THE CONFIGURATION OF FLEXIBLE ORGANIC MOLECULES

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1.1. Various types of labile molecular configuration are well known in organic chemistry. For example, processes have long been studied by means of which stereoisomers can undergo bond-rearrangement, as in racemisation, or in the Walden inversion. In the limiting case, when the half-life of any particular isomer is small compared with the time of experiment, say less than 10^3 seconds, the substance is best treated as a labile mixture of isomers. Such labile stereoisomerism can sometimes be detected by special techniques. For example, a labile acid can be combined with a stable optically active base, and on crystallisation of the salt the acid will be incorporated wholly in the form of a single stereoisomer. On liberation of the acid again in solution, observations can be made on this stereoisomer, but only a short period elapses before complete racemisation is again attained. Very fast changes of configuration are known, such as the " umbrella " switch of bonds in ammonia which has a half-life of about 10^{-10} sec.[1]

The labile configurations which form the special object of the present Review arise predominantly from rotation about single bonds. Owing to the fact that single bonds can have some double-bond character, brief reference is also made to geometrical isomerism about double bonds, in cases where the rate of isomerisation is rapid. Molecules which can form isomers by rotation about bonds are conveniently described as " flexible ", and the various configurations taken up may be described as " rotational isomers " * to distinguish them from other forms of isomerism. Energy differences between rotational isomers generally do not exceed 1—$10RT$ at room temperatures (see Section 7.4). In order to limit the scope of the Review, polymer chain molecules with more than about 30 units in the chain will not be included in any detail. Special experimental and statistical methods for dealing with flexible polymer molecules have been recently discussed in a number of summarising reviews.[2] A practical advantage of considering the smaller flexible molecules separately is that these can frequently be studied in more than one state of aggregation. As will be seen, a change of average molecular configuration frequently accompanies the passage of a flexible molecule from solid to liquid and from liquid to gas.

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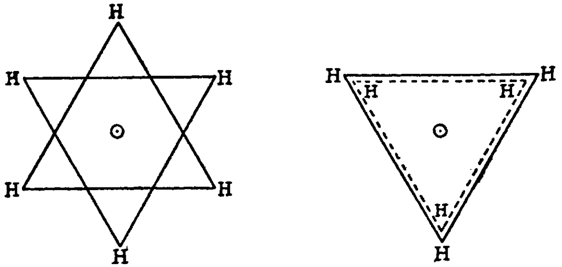
[1] Whiffen, *Quart. Reviews*, 1950, **4**, 141.

[2] Treloar, *Rep. Progr. Physics*, 1942, **9**, 113; Alfrey, " Mechanical Behaviour of High Polymers ", 1948, Interscience Publishers; Münster, *J. Polymer Sci.*, 1950, **5**, 333.

* The description " rotational tautomers " has also been proposed (Ref. 83) but is not in general use.

1.2. Some Examples of Rotational Isomers.—The simplest type of rotational isomerism arises from alternative orientations of groups around the C–C bond in ethane, and in substituted ethanes.[3] By way of illustration, in ethane, when the three terminal groups round each carbon atom are projected on to a plane normal to the C–C bond, their centres will lie at the apices of an (equilateral) triangle. The rotation of the groups on one carbon atom relative to those attached to the neighbouring atom can then be represented as in Fig. 1. The C–C bond lies perpendicular to the plane of the paper through O. The *trans*-arrangement passes into the *cis*-arrangement by rotation of the groups. Studies discussed below show that the potential energy increases on passing from *trans* to *cis*, though

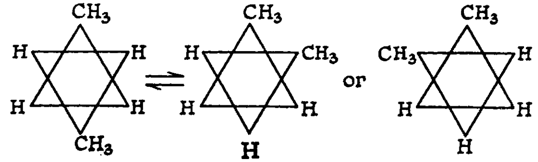


Point symmetry D_{3d}, *trans*- or staggered.

Point symmetry D_{3h}, *cis*- or eclipsed.

FIG. 1

Representation of ethane.



trans- (ΔH = 300—600 cals./mole).

Gauche (skew).

Gauche (skew).

Ratio of statistical weights, *trans* : gauche = 1 : 2.

FIG. 2*a*

n-*Butane : Representation of rotational isomers.*

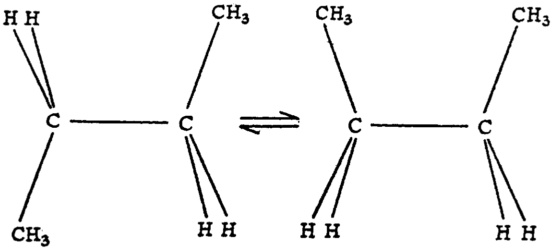


FIG. 2*b*

n-*Butane configurations of maximum* (trans) *and minimum* (cis) *stability.*

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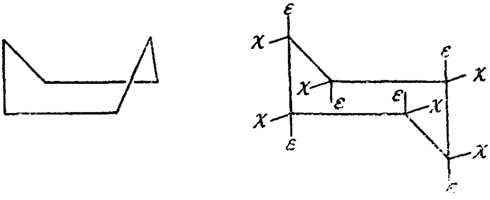
[3] Cabannes, *Rep. Progr. Physics*, 1945, **10**, 401.

even with substituents other than hydrogen the energy barrier is not normally sufficient to permit separation of the configurations. Spectroscopic analysis (see, *e.g.*, Sections 2.3, 3.1, 5.3) shows that at ordinary temperatures a small number of well-defined molecular configurations coexist, *i.e.*, the rotational states are not continuous.

Another simple example is presented by *n*-butane,[4] in which the *trans*-configuration is somewhat more stable than the gauche configuration. Diagrammatic representations are given in Fig. 2. It is evident that the number of possible rotational isomers becomes very large on extending the polymethylene chain. Statistical theory is required for a description of the properties of such large molecules. As will be seen below, not all these states are found in appreciable proportions in practice.

1.3. Effects of Ring Closure on Rotational Isomerism.—When the polymethylene chain is closed into a ring, the potential barriers which must be overcome in order to pass from one configuration to another are often considerably larger, owing to the fact that valency angles usually have to be deformed to permit the transition.[5] The possible arrangements in *cyclo*hexane were first discussed by Sachse.[6] Flexible " boat " molecules do not appear to be present in appreciable proportions under ordinary conditions.[7] It is important to distinguish between two groups of hydrogen atoms in the rigid " chair " form. In *cyclo*hexane (Fig. 3*a*), one set of six C–H bonds runs parallel to the principal axis of the carbon ring (ε bonds) and the other set of six H bonds makes an angle of 109° 28′ with this principal axis (χ bonds). Alternative nomenclature describes the ε bonds as polar and the χ bonds as equatorial.[8] When substituents other than hydrogen are present (i) the possibilities of tautomerism are much greater—*e.g.*, in



Boat form (flexible). Chair form (rigid).

FIG. 3*a*
cyclo*Hexane isomers.*

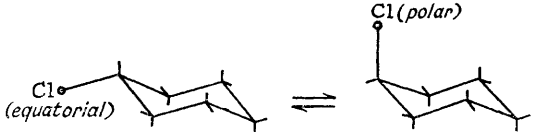


FIG. 3*b*
*Isomers of monochloro*cyclo*hexane* (*chair form*).

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[4] Pitzer, *Chem. Reviews*, 1940, **27**, 39.

[5] Langseth and Bernstein, *J. Chem. Phys.*, 1940, **8**, 403.

[6] *Ber.*, 1890, **23**, 1363.

[7] Hassel, *Research*, 1950, **3**, 504.

[8] Pitzer *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 977, 2488.

monochlorocyclohexane the χ chloro-molecule predominates and little of the ε chloro is present [7] (Fig. 3*b*). Well-known examples include tetralin and dekalin (cf. also ref. 9) and also sugar alcohols such as inositol, or halogen compounds such as Gammexane—and (ii) the obstacles to isomerisation can be so large as to permit a separation and study of individual geometrical isomers. Such separable isomers need no longer be treated statistically as " flexible ". Stable isomers lie outside the main object of this Review.[9]

Rotational isomers of polymethylene rings have not been much investigated in rings with $n > 6$. There is reason to believe that they behave more and more like the open-chain isomers, the larger the polymethylene ring.[15]

1.4. Other Types of Bond Rotation.—There is a large number of compounds in which free rotation about a C–C bond is affected to a greater or less extent by the possibility of a " stiffening " of this bond by conjugation. Studies on the restricted rotation in diphenyl compounds are fairly numerous.[10] Bond stiffening need not necessarily involve aromatic groups, and has been studied in a variety of compounds where the bond order lies between 1 and 2 (see Section 7.4). In the limiting case of bond order 2, in ethylene, the calculated barrier opposing " rotational isomerism " is about $100RT$ at ordinary temperatures [11] so that ethylene, unlike ethane, is not labile (see Section 7.4).

1.5. Flexible Molecules containing Nitrogen.—Little is known about the magnitude of potential barriers between different rotational isomers in short flexible molecules, *e.g.*, the polypeptides $R_1\cdot CHR_2\cdot CO\cdot NH\cdot CHR_2\cdot CO\cdot NH---$. It has been calculated that in the change from an ionised to a neutral polypeptide molecule the replacement of all the N^+ atoms by neutral N atoms leads to a contraction to 0·92 of the original length. This is attributed to the difference in bond angles between $C\text{–}\overset{+}{N}\text{–}C$ and C–N–C.[12] In such compounds the energy change accompanying isomerism is frequently modified by other energy changes such as those due to hydrogen-bond formation.[13] By way of example, the activation energy for muscle contraction has been estimated to be about 20 kcals. per mole.[14]

Only preliminary investigations have been made on the configuration of ring molecules containing hetero-atoms such as oxygen or nitrogen.[15]

1.6. Flexibility due to Bond-angle Changes.—This Review does not aim to include stereoisomeric changes wholly due to displacements of valency angles about individual atoms, such as those mentioned in Section 1.1. Certain border-line effects are however closely related to the rotational isomerism referred to in Section 1.2, because of the similar origin of the

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[9] Hückel, *Ann. Reports*, 1924, **21**, 92.

[10] See Gilman, " Advanced Treatise of Organic Chemistry ", 1947, Wiley.

[11] Mullikan and Roothan, *Chem. Reviews*, 1947, **41**, 203.

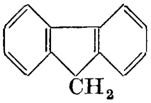
[12] Gombas and Hoffman, *J. Chem. Phys.*, 1950, **18**, 563.

[13] Bamford, Hanby, and Happey, *Proc. Roy. Soc.*, 1951, *A*, **205**, 30.

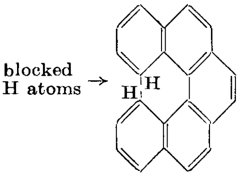
[14] Kahn, *J. Physical Chem.*, 1949, **53**, 977.

[15] Prelog, *J.*, 1950, 420.

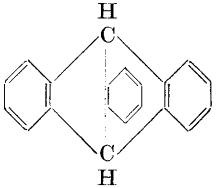
repulsion potentials which oppose isomerisation. Recently-discussed examples include the suggested isomerism in fluorene (I),[16] in 3 : 4-5 : 6-



(I.)



(II.)



(III.)

dibenzophenanthrene (II),[17] and in blocked triphenylmethane derivatives such as triptycene (III).[18]

2. Experimental Investigations of the Average Configuration of Flexible Molecules

In the following sections, evidence is considered separately for solid, liquid, surface, and gas phases. So far as possible, results obtained by experimental techniques are considered in the order : *X*-ray and electron diffraction, optical (infra-red, Raman, and ultra-violet), dielectric studies, volume studies, thermodynamic parameters. In the case of gases, various collision processes are considered first.

2.1. Physical Properties of Crystals containing Flexible Molecules.—*X*-Ray studies have shown that flexible polymethylene hydrocarbon chains crystallise with the chains fully extended in the *trans*-form [19] which permits the maximum intermolecular attraction per unit mass. As the melting point is approached, there is some evidence from *X*-ray studies on the increase in lattice dimensions [20] and from polymorphic transitions [21] that the chain molecules undergo rotation, or at least violent torsional oscillations, but no signs are found of any crumpling of the flexible molecules in the solid phase. Similar conclusions have been obtained for acids of the type $R\cdot[CH_2]_n\cdot CO_2H$. Crystals containing *cyclo*hexane and its derivatives could in principle incorporate more than one arrangement of bonds, but no examples appear to have been observed hitherto.[7]

2.2. Dielectric Studies on Solids containing Flexible Molecules.—Measurements of dielectric polarisabilities on crystals of mono- and di-ketones, $CH_3\cdot[CH_2]_r\cdot CO[CH_2]_s\cdot CH_3$ [22] and $CH_3\cdot[CH_2]_r\cdot CO\cdot[CH_2]_s\cdot CO\cdot[CH_2]_t\cdot CH_3$,[23] agree with the *X*-ray evidence showing that, although the molecules can undergo violent torsional oscillations or even rotations in the solid, on approaching the melting point, yet melting must precede any appreciable crumpling. When such long-chain molecules carrying dipoles (carbonyl

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[16] Iball, *Z. Krist.*, 1936, **94**, 397.

[17] Bell and Waring, *J.*, 1949, 2689.

[18] Dewar, " Electronic Theories of Organic Chemistry ", p. 205, O.U.P., 1949.

[19] Müller, *Proc. Roy. Soc.*, 1928, *A*, **120**, 454 ; cf. also Bunn, *ibid.*, 1942, *A*, **180**, 82.

[20] Müller, *ibid.*, 1930, *A*, **127**, 41.

[21] Cf. *idem*, *ibid.* ; Ubbelohde, *Trans. Faraday Soc.*, 1938, **34**, 289.

[22] Müller, *Proc. Roy. Soc.*, 1936, *A*, **158**, 403.

[23] *Idem*, *ibid.*, 1940, *A*, **174**, 137.

groups or ester groups) are present in solid solution in long-chain paraffins, the forces restraining torsional oscillation and rotation are lessened.[24] Measurements have been made of dielectric loss which permit calculation of the relaxation time τ for switch of the dipole from one equilibrium position to another. Theoretically,[25] $\log \tau = A + H_m/T$. The constant H_m which determines the activation energy for a switch in the crystal is found to depend on the chain length, $[CH_2]_m$. However, this increase is not linear with the number of CH_2 groups, as would be the case for a rigid chain. When m is small, $H_m \propto m$, but when m is large, H_m is independent of any further increase in chain length. This is interpreted to mean that, because of molecular flexibility, the chain rotates in segments to take up the new equilibrium position in the crystal.

2.3. Melting of Crystals containing Flexible Molecules.—2.3.1. *X*-Ray studies do not appear to have been carried out on liquids just above the melting point, where the evidence from premelting would suggest very considerable adlineation in the case of polymethylene compounds.[26] Even well above the melting point, *X*-ray measurements on liquid *n*-heptane and *n*-decane indicate appreciable adlineation of at least portions of the chain molecules.[27]

2.3.2. Comparisons have been made between the infra-red absorption spectra of crystals and melts of aliphatic hydrocarbons and simple derivatives : [28, 29] (i) For *iso*-compounds in which the molecules would not be flexible, the spectra are almost identical ; (ii) *n*-paraffins (which have now been studied up to C_{15}) show a large increase in the number of absorption lines on melting.

This increase of lines has been interpreted as due to a change into more than one rotational isomer on melting. Corresponding observations have been made with Raman spectra, which permit a quantitative evaluation of energy differences between the rotational isomers (see Section 3.1). Relative changes of intensities of these lines are observed as the temperature of the liquid is increased above the melting point.

From butane upwards, rotation about C–C bonds leads to a rapid increase in the number of possible isomers as the number of carbon atoms increases. Not all these are observed in practice ; [30] for instance, butane and pentane show two rotational isomers in appreciable quantities, and hexane and heptane three. In the case of the higher hydrocarbons the particular isomers present do not appear to have been completely defined.

2.3.3. Studies of the melting parameters of homologues of the *n*-paraffins and of simple derivatives $CH_3{\cdot}[CH_2]_n{\cdot}X$ show that for the higher paraffins

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[24] Jackson, *Proc. Roy. Soc.*, 1935, *A*, **150,** 197 ; Sellars, *ibid.*, 1938, *A*, **169,** 66 ; Daniel and Stark, *Trans. Faraday Soc.*, 1951, **47,** 149.

[25] Fröhlich, " Theory of Dielectrics ", O.U.P., 1949.

[26] Ubbelohde, *Quart. Reviews*, 1950, IV, 356.

[27] Katzov, *J. Chem. Phys.*, 1934, **2,** 841.

[28] Rank and Axford, *ibid.*, 1950, **18,** 51.

[29] Sheppard and Brown, *Discuss. Faraday Soc.*, " Spectroscopy ", 1950.

[30] Sheppard, Szasz, Rank, and Axford, *J. Chem. Phys.*, 1948, **16,** 704 ; Sheppard and Szasz, *ibid.*, 1949, **17,** 86.

where the crystal structure is similar the heats and entropies of fusion increase linearly with the number of carbon atoms in the chain :

$$\Delta H_f = H_0 + nH_1$$
$$\Delta S_f = S_0 + nS_1$$

When n is large, the freezing point converges to a limit, $T_{\text{limit}} = H_1/S_1$, as shown below.

Limiting freezing points of n-*paraffins and simple derivatives*

X =	T_{limit}, °K.	X =	T_{limit}, °K.
H (paraffins) . . .	408—417·5 (according to extrapolation formula used)	CO_2H (n even) .	389
		CO_2H (n odd) . . .	385

The linear increase of entropy of fusion with the number of CH_2 groups is most readily interpreted on the basis that the molecules in the liquid are flexible, so that the number of degrees of freedom in the liquid increases proportionally with the number of CH_2 groups. The formal thermodynamic relationship $\Delta S_f = \boldsymbol{R} \ln W_l/W_s$, where W_l = number of ways of realising liquid and W_s = number of ways of realising solid, implies this general conclusion, since W_s is substantially independent of n when the crystal structure is the same. Thus W_l increases rapidly with n. Even for the lower paraffins, where the crystal structure is not immediately comparable for homologues or isomers, the general rule still applies that the entropy of fusion of flexible molecules is higher than for the non-flexible *iso*-compounds, as shown below.

Comparative entropies of fusion of n- *and* iso-*paraffins* [31]

		ΔS_f (e.u.).			ΔS_f (e.u.).
C_4	*n*-Butane	8·26	C_6	*n*-Hexane	17·51
	*iso*Butane	9·55		2-Methylpentane . .	12·55
				2 : 2-Dimethylbutane .	0·80
C_5	*n*-Pentane	14·02			
	*iso*Pentane	10·88	C_7	*n*-Heptane	18·39
	*neo*Pentane	3·03		2-Methylhexane . . .	13·69
				2 : 2-Dimethylpentane .	9·38
				2 : 2 : 3-Trimethylbutane	2·12

Detailed specific-heat and volume-expansion curves of crystals of long-chain molecules show (i) that very considerable " premelting " becomes evident near the melting point ; (ii) that the specific heat of the solid some few degrees above the melting point substantially corresponds with that some few degrees below it.[26] This implies that the vibrations in the two phases do not differ to any major extent. Probably only very partial crumpling occurs when the solid is just melted. Data on the vapour suggest that crumpling increases with rise of temperature of the liquid.

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[31] U.S. Nat. Bur. Stand. Project 44 (1949).

Conjugation, as in the polyene Ph·CH:CH·CH:CHPh stiffens the chains and changes the basic relation between melting point and number of carbon atoms.[32a] In the compounds Ph·[CH:CH]$_n$·Ph, as n increases it seems likely from the theory of " ideal " solubility that even the polyene chain behaves as if it had some flexibility since there is no further decrease in solubility when $n > 5$.[32]

Melting of cyclo*Hexane and other Flexible Ring Compounds.*—In the case of *cyclo*hexane, it has been suggested that the melt may contain a small amount of the " boat " isomer which is concentrated in the last parts of the melt to freeze, and reverts to the equilibrium mixture of isomers.[33] Larger polymethylene rings do not appear to have been studied systematically. Thermodynamic parameters of fusion would be of great interest. Even the melting points (below) may refer to compounds in very different states of purity.

Melting points of higher cyclo*alkanes* [34]

Compound . . .	C_6H_{12}	C_7H_{14}	C_8H_{16}	C_9H_{18}	$C_{10}H_{20}$	$C_{11}H_{22}$
M.p. (° c.) . . .	6·40	− 12·00	13·5	9·7	10·8	− 7·2

3. Experimental Studies on Rotational Isomerism in Liquids

3.1. Changes of Rotational Isomerism in Liquids with Temperature : Optical Studies.—As was stated on p. 369, when a crystal containing flexible molecules is melted, the melt has been found to contain a mixture of rotational isomers. These differ somewhat in heat content, and the equilibrium mixture changes as the temperature rises.[35] From intensities in the Raman spectra of lines corresponding with the different isomers, changes in relative concentrations C_1, C_2 have been calculated.[30] The calculation proposed for tetrachloroethane is as follows.[36] If I_1 is the observed intensity of a Raman line corresponding with the more stable isomer in the mixture, and I_2 that of the less stable isomer, K_T, the equilibrium constant, is given by

$$C_1/C_2 = K_T = (I_1/I_2)(\alpha_1/\alpha_2)_T$$

where α_1, α_2 are the line intensities per molecule, so that $I_1 = \alpha_1 C_1$, etc.

$$\Delta H/RT^2 = \partial \ln K_T/\partial T$$

It is generally assumed that $(\alpha_1/\alpha_2)_T$ is independent of T,[30] and from the usual van't Hoff formula the observed change in K_T with temperature corresponds with a difference in heat content between the two forms (Fig. 4) :

$$\Delta H_{C_{2v}-C_2} = 1{\cdot}10 \text{ kcals./mole}$$

(for later estimates see Table V). Studies of this kind using the Raman

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[32] Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 182.

[32a] Kuhn and Grundmann, *Ber.*, 1936, **69**, 224.

[33] Thompson and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 349.

[34] Faraday, " Encyclopedia of Hydrocarbons ", 1949, Chemindex, Manchester.

[35] Kohlrausch, " Hand- und Jahrbuch der Chemische Physik ", 1943, p. 234.

[36] Langseth and Bernstein, *J. Chem. Phys.*, 1941, **9**, 110 (but see Table V for later estimates).

lines 432, 325, 835, and 789 cm.$^{-1}$ show that for butane [30] the fully extended *trans*-form (Fig. 2) is the most stable in the liquid, at any rate not too near the critical temperature. A similar conclusion has been reported for higher hydrocarbons [29, 30] and for fluorohydrocarbons.[37] Other values of ΔH are tabulated in Section 7.4. The proportion of isomers in liquid *cyclo*hexane appears to be controversial.[38, 7]

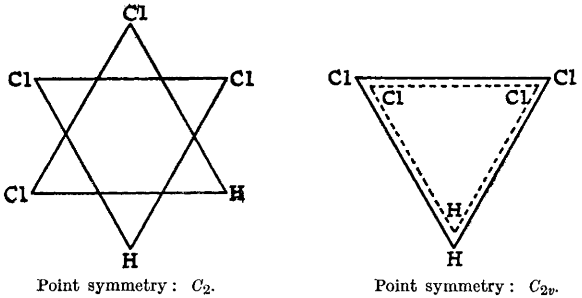

FIG. 4
Rotational isomers of tetrachloroethane.

The equilibrium between isomers can depend on the environment as well as on the temperature ; *e.g.*, in dichloro- and dibromo-ethane calculated differences of heat content are : [39]

Molecule.	ΔH, liquid, kcal./mole.	ΔH, gas, kcal./mole.
$C_2H_4Cl_2$	~ 0	1·2
$C_2H_4Br_2$	0·65	1·45

3.2 Dielectric Studies on Liquids.—Although the results would be of considerable interest, no work appears to have been published on the dielectric properties of melts containing flexible molecules (cf. Section 2.2). In dilute solution in non-polar solvents, when the flexible molecule carries more than one dipole on adjacent atoms the well-known dependence of total mean dipole moment $\bar{\mu}$ on temperature is observed : [40]

$$\bar{\mu}^2 = \frac{\mu_1{}^2 + 2\mu_2{}^2 \exp(\Delta H/RT)}{1 + 2\exp(-\Delta H/RT)}$$

where μ_1 and μ_2 are the individual dipole moments, and ΔH is the difference of energy between the two extreme configurations of the dipoles. A comprehensive theoretical discussion has been given by Lennard Jones

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[37] Szasz, *J. Chem. Phys.*, 1950, **18**, 1417 ; cf. also Bradley and Waghorn, *Proc. Roy. Soc.*, 1951, *A*, **206**, 65.

[38] Langseth and Bak, *J. Chem. Phys.*, 1940, **8**, 403 ; Schomaker and Stevenson, *ibid.*, p. 637 ; see Oosterhof and Hazebroek, *Discuss. Faraday Soc.*, 1951.

[39] Bernstein, *J. Chem. Phys.*, 1949, **17**, 256 ; Mizushima, *ibid.*, 1950, **18**, 754.

[40] See, *e.g.*, Le Fèvre, " Dipole Moments ", Methuen, 1948, p. 81 ; cf. also ref. 78.

and Pike.[41] In this instance values of ΔH involve partly electrostatic attractions and repulsions between the dipoles, and partly the repulsion forces involved in the rotation single bonds described in previous sections. *cyclo*Hexane derivatives have been discussed by Hassel.[42]

When the dipoles are carried on non-adjacent atoms, this would be expected to have a strong influence on the degree of crumpling in certain cases. In the liquid, the only published example appears to be the case of 1 : 4-dichlorobutane, where $\bar{\mu}$ is found to be independent of temperature.[43] Though no definitive interpretation can be given, it is possible that dipole orientation effects approximately compensate rotational isomerism in this molecule.

3.3. Volume Effects Associated with Flexible Molecules in Liquids.—Various studies of the molar volume of *n*-paraffins indicate that these are partly coiled even in the liquid phase, especially at higher temperatures. This can be brought out most readily by comparing the ratio of the molar volume of the *n*- with the corresponding *iso*-paraffin, at corresponding temperatures,[44] as in Table I : either boiling points or critical temperatures may be used.

TABLE I

Ratios of molar volumes and entropies of vaporisation

Paraffins.	Molar volumes.	
	Ratio at b.p.s.	Ratio at crit. temps.
n-Butane : *iso*butane	—	1·004
n-Pentane : *iso*pentane	1·0035	1·011
n-Hexane : *iso*hexane (di*iso*propyl)	—	1·028
n-Octane : *iso*octane (2 : 2 : 4-trimethylpentane)	1·0148	—
n-Octane : *iso*octane (di*iso*butane)	—	1·017

Molar volumes in a range of isomers have also been compared at constant temperature, instead of at corresponding temperatures. A relationship with the degree of chain branching has been claimed.[45] In heptanes, data include the following molar volumes (in ml.) : 2 : 4-dimethylpentane, 148·9 ; 2-methylhexane, 147·6 ; *n*-heptane, 146·0 ; 3-methylhexane, 145·8 ; 2 : 3-dimethylpentane, 144·2. A gradual trend with increasing chain branching has been observed in the molar refractivity.[46]

3.3.1. From absorption measurements of ultra-sonic vibrations in liquids, it is possible on the basis of the " free volume " theory of liquids [47] to calculate effective volumes of molecules from the quantity $MC^{1/3}/d$, where

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[41] *Trans. Faraday Soc.*, 1934, **30**, 830.

[42] *Ibid.*, p. 874.

[43] Oriani and Smyth, *J. Chem. Phys.*, 1948, **16**, 930.

[44] McCoubrey, McCrea, and Ubbelohde, *J.*, 1951, 1961 ; *critical volumes* : Partington, " Advanced Treatise on Physical Chemistry ", vol. 1, Longmans, 1949, p. 645.

[45] Audsley and Goss, *J.*, 1951, 121.

[46] Ubbelohde, *Rev. Inst. franç. du Pétrole et Ann. Combustibles liquides*, 1949, **4**, 488.

[47] Kittel, *Rep. Prog. Physics*, 1947, **11**, 205.

M = molecular weight, C = velocity of sound, d = density. A constant increment Δ_{CH_2} per CH_2 has been claimed in homologues, but studies have not yet covered sufficient isomers to permit any use of the results in elucidating molecular flexibility.[48]

3.3.2. *Partial Molal Volumes of Flexible Molecules in Dilute Solutions.*—It is of interest to compare partial molal volumes of flexible molecules, dissolved in solvents of about the same internal pressure, with molar volumes of the pure liquids. No systematic studies of the influence of flexibility appear to have been made for the short chains considered here.[49] (For colloids see Section 3.3.3.) Comparisons between *n*- and *iso*-paraffins would be of value. In a mixture of esters the partial molal volumes of both components have been found to be smaller than in either pure liquid. These geometrical effects may involve molecular flexibility.[50]

3.3.3. *Effective Molal Volumes of Flexible Polymethylene Hydrocarbons in Colloidal Micelles.*—It may be significant that the partial molal volume per CH_2 group in a micelle ranges between 13 and 14·8 ml. which is below that for liquid paraffins ($\sim$ 16·3 ml.) in which some crumpling seems likely. So far as it goes, the smaller partial molal volume suggests that CH_2 groups are closer packed and the molecules are less crumpled in the micelle than in the liquid, but the various factors have not been elucidated.[51] A similar observation has been made for the shift of a long-chain compound from solution to micelle.[51a]

3.4. Entropies of Vaporisation of Liquids composed of Flexible Molecules.—As has been detailed in Sections 2.2 and 2.3, there is considerable evidence that, on melting, flexible hydrocarbons pass from the fully extended *trans*-form to a mixture of rotational isomers. Further crumpling appears to take place on vaporisation.[46] Entropies of vaporisation of a sequence of isomeric octanes are illustrated in Table II.

It has been pointed out [52, 53] that entropies of vaporisation as a function

TABLE II

Trend in entropies of vaporisation of isomeric octanes at the boiling point with increased chain branching

Molecule.	Molar entropy of vaptn. (e.u.).	Molecule.	Molar entropy of vaptn. (e.u.).
n-Octane	20·96	2 : 2-Dimethylhexane	20·34
3-Ethylhexane . . .	20·91	3-Ethyl-2-methylpentane	20·21
2-Methylheptane . . .	20·55		
		2 : 2 : 3-Trimethylpentane	20·08
		2 : 2 : 3 : 3-Tetramethylbutane	19·92

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[48] Weissler and Del Grosso, *J. Amer. Chem. Soc.*, 1950, **72**, 4209.

[49] See, however, Hildebrand and Scott, *Ann. Rev. Phys. Chem.*, 1950, **1**, 75.

[50] Mears, *Trans. Faraday Soc.*, 1949, **45**, 966, 1066.

[51] Hartley, *Ann. Reports*, 1948, **45**, 33; but see also [51a] Stainsby and Alexander, *Trans. Faraday Soc.*, 1950, **46**, 587.

[52] Pitzer, *J. Chem. Physics*, 1939, **7**, 583.

[53] Staveley, *J.*, 1950, 3597.

of molecular structure should be compared under conditions such that $V_{\text{liquid}}/V_{\text{vapour}}$ = constant. From Table I this condition is satisfied by the present data.

As the branching increases the entropy of vaporisation decreases somewhat. Combined with the information from the ratio of molar volumes in liquid (Table I) and gas (Tables III and IV), the sequence of entropies indicates that the *n*-paraffins undergo a moderate increase in average crumpling on passing from liquid to gas.

3.5. Viscosities of Liquids containing Flexible Molecules.—For normal liquids, the activation energy E_η for the viscosity, obtained from a plot $\log \eta = A + E_\eta/RT$ should be approximately a quarter of the heat of vaporisation H_{vap}. A plot of $\frac{1}{4}H_{\text{vap.}}$ and of E_η for flexible hydrocarbons against the number of carbon atoms, shows that for the longer chains E_η falls below the value extrapolated from short chains. For such long-chain molecules movement through the liquid appears to occur in segments.[54] This behaviour is related to similar effects in the heats of fusion (Section 2.3) and in the activation energy for dielectric relaxation in the solid (Section 2.2).

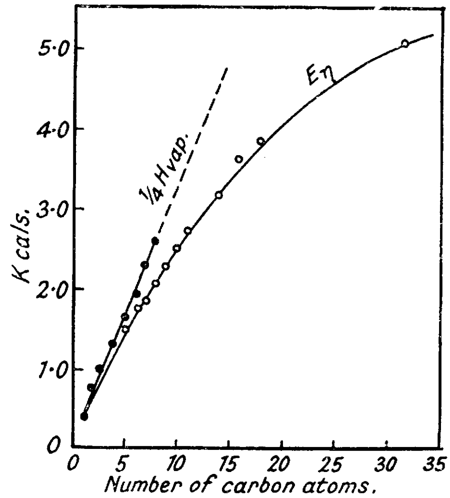

FIG. 5

Plots of $\frac{1}{4}H_{\text{vap.}}$ *and* E_η *for homologues.* (*Substantially copied from ref.* 54, *p.* 497.)

3.6. Compressibilities of Liquids containing Flexible Molecules.—The following table lists isothermal compressibilities per CH_2 group of a sequence of *n*-paraffins.[55] These figures suggest that the " free volume " per CH_2 group decreases as *n* increases. This could be accounted for if the longer molecules are proportionately more crumpled in the liquid at the temperature of measurement.

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[54] Eyring, Glasstone, and Laidler, " Theory of Rate Processes ", McGraw-Hill, 1947.

[55] International Critical Tables (1932).

Isothermal compressibilities, $\beta = 10^6(V_1 - V_2)/V_1(p_1 - p_2)$
(p *in megabars*)

n-Paraffin . .	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
β	157	132	120	111	104	96	90	86	82	78	74

4. Properties of Flexible Molecules in Surface Films on Liquids

4.1. In the sequence " solid film ⟶ " liquid " film ⟶ " gas " film for polymethylene compounds spread on water, the same general trend is observed as in the three-dimensional phases.[56] Fully stretched *trans*-molecules in solid films have room to crumple when the film expands.

Flexibility can readily be followed in the case of " radial " molecules, such as derivatives of pentaerythritol. For example, the surface tension–area plot of pentaerythritol tetrapalmitate shows that, as the surface film is compressed, the polymethylene chains, which initially lie flat, fold upwards, leaving the ester groups on the water surface.[57]

4.2. Sorption in Molecular Sieves and on Catalysts.—When zeolites absorb paraffins, the evidence suggests that the *n*-hydrocarbons enter the capillaries in the fully stretched *trans*-form ; for example, chabazite will occlude the hydrocarbons *n*-propane to *n*-heptane at decreasing rates, but will not occlude *iso*butane or the larger *iso*-paraffins.[58] The uncoiling which seems to be necessary before occlusion of *n*-paraffins can occur may account for the falling off in absorption rate with increasing chain length.

5. Collision Parameters of Flexible Molecules in the Gas Phase

5.1. In certain respects, the self-coiling of a flexible molecule is simplest to investigate in the gas phase, in which confusing effects due to the environment are at a minimum. Different collision diameters can be defined with respect to different processes in the gas. The most widely studied property has been the viscosity of the vapour. Average collision diameters for momentum transfer can be calculated in several ways, from measurements of gaseous viscosities at various temperatures. In a recent collection of new and older data [44] it has been shown that the average collision diameters of flexible *n*-paraffins are practically the same as for the isomeric branched paraffins over a range of temperatures (see Table III). Since there is no reason at present to suppose that the branched paraffin molecules are flexible, it appears from these ratios that *n*-paraffin molecules must be quite extensively crumpled in the gas and that the extent of crumpling does not change greatly with temperature.

Molecular collision diameters of the *n*-paraffins have also been calculated independently of any reference to the *iso*-paraffins, by applying the theories of Sutherland and of Hirschfelder, Bird, and Spotz [59] to the measured temperature variation of viscosities (see ref. 44, where earlier references

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[56] Adam, " Physics and Chemistry of Surfaces ", O.U.P., 1941, see especially p. 57.

[57] *Idem, ibid.*, p. 77.

[58] Barrer, *Quart. Reviews*, 1949, **3**, 293.

[59] *Chem. Reviews*, 1949, **44**, 205.

TABLE III

Ratio of collision diameters σ of normal and isomeric branched paraffins at various temperatures, from viscosities of vapours

Molecules.	T, ° K.	$\sigma_1^2 : \sigma_2^2$	Molecules.	T, ° K.	$\sigma_1^2 : \sigma_2^2$
C_4 (1) *n*-Butane	293·1	1·01	C_5 (1) *n*-Pentane	298·1	1·03
(2) *iso*Butane	373·1	1·00	(2) *iso*Pentane	373·1	1·02
	393·1	1·00			
C_7 (1) *n*-Heptane	380·1	1·07	C_8 (1) *n*-Octane	398·1	1·05
(2) *iso*Heptane	398·1	1·07	(2) *iso*Octane	416·9	1·05
(2 : 2 : 3-tri-	416·9	1·06	(2 : 2 : 4-tri-	436·5	1·05
methylbutane)	436·5	1·05	methylpentane)		

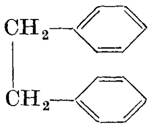
are given). The results (Table IV) give substantially the same conclusion as those in Table III. The fact that the ratio $\sigma^2_n : \sigma^2_{iso}$ is generally somewhat smaller than unity in Table IV and somewhat larger in Table III is probably due to the fact that the theories referred to correct in different ways for the increased average kinetic energy of collision as the temperature rises. The flexible, crumpled *n*-paraffins are somewhat more compressible on collision than the *iso*-paraffins.

TABLE IV

Molecular collision diameters calculated from the temperature coefficients of viscosities

Hydrocarbon.	Collision area (A.²) :		Hydrocarbon.	Collision area (A.²) :	
	Hirschfelder *et al.*	Sutherland.		Hirschfelder *et al.*	Sutherland.
n-Butane . . .	19·6	16·6	*n*-Heptane . .	—	26·7
*iso*Butane . .	22·4	17·1	*iso*Heptane . .	—	31·1
n-Pentane . .	26·2	19·6	*n*-Octane . .	34·7	27·9
*iso*Pentane . .	—	18·9	*iso*Octane . .	—	32·6
n-Hexane . .	27·4	25·4			

Results on collision diameters of flexible molecules other than the paraffins are not numerous. It is worth noting that dibenzyl appears to have the bunched-up configuration (IV) in the gas phase,[60] on average, whereas in the crystal [61] the molecule is packed in the stretched-out *trans*-configuration. As stated above, a change of average configuration with change of phase is not uncommon. All the *n*-paraffins crystallise in the fully extended *trans*-



(IV.)

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[60] Mack, *J. Amer. Chem. Soc.*, 1925, **47**, 2468.

[61] Robertson and Woodward, *Proc. Roy. Soc.*, 1934, *A*, **146**, 473.

configuration and there is a comparatively large change of configuration on vaporisation.

Collision diameters referring to other types of energy transfer have not yet yielded much information about the average configuration of flexible molecules in the gas phase. For diffusion in air, the hydrocarbons $C_{16}H_{34}$, $C_{17}H_{36}$, and $C_{18}H_{38}$ appear to be coiled into comparatively tight helices [62] as has been found for the shorter chains referred to in Tables III and IV.

So far as they have been determined,[63] collision diameters for energy transfer in heat conduction are comparable with those for momentum transfer in viscosity. Collision diameters in the " quenching " of fluorescence from atoms excited into metastable states have been investigated with respect to the influence of structure and molecular configuration (see following table). In this instance the quenching appears to depend on a summation of the individual bonds in the molecule and gives little information about average molecular configurations.

Effective collision diameters for quenching Hg 2537.[64]

Molecule.	σ, A.
C_2H_6	0·33
C_3H_8	1·13
n-C_4H_{10}	1·73
iso-C_4H_{10}	2·21
n-C_5H_{12}	2·94
iso-C_5H_{12}	3·52
neo-C_5H_{12}	1·22
n-C_6H_{14}	4·01
2-Methylpentane	4·54
2 : 2-Dimethylbutane	2·39
n-C_7H_{16}	5·39

5.2. Electron-diffraction Studies on Flexible Molecules.—When the molecules are flexible, electron-diffraction studies can give positions of the atoms averaged over the various configurations. Experiments have been most successful with heavy terminal groups to the flexible molecules such as 1 : 2-dibromoethane and 1-bromo-2-chloroethane,[65] 1 : 2-dibromopropane,[66] tetrachloroethane,[67] *meso*- and racemic 2 : 3-dibromobutane,[68] and acraldehyde and crotonaldehyde.[69] Such studies show that the predominant configuration is staggered. Energy barriers opposing rotation in hexachloroethane have been estimated to be 10—15 kcal./mole, from intensity measurements of electron-diffraction rings.[70] For 1 : 2-dichloroethane the

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[62] Shellard and Bradley, *Proc. Roy. Soc.*, 1949, *A*, **198**, 239.

[63] Lambert, *ibid.*, 1950, *A*, **200**, 262.

[64] Darwent, *J. Chem. Phys.*, 1950, **18**, 1532.

[65] Beach and Turkevich, *J. Amer. Chem. Soc.*, 1939, **61**, 303.

[66] Schomaker and Stevenson, *ibid.*, 1940, **62**, 2423.

[67] *Idem, J. Chem. Phys.*, 1940, **8**, 637.

[68] *Idem, J. Amer. Chem. Soc.*, 1939, **61**, 3173.

[69] Mackle and Sutton, *Trans. Faraday Soc.*, in the press.

[70] Morino and Iwasaki, *J. Chem. Phys.*, 1949, **16**, 216.

relative amounts have been estimated at 20% gauche and 80% *trans*-isomer.[71] For acraldehyde and crotonaldehyde relative amounts are between 6 : 1 and 3 : 1 of *trans* : *cis* at 35° c.[69]

Electron-diffraction studies have been applied to rotational isomers of various cyclic molecules with some success. Compounds include *cyclo*hexane and mono-derivatives,[7, 72] *cyclo*hexane-1 : 2-diol,[73] and *cis*- and *trans*-dekalin.[74]

5.3. Infra-red and Raman Studies on Vapours containing Flexible Molecules.—Raman studies on the vapours are considerably more difficult than on the liquids. For 1 : 2-dichloroethane Raman spectra support the evidence from infra-red spectra and dipole-moment measurements.[71] No accurate quantitative measurements have been obtained from infra-red absorption spectra. For hydrocarbons the general patterns from the gases are stated to correspond with those from the respective liquids (Section 3.1). For halogenated hydrocarbons the environment in the liquid is very different from that in the gas. Approximate evaluations of ΔH between isomers in the gas have been attempted for 1 : 2-dichloro- and 1 : 2-dibromo-ethane [70, 71] (cf. Fig. 6).

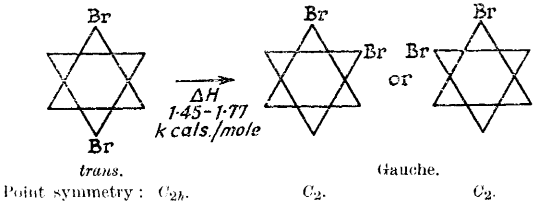

FIG. 6
Rotational isomers in 1 : 2-*dibromoethane.*

In view of the evidence from collision diameters in the gas phase (Section 5.1) Raman data on the vapours of polymethylene hydrocarbons at different temperatures should give useful complementary information. Spectroscopic studies have been published on various dimethyl*cyclo*hexanes.[75]

5.4. Dipole-moment Studies in the Gas Phase.—Studies on the dipole moments of flexible molecules in the gas phase are similar in principle to those in dilute solution (Section 3.2). Experimentally, they are more difficult to determine, but since the proportion of different configurations may be expected to change with the environment, complementary studies to those in liquid or solution are particularly desirable. Not many studies of the effect of a change of phase have been made. Temperature coefficients

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[71] Mizushima *et al.*, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1943, **40**, 417.
[71a] Mizushima *et al.*, *J. Chem. Phys.*, 1949, **17**, 591.
[72] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 1223.
[73] Ottar, *Acta Chem. Scand.*, 1947, **1**, 521.
[74] Hassel and Viervoll, *ibid.*, p. 149.
[75] Beckett, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2488.

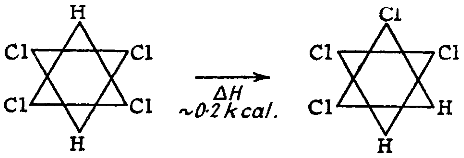
of mean dipole moment in the gas phase can be illustrated for chlorinated hydrocarbons : [76]

Variation of mean dipole moment with temperature (gas phase)

Molecule.	$\bar{\mu}$.	T, ° C.	$V_{\max}$, cals. mole^{-1}.
1 : 1 : 2-Trichloroethane .	1·45	105	2820
	1·47	258	
1 : 2-Dichloropropane . .	1·45	70	2500
	1·68	235	
1 : 4-Dichlorobutane . .	2·22 (invariant)	160—235	—

Earlier studies are summarised in the appendix to the Faraday Society Discussion on Dipole Moments.[77]

To determine which configurations are present, the individual bond moments must be evaluated from closely related compounds. From a recent study on 1 : 1 : 2-tri- and 1 : 1 : 2 : 2-tetra-chloroethane,[78] it has been estimated that the *trans*- and skew configurations of the tetrachloro-compound are present in approximately equal proportion (Fig. 7).



trans. Skew.

FIG. 7

Rotational isomers in tetrachloroethane.

The maximum height of potential barrier $V_{\max}$ opposing free rotation in molecules carrying dipoles has been assessed from plots of $\bar{\mu}$ against $1/T$.[81]

6. Thermodynamic Parameters of Flexible Molecules

6.1. Rotation about Single Bonds.—When the energy barrier opposing rotation about a bond is $\gg kT$, parts of the molecule undergo torsional oscillations about this bond. The specific heat and related thermodynamic parameters of such an oscillator can be described in terms of an Einstein function, with anharmonicity corrections, and no special features are present. When the barrier opposing rotation is $\ll kT$, the molecule exhibits " free rotation " about the bond, and the partition function Q corresponds with the well-known function for free rotators [79]

$$Q = \frac{1}{\sigma}\frac{\pi}{AB}\left(\frac{kT}{hc}\right)^2$$

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[76] Oriani and Smyth, *J. Chem. Phys.*, 1948, **16**, 930.

[77] *Trans. Faraday Soc.*, 1934, **30**, pp. i—lxxxvi.

[78] Thomas and Gwinn, *J. Amer. Chem. Soc.*, 1949, **71**, 2785.

[79] Eidenoff and Aston, *J. Chem. Phys.*, 1935, **3**, 379; Kassel, *ibid.*, 1936, **4**, 276.

where σ is the symmetry number, A is the moment of inertia of half of the molecule about the bond axis, and B is the overall moment of inertia. However, in most of the flexible molecules described in this Review the

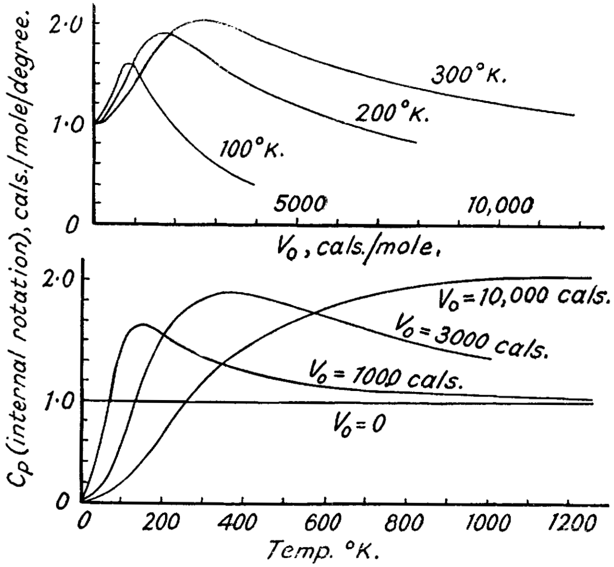

FIG. 8

Heat capacities for internal rotation as functions of temperature and potential barriers in ethane-like molecules (symmetrical top).

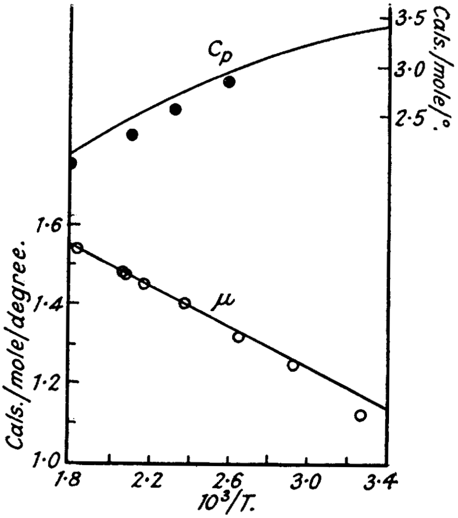

FIG. 9

Plots of experimental specific heats C_p and mean dipole moments $\bar{\mu}$ of 1 : 2*-dichloroethane compared with theoretical curves (V = 4130 cals./mole).*

barrier is of the same order of magnitude as kT. When this happens, the molecule behaves as a "hindered" rotator. Values of the energy $V_{\text{max.}}$ required to traverse the barrier are listed for typical molecules on p. 387. Thermodynamic functions for hindered rotators are too complicated to be reproduced here. Typical values of C_p (internal rotation) for ethane are reproduced in Fig. 8.[80] In addition to the procedure referred to in Section 5.4, two experimental procedures have been used to evaluate the magnitude of the potential barriers which hinder free rotation.

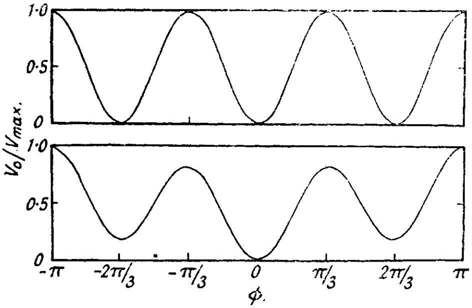

FIG. 10*a*

Rotational potential energy : in ethane (upper), $V(\phi) = \frac{1}{2}V_{\text{max.}}(1 - \cos 3\phi)$ *; in butane (lower),* $V(\phi) = \frac{1}{2}V_{\text{max.}}[0{\cdot}25(1 - \cos \phi) + 0{\cdot}75(1 - \cos 3\phi)]$.

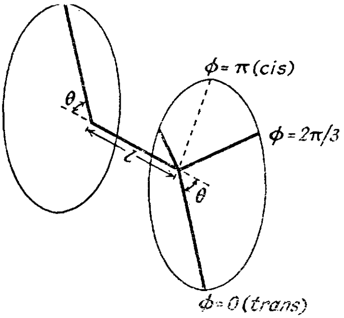

FIG. 10*b*

Definition of ϕ. *Successive positions of the* CH_2–CH_3 *bond in butane are shown at the right-hand side.*

(i) The experimental specific-heat curve is matched with theoretical curves so as to obtain the closest fit. Fig. 9 illustrates the procedure in the case of 1 : 2-dichloroethane.[81] One difficulty is that the potential function opposing rotation depends both on the nature of the bond and on the angle of twist ϕ away from the mutual orientation of lowest energy.

(ii) Entropies evaluated by integrating specific heat plots are compared with statistical values for various barriers.[4]

Fig. 10 illustrates conventional barriers for butane,[82] in which the

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[80] Herzberg, "Infra Red and Raman Spectra", Van Nostrand, 1945, p. 518.

[81] Gwinn and Pitzer, *J. Chem. Phys.*, 1948, **16**, 303.

[82] Taylor, *ibid.* p. 257 : cf. also Bresler and Frenkel, *Acta Physicochem, U.R.S.S.*, 1939, **11**, 485.

trans-configuration has the lowest energy (cf. Fig. 2*b*). According to the form of potential energy function assumed, different values are calculated for the maximum barrier to be traversed $V_{\text{max.}}$. A frequently used potential-energy function is (cf. ref. 83 for alternative potential functions)

$$V(\phi) = \tfrac{1}{2}V_{\text{max.}}(1 - \cos 3\phi)$$

6.2. Thermodynamic Parameters of Polymethylene Hydrocarbons.—When a molecule contains a sequence of hindered rotators, the rotational partition function becomes increasingly complex as the number of atoms increases. A particularly simple type of calculation for the equilibrium between rotational isomers may be illustrated for butane, for which the barrier is large compared with $\boldsymbol{R}T$ at ordinary temperatures [84] (cf. Section 7.4). If it is assumed that the difference in entropy between the pure *cis*- and pure *trans*- arises solely from the ratio of statistical weights, then in the equilibrium

$$K = cis/trans = (1 - x)/x\,;\quad \boldsymbol{R} \ln K = -\Delta F^\circ/T = \boldsymbol{R} \ln 2 - \Delta H_0{}^\circ/T$$

For the gas containing this mixture, the standard entropy includes a " mixture term ",

$$\Delta S_x = -\boldsymbol{R}[x \ln x + (1 - x) \ln (1 - x)]$$

On this basis, comparisons between computed entropies and entropies established from calorimetry and the third law have been quoted [85] (cf. ref. 92). Because of the small value of ΔH, thermodynamic functions are not very sensitive to the actual value assumed.

It has been shown [84] that with the energy difference ΔH of about 800 calories established for rotation about one C–C bond in butane, successive coiling, starting with the fully stretched *trans*-form in a polymethylene hydrocarbon, involves successive energy increases up to $n \times \Delta H$, where n is the number of C–C bonds. From this it has been claimed that the proportion of more highly coiled isomers should rapidly decrease with increase in steric repulsion energy. On this basis, even long-chain paraffins should show only a few isomers in appreciable concentration in the liquid. Although this is apparently confirmed by *n*-hexane (Section 2.3.2) in the liquid, the calculations which support mainly the stretched isomers neglect entropies of coiling [86] and do not agree with gas-collision diameters (Section 5.1). A final decision awaits further evidence.

6.3. Average Configuration of Polymethylene Hydrocarbons in the Gas Phase.—A simplified treatment of a flexible chain molecule starts with the (*trans*) chain fully extended along one co-ordinate axis, and considers the result of rotation about the successive C–C bonds [87] each of length $l = 1{\cdot}54$ A. For the " free rotator " model

$$(L_z)_n = l[1 + \cos \theta' + \cos^2 \theta' + \ldots] = l[(1 - \cos^n \theta')/(1 - \cos \theta')]$$

where θ' is the bond angle. A more detailed statistical theory due to

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[83] Pitzer, *Discuss. Faraday Soc.*, 1951. [84] *Idem, Chem. Reviews*, 1940, **27**, 39.

[85] *Idem, J. Chem. Physics*, 1937, **5**, 473 ; Pitzer and Gwinn, *ibid.* 1942, **10**, 428.

[86] Huggins, *ibid.*, 1940, **8**, 181.

[87] Burke and Laskowsky, *ibid.*, 1939, **7**, 465.

Taylor may be outlined by way of illustration. The " length " L of the line connecting the first and last, $(n + 1)$th, carbon atom is illustrated in Fig. 11. It is shown that the average square length $\langle L^2\rangle$ is given by the expression

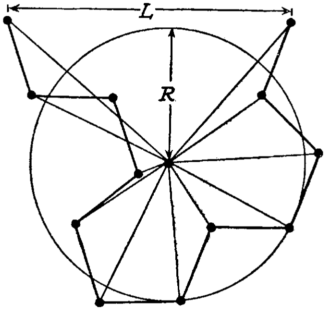

Fig. 11

Definition of average square length of a coiled molecule.

$$\langle L^2\rangle = l^2\left(\frac{1 + \cos\theta}{1 - \cos\theta}\right)\left(\frac{1 + a}{1 - a}\right)n$$

where θ is the supplement of the bond angle (180° – 109° 28′) and n is the number of bonds.

Rotation about each of the $n - 2$ " interior " bonds is assumed to be restricted by the same potential function $V(\phi)$, where the angle of rotation ϕ is defined as in Fig. 10*a*. The parameter a is the average value of $\cos\phi$. Using classical statistics to permit integration, we have

$$a = \frac{\int_0^\pi \exp\left[- V(\phi)/\boldsymbol{RT}\right]\cos\phi . \mathrm{d}\phi}{\int_0^\pi \exp\left[- V(\phi)/\boldsymbol{RT}\right] . \mathrm{d}\phi}$$

In this theory the selection of an appropriate potential barrier function must be specially discussed. $V(\phi)$ must be a three-fold function of ϕ because of the steric effects of the three neighbouring bonds. But whereas $V(\phi)$ has three-fold symmetry in ethane, yet in carbon chains the three barriers are not equal. Instead of the symmetrical function

$$V(\phi) = \tfrac{1}{2}V_{\mathrm{max.}}(1 - \cos 3\phi)$$

the function

$$V(\phi) = \tfrac{1}{2}V_{\mathrm{max.}}[x(1 - \cos\phi) + (1 - x)(1 - \cos 3\phi)]$$

has been proposed, where x is empirically selected to be 0·26 to fit thermodynamic data. The resultant function is illustrated in Fig. 10, and the temperature variation calculated for $\langle L^2\rangle$ is illustrated in Fig. 12. It can be shown that the average " radius " R

$$\langle R^2\rangle^{1/2} = \tfrac{1}{6}\langle L^2\rangle^{1/2}$$

As has been stated elsewhere,[44] the gas-collision diameters appear to have a much smaller temperature coefficient and do not confirm this theory :

this is still under investigation. In the limiting case where $V_{\text{max.}} = 0$, the rotation of the chain is " free ", and the average length corresponds with $a = 0$ in the equation.

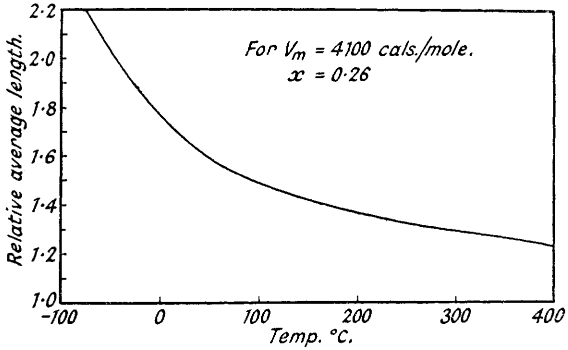

FIG. 12

Variation in $\langle L^2 \rangle$ with temperature for a flexible chain.

The absence of restricting potentials is commonly assumed in discussing the average configuration of high polymer molecules. Eyring [88] has proposed an alternative formula

$$\langle L^2 \rangle = l^2[n + 2(n - 1) \cos \theta + 2(n - 2) \cos^2 \theta + \ . \ . \ .]$$

for the freely coiling chain. These theories have been further developed for high-polymer chains [2] which are not dealt with in this Review.

7. General Conclusions

The general conclusions about the configuration of flexible molecules can be reviewed under the headings : (i) What are the predominant configurations in a mixture ? (ii) How do these change with environment at constant temperature $\left(\text{solid} \rightarrow \text{liquid} \begin{array}{l} \nearrow \text{gas} \\ \searrow \text{surface} \end{array}\right)$? (iii) How do they change with temperature under substantially constant environment ? From relative proportions at different temperatures it is possible to calculate : (iv) The energy difference ΔH between isomers. (v) The barrier $V_{\text{max.}}$ which must be surmounted in passing from one configuration to the next is obtained as in Section 6.1.

7.1. Predominant Configurations in a Mixture of Rotational Isomers.— As is discussed in Section 7.5, the simplest explanation of the potential barriers which lead to rotational isomerism is the repulsion between hydrogen atoms bonded to neighbouring carbon atoms. In the absence of dipole attractions, the most stable configuration with the minimum repulsion energy, is the *trans*-form, as recently shown for ethane.[89] Examples have been quoted above for ethane derivatives and for higher polymethylene hydrocarbons.

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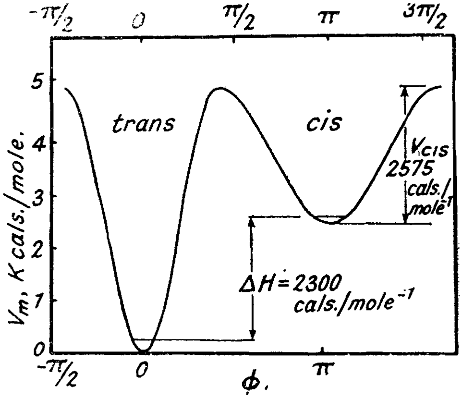
[88] *Phys. Review*, 1932, **39**, 746.

[89] Smith, *J. Chem. Phys.*, **17**, 139.

For cyclic hydrocarbons different bond angle strains are brought into play in the different rotational isomers. In *cyclo*pentane the configuration is still under controversy.[89a] For *cyclo*hexane and its derivatives in the absence of special effects, the chair form is predominant. No completely general statement can be made about the relative stabilities of " polar " and " equatorial " arrangements of substituents in *cyclo*hexane derivatives. Equatorial configurations appear to predominate in the examples so far studied.[90]

When more than one permanent dipole is present in the flexible molecule, important additional sources of potential energy arise. Generally, this additional energy is lowest when the dipoles point opposite ways, which again favours a *trans*-configuration in the gas phase. In the liquid phase (Section 7.2) the environment can substantially affect this generalisation.



$V_{\max.} = \Delta H + V_{cis}$.

FIG. 13

*Potential curve for rotation about the single bond in buta-*1 : 3*-diene.*

7.2. In the absence of permanent dipoles, condensed phases (solid and liquid) generally favour the configuration with the highest condensation energy. Thus polymethylene molecules are fully *trans* in the crystal, and probably largely *trans* just above the melting point. Crystal forces impose a unique isomer in all cases so far investigated by *X*-ray methods. Pairs of isomers crystallising together in a crystal compound would be theoretically possible, and would be of considerable interest. The nearest example known is in the structure of polythene where " crystalline regions " of *trans*-configuration are packed together with regions of random crumpling.[91]

When permanent dipoles are present, the general effect on passing from gas to liquid is to reduce the energy difference between different isomers, so that the mixture in the liquid tends to contain more nearly equal proportions than the gas at the same temperature.

[89a] Millar and Inskeep, *J. Chem. Phys.*, 1950, **18**, 1531.
[90] Beach, *Ann. Rev. Phys. Chem.*, 1950, **1**, 189.

TABLE V

Energy parameters for rotational isomerism about single bonds

Molecule.	Type of isomerism.	$V_{max.}$, cals./mole.	ΔH, cals./mole.	Ref.
C_2H_6	—	2750—3300	—	80, 92
C_3H_8	—	3300	—	,, ,,
n-C_4H_{10}	*trans*-gauche	3600—4100	760 (liq.)	80, 93, 30
iso-C_4H_{10}	—	3870	—	80
n-C_5H_{12}	*trans*-gauche	(assumed to be as in butane)	450 (liq.)	30
CMe_4	—	4200—4500	—	80, 92
n-C_6H_{14}	—	—	520 (liq.)	30
n-C_5F_{12}	*trans*-gauche	—	460 (liq.)	37
n-C_6F_{14}	,,	—	600 (liq.)	37
n-C_7F_{16}	,,	—	600 (liq.)	37
$CH_2Cl{\cdot}CH_2Cl$	*trans*-skew	4130	1200 (gas) zero (liq.)	71*a*, 81, 94
$CH_2Br{\cdot}CH_2Br$	,,	6100	1450 (gas) 650 (liq.)	,, ,, ,,
$CH_2Cl{\cdot}CHCl_2$	—	2800	see refs. (4000 ?)	76, 78
$CHCl_2{\cdot}CHCl_2$	*trans*-skew (gas) skew-*trans* (liq.)	—	200 (gas) 1100 (liq.)	78, 71 ,, ,,
$CH_3{\cdot}CCl_3$	—	2700	—	80
$CH_3{\cdot}CF_3$		3000		93
$COMe_2$	—	1400		92
$CH_3{\cdot}OH$	—	3400	—	,,
$CH_3{\cdot}SH$	—	1460	—	,,
$CH_3{\cdot}NH_2$	—	3000—1520	—	,,
$NHMe_2$	—	3460		91*a*
NMe_3	—	4270		,,
$C_2H_5{\cdot}OH$	—	$V_{max.}(CH_3)$ 3000 $V_{max.}(OH)$ 4410		92, 95
OMe_2	—	3100—2500		92
SMe_2	—	2000		,,
Butane-2-thiol		No rotational isomerism		96*a*
$ZnMe_2$	—	free		96
$HgMe_2$	—	free		,,
$SiMe_4$	—	1300		92
	Single bond C(aliph.)–C(aromat.)			
Toluene	—	0—1000		97
m- or *p*-Xylene	—	0—1000		,,
o-Xylene	—	2000 (avg.)		,,
	Cyclic molecules			
C_6H_{12}	chair → boat	—	6000	89
Dimethyl*cyclo*hexane	equatorial → polar	assumed as for butane	1800	7

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[91] Frith and Tuckett, *Trans. Faraday Soc.*, 1944, **40**, 251 ; Richards, *ibid.*, 1945, **41**, 127 ; Flory, *J. Chem. Phys.*, 1947, **15**, 684 ; 1949, **17**, 223 ; cf. also [91a] Aston, *Discuss. Faraday Soc.*, 1951.

[92] Aston, Isserow, Szasz, and Kennedy, *J. Chem. Phys.*, 1944, **12**, 336, which see for other references.

[93] Gulowsky and Levene, *ibid.*, 1950, **18**, 1297.

[94] Bernstein, *ibid.*, p. 897.

[95] Halford, *ibid.*, 1948, **16**, 560.

[96] Boyd, Thompson, and Williams, *Discuss. Faraday Soc.*, " Spectroscopy ", 1950, **9**, 154.

[96a] Rank, Schull, and Axford, *J. Chem. Phys.*, 1950, **18**, 392.

[97] Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803.

TABLE Va

Energy parameters for rotation about single bonds with order higher than unity

Molecule.	Bond length ("single bond").	Type of isomerism.	$V_{max.}$, cals./mole.	ΔH, cals./mole.	Ref.
$CH_3{\cdot}CH{:}CH_2$ . . .	1·52	—	800—2100*	—	80, 92
$CHEt{:}CH_2$ . . .		—	800	—	80
$CHMe{:}CHMe$ *trans* .	1·54 (?)	—	1950	—	91*a*
$CHMe{:}CHMe$ *cis* . .	1·54 (?)	—	450 (avg.)	—	,,
$CMe_2{:}CH_2$	1·54 (?)	—	1800		80
$CMe{:}CMe$	1·47	—	500 >	—	,,
$CH_2{:}CH{\cdot}CH{:}CH_2$ . .	1·46	— *trans* → *cis*	4900	2300	98
Values for ethylene derivatives are included below to illustrate the differences of magnitude.					
Rotation about double bonds					
$CH_2{:}CH_2$	1·34	—	60,000	—	11
$CHPh{:}CHPh$ . . .	1·44	*cis-trans*	40,000	—	54
$CHMe{:}CHMe$ . . .	—	*cis-trans*	18,000	1280	54, 99, 100
$CHCl{:}CHCl$ . . .	(1·34)	*trans-cis*	—	600	100, 101
$CHBr{:}CHBr$ . . .	—	*cis-trans*	—	340	101

* The lower value from calorimetric specific heat of gas, the higher from velocity of sound.

No generalisations appear to be possible about the predominant configuration in dilute solution.

7.3. A change with temperature in the relative amounts of rotational isomers depends on the differences in heat content and in entropy in the various phases. So far as they are known, differences in heat content are tabulated in Table V. Differences in entropy are generally assumed to be wholly due to differences in statistical weight of different isomers.

7.4. Energy differences between rotational isomers can conveniently be tabulated in terms of the difference in heat content ΔH and in terms of the maximum height $V_{max.}$ of the potential barrier to be traversed on passing from one isomer to another. Fig. 13 illustrates these potentials for buta-1 : 3-diene. Symbols used by various authors are somewhat confusing and have been rewritten where necessary for Table V.

In the above, values of ΔH are very considerably smaller than values of $V_{max.}$. It is interesting to note that $V_{max.}$ is apparently largest for the C–C bond and becomes smaller for the various hetero-atomic bonds.

From the similarity of the polar configuration of " chair " 1 : 2-dimethyl*cyclo*hexane with polar CH_3 groups to the gauche form of *n*-butane, the polar form is estimated to have a potential energy about 1·8 kcals. higher than for the equatorial configuration of CH_3 groups.

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[98] Aston and Szasz, *J. Chem. Phys.*, 1946, **14**, 28.

[99] Hill, *ibid.*, 1948, **16**, 430.

[100] Walsh, *Trans. Faraday Soc.*, 1951, **47**, 1.

[101] Maroney and Olsen, *J. Amer. Chem. Soc.*, 1934, **56**, 1320.

7.5. Origins of the Potential Barriers opposing Rotation about Bonds.— Two main types of explanation have been offered for the barriers opposing rotation about a single bond.

(i) Conventional ideas about the interaction between electrons bound to different atoms being used, the total repulsions between proximate hydrogen atoms have been summed in terms of individual repulsion potentials V_{ij} between atoms i, j, which are empirically assumed to be of the form $V_{ij} = 4{\cdot}99 \times 10^5/r_{ij}{}^5$ cals./g.-atom.[92] Calculated barriers on this basis are compared in the following table with values calculated from heat capacities. The test that this form of repulsion potential should give zero barrier for molecules such as dimethylzinc or dimethylmercury does not appear to have been made. For an alternative summation see ref. 102.

Comparison between calculated potential barriers from heat capacities and repulsion formulæ

	$V_{\text{max.}}$, cals./mole, from :			$V_{\text{max.}}$, cals./mole, from:	
	heat capacity.	calculation.[92]		heat capacity.	calculation.[92]
C_2H_6 . . .	3150	(3150)	$SiMe_4$ . . .	1300	1360
C_3H_8 . . .	3300	3170	OMe_2 . . .	3100	1600
CMe_4 . . .	4500	4230	SMe_2 . . .	2000	1260

An interpretation of the fifth-power repulsion law has been put forward in terms of the quadrupole–quadrupole interaction between the charges of one bond and those on a proximate bond.[103] By combining these with dipole effects, it has been shown that the staggered configuration has the lower energy for all possible modes. Net interactions from these causes are repulsive in both staggered and eclipsed forms. See also ref. 104.

(ii) Various quantum-mechanical possibilities have been reviewed.[105] In order to account for the observed height of the barrier in ethane, it has been suggested that various resonance forms with increased rotational barriers contribute to the structure. It may be significant that even where the bond order is greater than unity, as shown from bond lengths, the rotational barrier is not necessarily increased in propylene and dimethylacetylene, though it is increased in butadiene. No final conclusion seems possible at present about the various factors contributing to the rotational barriers. Additional experimental evidence about the magnitude of the C–H dipole in various molecules [106] and about the trend of heats of formation with the number of carbon atoms in the shorter paraffins [107] may yield contributory information about the origin of rotational barriers.

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[102] French and Rasmussen, *J. Chem. Phys.*, 1946, **14**, 389.

[103] Lassettre and Davis, *ibid.*, 1948, **16**, 151 ; Lassettre and Dean, *ibid.*, 1949, **17**, 317.

[104] Oosterhoff, *Discuss. Faraday Soc.*, 1951.

[105] Gorin, Walter, and Eyring, *J. Amer. Chem. Soc.*, 1939, **61**, 1876.

[106] Gent, *Quart. Reviews*, 1948, II, 383.

[107] Sidgwick, *Ann. Reports*, 1934, **31**, 45.