CCXLII.—*Alternation in the Heats of Crystallisation of the Normal Monobasic Fatty Acids. Part IV.*

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THE specific heats and heats of crystallisation of normal monobasic fatty acids, up to C_{20} for the even series and C_{15} for the odd, have already been measured (Garner and Randall, J., 1924, **125**, 881; Garner, Madden, and Rushbrooke, J., 1926, 2491). This paper describes the extension of the work to still higher members of the series, with the object of determining whether the straight-line relationship between Q, the molar heat of crystallisation, and n, the number of carbon atoms in the chain, is maintained for both odd and even acids. A careful study, involving a large number of experiments at different temperatures for each odd acid, was also made of the conditions governing the appearance of the α- and β-forms, and their transformation one into the other.

The results of Garner, Madden, and Rushbrooke (*loc. cit.*) for the even acids above C_{10} were expressed by the two equations

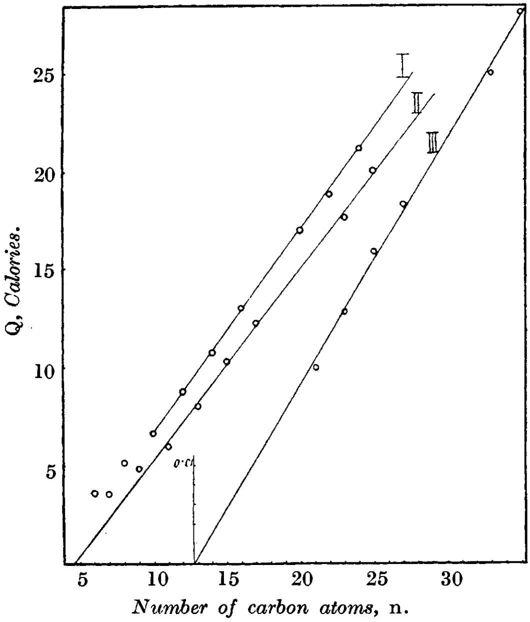
$$Q = 1{\cdot}030n - 3{\cdot}61 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Q/T = 0{\cdot}002652n - 0{\cdot}0043 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which were combined to give the following expression for the setting point :

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

FIG. 1.



I. Q–n *graph for even acids.* II. Q–n *graph for α odd acids.*
III. Q/T–n *graph for odd acids.*

The present work on the C_{22} and C_{24} acids fully confirms this equation, the linear relationship being maintained for both Q and Q/T against n (Fig. 1, curve 1, shows the heat of crystallisation plotted against n).

Table I gives the complete results for the even acids from C_{10} upwards. It will be seen that the observed setting points and those calculated from equation (3) are in good agreement.

Sufficient data have now been obtained for a similar treatment of the α odd acids. Curves II and III (Fig. 1) show the graphs for Q

TABLE I.

Setting Points and Heats of Crystallisation of the Even Acids.

Acid, C atoms.	Setting point (° Abs.). Obs.	Calc.	Diff.	Q (Cals./mol.).	Acid, C atoms.	Setting point (° Abs.). Obs.	Calc.	Diff.	Q (Cals./mol.).
10	304·2	301·0	+3·2	6·69	20	347·2	348·6	−1·4	16·95
12	316·8	318·0	−1·2	8.75	22	353·2	352·6	−0·4	18·75
14	326·7	329·4	−2·7	10·74	24	356·1	355·8	+0·3	21·10
16	335·3	337·4	−2·1	12·98	26	360·4	358·4	+2·0	—
18	—	343·8	—	—					

and Q/T respectively against n for these substances. Here again, as with the even members of the series, a linear relationship is obtained for both curves. From measurements of the intercepts and slopes, the following equations have been obtained for the α odd acids :

$$Q = 0{\cdot}9651n - 4{\cdot}49 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$Q/T = 0{\cdot}002505n - 0{\cdot}0071 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Combination of these two equations gives the setting point as

$$T = (0{\cdot}9651n - 4{\cdot}49)/(0{\cdot}002505n - 0{\cdot}0071) \quad . \quad . \quad . \quad (6)$$

This equation gives a curve of very similar shape to that obtained by Garner, Madden, and Rushbrooke for the even acids.

Table II gives the complete results for the α odd acids from C_{11} upwards. As with the even acids, the observed setting points and those calculated from the equation are in good agreement.

TABLE II.

Setting Points and Heats of Crystallisation of the α Odd Acids.

Acid, C atoms.	Setting point (° Abs.). Obs.	Calc.	Diff.	Q (Cals./mol.).	Acid, C atoms.	Setting point (° Abs.). Obs.	Calc.	Diff.	Q (Cals./mol.).
11	301·3	299·3	+2·0	5·99	19	—	341·8	—	—
13	314·1	316·2	−2·1	8·02	21	—	346·5	—	—
15	325·1	327·3	−2·2	10·30	23	351·7	350·4	+1·3	17·60
17	333·8	335·7	−1·9	12·22	25	355·9	353·6	+2·3	20·00

The equation for the even acids indicates a convergence temperature of 115·5°, and for the odd, 112·2°. The 3° difference in these temperatures is shown in Fig. 1 by the slight non-parallelism of the Q–n curves for the odd and even acids. This would seem to point to slightly different packing of the chains of these acids, possibly due to differences between the orientation of terminal groups in the two series. This point cannot be stressed, however, for the difference between the convergence temperatures is only slightly greater than the experimental error and the divergence obtained may, to some extent, be due to slight impurity in the acids.

The effect of impurity on the heat of crystallisation was investigated in the case of cerotic acid from beeswax, prepared by Professor Francis and found by *X*-ray analysis to be a mixture of at least two acids, C_{26} and C_{28}. The value obtained for the heat of crystallisation was 52·25 cals./g., which corresponds to that of an acid with a carbon content of 18, a result which is not in accordance either with the literature on this substance or with the results from *X*-ray analysis.

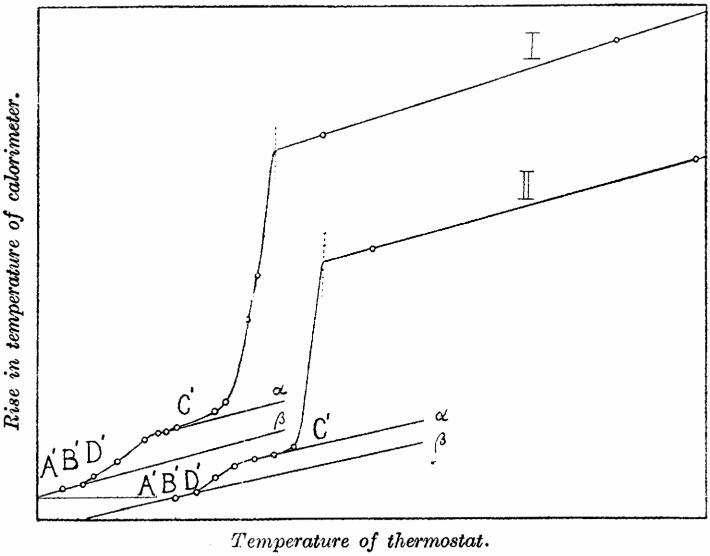
The low heat of crystallisation is not due to incomplete solidification, for cerotic acid gives a normal value for the specific heat for the temperature range 70—20°. The admixture of molecules of unequal chain length will probably lead to loose molecular packing in the neighbourhood of the terminal methyl group. The forces between the carboxyl groups are so strong that the arrangement in the neighbourhood of this group is likely to be unaffected. Any lack of contact between the methylene or terminal methyl groups will lead to a low value for the heat of crystallisation. It is intended to study the effect of mixing two straight-chain acids in the near future.

The transition between the α- and β-forms of the odd acids provides a further example of the phenomenon of unilateral equilibrium which has been recently discussed by Baur (*Z. physikal. Chem.*, 1928, **137**, 63). According to the law of Guldberg and Waage, the velocity of the reaction $A_1 \rightleftharpoons A_2$ at equilibrium is $k_1[A_1] - k_2[A_2] = 0$. The equilibrium is dynamic, and the velocity of the reaction is symmetrical about the equilibrium point. At equilibrium, $K = [A_2]/[A_1]$, and $K[A_1] - [A_2] = 0$. If Δ is placed equal to $K[A_1] - [A_2]$, and plotted against the velocity of the reaction, a straight line passing through the origin is obtained. In the case of many reactions, *e.g.*, $H_2 + I_2 \rightleftharpoons 2HI$, the slope of the line is the same whether the reaction is proceeding from the right or from the left, *i.e.*, the velocity of the reaction can be represented throughout by $k\Delta$.

In the three cases of equilibrium in the liquid state, quoted by Baur, there was a change of slope at the equilibrium point, where $\Delta = 0$. The slope of the line obtained when $K[A_1] - [A_2]$ is plotted against the velocity of the reaction changes at the equilibrium point in such a way that the velocity of the reaction is $k\Delta$ from the left and $k'\Delta$ from the right. The symmetry about the equilibrium point is thus destroyed. Baur has critically examined the literature dealing with this phenomenon and has come to the conclusion that in certain cases of inversion and transformation, there exists a true equilibrium which, however, can only be reached from one side of the reaction. He quotes experiments by Michael, Küster, Dienger, and Wislicenus.

The transition between the α- and β-forms of the odd acids is curious in that it affords examples of unilateral equilibrium in the solid state. The transformation for a number of acids has been studied by heating them in a thermostat at a temperature above that of the room but below their melting point, and measuring the amount of heat liberated when the solid and its container are immersed in a calorimeter at 20°. Figs. 2 and 3 show the curves obtained when the rise in temperature of the calorimeter is plotted against the temperature of the solid before immersion. Those in Fig. 2 were the values previously obtained for C_{13} and C_{15} by Mr. Rushbrooke, and those of Fig. 3 are the values found in the present investigation for C_{17} (I), C_{23} (II), and C_{25} (III). The rise in temperature depends on the previous treatment of the solid. The upper curve of each pair in Fig. 3 represents the temperatures obtained when the *molten* acid is placed in the thermostat and allowed to crystallise and come to equilibrium at temperatures above that of the room, and the lower curve that obtained by first cooling the acid to room temperature before placing it in the thermostat. The results shown in Fig. 2 were obtained by placing the molten acid in the thermostat in all experiments.

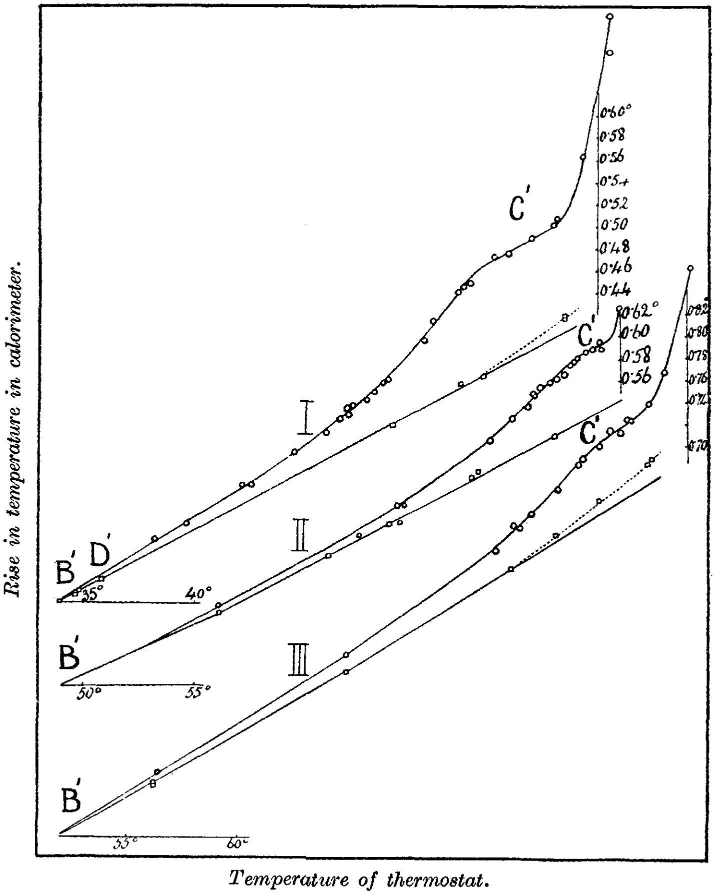
FIG. 2.



From the form of the upper curves, it will be seen that the solid form crystallising immediately below the melting point passes into another form with evolution of heat on lowering the temperature.

The solid first crystallising out is called the α-form, and that formed on further cooling, the β-form. The transition occurs over a temperature interval varying from 7° in the case of C_{13} to 22° for C_{25}. The values obtained at any temperature are independent of the time in the thermostat, provided that this exceeds 1½ hours.

FIG. 3.



Experiments were carried out with C_{25} to test whether or not the points on the upper curves obtained after 100 minutes' heating are equilibrium values. The acid crystallised at the high temperature was maintained at this temperature for 33 hours in Expt. 38 and for 6½ hours in Expt. 35, all the other conditions being the same. The values for the heat liberated were the same in the two experiments, and lie on the curve.

For C_{17}, C_{23}, and C_{25}, the lower curve shows no evidence of the occurrence of any change of state. Thus, although the transformation $\alpha \rightharpoondown \beta$ can occur on lowering the temperature, the reverse change cannot be brought about by raising the temperature. A test was made with C_{25} from the β side of the transformation, to see if the β-form could be transformed into the α-form in a reasonable time. In Expt. 34, the solid β-form was maintained for $6\frac{1}{2}$ hours at 78° and in Expt. 33 for $1\frac{1}{2}$ hours at the same temperature. Identical results were obtained, and no apparent transition into the α-form was observed.

The lack of reversibility in the $\alpha \rightharpoondown \beta$ transition is supported by the observations of Piper (*Trans. Faraday Soc.*, 1929, **25**, 348), who has measured the X-ray spacings of monobasic fatty acids. He finds that the powdered crystals of the odd acids may show simultaneously more than one spacing. These spacings he designates as A′, B′, C′, and D′ to distinguish them from the spacings of the even acids. It is exceptional for the C′ spacing to appear at low temperatures. After fusion, and just below the melting point, he obtains the C′ spacing only; if the temperature is allowed to fall below a certain transition value, then the A′, B′, and D′ spacings may appear. For acids with more than 13 carbon atoms, Piper has never found it possible to convert the A′, B′, and D′ into the C′ spacing on raising the temperature. The A′, B′, and D′ spacings for acids with more than 13 carbon atoms are *apparently* stable up to the melting point. The α-form gives the C′ spacing of Piper and the β-form gives either one or all of the A′, B′, and D′ spacings.

The unilateral equilibrium $\alpha \rightharpoondown \beta$ is not observed in the cases of acids C_9 and C_{11}. Here the equilibrium can be approached from both sides (*loc. cit.*; see also de Boer, *Nature*, 1927, **119**, 1634). We have not studied C_{13} and C_{15} from this point of view, but the work of Piper is convincing with respect to these acids. The phenomenon of unilateral equilibrium thus makes its appearance as the carbon chain is lengthened from 11 to 13 carbon atoms. Its appearance is associated with a marked change in the nature of the X-ray spacings given by the β-form. At this point, there is an increase in complexity of the spacings found by X-ray analysis for the crystals at room temperature. For C_{11}, Piper finds only the A′ spacing, but for C_{13} and C_{15} the three spacings A′, B′, and D′ occur. The β-forms of C_{13} and C_{15} are thus mixtures of three modifications. C_{17} shows B′ and D′, and higher acids only the B′ spacing (see Table III).

The occurrence of several spacings side by side in these one-component systems is a matter of considerable interest. Piper's work on the even acids indicates that they are not affected by changes of temperature, and thus the forms giving rise to these spacings are probably not in equilibrium with one another. Metastable forms would be expected to occur with lengthening of the hydrocarbon chain so that the appearance of the B′ and D′ spacings for the first time at C_{13} is readily understood if these spacings are given by metastable modifications. An explanation of the non-occurrence of these forms in the case of C_{11} is that with this acid they pass readily into the A′ spacing. Not only are B′ and D′ metastable over the lower temperature range for C_{13}, but also the A′ spacing is metastable in the higher temperature range where C′ is the stable spacing. The transition phenomena and the first appearance of the B′ and D′ spacings are thus explicable on the same basis.

The heats of transition $\alpha \rightarrow \beta$ are now known from C_9 to C_{25},* except for a few gaps, and are given in Table III. It will be observed that a discontinuity occurs between C_{11} and C_{13}; this corresponds to the appearance of the B′ and D′ spacings in the β-form. A steady value of 1·5 Cals. is reached from C_{17} onwards, and this is probably the heat of transition of the C′ into the B′ spacings.

TABLE III.

No. of C atoms	9	11	13	15	17	23	25
Spacings :							
α-form	C′	C′	C′	C′	C′	C′	C′
β-form		A′	A′ B′ D′	A′ B′ D′	— B′ D′	— B′ —	— B′ —
Transition interval ...	−5° to −11°	+17° to +12·5°	+23° to +16°	+34° to +28°	+53° to +37°	+72° to +54°	+76° to +54°
$Q_{\alpha-\beta}$ (Cals./mol.)	1·37	1·84	0·94	1·20	1·55	1·62	1·47

Another feature of the curves shown in Figs. 2 and 3 is the lack of sharpness in melting and transition. These changes take place not at one temperature, as is found for many substances, but over a range of temperatures. Were it not for the fact that the melting and setting points of the acids used agree with the highest values yet observed for these acids, one would be inclined to ascribe this lack of sharpness to impurity : the well-known difficulty met with in the purification of long-chain acids might be the cause of these phenomena. Professor Francis is shortly publishing an account of the difficulties involved in the separation of the acids present in cerotic, arachidic, and other acids, which brings out very clearly the nature of the difficulties. In none of the five cases so far studied

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* C_7 does not give a β-form. The transition temperature is probably too low for the change $\alpha \rightarrow \beta$ to occur.

in detail do the changes of state occur sharply, although acids from different sources have been employed, and purified as long as any change in melting point could be observed.* It is thus not improbable that the effects observed are due to some cause other than that of impurity.

The melting point of these acids depends on the thickness of the crystalline film. Meissner (*Z. anorg. Chem.*, 1920, **110**, 169), by using the method suggested by Tammann (*ibid.*, p. 166), in which wedge-shaped lamellæ are formed between a cylindrical lens and a metal plate, obtained a decrease of 0·3° in the melting point of myristic acid as the thickness diminished from 10 μ to 0·8 μ. The gradual melting of these acids may be associated with this fact. Melting may first occur along the line of junction between the differently oriented crystal grains, due to the action of unsymmetrical forces. The thickness of the molten film would be expected to increase with rise in temperature. The same phenomenon could arise during the transition $\alpha \rightarrow \beta$, and this, together with the irreversible phenomena observed, would account for the transition interval found for these acids.

EXPERIMENTAL.

With the exception of the C_{17} acid, which was obtained from the Eastman Kodak Company and recrystallised until it gave a constant setting point, all the acids were prepared by Professor Francis and Dr. Malkin in the Bristol laboratory. They were white crystalline substances, melting to practically colourless liquids which tended to become slightly yellow towards the end of the series of experiments—this may be due to the formation of small quantities of salts with the alkali of the glass. In the case of cerotic acid, a minute amount of soap was found to be present in the acid at the end of the experiments.

The experimental procedure was identical with that described in a previous paper (Garner and Randall, J., 1924, **125**, 881). The water equivalent of the calorimeter was determined at the beginning of the work, with the container used by previous investigators : the mean of six determinations gave a value of 345·9, compared with 345·5 obtained by Rushbrooke. The water equivalent was again determined at the end of the work, when another container made of different glass was used. A mean of eight determinations gave a value of 345·4, showing that the water equivalent had remained constant for two years. In all calculations of specific heat and heat

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* Melting points of these acids as determined by Professor Francis lie about 1° higher than the setting points.

of crystallisation, the water equivalent was taken as 345·7, the mean of the two series of determinations.

For C_{22}, C_{24}, cerotic acid, and some experiments with C_{17}, the acid containers were made of glass used by Garner, Madden, and Rushbrooke. For C_{23}, C_{25}, and part of the C_{17} series, new glass of different specific heat was used. The values of the specific heat over three ranges of temperature for the new glass were :

Temp. range	18—56°	17—78°	18—99°
Specific heat	0·1999	0·2018	0·2049

The specific heats and heats of crystallisation of C_{22}, C_{24}, and cerotic acid were calculated as described previously. In the case of C_{17}, C_{23}, and C_{25}, where the temperature coefficient of the specific heat was high, a graphical method was employed (see previous papers). The temperature coefficients of the specific heat of C_{17}, C_{23}, and C_{25} are given in Table IV, where they are compared with the results of Parks and Kelley (*J. Amer. Chem. Soc.*, 1925, **47**, 3089) on palmitic acid. The high values for the temperature coefficient near the melting point may indicate some transformation occurring in the solid state. If this is so, the values given for the heat of transition will be rendered somewhat uncertain. In the calculation of the heats of transition, the mean specific heats of the following ranges of temperature are taken as the basis of calculation : 33·95—52·97° for C_{17}, 56·1—71·15° for C_{23}, and 56·2—72·2° for C_{25}.

TABLE IV.

Temperature Coefficients of Specific Heat.

Acid.	Temp. range.	Temp. coeff.	Acid.	Temp. range.	Temp. coeff.
*C_{16}	$-57·6$ to $-35·1°$	1289×10^{-6}	C_{23}	26·4—45·3°	2973×10^{-6}
	$-35·1$,, 1·9	2622		45·3—63·1	4916
	1·9 ,, 19·5	2727	C_{25}	27 —45·8	1925
C_{17}	26—43·5	3383		45·8—64	4641

* Parks and Kelley (*loc. cit.*).

The experimental data for the specific heats and heats of crystallisation are given in the following tables. Those for cerotic, behenic, and lignoceric acids are given in full, for they contain the minimum of data necessary for a recalculation. For the other three acids, the data are restricted to results above the m. p., and those at the lowest temperature in each case. Other results are represented on the curves of Fig. 3, from which the specific heats of the α-forms and the heat of transition α ⟶ β are read off directly.

The temperature of the thermostat is given in the second column, and the temperature of the calorimeter varied from 17° to 20°. In many of the experiments carried out on the specific heat below the melting point, the acid was solid on being placed in the thermostat for heating. In other experiments, however, the acid was molten when placed in the thermostat, and was allowed to crystallise at the high temperature. By this means, the α-form of the odd acids was obtained. The length of time necessary for complete crystallisation was tested with margaric acid in Expts. 32 and 33, which were carried out under identical conditions, except that in 32, the time allowed for crystallisation before the acid was added to the calorimeter was 80 mins., and in 33, 125 mins. Results showed that 80 mins. was not long enough for complete crystallisation. Expts. 34 and 35 led to the same conclusion. In Expts. 35 and 36, the same rise was obtained for 110 mins. and for 160 mins., respectively. Therefore in all succeeding experiments involving crystallisation at a high temperature, a minimum time of 110 mins. was allowed.

Behenic acid : setting point, 79·15°.

[Weight of acid, 6·2013 g.; glass (old), 4·5123 g.; platinum, 0·2012 g.; nickel, 1·9026 g.]

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
1—3	71·68°	53·67°	$0{\cdot}634_2$°
4—8	108·91	89·86	$2{\cdot}101_6$
9—14	79·93	61·07	1·715

I. From Expts. 1—3 (71·68—18·01°), $\sigma_S = 0{\cdot}4854$ cal./g.
II. ,, ,, 4—8, 9—14, and I, $\sigma_L = 0{\cdot}5556$ cal./g.;
$Q = 55{\cdot}09$ cal./g.

Lignoceric acid : setting point, 83·14°.

[Weight of acid, 4·8016 g.; glass (old), 4·0323 g.; platinum, 0·1886 g.; nickel, 3·9831 g.]

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
1—3	78·34°	60·16°	$0{\cdot}602_8$°
4—8	87·11	68·54	$1{\cdot}490_2$
9—12	109·33	90·13	$1{\cdot}750_3$

I. From Expts. 1—3 (78·34—18·18°), $\sigma_S = 0{\cdot}4656$ cal./g.
II. ,, ,, 4—8, 9—12, and I, $\sigma_L = 0{\cdot}5855$ cal./g.;
$Q = 57{\cdot}27$ cal./g.

Cerotic acid : setting point, 76·05°.

[Weight of acid, 5·808 g.; glass (old), 4·532 g.; platinum, 0·1886 g.; nickel, (Expts. 1—2) 1·916 g., (Expts. 3—11) 1·807 g.]

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
1—2	64·61°	46·83°	$0{\cdot}518_1$°
3—4	70·67	53·31	$0{\cdot}596_2$
5—8	78·96	60·51	1·554
9—11	109·25	90·10	$1{\cdot}939_6$

I. From Expts. 1—2 (64·61—17·78°), $\sigma_S = 0{\cdot}4711$ cal./g. } Mean = 0·4750
II. ,, ,, 3—4 (70·67—17·36°), $\sigma_S = 0{\cdot}4789$ cal./g. } cal./g.
III. ,, ,, 5—8, 9—11, I, and II, $\sigma_L = 0{\cdot}5712$ cal./g.;
$Q = 52{\cdot}25$ cal./g.

Margaric acid : setting point, 60·81°.

Expt. No.	Acid, g.	Glass, g.	Platinum, g.	Nickel, g.
3—12	7·0661	5·5713 (Old)	0·1879	2·6156
19—21	6·5297	5·5607 (Old)	0·1457	3·6431
24—26	,,	,, ,,	,,	3·9831
59—63	6·0245	3·6876 (New)	0·1118	1·0442

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.	Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
3—5	52·57°	35·06°	0·462$_3$°	24—26	99·13°	79·70°	2·077$_8$°
10	39·36	21·80	0·275$_2$	59	52·97	33·77	0·351$_3$
11, 12	30·26	12·61	0·159$_2$	63	33·95	15·27	0·149$_8$
19—21	64·23	44·93	1·548$_8$				

I. From Expts. 10, 11, 12 (18—39·36°), σ_{s_β} = 0·4302 cal./g.
II. ,, ,, 3—5, 10 (39·36—52·57°), σ_{s_β} = 0·5063 cal./g.
III. ,, ,, 63 (18—33·95°), σ_{s_β} = 0·4236 cal./g.
IV. ,, ,, 63, 59 (33·95—52·97°), σ_{s_β} = 0·4828 cal./g.
V. ,, ,, 19—21, 24—26, and IV, σ_L = 0·5604 cal./g.
Q_α = 45·19 cal./g.;
Q_β = 50·93 cal./g.

Heat of transition $\alpha \longrightarrow \beta$ = 1·55 Cals./mol.

Tricosanic acid : setting point, 78·69°.

[Weight of acid, 4·6976 g.; glass (new), 3·6724 g.; platinum, 0·1462 g.; nickel, 2·9586 g.]

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.	Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
5	71·15°	52·09°	0·499$_8$°	11—13	108·79°	89·14°	0·644$_9$°
8	56·10	37·41	0·342$_7$	14—17	87·16	68·05	1·411$_9$
9	34·62	16·39	0·142$_0$				

I. From Expt. 9 (18—34·62°), σ_{s_β} = 0·4166 cal./g.
II. ,, ,, 9, 8 (34·62—56·1°), σ_{s_β} = 0·4728 cal./g.
III. ,, ,, 8, 5 (56·1—71·15°), σ_{s_β} = 0·5603 cal./g.
IV. ,, ,, 11—13, 14—17, and III, σ_L = 0·5762 cal./g.
Q_α = 49·66 cal./g.;
Q_β = 54·23 cal./g.

Heat of transition of $\alpha \longrightarrow \beta$ = 1·62 Cals./mol.

Pentacosanic acid : setting point, 82·91°.

[Weight of acid, 5·8457 g.; glass (new), 5·8360 g.; platinum, 0·1607 g.; nickel, none used.]

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.	Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
4—7	87·72°	67·66°	1·737$_5$°	29	56·20°	38·88°	0·418$_1$°
8—11	109·81	90·10	2·037$_1$	30	56·20	38·54	0·411$_9$
28	77·20	54·24	0·610$_8$	32	35·46	16·90	1·174$_8$

I. From Expt. 32 (20—35·46°), σ_{s_β} = 0·4146 cal./g.
II. ,, ,, 32, 29, 30 (35·46—56·20°) σ_{s_β} = 0·4508 cal./g
III. ,, ,, 28, 29, 30 (56·2—72·2°), σ_{s_β} = 0·5351 cal./g.
IV. ,, ,, 4—7, 8—11, and III, σ_L = 0·5769 cal./g.;
Q_α = 52·30 cal./g.;
Q_β = 56·14 cal./g.

Heat of transition of $\alpha \longrightarrow \beta$ = 1·47 Cals./mol.

The values for the mean specific heats of the higher members of the series in the liquid state, *viz.*,

Acid…………………	Cerotic	C_{17}	C_{22}	C_{23}	C_{24}	C_{25}
σ_L …………………	0·57	0·56	0·56	0·58	0·59	0·58

support the observations of Garner, Madden, and Rushbrooke (*loc. cit.*) that there is a slight rise in specific heat in the liquid state as the series is ascended.

The values for the heat of transition of the α- to the β-form are constant within the experimental error for the three acids investigated (*viz.*, 1·55, 1·62, and 1·47 Cals./mol. for C_{17}, C_{23}, and C_{25}, respectively).

Summary.

(1) The heats of crystallisation of the following acids have been measured and are given in Cals./g.-mol.: Margaric, 12·22; tricosanic, 17·60; pentacosanic, 20·00; behenic, 18·75; lignoceric, 21·10; that of cerotic acid is 52·25 cals./g. Q and Q/T when plotted against n give linear relationships. Cerotic acid is an exception, but this is a mixture of at least two acids.

(2) The equation $T^\circ_m = (0{\cdot}9651n - 4{\cdot}49)/(0{\cdot}002505n - 0{\cdot}0071)$ has been obtained for the setting points of the odd acids, and gives a curve of similar shape to that previously obtained for the even acids. There is a difference of 3° in the convergence temperatures of the odd and even acids, which is almost within experimental error.

(3) A detailed study of the transition of the α- and β-forms of the odd acids has been made, and the heats of transition $\alpha \rightarrow \beta$ have been measured. For acids above C_{11} the change $\beta \rightarrow \alpha$ does not occur readily on raising the temperature. This lack of reversibility is considered to provide a further example of unilateral equilibrium. The results are correlated with the X-ray measurements of Piper, and in agreement with his results, it is shown that metastable forms make their appearance on passing from C_{11} to C_{13}.

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