Phase Behaviour of n-Alkanes and Polyethylene

A Thermodynamic Study

BY C. M. L. ATKINSON AND M. J. RICHARDSON

Division of Molecular Science, National Physical Laboratory,
Teddington, Middlesex

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Free energies of fusion, and derived thermodynamic properties, are reported for a series of pure long chain n-alkanes, containing from 19 to 42 carbon atoms, in the temperature range $-35°C \rightarrow$ melting point. Orthorhombic, monoclinic (for which the sub-cell is orthorhombic), triclinic, and hexagonal phases are investigated and the properties of the corresponding polyethylene structures extrapolated using the Flory-Vrij equation. The orthorhombic form (extrapolated m.p., 141·6°C) is always stable under normal conditions but the triclinic modification is only 3-4 J g^{-1} less stable and, once formed, will remain indefinitely at all temperatures until these are such that there is considerable lattice mobility.

In treating bulk polymer crystallization and the growth of polymer single crystals from dilute solution a quantity of major importance is the free energy of fusion of the perfectly ordered crystal of infinite, fully extended chains, ΔG_∞, and its variation with temperature. This is usually estimated [1] by means of equations which directly involve the heat ΔH_∞ of fusion of such chains at their melting point $T_{m\infty}$, the temperature dependence of ΔH_∞, and $\Delta T = T_{m\infty} - T$. There is an approximately 4°C discrepancy between the predicted (145·5°C) [2] and observed [3, 4] melting points of extended chain polyethylene so that in the range 120-130°C, where the crystallization kinetics of this polymer are most conveniently studied, ΔT is ~20 % uncertain. At low temperatures, where this effect is less serious, the heat of fusion is unknown. This region (60-100°C) has become important with the preparation of polyethylene single crystals.

Direct calorimetric measurements of the free energy of fusion of semi-crystalline polymers are difficult because in a temperature range that may extend as much as 70-80°C below the melting point (the actual figure being greatly influenced by the nature of the thermal treatment the polymer has received), irreversible annealing processes occur, and it is not possible to extract the reversible entropy of fusion without making assumptions.[4] There are in general two routes to the properties of the perfectly ordered, infinite polyethylene crystals—the extrapolation of measurements on either n-alkanes of suitable crystal structure,[5] or polymers of differing crystallinity to 100 % crystallinity.[6] This paper reports the free energy, heat and entropy of fusion of a series of pure n-alkanes. These permit the determination of the thermodynamic properties of orthorhombic, triclinic and hexagonal polyethylene. The first is the normal form, found in bulk and solution-crystallized material; the triclinic form occurs in polyethylene produced by the decomposition of diazomethane and in severely cold-worked polymer;[7] hexagonal polyethylene is unknown.

Our interest in the thermodynamic properties of fully extended chain polyethylene is a result of earlier work on the surface energy of polyethylene single crystals.[8] In this, irreversible entropy effects were assumed to cancel for the two polymers investigated. The resulting surface energy was a small difference between two large quantities and it is desirable to obtain independent estimates of the requisite thermodynamic parameters. At the same time, long chain n-alkanes are of interest in their own right. Their complex phase behaviour [9] is determined by the interaction of bulk and surface effects. This latter relates to the efficiency of chain end packing which, for geometrical reasons, is different as the number of chain atoms is odd or even. The results reported here throw light on the relative stability of the several phases.

EXPERIMENTAL

PURE n-ALKANES

Even-numbered n-alkanes up to C36 are available commercially. These contain varying amounts of (mainly) homologous impurities which can have a profound effect on the phase behaviour [9] so all materials were carefully purified. Alkanes or their precursors were generally freed from impurities by low pressure distillation in a spinning band column and analyzed by high temperature (200-350°C) vapour-phase chromatography using an argon ionization detector.

After distillation nonadecane, tricosane, tetracosane (B. Newton Maine) and octacosane (Koch-Light) contained less than 0·1 % of impurities.

Docosane and hexacosane were kindly donated by Dr. A. R. Hawdon of this laboratory. They had been prepared by the electrolysis of zone-refined lauric or myristic acids and were of 99·7 % (0·3 % C21) and 99·8 % (0·1 %, each C25/28) purity respectively.

Tetratriacontaine and dotetracontane were prepared by the electrolysis of stearic (B. Newton-Maine) or behenic (Univol U344, kindly donated by the Universal Oil Co., Hull) acids. These were purified by the distillation of their methyl esters. No impurities were detectable in the fractions eventually electrolyzed. Electrolysis [10] was carried out in boiling methanol in a cell fitted with a reflux condenser. The insoluble reaction product was filtered from the hot methanol, further extracted with boiling methanol and recrystallized from petroleum ether. This treatment effectively removed all products of the disproportionation side reaction from C34 and most from C42, although in this case the material used appeared to contain some 0·2 % of low molecular weight compounds. This may be an artefact due to cracking of the hydrocarbon in the hot (325°C) chromatography column.

Hexatriacontane and octatetracontane were prepared (the latter by Dr. A. R. Hawdon) by a Wurtz reaction [11] on the corresponding " half " halides. Octadecyl bromide (Eastman Kodak) was freed of homologous impurities by distillation. Some cracking to octadec-1-ene invariably occurred but this was not serious as it was readily separated from the Wurtz product. The precursor of octatetracontane was tetracosyl iodide prepared from zone-refined behenic acid of 95 % purity and it was assumed that the final product was of similar purity (chromatographic analysis was not possible).

CALORIMETRY

The adiabatic calorimeter is shown in fig. 1. A minimum temperature of −35°C could be obtained by means of an external cooling coil. A description of the experimental procedure has been given.[8] Two additional calibrations with Calorimetry Conference alumina, to cover the expanded temperature range, gave enthalpy changes from −35→100°C that were trivially (0·04, 0·05 %) lower than found by Furukawa, Douglas, McKoskey and Ginnings.[12] All measurements were made on melt-crystallized material. n-Alkanes were melted in the evacuated calorimeter and a cooling curve observed. Solidification (with no supercooling) to the hexagonal form was complete in about 2 h, transition (following some supercooling) to the low temperature form (column 1, table 1) took approximately another hour. Variants on this cycle involving either careful annealing of the solid for periods of several hours at temperatures just below the melting or transition points, or " quenching " the calorimeter with compressed air (when cooling to the low temperature form was complete in less than half an hour), had no discernible effect on the observed enthalpy and entropy changes. The material investigated had, therefore, an essentially equilibrium structure. At the same time, the thermodynamic cycle was totally reversible as testified by the numerous identical solid→liquid repeat experiments (a partial exception, C34, is discussed below).

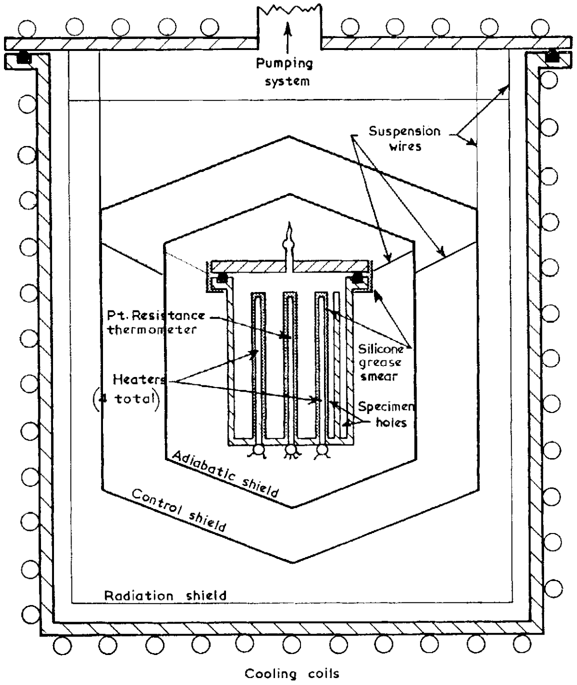

FIG. 1.—Schematic diagram of calorimeter (not to scale). For clarity only two of the specimen holes are shown.

RESULTS

GENERAL

Enthalpy $H_t^{t_r}$, and entropy $S_t^{t_r}$ changes from solid at temperature t to liquid at a reference temperature t_r were calculated as described [8] previously. There is thermal evidence for some residual order in the liquid immediately above the melting point.[13] This appears to be dissipated in a few degrees and for this reason t_r was always 10°C or more above the melting point. The isothermal enthalpy ΔH_t (fig. 2), entropy ΔS_t, and Gibbs free energy ΔG_t, of melting (solid→supercooled liquid) were then computed for the experimental temperatures, using the above data and (1) to represent the supercooled liquid.[13]

$$c_{p,\,l} = 2{\cdot}114+3{\cdot}11\times10^{-3}\,t+1{\cdot}9\times10^{-6}\,t^2 \quad \text{J g}^{-1}\,\text{deg.}^{-1},\ t^\circ\text{C}. \tag{1}$$

(this is independent of the number of carbon atoms in the alkane). For the low temperature forms the free energies of fusion were next fitted to a cubic equation in temperature. The coefficients for the various hydrocarbons are given in table 1. The standard error of individual points for such a fit was about 0·01 J g^{-1} (ΔG_N varies from 0 at the melting point to 79·1 J g^{-1} for C42 at -30°C). Finally, the free energy polynomial was used to compute the enthalpy, entropy and free energy of fusion and, together with (1), the solid heat capacity $c_{p,s}$ at rounded temperatures. The first three of these quantities are reproduced with negligible loss of accuracy over the whole temperature range with the exception of the region (*ca.* 10°C) immediately below the transition point (fig. 2), where ΔH and ΔS are experimentally less than calculated owing to pre-melting effects. The effects virtually compensate for ΔG.

TABLE 1.— FREE ENERGY ΔG_N OF FUSION OF VARIOUS n-ALKANES

$$\Delta G_N = A_0 + A_1 t + A_2 t^2 + A_3 t^3,\ t\text{°C}$$

structure	N	A_0 J g^{-1}	A_1 J g^{-1} deg.$^{-1}$	$A_2 \times 10^4$ J g^{-1} deg.$^{-2}$	$A_3 \times 10^6$ J g^{-1} deg.$^{-3}$
triclinic	22	33·74	−·7398	− 9·12	3·62
	24	38·12	−·7290	− 9·54	3·74
	19	22·04	−·7411	− 6·26	7·00
orthorhombic	23	33·58	−·7205	− 8·19	4·51
	42	59·96	−·6724	− 9·83	3·78
	26	40·98	−·7097	− 9·62	4·19
monoclinic	28	44·85	−·7025	− 9·85	3·92
	36	55·38	−·6811	−10·36	3·60
?(impure alkane)	48	58·20	−·6301	− 9·98	7·44

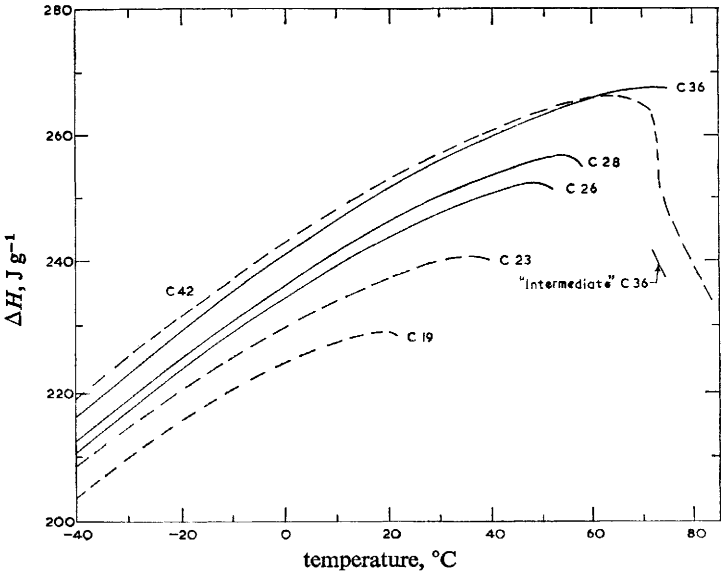

FIG. 2.—Heats of fusion of n-alkanes. Premelting, shown by the decrease in ΔH at the upper end of each curve, is evident near the transition temperature. Orthorhombic alkanes, broken lines; monoclinic alkanes, full lines.

The calculated $c_{p,s}$ diverges slightly, ±1 ‰, from the experimental at the low temperature limit and considerably near the melting or transition temperature where the simple cubic form of ΔG fails to reproduce the infinite heat capacity at the phase transition. The free energy polynomials are merely convenient mathematical devices for accurately presenting our experimental results; in themselves they have no fundamental meaning. Although the true form may well be different, the polynomials of table 1 are adequate to reproduce the second differential (and hence $c_{p,s}$) correctly up to the premelting range. Later, when deriving the properties of polyethylene we shall note the loss of some of this internal consistency.

No details are given of the thermal behaviour of the low temperature structure in the vicinity of the transition where anomalous effects are noted—these are covered here by the general term " premelting " the nature of which we leave unspecified.[14] A major object of the present work was to determine heats, etc. of fusion at low temperatures (i.e., to supercooled liquid) where such effects are absent.

HEXAGONAL PHASE

The n-alkanes C19-C36 undergo a solid-solid transition to a hexagonal form a few degrees below the melting point. It is possible to supercool this below the transition temperature (C19/23/34/36 by 0·6°, C22 2·2°, C24 3·3°, C26 4·4°C and C28 3·6°C) sometimes briefly extending the normal temperature range over which the form exists by a factor of 2-3. Adiabatic calorimetry cannot take full advantage of this because of the time required for the initial thermal equilibration and the slow rate of heating. Our minimum temperatures are therefore those at which this now metastable form remains unchanged for about 1 h. Because of the limited stability range of the hexagonal form it is not possible to ignore " premelting " behaviour and our results must necessarily be treated with this in mind. Consider, e.g., the maximum observed heat of fusion of the hexagonal alkanes examined (table 2). This, 178·3 J g^{-1}, is found with nonadecane, the shortest hydrocarbon investigated. At first sight absurd, this result becomes meaningful when it is realised that hexagonal C19 exists over a 10°C range and the 178·3 J g^{-1} refers to the temperature farthest removed from the melting point. Evidently, premelting effects are analogous to, but greater than, those shown in fig. 2 for the low temperature structures. For this reason we restrict ourselves, in table 2, to giving ΔG and ΔH as functions of temperature. The specific heat, large (4 J g^{-1} deg^{-1} or more) compared with that of the low temperature form, shows considerable curvature but may be calculated from the data of table 2 and eqn. (1).

TABLE 2.—EXPERIMENTAL ENTHALPIES ΔH_N AND FREE ENERGIES ΔG_N OF FUSION OF HEXAGONAL n-ALKANES

N	temp., °C	ΔH_N, J g^{-1}	ΔG_N, J g^{-1}	N	temp., °C	ΔH_N, J g^{-1}	ΔG_N, J g^{-1}
19	23·949	178·3	4·246	26	51·674	167·6	2·237
	25·281	174·8	3·474		53·159	165·4	1·488
	28·102	169·0	1·880		54·722	162·1	·709
	30·359	155·8	·681		55·524	155·8	·290
22	41·700	163·5	1·177	28	55·329	173·6	2·891
	42·254	162·0	·890		56·467	171·0	2·307
	43·344	158·9	·335		57·627	168·7	1·720
					58·806	166·7	1·131
23	40·241	177·8	3·584				
	43·013	164·7	2·098	34	70·057	173·2	1·321
	44·231	160·2	1·479		71·699	169·3	·506
	45·600	153·5	·804				
				36	73·582	177·3	1·110
24	48·596	163·1	1·021		74·131	176·1	·837
	49·740	161·5	·453		74·672	174·8	·560

INDIVIDUAL n-ALKANES

TETRATRIACONTANE

The behaviour of this hydrocarbon in the low temperature region was at variance with all others. The structure obtained by cooling the hexagonal form appeared metastable and slowly changed above about 50°C releasing heat. It was never possible to select conditions whereby the change was essentially complete; at the same time it was not possible to obtain the pure metastable form because of the finite cooling rate of the calorimeter (change occurred in cooling to 50°C). In the hexagonal and liquid states the behaviour of C34 was normal; only the low temperature form was anomalous. Measured heats of fusion were less than those calculated using the data given in table 3 for the orthorhombic or monoclinic forms (e.g., 235·4-236·9 J g^{-1} at 0°C compared with 239·8, orthorhombic, or 240·5, monoclinic). The difference is small but measurable. The crystallographically impure alkane will contain numerous lattice imperfections and a ΔH value less than some mean of those of the two forms is reasonable. In the absence of a pure low-temperature structure we restrict our attention for this compound to the hexagonal and liquid [13] phases.

HEXATRIACONTANE

As indicated by Schaerer, Busso, Smith and Skinner [15] this alkane exhibited two solid-solid phase transitions. In the restricted range of 20°C below the final melting point, ΔG was essentially linear with temperature for all phases and the extrapolated melting points were 74·99°C (monoclinic), and 75·22°C (" intermediate ") and 75·81° C (hexagonal) the corresponding heats of fusion being 269,241 and 174 J g^{-1}. The observed monoclinic-" intermediate" and " intermediate "-hexagonal transition temperatures were 72·95 and 73·74°C respectively with an extrapolated monoclinic-hexagonal transition at 73·51°C. The " intermediate " structure supercools some 3°C but the transition to the monoclinic form, when it occurs, seems complete. The " intermediate " phase has been reported to be orthorhombic,[16] but thermodynamically this is not so.

DOTETRACONTANE

We first assumed this was monoclinic. It soon became evident, however, that the properties were those of an orthorhombic alkane. In addition, there is a small phase transition (ΔH (transition) = 17 J g^{-1}) of unknown origin at about 71·5 (±·3)°C. The high-temperature phase supercools to 65-66°C and melts at 83·77°C. This temperature is close to Broadhurst's extrapolated hexagonal melting point,[9] but ΔH (251·4 J g^{-1} at 71·5°C) is much too large for this.

OCTATETRACONTANE

This was believed to contain some 5 % of homologous impurities (mainly C46). Our results demonstrate the effects of these. For example, ΔH at 0°C is 229 J g^{-1}, whereas the calculated value is 246 J g^{-1} (orthorhombic or monoclinic). Gross premelting behaviour is discernible 40°C or more below T_m, 88·5°C, which is some 2°C below the predicted value.[9] For these reasons we include this hydrocarbon only to emphasize the need for purity in accurate thermodynamic measurements of this type.

DISCUSSION

We now derive the free energy of fusion of several forms of polyethylene and consider present knowledge of the phase behaviour of this polymer in the light of these results. The molar Gibbs free energy ΔG_{mN} of fusion (in general molar quantities are given the subscript m) of an N-mer (an n-alkane containing N carbon atoms) is given by [2]

$$\Delta G_{mN} = N\Delta G_{m\infty} + \Delta G_e - \boldsymbol{R}T\ln N, \tag{2}$$

where $\Delta G_{m\infty}$ is the molar free energy of fusion of the repeat (—CH_2—) unit and ΔG_e the excess end group contribution (end effects will always be considered in molar terms and we drop the subscript in this case). The term in $\ln N$ accounts for the entropy of disruption on melting of regularly packed terminal methyl groups of adjacent layers.[2] The present measurements refer to melt-crystallized material and ΔG_e is an interfacial, rather than surface, free energy. No account is taken of lattice imperfections which are assumed to be negligible in comparison with interfacial effects—no differences were found between quenched and annealed alkanes. The additional term in N^{-1} suggested by Broadhurst [17] is not included; it has a negligible effect on the thermodynamic properties in the temperature range of interest here. Experimentally $\Delta G_{mN} + \boldsymbol{R}T\ln N$ is linear in N as shown in fig. 3. Curves for the orthorhombic and monoclinic forms have only three points each, concentrated at the extremes, so individually there could still be considerable curvature. Collectively, however, the observed parallel behaviour (which is to be expected, see below) over different ranges of N is strong evidence for the validity of (2) and the accuracy of the experimental data. Individual data points were fitted, using a multiple regression analysis, to an equation of the form

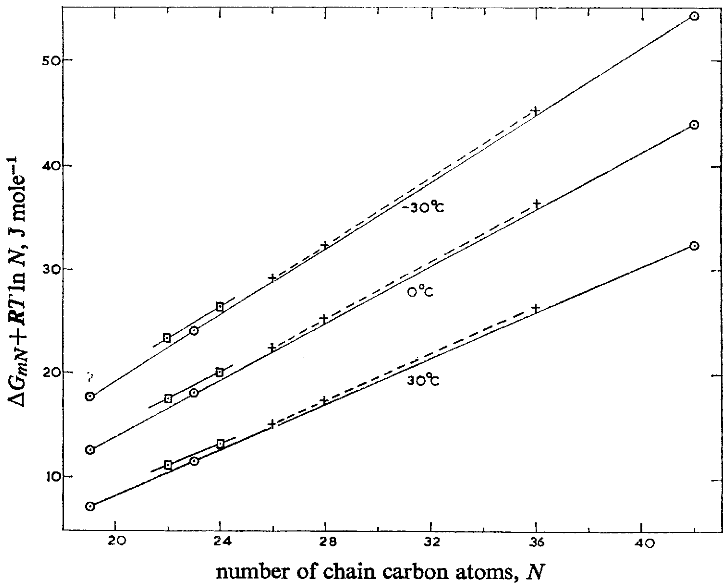

FIG. 3.—The molar free energy of fusion, $+\boldsymbol{R}T\ln N$, as a function of N (the number of chain carbon atoms), temperature, and structure. ⊙, orthorhombic; +, monoclinic; ☐, triclinic alkanes. (The point for C19 at 30°C is extrapolated from the data of table 1).

$$\Delta G_{mN} + \boldsymbol{R}(t+273{\cdot}15)\ln N = N(A+Bt+Ct^2+Dt^3)+a+bt+ct^2, \tag{3}$$

the input variables being the left-hand side of eqn. (3), N, t, and the various powers and products of these last two. The combination in (3) of temperature cubic and quadratic for $\Delta G_{m\infty}$ and ΔG_e respectively gave an excellent representation of the properties of individual alkanes of a given structure.

TRICLINIC STRUCTURES

Although our data only cover a wide temperature range for two similar chain lengths (C22 and C24) we can also use the melting points [9] ($\Delta G_{mN} = 0$) of the lower triclinic alkanes (even numbers C8-C20) which melt directly from this form without going through a transition to a hexagonal phase.

TABLE 3.—BULK $\Delta G_{m\infty}$ AND INTERFACIAL ΔG_e FREE ENERGIES OF FUSION OF SEVERAL n-ALKANE STRUCTURES

$$\Delta G_{m\infty} = A + Bt + Ct^2 + Dt^3 \text{ J(mole —CH}_2\text{— unit)}^{-1},\ t\,^\circ\text{C}$$
$$\Delta G_e = a + bt + ct^2 \text{ J mole}^{-1},\ t\,^\circ\text{C}$$

phase	approx. experimental range (°C)	A J mole^{-1}	B J mole^{-1} deg.$^{-1}$	$C\times10^2$ J mole^{-1} deg.$^{-2}$	$D\times10^5$ J mole^{-1} deg.$^{-3}$	a J mole^{-1}	b J mole^{-1} deg.$^{-1}$	c J mole^{-1} deg.$^{-2}$
triclinic	−40-50	1320	−8·30	−1·70	5·6	−11540	−21·5	·088
orthorhombic	−40-70	1369	−8·30	−1·70	5·2	−13480	−17·4	·110
monoclinic	−40-70	1369	−8·30	−1·70	5·2	−13110	−16·8	·094
hexagonal	20-75	980	−5·91	−3·73	24·7	−7460	1·34	·438
" high temperature "	70-80	1376	−9·80	—	—	−15220	34·7	—

TABLE 4.—CALCULATED AND EXPERIMENTAL ENTHALPIES ΔH_{mN} OF FUSION TRICLINIC AND ORTHORHOMBIC n-ALKANES

		ΔH_{mN}, J mole^{-1}				ΔH_{mN}, J mole^{-1}	
N	temp., °C	expt. ref. (18)	calc. table 3, parameters	N	temp., °C	expt.	calc. table 3, parameters
	TRICLINIC [1]			20	36·6 [2]	(69900) [3]	70070
6	−95·3	13080	13320	22	43·7 [2]	(77200) [3]	78430
8	−56·8	20740	20670	24	49·7 [2]	(86200) [3]	86780
10	−29·7	28720	28570				
12	− 9·6	36840	36730		ORTHORHOMBIC [4]		
14	5·9	45070	45000	11	−43·2	29330 [5]	28830
16	18·2	53360	53340	13	−23·2	37080 [5]	36930
18	28·2	61710	61700	15	− 3·2	45530 [5]	45580
				17	6·9	53690 [5]	53750

[1] temperatures are melting points (ref. (18)); [2] calculated melting points (triclinic parameters, table 3); [3] ref. (15), approximate values only; [4] temperatures just below transition; [5] data of ref. (18) and eqn. (1).

The constants of the polynomials in eqn. (3) are given in table 3, and reproduce the observed $\Delta G_{mN} + RT \ln N$ (which varies from 3770 J mole^{-1} at the melting point of C8 to 26420 J mole^{-1} for C24 at −30°C) with a standard error of 10 J mole^{-1}. The accuracy of the polynomials may be demonstrated by comparing calculated and experimental [18] properties. Results are summarized in table 4 where the agreement is excellent even at temperatures well below our experimental range (−35→50°C). Molar quantities are used to show that the heat of fusion *at the melting point* is linear in N, the increment is 4180 J (CH$_2$ unit)$^{-1}$. The extrapolated melting point of triclinic polyethylene is 138°C where the heat of fusion is 4000 J (—CH$_2$— unit)$^{-1}$. In view of the lengthy extrapolation from 50 to 140°C the two heats of fusion are in good agreement. The high temperature figures are approximate, but they do show that the behaviour of ΔG_∞ is reasonable well above the experimental range for n-alkanes.

A sensitive test of the parameters of eqn. (3) is the calculation of $\Delta c_p = c_{p,l} - c_{p,s}$ and thus, together with (1), $c_{p,s}$. Calculated specific heats are 1-2 % lower than observed. This is good agreement but the true figure is probably better as (1) may be slightly in error at the lowest temperatures (it is based on measurements in the 30-180°C range). The parameters given in table 3 therefore represent the thermodynamic behaviour of the triclinic n-alkanes with a high degree of accuracy in the range $-35 \rightarrow 50$°C and may be used with some confidence in extrapolating outside this range.

ORTHORHOMBIC AND MONOCLINIC STRUCTURES

These are very similar. The internal structure is the same in both cases,[19] differences only arise in the packing of the end groups. In eqn. (2), therefore, the two forms should give lines of identical slope ($\Delta G_{m\infty}$) but different intercept (ΔG_e).

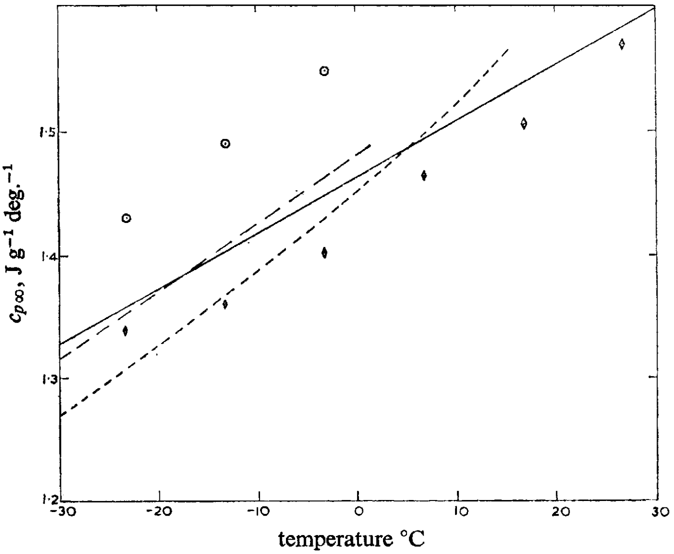

FIG. 4.—The specific heat of extended chain orthorhombic polyethylene via eqn. (4) and monoclinic (full line) or orthorhombic (broken line) results. Dotted line, parameters of table 3 and eqn. (1); ◇, Wunderlich;[20] ○, Broadhurst.[5]

Molar free energies of fusion of C19, C23 and C42 and of C26, C28 and C36 are linear (our assumption that C42 is orthorhombic is based on this) and parallel (the slopes differ by about 1 %). For consistency in discussing n-alkane phase behaviour, we take the mean value of $\Delta G_{m\infty}$ and recalculate ΔG_e for the two structures on this basis (use of a mean $\Delta G_{m\infty}$ leads to changes of, at most, 2 % in ΔG_e). Results are shown in table 3. Calculated and observed [18] heats of fusion of orthorhombic n-alkanes, compared a few degrees below the transition temperature, are shown in table 4. The agreement is again good. Calculated specific heats may differ by a few percent from observed values. This moderate agreement indicates the need for caution in using higher derivatives of our polynomials. These are merely convenient summaries of our results. This is clearly shown when considering the specific heat of extended chain polyethylene. Double differentiation of (2) gives

$$C_{p,N} = NC_{p,\infty} + C_{pe} \tag{4}$$

where $C_{p,N}$ and $C_{p,\infty}$ are the molar heat capacities of solid N-mer and repeat units respectively and $C_{p,e}$ the excess end-group contribution. (Experimentally, analogous terms for the liquid phase that occur in the differential form of (2) are equal).[13] Observed molar heat capacities are indeed linear in N, the orthorhombic form to 0°C and the monoclinic to 30°C. At higher temperatures, premelting starts and gross deviations occur. The derived specific heat $c_{p,\infty}$ of polyethylene is shown in fig. 4 values derived from the two different forms are within about 1 % of each other. The data of Wunderlich,[20] direct measurements on extended chain polyethylene using a differential scanning calorimeter, are also plotted in fig. 4; our values are in good agreement with these and a theoretical estimate.[21] No correction has been made corresponding to that of Broadhurst [5] who found it necessary to compensate for non-excited optical vibrations to give a required melting point of 141·1°C. These " corrected " values are also displayed in fig. 4 along with the " orthorhombic " $c_{p,\infty}$ calculated using the mean parameters of table 3. The large deviations of the last from our directly extrapolated values (eqn. (4)) emphasize our remarks regarding higher derivatives.

HEXAGONAL STRUCTURES

Although all alkanes in the range C19-C36 that were investigated have a hexagonal form, information for each is limited to the free energy of fusion over at most a few degrees. The total temperature span covered is about 20-75°C with little overlap and many gaps. These may be reduced and the temperature range extended by using the melting points of the hexagonal form [9] and certain transition temperatures. Many of the melting points are for materials of uncertain purity but fortunately homologous impurities have little effect on the hexagonal-melt transformation [9] and their use is permissible. Solid-solid transitions, on the contrary, are much affected by such impurities and only the orthorhombic-hexagonal transition temperatures of carefully characterized C 11/13/15 and 17 [18] have been used. ΔG_{mN} was calculated using the orthorhombic parameters of table 3. Fitting the results to the polynomials of eqn. (3) gives the hexagonal parameters of table 3. Free energies are estimated to be correct to ± 2 % at 50°C and ± 4 % at 30 and 70°C.

So far we have not considered the validity of the $RT\ln N$ term of eqn. (2) and (3) when applied to the hexagonal phase, in which the component molecules are rotating. The above term is an entropy contribution [2] from the disruption on melting of regular terminal methyl-terminal methyl sequences in adjacent monolayers. Is this " link " from one monolayer to another preserved in the hexagonal phase or have adjacent methyl group arrays become randomized with respect to each other? $\Delta G_{m\infty}$ and ΔG_e were recalculated omitting the logarithmic term. The resulting parameters gave poorer agreement with experimental results. More significantly, on omission of the queried term the heat of fusion of hexagonal polyethylene at 75°C is predicted to be less than the experimental value for C36 at this temperature. This is grossly in error and we conclude that methyl group pairing remains in hexagonal alkanes. The parameters of table 3 give the free energy of fusion of hexagonal polyethylene with an uncertainty of a few percent; this is sufficient to cause significant loss of accuracy even in ΔH_∞ which we estimate to be 200 ± 10 J g^{-1} in the 20-75°C range.

PHASE BEHAVIOUR OF POLYETHYLENE

The free energy and heat of fusion of the several forms of polyethylene, calculated with the parameters of table 3, are shown in fig. 5 and 6 respectively. The low-temperature extrapolations (< -35°C) are substantially correct since for the lower alkanes ΔG and ΔH are well represented by these parameters. The extrapolated melting points are 141·6°C (orthorhombic) and 138·0°C (triclinic). The former is very close to the highest reported experimental melting points [3, 4] although a method extrapolating the melting points of the n-alkanes gives 145·5°C.[2] Whatever the absolute value, the melting point of the orthorhombic form is undoubtedly higher than that of the triclinic modification. The wide angle X-ray pattern [22] of the latter disappears at about 100°C where we suggest there is sufficient lattice mobility to allow transition to the more stable orthorhombic structure. This stability persists below -100°C (and the curves slowly diverge as the temperature decreases) but the free energy difference is only 3-4 J g^{-1} so the metastable triclinic form can exist indefinitely at, say, room temperature. The difference between the two structures is roughly that the centre atom of the orthorhombic unit cell is approximately at right-angles to its four neighbours whereas in the less stable form the zigzag planes of all molecules are parallel. Teare and Holmes [23] have pointed out how cold working favours the transformation to the latter state. The triclinic phase may even become stable at high pressures (as in cold working) although specific volume changes on melting, which give $(\partial \Delta G/\partial p)_T$, are nearly equal for the two forms.[7] Teare and Holmes suggest that in rapid crystallization " mistakes " (chains trapped in an incorrect orientation) may occur, resulting in the triclinic form. This is at variance with the results of Fatou, Baker and Mandelkern [22] who found no trace in quenched material. It only occurred at low temperatures (<100°C) subsequent to extensive crystallization at higher temperatures. Under these conditions crystallization is substantially complete, residual crystallization is hampered, and " mistakes " of the

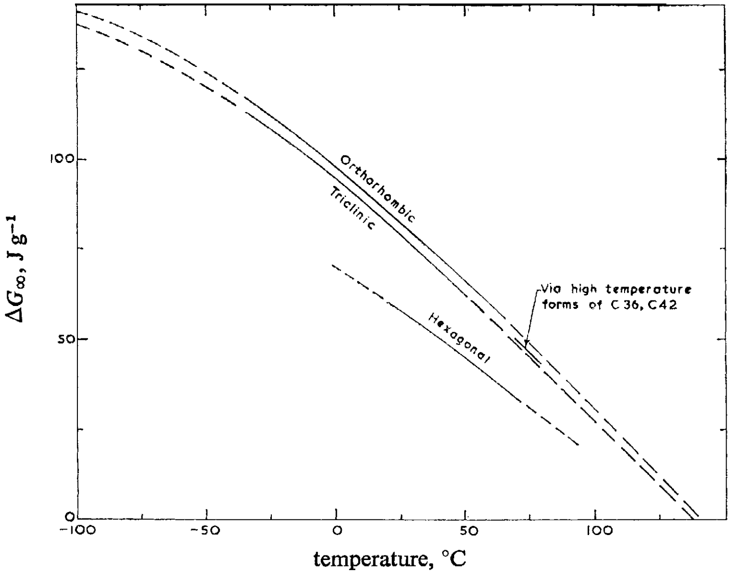

FIG. 5.—The free energy of fusion of extended chain polyethylene structures. Broken lines represent extrapolated values (data of table 3).

type suggested by Teare and Holmes may now become relatively common. ΔH for the two froms differs by only about 2 % rendering void most enthalpic methods of detecting the metastable phase, even in relatively large concentration.

The hexagonal phase is considerably less stable than the forms discussed above. At the same time the temperature variation is less than for these and a transition to the hexagonal form, akin to that found in the alkanes, is in principle possible at high temperatures (a triclinic-hexagonal transition is indeed observed in certain polyamides at high temperatures).[24] Experimentally, however, there is no evidence for this and we assume that the free energy curves of this and the stable form intersect above the melting point of the latter. Since $\Delta G_{m\infty}$ is of restricted accuracy for the hexagonal structure no attempt is made to extrapolate the cross-over temperature from the data of table 3.

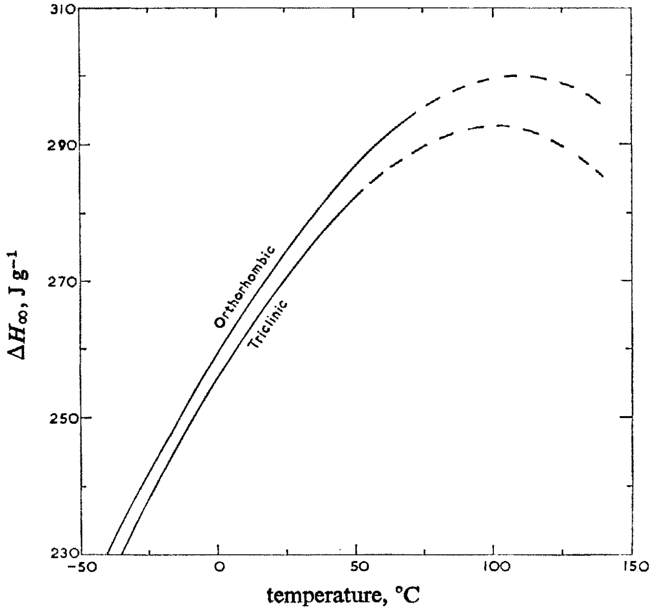

Fig. 6.—The heat of fusion of extended chain orthorhombic and triclinic polyethylene. Broken lines represent extrapolated values (data of table 3).

INTERFACIAL EFFECTS AND THE STRUCTURE OF n-ALKANES

The interfacial free energies of all structures investigated are shown in fig. 7. Orthorhombic and monoclinic forms are directly comparable on this basis as $\Delta G_{m\infty}$ is the same for both these phases. Thermodynamically the monoclinic structure is the more stable but Broadhurst[9] has indicated how symmetry conditions prevent N-mers with N_{odd} crystallizing in a monoclinic form. All high N_{even} alkanes would, however, be expected to have this form and it is therefore surprising to find orthorhombic C42. This occurs following a solid-solid transition at about 65°C and it may be metastable—although annealing of this form at 70°C for 15 h had no effect. In this connection we cite the work of Ohlberg[25] on the structure of melt-crystallized alkanes as a function of time. Initial solidification led to a crystallographic mixture which changed only slowly (over a period of months) to the stable form predicted by

Broadhurst. In the present work both monoclinic and triclinic C26 could be obtained by varying the conditions of crystallization. The parameters given in table 3 show that the triclinic form is slightly more stable but the difference is so small that the actual structure is probably determined by kinetic factors. Lower, even-numbered alkanes are unambiguously triclinic and higher ones monoclinic. The stability of the triclinic phase is attributable to more efficient end-group packing, the resulting methyl-methyl group dispersion forces being stronger (ΔH_e is some 3000 J mole^{-1} larger) for methyl groups in triclinic as opposed to monoclinic structures. Above C26 these effects are less important and the crystal structure is determined by the greater stability of the orthorhombic sub-cell of the bulk phase.

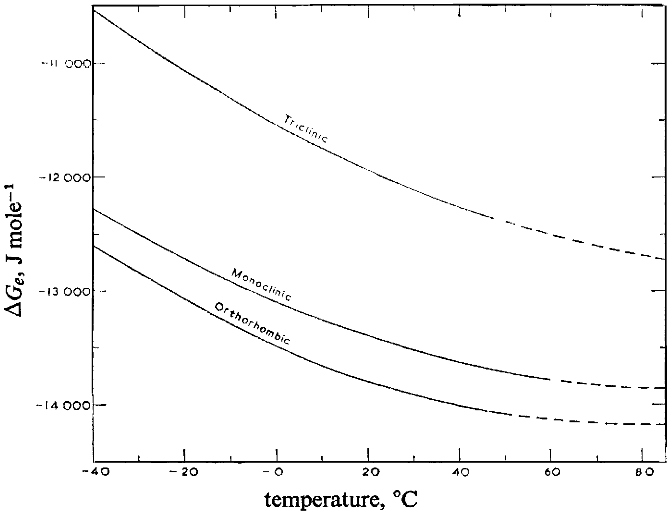

FIG. 7.—The interfacial free energy of various alkane structures. Broken lines represent extrapolated values (data of table 3).

Ohlberg [25] suggested that the phase of unknown structure which appeared as a minor component in diffraction patterns of C32 and C36 was the precursor of a stable phase of long chain alkanes. This could account for our " intermediate " C36 and high temperature form of C42. Assuming that the two have the same structure we may derive the " high temperature " parameters of table 3 ; the restricted 70-80°C range is emphasized. The stability of this phase is again due to end effects, the bulk phase being less stable than that of orthorhombic polyethylene (fig. 5). Because of the restricted input data no attempt is made to find the temperature and molecular weight range of this structure. For C34 the calculated free energies of fusion of the " high temperature " and monoclinic forms are equal just below the melting point. This might explain the anomalous behaviour of our C34.

In general, solution of the free energy equations using the data of table 3 give the melting points of hexagonal and triclinic alkanes to better than 0·1°C. Transition temperatures are reproduced less accurately, deviations of a degree from the values tabulated in [9] being common (impurity errors in the experimental transition temperatures are expected to be, at most, a few tenths of a degree). This reflects the uncertainties in our bulk and interfacial free energies. Relatively small changes in thermodynamic properties have such gross effects on transition temperatures because these are determined by the intersection of two free energy curves of similar shapes and with slopes of the same order. Because of this, our suggested errors for ΔG_∞

(hexagonal) may be high; ±4 % in ΔG_{∞} implies possible errors of several degrees in the calculated transition temperature which are certainly not found.

The interfacial free energies of fig. 7 may be separated into enthalpy and entropy contributions (fig. 8). The lower intermolecular crystal energy implied by the negative value of ΔH_e may be ascribed to the weaker dispersion forces of the terminal methyl groups with respect to methylene.[2] The change with temperature shows how the methyl group separation increases relative to methylene. A positive value of ΔS_e implies some loss of the precise ordering possible if all lattice units were methylene groups. Opposed to this is the effect of thermal energy which permits increasing motion of the whole molecule with rising temperature so the relative effect of this disordering term decreases as the thermal energy is increased. In the derivation of (2) an additional, negative, constant has been absorbed in ΔS_e.[2] The apparent extrapolated change of sign of ΔS_e is due to the increasing influence of this constant term. The interfacial free energy curves of fig. 7 are nearly linear (deviations amount to only ±1 %) up to about 50°C, the approximate upper limit of most alkane measurements. We have, however, refrained from representing ΔG_e in this way as direct enthalpy measurements show unambiguously that ΔH_e is the strong function of temperature shown in fig. 8. In view of the extrapolations involved in both methods, there is good agreement between the orthorhombic interfacial free energy at the melting point of polyethylene as derived by Flory and Vrij [2] (13300 J mole^{-1}) and the present value (13700 J mole^{-1}), despite the different enthalpy and entropy components. The small change in ΔG_e with temperature (a mean, ±10 %, covers all values) is to be contrasted with the changes in the *surface* free energy of polyethylene crystals [26] which contain re-entrant chains.

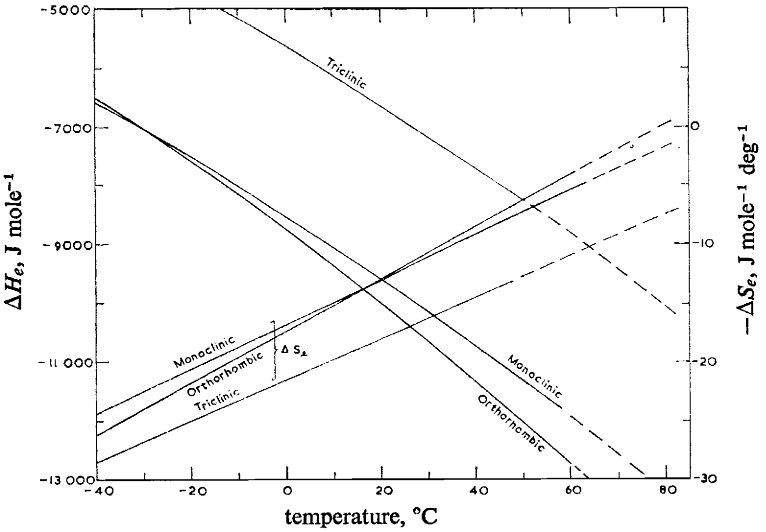

FIG. 8.—Interfacial enthalpies and entropies (sign reversed for clarity) of various alkanes. Broken lines represent extrapolated values (data of table 3).

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