The Melting Temperatures of the n–Paraffins and the Convergence Temperature for Polyethylene

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The extrapolation of the melting points, T_m, of the n-paraffins to large chain lengths ($n \to \infty$) is reexamined in order to resolve the differences in the proposed values of the convergence temperature $T_0 = \lim_{n \to \infty} T_m$. Experimental liquid entropies can be made consistant with a term, $R \ln n$, proposed by Flory and Vrij. This term effectively replaces the well-known expression $T_m = T_0 (n+a)/(n+b)$ with an expression $T_m = T_0 (n+a)/(n + \ln n + b)$; thus, slowing the convergence rate and increasing T_0 from 141.1 °C to 144.7 °C. Independent estimates of the parameters in the melting relationship were obtained from thermodynamic data and the least squares estimate of $T_0 = 144.7$ °C (calculated from 33 melting points with a standard deviation of $T_m = 0.3$ °C) could not be altered by more than ± 0.5 °C by any reasonable variation of the parameters. A simplified melting expression is obtained for polyethylene which includes both the chain end and fold surface energies, and it is shown that chain end effects partly account for the discrepancy between the 144.7 °C convergence temperature and experimental melting temperatures (~ 139 °C) of extended chain polyethylene crystals.

Key Words: Convergence temperature, melting temperatures, methyl surfaces, n-paraffins, polyethylene, thermodynamic properties.

1. Introduction

In 1962, I published a paper [1][1] which was intended to establish on thermodynamic grounds an analytical expression $T_m = f(n)$ for the orthorhombic normal paraffin melting temperatures, T_m, as a function of the number of carbon atoms per molecule, n. That work resulted in an expression,

$$T_m = T_0 \frac{n+a}{n+b} \tag{1}$$

of well-known form in use since 1931. The constants were found to be $a = -1.5$, $b = 5.0$, and $T_0 = \lim_{n \to \infty} T_m(n) = 414.3$ °K (141.1 °C) with an estimated error of ± 2.4 °K.

In 1963 Flory and Vrij [2] reexamined the thermodynamic basis for the paraffin melting equation and modified the assumption [1] of a linear dependance of the liquid entropy on n, by adding a term, $R \ln n$, to account for the disordering of the methyl layers during melting. The effect of this additional term was to raise the value of T_0 from 414.3 °K (141.1 °C) as predicted by eq (1) to 418.5 ± 1 °K (145.3 °C). The difference between these two values is quite significant

when calculating, for instance, the surface free energy of polyethylene crystals from melting data or crystal growth rates. It is the primary purpose of this paper to investigate this discrepancy and to establish more firmly a value for T_0.

2. Liquid Entropies

The n-paraffin melting relationship, $\Delta G(T_m, n) = \Delta H(T_m, n) - T_m \Delta S(T_m, n) = 0$, can be obtained following Flory and Vrij by equating the Gibbs free energy of fusion (written as a function of temperature and n) to zero. If the dependence of ΔG on n is linear, one obtains equation (1). If not, one obtains a more general form of (1) where a and b are functions of n. The limiting value, T_0, depends on the functional form of $\Delta G(T_m, n)$. The solid enthalpies and entropies and the liquid enthalpies are experimentally observed to be linear with n [3], and the problem centers around the functional form of the liquid entropies, $S_l(T, n)$, which experimentally are found to show some nonlinearity. This nonlinearity in $S_l(T, n)$ appears in $\Delta G(T, n)$ and alters T_0 in a way which depends on the magnitude and functional form of the nonlinear terms.

Since it is the liquid entropy that supplies the nonlinear terms to the melting relationship one can investigate these terms independently of the melting temperatures by looking at the n-dependence of experi-

mental liquid entropies. Experimental liquid entropies for the n-paraffins from C_5H_{12} through $C_{18}H_{38}$ at 300 °K are listed in table 1.[2] If S_l were linear, then differences between consecutive values of $S_l = S_{cl}n + S_{el}$ would be constant, and if $(S_l - R \ln n)$ were linear as indicated by the work of Flory and Vrij then differences between consecutive values of $(S_l - R \ln n) = S_{cl}n + S_{el}$ would be constant. These differences are plotted in figure 1 as a function of n. Figure 1 shows that neither S_l nor $S_l - R \ln n$ are linear with n, and that the $R \ln n$ term is too strong and overcompensates for the non-linearity in S_l. The magnitude of the $R \ln n$ term could be reduced or alternatively a term like $1/n$ could be added with or without the $R \ln n$ term. Included in figure 1 are consecutive differences of the function $(S_l - R \ln n - 5.6/n)$ which do not show any increasing or decreasing trend with n.

FIGURE 1. *Differences between experimental liquid entropies,* S_1, *(open circles);* $S_1 - R \, ln \, n \, (triangles);$ *and* $S_1 - R \, ln \, n - 5.6/n \, (closed circles),$ *for consecutive* n-paraffins at 300 °K *versus average number of carbon atoms.*

TABLE 1. *Experimental values of the absolute liquid entropies in cal/mol · deg at 300 °K for the* n-paraffins with from 5 to 18 carbon atoms per molecule

n	S_l(cal/mol/deg)
5	63.21[a]
6	71.05
7	78.86
8	86.67
9	94.505
10	102.272
11	110.019
12	117.869
13	125.591
14	133.407
15	141.111
16	148.865
17	156.68
18	164.37[b]

[a]Data obtained from the U.S. Bureau of Mines, Bartlesville, Oklahoma.
[b] The value for C_{18} was extrapolated to 300 °K from its melting point, 301.3 °K.

A more formal analysis of the entropy data is given in table 2 which shows coefficients and standard devia-

tions resulting from least squares fits of the liquid entropy data for several functions. The lowest standard deviation was obtained using $S_l = S_{cl} + S_{el} + R \ln n + c/n$, but the fit using $S = S_{cl} + S_{el} + cR \ln n$ was also quite satisfactory. The inclusion of a $1/n^2$ term seems an unnecessary complication. But we are still not able to select unambiguously a functional form for S_l based on the data alone. In order to clarify this situation we have examined the statistical theory of polymer chains based on the liquid lattice model. This model allows one to calculate an expression for the entropy of a polymer chain in its liquid phase and leads not only to an unalterable $R \ln n$ term as pointed out by Flory and Vrij but also predicts terms in powers of $1/n$ (see appendix A).

It seems most reasonable to conclude then that the correct expression for the liquid entropy of the n-paraffins as a function of n and T is

$$S_l(n, T) = S_{cl}(T)n + S_{el}(T) + R \ln n + 5.6/n, \qquad (2)$$

where terms in $1/n^2$ have been ignored as has the temperature dependence of the relatively unimportant $1/n$ term.

TABLE 2. *Least square fits of the liquid* n-paraffins entropies at 300 °K for several functions

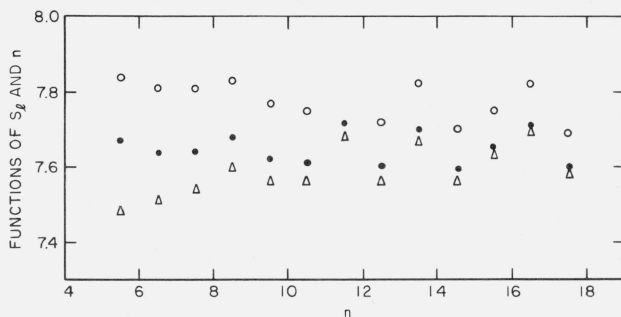| Function	Standard deviation of function	Constants and their (standard deviations)			
		S_c	S_e	c	d
$S_l = S_{cl}n + S_{el}$	(0.061)	7.78 (0.004)	24.4 (0.05)		
$S_l = S_{cl}n + S_{el} + cR \ln n$	(0.028)	7.71 (0.010)	23.4 (0.14)	0.38 (0.06)	
$S_l - R \ln n = S_{cl}n + S_{el}$	(0.092)	7.59 (0.006)	21.9 (0.02)		
$S_l - R \ln n = S_{cl}n + S_{el} + c\left(\dfrac{1}{n}\right)$	(0.027)	7.65 (0.005)	20.7 (0.11)	5.61 (0.49)	
$S_l - R \ln n = S_{cl}n + S_{el} + c\left(\dfrac{1}{n}\right) + d\left(\dfrac{1}{n}\right)^2$	(0.028)	7.66 (0.016)	20.4 (0.50)	7.73 (4.61)	−6.04 (13.0)

3. Melting Equation

By expanding $\Delta G = \Delta G_c n + \Delta G_e - RT \ln n - 5.6 T/n$ about $T = T_0$ (see reference 2 for details) one finds,

$$n\Delta H \frac{\Delta T}{T_0} - n\frac{\Delta C_p}{2T_0}(\Delta T)^2 - T_m\left[R \ln n + 5.6\left(\frac{1}{n}\right)\right]$$

$$= T_m\Delta S_e - \Delta H_e + \frac{\Delta C_{pe}}{2T_0}(\Delta T)^2 \qquad (3)$$

which differs from Flory and Vrij's eq (8) only in that it includes the $(1/n)$ term and the ΔC_{pe} term which they chose to neglect. Direct calculations show that neglected terms remain below 1 percent of the magnitude of the leading terms in eq (3). Here $\Delta T = T_0 - T_m$; $-\Delta H/T_0$ and $-\Delta C_p/T_0$ are the first and second temperature derivatives of ΔG_c at $T = T_0$; $-\Delta S_e$ and $-\Delta C_{pe}/T_0$ are the first and second temperature derivatives of ΔG_e at $T = T_0$; and $\Delta H_e = \Delta G_e + T_0\Delta S_e$. Rewriting (3) in the form of (1) one obtains,

$$T_m = T_0 \frac{n + \dfrac{\Delta H_e - T_0\Delta C_{pe}/2}{\Delta H - T_0\Delta C_p/2}}{n + \dfrac{T_0}{\Delta H - T_0\Delta C_p/2}\left[\left(\Delta S_e - \dfrac{\Delta C_{pe}}{2}\right) + R \ln n + 5.6\left(\dfrac{1}{n}\right) - \left(\dfrac{\Delta C_p}{2}n + \dfrac{\Delta C_{pe}}{2}\right)\dfrac{\Delta T}{T_0}\right]}. \qquad (4)$$

This result is equivalent, except for the $\ln n$ and $(1/n)$ terms, to eq (1.6) in reference [1]. Equation (4) can be abbreviated as

$$T_m = T_0 \frac{n + a}{n + B(n)}$$

which can now be treated as a generalization of (1). One can calculate from experimental T_m values

$$B(n) = \frac{T_0}{T_m}(n + a) - n, \qquad (5)$$

and these $B(n)$ values are shown in figure 2 for various values of T_0 and a. The quantity $B(n)$ can also be expressed from equation (4) in the following form:

$$B(n) = \frac{T_0}{\Delta H - T_0\Delta C_p/2}\left[\left(\Delta S_e - \frac{\Delta C_{pe}}{2}\right)\right.$$

$$\left. + R \ln n + \frac{5.6}{n} - \left(\frac{\Delta C_p}{2}n + \frac{\Delta C_{pe}}{2}\right)\left(1 - \frac{T_m}{T_0}\right)\right]. \qquad (6)$$

The thermodynamic quantities in eq (6) were assigned values as follows. The molar entropies and enthalpies for the liquid and solid n-paraffins (see footnote 2) were plotted as a function of n. The slopes and intercepts of these curves equal respectively $S_c(T)$, $H_c(T)$ and $S_e(T)$, $H_e(T)$ and differences between the liquid and solid values gave $\Delta S_c(T)$, $\Delta H_c(T)$ and $\Delta S_e(T)$, $\Delta H_e(T)$ which were then extrapolated to $T = T_0$ to give ΔH, ΔS, ΔS_e, and ΔH_e. ΔC_p and ΔC_{pe} were taken as the slopes of the $\Delta H(T)$ and $\Delta H_e(T)$ curves at $T = T_0$. (A more detailed description of this procedure can be found in [3].) The results of these calculations are summarized in table 3. Numbers from table 3 were used to evaluate the various terms in eq (6) and these terms are shown in figure 3.

TABLE 3. *The values of several quantities at 418 °K determined from thermodynamic data on the n-paraffins*

Quantity	Value	Estimated possible error [a]
ΔH	1000	± 25 cal/mol
ΔC_p	0.5	± 0.5 cal/mol deg
ΔG_e	-3400	± 500 cal/mol
ΔH_e	-3000	± 500 cal/mol
ΔS_e	1.0	± 0.5 cal/mol deg
ΔC_{pe}	-8.0	± 4.0 cal/mol deg

[a] The estimates of error are intentionally pessimistic and serve only as a guide in examining the sensitivity of eq (4) to extreme variations of these quantities.

Figures 2 and 3 are useful for getting a feeling for how the various terms in $B(n)$ affect T_0 and a. In figure 2 the change in shape of $B(n)$ at small n is associated with a change in a, whereas a change in the slope of $B(n)$ at large n is associated with a change in T_0. Figure 3 shows that the term which accounts mostly for the shape of $B(n)$ at large n is the $\ln n$ term and that the remaining three n-dependent terms in $B(n)$ mostly affect the shape of $B(n)$ at small n. The quantity $(\Delta S_e - \Delta C_{pe}/2)$ is treated here as an adjustable parameter and is used to regulate the vertical position of $B(n)$.

When $B(n)$ was assumed constant as was done in [1], curve fitting of the melting equation gave $a = -1.5$ and $T_0 = 414.3$ °K. These results can be anticipated from figure 2 which shows that straightest curve is the $a = -1.5$ curve and the flattest curve would be for T_0 a little less than 415. Including a $\ln n$ term and a partially compensating ΔC_p term in $B(n)$ as was done by Flory and Vrij gives $B(n)$ a shape similar to the $a = -3.0$ curve and a large-n slope similar to the 419 °K curve. Thus one can anticipate their results of $T_0 = 418.5$ °K and $a = -2.7$. In this present paper we are adding to $B(n)$ the $1/n$ and ΔC_{pe} terms and from figure 3 we can anticipate that these will raise the small-n end of the curve and thus significantly reduce the magnitude of a but only slightly lower the large-n slope and thus only slightly reduce the T_0 value found by Flory and Vrij.
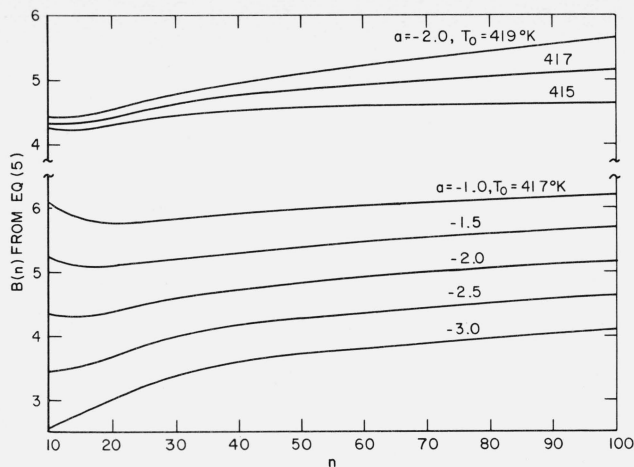
FIGURE 2. B(n), *calculated using eq (5), as a function of* n *for different values of parameters* T_0 *and* a.
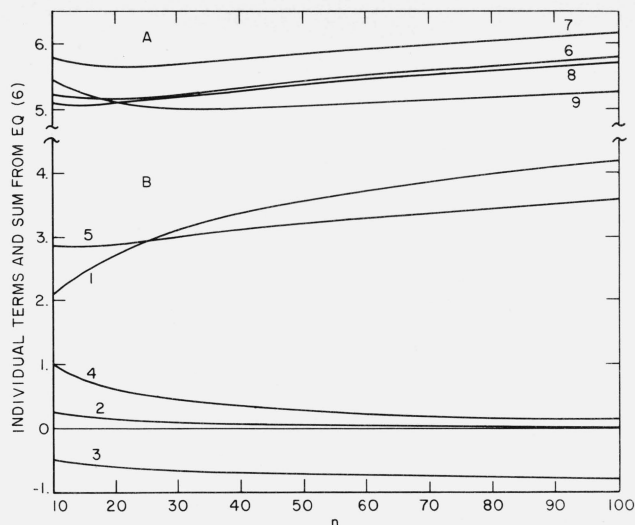

FIGURE 3. A. B(n), *calculated from eq (6) using different values for the thermodynamic quantities.* B. *Values of the four variable terms in eq (6) and their sum using the values in table 3 and* $T_0 = 418\,°K$.

The curves are (1) $b_0 R \ln n$ (where $b_0 = T_0/(\Delta H - T_0 \Delta C_p/2) = 0.47$); (2) $5.6\ b_0(1/n)$, (3) $b_0(\Delta C_p/2)n(\Delta T/T_0)$, $\Delta C_p = 0.5$; (4) $b_0(\Delta C_{pe}/2)(1 - T_m/T_0)$, $\Delta C_{pe} = -8$; (5) sum of curves 1–4, (6) same as (5) with $b_0(\Delta S_e - \Delta C_{pe}/2) = 5\ b_0$ added, (7) same as (6) with $\Delta C_{pe} = -12$, (8) same as (6) with $\Delta C_p = 1.0$, (9) same as (6) with $\Delta C_p = 2.0$.

In other words, the $\ln n$ term is the crucial one in $B(n)$ as far as establishing T_0 is concerned, and the constants in the other terms can be varied within the generous range of uncertainties given in table 3 without appreciably affecting T_0. In the following section the results of fitting the melting temperatures to eq (4) will be shown to verify these anticipated results.

4. Fitting the Melting Data

Previously, eq (1) was fit to 14 values of T_m for the orthorhombic-liquid transition of the n-paraffins with $44 \leqslant n \leqslant 100$ [1]. Flory and Vrij calculated 19 additional values for $11 \leqslant n < 44$ from data on the enthalpies and temperatures of the orthorhombic-hexagonal and hexagonal-liquid transitions. The resulting 33 values are listed in their paper. The values for the five shortest paraffins were found to be smaller by 0.1, 0.3, 0.2, 0.2, and 0.1 °C respectively than those given by Flory and Vrij, based on quadratic extrapolations of experimental free energies.

These data were fit by least squares using an Omnitab program to eq (4) in the form:

$$T_m(n) = T_0\left(\frac{n}{n + B(n)}\right) + T_0 a\left(\frac{1}{n + B(n)}\right),$$

where $B(n)$ is given by eq (6).

Such a fit yields least squares estimates of T_0 and $T_0 a$ with the assumption that the bracketted terms are known functions of n and that all experimental uncertainty is contained in $T_m(n)$. Thus all constants in $B(n)$ had to be assigned values before fitting. To adapt to these restrictions we assigned values to ΔC_p, ΔC_{pe} and the factor $T_0/(\Delta H - T_0 \Delta C_p/2)$ from table 3 and then did the least squares fitting for each of a series of closely spaced values of $(\Delta S_e - \Delta C_{pe}/2)$. The best value for $(\Delta S_e - \Delta C_{pe}/2)$ was taken as that which gave a minimum standard deviation in T_m for fixed values of ΔC_p, ΔC_{pe}, and $T_0/(\Delta H - T_0 \Delta C_p/2)$. This method yields a pseudo-least-squares value for $(\Delta S_e - \Delta C_{pe}/2)$, and the standard deviations were adjusted to account for this third constant. The other constants in $B(n)$ could have been handled in the same way except that the fit was fairly insensitive to them. Instead, the values of ΔC_p, ΔC_{pe}, and $T_0/(\Delta H - T_0 \Delta C_p/2)$ were varied either together or singly within the range allowed by table 3 and the fit was repeated each time yielding new values for T_0, $T_0 a$ and $(\Delta S_e - \Delta C_{pe}/2)$. In this way the effect of variations in the assigned constants on the values of the derived constants could be observed directly. To eliminate the difficulty of having the ratio $\Delta T/T_0$ appear in $B(n)$, calculated values for this ratio were fed back into $B(n)$ until the calculated T_0 became constant. The results were quite insensitive to the initially assumed value of $\Delta T/T_0$, and T_0 converged to a constant value to better than 4 figures after 2 iterations.

Using $T_0/(\Delta H - T_0 \Delta C_p/2) = 0.47$, $\Delta C_p = 0.5$ and $\Delta C_{pe} = -8.0$ gave best fit values of $T_0 = 417.9\ °K$, $a = -1.5$ and $(\Delta S_e - \Delta C_{pe}/2) = 5$. The values in table 3 give independently $a = -1.5$ and $(\Delta S_e - \Delta C_{pe}/2) = 5$, which is encouraging agreement. The standard deviations for T_m and T_0 based on 33 minus 3 degrees of freedom were calculated to be 0.30 and 0.12 °K respectively.[3] Changing the assumed values of ΔC_p, ΔC_{pe}, and $T_0/(\Delta H - T_0 \Delta C_p/2)$ within the limits allowed in table 3 did not alter the calculated value of T_0 by more than ± 0.5 °K. The results are as anticipated by the arguments of the previous section.

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[3] For comparison, the melting data were fit to eq (1) and gave $T_0 = 413.8$ °K with standard deviations of 0.36 and 0.14 °K respectively. Hence, eq (4) does offer some improvement of fit over eq (1).

The results lead strongly to the conclusion that T_0 is very nearly equal to 417.9 °K. To apply an uncertainty based on three standard deviations (3×0.12 °K) is misleading since it does not take account of uncertainties in the functional form of (4), but it is difficult to see how T_0 could be altered by more than 0.5 °K by any reasonable means. Hence, the results essentially confirm those of Flory and Vrij with a slight but significant reduction in their estimate of $T_0 = 418.5 \pm 1.0$ °K because of two relatively small terms which they neglected.

5. Discussion

The highest experimentally observed melting temperature for polyethylene is 138.7 °C, and for polymethylene, 141.4 °C [6, 7]. Both of these were extended-chain pressure-crystallized specimens. Brown and Eby [8] used a form of eq (1) to extrapolate the melting temperatures of polyethlene to infinite molecular weight and found $T_0 = 143.5$ °C. By the same procedure Fujiwara and Yoshida [9] found $T_0 = 144.8$ °C. Weeks [10] used a plot of crystallization versus melting temperatures and extrapolated the data to the line $T_c = T_m$ to find $T_0 = 145.5$ °C. Thus, a value of T_0 (paraffins) $\simeq 145$ °C is not out of line with extrapolated values for T_0 (polyethylene), but is significantly higher than experimentally observed melting points for extended chain polyethylene where there should be no effect from chain folded surfaces. An overall explanation of the melting data for polyethylene seems still to be lacking.

It is of interest to examine eq (3) in the limit of large n,

$$T_m \text{ (paraffins, } n \gg 1) = T_0 \left(1 + \frac{\Delta G_e - R T_0 \ln n}{n \Delta H} \right) \quad (7)$$

For a polymer, one would observe some contribution from the $R \ln n$ term if the chain ends were ordered in the crystal. Given a narrow length-fraction of polyethylene, one might find a high degree of chain end ordering in extended chain crystals, and very little chain end ordering in the folded chain crystals. Assume that ΔG_e is the same for any type of crystal and that a term $R T_0 \ln \alpha n$ takes care of end group ordering effects where α has a value from $1/n$ (completely disordered) to 1 (completely ordered), depending on n, the distribution in length and the mode of crystallization. Assume further that ΔG_f is the free energy contributed to the crystal by a mole of folds in excess of that attributable to the associated CH_2-groups if in a nonfolded configuration, and that the folds, when present in the crystal, occur in regular planes separated by n_f carbon atoms. We can now modify eq (7) as follows,

T_m (polyethylene, $n \gg 1$)

$$= T_0 \left[1 + \frac{\Delta G_e - T_0 R \ln \alpha n}{n \Delta H} - \frac{\Delta G_f}{n_f \Delta H} \right] \quad (8)$$

in order to explicitly account for both chain ends and folds.

Equation (8) can be compared to the well-known equation,

$$T_m = T_0' \left[1 - \frac{2 \sigma_e}{l \Delta h_f} \right]. \quad (9)$$

Here $\sigma_e = -(C/2A) \Delta G_f$ erg/cm², $A = 18.5 \times 10^{-16}$ cm² $=$ the effective cross-sectional area of a CH_2 chain, $C = 6.95 \times 10^{-17}$ ergs-moles/cal-molecule is a dimensional conversion constant, $l = 1.27\, n_f \times 10^{-8}$ cm and $\Delta h_f = (C/1.27 \times 10^{-8} A) \Delta H = 2.96 \times 10^9$ ergs/cm³ is the heat of fusion of a CH_2 chain crystal.

One can now write (8) in the form of (9) to a good approximation by letting

$$T_0' = T_0 \left[1 + \frac{\Delta G_e - T_0 R \ln \alpha n}{n \Delta H} \right] \quad (10)$$

where T_0' is the effective convergence temperature for a polymer containing end groups. T_0' was calculated using $T_0 = 417.9$, $\Delta G_e = -3{,}400$ cal/mole, $\Delta H = 1000$ cal/mole for the two limiting values of α_0, and the results are shown in figure 4, plotted as a function of the number of chain ends per 1000 carbon atoms.

Notice that the apparent convergence temperature for our hypothetical polyethylene is lower when the chain ends are ordered ($\alpha = 1$) than when the chain ends are disordered ($\alpha = 1/n$). This result is of interest primarily because the experimental results mentioned at the beginning of this section give higher values for
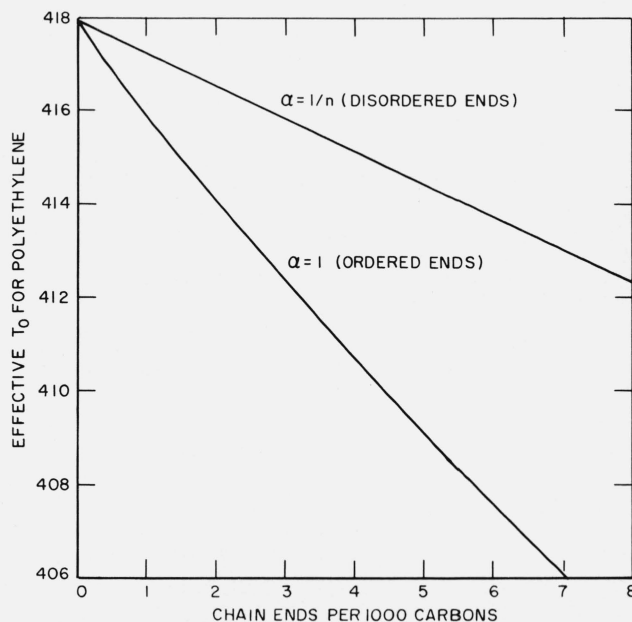

FIGURE 4. *Effective* T_0 *for polyethylene fractions as a function of the number of chain ends (calculated from eq (10)).*

The $\alpha = 1$ line represents the case of extended chain crystals with ordered methyl layers and the $\alpha = 1/n$ line applies to chain folded crystals where the chain ends are supposed to be randomly ordered in the crystal.

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T_0' for folded crystals of polyethylene than the actual measured values for extended chain polyethylene. (The former would presumably exhibit more randomization of ends than the latter.) Also notice that the depression in T_0' is not insignificant for typical polyethylene where the weight average molecule has about 1000 carbons (2 ends per 1000 carbons) [7]. We shall not procede further to include the additional effects of length distribution and side branching but merely emphasize the significant point here that chain ends play an important part in calculating thermodynamic quantities for polyethylene and one can use the $T_0 = 417.9$ °K calculated in this paper only if one includes $\Delta G_e - RT_0 \ln n$ *explicity* in polyethylene melting expressions like (8).

Finally, it should be mentioned that the increase in T_0 to 144.7 °C does not greatly alter the results in reference [3] where the thermodynamic properties of an infinite CH_2 chain crystal and liquid were obtained from paraffin data. Also the introduction of the $R \ln n$ term does not affect those results since the nonlinearity, although not understood, was recognized and taken into account empirically in that paper.

6. Appendix A

In order to examine the theoretical form of the liquid-glass entropy difference, ΔS_{lg}, as predicted by the liquid lattice theory (for a general discussion of the theory see Miller [4]), it is convenient to start with eq 20 in reference [5].[4] This equation includes the important effects of chain stiffness. Letting their z, the primary valance of the backbone chain atoms, equal 4 and writing ΔS_{lg} as a molar quantity, eq 20 [5] is,

$$\Delta S_{lg}/R = n \ln(V_0/S_0) + np \ln(V_0/S_0^2)$$
$$+ \ln 3(n-1) + (n-3)A \qquad (A.1)$$

where R = molar gas constant, n = number of carbon atoms in the chain, $p = n_0/n\, n_x$ = fraction of vacant, n_0, to occupied, $n\, n_x$, lattice sites (n_x = number of n −mers), $V_0 = n_0/(n\, n_x + n_0) = p/(1+p)$ = volume fraction of vacant to total lattice sites, $S_0 = 2n_0/[(n+1)n_x + 2n_0]$ and

$$A = \ln[1 + 2\exp(-\Delta\beta)] + \frac{2\Delta\beta \exp(-\Delta\beta)}{1 + 2\exp(-\Delta\beta)}$$

where $\Delta\beta = (\epsilon_2 - \epsilon_1)/RT$ and $(\epsilon_2 - \epsilon_1)$ is the energy difference between the trans and gauche configurations for a carbon-carbon bond.

Ignoring p compared to 1 (the derivation was carried out without simplications and gave essentially the same results), writing $V_0/S_0 = (1/2)(1 + 1/n)$ and dropping the

second term in (A.1) gives,

$$\Delta S_{lg}/R = n \ln(1/2)(1+1/n) + \ln 3n(1+1/n) + (n-3)A$$
$$= n(-\ln 2 + A) + (\ln 3 - 3A) + \ln n + (n+1)\ln(1+1/n).$$

Expanding,

$$\ln(1+1/n) = (1/n - 1/2n^2 + 1/3n^3 \ldots)$$

and

$$\Delta S_{lg}/R = n(-\ln 2 + A) + (1 + \ln 3 - 3A)$$
$$+ \ln n + 1/2\,(1/n) - (1/6)(1/n^2). \qquad (A-2)$$

Thus we have in addition to the linear and constant terms an unalterable $\ln n$ term and a power series in $(1/n)$.

Of some further interest are the predicted magnitudes of the coefficients. Letting $(\epsilon_2 - \epsilon_1) = 500$ cal/mole, then $A = 1.0$ at 300 °K and we have,

$$(\Delta S_{lg}/R) = 0.3n - 0.9 + \ln n + (1/2)(1/n) - (1/6)(1/n^2).$$

Experimentally, the liquid crystal entropy differences at 300 °K for the n-paraffins fit roughly,

$$(\Delta S_{lc}/R) = 1n + 0.5 + \ln n + 2.6(1/n) - 3(1/n^2).$$

The agreement is not good but we can improve things somewhat by taking account of the extra volume of a CH_3 group compared to a CH_2 group. From the x-ray length of the orthorhombic phase $l = (1.27\, n + 2) \times 10^{-8}$ cm indicating an effective CH_3 length of roughly twice a CH_2 length. Replacing n by $n+2$ gives,

$$(\Delta S_{lg}/R) = 0.3n - 0.3 + \ln n$$
$$+ 2.5\,(1/n) - 3.2\,(1/n^2) + \ldots$$

Even the discrepancy in the constant term is now not too disturbing, and the numerical agreement lends some support to the adoption of the above form for ΔS_{lc}.

7. References

[1] M. Broadhurst, J. Chem. Phys. **36**, 2578 (1962).
[2] P. J. Flory and Vrij, J. Am. Chem. Soc. **85**, 3548 (1963).
[3] M. Broadhurst, J. Res. NBS, **67A** (Phys. and Chem.) No. 3, 233 (1963).
[4] A. R. Miller, The Theory of Solutions of High Polymers (The Clarendon Press, Oxford, 1948).
[5] J. H. Gibbs and E. A. Dimarzio, J. Chem. Phys. **28**, 373 (1958).
[6] T. Arakawa and B. Wunderlich, J. Polymer Sci. **A2**, 53 (1966).
[7] T. Arakawa, Ph. D. Thesis, Cornell University, 1965.
[8] R. G. Brown and R. K. Eby, J. Appl. Phys. **35**, 1156 (1964).
[9] Y. Fujiwara and T. Yoshida, Polymer Letters **1**, 675 (1963).
[10] J. J. Weeks, J. Res. NBS **67A** (Phys. and Chem.) No. 5, 441 (1963).
[11] J. P. Colson and R. E. Eby, J. Appl. Phys. **37**, 3511 (1966).

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[4] This equation actually deals with the configurational entropy difference between the liquid and a zero configurational entropy glass and hence should equally well apply to the configurational entropy difference between the liquid and ordered crystal.