CCCXXVIII.—*Alternation in the Heats of Crystallisation of the Normal Monobasic Fatty Acids. Part II.*

By W. E. GARNER, F. C. MADDEN, and J. E. RUSHBROOKE.

THE heats of crystallisation of five of the members of the homologous series of normal monobasic fatty acids have been reported previously (J., 1924, **125**, 881). The investigation of this homologous series has now been extended and the heats of crystallisation of seven more acids have been established. With the exception of stearic acid, the heats of all the even acids up to C_{20} are now known, and of the odd acids there are but three missing over this range.

The data which are available both from our own experiments and those of others are summarised in Table I and in the figure. It will be seen that the alternation in the heats of crystallisation (curve II) is as definite as for the melting points (curve I), but that it is essentially different in character. The melting-point curves of the odd and even members converge and approach a maximum value as the length of the carbon chain increases, whereas the curves for the heats of crystallisation diverge up to the tenth member and then take a parallel course. The heats of crystallisation are linear above decoic acid and for the higher members they are given by

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

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

relationship between Q and n is evident from the differences ΔQ in Table I. Above C_{10} these differences are constant within experimental error.
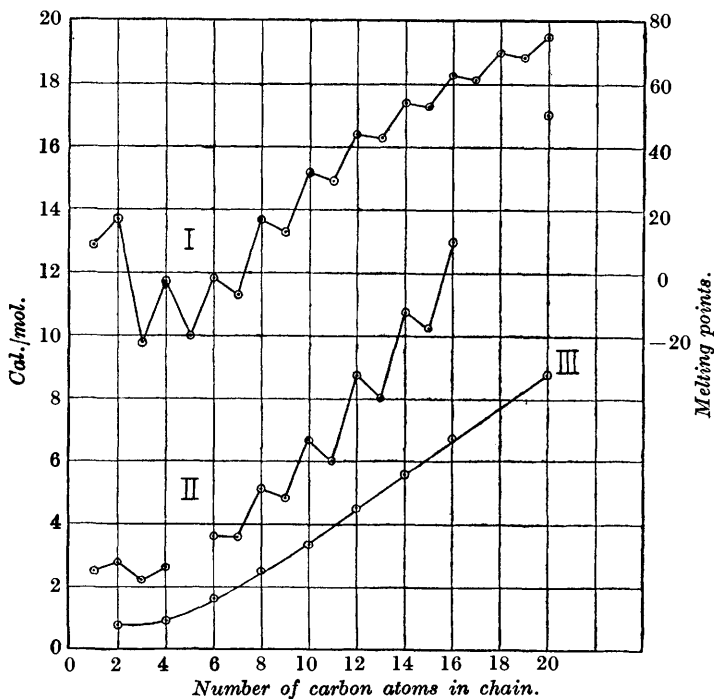
I *Melting points.*   II *Heats of crystallisation.*   III *Q/T.*

TABLE I.

No. of C atoms and setting point (Abs. Temp.).		Heat of crystallisation, Q (Cal./mol.).		ΔQ for $2CH_2$.	
Odd.	Even.	Odd.	Even.	Odd.	Even.
1 (281·5)	2 (289·5)	2·52*	2·77*	−0·26	−0·13
3 (251)	4 (270)	2·26†	2·64‡	—	0·96
5 (253)	6 (271·5)	—	3·60	—	1·51
7 (261·75)	8 (289·5)	3·58	5·11	1·27	1·58
9 (285·5)	10 (304·5)	4·85	6·69	1·14	2·06
11 (301·5)	12 (316·8)	5·99	8·75	2·03	1·99
13 (314·7)	14 (326·7)	8·02	10·74	2·28	2·24
15 (325·5)	16 (335·8)	10·30	12·98	—	1·98
17 (334·5)	18 (343·75)	—	—	—	1·98
19 (342·5)	20 (349·5)	—	16·95		

* Landolt-Börnstein, Tabellen, 1912, IV, p. 830.

† Massol and Faucon (from equation, $M(l + s)/T = 30$) ; *Compt. rend.*, 1909, **149**, 345.

‡ Parks and Anderson (*J. Amer. Chem. Soc.*, 1926, **48**, 1506).

The increment in the heat of crystallisation of the odd members on adding two methylene groups to the chain approaches the same constant value as is found for the even acids. From this it may be inferred that the packing of the methylene groups in the crystalline state is the same for the odd as for the even members. The suggestion that this was the case was made in the previous paper (*loc. cit.*, p. 885) and was supported by measurements on the molecular volumes of these acids in the solid state (Garner and Ryder, J., 1925, **127**, 720). The alternations in Q can therefore only be ascribed to an alternation in the arrangement of the terminal groups * as we pass from member to member.

In curve III, Q/T is plotted against n for the even acids (T in °Abs). This is linear above C_{10} and nearly so down to C_6. For the acids above decoic the following equation holds :

$$Q/T = -0.0043 + 0.002652n \quad . \quad . \quad . \quad (2)$$

where the coefficients have been calculated by the method of least squares. Combining (1) and (2) one obtains

$$T = (1.030n - 3.61)/(0.002652n - 0.0043) \quad . \quad . \quad (3)$$

as the equation for the melting-point curve of the even acids above decoic. From this equation, the melting-point curve should reach its maximum value at 115°. A similar value may be calculated for the odd acids, but as these crystallise in two forms, the determination of the heat of crystallisation of the form stable at the melting point is more difficult than for the even acids, and the values of Q are less accurate.

Equation (3) assumes that the linear relationships for Q and Q/T persist up to $n = \infty$; very strong arguments must be forthcoming before such assumptions are worthy of serious consideration, especially in the case of Q/T. The arguments which can be adduced in support are of a twofold character : (*a*) those based on the experimental results obtained on the melting points and heats of combustion of the normal dibasic fatty acids, and (*b*) a theoretical deduction of the relationship between the heat of crystallisation and melting point, based on statistical laws.

The Dibasic Fatty Acids.—The melting points of the even acids in this homologous series decrease and those of the odd acids increase with lengthening of the carbon chain. The melting-point curves converge so rapidly that by $n = 30$ the temperatures for the odd and even acids are identical within 2 or 3°. From the values given in Beilstein, the convergence temperature is approximately 118°, and from the results of Fairweather (*Phil. Mag.*, 1926, **1**, 944) on the even members, 123°. These values are as near to that of the

* See subsequent note.

convergence temperature of the monobasic acids as can be expected in view of experimental errors in the coefficients of equation (3).

For molecules of straight-chain compounds in which n approaches infinity, the effect of the terminal groups becomes negligible, and the physical properties of the crystal will be mainly determined by the hydrocarbon chain. Hence the agreement between the convergence temperatures mentioned above can have no other meaning than that the packing of the hydrocarbon chain in the mono- and di-basic acids is the same. This conclusion is supported by the work of Verkade, Hartmann, and Coops (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 859), who have measured the heats of combustion of the members of the dibasic acids with 2 to 12 carbon atoms. The difference between the heat of combustion of an odd acid and the mean of those for the next lower and higher acids is given below :

2		4		6		8		10		12
	3		5		7		9		11	
Diff.	−2·15		+1·85		+1·50		+1·35		+1·60	Cal./mol.

Excluding the first difference, the mean is 1·58 * Cal./mol. This should also be the difference between the mean heat of crystallisation of two adjacent even acids and that for the intermediate odd acid. These have not been determined for the dibasic acids but are available for the monobasic acids :

6		8		10		12		14		16
	7		9		11		13		15	
Diff.	0·78	1·05		1·73		1·73		1·56	Cal./mol.

The mean of the last three is 1·67 Cal./mol.* The two means are in agreement within experimental error. These facts are suggestive : the differences between the odd and even mono- and di-basic acids very probably have a similar physical origin ; therefore there is every reason to expect that the convergence temperatures for the two homologous series will be identical.

Kinetic Theory of Melting of Members of an Homologous Series.

The general character of the structure of the crystals of straight-chain compounds has been made manifest by the X-ray method of

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* It is of interest to note that these differences are equal in magnitude to the heat liberated on sublimation of a methylene group (see Smiles, " Physical Properties and Chemical Constitution," 1910, for the heat of evaporation from the liquid state). If one of the methylene groups in the crystal molecules of the odd acids is in a state analogous to the gaseous state, *i.e.*, is not within the sphere of influence of adjacent hydrocarbon chains, then during crystallisation the group in question undergoes changes analogous to those occurring during evaporation from the liquid state. Its heat of crystallisation is thus negative and about 0·6 Cal./mol.

analysis (Müller and Shearer, J., 1923, **123**, 2043, 3152, 3156). The molecules of these compounds are arranged in straight chains with their methylene groups placed alternately on opposite sides of the chains. Contact between the molecules is made through the methylene and terminal groups. On the faces of the crystal, the molecules are attached by $\frac{1}{2}(n-2)$ methylene groups and the two terminal groups. In the process of melting the conjoined groups separate and the molecule enters the liquid state; on solidification, the reverse change occurs. A consideration of the kinetics of these processes may serve to elucidate some of the problems which arise in the study of the melting points of homologous series and other organic compounds.

On account of the rotation which can occur at the carbon–carbon linking, a molecule which is attached to the surface at a number of points may leave it in stages, in each of which one point of attachment is broken at a time. In the case of a straight-chain compound, the methylene groups in the middle of the chain being immovable when the ends of the chain are fixed, a molecule must leave the surface beginning at a terminal group and progressively untwisting itself until it is finally completely detached. We have thus to take into account in the case of a single molecule a succession of processes of which the probabilities will be given by equations of the type $P = ke^{-q/KT}$, where q is the energy of activation in ergs per molecule, k is a constant,* K the Boltzmann constant, and T the absolute temperature.

It can be readily shown that the probability P' that a molecule will leave the solid surface is given by

$$P' = k_1'^{\frac{1}{2}(n-2)} . k_2' . k_3' e^{-\{\frac{1}{2}(n-2)q_1' + q_2' + q_3'\}/KT} \quad . \quad . \quad (4)$$

where q_1', q_2', and q_3' are the energies of activation in ergs per molecule for methylene, methyl, and carboxyl groups, respectively, and k_1', k_2', and k_3' are corresponding constants dependent on spatial considerations, times of relaxation, etc., about which very little is known.

Also, the probability that a molecule near a crystal face will leave the liquid state is given by a similar equation

$$P'' = k_1''^{\frac{1}{2}(n-2)} . k_2'' . k_3'' . e^{-\{\frac{1}{2}(n-2)q_1'' + q_2'' + q_3''\}/KT} . \left[\frac{x}{x + (n-2)y + z}\right] (5)$$

where q_1'', q_2'', q_3'' are the energies of activation, etc., $x/[x + (n-2)y + z]$ is a factor which has been introduced to allow for the fact that the longer the carbon chain the smaller the probability

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* The nature of k has been discussed previously for homogeneous reactions (*Phil. Mag.*, 1925, **49**, 463).

that an activated terminal group will collide with the surface in the right place; x and z are the areas of the terminal groups exposed on the face of the crystal, and y is the area of the methylene group. Approximately, $x = y = z$, and the factor becomes $1/n$. At the melting point, $P' = P''$, therefore

$$(k_1'/k_1'')^{\frac{1}{2}(n-2)} . (k_2'/k_2'')(k_3'/k_3'') . n = e^{-\{\frac{1}{2}(n-2)q_1+q_2+q_3\}/KT} \quad . \quad (6)$$

where $q_1 = q_1'' - q_1'$, etc. A similar equation [(7), not given] holds for the member with $n + 2$ carbon atoms. On dividing (7) by (6) and assuming a constancy of k_1', k_2', k_3', etc. with increase in temperature, we obtain

$$\log_e \{k_1'(n + 2)/k_1''n\} = q_{n+2}/KT_{n+2} - q_n/KT_n$$

where q_{n+2} and q_n are the heats of crystallisation per molecule of the $(n + 2)$th and nth members of the homologous series. T_{n+2} and T_n are the melting points.

For a gram-molecule,

$$\log_{10}\{k_1'(n + 2)/k_1''n\} = Q_{n+2}/4.57T_{n+2} - Q_n/4.57T_n = \\ 5.30/4.57 = 1.15 \quad . \quad . \quad (8)$$

For members above C_{10}, $\log(n + 2)/n$ is small compared with $\Delta Q/T$ for two adjacent even members, and when n is large

$$\Delta(Q/4.57T) = \log_{10} k_1'/k_1''.$$

k_1' is dependent on the time which elapses between the activation of a methylene group on the surface and its detachment. Since this time is determined by intramolecular changes, k_1' should be independent of temperature. k_1'' is a similar factor for the processes occurring on crystallisation. In the analogous processes occurring in chemical change, the logarithms of factors of a similar nature to the above are constant over a range of temperature of $100°$ within experimental error. There is thus every reason to expect $\log k_1'/k_1''$ to be constant on theoretical grounds and this view is supported by the constancy of $\Delta(Q/4.57T)$ found for the acids C_{10} to C_{20}.

The Lower Members of Homologous Series.

The departure from the linear relationships (1) and (2) in the cases of the lower members (see figure) is an indication of an important physical difference between the higher and the lower members in either the liquid or the solid states. This physical difference *gradually* disappears as the series is ascended. An examination of a number of physical properties for the series of monobasic acids, *e.g.*, the specific heats and specific volumes in the liquid state, the volume of the crystal, length of crystal molecule from X-ray

measurements,* etc., fails to reveal the nature of this physical difference.

From the heats of crystallisation in Table I some light can be thrown on the matter. The heat of crystallisation of the methylene group is 1·030 Cal. for the acids above C_{10}. Assuming this to be constant even for the lower members, the heats of crystallisation of the terminal groups may be calculated. They change from $+ 2·77$ for C_2 up to $- 1·55$ for the higher members :

C_2.	C_4.	C_6.	C_8.	C_{10}.	C_{12}.	C_{14}.	C_{16}.	C_{20}.
$+2·77$	$+0·58$	$-0·52$	$-1·07$	$-1·55$	$-1·55$	$-1·62$	$-1·44$	$-1·59$

From a study of a solid model, in the construction of which Bragg's dimensions for carbon, hydrogen, and oxygen atoms, and Müller and Shearer's structure for the fatty acids are assumed, a physical interpretation of the above change can be given. It is found that the area of the cross-section of the crystal cell of the higher acids is determined entirely by the methylene groups and that the methyl and carboxyl groups † can rotate freely within the crystal without touching adjacent molecules. The empty spaces between the adjacent methyl and carboxyl groups of neighbouring molecules disappear on liquefaction, for all of the groups can come into contact in the liquid state. The increase in the density of packing of these groups which occurs on liquefaction would account for the negative heat of crystallisation in the higher members.

In crystals of acetic acid, where there are no methylene groups, the terminal groups must be in contact and hence possess a positive heat of crystallisation. Judging from the above values, as more and more methylene groups are introduced into the molecule, the terminal groups are forced farther and farther apart, their heat of crystallisation changes sign, and finally a constant negative value is attained.

In terms of equation (6), we are no longer justified in assuming that the values of k_2 and k_3 for the terminal groups are constant for the lower members, hence equation (8) no longer represents the facts, but the above interpretation cannot readily be formulated mathematically.

No further light has been thrown on the β-odd acids. Indeed, as the following scheme shows, there is some disturbing factor operating

Heat of α—β transition for odd acids.

	9	11	13	15
$Q_{\alpha-\beta}$	1·37	1·84	0·94	1·20 Cal./mol.

* This has not been determined accurately for the lower acids.

† For structure of carboxyl group, see Garner and Ryder (*loc. cit.*).

during the α—β change which does not affect the change from the liquid to the α-form. The deviations are outside the experimental error. The heat of transition of C_{11} has been redetermined in a new apparatus, and the previously published value confirmed. It is possible that the β-form is a mixture of two modifications which occur in inner equilibrium with one another in the solid state. It has been observed that when a trace of water is present in an odd acid the transition α—β occurs with a marked swelling of the solid which very frequently is accompanied by a rupture of the container. The density of the β-form is, however, greater than that of the α-form. In the absence of water, the change from one form to the other is much less evident. This question calls for further investigation, for the work of Smits suggests the possibility that the transition would not occur if the acids were very carefully dried.

On the basis of the above considerations, we venture to put forward two hypotheses : (1) *the convergence temperature of all homologous series lies in the neighbourhood of* 120° *;* and (2) *the melting-point curve of the higher members of any homologous series is given by the relationship* $T = (x + 1 \cdot 030n)/(y + 0 \cdot 00265n)$, where x and y are coefficients depending on the terminal groups.

EXPERIMENTAL.

A number of the monobasic acids were obtained from Kahlbaum, *e.g.*, C_6, C_7, C_{14}, and C_{16}, and others, C_{13}, C_{15}, and C_{17}, from the Eastman Kodak Co. These acids were not quite pure, melting, as a rule, 2—3° below the correct m. p. They were purified by distillation or crystallisation until a constant setting point was obtained. The specimen of eicosoic acid was kindly lent to us by Mr. N. K. Adam.

The details of the experimental technique have been described previously. Two calorimeters were used; one was constructed by Mr. Rushbrooke for the determination of the heats of crystallisation of about 5 g. of material, and had a water-equivalent of 345·3; this was used for C_{13}, C_{14}, C_{15}, and C_{20} acids. The other had been used previously by Garner and Randall (*loc. cit.*). The water-equivalent of this calorimeter was now found to be 691·4, in agreement with the previous value of 690·5.

The specific heat of the glass forming the container was determined for two new ranges of temperature. The values for all the ranges are given in Table II.

TABLE II.

Temp.	20—100°	19—77°	19—44°	18—0°	18— -13°	18— -35°
Sp. heat.	0·2005	0·1962	0·1878	0·1835	0·1803	0·1799

The mean specific heat of nickel between $-33°$ and $20°$ was

found to be 0·1001; for other ranges of temperature the values of Schlett (Tabellen) were taken.

The same methods of calculation of the specific heats and heats of crystallisation were adopted as described previously, except that for C_{13} and C_{15} acids a graphical method was employed as well. The experimental data are recorded in Tables III—X. In the majority of cases, the means of duplicate experiments are given. The degree of reproducibility of results was of the same order as in the previous investigation (loc. cit.), where individual experimental results are given.

TABLE III.

(Caproic acid : setting point, − 3·6°).

Exp. No.	Temp. range.	Weight of				Fall in temp.	Rise in temp.
		Acid.	Glass.	Platinum.	Nickel.		
1—3	0—23°	7·6714	4·5256	0·2524	1·8985	22·53°	$0·161_3°$
4—6	−10—19	,,	,,	,,	,,	28·30	$0·543_0$
7—9	−33—18·5	,,	,,	,,	,,	51·70	$0·694_3$

    I.   From 1, 2, and 3, $\sigma_l = 0·5105$.

    II. From 4 to 9, and I, $\sigma_s = 0·4495$; $Q = 31·15$ cal./g.

TABLE IV.

(Heptoic acid : setting point, −7·5°).

Exp. No.	Temp. range.	Weight of				Fall in temp.	Rise in temp.
		Acid.	Glass.	Platinum.	Nickel.		
1—3	0—20°	11·6806	4·6955	0·266	2·401	20·86°	$0·207_0°$
4—6	30—20	,,	,,	,,	,,	9·73	$0·097_7$
7	−15—20	,,	,,	,,	,,	34·49	0·800
8						39·97	0·857
9						35·95	0·824
10	−35—19	11·8990	5·9224	0·266	1·8982	56·66	1·040
11						49·65	0·981
12						55·04	1·024

    I.   From 1 to 6, $\sigma_l = 0·4928$.

    II. From 7 to 12, and I, $\sigma_s = 0·4752$; $Q = 27·50$ cal./g.

TABLE V.

(Nonoic acid : setting point, 12·35°).

Exp. No.	Temp. range.	Weight of materials.	Fall in temp.	Rise in temp.
1	−33—16°	{As in previous	49·58°	0·963°
2	−42—16	paper. }	58·86	1·0265

Combining these results with those of Garner and Randall (loc. cit.),

$$\sigma_\beta = 0·3653; \quad Q = 39·29 \text{ cal./g.}$$

TABLE VI.

(Tridecoic acid : setting point, $41 \cdot 1°$).

Weight of			
Acid. 8·7132	Glass. 6·4994	Platinum. 0·2008	Nickel. 2·9781

No. of exp.	Range of temp.	Fall in temp.	Rise in temp.	No. of exp.	Range of temp.	Fall in temp.	Rise in temp.
1—3	0—18°	17·47°	0·259$_7$°	8	34—17°	17·52°	0·384°
4	26—17	10·02	0·160	9	36—17	18·86	0·405
5	28—17	11·93	0·191	10	38—17	21·28	0·460
6	30—17	13·25	0·276	11—13	44—17	25·66	1·467$_7$
7	32—17	15·59	0·342	14—16	76—17	58·79	2·085$_3$

By a graphical method one obtains

$$Q_\alpha = 37 \cdot 43 \text{ cal./g.}; \quad Q_\beta = 41 \cdot 81 \text{ cal./g.}; \quad \sigma_l = 0 \cdot 5456 \text{ cal./deg.};$$
$$\sigma_\alpha = 0 \cdot 4307 \text{ cal./deg.}; \quad \sigma_\beta = 0 \cdot 4322 \text{ cal./deg.}$$

TABLE VII.

(Myristic acid : setting point, $53 \cdot 7°$).

Weight of			
Acid. 6·4092	Glass. 4·1884	Platinum. 0·2008	Nickel. 3·0904

No. of exp.	Range of temp.	Fall in temp.	Rise in temp.	No. of exp.	Range of temp.	Fall in temp.	Rise in temp.
1—7	43—24°	19·24°	0·248$_4$°	12—19	84—23°	62·01°	1·682$_8$°
8—11	57—24	32·93	1·300$_5$				

    I. From 1 to 7, $\sigma_s = 0 \cdot 5209$ cal./deg.
    II. From 8 to 19, and I, $\sigma_l = 0 \cdot 5157$; $Q = 47 \cdot 07$ cal./g.

TABLE VIII.

(Pentadecoic acid : setting point, $52 \cdot 1°$).

Weight of			
Acid. 10·3201	Glass. 6·4279	Platinum. 0·2008	Nickel. 3·9136

No. of exp.	Range of temp.	Fall in temp.	Rise in temp.	No. of exp.	Range of temp.	Fall in temp.	Rise in temp.
1—2	30—20°	8·13°	0·161°	29—30	42—20°	19·37°	0·504$_5$°
3—7	32—20	9·30	0·169$_4$	31—35	45—20	22·04	0·592
8—9	33·5—20	11·20	0·238	36—37	47—20	24·53	0·671
10—11	36—20	13·42	0·317	38—39	49—20	25·77	1·087
12—18	38—20	15·59	0·430$_6$	40—41	50—20	26·70	1·314
19—20	40—20	16·10	0·451$_5$	42—45	55—20	31·94	2·027$_0$
21—28	41—20	18·21	0·486$_8$	46—49	88—20	61·52	2·656$_0$

$$Q_\alpha = 42 \cdot 47 \text{ cal./g.}; \quad Q_\beta = 47 \cdot 40 \text{ cal./g.}; \quad \sigma_l = 0 \cdot 5316 \text{ cal./deg.};$$
$$\sigma_\alpha = 0 \cdot 4668 \text{ cal./deg.}; \quad \sigma_\beta = 0 \cdot 4603 \text{ cal./deg.}$$

TABLE IX.

(Palmitic acid : setting point, 62·3°).

Exp. No.	Temp. range.	Weight of				Fall in temp.	Rise in temp.
		Acid.	Glass.	Platinum.	Nickel.		
1—3	22—100°	12·5535	6·2055	0·266	1·8990	77·01°	1·803$_0$°
4—5	22— 68	,,	,,	,,	,,	46·40	1·438
6	22— 66	,,	,,	,,	,,	44·48	1·405
7—9	22— 56	,,	,,	,,	,,	34·03	0·393$_3$
10—12	22— 53	,,	,,	,,	,,	33·50	0·367$_3$

    I.   From 10 to 12, $\sigma_s = 0\cdot4920$.

   II. From 4 to 6, 10 to 12, and I, $\sigma_l = 0\cdot5416$; $Q = 50\cdot59$ cal./g.

[Mrs. Stratton and Partington (*Phil. Mag.*, 1924, **48**, 1085), working with very carefully purified palmitic acid (setting point 62·65°), by electrical heating at the melting point obtained $Q = 51\cdot03$ cal./g.]

TABLE X.

(Eicosoic acid : setting point, 74·2°).

Exp. No.	Temp. range.	Weight of				Fall in temp.	Rise in temp.
		Acid.	Glass.	Platinum.	Nickel.		
1—3	56—20°	10·3867	4·7523	0·2008	2·5944	32·65°	0·563$_7$°
4—6	66—20	,,	,,	,,	,,	42·43	0·756$_7$
7—9	77—20	,,	,,	,,	,,	51·97	2·568$_3$
10—12	100—20	,,	,,	,,	,,	74·21	3·030$_7$

    I.   From 1 to 3, $\sigma_s = 0\cdot4597$ cal./deg.

   II.   From 4 to 6, $\sigma_s = 0\cdot4772$ cal./deg.

  III. From 7 to 12, and II, $\sigma_l = 0\cdot5663$ cal./deg.; $Q = 54\cdot24$ cal./g.

TABLE XI.

Mean specific heat in liquid state.

6	7	8	9	10	11	12	13	14	15	16	20
0·51	0·49	0·51	0·50	0·50	0·52	0·51	0·55	0·52	0·53	0·54	0·57

The mean specific heats of the acids in the liquid state over a temperature range of approximately 30° just above the melting point show no evidence of the presence of alternation; there is a slight rise in specific heat as the series is ascended.

The average mean specific heat of the solid form stable at the melting point is 0·46, somewhat lower than the mean for the liquid acids. It was not convenient to measure these over comparable ranges of temperature. Thus it is impossible to draw any conclusions as to the presence or absence of alternation in the mean specific heats of the solids.

Summary.

The heats of crystallisation of caproic, heptoic, tridecoic, myristic, pentadecoic, palmitic, and eicosoic acids have been determined.

These values, together with those previously published, show a very marked alternation as the series of acids is ascended.

Above decoic acid, the heat of crystallisation of the even acids is given by the equation $Q = - 3 \cdot 61 + 1 \cdot 030\ n$, where n is the number of carbon atoms in the chain, and the melting points of these acids are given by $T = (- 3 \cdot 61 + 1 \cdot 030n)/(- 0 \cdot 0043 + 0 \cdot 002652n)$. This equation has been shown to have a statistical basis.

Similar equations have been obtained for the odd acids, and the conclusion is drawn that the arrangement of the methylene groups is the same for both the even and the odd acids in the solid state.

The convergence temperature for the monobasic acids is $115°$, in agreement with that for the dibasic acids.

The heat of crystallisation of the terminal methyl and carboxyl groups changes from a positive to a negative value as the number of carbon atoms changes from 2 to 10.

The heat of transition of the α- to the β-form of the odd acids is erratic owing to the presence of a disturbing factor, very possibly water.

There is no alternation in the specific heats of the acids in the liquid state.