CXCI.—*Melting Points and Heats of Crystallisation of Homologous Series. Part III. Myristic Acid Derivatives.*

By W. E. Garner and J. E. Rushbrooke.

It has been shown previously (J., 1926, 2491) that the heat of crystallisation of the monobasic fatty acids above C_{10} increases by 2·060 Cal. for every two methylene groups added to the carbon chain; and also that for an even member the heat of crystallisation divided by the absolute melting point increases regularly as the series is ascended. From these two relationships the empirical equation (1) was derived for the melting points of the even members of the monobasic acids :

$$T = (-3{\cdot}61 + 1{\cdot}030n)/(-0{\cdot}0043 + 0{\cdot}002652n) \quad . \quad . \quad (1)$$

where n is the number of carbon atoms in the chain.

If it be assumed that the increment in the heat of crystallisation per methylene group is the same for all homologous series above C_{10}, then an equation of a general character, (2), would be expected to be valid for all series:

$$T = (x + 1{\cdot}030n)/(y + 0{\cdot}002652n) \quad . \quad . \quad . \quad . \quad (2)$$

where x and y are constants depending on the nature of the terminal groups.

In order to check the applicability of equation (2) to any particular series it is necessary to know the value for the heat of crystallisation of one of the even members of the series. In the present investigation, the data necessary for such a test have been procured in the case of the monobasic amides, alcohols, and methyl and ethyl esters. The amides, like the acids, form a series in which the melting points alternate from the odd to the even members, but the alcohols and esters are non-alternating.

The fourteenth member of each of these series was chosen for the test, and the results are in Table I. From the values of x and y in this table, the melting points (*i.e.*, the setting points or equilibrium values) of the members of five homologous series have been calculated and these are given by the continuous lines in the diagram. The experimental values of the melting points culled from numerous sources are shown in the diagram by vertical lines, the length of which indicates their range. The agreement between the calculated and the experimental melting points is within 1—2% and is as good as could be expected in view of the fact that the melting points of homologous series are not known with great accuracy, and that a small change in the constants of equation (2) produces a marked change in the calculated curve.*

TABLE I.

Substance.	Setting point, $t°$.	Q (Cal./mol.).	Q/T.	x.	y.	Heat of cryst. of terminal groups.
I. Alternating series.						
Myristic acid ...	53·7°	10·74	0·03287	−3·68	−0·00426	−1·62
Myristamide ...	103·0	12·92	0·03436	−1·50	−0·00277	+0·56
II. Non-alternating series.						
Methyl myristate	18·35	10·63	0·03647	−3·79	−0·00066	−1·73
Ethyl myristate	11·0	11·17	0·03933	−3·25	+0·00220	−1·19
Myristyl alcohol	37·7	11·76	0·03785	−2·66	+0·00072	−0·60

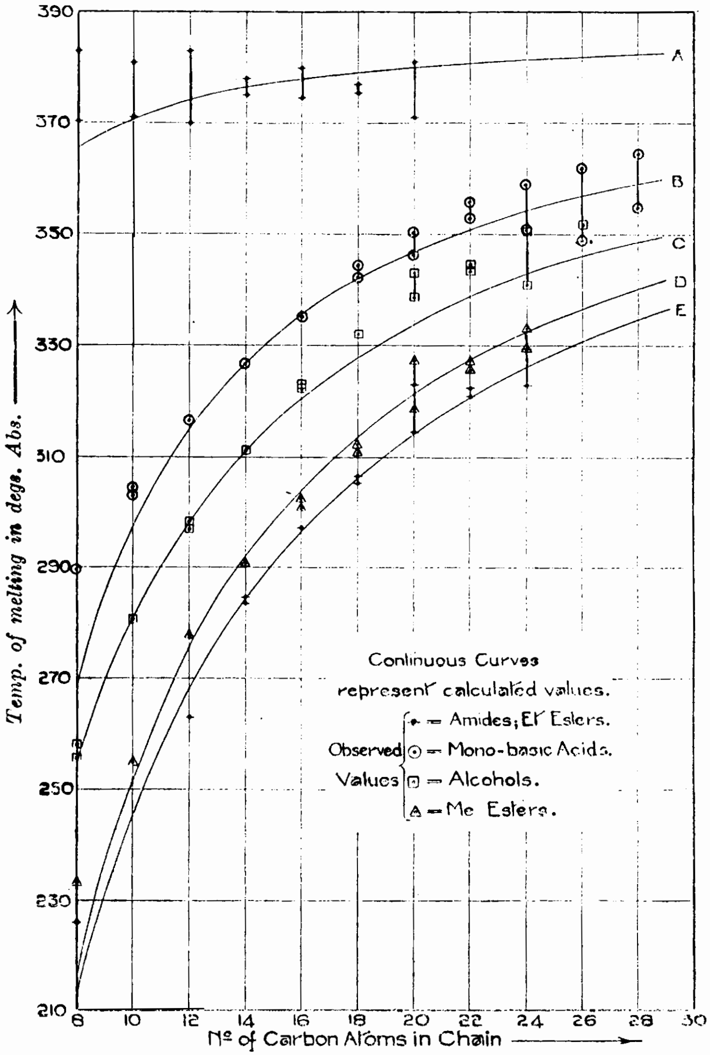
The melting points as determined by the ordinary method may or may not be identical with the equilibrium values for these temperatures given by the setting points. Partington and Stratton (*Phil. Mag.*, 1924, **48**, 1089) have recorded that the setting point of palmitic acid is lower than its melting point, and we also have observed the same phenomenon with palmitic and eicosoic acids. As Smits has shown (" The Theory of Allotropy," 1922), the melting

---

* It is desirable that the constants in equation (2) be determined more accurately by measurements of the heats of crystallisation of higher members of the monobasic acid series.

point varies with the rate of heating if equilibrium between the various molecular forms in the liquid or solid states is established slowly. Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 905) have

FIG. 1.



observed that the melting points of the long-chain fatty acids decrease after the solids have been kept for a long time. This points to slow changes occurring in the solid state and indicates that the phase equilibria are not established rapidly. It would therefore be expected that the melting points of these substances would vary with the rate of heating, and this would account for the wide range of the experimental values.

The melting points of the alcohols and acids recorded by Levene and Taylor and others for the 18—26th members lie on a curve which is 4—5° higher than the calculated curve. It is not unlikely that this discrepancy is due to the fact that the experimental melting points are not equilibrium values. In the case of the esters, the divergences from the theoretical curve are not large over the whole range from $n = 8$ to $n = 28$.

The agreement is of such a nature as to provide some justification for further work along these lines.

Up to the present, very few quantitative relationships, other than those of a thermodynamical character, have been discovered between the melting points of organic compounds and their other physical properties. This lack of quantitative knowledge applies not only to the melting points but also to other properties which are likewise sensitive to changes in chemical constitution. The factors determining the numerical values of constitutive properties are imperfectly understood and it is difficult to discuss even qualitatively their dependence on chemical constitution.

On account of the similarity which exists between the processes occurring at the melting point and those associated with chemical change, it is not unlikely that the application of the laws of chemical change to melting-point phenomena will yield information of importance for the study of the relationship between melting point and chemical constitution. In the previous paper (*loc. cit.*, p. 2496) a theoretical equation for the melting points of homologous series was deduced along these lines:

$$T = \frac{Q}{4 \cdot 57}\left\{\tfrac{1}{2}(n-2)\log\frac{k_1''}{k_1'} + \log\frac{k_2''}{k_2'} + \log\frac{k_3''}{k_3'} + \log n\right\} \quad . \quad (3\text{A})$$

This equation, which applies only to those homologous series in which no chemical association occurs in the liquid and solid states, contains four variables—the melting point, T, the heat of crystallisation, Q, a number of probability factors, and the number of carbon atoms in the chain, n.

This equation can be expressed in a more convenient form by adopting the conception that for each group in the molecule there is an *equilibrium constant* which determines its distribution between the solid and the liquid phase. This involves making the hypothesis that the groups forming the carbon chain can detach themselves from the surface of the crystal or rejoin the surface independently of their neighbours. This is rendered highly probable by the possibility of rotation of the groups about the single C—C linkings. There is, however, a limitation to this freedom of movement of individual groups; any group situated between two others, which are themselves attached to the surface, is incapable of movement. Thus the equilibrium constant refers only to those groups which are in such a position that they can move away from or attach themselves to the surface. Of these groups, some will be in the liquid and some in the solid phase. The ratio of those in the solid to those in the liquid phase, or the equilibrium constant, κ, is given by $\kappa = (k''/k')e^{+Q/RT}$, where Q is the heat of crystallisation of the group in question, T is the absolute temperature, and k'' and k' are the probability factors discussed previously (*loc. cit.*). The equilibrium constant of any group will vary with temperature in an analogous manner to the equilibrium constant of chemical change.

According to this view the melting points for long-chain compounds will be given by

$$T = \log_e [\kappa_1{}^{\frac{1}{2}(n-2)} . \kappa_2 . \kappa_3 . n] \quad . \quad . \quad . \quad . \quad (3\textsc{b})$$

where κ_1, κ_2, and κ_3 are the equilibrium constants of the methylene group and of the two terminal groups respectively. The value of κ_1 is readily evaluated as follows: For a carbon chain of infinite length, the melting point is 118°; at this temperature, $\kappa_1 = (k_1''/k_1')e^{+Q_1/RT}$, since the probability of attachment of a methylene group at the melting point is equal to the probability of its detachment. The equilibrium constant at any other temperature can readily be calculated from the above equation.

The values of the equilibrium constants of the terminal groups are not yet known, but there is no great difficulty in the way of their determination. A study of the heats of crystallisation of the hydrocarbons and the dibasic acids, together with the data already known, should give these directly.

The application of equation (3B) to the compounds given in Table I is complicated by the fact that the acids are chemically associated to double molecules in the solid and liquid states, whereas the esters occur as single molecules in the solid state (compare Müller and Shearer, J., 1923, **123**, 2043, 3152, 3156). The amides have not yet been investigated by X-ray methods, but on account of the similarities between the $-CO_2H$ and $-CO{\cdot}NH_2$ groups and also since the amides and acids give alternating series, it will be assumed that the amides, like the acids, are chemically associated in the solid and liquid states. It is necessary to discuss the alternating and non-alternating series separately.

Alternating Series.—The melting points of alternating series will be given by a modified form of equation (3A). The molecules are practically twice the length of corresponding members of the non-alternating series, the heat of crystallisation per g.-mol. is doubled, and log n in equation (3A) is replaced by $\frac{1}{2}$ log $2n$ in (4A) :

$$T = \frac{Q}{4{\cdot}57}\left\{\tfrac{1}{2}(n-2)\log\frac{k_1''}{k_1'} + \log\frac{k_2''}{k_2'} + \log\frac{k_3''}{k_3'} + \tfrac{1}{2}\log 2n\right\} \quad (4\text{A})$$

and

$$T = \log_e\left[\kappa_1{}^{\frac{1}{2}(n-2)} . \kappa_2 . \kappa_3 . (2n)^{\frac{1}{2}}\right] \quad . \quad . \quad . \quad . \quad (4\text{B})$$

When $n = 14$, the numerical value for the terms in the brackets is 7·18 (for myristic acid). If we replace $\frac{1}{2}$ log $2n$ by log n, the value increases to 7·60. This change alone would lower T by 18°. Thus association has by no means an insignificant effect on the melting points of homologous series.

If our assumptions be correct, the amide will differ from the acid only in the value of the equilibrium constants of the chemically associated groups $(\text{-CO}{\cdot}\text{NH}_2)_2$ and $(\text{-CO}_2\text{H})_2$. The equilibrium constants for these groups are given by $\kappa_3 = (k_3''/k_3')e^{+2Q_3/RT}$, where Q_3 is the heat of crystallisation of the terminal group. Q_3 for the amide is 2·18 Cal. greater than for the acid, and this difference will affect κ_3 very materially and through it the melting point; k_3''/k_3' may be different for the two substances, but the values of this ratio are unknown.

It is clear, however, that the main factor which is responsible for the amide melting 50° higher than the acid is the high heat of crystallisation of the $(\text{-CO}{\cdot}\text{NH}_2)_2$ group. In (4A), if we assume that the terms in the brackets are the same for the amide and the acid, then Q/T = constant. Q/T for the amide is 0·03436, and for the acid 0·03287, and these values are sufficiently in agreement to warrant the above conclusion.

Non-alternating Series.—The ethyl ester possesses one more point of attachment in the crystal than the methyl ester. This is due to the additional methylene group in the alkyl chain. The equilibrium constant for this group, κ_4, is equal to $(k_4''/k_4')e^{+Q_4/RT}$, where Q_4 is its heat of crystallisation. $Q_4 = 0{\cdot}54$ instead of the normal value 1·03 Cal. found for the acid chain. The equilibrium constant, κ_4, is lower than κ_1 for the groups of the acid chain, or, in other words, the tendency for the methylene group in the alkyl chain to enter the solid state is much lower than for the same group in the acid chain. Thus the low melting point of the ethyl esters, when compared with the methyl esters, can be ascribed to the low heat of crystallisation of the methylene group in the alkyl chain.

EXPERIMENTAL.

The esters of myristic acid and myristyl alcohol were obtained from Eastman Kodak Co., and were purified by distillation or crystallisation until a constant setting point was obtained. Myristamide was prepared from a pure specimen of myristic acid and purified by crystallisation.

The details of the experimental technique were as described previously. The calorimeter had a water equivalent of 345·3 cal./deg.

The experimental data are recorded in Tables II—V. The heats of crystallisation of myristamide and myristyl alcohol are probably correct to within 0·5% and those of the esters to within 1%.

TABLE II.

Myristamide : setting point, 103·5°.

(Weight of substance, 6·5294 g.; glass, 3·8847 g.; platinum, 0·2008 g.; nickel, 3·3121 g.)

Expt. No.	Temp. range.	Fall in temp.	Rise in temp.	Expt. No.	Temp. range.	Fall in temp.	Rise in temp.
1— 4	64—15°	50·73°	0·586°	11—12	110—15°	95·75°	2·273°
5— 7	100—15	84·75	1·045	13—14	127—15	112·68	2·545
8—10	110—15	95·56	2·278	14—17	139—15	123·94	2·725

I. From 1—7, σ_S = 0·535 cal./deg.
II. From I and 8—17, σ_L = 0·640 cal./deg.; Q = 56·84 cals./g.

A large number of measurements were made over the temperature range 110—139° in order to make quite sure that the high value for σ_L given above was correct. The amide when fused had a pale yellow colour which could not be removed by repeated crystallisation.

TABLE III.

Myristyl alcohol : setting point, 37·7°.

(Weight of substance, 10·9602 g.; glass, 6·1894 g.; platinum, 0·2008 g.; nickel, 3·9133 g.)

Expt. No.	Temp. range.	Fall in temp.	Rise in temp.	Expt. No.	Temp. range.	Fall in temp.	Rise in temp.
1—3	1—18°	−17·13°	−0·297°	9	34—18°	+15·97°	+0·333°
4	24—18	+ 6·36	+0·119	10—12	39—18	21·23	2·146
5	26—18	8·31	0·156	13	56—18	37·48	2·538
6	28—18	10·09	0·194	14—15	60—18	42·43	2·643
7	30—18	12·08	0·233	16—18	66—18	47·73	2·785
8	32—18	14·01	0·279	19	75—18	57·35	3·032

I. From 1—9, σ_S = 0·432 cal./deg.
II. From I and 10—19, σ_L = 0·612 cal./deg.; Q = 54·86 cal./g.

Myristyl alcohol occurs in two solid modifications, one of which is unstable between 0° and 34°. The above value of Q refers to the modification stable at room temperature.

TABLE IV.

Methyl myristate : setting point, 18·35°.

(Weight of substance, 10·9144 g.; glass, 6·1791 g.; platinum, 0·2008 g.; nickel, 3·0904 g.)

Expt. No.	Temp. range.	Fall in temp.	Rise in temp.	Expt. No.	Temp. range.	Fall in temp.	Rise in temp.
1—3	1—13°	−12·25°	−0·232°	6— 8	20—13°	6·96°	1·526°
4	3—13	− 9·92	−0·190	9—11	50—13	36·93	2·155
5	6—13	− 6·95	−0·135				

I. From 1—5, $\sigma_S = 0·475$ cal./deg.

II. From I and 6—11, $\sigma_L = 0·526$ cal./deg.; $Q = 43·90$ cal./g.

In experiments 6—11, the ester took 60 minutes before crystallisation was complete, as compared with 20—25 minutes for the amide and alcohol. On account of the long middle period, a radiation correction of approx. 0·04° was sometimes applied. This makes the above value of Q less accurate than those of the amide and the alcohol, but the error is not greater than 1%.

TABLE V.

Ethyl myristate : setting point, 11·0°.

[Weight of substance, 11·0523 g.; glass, 4·6576 g.; platinum 0·2008 g.; nickel (except Expts. 6—8), 2·034 g.; nickel (Expts. 6—8), 2·1498 g.]

Expt. No.	Temp. range.	Fall in temp.	Rise in temp.	Expt. No.	Temp. range.	Fall in temp.	Rise in temp.
1	0—15°	−14·58°	−1·678°	6— 8	45—15°	30·09°	0·579°
2	3—15	−11·99	−1·619	9—11	−9—15	−23·99	−1·842
3—5	6—15	−9·32	−1·500				

I. From 6—8, $\sigma_L = 0·500$ cal./deg.

II. From I, 1—5, and 9—11, $\sigma_S = 0·498$ cal./deg.; $Q = 43·6$ cal./g.

Sixty minutes elapsed before the melting of the ester was complete.

Summary.

The heats of crystallisation of a number of derivatives of myristic acid have been determined, and the results have been employed in the calculation of the melting points of certain homologous series, *viz.*, the amides, methyl and ethyl esters of the monobasic fatty acids, and the monohydric alcohols. The calculated melting points are in good agreement with the experimental values.

The effect of the chemical constitution of the polar terminal group on the melting point has been discussed from the standpoint of the theory of melting points put forward previously. The heat of crystallisation of the terminal group is shown to play a dominant part in determining the *equilibrium constant* of the group and, through it, the melting point.

THE RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON.
[*Received, May 5th,* 1927.]