm., measured by calibration with mercury. The fall in the liquid level during capillary flow was measured at intervals to  $\pm 0.01$  mm. with a cathetometer. After passing through the capillary the vapours were condensed in liquid air. The spiral gauge generally showed that the pressure on this side was negligible. The temperature of the bath oil around the capillary was maintained electrically to  $\pm 0.25^\circ$ . The capillary tube was a "Veridia" capillary supplied by Chance Brothers. Calibration with a mercury pellet showed that it had a uniform diameter of  $0.992 \times 10^{-2}$  cm.  $\pm 0.03\%$  over the length used (*ca.* 20 cm.). In the calculations which follow, no correction has been made for possible effects of multi-

layer absorption on the effective diameter of the capillary, or on the slip correction. Multilayers thicker than  $5 \times 10^{-6}$  cm. could have an appreciable effect in decreasing flow and thus increasing the apparent viscosity.

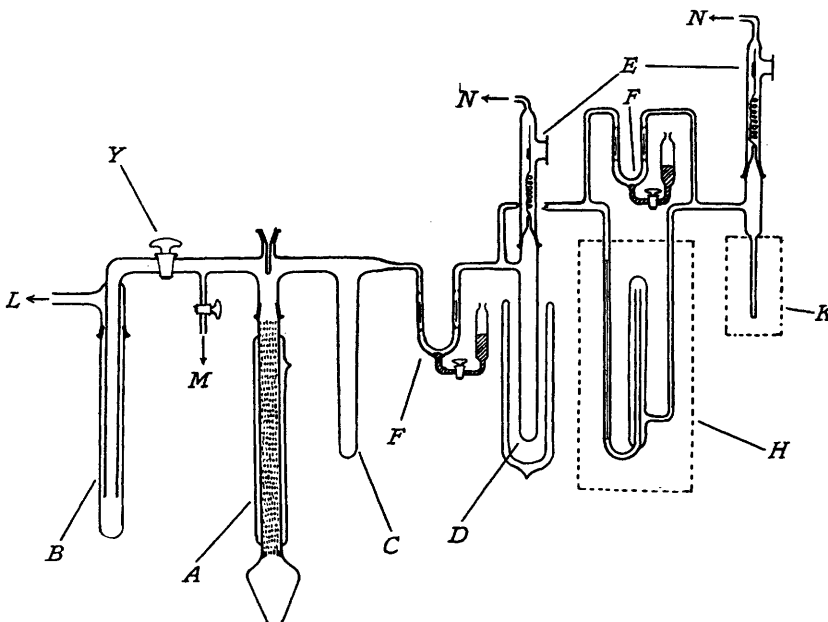
To avoid *ad hoc* end corrections, the resistance of the viscometer was calibrated with dry air. For this purpose a volume of about 6 l. of air at measured pressure was connected to one side of the capillary, and the other side was kept effectively at zero pressure by continuous pumping.

By use of the values  $\eta_{293} = 1795 \times 10^{-7}$  and  $\eta_{273} = 2171 \times 10^{-7}$  c.g.s. units (temp. are K.) for air (Johnson and McCloskey, *J. Phys. Chem.*, 1940, 44, 1038), the average of four independent determinations at each temperature was found to be  $r^4/L = 389.8 \times 10^{-12}$  with a mean deviation of  $\pm 0.4\%$ . In calculating viscosities the standard Poiseuille equation was used, *viz.* :

$$\eta = \frac{r^4}{L} \times \frac{p_1^2 - p_2^2}{16} \times \frac{273\rho}{760T} \times \frac{t}{m}$$

where  $m$  is mass transpired in time  $t$  seconds (measured in terms of the volume of liquid evaporated),  $\rho$  is the density of vapour at N.T.P.,  $T$  is the capillary temperature in  $^{\circ}\text{K.}$ ,  $p_1$  and  $p_2$  are the pressures (dynes/cm.<sup>2</sup>) on either side of the capillary,  $r$  is the radius of the capillary, and  $L$  is its length in cm.  $\eta$  is the coefficient of viscosity.

FIG. 1.



A, Fractional distillation unit, in which liquid is introduced into the apparatus. B, Liquid-air trap. C, Tube for bulb-to-bulb distillation from C to D. D, Condensation point for vapours after they pass through the capillary. E, Pyrex-spiral pressure gauges. F, Mercury-seal taps. H, Capillary arrangement, showing preheater and surrounding thermostat bath. K, Graduated tube, with thermostat bath. L, Lead to Hyvac rotary and diffusion pumps. M, Lead to manometric system, by means of which the pressure inside the apparatus can be measured during fractionation. N, Leads to manometric system, so that the air pressure inside the gauge jackets can be measured.

By way of illustration data for cyclopentane are recorded in detail (Table II).

TABLE II.  
Flow data for cyclopentane.

Temp. of capillary.	Drop in liq. level, <i>d.</i>	Driving pres- sure, cm. Hg.	$\eta$ , poises.	$\eta$ , corr. for slip, poises.	Temp. of capillary.	Drop in liq. level, <i>d.</i>	Driving pres- sure, cm. Hg.	$\eta$ , poises.	$\eta$ , corr. for slip, poises.		
18.5°	0.765	5.490	9.55	826	845	109.0	0.773	2.850	8.80	1021	1044
18.5	0.765	5.400	9.55	837	853	109.0	0.773	2.850	8.75	1010	1033
18.5	0.765	5.620	9.75	830	846	109.0	0.773	2.370	8.00	1015	1038
19.0	0.765	5.700	9.65	811	828	140.0	0.773	2.260	8.40	1085	1114
19.0	0.765	5.900	9.65	784	801	140.0	0.773	2.040	7.86	1050	1079
76.0	0.763	4.800	10.60	973	997	140.0	0.773	1.950	7.70	1059	1086
79.0	0.767	4.220	9.90	952	970	140.0	0.773	2.310	8.60	1113	1142
75.0	0.765	4.400	10.10	966	984	176.0	0.773	2.160	8.75	1133	1164
109.0	0.773	2.760	8.71	1031	1054	176.0	0.775	2.600	9.60	1134	1163

TABLE III.  
Summarised viscosity data.

	$\eta$ , poises.	Precision ( $\pm$ ).	No. of independent observations.	Temp. (K.).	$\alpha$ .	
<i>n</i> -Butane (Titani) .....	739	—	—	293.1	0.177	
	787	—	—	323.1	0.174	
	947	—	—	373.1	0.155	
	998	—	—	393.1	0.151	
<i>iso</i> Butane (Titani) .....	744	—	—	293.1	0.175	
	792	—	—	323.1	0.173	
	947	—	—	373.1	0.155	
	995	—	—	393.1	0.152	
<i>cyclo</i> Pentane (present work), $p_1 \sim 90$ mm. Hg ...	835	16	5	292.6	0.171	
	985	9	3	352.1	0.159	
	1042	7	4	382.1	0.157	
	1105	23	5	413.1	0.154	
	1164	1	2	449.1	0.152	
<i>iso</i> Pentane (present work), $p_1 \sim 75$ mm. Hg ...	693	8	4	291.1	0.209	
	807	11	3	341.1	0.194	
	978	13	3	415.1	0.177	
	1108	14	4	453.1	0.163	
	„ (Bleakney) .....	695	—	—	298.1	0.211
	860	—	—	373.1	0.191	
<i>n</i> -Pentane (Bleakney) .....	676	—	—	298.1	0.217	
	841	—	—	373.1	0.195	
„ (Titani) .....	662	—	—	298.1	0.221	
	868	—	—	373.1	0.189	
	911	—	—	395.1	0.185	
	995	—	—	432.1	0.177	
	1126	—	—	492.1	0.167	
	1191	—	—	523.1	0.163	
Benzene (present work), $p_1 \sim 70$ mm. Hg .....	744.7	14	5	295.1	0.204	
	846.1	10	4	327.1	0.189	
	979.3	6	4	374.1	0.174	
	1030.0	5	3	406.1	0.173	
	1134.4	18	5	451.1	0.165	
„ (Nasini) .....	736	—	—	289.1	0.204	
	802	—	—	314.1	0.195	
	941	—	—	373.6	0.181	
	1074	—	—	423.1	0.169	
	1176	—	—	470.3	0.163	
„ (Titani) .....	738	—	—	281.1	0.203	
	918	—	—	323.1	0.173	
	1031	—	—	403.1	0.172	
	1110	—	—	434.1	0.166	
	1198	—	—	468.1	0.160	
	<i>n</i> -Hexane (present work) $p_1 \sim 68$ mm. Hg .....	614.3	4	5	288.1	0.256
737.6		8	3	349.1	0.235	
796.2		2	3	376.1	0.286	
835.0		9	5	395.1	0.221	
904.6		5	3	423.1	0.211	
981.1		8	4	462.1	0.203	
„ (Titani) .....		866	—	—	394.1	0.213
		958	—	—	434.1	0.226
	1021	—	—	462.1	0.195	
Hex-1-ene (present work), $p_1 \sim 68$ mm. Hg ...	681.1	10	5	301.1	0.234	
	772.5	3	5	348.1	0.221	
	902.8	9	3	398.1	0.203	
	931.6	6	5	419.1	0.202	
	1000.2	5	5	450.1	0.195	
Methylcyclopentane (present work), $p_1 \sim 85$ mm. Hg .....	762	14	6	293.1	0.206	
	837	6	4	341.9	0.203	
	891	13	5	378.7	0.200	
	1019	16	3	414.6	0.183	
	1097	10	5	450.5	0.177	

TABLE III—continued.

	$\eta$ , poises.	Precision ( $\pm$ ).	No. of independent observations.	Temp. (K.).	$\alpha$ .
<i>n</i> -Heptane (Melaven and Mack) .....	717	—	—	373.1	0.270
	811	—	—	423.1	0.254
	922	—	—	475.1	0.237
	1080	—	—	524.1	0.212
2 : 2-Dimethylpentane (Melaven and Mack) ...	734	—	—	343.1	0.253
	769	—	—	374.1	0.252
	827	—	—	405.1	0.244
	900	—	—	449.1	0.236
	1048	—	—	535.1	0.221
<i>n</i> -Octane (present work), $p_1 \sim 20$ mm. Hg .....	689	19	8	379.5	0.302
	762	2	3	419.4	0.287
	800	18	8	446.7	0.282
	875	3	3	473.8	0.266
2 : 2 : 4-Trimethylpentane (present work), $p \sim 35$ mm. Hg	727	12	3	374.8	0.285
	770	11	3	402.1	0.278
	817	15	5	433.4	0.272
	898	17	2	467.1	0.257
<i>cyclo</i> Octane (present work), $p_1 \sim 20$ mm. Hg ...	703	4	2	398.6	0.301
	708	19	4	414.1	0.304
	755	7	3	442.6	0.295
	805	6	4	478.1	0.288

References : Titani, *Bull. Chem. Soc. Japan*, 1929, **4**, 277; 1930, **5**, 98; Bleakney, *Physics*, 1932, **3**, 123; Nasini, *Proc. Roy. Soc.*, 1929, *A*, **123**, 692; Melaven and Mack, *J. Amer. Chem. Soc.*, 1932, **54**, 888; Titani, quoted by Schuil, *Phil. Mag.*, 1939, **28**, 679; Everhart, Hare, and Mack, *J. Amer. Chem. Soc.*, 1933, **55**, 4894.

TABLE IV.

*Interpretation of temperature coefficients of viscosity (Sutherland's equation).*

Hydrocarbon.	Sutherland's constant.	Collision area, $A$ , sq.A.	Hydrocarbon.	Sutherland's constant.	Collision area, $A$ , sq.A.
<i>n</i> -Butane (T) .....	358	16.6	<i>n</i> -Heptane (M) .....	445	26.7
<i>iso</i> Butane (T) .....	330	17.1	<i>iso</i> Heptane (E) .....	257	31.1
<i>n</i> -Pentane (T) .....	383	19.6	<i>n</i> -Octane (W) .....	577	28.2
<i>iso</i> Pentane (W) .....	468	19.2	2 : 2 : 4-Trimethylpentane (W) .....	394	32.9
<i>cyclo</i> Pentane (W) .....	140	27.0	<i>cyclo</i> Octane (W) .....	205	47.0
Benzene (W) .....	344	22.1	References (for details see Table III) : T = Titani; W = present work; M = Melaven and Mack; E = Everhart <i>et al.</i>		
<i>n</i> -Hexane (W) .....	384	25.6			
Hex-1-ene (W) .....	392	23.8			
<i>cyclo</i> Hexane (T) .....	351	21.2			
Methylcyclopentane (W) ...	293	24.3			

The Poiseuille value of  $\eta$  was corrected for slip by means of the standard formula  $\eta_{corr.} = \eta(1 + 4\eta/\epsilon r)$ , where the slip coefficient  $\eta/\epsilon$  is given by

$$\eta/\epsilon = \frac{1.70\sqrt{3RT/M}}{(p_1 + p_2)}$$

where  $M$  is molecular weight and the other symbols have their usual meanings. The numerical values of  $(\eta_{corr.} - \eta)$  at the pressures and temperatures used ranged from 1 to 4% of  $\eta$ .

The correction for non-axial flow at the ends of the capillary was less than 0.1% and was neglected. Flow rates were in all cases less by a factor of about 20 than the Reynolds number for turbulent flow.

Bleakney (*Physics*, 1932, **3**, 123) proposed an empirical correction for the variation of viscosity with gas pressure. Insufficient information is available for application of systematic corrections, and for comparative reasons no allowance for any pressure variation has been made in Tables III and IV.

The Poiseuille flow equation should be corrected if the behaviour of the vapour differs appreciably from that of a perfect gas, and if this correction is not applied there will be an apparent variation with temperature of the calculated  $\eta$ . The most convenient way of introducing this correction is to use the equation

$$pV = n(RT + Bp)$$

in place of  $pV = nRT$  in deriving the Poiseuille formula. The flow equation becomes :

$$\eta = \frac{r^4}{8L} \times \frac{273\rho}{760T} \times \frac{t}{m} \left[ \frac{p_1^2 - p_2^2}{2} - \frac{B}{3} \frac{p_1^3 - p_2^3}{RT} \right]$$

# 1966 McCoubrey, McCrea, and Ubbelohde: The Configuration of

Since  $p_2 \sim 0$ , the resultant correction can be reduced to the form:

$$\eta_{\text{apparent}} = \eta_{\text{ideal}}(1 - 2Bp/3RT)$$

where  $\eta_{\text{apparent}}$  is the apparent viscosity at  $p$ ,  $T$ , and  $\eta_{\text{ideal}}$  is the viscosity under limiting conditions of ideal gas laws. From Berthelot's equation,  $B$  is negative. By way of illustration, the numerical magnitude of the second term can be calculated at  $T = 323^\circ \text{K}$ , viz.: benzene = 0.0018, cyclohexane = 0.0022, and  $n$ -hexane = 0.0023. These values refer to an arbitrary  $p = 5 \text{ cm. Hg}$  and would be larger at lower temperatures or higher pressures (for the  $B$  values see Lambert, Roberts, Rowlinson, and Wilkinson, *Proc. Roy. Soc.*, 1949, *A*, **196**, 113).

It should be noted that any dimerisation or cluster formation has an effect on the collision area quite apart from the above correction to the Poiseuille equation for hydrodynamic flow.

Unfortunately, values of  $B$  are not available for all the molecules used in the present investigation, so that for comparative purposes the variation of viscosity with temperature from this cause is best left uncorrected in all the data. However, in evaluating "straight lines" for Sutherland plots anomalous data at the lowest temperatures of measurement for isooctane and cyclooctane were not included.

## RESULTS.

New results on molar volumes at the b. p. are recorded in Table I. B. p.s are used to give corresponding temperatures. New results on viscosities are conveniently summarised in the form of the parameter  $\mathfrak{A} = \sqrt{MT}/\eta$ , where  $M$  is the mol. wt. and  $T$  the temperature in  $^\circ\text{K}$ .  $\eta$  is measured in poises.

In the simplest form of kinetic theory of momentum transfer, the molecular diameter  $\sigma$  is related to this parameter according to the equation:

$$11\sigma^2 = \frac{3}{2}\sqrt{k/N\pi} \times \sqrt{MT}/\eta = 5.694 \times 10^{-21} \mathfrak{A} \quad \dots \quad (1)$$

where  $N$  is Avogadro's number (taken as  $6.023 \times 10^{23}$ ) and  $k$  is Boltzmann's constant (taken as  $1.380 \times 10^{-16}$ ).

These results are recorded in Table III. As will be seen below, the precision achieved in the present experiments is about the same as that in the most self-consistent previous work. Lines of closest fit were calculated by standard probability theory, using the straight-line equation (3 below). Deviations of individual mean values from these lines (Fig. 3, i—iii, p. 1969) may be compared with the scatter of individual results on which these means are based (Table III, "Precision"). The deviations accord with the experimental scatter except for one point with methylcyclopentane and one with hex-1-ene. Where necessary, further independent observations were made with different samples, but these did not remove the discrepancy. It may be that the straight-line equation assumed for purposes of computation breaks down for these molecules.

## DISCUSSION.

*Coiling of n-Paraffins in Vapour and Liquid.—Variation of  $\mathfrak{A}$  with molecular structure.* As with other gas-kinetic parameters, the theoretical interpretation of viscosities in terms of molecular structure and modes of energy transfer has not been completely worked out for polyatomic molecules. A review up to 1934 has been given by Loeb ("Kinetic Theory of Gases," McGraw Hill, 1936). Mathematical refinements have been discussed by Chapman and Cowling ("Mathematical Theory of Non-Uniform Gases," Cambridge Univ. Press, 1939) but are not readily amenable to computation from observed viscosities. Rather elaborate computations by Hirschfelder, Bird, and Spotz (*J. Chem. Physics*, 1948, **16**, 968; *Chem. Reviews*, 1949, **44**, 205; *Trans. Amer. Soc. Mech. Eng.*, 1949, 921) are discussed below.

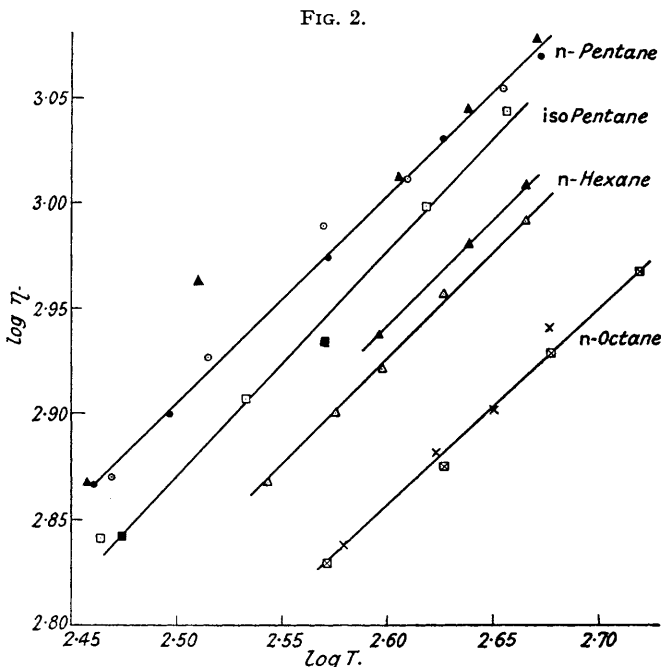
Although no complete theoretical treatment can at present be applied, advantage can be taken of the structural variations available within a range of homologues and isomers to establish some definite conclusions about average molecular configurations.

In the crudest approximation, the viscosity parameter  $\mathfrak{A}$  and the molecular diameter  $\sigma$  effective for momentum transfer are treated as independent of temperature. Table III permits a preliminary survey of the variation of  $\mathfrak{A}$  with molecular structure, in a series of closely related compounds.

So far as possible, the same temperature must be chosen for comparison. This is usually possible for isomers, but for homologues there are experimental limitations set by the vapour-pressure range in which data can conveniently be obtained. Notwithstanding these limitations, it is evident by inspection of Table III that at the same temperatures the normal paraffins have approximately the same effective diameter as the isomeric branched paraffins. For butane the difference between the  $n$ - and  $iso$ -compounds is less than the experimental error. At longer chain length, the  $n$ -compounds tend to have rather higher  $\mathfrak{A}$  than the branched isomers, but even for octane the difference is not more than a few units per cent. The cyclic compounds cyclopentane and methylcyclopentane show a smaller  $\mathfrak{A}$  than the paraffins with the same number of carbon atoms, but  $\mathfrak{A}$  for cyclooctane resembles that for  $n$ -octane.

The simplest interpretation of this broad general conclusion is that in molecular collisions with similar molecules the *n*-paraffins behave as if on average their area corresponds with coiling into close-packed configurations. More detailed ratios are given in Table V below.

*Molar volumes and entropies of vaporisation in relation to structure.* In Table I, the molar volumes are recorded at the respective boiling points of the liquids, since these give approximately corresponding temperatures. On the average each *n*-paraffin occupies a volume which is the same within a few units per cent. as that of the isomeric branched paraffin. This again implies the broad conclusion that the average configuration of the *n*-paraffins must correspond with close-packed helices. A drift towards smaller parachors which is observed as molecular branching increases (Gibling, *J.*, 1941, 299) does not exceed 2–3% in the C<sub>7</sub>–C<sub>9</sub>-series. Owing to complications of molecular interference in the liquid phase, not more than a broad general comparison seems feasible at present. The smaller space requirements of cyclic molecules is again apparent and in this case is shown also by cyclooctane.



○, □, △, ×, Present work ; ●, Nasini ; ▲, Titani ; ⊠, Melaven and Mack ; ■, Bleakney (for refs. see Table III).

Additional general information about the relative coiling of the flexible molecules in the liquid and the vapour may be obtained from a consideration of entropies of vaporisation (Table I, cf. Ubbelohde, *loc. cit.*). The *n*-paraffin has generally a slightly higher entropy of vaporisation than the *iso*-compound, which may imply that a rather broader distribution of configurations is assumed when the flexible *n*-paraffin molecules pass from liquid to vapour.

On this basis, the difference between isomeric *n*- and *iso*-compounds would be attributed to a change of entropy with coiling. The cyclic compounds have uniformly higher entropies of vaporisation than the paraffins with the same number of carbon atoms. This may be because for these rings in the liquid phase molecular rotation about an axis perpendicular to the symmetry axis is strongly hindered, so that the average molecular volume occupied in the liquid is smaller and the entropy of vaporisation larger than for the normal and branched-chain paraffins.

*Interpretation of the temperature coefficient of viscosity.* More refined information about the collision processes between polyatomic molecules can be obtained from the observed temperature variations.

Before theoretical analysis of the results is attempted, the accuracy of the temperature coefficients may be assessed. Straight lines (or shallow curves) are very generally obtained by plotting the relation,

$$\log \eta = A + x \log T \dots \dots \dots (2)$$

where  $\alpha > \frac{1}{2}$  (Licht and Stechert, *J. Phys. Chem.*, 1944, **48**, 23). Such plots permit a test of concordance when the same molecule has been studied by different observers. Fig. 2 gives comparative plots for benzene, isopentane, *n*-hexane, and *n*-octane. The data overlapping our present results were in most cases obtained with capillary viscometers; a rotating cylinder was used for isopentane (see refs. to Table III). It will be seen from Fig. 2 that the agreement between different observers is usually within 1% for benzene; for *n*-hexane our values lie about 4% below those of Titani. For isopentane our results accord with those of Bleakney within about 2.5%. For *n*-octane the concordance is generally within 1% with the results of Melaven and Mack. Except for Titani's data for *n*-hexane, the agreement is about as good as present experimental methods permit. However, the divergences make it unsafe to combine the results of more than one observer in calculating temperature coefficients, since these involve a first differential of the experimental data. The sources of the observations selected for calculation are given in Table IV. Various authors have claimed that Sutherland's equation is the most straightforward two-constant equation for the temperature coefficient of gaseous viscosity (Licht and Stechert, Loeb, and Schuil, *loc. cit.*). This can be written:

$$\eta = KT^{3/2}/(T + C) \quad \dots \quad (3)$$

where  $K$  and  $C$  are constants to be evaluated by experiment. In the notation of the present paper

$$K'\alpha = 1 + C/T$$

For purposes of computation it was more convenient to use the variables  $T$  and the expression

$$T^{3/2}/\eta = \alpha T$$

in evaluating lines of closest fit by standard methods. The best values of the constants are recorded in Table IV; this records nominal collision areas  $A$ , which are related to the constant  $K$  in equation 3 by the expression:

$$A/(1 + e) = 1.594 \times 10^{-18} \sqrt{M}/K = \frac{0.086 \rho_0 \bar{c}}{N\eta(1 + C/T)}$$

where  $\rho_0$  is the density at N.T.P. and  $\bar{c}$  is the R.M.S. velocity at  $T$ . Chapman's correction term  $e$  ranges from 0.001 to 0.006 (Chapman, *Phil. Trans.*, 1916, **211**, 279) and is neglected.

In Fig. 3 some of the calculated lines of closest fit according to equation (3) are plotted for comparison with individual results. Although a straight-line equation represents the experimental results with moderate accuracy, it is found that equation (2) frequently gives a more nearly linear plot. Furthermore, for isooctane and cyclooctane the measured viscosities at the lowest temperatures do not fit equation (3) at all. To avoid confusion these points (Table III) have not been included in Fig. 3.

Probably on account of deviations from straight-line equations, molecular parameters calculated by different authors, using equation (3) show considerable discrepancies, even though individual values of viscosities are in good agreement. The Sutherland constant  $C$  involves extensive extrapolation and is sensitive to the precise straight line assumed.

In examining Table IV, it must be remembered that the theoretical basis for Sutherland's formula is a particular interpretation of the change of  $\eta$  with temperature. Sutherland's theory is that the average relative velocity of approach of the molecules increases with rise in temperature, and this lowers the apparent collision area. But if there is any other source of temperature variation of viscosity this might distort the Sutherland interpretation of the temperature coefficients. For example, if the flexible molecules are coiled, the average degree of coiling might vary with temperature (see below). Such a variation would give spurious values to the constants  $C$  and  $K$  in equation (3). Again, cyclic molecules can crumple if  $n \geq 6$  and, particularly at higher temperatures, the relative proportions of various configurations in equilibrium can change appreciably with temperature. Furthermore, if the molecules are associated in pairs or clusters in the gas owing to van der Waals attractions this could give an abnormally large apparent collision diameter particularly at the lower temperatures.

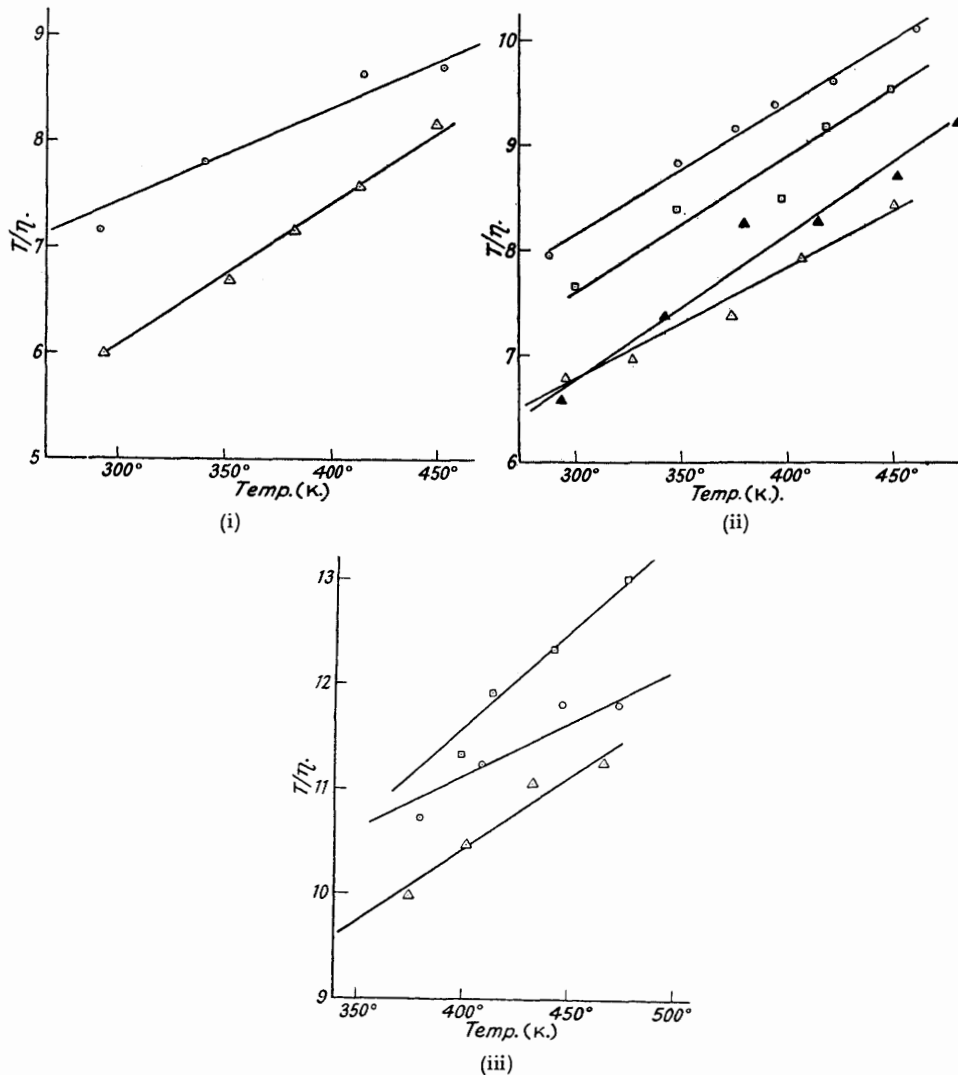
Evidence for association has been put forward on the basis of second virial coefficients (Hirschfelder, McClure, and Weeks, *J. Chem. Physics*, 1942, **10**, 201). In view of these restrictions on the Sutherland theory in the case of flexible molecules comparisons in Table IV should in the first instance be made between closely similar molecules. The Sutherland collision areas of the branched-chain paraffins are only slightly larger than those of the *n*-paraffins, thus confirming the broad conclusions from the viscosities themselves. Introduction of a double bond



at one end of *n*-hexane decreases the collision area; this is similar to the effect reported by Bleakney for pent-2-ene (*loc. cit.*).

The large apparent values of *A* for the cyclic compounds are anomalous and are very tentatively attributed to the fact that molecular association in the vapour is an additional source of temperature variation of viscosity. A similar anomaly has been reported for mesitylene (Everhart *et al.*, *loc. cit.*).

FIG. 3.  
Sutherland plots for calculated lines of closest fit.



(i) ○, isoPentane; △, cycloPentane. (ii) ○, n-Hexane; □, Hex-1-ene; △, Benzene; ▲, Methylcyclopentane. (iii) □, cycloOctane; ○, n-Octane; △, 2:2:4-Trimethylpentane.

*Other computations of molecular interaction.* Preliminary computations of "collision areas" were also made by the method described by Hirschfelder, Bird, and Spatz (*loc. cit.*). This method uses Lennard-Jones attraction and repulsion functions between the molecules, based on the virial coefficients. Hirschfelder, Bird, and Spatz had already reported that the *n*-hydrocarbons show large discrepancies in the force constants as evaluated from boiling-point data, compared with those evaluated from viscosities (*loc. cit.*). Graphical approximations using tables of functions calculated by these authors gave no substantially new information for the

hydrocarbons investigated by us. Results are collected in Table V. The anomaly of the cyclic compounds and the somewhat larger  $r_0$  of the 2 : 2 : 4-trimethylcyclopentane are again apparent.

The comparisons in Table V cannot be pushed very far, since if the Taylor theory is correct (see below), a contribution to the overall temperature coefficient of viscosity would arise from the shrinking together of the coiled molecule as the temperature rises, and neither the Sutherland nor the Hirschfelder interpretation of temperature coefficient in terms of change of average molecular velocities can be fully adequate.

TABLE V.

*Hirschfelder parameters computed graphically from present results.*

	Molecular diameters, $r_0$ (A.).	Best $\epsilon/k$ ( $\pm 25$ ).		Molecular diameters, $r_0$ (A.).	Best $\epsilon/k$ ( $\pm 25$ ).
<i>cyclo</i> Pentane .....	6.69	100	<i>n</i> -Octane .....	6.83	450
<i>iso</i> Pentane .....	5.25	450	2 : 2 : 4-Trimethylpentane	7.44	300
<i>n</i> Hexane .....	6.51	300	<i>cyclo</i> Octane .....	8.68	150
Benzene .....	5.78	250			

*Relation between effective collision area and degree of coiling.* In the conclusions outlined above, the working assumption has been made that since the effective collision area in the vapour is approximately the same for a *n*-paraffin as for the *iso*-isomer, the *n*-paraffin must be coiled into close-packed configurations and cannot, for example, be stretched out as a zigzag. This assumption can be substantiated, for example, by the use of atomic models. Melaven and Mack (*loc. cit.*) have described a "shadowgraph" technique for computing average collision area in terms of average configuration, which likewise supports the above assumption.

Two further points in the interpretation of the present results refer to the possible effect of temperature on the degree of coiling, and to the possibility that the apparent collision area of a flexible molecule may not be the same in heteromolecular as in homomolecular collisions.

*Temperature Effects in the Average Degree of Coiling of Flexible Polymethylene Molecules.*—The collision parameters and the molecular volumes recorded above both indicate that flexible *n*-hydrocarbons in the  $C_5$ — $C_8$ -range are on the average highly coiled. But the experimental methods cannot as yet indicate whether the average degree of coiling changes appreciably with temperature.

Two theoretical arguments throw some light on this possibility. If there is initially a fully stretched zigzag, in which all the carbon atoms lie in one plane, and if there is no energy change on coiling, then by rotation about the C—C bonds the molecules will assume a range of configurations such as to raise the entropy of coiling to a maximum. The most probable "radius" of the crumpled molecule and average configuration can be calculated by statistical theory. Calculations on this basis have been proposed by Eyring (*Phys. Reviews*, 1932, **39**, 746) and by H. Kuhn (*J. Chem. Physics*, 1947, **15**, 843). If on the other hand energy changes are involved when the molecule is coiled, the combined energy and entropy effects lead to a change of the average coiling with temperature. W. J. Taylor (*ibid.*, 1948, **16**, 258) has made use of the suggestion that as the  $CH_2$  groups are moved with respect to their nearest neighbours, by rotation about the C—C bonds, a repulsion potential between these nearest neighbours passes through maxima and minima dependent on the angles between C—H bonds in adjacent groups (cf. Pitzer, *ibid.*, 1937, **5**, 469; Kistiakowsky and Stitt, *ibid.*, 1939, **7**, 289). This "steric hindrance" potential, if correct, would lead to a contraction in average chain length of about 15—25% in the temperature range 0—200°. The consequent decrease in apparent collision area if inserted in equation (3) would affect the rise in  $\eta$  observed as the temperature rises (Table III).

If  $dA/dT$  is negative as required by Taylor's theory, the estimated areas in Table IV tend to be too large for the flexible molecules. This must be left for further research. Though Taylor's theory has been worked out in detail only for long chains, the behaviour predicted from it for octane and upwards appears to be in conflict with kinetic data.

By using equation (2) for interpolation of the data in Table II, it is possible to make quite precise calculations of the ratio of  $\sigma^2$  for normal and branched isomers at different temperatures, according to equation (1). Some of these ratios are given as illustration in Table VI. It will be seen that the trend with temperatures of  $[\sigma^2(\text{normal})/\sigma^2(\text{iso})]$  is notably smaller than would be expected on the basis of Taylor's theory, and is, if anything, in the opposite sense. Values for the *cyclo*-compounds are also included though, for reasons stated above, the ratios may be influenced by molecular association.

TABLE VI.  
Ratios of collision areas of paraffins.

	Temp. (K.).	$\sigma_1^2/\sigma_2^2$ .
<i>n</i> -C <sub>4</sub> H <sub>10</sub> : CH <sub>3</sub> ·CH(CH <sub>3</sub> ) <sub>2</sub> .....	293·1	1·01
	373·1	1·00
	393·1	1·00
<i>n</i> -C <sub>5</sub> H <sub>12</sub> : C <sub>2</sub> H <sub>5</sub> ·CH(CH <sub>3</sub> ) <sub>2</sub> .....	298·1	1·03
	373·1	1·02
<i>cyclo</i> Pentane : C <sub>2</sub> H <sub>5</sub> ·CH(CH <sub>3</sub> ) <sub>2</sub> .....	316·2	0·83 *
	354·8	0·83
	398·1	0·87
Methylcyclopentane : <i>n</i> -C <sub>6</sub> H <sub>14</sub> .....	316·2	0·83 *
	436·5	0·87
<i>n</i> -C <sub>7</sub> H <sub>16</sub> : (CH <sub>3</sub> ) <sub>2</sub> CH·C(CH <sub>3</sub> ) <sub>3</sub> .....	380·1	1·07
	398·1	1·07
	416·9	1·06
	436·5	1·05
<i>n</i> -C <sub>8</sub> H <sub>18</sub> : (CH <sub>3</sub> ) <sub>2</sub> CH·CH <sub>2</sub> ·C(CH <sub>3</sub> ) <sub>3</sub> .....	398·1	1·05
	416·9	1·05
	436·5	1·05
<i>cyclo</i> Octane : (CH <sub>3</sub> ) <sub>2</sub> CH·CH <sub>2</sub> ·C(CH <sub>3</sub> ) <sub>3</sub> .....	436·5	1·11 *
	457·1	1·13

\* Equation (1) is not immediately applicable for calculating  $\sigma_1^2 : \sigma_2^2$  if there is appreciable dimerisation or clustering. The dimer has a larger mol. wt. and failure to allow for this gives a ratio in which the value of  $\sigma$  appears too small for the more highly clustered molecules.

*Homomolecular and heteromolecular collision areas.* In the collision between two molecules of the same mass, to which the present data refer, possible crumpling during the collision seems likely to play a greater part than during heteromolecular impact between flexible molecules and light molecules such as hydrogen. Different apparent collision areas might be expected for the flexible hydrocarbon in the two cases. Molecules such as oxygen and nitrogen do not differ greatly in mass from the CH<sub>2</sub> group. Diffusion studies of the C<sub>16</sub>—C<sub>18</sub>-polymethylene molecules in air (Bradley and Shellard, *Proc. Roy. Soc.*, 1949, *A*, **198**, 239) lead to conclusions about coiling in the gas phase which roughly correspond with present conclusions. The special case of collisions with hydrogen is being further investigated in view of the interesting catalytic rôle of hydrogen in certain hydrocarbon reactions (Small and Ubbelohde, *J.*, 1950, 723).

QUEEN'S UNIVERSITY, BELFAST.

[Received, February 26th, 1951.]