296. *The Melting Points of Long-chain Carbon Compounds.*

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THE heats of crystallisation and specific heats of the members of a number of homologous series, *viz.*, the aliphatic monobasic acids, their ethyl and methyl esters, and the straight-chain hydrocarbons, have now been determined experimentally, and the data are of importance in that they extend our knowledge of the physical properties of the hydrocarbon chain and of the nature of the factors influencing the melting points of homologous series.

The lower members of homologous series show anomalies of m. p. which frequently give rise to a minimum on the m. p. curve at about $n = 5$, and there are corresponding anomalies in the heats of crystallisation, etc., in this region (cf. Garner and King, J., 1931, 578). The heats, X-ray spacings, etc., of the lower members of the series have not been extensively studied—only those of the monobasic aliphatic acids are in any respect complete (Gibbs, J., 1924, **125**, 2622)—so the causes of the anomalies are still somewhat obscure. The anomalies disappear when the hydrocarbon chain contains more than 10 carbon atoms, and two regularities emerge from the experimental results. First, the odd and even members being considered as separate series, the molar heat of crystallisation increases linearly with the number of methylene groups in the hydrocarbon chain, and hence the increment in the heat of crystallisation due to the introduction of a methylene group into the chain becomes constant for the higher members of any one series : this increment, however, does not possess the same value for all series (see table, col. 2). Secondly, the increment in the entropy of crystallisation per methylene group is constant for any one series; this is of considerable significance for the theory of melting points, and is discussed later (p. 1369). The entropy increments can only be determined for those forms stable at the m. p. The values for six series are now known and are given in the table. Five of these are illustrated in the figure.

	Series.	Heat of crystn. per CH_2, kg.-cals.	Entropy per CH_2 group, $\times 10^6$.	Average sp. heat of solid forms, cal./g.	Average sp. heat of liquid for range 30° above m.p., cals./g.	Area of hydrocarbon chain, A.^{2}.	Convergence temp. (calc.).	Heat of crystn. of terminal groups, kg.-cals.
Tilted forms.	Even acids	1·03	2652	0·48	0·53	18·3	388·5°	−1·55
	Odd acids	0·97	2505	0·44	0·54		385·2	−2·56
	Even methyl esters	1·08	2839	0·43	0·52		381·5	−1·98
	(T.) Hydrocarbons	1·0		0·44	0·57	18·3		
	(T.) Ethyl esters	1·04		0·43	0·52	18·5		
Vertical forms.	(V.) Odd ethyl esters	0·84	2240	0·63	0·50			−3·90
	(V.) Even ethyl esters	0·71	1796	0·71	0·52	19·6	394·2	−1·86
	(V.) Even hydrocarbons	0·61	1491	1·05	0·57	19·9	408·0	−0·53

An examination of the increments per methylene group for different series (table) shows that the long-chain compounds may be sharply divided into two classes. There is

one group for which the increments both in the heats and in the entropies of crystallisation are the same within experimental error. This group gives specific heats for the solid in equilibrium with the melt which are normal in the sense that the values are lower than those for the liquid state (cols. 4 and 5). X-Ray analysis of the solids of this group by Müller, Piper, Malkin, and others has shown that the axes of the hydrocarbon chains are tilted with respect to the planes holding the terminal groups. The angle of tilt varies from one homologous series to another, but the variations do not appear to have much effect on the physical properties recorded in the table; *e.g.*, the cross-sectional area of the chains taken at right angles to the axes of the chains is unaffected (col. 6). In this group, the hydrocarbon chains are in the state of closest packing, possessing a cross-sectional area of $18 \cdot 3$—$18 \cdot 5 \times 10^{-16}$ cm.^{2}.

In the other group, which includes the hydrocarbons and ethyl esters, the values of the increments in the heats and entropies of crystallisation are lower, and the specific heats, cross-sectional areas, and coefficients of expansion are higher, than those of the first group. Also, the values obtained vary from one series to another. X-Ray analysis shows that in

Entropies of crystallisation for various homologous series.
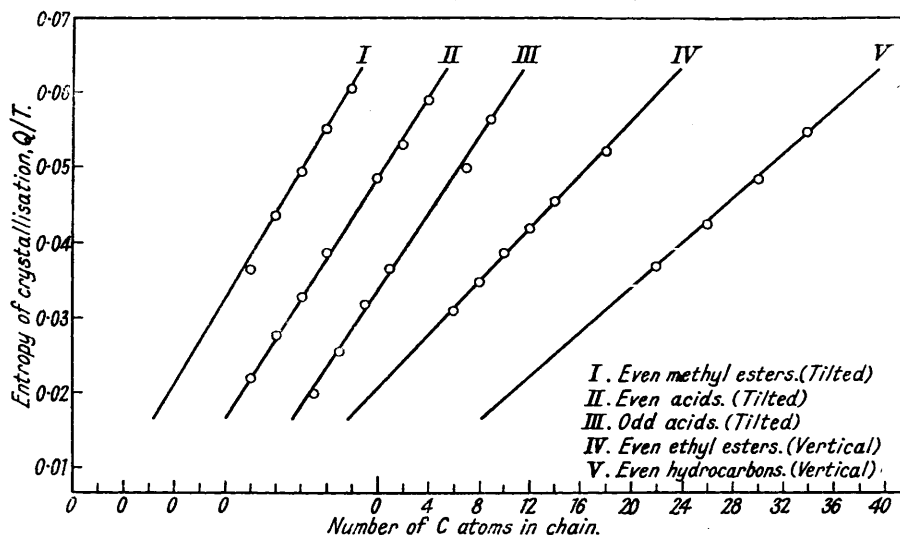
this group the chains are vertical with respect to the planes containing the terminal groups, and dielectric-constant and molecular-volume measurements by Buckingham (*Trans. Faraday Soc.*, 1934, **30**, 377) have shown that not only are these vertical chains less closely packed than the tilted chains, but they also possess considerably higher mobility in the solid state. The results obtained are in accord with the hypothesis that the vertical chains are oscillating or rotating about the axis of the chains. The high values obtained for the specific heats indicate that the energy of oscillation of the chains increases rapidly with increase in temperature, and this is further borne out by the high coefficients of expansion of the solid state. The low heat and entropies of crystallisation would be expected on this hypothesis, since, on account of the possession of oscillation energy, less thermal energy will be required to tear the chains from the surface of the solid.

In view of the very marked differences between the physical properties of the vertical and the tilted forms of the hydrocarbon chain, it would appear to be advisable to classify the polymorphic modifications of long-chain compounds into the two main groups, tilted and vertical forms, and to discard the use of the terms α, β, and γ to designate these polymorphic modifications. This sub-division into tilted and vertical forms has considerable justification in that the former give rise to alternating and the latter to non-alternating homologous series (Malkin, *Nature*, 1931, **127**, 126; J., 1931, 2796).

Theory of Melting Points.—The fact that the entropy of crystallisation increases linearly

with chain length is of importance for the theory of the melting points. The entropy increment must be associated with an increasing probability of the solid state as against the liquid, as the hydrocarbon chain is lengthened. Since the entropy increases by ΔS for each methylene group, the entropy of crystallisation must include the term $\log_e w^n$, where w is the probability of some state or configuration of the methylene group and n is the number of carbon atoms in the chain. The source of this term can be traced with fair certainty.

We shall consider the process of melting such as would occur at the crystal faces parallel to the c axis. On these faces the molecules are lying lengthwise in the surface and are each held to the surface by $\frac{1}{2}(n-2)$ methylene groups and two terminal groups. It is possible to account for the nature of the entropy increment if we assume that, in the process of melting, these contacts are broken one at a time by rotation about the C—C linkings, and that the probability of the breaking of each contact obeys an equation of the type $w = ke^{-q/RT}$, where q is the activation energy of the process (cf. Garner, Madden, and Rushbrooke, J., 1926, 2494). There is only one alternative to this assumption, *viz.*, that all of the contacts are broken at one and the same time, and this seems to be a very improbable mechanism. It was shown in the earlier paper that the relationship governing the melting point was

$$(k'_1/k''_1)^{\frac{1}{2}(n-2)} \cdot (k'_2/k''_2) \cdot (k'_3/k''_3) \cdot f(n) = e^{-q/kT} = e^{-Q/RT} \quad . \quad . \quad . \quad (1)$$

where k'_1, k'_2, and k'_3 refer to the process of melting and are the frequencies with which the methylene and the two terminal groups receive activation energy from the solid lattice, and k''_1, k''_2, and k''_3 refer to similar frequencies applying to the process of crystallisation; q and Q are the heats of crystallisation per molecule and g.-mol. respectively, and T is the absolute temperature of the m. p. As the chain is lengthened, the chance of molecules colliding with the surface in the right place diminishes, and the function $f(n)$ is introduced to take account of this. The precise nature of the function is not accurately known. It has been discussed elsewhere, and it was shown that it is very probably responsible for the minima which occur at about $n = 5$ on the m. p. curves.

From (1), it can be shown that the entropy increment for two methylene groups is given by

$$Q_n/T_n - Q_{n-2}/T_{n-2} = R \cdot \log_e k'_1/k''_1 + R \cdot \log_e f(n)/f(n-2) \quad . \quad . \quad (2)$$

and for long chains the last term can be neglected (cf. J., 1931, 578). Thus the probability w referred to above is k'_1/k''_1, where k''_1 is now the frequency of rotation about the C—C bond in the liquid state. Since k''_1 is probably a constant for all homologous series, the variations in the entropy increment which occur are to be ascribed to different values of k'_1.*

Convergence of the Melting Points of Homologous Series.—In the consideration of this question, the dimensions of the terminal and the methylene groups are important. These will vary with the nature of the environment, and since expansion occurs on melting, they will, in general, be greater in the liquid than in the solid state. In the crystal, both the terminal and the methylene groups are compelled to take up the same area of cross-section, and it is unlikely that either would occupy this area exactly if effects due to the other were absent. Both will be subject to some distortion either of compression or of expansion, which can, however, be reduced by modification of the angle of tilt of the chain. The area of cross-section of the methylene chains measured normally to their long axis can vary from 18·3 to 19·9 A.² according to whether the chain is tilted or vertical. It will not, however, be possible by a modification of the angle of tilt to remove the distortion completely, for the localised forces of attraction between the methylene groups will severely restrict the possible angles of tilt. Thus the change in the dimensions of the terminal group which occurs on passing from the liquid to the solid state will vary with the length of the methylene chain, but the

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* The view put forward in our previous paper (J., 1934, 1451), *viz.*, that the straightening of the hydrocarbon chain occurs in the liquid state previous to the entry of the molecule into the solid state, can be shown to lead to incorrect conclusions with regard to the rates of crystallisation of long-chain compounds, and therefore must be discarded as not in accord with the facts. Hence, it has been necessary to return to the earlier mechanism set out above.

dimensions of these groups should, however, approach constant values as the hydrocarbon chain is lengthened.

The heats of crystallisation increase linearly with the number of methylene groups when there are more than 8—10 such groups in the molecule. If calculations are made of the contribution of the heats of crystallisation of the terminal groups to the total heat from those of compounds with more than 10 methylene groups, negative values are always obtained (see table). This shows that the interaction of the terminal groups with their environment in the crystal is less in the solid than in the liquid state. Therefore, when the chain length exceeds $n = 10$, the terminal groups must be in an expanded state.

As the chain is progressively shortened below $n = 10$, there is a positive departure from the linear relationship between Q and n, the lower members giving a higher heat than expected. This may be taken to mean that, as the number of methylene groups is reduced, the interaction between the terminal groups of adjacent chains is becoming larger, and hence the heats of crystallisation of these groups is becoming more positive. In the case of acetic acid, where the restriction due to the presence of methylene groups has disappeared, the molar heat of crystallisation of the terminal groups is at its maximum value, viz., $Q = 2 \cdot 77$, and this is actually larger than the molar heat of crystallisation of butyric acid which contains two extra methylene groups, viz., $Q = 2 \cdot 62$.

On account of the negative heats and entropies of crystallisation found to exist in the neighbourhood of the ends of the chains, there is a marked tendency for these ends to enter the liquid state, and this markedly reduces the m. p.'s of the lower members of homologous series.* The m. p.'s rise as the chain is lengthened, because these terminal effects become of less importance, and ultimately, as the methylene chain becomes dominant, the m. p.'s approach a limiting value which is called the convergence temperature.

The convergence of the m. p.'s of homologous series has been experimentally realised only with the dibasic aliphatic acids, where they converge so rapidly that by $n = 30$ the m. p.'s of odd and even acids are identical to within 2—3°. From the values given in Beilstein, the convergence temperature for these acids is 391° Abs., and from the results of Fairweather (*Phil. Mag.*, 1926, **1**, 944) on the even members, 396° Abs. The convergence temperature is the m. p. of a very long hydrocarbon chain, so long that the effects of the terminal groups may be neglected, so this temperature can be calculated from the properties of the methylene groups, viz., $T_c = \Delta Q / \Delta S$. The values obtained in this manner are set out in the table for the tilted and the vertical forms. The accuracy of T_c is not very high in some cases on account of experimental error in the determination of the heats of crystallisation. The most accurate values are those for the even acids (389°) and for the α-even ethyl esters (394·2°), and these lie very close to the experimentally determined convergence temperatures for the dibasic acids, in spite of the fact that the acids possess tilted chains and the esters vertical chains at the m. p.

Relative Stability of the Tilted and the Vertical Chains.—Since the convergence temperatures of the vertical and the tilted forms do not differ greatly, it must be concluded that the two types of packing in the crystal possess very nearly equal stabilities. It can therefore be readily understood why the mode of packing of the hydrocarbon chains should be decided by the nature of the terminal groups. In the case of series where the terminal groups are strongly associated, e.g., in the acids and methyl esters, the constraint due to these groups is so great that the tilted forms are stable at the m. p. even up to $n = 30$ or 40. On the other hand, where there is little tendency towards association, as for the ethyl esters and hydrocarbons, the vertical forms are stable at the m. p. in the case of the higher members of the series. There is, however, a switch over to the tilted forms in the case of the ethyl esters when n is less than 22, due to the greater rôle played by the terminal groups in the shorter-chain compounds. The experimental evidence so far obtained indicates that the vertical forms will be stable at the m. p. of compounds with very long chains, and this is supported by the fact that the convergence temperatures for the vertical are somewhat higher than those for the tilted forms (see table).

* An exception occurs in the case of the odd dibasic aliphatic acids where the m. p. falls as the chain is lengthened, but there are no data on the heats of crystallisation.

SUMMARY.

The heat and entropy increments per methylene group are constant for members of homologous series when the number of carbon atoms in the chain exceeds 10. The polymorphic modifications of long-chain compounds can be sharply divided into two classes, *viz.*, those with vertical and those with tilted chains. For the former, the heat and entropy increments of crystallisation are small and variable from series to series, but for the latter, they are large and constant for all series so far investigated. The vertical forms possess oscillating or rotating chains, and abnormally high specific heats, coefficients of expansion, and cross-sectional areas of the chains in the solid state.

The theory of the convergence of the melting points of long-chain compounds is discussed, and the rise in the melting points with increasing chain length is ascribed to negative heats of crystallisation in the neighbourhood of the terminal groups. It is concluded that the vertical chains are more stable than the tilted chains at the melting point for compounds with very long chains.