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**Melting Points of Linear-Chain Homologs. The Normal Paraffin Hydrocarbons**By P. J. FLORY AND A. VRIJ<sup>1</sup>

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A term  $R \ln n$  should be included in the molar entropy of fusion of long chain molecules in ordered crystalline array (e.g.,  $n$ -paraffin hydrocarbons),  $n$  being the number of repeating units (e.g.,  $\text{CH}_2$ ). This hitherto unrecognized term, which takes account of the disjunction of terminal groups of neighboring chain molecules, exerts a considerable effect on the convergence of the melting point  $T_m$  to its limit  $T_m^0$  for  $n = \infty$ . Experimental  $T_m$ 's for  $n$ -paraffin hydrocarbons from  $n = 11$  to 100 are represented to an accuracy of  $\pm 0.5^\circ$  by a melting point-chain length relationship of the form obtained by including  $R \ln n$  in the molar entropy of fusion. The limiting melting point  $T_m^0$  thus found,  $145.5 (\pm 1^\circ)$ , is several degrees higher than has been indicated by previous empirical extrapolations unguided by the presence of this term. It is  $7^\circ$  above the experimental melting point observed for carefully crystallized linear polyethylene. The latter disparity is largely accountable in terms of the small thickness of the crystalline lamellae occurring in polyethylene and the large interfacial free energy indicated by several unrelated observations.

Melting points for the normal paraffin hydrocarbon<sup>2</sup> homologs  $\text{H}-(\text{CH}_2)_n-\text{H}$  have been treated heretofore on the supposition that both the enthalpy and the entropy of fusion may be adequately represented by linear expressions, each comprising a term proportional to  $n$  and an additive constant for contributions associated with the end groups. The melting point  $T_m$  is expected on this basis to be related to the chain length  $n$  as

$$T_m = \Delta H^*(n + a)/\Delta S^*(n + b) = T_m^*(n + a)/(n + b) \quad (1)$$

where  $\Delta H^*$  and  $\Delta S^*$  represent, respectively, the enthalpy and entropy of melting per  $\text{CH}_2$  group in the limit  $n = \infty$ , and  $a\Delta H^*$  and  $b\Delta S^*$  are the end-group contributions. It is to be noted however that  $T_m^*$ , and other parameters appearing in eq. 1 as well, will depend in general on the temperature and should not, on the basis set forth above for this equation, be treated as constants. Revisions appropriately taking account of the dependence of  $T_m^*$  on temperature were introduced by Broadhurst.<sup>2f</sup> His analysis retains, however, the basic assumption of linearity of the enthalpy and of the entropy with  $n$  at constant temperature.

Linearity of the enthalpy of fusion with the chain length can safely be accepted as a sound approximation—for higher members of the series at any rate. Experimental enthalpies of fusion for the normal paraffin hydrocarbons, in conjunction with the corresponding quantity for linear polyethylene, support this assertion within the limits of accuracy with which these quantities are known.<sup>3</sup> Linearity of the entropy of fusion is another matter. It cannot be so represented as the following argument will show. Chain molecules in the crystalline state are laid end to end with terminal (e.g., methyl) groups juxtaposed in successive layers of the crystal lattice. In effect, the end groups are paired one to another in such a way as to perpetuate the sequence of chain units from one molecule to the next throughout successive layers of the lattice. Upon melting, this pairing is destroyed. Disruption of pairs contributes a term to the entropy of fusion, this contribution being in addition to the more obvious contributions from the disorder characteristic of the liquid state. The latter category may include entropies associated with intramolecular randomization of the configurations of the chain molecules, and with intermolecular disordering in the mutual arrangement of

chain units belonging to neighboring molecules, in analogy to the disordering which accompanies melting of simple molecular liquids.

Consider the terminus of a chain molecule in the melt. It will be surrounded by neighboring molecules, or rather by segments thereof. A segment is loosely defined as an approximately isometric subdivision of the chain molecule, its size being so chosen as to afford optimum representation of the radial distribution of chain elements about one another in terms of sets of neighbor sites each of which is occupied by exactly one segment. Let  $x$  represent the number of segments in a chain molecule. Now the coordination sphere about a terminal segment in the melt will on the average be occupied by 1st, 2nd, 3rd, . . .  $x$ -th segments of chain molecules at random. But in the paired state a particular first neighbor site is reserved for the terminal segment of another molecule. Elimination of pairing permits the site in question to be occupied by any one of the  $x$  segments of a molecule. The associated entropy increase is  $k \ln x$  per molecule. The magnitude of this term depends of course on the precise definition of a chain segment. Although  $x$  cannot in general be identified with  $n$ , it may be taken proportional to  $n$ . Fortunately, the constant of proportionality between  $x$  and  $n$  is of little importance for the purpose at hand. It suffices to write

$$\Delta S_{\text{unpairing}} = R \ln x = R \ln n + C \quad (2)$$

where  $C = R \ln (x/n)$  is treated as a constant.

While the foregoing direct deduction of the logarithmic term is both sufficient and general, it is worthy of note that the same result is furnished by the lattice theory of chain liquids.<sup>4</sup> There we find for the molar entropy of disorientation of a perfect array of  $x$ -meric chain molecules, in absence of a second component

$$\Delta S_{\text{disorient}} = R(x - 1) \ln [(z - 1)/e] + R \ln x \quad (3)$$

where  $z$  is the coordination number of the lattice. The first term arises from randomization of the molecular conformation subject to the restriction to single occupancy of each lattice cell. This term is linear in  $x$ , and therefore in  $n$ ; it may be included with intermolecular effects not taken into account by the lattice model, but likewise linear in  $n$ . The second term corresponds to eq. 2. As will be apparent, however, from examination of the argument indicated in the paragraph above, this term is not conditional on the validity of the specific model used in deriving eq. 3.

The relevant quantity for treating the melting point is the entropy of fusion per repeating unit ( $\text{CH}_2$ ). Hence, eq. 2 contributes a term in  $n^{-1} \ln n$  to the melting relationship. This term converges to zero slowly—more slowly than terms in  $n^{-1}$  prescribed by

(4) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 503.

(1) Postdoctoral fellow, 1962–1963.

(2) (a) W. E. Garner, K. Van Bibber, and A. M. King, *J. Chem. Soc.*, 1533 (1931); (b) K. H. Meyer and A. Van der Wyk, *Helv. Chim. Acta*, **20**, 1313 (1937); (c) A. H. Etesam and M. F. Sawyer, *J. Inst. Petrol.*, **25**, 253 (1939); (d) C. G. Gray, *ibid.*, **29**, 226 (1943); (e) G. Stållberg, S. Stållberg-Stenhagen, and E. Stenhagen, *Acta. Chem. Scand.*, **6**, 313 (1952); (f) M. G. Broadhurst, *J. Chem. Phys.*, **36**, 2578 (1962).

(3) F. W. Billmeyer, Jr., *J. Appl. Phys.*, **28**, 1114 (1957).

simple additivities of end-group effects (eq. 1). Hence, the course of the extrapolation of  $T_m$  to its limit  $T_m^0$  for  $n = \infty$  turns out to be altered by the logarithmic term.

In this paper we incorporate the foregoing logarithmic term in an analysis of the melting points for a homologous series of chain molecules. The melting points of the normal paraffin hydrocarbons in the orthorhombic crystalline form are interpreted in this manner. The treatment establishes a basis for relating the melting points of systems comprising chain molecules of infinite length with the melting points for finite chains of uniform length having their end groups assembled in layers which repeat with regularity throughout the crystal.

**Melting Relationships.**—For convenience, we adopt the artifice of considering melting to occur in two hypothetically differentiated steps. In the first of these the intersegment disorder and volume characteristic of the liquid state are established, but the intermolecular pairing of end groups one to another is preserved. (The end groups no longer occur in planar arrays, however.) In the second step the pairing of end groups is abolished, whereupon they relocate amongst neighboring segments at random. The molar free energy change in the first step is assumed to depend linearly on the chain length; *i.e.*, the contributions of end groups will be represented by an additive term taken to be independent of  $n$ . This term will include, for example, the disproportionate contribution of end groups to the intermolecular energy of the crystal owing to interactions peculiar to them; a possible diminution of the magnitude of the lattice energy resulting from distortion by end groups is to be included in this term, etc. Parallel end-group effects on the enthalpy and entropy of the liquid phase are also to be incorporated in this term.

The second step will involve the unpairing entropy given by eq. 2. On this basis we express the molar free energy of melting of the chain comprising  $n$  repeating units at an arbitrary temperature  $T$ , as

$$n\Delta G_n = n\Delta G + \Delta G_e - RT \ln n \quad (4)$$

where  $\Delta G$  is the free energy of fusion *per repeating unit* in the limit  $n = \infty$  at the temperature  $T$ ;  $\Delta G_e$  is the end-group contribution assumed to be the same for all  $n$ . The constant  $C$  of eq. 2 is absorbed in  $\Delta G_e$ .

Expanding  $\Delta G$  and  $\Delta G_e$  about the limiting melting temperature  $T_m^0$  for  $n = \infty$ , we obtain

$$\Delta G = \Delta S\Delta T - (\Delta C_p/2T_m^0)(\Delta T)^2 - (1/6T_m^0)^2(\Delta C_p - T_m^0\Delta C_p')(\Delta T)^3 - \dots \quad (5)$$

and

$$\Delta G_e = \Delta H_e - T_m^0 \Delta S_e + \Delta S_e \Delta T - (\Delta C_{p,e}/2T_m^0)(\Delta T)^2 + \dots \quad (6)$$

where

$$\Delta T = T_m - T_m^0$$

and

$$\Delta C_p' = (\partial \Delta C_p / \partial T)_p$$

The various derivatives of the free energy occurring as coefficients in these expressions, *e.g.*,  $\Delta S$ ,  $\Delta H_e$ , etc., must be assigned their values at the temperature  $T_m^0$ .

At the melting point  $T_m$  for a given  $n$ ,  $\Delta G_n = 0$ . From eq. 4, 5, and 6 and the extension of the scheme of symbols to include  $\Delta H = T_m^0 \Delta S$  for the enthalpy of fusion per repeating unit at the temperature  $T_m^0$ , we obtain therefore

$$n[\Delta H\Delta T - (\Delta C_p/2)(\Delta T)^2 - (1/6)(\Delta C_p/T_m^0 - \Delta C_p')(\Delta T)^3 - \dots] - RT_m T_m^0 \ln n \dots = [T_m T_m^0 \Delta S_e - T_m^0 \Delta H_e + (\Delta C_{p,e}/2)(\Delta T)^2 + \dots] \quad (7)$$

with  $\Delta T = T_m^0 - T_m$ . To a generally sufficient approximation

$$(n\Delta H/R)\Delta T - (n\Delta C_p/2R)(\Delta T)^2 - T_m T_m^0 \ln n \approx (T_m^0/R)(T_m \Delta S_e - \Delta H_e) \quad (8)$$

TABLE I

MELTING POINTS FOR NORMAL PARAFFIN HYDROCARBONS  
Experimental data taken from Broadhurst's<sup>6</sup> compilations;  
see text

$n$	$T_{tr}$	$T_m'$	$T_m$
11	236.6	247.6	245.0
13	255.0	267.8	265.1
15	270.9	283.1	280.5
17	283.7	295.1	292.7
19	295.2	305.2	302.9
21	305.7	313.4	311.5
23	313.7	320.7	318.7
25	320.2	326.7	324.7
27	326.2	332.0	330.1
29	331.4	336.6	334.9
31	335.7	340.9	339.3
33	340.6 <sup>a</sup>	344.3	343.2
34	342.6	345.9	345.0
35	345.1	347.7	347.0
36	347.0	349.1	348.6
38	350.6 <sup>a</sup>	352.2	351.8
39	352.3 <sup>a</sup>	353.5	353.2
40	353.9 <sup>a</sup>	354.7	354.5
43	358.4 <sup>a</sup>	358.5	358.5
44			359.6
46			361.2
50			365.3
52			367.2
54			368.2
60			372.4
62			373.7
64			375.3
66			376.8
67			377.3
70			378.5
82			383.5
94			387.0
100			388.4

<sup>a</sup> Smoothed values.

The molar enthalpy fusion of an  $n$ -mer is given correspondingly by

$$n\Delta H_n = n[\Delta H - \Delta C_p \Delta T + (\Delta C_p'/2)(\Delta T)^2 + \dots] + \Delta H_e - \Delta C_{p,e} \Delta T \quad (9)$$

and

$$n\Delta C_{p,n} = n(\Delta C_p - \Delta C_p' \Delta T) + \Delta C_{p,e} \quad (10)$$

**Melting Points in the Normal Paraffin Hydrocarbon Series.**—We confine attention to melting of the  $n$ -paraffin hydrocarbons in the orthorhombic crystalline form. This is the stable form at low temperatures for odd  $n \geq 9$  and for even  $n \geq 44$ . Transition from the orthorhombic to the hexagonal form precedes melting for odd  $n$  in the range  $11 \leq n \leq 43$  and for even  $n$ ,  $34 \leq n \leq 42$ ; for even  $n \leq 32$  a stable orthorhombic form apparently does not occur at any temperature. For all  $n \geq 44$  the orthorhombic form melts without polymorphic transition. For those members of the series which undergo transition from the orthorhombic to the hexagonal form before melting, the melting point  $T_m$  for the metastable orthorhombic form may be calculated from the observed melting point  $T_m'$  of the hexagonal modification, the temperature  $T_{tr}$  for the orthorhombic  $\rightarrow$  hexagonal transition, and the latent enthalpies of melting  $\Delta H_n$  and transition  $\Delta H_{tr,n}$  through use of the thermodynamic relationship (for small differences  $T_m' - T_m$ )

$$T_m = T_m' - (T_m' - T_{tr})\Delta H_{tr,n}/\Delta H_n \quad (11)$$

Melting points  $T_m$  of the orthorhombic crystal forms of the  $n$ -paraffin hydrocarbons from  $C_{11}$  to  $C_{100}$  used in the calculations discussed below are presented in the fourth column of Table I. Experimental data in

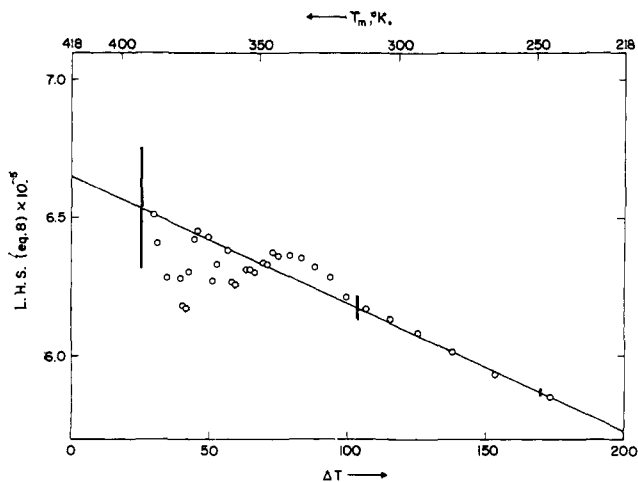


Fig. 1.—Left-hand side of eq. 8 plotted against  $\Delta T = T_m^0 - T_m$  (lower abscissa scale) and  $T_m$  in  $^{\circ}\text{K}$ . (upper abscissa scale) assuming  $T_m^0 = 418^{\circ}\text{K}$ .,  $\Delta H = 950$  cal. (mole  $\text{CH}_2$ ) $^{-1}$ , and  $\Delta C_p = 1.0$  cal. deg. $^{-1}$  (mole  $\text{CH}_2$ ) $^{-1}$ .

this table have been taken from Broadhurst's<sup>5</sup> tabulations. These include the transition temperatures  $T_{tr}$  for the orthorhombic  $\rightarrow$  hexagonal transition, the melting points  $T_m'$  for the latter form for members of the series in the range  $11 \leq n \leq 43$ , and the directly observed melting points  $T_m$  for the orthorhombic form for members of the series in the range  $44 \leq n \leq 100$ . Values of  $T_m$  (column 4) for hydrocarbons in the former range have been calculated using eq. 11 from  $T_m'$  and  $T_{tr}$ , together with the required enthalpies of fusion and transition (Broadhurst<sup>5</sup>). The correction from the observed  $T_m'$  (hexagonal) to  $T_m$  (orthorhombic) invariably is small.

The  $a$  and  $b$  crystallographic spacings transverse to the chain axis vary by less than 1% from  $n = 23$  to  $n = \infty$  (polyethylene).<sup>6-8</sup> The  $c$ -axis spacing is accurately linear with  $n$ , the intramolecular C-C distance projected on the  $c$ -axis being 1.270 Å. throughout the series. This concordance in the crystalline dimensions lends strong support for the assumption of linearity of the intramolecular energy and entropy in the crystalline state. That the thermodynamic functions for the liquid state can be similarly expressed, insofar as intermolecular effects other than end-group pairing are concerned, seems assured by the observation that the liquid specific volume is approximately linear with  $n^{-1}$  at constant temperature. The specific volume of each homolog at its melting point turns out, incidentally, to be very nearly independent of  $n$ .

Early estimates of  $\Delta H$  were attempted by extrapolation of the latent enthalpies of fusion of the  $n$ -paraffin hydrocarbons.<sup>3,9</sup> For homologs in the range from  $n = 5$  to 32 the molar enthalpies of fusion increase approximately linearly with  $n$ , and the slope, amounting to 910–930 cal. deg. $^{-1}$  (mole  $\text{CH}_2$ ) $^{-1}$ , was taken to represent the limiting value,  $\Delta H$ . The data are of restricted accuracy and the length of the extrapolation to  $n = \infty$  is excessive. The numerical result is supported, however, by calorimetric measurements of Wunderlich and Dole<sup>10</sup> on linear polyethylene. Quinn and Mandelkern<sup>11,12</sup> applied the melting point de-

(5) M. G. Broadhurst, *J. Research Natl. Bur. Standards*, **A66**, 241 (1962).

(6) A. Miller, *Proc. Roy. Soc. (London)*, **A120**, 437 (1928).

(7) J. M. Robertson, "Organic Crystals and Molecules," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 169.

(8) A. E. Smith, *J. Chem. Phys.*, **21**, 2229 (1953).

(9) M. Dole, W. P. Hettlinger, Jr., N. R. Larson, and J. A. Wethington, *J. Am. Chem. Soc.*, **77**, 781 (1955).

(10) B. Wunderlich and M. Dole, *J. Polymer Sci.*, **24**, 201 (1957).

(11) F. A. Quinn, Jr., and L. Mandelkern, *J. Am. Chem. Soc.*, **80**, 3178 (1958).

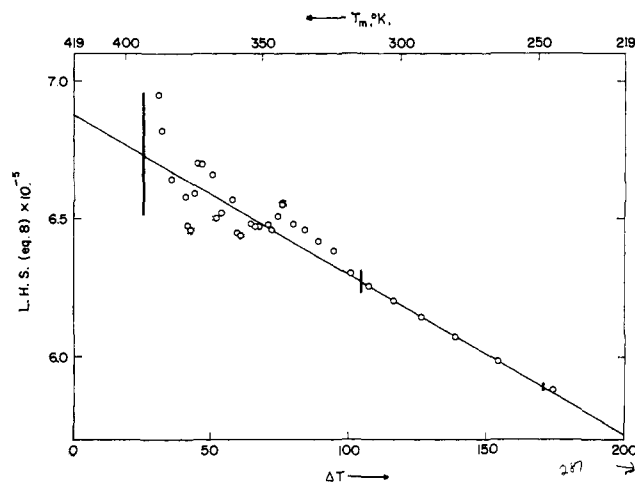


Fig. 2.—Left-hand side of eq. 8 plotted against  $\Delta T$  assuming  $T_m^0 = 419^{\circ}\text{K}$ .; other quantities as in Fig. 1.

pression method which gives  $\Delta H$  directly without need of correction. They found  $\Delta H = 960 (\pm 30)$  cal. mole $^{-1}$ .<sup>12</sup> We have accordingly adopted the value of 950 cal. mole $^{-1}$  in the principal calculations presented below.

Whereas the heat capacities of the liquid  $n$ -paraffin hydrocarbons and polyethylene are fairly well established, corresponding data for the crystalline forms are sparse. The specific heat measurements of Finke,<sup>13</sup> *et al.*, on the  $n$ -paraffin homologs in the range  $n = 12$ –16 yield  $\Delta C_p = 1.75$ –1.80 deg. $^{-1}$  (mole  $\text{CH}_2$ ) $^{-1}$  at the melting point for each hydrocarbon. Within this limited range there is no evidence of a trend with  $n$  in the value of  $\Delta C_p$  at  $T_m$ . The heat capacity of crystalline polyethylene is not known with any degree of accuracy above about 50° owing to complications arising from premelting.<sup>9,10,14</sup> Lengthy extrapolations based on empirical expressions given by Wunderlich and Dole<sup>10,14</sup> lead to the implausible result  $\Delta C_p \cong 0$  at  $T_m^0$ . Inasmuch as treatment of the melting points according to eq. 8 is fairly insensitive to  $\Delta C_p$ , we have chosen the value 1.0 cal. deg. $^{-1}$  (mole  $\text{CH}_2$ ) $^{-1}$  for this quantity. This choice finds partial justification in the representation of the enthalpies of fusion according to eq. 9, as we show later in this paper.

The left-hand side (l.h.s.) of eq. 8 is plotted against  $\Delta T = T_m^0 - T_m$  in Fig. 1 with arbitrary choice of  $T_m^0 = 418^{\circ}\text{K}$ . and in Fig. 2 with  $T_m^0 = 419^{\circ}\text{K}$ .; the values of  $\Delta H$  and  $\Delta C_p$  given above have been used in each instance. The first of the three terms in the l.h.s. of eq. 8 dominates the other two throughout the range concerned. The second term decreases from about 15% of the first term for  $n = 11$  to 3% at  $n = 100$ . The third term, involving  $\ln n$ , is much larger than the second term and its relative contribution increases with  $n$ . It is about one-fourth of the leading term at  $n = 11$ , and half of it at  $n = 100$ .

The plots shown in Fig. 1 and 2 are extremely sensitive in the range of high  $n$  (small  $\Delta T$ ) to the experimental value of  $T_m$  and to the value assigned to  $T_m^0$ . Vertical bars serve to illustrate the effect of shifting  $T_m$  by  $\pm 0.5^{\circ}$ . The effect of changing  $T_m^0$  by  $\pm 1^{\circ}$  is apparent from comparison of the two figures. In Fig. 1 ( $T_m^0 = 418^{\circ}\text{K}$ .) points in the upper range of  $n$  tend to fall somewhat below the straight line drawn

(12) L. Mandelkern, *Rubber Chem. Tech.*, **32**, 1392 (1959); see p. 1403 for revision of the enthalpies of fusion originally reported in ref. 11.

(13) H. L. Finke, M. E. Gross, G. Waddington, and H. M. Huffman, *J. Am. Chem. Soc.*, **76**, 333 (1954). Heat capacities of crystalline and liquid phases at temperatures outside the melting range were extrapolated linearly to  $T_m$  for the purpose of deducing the  $\Delta C_p$  values cited in the text.

(14) B. Wunderlich, *J. Chem. Phys.*, **37**, 1203 (1962).

through points representing lower  $n$ 's, and in Fig. 2 ( $T_m^0 = 419^\circ\text{K.}$ ) they lie somewhat above the analogous line. For  $T_m^0 \leq 417^\circ\text{K.}$  and  $T_m^0 \geq 419^\circ\text{K.}$  the divergence in the range of large  $n$  is severe. Thus a value of  $418.5 (\pm 1)^\circ\text{K.}$  is indicated for  $T_m^0$ , this result being subject, however, to the values chosen above for  $\Delta H$  and  $\Delta C_p$ .

We have carried out similar calculations for  $\Delta H = 900$  and  $1000 \text{ cal. mole}^{-1}$ , and for  $\Delta C_p = 1.6$  and  $2.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . Although intercepts and slopes are altered, the values of  $T_m^0$  required for optimum representation of the experimental data for large  $n$  remain within the range indicated above. Thus, analysis according to eq. 8 leads quite unambiguously to  $T_m^0 = 418.5 (\pm 1)^\circ\text{K.}$  for the limiting melting point of the orthorhombic crystalline form in the  $n$ -paraffin hydrocarbon series.

Our value of  $T_m^0$  exceeds Broadhurst's<sup>2,5</sup>  $414.3 (\pm 2.4)^\circ\text{K.}$  obtained by empirical extrapolation of  $T_m$  for the hydrocarbons above  $n = 44$ . Results similar to his were deduced previously by others,<sup>2</sup> with the exception of Meyer and Van der Wyk,<sup>2b</sup> who found  $T_m^0 = 418^\circ\text{K.}$

The slope and intercept of the line drawn in Fig. 1 ( $T_m^0 = 418^\circ\text{K.}$ ), interpreted according to the right-hand member of eq. 8, yields  $\Delta H_e = -2200 \text{ cal. mole}^{-1}$  and  $\Delta S_e = 2.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . From Fig. 2 ( $T_m^0 = 419^\circ\text{K.}$ ),  $\Delta H_e = -2100 \text{ cal. mole}^{-1}$  and  $\Delta S_e = 2.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . A negative value of  $\Delta H_e$  accords with expectation, for it signifies diminution of the magnitude of the intermolecular crystal energy by the end-group layers, due in part perhaps to the lower dispersion interactions of  $\text{CH}_3$  groups compared with  $\text{CH}_2$ . A positive value for  $\Delta S_e$ , the negative contribution from  $C$  of eq. 2 notwithstanding, is attributable to relaxation of the precise positioning and orientation of the terminal segment (methyl group) in the crystal lattice.

Neglecting terms in  $\Delta C_p'$  and  $\Delta C_{p,e}$  in eq. 9, we obtain for the enthalpy of fusion per  $\text{CH}_2$  group of the homolog of chain length  $n$

$$\Delta H_n = \Delta H - \Delta C_p \Delta T + \Delta H_e/n \quad (9')$$

Substitution of the values used above for  $\Delta H$  and  $\Delta C_p$ , together with  $\Delta H_e = -2150 \text{ cal. mole}^{-1}$ , yields

$$\Delta H_n = 950 - \Delta T - 2150/n \quad (12)$$

The enthalpies of fusion calculated for eq. 12 for selected values of  $n$  are compared in Table II with those

TABLE II  
ENTHALPIES OF FUSION

$n$	$\Delta T, ^\circ\text{C.}$	$\Delta H_n, \text{ cal./mole CH}_2$	
		Calcd. eq. 12	Obsd.
15	138	669	700
19	116	721	750
25	94	770	800
29	84	792	805
30	(82)	796	795
43	60	840	800

observed.<sup>2f</sup> Agreement is within about 5%. Thus, the parameters chosen offer a consistent account of both the melting points and the enthalpies of fusion, within the limits of reliability with which the latter quantities are known.

### Discussion

Equation 8 matches the melting points for orthorhombic  $n$ -paraffin hydrocarbons from  $n = 11$  to 100 with an error exceeding  $\pm 0.5^\circ$  in only three instances (see Fig. 1 and 2). The parameters involved, though five in number, are greatly restricted by independent considerations. Thus,  $\Delta H$  has been assigned its value

established by experiments on polyethylene. The fit is insensitive to  $\Delta C_p$  in any case; moreover, this quantity has been so chosen as to render eq. 9 compatible with the observed enthalpies of fusion and the value of  $\Delta H_e$  indicated by the slopes and intercepts in the figures. This leaves  $T_m^0$ ,  $\Delta H_e$ , and  $\Delta S_e$  for unrestricted choice. The first of these quantities is the most critical by far; sensitivity of the fit to  $\Delta S_e$  and  $\Delta H_e$  diminishes in this order. Thus, the success of eq. 8 in matching the experimental melting points over a wide range, and with the accuracy cited above, is significant.

**Comparison of the Melting Point for Polyethylene with  $T_m^0$ .**—The limiting melting point  $T_m^0$  for the  $n$ -paraffin hydrocarbon series must be coincident with the melting point for linear polyethylene of infinite chain length arranged in indefinitely large crystallites of perfect order apart from the normal complement of equilibrium defects. This assertion follows directly from the equivalence of the crystal structures for polyethylene and the  $n$ -paraffin hydrocarbons and the virtual identity of their unit cell dimensions. Yet the melting point observed for linear polyethylene of high molecular weight, crystallized with minimum undercooling, is  $138.5^\circ$ ,<sup>15</sup> a full  $7^\circ$  below  $T_m^0$  established by extrapolation. This unexpectedly large discrepancy commands close examination inasmuch as it bears in an important way on the significance of melting points of macromolecular crystals generally.

The crystalline regions in macromolecules (copolymers excepted<sup>16</sup>) characteristically occur as thin lamellae, the chain axes being arranged in the direction perpendicular to the plane thereof. Low angle X-ray diffraction maxima, believed to represent the interlamellar spacing, indicate values for the lamellar thickness ranging from a few hundred to over a thousand angstrom units. According to various lines of evidence, a very large interfacial free energy  $\sigma_e$  is associated with the lamellae surfaces, *i.e.*, the 001 crystal surfaces. Cormia, Price, and Turnbull<sup>17</sup> concluded that  $\sigma_e \cong 168 \text{ ergs cm.}^{-2}$  on the basis of rates of nucleation in small droplets of polyethylene. Richardson, Flory, and Jackson<sup>18</sup> arrived at an almost identical value of  $170 \text{ ergs cm.}^{-2}$  by analysis of the melting of random copolymers in which the principal unit is  $\text{CH}_2$ . An earlier estimate of  $95 \text{ ergs cm.}^{-2}$  by Mandelkern, Posner, Diorio, and Roberts<sup>19</sup> from the dependence of the low angle X-ray spacings on the crystallization temperature of polyethylene was predicated on  $T_m^0 = 137.5^\circ$ . Choice of a higher value in keeping with the  $T_m^0$  found above brings the result for  $\sigma_e$  into the range of the other two results quoted.<sup>20</sup> Such a large interfacial free energy finds qualitative explanation in the difficulty in dissipating order among chains emanating from the 001 face of a lamellar crystallite of essentially unlimited dimensions.<sup>21</sup>

The depression of the melting point  $\Delta T_\zeta = T_m^0 - T_{m,\zeta}$  attributable to the finite thickness  $\zeta$  of the crystal is given, on the basis of elementary thermodynamic considerations, by

$$\Delta T_\zeta = (2\sigma_e T_m^0 / \Delta H) \zeta^{-1} \quad (13)$$

Let  $\zeta$  be expressed as the number of  $\text{CH}_2$  groups in a chain extending through the crystallite. Then, ac-

(15) R. Chiang and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 2857 (1961).

(16) J. B. Jackson, P. J. Flory, and R. Chiang, *Trans. Faraday Soc.*, **59**, 1906 (1963); J. B. Jackson and P. J. Flory, *Polymer*, in press.

(17) R. L. Cormia, F. P. Price, and D. Turnbull, *J. Chem. Phys.*, **37**, 1333 (1962).

(18) M. J. Richardson, P. J. Flory, and J. B. Jackson, *Polymer*, **4**, 221 (1963).

(19) L. Mandelkern, A. S. Posner, A. R. Diorio, and D. E. Roberts, *J. Appl. Phys.*, **32**, 1509 (1961).

(20) L. Mandelkern, private communication.

(21) P. J. Flory, *J. Am. Chem. Soc.*, **84**, 2857 (1962)

cording to the values given above,  $\sigma_e = 4600$  cal. per mole of chains intersecting the interface plane. By substitution in eq. 13, we thus obtain

$$\Delta T_{\zeta} = 4000\zeta^{-1} \quad (14)$$

For polyethylene samples crystallized at  $131^\circ$  according to the procedure of Chiang and Flory<sup>15</sup> and exhibiting a melting temperature of  $138.5^\circ$ , the low angle X-ray spacing is approximately  $1100 \text{ \AA}$ .<sup>22</sup> Allowing for the presence of approximately 20% of amorphous material, and assuming this to occur between the crystalline lamellae, we arrive at  $\zeta = 900 \text{ \AA}/1.25 \text{ \AA} = 720$ ; hence, according to eq. 14,  $\Delta T_{\zeta} = 5.5^\circ$ . This estimate accounts for most of the discrepancy between the observed melting point for linear polyethylene and our value for  $T_m^0$  established by extrapolation.

The low angle X-ray spacing used in the calculation above pertains to samples crystallized at  $131^\circ$  and subsequently examined at room temperature. Recrystallization may of course have occurred during melting, with the result that lamellae of somewhat greater thickness were produced; on this basis a larger value of  $\zeta$  might have been appropriate for insertion in eq. 14. On the other hand, partial melting as  $T_m$  is approached would tend to diminish  $\zeta$ , and this would introduce an opposite effect on the calculated  $\Delta T_{\zeta}$ . Additionally to be borne in mind are (a) the uncertainty in the value of  $\sigma_e$  and (b) the likelihood of contributions to  $\Delta T$  from other nonequilibrium defects in the crystalline array. These vitiating factors notwithstanding, we conclude that the disparity between the observed melting temperature for polyethylene and  $T_m^0$  can reasonably be attributed in large part to the finite dimensions of the polyethylene crystallites in the direction of their chain axes.

Hoffman and Weeks,<sup>23</sup> by extrapolating the increase of melting point of linear polyethylene with its crystallization temperature, have arrived at a value of  $145^\circ$  for  $T_m^0$ . Their method rests on the assumption that crystalline imperfection, including finite crystal size, is determined by the degree of supercooling prevailing during crystallization. Hence, the coincidence of their result with our value obtained by extrapolation of melting points for the  $n$ -paraffin hydrocarbons supports the explanation given above for the depressed melting point of polyethylene as normally determined.

**Partial Melting of Molecular Crystals of Chain Molecules.**—Up to this point we have considered only the extreme states of perfect crystalline order and of completely melted liquids. The possibility that, for chain molecules of large but finite  $n$ , intermediate states may exist under favorable circumstances has been disregarded. It is at least conceivable that molecular crystals may undergo partial melting with disruption of the planar arrays of terminal ( $\text{CH}_3$ ) groups as a prelude to final melting.<sup>24</sup> Participation of long-chain molecules in crystals of arbitrarily specified length ( $< n$ ) was discussed in detail some years ago.<sup>25</sup> Theoretical relationships predicted stable forms of crystallites of length less than  $n$  over a finite temperature range below the melting point; the optimum length was shown to depend on the effective interfacial free energy and on the concentration.<sup>25</sup> The treatment referred to was specialized to the case of low degrees of crystallization and involved an approximation which becomes

(22) S. S. Pollack, W. H. Robinson, R. Chiang, and P. J. Flory, *J. Appl. Phys.*, **33**, 237 (1962).

(23) J. D. Hoffman and J. J. Weeks, private communication; also *J. Research Natl. Bur. Standards*, **66A**, 13 (1962).

(24) We are indebted to Professor Leo Mandelkern for directing our attention to the possible significance of this case.

(25) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

inaccurate for higher degrees. We present here a simplified treatment better suited to incipient partial melting in the end-group layers of molecular crystals of long-chain compounds.

Let  $m$  units ( $\text{CH}_2$ ) from the terminal sequences of each molecule be melted;  $n - m$  consecutive units from the mid-section of the molecule occupy a crystalline zone comprising similar sequences from neighboring chains. Inasmuch as the fairly drastic alteration in intramolecular configuration associated with melting can only be accomplished through simultaneous disordering of neighbors, all molecules will be constrained to adopt approximately the same value of  $m$ . The partially melted crystal is thus envisioned as consisting of a succession of layers of crystalline and amorphous zones, terminal units of chains being allocated to the latter.

The molar free energy change associated with partial melting in this fashion will involve, in addition to a term  $m\Delta G$  and interfacial terms, a contribution  $-RT \ln(m + 1)$  arising from the  $m + 1$  possible locations of the molecule such that terminal units are excluded from the interior of the crystalline zone. The interfacial free energy associated with each interzonal boundary should resemble the same quantity  $\sigma_e$  for the homologous polymer. Accordingly, the molecular free energy change associated with partial melting may be expressed as

$$(\Delta G)_m = m\Delta G - RT \ln(m + 1) + 2\sigma_e + \Delta G_e \quad (15)$$

where  $-\Delta G_e$  (see above) is the "defect" free energy for the end-group layers destroyed by partial melting. Equating  $\partial(\Delta G)_m/\partial m$  to zero, and substituting  $\Delta G = \Delta H\Delta T/T$  where  $\Delta T = T_m^0 - T$ , we obtain for the optimum extent of melting

$$m^* + 1 = RT^2/\Delta H\Delta T \quad (16)$$

Substitution of this result into eq. 15 yields

$$(\Delta G)_{m^*} \cong RT[1 - \ln(RT^2/\Delta H\Delta T)] + 2\sigma_e + \Delta G_e$$

By imposing the inequality  $(\Delta G)_{m^*} < 0$  we find

$$\ln(RT^2/\Delta H\Delta T) > 1 + (2\sigma_e + \Delta G_e)/RT \quad (17)$$

as the condition for partial melting.

Insertion of numerical values for the  $n$ -paraffin hydrocarbons in the left-hand member yields

$$\ln(370/\Delta T) > 1 + (2\sigma_e + \Delta G_e)/RT \quad (17')$$

If  $\sigma_e$  is assigned the value estimated for polyethylene and  $\Delta G_e$ , a negative quantity, is taken from the analysis of melting data above, the right-hand member is  $\cong 8$ , and this requires  $\Delta T < 0.12^\circ$ . By way of comparison,  $\Delta T = 30^\circ$  at the melting point of  $n$ -heptane ( $n = 100$ ). A melting point  $T_m$  very close to  $T_m^0$  is required on this basis if partial premelting is to precede final melting, and this condition will be met only for  $n \gg 100$ .

It should be acknowledged that the appropriate value for  $\sigma_e$  may be much less than that for infinite chains. The configurational constraints at the interzonal layers, which are severe for infinite chains,<sup>22</sup> should be partially alleviated by termination of the trajectories of finite chains in the intercrystalline zones. To the extent that the large value of  $\sigma_e$  indicated for polyethylene is contingent upon those constraints, a smaller value of  $\sigma_e$  may be anticipated under the conditions here considered. As is apparent from eq. 17, however, incidence of partial melting would seem to require indeed  $2\sigma_e + \Delta G_e$  small and  $n$  large.

In conclusion, the expectation that  $2\sigma_e$  will exceed the "defect" free energy  $-\Delta G_e$  for end-group layers supports the view that molecular crystals with end groups aligned in planes will be the most stable form at low temperatures for all  $n$ . Moreover, the difference between these quantities should suffice to suppress

partial melting, as a prelude to complete disappearance of a crystalline phase, throughout the accessible range of  $n$  within which pure compounds are available. This assertion is, of course, substantiated by evidence on the narrow melting ranges ( $\leq 1^\circ$  which is  $\ll \Delta T$ ) for the  $n$ -paraffin hydrocarbons.<sup>26</sup> For sufficiently large  $n$  the molecular crystals stable at low temperatures should, according to eq. 17, undergo partial premelting

(26) W. F. Seyer, R. F. Peterson, and J. L. Keays, *J. Am. Chem. Soc.*, **66**, 179 (1944).

to "crystallites" having a dimension  $\zeta < n$ , assuming of course that equilibrium prevails. The value of  $n$  required may, however, be very large (e.g.,  $> 10^4$ ). This predicted transformation in advance of final melting establishes an essential connection between the melting of pure chain homologs of finite  $n$  and the limiting case  $n = \infty$ .

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

## Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constants of 1,2,5-Thiadiazole<sup>1a</sup>

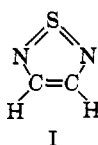
BY SR. VICTOR DOBYNS<sup>1b</sup> AND LOUIS PIERCE<sup>1c</sup>

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The microwave spectra of four isotopic species of 1,2,5-thiadiazole have been assigned and analyzed. The value of the inertial defect indicates that the molecule is planar in the ground vibrational state. Moments of inertia obtained from the analyses of the spectra together with the center of mass condition give the following structural parameters: S-N =  $1.631 \pm 0.003$  Å., C-N =  $1.328 \pm 0.003$  Å., C-C =  $1.420 \pm 0.003$  Å., C-H =  $1.079 \pm 0.003$  Å.,  $\angle$ NSN =  $99^\circ 33' \pm 10'$ ,  $\angle$ CCN =  $113^\circ 46' \pm 10'$ ,  $\angle$ CCH =  $126^\circ 14' \pm 10'$ . The dipole moment is  $1.565 \pm 0.015$  D. Quadrupole coupling constants are  $|\chi_{AA}| < 1$  Mc. and  $\chi_{CC} - \chi_{BB} = 5.2 \pm 0.3$  Mc. These were obtained by a direct comparison of two corresponding transitions of thiadiazole and diazine, a molecule whose quadrupole coupling constants have previously been determined from microwave data. An analysis of the hyperfine structure for high  $J$   $Q$ -branch transitions using a limiting expression for the splittings confirmed the value and sign of  $\chi_{CC} - \chi_{BB}$ . Relative intensities of the components of the hyperfine multiplets are consistent with the assumption that the molecule is planar in the ground-vibrational state. Quadrupole energies for a molecule having two equivalent nuclei of spin 1 are tabulated.

### I. Introduction

1,2,5-Thiadiazole, a five-membered heterocyclic ring compound, was initially prepared and identified by Carmack, Weinstock, and Shew.<sup>2a,b</sup> These authors conducted an extensive study of the chemical and physical properties of this compound and its substituted derivatives, and on the basis of this study proposed the structure, I, as best representing the properties ob-



served. On considering the known isoelectronic relationship between thiophene and benzene and between quinoxaline and 2,1,3-benzothiadiazole, they predicted a close chemical relationship between 1,2,5-thiadiazole and pyrazine since these are also isoelectronic. Chemical evidence supported these predictions and indicated that the ring does not possess purely dienoid character. Similarity between aromatic compounds containing the  $-\text{CH}=\text{CH}-$  group and those in which the vinyl group has been replaced by  $-\text{S}-$  had been noted previously.<sup>3</sup> Assuming that sulfur can expand its valence shell to ten electrons,<sup>4</sup> all resonance forms of the vinyl group become possible for the sulfur atom. For this reason they investigated properties dependent on mobile electrons, comparing the ultraviolet spectra and polarographic behavior of 1,2,5-thiadiazole with that of pyrazine. On the basis of the experimental results, these authors proposed the structure already noted.

(1) (a) This research was supported by a grant from the National Science Foundation. (b) Recipient, du Pont Teaching Assistant Award 1961-1962. (c) Alfred P. Sloan Foundation Fellow.

(2) (a) M. Carmack, L. M. Weinstock, and D. Shew, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959, p. 37P. (b) L. M. Weinstock, *Dissertation Abstr.*, **19**, 3136 (1959).

(3) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

(4) L. Pauling and V. Shomaker, *J. Am. Chem. Soc.*, **61**, 1773 (1939).

Preliminary electron diffraction results of Bonham and Momany<sup>5</sup> likewise suggested that the system is highly aromatic. Their work indicated that the C-C bond distance is nearly that of benzene and that the C-N bond distance is considerably shorter than the structure proposed by Carmack, Weinstock, and Shew would imply. It should be noted that the experimental uncertainties in the measurement of these two parameters were rather large. Their results indicate that the ring is planar to within 0.1 Å.

The present work is concerned with the determination of the structure, dipole moment, and quadrupole coupling constants of 1,2,5-thiadiazole from its microwave spectrum.

### II. Experimental

Samples of  $\text{C}_2\text{H}_2\text{N}_2\text{S}$  and  $\text{C}_2\text{D}_2\text{N}_2\text{S}$  were kindly provided by M. Carmack. These were purified by gas chromatography. A proton nuclear magnetic resonance spectrum (60 Mc.) was run in tetramethylsilane, giving a chemical shift of 516.7 c.p.s. to low field with respect to the solvent and evidence of two equivalent protons.

### III. Microwave Spectrum and Dipole Moment

A Stark modulated spectrometer (100 kc.) was used for measuring the rotational transitions of five isotopic species of 1,2,5-thiadiazole in the region 8 to 30 kMc. The species  $\text{C}_2\text{H}_2\text{N}_2^{34}\text{S}$  (4.22%),  $\text{C}^{13}\text{CH}_2\text{N}_2\text{S}$  (2.22%), and  $\text{C}_2\text{H}_2\text{N}^{15}\text{NS}$  (0.73%) were observed in natural abundance.

Hyperfine structure arising from quadrupole effects was partially resolvable for the  $\text{C}_2\text{H}_2\text{N}_2\text{S}$  and  $\text{C}_2\text{D}_2\text{N}_2\text{S}$  species. The Hamiltonian for the interaction of several quadrupolar nuclei with the molecular field may be expressed as

$$H_Q = \sum_i \frac{eQ_i(\partial^2 V/\partial z^2)_i}{2J(2J-1)I_i(2I_i-1)} \left[ 3(I_i \cdot J)^2 + \frac{3}{2}(I_i \cdot J) - I_i^2 \cdot J^2 \right] \quad (1)$$

where  $(\partial^2 V/\partial z^2)_i$  represents the second derivative of the electrostatic potential with respect to a space-fixed

(5) R. A. Bonham and F. A. Momany, *ibid.*, **83**, 4475 (1961).