

CCXI.—*The Melting Points and Heats of Crystallisation of the Normal Long-chain Hydrocarbons.*

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In an earlier paper (Garner, Madden, and Rushbrooke, J., 1926, 2491), it was suggested that the increment in the heat of crystallisation due to the addition of two methylene groups to the hydrocarbon chain might be the same for all normal homologous series. It was also pointed out that the convergence temperature for the melting point of homologous series, which depends on the heat of crystallisation of the methylene groups, should, in such circumstances, be identical for all series. The increment in the heat of crystallisation for the higher members of the normal monobasic fatty acids was found to be 2.06 Cals. for the even acids, and 1.93 Cals. for the odd acids. The small difference between the two values lies within the experimental error of the determination for the odd acids. The convergence limits were calculated to be 115.5° for the even and 112.2° for the odd acids (Garner and King, J., 1929, 1849). The experimental convergence limit for the dibasic acids is approximately 120° . In the present investigation, the values for the increment in the heat of crystallisation and the convergence limit have been determined for the hydrocarbons with an even number of carbon atoms in the chain.

The heats of crystallisation of the following aliphatic hydrocarbons have been determined: docosane, hexacosane, triacontane, tetratriacontane, and pentatriacontane. All of these exist in two enantiotropic forms, α and β , similar to those previously found for the odd fatty acids (Garner and Randall, J., 1924, 125, 881). The form stable at the melting point, α , passes into the β -form at temperatures lying a few degrees below the melting point (Table I).

TABLE I.

Transition temperature of the hydrocarbons.

No. of carbon atoms.....	22	26	30	34	35
Setting point	43.8°	56.1°	65.5°	72.4°	74.0°
Transition temperature (degrees below setting point).....	3.6	6	6.5	4.5	2.5

The α -form possesses a glass-like appearance, and this becomes white on transition to the β -form. The transition can very readily be seen by melting and cooling the hydrocarbons in thin films between glass plates. In the case of the higher members of the odd acids, the transition $\beta \rightarrow \alpha$ did not occur, but in the case of the C_{30} hydrocarbon the transition was reversible. Müller (J., 1925,

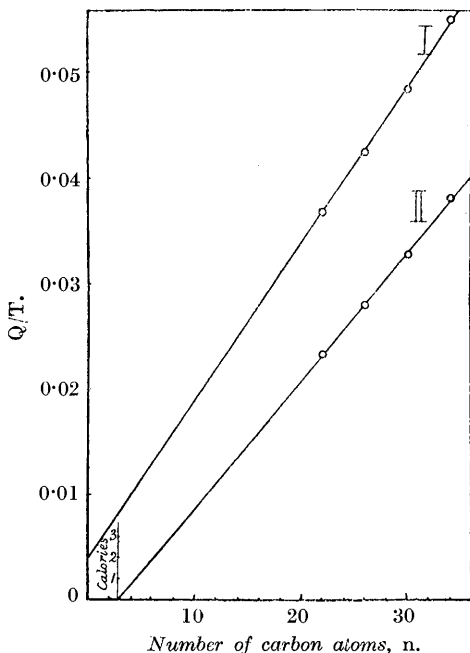
127, 599) has previously recorded the existence of two X-ray spacings for C_{18} and C_{20} hydrocarbons, and later he showed that $C_{22}H_{46}$ also gave two spacings. These spacings very probably correspond to our α - and β -forms, at least in the case of $C_{22}H_{46}$ (see later).

The heats of crystallisation of the two forms of the even hydrocarbons and the heat of transition are given in Table II. The heat

TABLE II.

No. of carbon atoms.	Heat of crystallisation, kg.-cals./mol.		Heat of transition, kg.-cals./mol.
	α -Form.	β -Form.	
22	11.70	18.60	6.90
26	14.04	22.41	8.37
30	16.45	25.17	8.72
34	19.11	30.59	11.48

FIG. 1.



I. Q/T - n Graph for even hydrocarbons. II. Q - n Graph for even hydrocarbons.

of crystallisation, Q , and the entropy of crystallisation, Q/T , for the α -forms are plotted against n in Fig. 1. Measurements of the slopes and intercepts of Curves I and II lead to the following equations:

$$Q = 0.6085n - 1.75 \quad \dots \quad (1)$$

$$Q/T = 0.001491n + 0.00404 \quad \dots \quad (2)$$

It will be noted that the heat of crystallisation of two methylene groups for the α -forms is 1.22 instead of 2.06 found for the even acids. There are thus two very different modes of packing hydrocarbon chains in the crystals of straight-chain compounds. It is very remarkable that, in a molecule containing 34 carbon atoms, the nature of the terminal group should decide the mode of packing.

The increment for the β -forms of the hydrocarbons is approximately the same as that for the acids, and this may mean that the type of packing of the methylene groups is similar in the two cases.

Müller (*Proc. Roy. Soc.*, 1930, *A*, **127**, 417) finds that the short X-ray spacings of the two forms of the hydrocarbons are very dissimilar. Since these spacings correspond with molecular distances across the hydrocarbon chain, they are an indication of marked differences in the mode of association of the chains in the two types of crystal. Our results show that these differences are of such a radical character as to affect the heats of crystallisation.

The heat of crystallisation of a terminal methyl group can be calculated from equation (1) if it be assumed that all of the methylene groups have the same heat of crystallisation; this gives $Q_{\text{CH}_3} = -0.27$. It was shown in the case of the acids that $Q_{\text{CH}_3} + Q_{\text{CO}_2\text{H}} = -1.55$. Therefore $Q_{\text{CO}_2\text{H}} = -1.28$ Cals. It is considered that the negative values for the heat of crystallisation of the terminal groups are due to a lack of lateral contact between the carboxyl and the methyl group in the crystal. The heat of crystallisation of the former is more negative than that of the latter because, in the liquid state, the former groups are already associated in pairs.

Equation for the Setting Points of Hydrocarbons.—Dividing equation (1) by (2), we obtain equation (3) connecting the setting point T with the number of carbon atoms in the chain :

$$T = (0.6085n - 1.75)/(0.001491n + 0.00404) \quad . \quad . \quad (3)$$

This is similar in form to the equation shown to fit the melting-point curves of the acids between C_{10} and C_{24} . It gives a convergence temperature of 135° , which is about 20° higher than for the monobasic and dibasic acids. Equation (3) has been used to calculate the setting points of the hydrocarbons from C_5H_{12} to $\text{C}_{70}\text{H}_{142}$. The degree of correspondence between the calculated and the observed values will be seen from Table III, in which Δ denotes the difference between the two values.

It will be noted that the agreement above C_{20} is good, but that for the hydrocarbons with shorter chains the experimental value is always higher than the calculated value. Similar discrepancies are found for all homologous series yet investigated. The melting points of the lower members of the series are not given accurately

TABLE III.

Calculated and observed setting points (absolute temperatures) of hydrocarbons.

No. of C atoms.	Ref.	Setting pt.			No. of C atoms.	Ref.	Setting pt.		
		Obs.	Calc.	Δ .			Obs.	Calc.	Δ .
5	P	143.4°	112.4°	-31.0°	20	P	309.7°	307.7°	-2.0°
6	P	178.6	146.3	-32.3	22	K	316.8	316.0	-0.8
7	P	182.2	173.4	-8.8	26	K	329.1	328.6	-0.5
8	P	215.6	195.2	-20.4	30	K	338.5	338.6	+0.1
9	I.C.T.	222.0	213.4	-8.6	34	K	345.4	346.0	+0.6
10	I.C.T.	241	228.8	-12.2	35	K	347.0	347.7	+0.7
11	I.C.T.	246.5	241.9	-4.6	36	G	349	349.2	+0.2
12	I.C.T.	261	253.2	-7.8	40	C	353.8	354.6	+0.8
13	I.C.T.	266.8	263.1	-3.7	50	C	365.1	365.0	-0.1
14	I.C.T.	278.5	271.7	-6.8	54	G	368	367.9	-0.1
15	I.C.T.	283	279.4	-3.6	60	C	371.9	371.8	-0.1
16	I.C.T.	293	286.3	-6.7	62	G	373.5	372.9	-0.6
17	M	295	292.7	-2.3	64	G	375	374.0	-1.0
18	M	301	298.0	-3.0	70	C	378.3	377.2	-1.1
19	M	304	303.1	-0.9					

References :

P = Parks, Huffmann, and Thomas; Parks and Huffmann (*loc. cit.*).

I.C.T. = International Critical Tables.

M = Müller, *Proc. Roy. Soc.*, 1930, **127**, 805.

K = King, present research.

G = Gascard, *Ann. Chim.*, 1921, **15**, 332.

C = Carothers, Hill, Kirby, and Jacobson, *J. Amer. Chem. Soc.*, 1930, **52**, 5279.

by equations similar to (3); those of the lower acids have been discussed previously (King and Garner, this vol., p. 578), and it has been shown that the discrepancy is in part due to an effect which the length of chain has on the probability of crystallisation. It is not possible to examine the hydrocarbons in this way on account of lack of knowledge of thermal data for the lower hydrocarbons.

A possible cause of part of the deviation may be gathered from the work of Müller, who shows that the form stable at the melting point is not the same for the short-chain as for the long-chain paraffins. Also, from Table III, it appears that there is alternation in the melting points of the short-chain hydrocarbons. Thus, from the experimental results available, it would appear unlikely that the melting points of the hydrocarbons can be represented by one equation. This is confirmed by the alternation in the heats of crystallisation of hydrocarbons containing 5, 6, 7, and 8 carbon atoms (see p. 1537).

The long X-ray spacings of the hydrocarbons used in this research have been measured by Piper and Malkin (*Nature*, 1930, **126**, 278), and are recorded below :

No. of carbon atoms	26	30	34
Long spacings $\left\{ \begin{array}{l} A \\ C \end{array} \right.$	35.0	40.5	45.3
	31.05	—	40.00

The *A*-spacing agrees with that given by Müller, and very probably corresponds with the α -form. It would appear that the β -form sometimes gives the *B*- and sometimes the *C*-spacing.

The heats of crystallisation of pentane, hexane, heptane, octane, and eicosane have been determined by Parks, Huffmann, and Thomas (*J. Amer. Chem. Soc.*, 1930, **52**, 1032) and by Parks and Huffmann (*ibid.*, p. 4385), and are given below :

<i>n</i>	5	6	7	8	20
<i>Q</i> (Cals./mol.)	2.001	3.004	3.381	4.796	14.68

The hydrocarbons 5—8 give the *B*-spacing, and 20 gives both *A*- and *B*-spacings (Müller). Since the above authors do not mention the fact that eicosane occurs in two forms, it is not clear whether their heat of crystallisation for this hydrocarbon refers to the α - or the β -form.

EXPERIMENTAL.

The hydrocarbons were prepared by the electrolysis of the potassium salts of the respective fatty acids. For docosane, the lauric acid used in the measurements of the heat of crystallisation was converted into the potassium salt and electrolysed according to the method of Petersen (*Z. Elektrochem.*, 1906, **12**, 141).* The hydrocarbon was fractionally crystallised several times until a constant setting point of 43.8° was obtained.

For hexacosane and tetratriacontane, Kahlbaum's purest myristic and stearic acids respectively were used as starting points. The ethyl esters were prepared and fractionated to a constant setting point. The hydrocarbons obtained from the respective acids were repeatedly crystallised and distilled, and further purified by heating at approximately 130° for two hours with concentrated sulphuric acid, in the manner suggested by Professor Chibnall. This had the effect of raising the setting point from 56.0° to 56.1° in the case of the former, and from 72.1° to 72.4° for the latter.

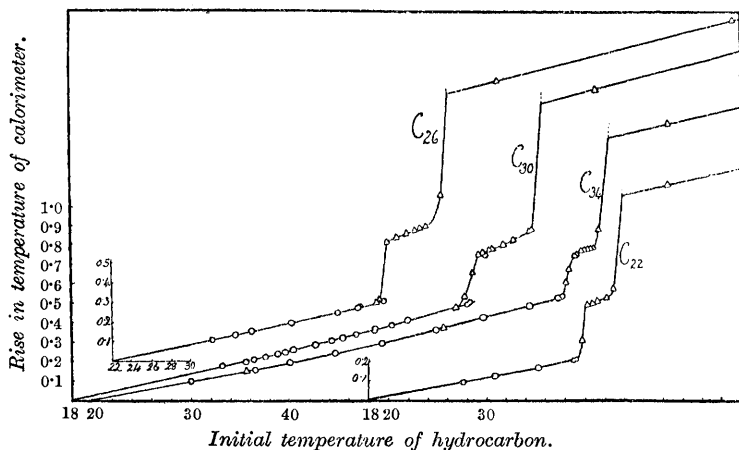
Triacontane was kindly supplied by Professor Francis. This had been prepared from Kahlbaum's palmitic acid, and treated as above. After several distillations in a vacuum, it gave a final setting point of 65.5°. Neither this hydrocarbon nor docosane was treated with sulphuric acid before the heat of crystallisation measurements were made. Professor Chibnall, however, found that after treatment the setting point of the latter was raised by 0.2° and that of the former remained unaltered.

The experimental procedure adopted in measuring the heats of crystallisation was that described in a previous paper (Garner and Randall, *loc. cit.*). The duration of the heating in the thermostat

* Attempts to make $C_{42}H_{86}$ by this method have as yet been unsuccessful.

varied from 8 or 9 hours to 80 minutes. Immediately below the melting point, equilibrium is established slowly, and hence a long period was necessary. For the β -form, 80 minutes in the thermostat was long enough for equilibrium to be reached. $3\frac{1}{2}$ Hours were allowed for the transition $\beta \rightarrow \alpha$ form, as this change proceeds slowly.

FIG. 2.



The experimental data are shown graphically in Fig. 2, where the rise in temperature of the calorimeter is plotted against the initial temperature of the hydrocarbon; Δ indicates points obtained when the solid had been cooled to its initial temperature from above the melting point, and \odot points obtained when the solid acid was heated from room temperature to its initial temperature. It will be

Docosane (Setting point = 43.8°).

(Wt. of hydrocarbon = 4.547 g.; glass = 6.002 g.; platinum = 0.1641 g.; nickel = 0.7253 g.)

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
3	35.18°	18.00°	0.172 ₈ °
5	41.33	23.70	0.510 ₇
7	40.33	23.26	0.498 ₄
10	39.00	21.75	0.215 ₃
12—14	48.60	30.10	1.103 ₈
15—18	73.89	56.02	1.398 ₉
I.	From Expt. 3 (17.18—35.18°),	$\sigma_{s\beta} = 0.4338$ cal./g.	
II.	„ Expts. 3, 10 (35.18—39.00°),	$\sigma_{s\beta} = 0.5572$ „	
III.	„ „ 5, 7 (40.33—41.33°),	$\sigma_{s\alpha} = 1.030$ „	
IV.	„ „ 12—14, 15—18, and I,	$\sigma_L = 0.5590$ „	
		$Q_\alpha = 11.70$ Cals./mol.	
		* $Q_\beta = 18.60$ „	
		Heat of transition $\alpha \rightarrow \beta = 6.90$ „	

* An earlier, independent series gave 18.42 Cals./mol.

observed in the curve for tetratriacontane that the same values are obtained at 36° and 56° irrespective of the side from which equilibrium is approached.

The heats of crystallisation were determined by a graphical method described in previous papers. In order to obtain the heat of crystallisation of the β -form, the specific heats from 20° to 40° approximately were employed. The results are given in the tables. The temperature of the thermostat is given in col. 2, and the temperature of the calorimeter varied from 16° to 23°. The glass used in the container was the same as that used previously.

Hexacosane (Setting point = 56.1°).

(Treated with concentrated sulphuric acid.)

(Wt. of hydrocarbon = 5.563 g.; glass = 6.036 g.; platinum = 0.1634 g.)

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
2	40.07°	17.77°	0.192 ₆ °
4	49.60	27.18	0.306 ₄
6	44.82	22.04	0.241 ₃
8	50.90	27.71	0.626 ₃
11	53.82	31.10	0.688 ₀
17—20	61.20	38.35	1.430 ₃
21—23	85.32	63.01	1.750 ₃
I.	From Expt. 2 (22.30—40.07°),	$\sigma_{S\beta} =$	0.4419 cal./g.
II.	„ Expts. 2, 6 (40.07—44.82°),	$\sigma_{S\beta} =$	0.4578 „
III.	„ „ 6, 4 (44.82—49.60°),	$\sigma_{S\beta} =$	0.5554 „
IV.	„ „ 8, 11 (50.90—53.82°),	$\sigma_{S\alpha} =$	0.9554 „
V.	„ „ 17—20, 21—23, and I,	$\sigma_L =$	0.5614 „
		$Q_\alpha =$	14.04 Cals./mol.
		$Q_\beta =$	22.41 „
		Heat of transition $\alpha \rightarrow \beta =$	8.37 „

Triacontane (Setting point = 65.5°).

(Wt. of hydrocarbon = 5.629 g.; glass = 6.112 g.; platinum = 0.1641 g.)

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
2	37.64°	21.15°	0.237 ₂ °
14	48.56	30.67	0.364 ₅
16	48.61	30.76	0.360 ₄
21	58.19	40.29	0.501 ₃
25	61.75	45.62	0.820 ₅
27	59.21	41.82	0.755 ₃
32—35	100.37	81.98	1.985 ₅
36—41	71.20	53.18	1.599 ₁
I.	From Expt. 2 (16.49—37.64°),	$\sigma_{S\beta} =$	0.4572 cal./g.
II.	„ Expts. 2, 14, and 16 (37.64—48.58°),	$\sigma_{S\beta} =$	0.5512 „
III.	„ „ 14, 16, and 21 (48.58—58.19°),	$\sigma_{S\beta} =$	0.6474 „
IV.	„ „ 25, 27 (61.75—59.21°),	$\sigma_{S\alpha} =$	0.9792 „
V.	„ „ 32—35, 36—41, and I,	$\sigma_L =$	0.5722 „
		$Q_\alpha =$	16.45 Cals./mol.
		$Q_\beta =$	25.17 „
		Heat of transition $\alpha \rightarrow \beta =$	8.72 „

Tetratriacontane (Setting point = 72.4°).

(Treated with concentrated sulphuric acid.)

(Wt. of hydrocarbon = 4.518 g.; glass = 5.918 g.; nickel = 0.7249 g.; platinum = 0.1371 g.)

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
4	40.05°	20.02°	0.192 ₂ °
3	49.42	29.73	0.296 ₁
2	59.64	40.58	0.429 ₉
23	67.26	48.63	0.540 ₄
8	70.83	51.57	0.791 ₇
25	69.48	50.04	0.762 ₀
9—12	78.60	59.26	1.431 ₇
14—16	99.78	79.97	1.667 ₃
I. From Expt. 4 (20.03—40.05°),		$\sigma_{S\beta} =$	0.4428 cal./g.
II. „ Expts. 4, 3 (40.05—49.42°),		$\sigma_{S\beta} =$	0.5249 „
III. „ „ 3, 2 (49.42—59.64°),		$\sigma_{S\beta} =$	0.6521 „
IV. „ „ 2, 23 (59.64—67.26°),		$\sigma_{S\beta} =$	0.7591 „
V. „ „ 8, 25 (69.48—70.83°),		$\sigma_{S\alpha} =$	1.264 „
VI. „ „ 9—12, 14—16, and I,		$\sigma_L =$	0.5725 „
		$Q_a =$	19.11 Cals./mol.
		$Q_\beta =$	30.59 „
		Heat of transition $\alpha \rightarrow \beta =$	11.48 „

Pentatriacontane (Setting point = 74.0°).

(Wt. of hydrocarbon = 5.621 g.; glass = 6.026 g.; platinum = 0.1641 g.)

Expt. No.	Upper temp.	Fall in temp.	Rise in temp.
20	41.04°	24.40°	0.267 ₁ °
3	56.26	39.83	0.457 ₀
1	64.73	48.12	0.575 ₅
12	67.05	50.34	0.615 ₁
7	72.22	54.51	0.942 ₆
10	71.76	54.17	0.939 ₉
13—15	99.68	81.41	1.991 ₀
16—19	78.70	60.70	1.716 ₄
I. From Expt. 20 (41.04—16.64°),		$\sigma_{S\beta} =$	0.4441 cal./g.
II. „ Expts. 20, 3 (41.04—56.26°),		$\sigma_{S\beta} =$	0.5220 „
III. „ „ 3, 1 (56.26—64.73°),		$\sigma_{S\beta} =$	0.6324 „
IV. „ „ 1, 12 (64.73—67.05°),		$\sigma_{S\beta} =$	0.8305 „
V. „ „ 7, 10 (71.76—72.22°),		$\sigma_{S\alpha} =$	0.3369 „
VI. „ „ 13—15, 16—19, and I,		$\sigma_L =$	0.5656 „
		$Q_a =$	20.65 Cals./mol.
		$Q_\beta =$	30.47 „
		Heat of transition $\alpha \rightarrow \beta =$	9.82 „

The values for the specific heats of the liquid state, viz.,

Hydrocarbon	C_{22}	C_{26}	C_{30}	C_{34}	C_{35}
σ_L	0.56	0.56	0.57	0.57	(0.56)

show that there may be a slight tendency to increase as the series is ascended, as was the case with the fatty acids.

The heats of transition of the α - to the β -form are approximately four times as great as those of the fatty acids.

The specimen of pentatriacontane was kindly lent to us by Professor Chibnall.

Summary.

(1) The heats of crystallisation of the following hydrocarbons, all of which exist in two forms, α and β , have been measured, and are given as kg.-cals./g.-mol. for the α -form: $C_{22}H_{46}$, 11.7; $C_{26}H_{54}$, 14.04; $C_{30}H_{62}$, 16.45; $C_{34}H_{70}$, 19.11; $C_{35}H_{72}$, 20.65.

The heat of crystallisation, Q , and also Q/T , when plotted against n , the number of carbon atoms, give linear relationships.

(2) The equation $T = (0.6085n - 1.75)/(0.001491n + 0.00404)$ has been obtained for the setting points of the hydrocarbons, and gives very good agreement with the observed values between C_{20} and C_{70} . The convergence temperature is 135° , as compared with 116° for the even fatty acids, and 112° for the odd acids.

(3) The increment in the heat of crystallisation for one methylene group is 0.608 Cal. for the α -form, and 1.0 Cal. for the β -form, as compared with 1.03 Cal. for the fatty acids.

(4) The heat of transition of the $\alpha \rightarrow \beta$ form is 6—11 Cals., and varies with the chain length.

In the preliminary work in this investigation the presence of the two forms was overlooked, so that it was necessary to repeat the determinations. Our thanks are due to Professor Chibnall for advice on the final purification of the hydrocarbons, and to the Colston Society for a grant for the purchase of chemicals.

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