317. *The Heats of Crystallisation of the Ethyl Esters of the Monobasic Aliphatic Acids.*

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The heats of crystallisation and transition and the specific heats of some of the members of the homologous series of monobasic fatty acids and hydrocarbons have already been determined, and the bearing of the data on the melting points of these series has been discussed (Garner and Randall, J., 1924, **125**, 881; Garner, Madden, and Rushbrooke, J., 1926, 2491; Garner and Rushbrooke, J., 1927, 1351; Garner and King, J., 1929, 1849; King and Garner, J., 1931, 578; Garner, van Bibber, and King, J., 1931, 1533). In this paper are reported the corresponding values for the ethyl esters of the monobasic fatty acids.

A summary of the thermal data now available is given in Table I, together with other information which is relevant to the problem in hand, *viz.*, that of the interpretation of the melting-point phenomena of homologous series. From this table, the effect of variations in the tilt of the hydrocarbon chains in the solids on the thermal properties of long-chain

TABLE I.

Homologous series.	No. of C atoms in chain.	Spacing and angle of tilt of chain. Spacing.	Angle.	Heat of crystn. per CH_2 (Cals.).	Sp. heat (aver.) (cals./g.).	Heat of crystn. of terminal groups (Cals.).	Convergence temp. (calc.).
Acids.							
Even	6—26	C	59° 12′	1·03	0·48	Above C_{10} −1·55	115·5°
Odd, α	7—25	C′	59° 12′	0·97	0·44	,, C_{11} −2·56	112·2
,, β	9—25	B′ (Main)	59° 12′		0·44		
		D′	74° 36′				
		A′	90° for low members.				
(See Garner and King, J., 1929, 1856).							
Hydrocarbons.							
Even, α	22—34	A	90° *	0·609	1·05	−0·53	135
,, β	,,	B	72° 48′ *	1·0	0·44		
		C	61° 30′ *				
Ethyl esters.							
Even, α	18—30	A	90° *	0·708	0·71	−1·86	121·2
,, β	20—26		64° 26′ *	1·04	0·43		
	18—26		67° 30′ †				
	12—18			0·763	0·42	+2·16	

* S. H. Piper, private communication.
† Malkin (J., 1931, 2796).

compounds can be clearly seen. If the chain be tilted with respect to the planes holding the terminal groups, then the heat of crystallisation per methylene group is about 1 kg.-cal., and the specific heats of the solids about 0·45 cal./g. at room temperatures. When the chains are vertical, as in the α-forms of the esters and hydrocarbons, the heat of crystallisation per methylene group is much lower and the specific heats much higher than for the tilted forms. The reason for these differences was made evident by the investigation of Buckingham (*Trans. Faraday Soc.*, 1933, **30**, 377) into the dielectric constants and densities of ethyl behenate in the solid state, which has shown that the dipole possesses a greater freedom of movement and the hydrocarbon chains occupy a larger volume in the vertical than in the tilted form. The movement which occurs in the vertical form most probably consists in an oscillation of the hydrocarbon chain about its long axis (cf. Pauling, *Physical Rev.*, 1930, **36**, 443). The energy involved in the oscillation is evidently greater for the hydrocarbons than for the esters, since the specific heats are greater, *viz.*, 1·05 as compared with 0·71. Consequently, the energy required to separate the hydrocarbon chains in melting is less for hydrocarbons (0·61 kg.-cal. per methylene group) than for the esters (0·71 kg.-cal.), and in general, less for the vertical than for the tilted forms.

The relationship between the m. p.'s of homologous series and their thermal properties can best be brought out by reference to a simple theory of the melting process which has, in part, been developed in the earlier papers. The theory is not applicable to the first few members of a series because of abnormal effects due to the terminal groups. If it be assumed, in the first place, that the molecules in the liquid have the same shape as in the solid, *i.e.*, consist of rods with the carbon atoms arranged in a zig-zag pattern, then the melting process can be described relatively simply. The probability that a rod molecule will collide with the surface of the solid in the right place to form a unit of the solid lattice will vary inversely with its length, and can be represented as a first approximation by $p' = k'/n$, where k' is a constant and n the number of atoms in the chain. The reverse process, the removal of a molecule from the surface, requires an activation energy equal to the heat of crystallisation, and the probability in this case is $p'' = ve^{-Q/RT}$, where Q is the heat of crystallisation and v the rate at which the energy is supplied by the lattice and from the liquid. At the m. p., $p' = p''$, and (1) $k/n = ve^{-Q/RT_m}$, or (2) $\log_e n + \text{const.} = Q/RT_m$, if we assume that $\log_e k/v$ does not vary very much from one member to another and is practically independent of temperature; (2) is not in accord with the facts, for it has been shown that Q/T_m varies linearly with n for all of the homologous series yet investigated.

Our assumption that all of the molecules in the liquid state are in the form of rods must be in error, since rotation can occur about the C–C linking, and hence a correction must be made to (2) by multiplying the term on the left by the fraction of molecules which actually exist in the linear form in the neighbourhood of the solid surface. The probability that a molecule will occur in the linear form will evidently decrease with increase in n. Consider the shortest possible unit with two methylene groups, and let τ be the probability of the linear form in this case; then the probability of the linear form for a molecule with n atoms in the chain will evidently be τ^{n-1}, and $p' = k'\tau^{n-1}/n$, and the equation for the equilibrium at the m. p. becomes

$$(3)\ \log_e n - (n-1)\log_e \tau + \text{const.} = Q/RT_m$$

This is in agreement with the experimental results, for since $\log_e n$ and the constant are small compared with $(n-1)\log_e \tau$, Q/T_m varies linearly with n. Also, calculation of τ from successive members of the homologous series (Table II) gives values of the right order for the probability of the linear form. For the acids, within experimental error, τ is a constant along the chain down to $n = 10$, but below this it increases owing to the action of the terminal groups on the nearby methylene groups. τ varies for different series between 0·25 and 0·5 for one chemical link, and this variation may be taken to indicate that the straightening of the chain actually occurs in contact with the solid surface, and possibly in a unimolecular film on the surface. It would be expected that τ would be a constant for all series if the straightening occurred in the body of the liquid.

TABLE II.

Values of τ for different homologous series.

n (Even acids)......	4		6		8		10		12		14		16		18		20		22		24
τ		0·509		0·390		0·376		0·265		0·286		0·246		0·295		0·295		0·364		0·218	
n (Hydrocarbons)	24		26		30		34														
τ		0·507		0·489		0·443															
n (Ethyl esters, α)	18		20		22		24		26		30										
τ		0·398		0·399		0·430		0·430		0·442											
n (Ethyl esters, β)	12		14		16		18														
τ		0·458		0·444		0·398															
n (Odd acids)	9		11		13		15		17		21		23		25						
τ		0·420		0·261		0·229		0·307		0·341		0·341		0·223							

The value of τ increases in the order, acids<ethyl esters<hydrocarbons, and this is the order of the m. p.'s of compounds in these series *with an equal number of carbon atoms in the molecule.* It must be borne in mind, however, that the acids exist as double and the esters as single molecules in the solid state, and this is also very probably true of the liquid state, for in non-dissociating solvents, the acids undoubtedly exist as double molecules. For chain compounds 22 carbon atoms long, the following data summarise the position, temperatures being on the absolute scale.

Homologous series.	T_m.	Q (Cals./ g.-mol.).	q, terminal group (cals.).	q, methylene group (Cals.).	τ.	Convergent temp., calc.
Odd acids	301·3°	11·98	−5·12	0·97	0·272	385·2°
Even acids *	310·5	15·44	−3·10	1·03	0·279	388·5
Ethyl esters, α	313·4	10·93	−1·86	0·71	0·420	394·2
Hydrocarbons, α	316·8	11·70	−0·53	0·61	0·479	408·0

* Mean of twice 10th and 12th members.

The values of the heat of crystallisation give little clue to the order of the m. p.'s or the convergence limits, but this order is in line with the values of τ. The general run of the melting-point curves above $n = 10$ is mainly determined by the value of τ. Now τ varies inversely as the heat of crystallisation of the methylene groups and directly as the looseness of packing and the amplitude of the oscillation of the methylene chains. Thus *the attachment of a long-chain molecule to the surface of the solid occurs the more readily the greater the oscillation of the chain.* This appears to be the most important factor determining the order of the melting points.

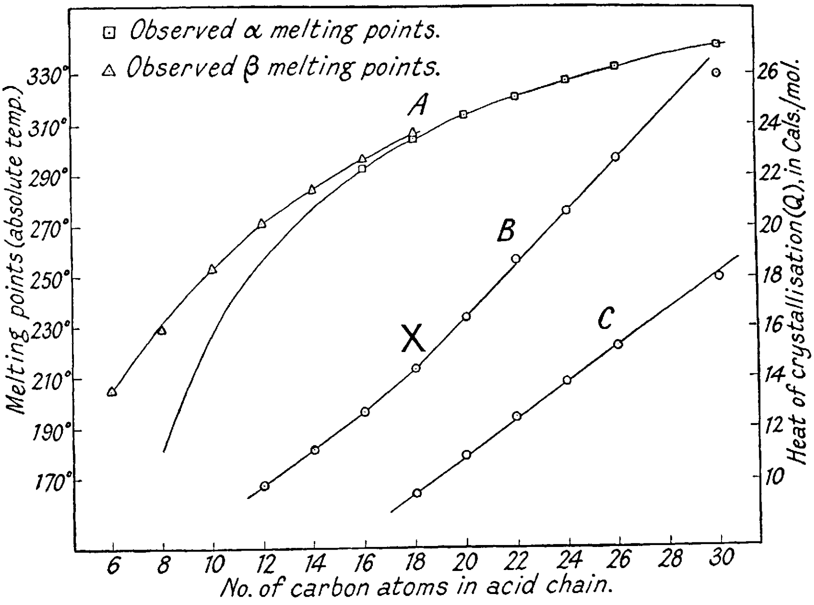
The ethyl esters give two melting-point curves which cut in the neighbourhood of $n = 20$ The equations to the curves are:

(4) $T_m = (0{\cdot}7630n + 0{\cdot}63)/(0{\cdot}00179n + 0{\cdot}01475)$ up to $n = 20$
(5) $T_m = (0{\cdot}7081n - 3{\cdot}28)/(0{\cdot}001796n - 0{\cdot}0012)$ above $n = 20$,

and these curves, together with the experimentally determined setting points, are given in Fig. 1. On the same diagram are recorded the heats of crystallisation at the setting points of the two solid forms, (C) being that for the α- or vertical form, and B that for the β- or tilted form. The β-forms are stable at the m. p. for members below $n = 20$, and the α-forms stable above. The point of intersection cannot be determined exactly, since there is hysteresis in the conversion of one form into the other similar to that observed with quartz (see Table III, and Fig. 2).

The tilted forms of the esters are very complex, and this complexity is mainly due to rearrangements occurring about the ester group. They undergo a phase change of the first order, which is recognisable by changes occurring in the slopes of the dielectric-constant curves, in the coefficient of expansion, and in the specific heats of the solid phase, but is not accompanied by changes in the long X-ray spacings or in the tilt of the chains. The magnitude of the effects observed at the phase-change point decreases progressively as the chain shortens, until at $n = 20$ it is not observable on the heat-content curve. On curve B are recorded the heats of crystallisation of the tilted forms stable below the phase change point. Above $n = 18$ the slope of curve B is the same as that of the acids and the β-forms of the hydrocarbons, the heat per methylene group being 1 kg.-cal. Below $n = 20$, there is a change of slope at X, curve B now becoming parallel to curve C. There is no marked change in the specific heats on passing through X, so that there can be little change in the energy of oscillation of the chains. Also, the long X-ray spacings, although only measured down to ethyl palmitate (Malkin, *loc. cit.*), vary linearly with n, so there is no change of tilt of the chains at X. It must therefore be concluded that the change at X is due to some rearrangement occurring about the ester group. In order to throw further light on this point, Buckingham has measured the dielectric constants of ethyl palmitate in the solid state, and finds that the dipole possesses a much higher mobility than in the β-forms of ethyl behenate. Hence, all the experimental evidence points to the same explanation of the change in slope at X, *viz.*, that it is due to a change in the mode of packing the ester group.

FIG. 1.



In accordance with the argument advanced earlier, the β-forms which possess non-oscillating chains should melt lower than the α-forms, and this is probably true down to $n = 20$, where the esters begin to behave in an anomalous manner. The rearrangement occurring in the packing of the ester group alters the relative stability of the α- and β-forms and brings about the crossing of the melting-point curves. The rearrangement must be of such a character as to increase the probability of adhesion of the molecule at the solid surface.

As we have seen, the terminal groups decide the mode of packing of the hydrocarbon chains even though the chains be 34 carbon atoms long. There is, however, a more specific action of the terminal groups which extends for 8 atoms along the chain. This shows itself in a departure of Q and Q/T from the linear relationships found to hold for the higher members, and in the case of the acids it is found to increase the value of τ for the methylene groups near the end of the chain. The experimental data available for the lower members of homologous series are, however, so scanty that it would serve no useful purpose to discuss these effects at any length at this stage.

EXPERIMENTAL.

The ethyl esters of palmitic and stearic acids were obtained by esterification of Kahlbaum's purest acids with sulphuric acid and ethyl alcohol, and purified by fractional distillation and crystallisation from ethyl alcohol until a constant setting point was reached. Ethyl laurate was prepared in the same way from pure lauric acid, setting point = 43·75°, and purified by fractional distillation. Ethyl behenate was prepared from Kahlbaum's erucic acid which had been esterified and fractionally distilled, and afterwards reduced with hydrogen to the behenate. The ethyl behenate was fractionally distilled, and crystallised from ethyl alcohol to a constant setting point. The esters of the C_{24}, C_{26}, and C_{30} acids were very kindly supplied to us in a high state of purity by Professor Francis. They had been synthesised from very pure behenate. The ester of the C_{20} acid was very kindly prepared by Dr. Malkin from recrystallised and fractionally distilled ethyl stearate prepared from Kahlbaum's pure stearic acid. The setting points of these and other esters are given in Table III, together with those calculated from equations (4) and (5).

TABLE III.

Calculated and Observed Setting Points of Even Ethyl Esters.

	Setting point.					Setting point.			
No. of C atoms in chain.	Calc. from α curve.	Obs.	Δ.	Ref.	No. of C atoms in chain.	Calc. from β curve.	Obs.	Δ.	Ref.
30	341·0°	341·3°	+0·3°	K. & G.	18	305·9°	306·4° *	+0·5°	Sm. †
26	332·4	332·6	+0·2	K. &. G.	16	295·9	296·2	+0·3	K. & G.
24	327·1	327·2	+0·1	K. & G.	14	284·1	284·0	−0·1	G. & R.
22	321·0	320·8	−0·2	K. & G.	12	270·1	271·3	+1·2	K. & G.
20	313·4	313·4	0·0	K. & G.	10	253	253·1 *	+0·1	D.†
18	304·2	304·1	−0·1	K. & G.	8	231·6	229 *	−2·6	T.†
16	292·3	292·3	0·0	P. & M.†					D.†
					6	204·4	205·5 *	+1·1	S.†

* Indicates m. p.

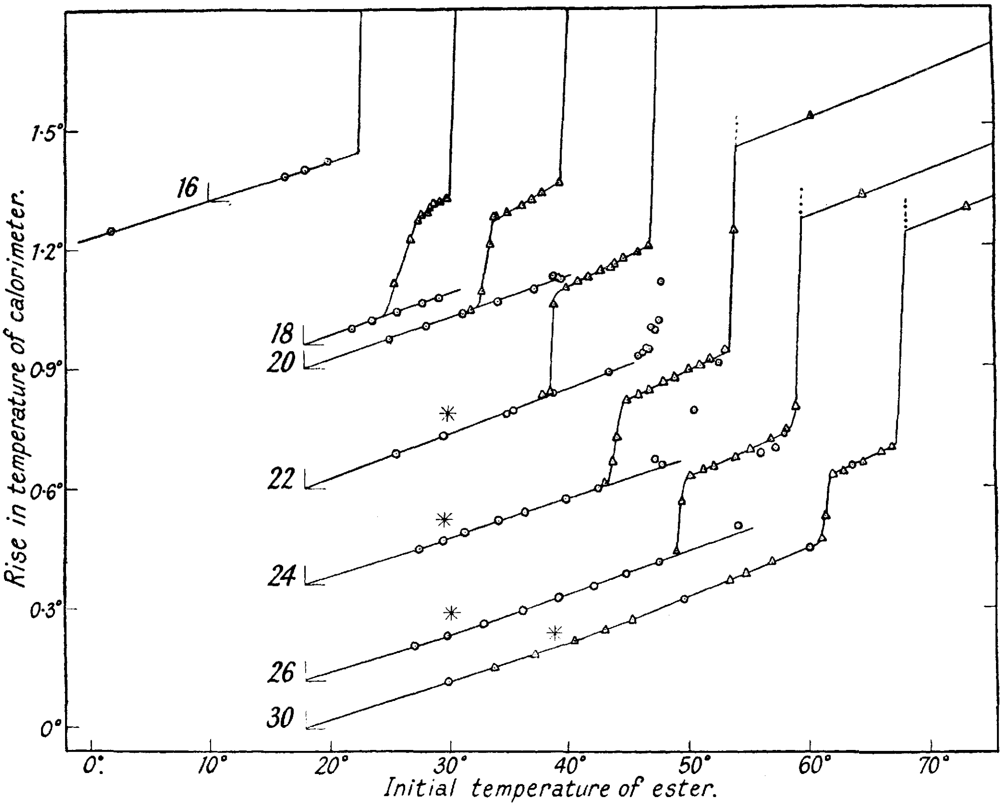
† Indicates values quoted by Phillips and Mumford (*Rec. trav. chim.*, 1933, **52**, 183).

Sm. = Smith (J., 1931, 802).
K. & G. = King and Garner, present research.
G. & R. = Garner and Rushbrooke (*loc. cit.*).
P. & M. = Phillips and Mumford (*loc. cit.*).
D. = Deffet (*Bull. Soc. chim. Belg.*, 1931, **40**, 385).
T. = Timmermans (*ibid.*, 1923, **31**, 389).
S. = Simon (*ibid.*, 1929, **38**, 47).

Purity of the Esters.—The physical properties of homologous series are not all equally sensitive to the presence of impurity. X-Rays will detect homologous impurities in amount exceeding 1—2%, but the setting points are more sensitive than this, *viz.*, to about 0·1%. One of the best criteria is the specific heat, for this shows an increase near the m. p. if impurity is present. Of the esters used, those of $n = 14$ and $n = 30$ do not attain the standard set by the rest. The specific heat of $n = 14$ in the solid state shows that some impurity is probably present. Ethyl behenate is probably the purest, for in tests made within 0·04° of the m. p. it appeared to be completely solid. It is the ester most easily prepared in the pure state. The esters of n = 16, 18, 20, 24, and 26 showed no signs of the presence of impurity in the course of the investigation, but they were not subjected to the same test as the behenate. Fortunately, the heats of crystallisation of the α-forms are not very sensitive to impurities, so that there is little difficulty in determining these values. The properties of the β-forms are, however, more sensitive.

Procedure.—The determinations of the specific heats and heats of crystallisation of the esters were carried out in the same apparatus and in a manner identical with that used previously for the acids and hydrocarbons (*loc. cit.*). The water-equivalent of the calorimeter remained unchanged throughout the series of experiments.

FIG. 2.



The low setting point of ethyl palmitate made it necessary for the crystallisation experiments to be carried out at 10°, but in all other cases, except that of ethyl laurate, the calorimeter temperature was approximately 18°. For this ester the calorimeter temperature was maintained at approximately 21°, and a cryostat in which liquid sulphur dioxide and liquid ammonia could be boiled under reduced pressure was used to give the low temperature necessary for the solidification of this ester.

Experimental Data.—Only the experimental data essential for the calculation of specific heats and heats of crystallisation are given below. The complete experimental data, except those for ethyl laurate, are shown graphically in Fig. 2.

Ethyl laurate (setting point = $-1·70°$).

(Wt. of ester, 5·195 g.; glass, 5·873 g.; platinum, 0·1333 g.)

Expt. No.	Initial temp. of ester.	Fall in temp.	Rise in temp.	Expt. No.	Initial temp. of ester.	Fall in temp.	Rise in temp.
1—3	30·597°	10·229°	$0·110_7$°	7—9	− 9·20°	−30·790°	$-0·970_2$°
4—6	4·250	−15·837	$-0·171_5$	12—14	−32·876	−54·085	$-1·165_0$

$\sigma_L = 0·4825$ cal./g.; $\sigma_{S_\beta} = 0·3378$ cal./g.; $Q_\beta = 9·745$ Cals./g.-mol.

Ethyl palmitate (setting point = 23·2°).

(Wt. of ester, 5·205 g.; glass, 5·631 g.; platinum, 0·1246 g.)

Expt. No.	Initial temp. of ester.	Fall in temp.	Rise in temp.	Expt. No.	Initial temp. of ester.	Fall in temp.	Rise in temp.
1	20·11°	10·85°	0·108$_9$°	5, 8, 9	54·32°	44·11°	1·153$_8$°
2	18·22	7·26	0·068$_2$	6, 10, 11, 13	28·42	18·66	0·873$_3$
3	16·50	6·50	0·060$_3$				

σ_{S_β} = 0·3931 cal./g.; σ_L = 0·4979 cal./g.; Q_β = 12·68 Cals./g.-mol.

Ethyl stearate (setting point = 31·05°).

(Wt. of ester, 5·370 g.; glass, 5·846 g.; platinum, 0·1358 g.)

1	27·98	10·54	0·111$_1$	22	30·097	12·27	0·368$_7$
13	28·91	11·57	0·356$_3$	23	28·92	10·82	0·349$_0$
18	28·59	10·67	0·343$_2$	6—9	36·13	17·96	0·920$_8$
20	29·53	11·06	0·351$_5$	10—12	60·953	43·369	1·218$_9$

σ_{S_β} = 0·4504 cal./g.; σ_{S_α} = 0·9227 cal./g.; σ_L = 0·4994 cal./g.; Q_β = 14·31 Cals./g.-mol.;
Q_α = 9·436 Cals./g.-mol.

Heat of transition $\alpha \longrightarrow \beta$ = 4·874 Cals./g.-mol.

Ethyl ester of C_{20} *acid* (setting point = 40·36°).

(Wt. of ester, 5·224 g.; glass, 5·903 g.; platinum, 0·1358 g.)

5	37·42	19·36	0·197$_6$	17	38·05	20·95	0·447$_8$
6	36·43	18·19	0·409$_3$	23	24·10	15·95	0·381$_1$
9	35·08	16·61	0·386$_7$	11—14	45·72	27·79	1·034$_6$
10	34·11	15·84	0·378$_1$	15—18	70·70	52·63	1·325$_4$
12	37·16	19·04	0·421$_4$				

σ_{S_β} = 0·4383 cal./g.; σ_{S_α} = 0·7209 cal./g.; σ_L = 0·5271 cal./g.; Q_α = 10·93 Cals./g.-mol.;
Q_β = 16·39 Cals./g.-mol.

Heat of transition $\alpha \longrightarrow \beta$ = 5·46 Cals./g.-mol.

Ethyl behenate (setting point = 47·8°).

(Wt. of ester, 5·838 g.; glass, 6·253 g.; platinum, 0·1249 g.)

4	38·80	20·67	0·235$_2$	19	46·01	27·25	0·581$_7$
5	25·70	7·72	0·086$_7$	8, 16, 17	53·53	35·08	1·267$_4$
13	40·02	21·91	0·499$_6$	22—25	76·77	58·02	1·570$_7$

$\sigma_{S_{\beta_2}}$ = 0·4422 cal./g.; $\sigma_{S_{\beta_1}}$ = 0·4477 cal./g.; σ_{S_α} = 0·6512 cal./g.; σ_L = 0·5450 cal./g.;
Q_α = 12·42 Cals./g.-mol.; Q_β = 18·63 Cals./g.-mol.

Heat of transition $\alpha \longrightarrow \beta$ = 6·21 Cals./g.-mol.

Ethyl ester of C_{24} *acid* (setting point = 54·2°).

(Wt. of ester, 4·935 g.; glass, 5·800 g.; platinum, 0·1218 g.)

34	27·64	9·49	0·089$_8$	10	45·00	26·18	0·454$_6$
26	42·58	23·53	0·232$_5$	12—15	60·36	41·62	1·162$_6$
30	31·39	13·81	0·133$_6$	17—19	84·65	65·81	1·436$_4$
7	52·02	33·43	0·555$_2$				

$\sigma_{S_{\beta_2}}$ = 0·418 cal./g.; $\sigma_{S_{\beta_1}}$ = 0·4613 cal./g.; σ_{S_α} = 0·7238 cal./g.; σ_L = 0·5325 cal./g.;

Q_α = 13·82 Cals./g.-mol.; Q_β = 20·57 Cals./g.-mol.

Heat of transition $\alpha \longrightarrow \beta$ = 6·75 Cals./g.-mol.

Ethyl ester of C_{26} *acid* (setting point = 59·6°).

(Wt. of ester, 4·876 g.; glass, 5·704 g ; platinum, 0·1208 g.)

22	29·93	12·80	0·121$_1$	15	56·93	38·26	0·594$_5$
19	36·26	18·18	0·177$_0$	4, 5, 7	64·74	46·51	1·210$_2$
20	47·66	29·72	0·295$_8$	10, 11, 13	88·43	69·79	1·471$_5$

$\sigma_{S_{\beta_2}}$ = 0·4271 cal./g.; $\sigma_{S_{\beta_1}}$ = 0·4798 cal./g.; σ_{S_α} = 0·7343 cal./g.; σ_L = 0·5332 cal./g.;
Q_α = 15·22 Cals./g.-mol.; Q_β = 22·66 Cals./g.-mol.

Heat of transition $\alpha \longrightarrow \beta$ = 7·44 Cals./g.-mol.

Ethyl ester of C_{30} *acid* (setting point = 68·3°).

(Wt. of ester, 4·749 g.; glass, 5·869 g.; platinum, 0·1358 g.)

24	33·80	16·59	0·160$_1$	8	67·11	48·99	0·704$_4$
20	57·01	39·87	0·425$_1$	9, 10, 11, 15	73·30	54·81	1·297$_5$
21	45·36	29·01	0.287$_2$	17, 18, 28	91·30	73·46	1·507$_2$

$\sigma_{S_{\beta_2}}$ = 0·4447 cal./g.; $\sigma_{S_{\beta_1}}$ = 0·6389 cal./g.; σ_{S_α} =0·7884 cal./g.; σ_L = 0·5451 cal./g.;
Q_α = 17·93 Cals./g.-mol.; Q_β = 25·98 Cals./g.-mol.

Heat of transition $\alpha \longrightarrow \beta$ = 8·05 Cals./g.-mol.

The heat content of the esters is shown in Fig. 2, in which, following the convention used in the earlier papers, points obtained by cooling the solid to its initial temperature from above the m. p. are indicated by △, and points obtained by heating the solid ester from room temperature to its initial temperature are indicated by ⊙. Circumstances to be noticed in connexion with Fig. 2 are : (1) the greater slope of the curves for the α-forms, (2) the change of slope in the β-forms of the long-chain esters, which occurs in the case of ethyl behenate at the point (*) where this ester undergoes a phase change of the first order (cf. Buckingham, *loc. cit.*), and (3) the hysteresis in the conversion $\alpha \longrightarrow \beta$, which becomes less pronounced as the chain length increases. It will be observed that the phase change in the β-forms decreases as the chain shortens, and disappears at about $n = 18$. The recorded heats of crystallisation of the β-forms are those obtained by extrapolating the lower straight line (called β_2) back to the m. p., and the heats of transition $\alpha \longrightarrow \beta$ are those for the change at the m. p. The heats of crystallisation and transition, the specific heats, and temperatures of transition, are summarised in Table IV.

TABLE IV.

Heats of Crystallisation and Transition, Specific Heats, and Transition Temperatures of Ethyl Esters.

No. of C atoms in chain.	Heat of crystn. (Cals./g.-mol.).		Heat of transtn. $\alpha \longrightarrow \beta_2$ at s.p. (Cals./g.-mol.).	Specific heats (cals./g.).	Solid.		Transition temps.		Setting point.
	α.	β.		Liquid.	α.	β_1.	$\alpha \longrightarrow \beta$.	$\beta \longrightarrow \alpha$.	
12		9·745		0·48		0·34			−1·7°
14*		11·17		0·50		(0·50)			11·0
16		12·68		0·50		0·39			23·2
18	9·436	14·31	4·874	0·50	(0·92†)	0·45	27°		31·05
20	10·93	16·39	5·46	0·53	0·72	0·44	33·5	(39°)	40·36
22	12·42	18·63	6·21	0·55	0·65	0·44	39	46	47·8
24	13·82	20·57	6·75	0·53	0·72	0·42	44·5	47·5—50	54·2
26	15·22	22·66	7·44	0·53	0·73	0·43	49·5	54	59·6
30	17·93	25·98	8·05	0·55	0·79	0·45	61·5	63·5	68·3

* Garner and Rushbrooke, *loc. cit.*

† This high value is caused by difficulties in measuring accurately the specific heat of ethyl stearate, owing to the instability of the α-form of this ester (cf. Fig. 2).

SUMMARY.

The thermal data for the ethyl esters of the monobasic acids between $n = 14$ and $n = 30$ have been determined. These esters exist in two main forms, one with a vertical and the other with a tilted chain. The form stable at the melting point possesses a vertical chain when $n > 20$ and a tilted chain when $n < 20$. The heats of crystallisation of the vertical forms vary linearly with n, but there is a change of slope for the tilted forms at $n = 20$. This is attributed to a change in the mode of orientation of the ester group in the lattice.

On comparing these data with those available for other homologous series, it is seen that the vertical forms possess a much higher specific heat and a much lower heat of crystallisation of the methylene groups than the tilted forms. This is due to a greater amplitude of oscillation of the chain about its main axis. The vertical forms possess, in general, the highest melting point, and this is ascribed to a greater rate of attachment of the chain to the surface of the solid.

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