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The Melting Points of Ultralong Paraffins and Their Homologues

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Because of the recent availability of the melting points of several ultralong normal paraffins, the melting behavior of normal paraffins has been investigated. Taking the melting point of polyethylene to represent the melting point of an ultralong paraffin, a new function has been established to represent the melting points of alkanes from the carbon number 32 onwards. Adopting the same value for the limiting melting point of an ultralong paraffin, equations are derived for the melting points of several homologous series.

KEY WORDS: alkanes; cycloalkanes; alkanamines; alkanols; halogenated alkanes; polyethylene.

1. INTRODUCTION

The crystallization of ultralong normal paraffins and their melting points are of considerable interest to both the thermodynamicists and the organic chemists. They are also of great interest to the polymer chemists because they are the oligomers of polyethylene. Due to the refinements in the techniques for the preparation of the ultralong normal paraffins, Ungar et al. [1] have been successful in reaching the length of $C_{390}H_{782}$ and determined the melting points of six normal alkanes in the range C_{102}–C_{390}. The $C_{390}H_{782}$ has a melting point of 405.2 K. Arakawa and Wunderlich [2] have determined the melting point of extended chain polyethylene to be 414.6 K. In addition to these data, Wunderlich and Czornyj [3] list the melting points of several high molecular weight polyethylene crystals.

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Many attempts have been made by various authors [3–16] to determine the melting point of polyethylene from the analysis of the melting point of normal alkanes. For the paraffins above the carbon number 44 the melting point has been shown by Broadhurst [4, 5] to be given by the formula[2]

$$T_m = T_0(n + a)/(n + b) \tag{1}$$

Thus Broadhurst predicted a value of 414.3 K for the melting point of polyethylene. Variation of Eq. (1) was used by various authors [11–16] to represent the melting points of normal alkanes. A value of 418 K was reached by some of these authors. Flory and Vrij [8] examined the thermodynamic basis of the paraffin melting equation and added an extra term, $R \ln n$, to account for the disordering of the methyl layers during melting. On this basis Flory and Vrij estimated the melting point of polyethylene to be 418.5 K. Broadhurst [6] taking the extra term, $R \ln n$, into consideration modified Eq. (1) as follows:

$$T_m = T_0(n + a)/(n + \ln n + b) \tag{2}$$

Using an equation based on the above concept, Broadhurst calculated the convergence temperature for polyethylene to be 418.0 K. The melting points estimated by Flory and Vrij and also by Broadhurst are much higher than the experimentally determined value of 414.6 K.

We have looked at the problem of extrapolation of the melting points from the standpoint of the equations developed by Kreglewski [17, 18] for the dependence of normal boiling point and critical temperature on the chain length. Kreglewski also based his equations on the theory of Flory et al. [7]. Kreglewski's equations are the following:

$$\ln[(T_c^\infty - T_c)/K] = a - bm^{2/3} \tag{3}$$

$$\ln[(T_b^\infty - T_b)/K] = a - bm^{2/3} \tag{4}$$

where m is the number of CH_2 groups in the molecule, T_c^∞ is the critical temperature of an ultralong paraffin, and T_b^∞ is the normal boiling point of an ultralong paraffin. Others [19, 20] have extended Kreglewski's equations to various homologous series assuming T_c^∞ and T_b^∞ to be the same for all the homologous series. We have felt that the same concept can be used to determine the infinite melting point of a normal paraffin. The melting points of the paraffins, however, depend upon the crystalline state of the paraffin, which in turn depends on the odd and even number of the

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[2] Explanation of symbols and the associated units is given under Nomenclature.

carbon atoms at least for the first 30 normal alkanes. Above the carbon number 30 the even–odd effect vanishes and the melting points fall on a smooth curve. According to Kreglewski [17], the function $m^{2/3}$ corresponds to the effective chain length. We used the melting points of normal paraffins in the range C_{32} to C_{390} and using the relation

$$\ln[(T_m^\infty - T_m)/K] = a - bn^{2/3} \tag{5}$$

determined the melting point of an ultralong paraffin to be 405.4 K. This value is unfortunately too low to be considered the melting point of polyethylene which is now known very accurately to be 414.6 K. The reason for this discrepancy has been finally traced by us to be lying not in the value for the melting point of polyethylene but in the function $n^{2/3}$. The function $n^{2/3}$ which is supposed to represent the effective chain length in an ultralong paraffin is applicable to alkanes in the liquid state and not to the crystalline state, which is characterized by short- and long-range order in addition to other effects such as folding. The effective chain length should therefore be different in the crystalline state. We have therefore accepted the literature value for the melting point of polyethylene as the T_m^∞ and optimized the chain length function. Accordingly, we have found the exponent to be 1/25 instead of 2/3. We have tested the melting point function with the exponents in the range 1/10 to 1/50. The results are good for all these exponents. The optimum value has been fixed by us to be 1/25 mainly from the consideration of the overall fit and the standard deviation. We assume that the effective chain length incorporates into itself various effects related to melting. The value of $n^{1/25}$ increases monotonically from 1 for methane to about 2 for ultralong paraffins. Such a monotonic function is consistent with the enthalpies of fusion of the paraffins which also increase monotonically. Thus we have the following expression for representation of the melting points of alkanes above the carbon number 31.

$$\ln[(T_m^\infty - T_m)/K] = a - bn^{1/25} \tag{6}$$

It is quite amazing that this new function fits the data of alkanes even from the carbon number 16 to a deviation within 1 K. The limiting value for the T_m is strictly applicable to the normal paraffin chains, with the repeating unit CH_2. When the repeating unit is CF_2 as in perfluoroalkanes, the infinite melting point would be different. Bunn [21] reported a value of 603 K for the polymer with CF_2 as the polymer unit.

2. RESULTS AND DISCUSSION

Except for normal alkanes and a few homologous series, the melting points are not known for high molecular weight compounds of the homologous series. We have therefore assumed that the limiting melting point in any homologous series to be the same as for the normal paraffins. If not mentioned otherwise, the melting points have all been taken from the TRC Thermodynamic Tables [22]. The references for the melting points are too numerous to be listed in this paper. It is pertinent to point out here that the TRC tables report the values as the freezing points but in many cases they are the melting points. The freezing points are slightly lower than the melting points determined at 1 atmospheric pressure. Since we are interested in the melting points of the higher members only, it really does not matter whether we use the melting points or the freezing points for the lower members of the series.

We have used the melting points that have been determined experimentally in a number of cases and in a few cases graphically extrapolated values. The results for alkanes are shown in Table I. The constants of Eq. (6) have been listed in Table II for various homologous series of the general formula $Y-(CH_2)_m-H$. It appears that the even–odd effect of the carbon number on the melting point in any homologous series depends on the functional group Y. With some functional groups the even–odd effect vanishes even from the carbon number 15. Typical results illustrating the above points are shown in Table III with respect to 2-alkanones.

1. Normal Paraffins. We have used the TRC selected melting points up to C_{40}. In the carbon range 41 to 100, we used the values collected by Broadhurst [4] and Seyer et al. [16]. We have also obtained the melting points for alkanes with carbon numbers 48, 57, 58, 120, and 140 from other sources [23–26]. All other values above C_{100} are from Ungar et al. [1]. We have found that above the carbon number 1,000,000 the melting point reaches the limiting value of 414.6 K. This high carbon number is quite consistent with the numbers cited for the polyethylene chains which are also shown in Table I. They are, however, excluded in the data set used for the determination of the melting point equation for the alkanes.

2. Cycloalkanes. The TRC Thermodynamic Tables list the melting points from cyclopropane to cyclooctadecane. Sondheimer et al. [27, 28] synthesized several cycloalkanes in the range C_{21} to C_{54} and determined their melting points. Ruzica et al. [29–33] also synthesized several cycloalkanes and studied their melting behavior. In recent years cycloalkanes were studied with considerable interest [34–39]. We obtained the melting points of cycloalkanes with carbon numbers 48, 72, and 96 from Drotloff and Moller [38]. Therefore we have used the melting points of cycloalkanes with the carbon numbers 32, 36, 40, 42, 45, 48, 54, 72, and 96 and derived the melting point equation for this series. It appears that many more cycloalkanes were synthesized and studied [34, 39] but their melting

Table I. Comparison of the Calculated and Observed Melting Points of Normal Paraffins[a]

n_C	T_m (obs.) (K)	T_m (cal.) (K)	Dev. (K)	Weight	Ref. No.
1	90.68	−590.68	681.36	0.0	22
2	90.35	−194.89	285.24	0.0	22
3	85.47	−37.28	122.75	0.0	22
4	134.79	50.24	84.55	0.0	22
5	143.42	106.79	36.63	0.0	22
6	177.83	146.72	31.10	0.0	22
7	182.57	176.60	5.97	0.0	22
8	216.39	199.90	16.48	0.0	22
9	219.66	218.65	1.01	0.0	22
10	243.51	234.09	9.42	0.0	22
11	247.57	247.06	0.52	0.0	22
12	263.57	258.12	5.45	0.0	22
13	267.76	267.68	0.08	0.0	22
14	279.01	276.03	2.98	0.0	22
15	283.07	283.40	−0.33	0.0	22
16	291.31	289.96	1.35	0.0	22
17	295.13	295.84	−0.70	0.0	22
18	301.31	301.13	0.18	0.0	22
19	305.04	305.94	−0.90	0.0	22
20	309.58	310.32	−0.74	0.0	22
21	313.65	314.32	−0.67	0.0	22
22	317.55	318.01	−0.46	0.0	22
23	320.75	321.41	−0.66	0.0	22
24	324.05	324.56	−0.51	0.0	22
25	326.85	327.49	−0.64	0.0	22
26	329.55	330.21	−0.66	0.0	22
27	332.15	332.76	−0.61	0.0	22
28	334.55	335.14	−0.59	0.0	22
29	336.85	337.38	−0.53	0.0	22
30	338.95	339.48	−0.53	0.0	22
31	341.05	341.47	−0.42	0.0	22
32	342.85	343.34	−0.49	1.0	22
33	344.55	345.11	−0.56	1.0	22
34	346.25	346.79	−0.54	1.0	22
35	347.85	348.38	−0.53	1.0	22
36	349.35	349.90	−0.55	1.0	22
37	350.85	351.34	−0.49	1.0	22
38	352.15	352.71	−0.56	1.0	22
39	353.45	354.02	−0.57	1.0	22
40	354.65	355.28	−0.63	1.0	22
41	355.50	356.47	−0.97	1.0	4
41	354.85	356.47	−1.62	1.0	16

[a] Calculated using Eq. (6) with $a = 24.71207$; $b = 17.79905$.

Table I. *(Continued)*

n_C	T_m (obs.) (K)	T_m (cal.) (K)	Dev. (K)	Weight	Ref. No.
42	357.30	357.62	−0.32	1.0	4
42	356.05	357.62	−1.57	1.0	16
43	358.50	358.72	−0.22	1.0	4
43	356.95	358.72	−1.77	1.0	16
44	359.60	359.77	−0.17	1.0	4
45		360.78			
46	361.30	361.75	−0.45	1.0	4
47		362.69			
48	361.40	363.59	−2.19	1.0	23
49		364.46			
50	365.30	365.29	0.01	1.0	4
51		366.10			
52	367.00	366.88	0.12	1.0	4
53		367.63			
54	368.20	368.36	−0.16	1.0	4
55		369.06			
56		369.74			
57	369.65	370.40	−0.75	1.0	24
58	370.15	371.04	−0.89	1.0	25
59		371.66			
60	372.40	372.26	0.14	1.0	4
60	372.05	372.26	−0.21	1.0	16
61		372.84			
62	373.70	373.41	0.29	1.0	4
63		373.96			
64	375.30	374.49	0.81	1.0	4
65	376.80	375.01	0.74		
66	376.80	375.52	1.28	1.0	4
67	377.30	376.01	1.29	1.0	4
68		376.49			
69		376.96			
70	378.50	377.41	1.09	1.0	4
71		377.85			
72		378.28			
73		378.71			
74		379.12			
75		379.52			
75.4[b]	380.80	379.67	1.13	0.0	3
76		379.91			
77		380.29			
78		380.66			

[b] The quantity n_c calculated from the weight average molecular weight of polyethylene crystals. For details see Ref. 3.

Table I. *(Continued)*

n_C	T_m (obs.) (K)	T_m (cal.) (K)	Dev. (K)	Weight	Ref. No.
79		381.03			
80		381.38			
81		381.73			
82	383.50	382.07	1.43	1.0	4
83		382.41			
84		382.73			
84.8^b	383.45	382.99	0.46	0.0	3
85		383.05			
86		383.36			
87		383.67			
88		383.97			
89		384.26			
90		384.55			
91		384.83			
92		385.11			
93		385.38			
94	387.00	385.64	1.36	1.0	4
95		385.90			
96		386.16			
97		386.41			
98		386.66			
99		386.90			
100	388.40	387.14	1.26	1.0	4
102	388.90	387.60	1.30	1.0	1
120	392.20	391.12	1.08	1.0	26
140	394.20	394.05	0.15	1.0	26
150	396.40	395.24	1.16	1.0	1
198	399.80	399.42	0.38	1.0	1
246	401.80	402.07	−0.27	1.0	1
294	403.60	403.91	−0.31	1.0	1
335.0^b	408.10	405.09	3.01	0.0	3
377.8^b	409.30	406.06	3.24	0.0	3
390	405.20	406.30	−1.10	1.0	1
515.3^b	409.15	408.16	0.99	0.0	3
912.3^b	411.20	410.80	0.40	0.0	3
3,863.2^b	412.65	413.65	−1.00	0.0	3
6,001.4^b	413.65	413.99	−0.34	0.0	3
10,000		414.24			
100,000		414.57			
1,000,000		414.60			

points were not reported. We have therefore presented in Table IV our calculated values for those cycloalkanes along with our results for the other cycloalkanes.

3. 1-Alkylcyclopentanes. The TRC Thermodynamic Tables list the melting points up to C_{40} but the values are experimental only for 12 of them. The constants listed in Table II are obtained on the basis of

Table II. Values of the Constants of Eq. (6) for Various Homologous Series[a]

Homologous series	a	b	SD[b]	n^{*}[c]
Normal alkanes	24.71207	17.79905	0.947	31
Cycloalkanes	30.35974	22.57216	1.92	31
1-Alkylcyclopentanes	27.16582	19.80791	0.341	22
1-Alkylcyclohexanes	28.58733	21.11261	0.438	25
1-Alkenes	29.29506	19.13557	0.009	21
1-Alkynes	26.42416	19.32058	0.637	15
1-Alkylbenzenes	28.71740	21.18813	0.148	16
1-Alkylnaphthalenes	25.15359	18.06739		25
2-Alkylnaphthalenes	26.00394	18.80971		25
1-Fluoroalkanes	26.55369	19.44985		30
1-Chloroalkanes	25.67164	18.64411		30
1-Bromoalkanes	24.48168	17.59152	0.168	22
1-Iodoalkanes	22.55096	15.95350	1.29	30
1-Alkanols	24.11107	17.55276	0.736	21
2-Alkanols	24.26195	17.64788		30
n-Alkanoic acids	20.89539	14.85653	1.10	22
1-Alkanals	26.25112	19.17364		30
2-Alkanones	23.80299	17.20223	0.278	15
Methyl alkanoates	26.62865	19.52636	1.85	22
Ethyl alkanoates	30.02291	22.44980	1.17	22
n-Alkyl methanoates	25.67164	18.64411		28
n-Alkyl ethanoates	27.71664	20.42408	1.89	20
Dialkyl ethers	24.56745	17.18798		28
1-Alkanethiols	25.39403	18.39017		30
2-Alkanethiols	24.86143	17.90249		30
2-Thioalkanes	24.60585	17.66823		30
1-Alkanamines	22.85642	16.32426		22
Dialkyl amines	24.67382	17.72836		28
Trialkyl amines	26.84949	19.07693	0.94	36
1-Alkanenitriles	26.55369	19.44985		30

[a] The constants of Eq. (6) are to be used with the value of 414.6 K for the limiting melting point.

[b] The standard deviation is not shown when graphically extrapolated melting points are used.

[c] The quantity n^{*} is the number of carbon atoms above which Eq. (6) is applicable in this series.

the experimental melting points of 1-hexadecylcyclopentane, 1-octadecylcyclopentane, and 1-henicosylcyclopentane. In this series, the even–odd effect on the melting point appears to diminish from the carbon number 21 itself.

4. *1-Alkylcyclohexanes.* The TRC Thermodynamic Tables list the melting points up to C_{40} but the values are experimental only for 15 of them. Using the experimental melting points for 1-octadecylcyclohexane, 1-icosylcyclohexane, and 1-docosylcyclohexane, we determined the constants reported in Table II. The even–odd effect on the melting point vanishes from the carbon number 18 itself in this series. We recommend the values that can be obtained through Eq. (6).

5. *1-Alkenes.* The TRC Thermodynamic Tables list the melting points of 1-alkenes up to 1-tetracontene but the values are experimental for only 24 of them. In deriving the constants of Eq. (6) for this series we used the experimental melting points of 1-docosene, 1-heptacosene, 1-hentriacontene, and 1-tritriacontene. The even–odd effect vanishes in this series from carbon number 21. We recommend our melting point equation for this series.

Table III. Comparison of the Calculated and Observed Melting Points of 2-Alkanones[a]

n_C	T_m (obs.) (K)	T_m (cal.) (K)	Dev. (K)	Weight	Ref. No.
3	178.45	74.94	103.51	0.0	22
4	186.46	138.73	47.73	0.0	22
5	196.29	180.23	16.06	0.0	22
6	217.35	209.68	7.67	0.0	22
7	238.15	231.82	6.33	0.0	22
8	252.85	249.14	3.71	0.0	22
9	265.65	263.12	2.53	0.0	22
10	276.25	274.67	1.58	0.0	22
11	285.95	284.40	1.55	0.0	22
12	293.65	292.72	0.93	0.0	22
13	300.65	299.92	0.73	0.0	22
14	307.15	306.23	0.92	0.0	22
15	313.15	311.81	1.34	0.0	22
16	317.15	316.78	0.37	0.0	22
17	321.15	321.24	−0.09	0.0	22
18	325.15	325.27	−0.12	1.0	22
19	329.15	328.92	0.23	1.0	22
20	332.15	332.26	−0.11	1.0	22

[a] Calculated using Eq. (6) with $a = 24.82267$; $b = 18.07148$.

6. 1-Alkynes. The TRC Thermodynamic Tables list the melting points in this series up to C_{40} but only for 16 of them in the low molecular weight range the values are experimental. In deriving the constants of Eq. (6) we used the experimental melting points of 1-heptadecyne, 1-octadecyne, and 1-nonadecyne. The even–odd effect seems to vanish in this series from carbon number 15 itself.

7. 1-Alkylbenzenes. Although the TRC Thermodynamic Tables list the melting points up to C_{40}, only for 11 of these compounds the values are experimental. We have used the experimental melting points of 1-hexadecylbenzene, 1-octadecylbenzene, and 1-icosylbenzene and determined the constants of Eq. (6). The even–odd effect vanishes in this series from the carbon number 21 and we recommend Eq. (6) for this series.

8. 1-Alkylnaphthalenes. The TRC Thermodynamic Tables list the melting points for 13 compounds up to 1-dedecylnaphthalene. All of them are experimental. We have obtained from the literature [40] the melting point of 1-pentadecylnaphthalene. Using the melting point of 1-pentadecylnaphthalene and graphically extrapolated values for 1-icosylnaphthalene and 1-docosylnaphthalene, we derived the constants of Eq. (6).

Table IV. Comparison of the Calculated and Observed Melting Points of Cycloalkanes[a]

n_C	T_m (obs.) (K)	T_m (cal.)[b] (K)	Dev. (K)	Weight	Ref. No.
32	331.65	330.57	1.08	1.0	27
36	343.65	340.26	3.39	1.0	27
40	347.65	348.00	−0.35	1.0	27
40	349.65	348.00	1.65	1.0	28
42	351.21	351.32	−0.11	1.0	38
45	353.65	355.74	−2.09	1.0	27
48	359.00	359.61	−0.61	1.0	38
50		363.02			
54	363.65	366.04	−2.39	1.0	28
72	379.30	378.86	0.44	1.0	38
96	389.00	388.39	0.61	1.0	38
120		394.04			
144		397.77			
168		400.40			
192		402.36			
216		403.87			
288		406.84			

[a] Results are shown from cyclodotriacontane.

[b] Calculated using Eq. (6) with $a = 30.35974$; $b = 22.57216$.

9. 2-Alkylnaphthalenes. The TRC Thermodynamic Tables list the melting points up to 2-decylnaphthalene. They are all experimental. Data are insufficient to apply Eq. (6) to this series. We used graphically extrapolated melting points of compounds with carbon numbers 28, 30 and 32.

10. 1-Fluoroalkanes. The TRC Thermodynamic Tables list the melting points up to C_{40}. The melting points for only 10 of the lower members of this series are experimental. The tablemaker for this series carried the even–odd effects up to the 40th member of this series. We consider this to be unusual, judging mainly from the behavior of 1-chloroalkanes, 1-bromoalkanes, and 1-iodoalkanes. The even–odd effect, according to us, diminishes in this series from carbon number 31. Accordingly, we used the graphically extrapolated melting points for 31, 32, and 33 members of this series and derived the constants shown in Table II.

11. 1-Chloroalkanes. The TRC Thermodynamic Tables list the melting points up to C_{40} but the values are experimental only for 11 of them. We used the experimental melting point for 1-chlorotiacontane and graphically extrapolated melting points of 1-chlorohentriacontane and 1-chlorodotriacontane to derive the constants recorded in Table II for this series.

12. 1-Bromoalkanes. The TRC Thermodynamics Tables list the melting points up to C_{40} for this series. The melting points are based on experiment for 22 of these compounds. We used the experimental melting points for compounds with carbon numbers 20, 22, and 30 to derive the constants recorded in Table II for this series.

13. 1-Iodoalkanes. There are quite a number of experimental melting points for compounds of this series with carbon numbers above C_{30}. We derived the constants for this series using the melting points of 1-iodoalkanes with carbon numbers 30, 31, 32, and 36. The even–odd effect seems to vanish above C_{25} in this series. We recommend our values for this series.

14. 1-Alkanols. The TRC Thermodynamic Tables list the melting points up to 1-icosanol. We collected the melting points of eight more 1-alkanols in the range C_{22} to C_{32} from the literature [41]. Our equation is based on the melting points of 1-alkanols with the carbon numbers 22, 23, 24, 26, 28, 29, 30, and 32. The even–odd effect vanishes in this series from 1-docosanol and we recommend our equation for this series. The calculated and the observed melting points are compared in Table V for this series from 1-henicosanol.

Table V. Comparison of the Calculated and Observed Melting Points of 1-Alkanols[a]

n_C	T_m (obs.) (K)	T_m (cal.)[b] (K)	Dev. (K)	Weight	Ref. No.
21		341.99			
22	344.15	344.62	−0.47	1.0	41
23	347.65	347.84	−0.19	1.0	41
24	350.15	349.30	0.85	1.0	41
25		351.40			
26	353.15	353.35	−0.20	1.0	41
27		355.17			
28	356.45	356.88	−0.43	1.0	41
29	357.65	358.48	−0.83	1.0	41
30	361.15	359.99	1.16	1.0	41
31		361.41			
32	362.55	362.76	−0.21	1.0	41

[a] Results are shown from 1-henicosanol.

[b] Calculated using Eq. (6) with $a = 24.11107$; $b = 17.55276$.

15. 2-Alkanols. The TRC Thermodynamic Tables list the melting points of the first 18 members of this series. We used the graphically extrapolated melting points for 2-alkanols with carbon numbers 30, 31, and 32 to derive the melting point equation for this series.

16. n-*Alkanoic acids.* The values listed in the TRC Thermodynamic Tables for the first 20 members are all based on experiment. We collected from the literature [41] the melting points of docosanoic acid, tetracosanoic acid, hexacosanoic acid, octacosanoic acid, triacontanoic acid, and dotriacontanoic acid and used the last six of them to derive the constants listed in Table II. We recommend our equation for this series. The calculated and observed melting points are compared in Table VI for this series beginning from 1-henicosanoic acid.

17. 1-Alkanals. The TRC Thermodynamic Tables list the melting points for the first 20 members of this series, out of which only 15 are based on experiment. We have used the graphically extrapolated melting points of compounds with the carbon numbers 30, 31, and 32 to derive the melting point equation for this series. Our results appear to be good.

18. 2-Alkanones. The TRC Thermodynamic Tables list the experimental melting points for the first 18 members of this series. We used the melting points of the last three compounds in that list to determine the constants of Eq. (6). We recorded the results for this series in Table III. It

Table VI. Comparison of the Calculated and Observed Melting Points of *n*-Alkanoic acids[a]

n_C	T_m (obs.) (K)	T_m (cal.)[b] (K)	Dev. (K)	Weight	Ref. No.
21		353.36			
22	354.15	355.24	−1.09	0.0	40
23		356.99			
24	359.15	358.62	0.53	1.0	41
25		360.14			
26	362.05	361.57	0.48	1.0	41
27		362.91			
28	363.55	364.17	−0.62	1.0	41
29	363.65	365.36	−1.71	1.0	41
30	366.75	366.48	0.27	1.0	41
31		367.54			
32	369.55	368.55	1.00	1.0	41

[a] Results are shown from 1-henicosanoic acid.

[b] Calculated using Eq. (6) with $a = 20.89539$; $b = 14.85653$.

can be seen from those results that the even–odd effect of the carbon number on the melting point vanishes above the carbon number 15.

19. Methyl Alkanoates. The TRC Thermodynamic Tables list the values for the first four members of this series. We were able to get the melting points of several higher members of this series from the literature [40–42]. We used the melting points of eight methyl alkanoates in the carbon range 22 to 31 and derived the constants reported in Table II. The even–odd effect seems to vanish in this series from C_{22}. The calculated and observed melting points are compared in Table VII beginning from methyl icosanoate.

20. Ethyl Alkanoates. The TRC Thermodynamic Tables list the values for the first four members of this series. We collected from the literature [40–42] the melting points of 14 higher members of this series. Using the melting points of ethyl docosanoate, ethyl tricosanoate, ethyl tetracosanoate, ethyl octacosanoate, and ethyl triacontonoate we determined the constants reported in Table II. The even–odd effect appears to diminish in this series from the carbon number 22. The calculated and observed melting points are compared in Table VIII beginning from ethyl icosanoate.

21. n-*Alkyl Methanoates.* The TRC Thermodynamic Tables list the experimental melting points for all of the first eight members in this series and the pentadecyl methanoate. We used the graphically extrapolated

Table VII. Comparison of the Calculated and Observed Melting Points of Methyl Alkanoates[a]

n_C	T_m (obs.) (K)	T_m (cal.)[b] (K)	Dev. (K)	Weight	Ref. No.
21	318.95	317.72	1.23	0.0	40
22	322.15	321.62	0.53	0.0	40
23	327.15	325.20	1.95	1.0	40
24	326.55	328.51	−1.96	1.0	40
25	332.65	331.57	1.08	1.0	40
26		334.42			
27	336.95	337.07	−0.12	1.0	41
28	337.15	339.54	−2.39	1.0	40
29	341.65	341.86	−0.21	1.0	42
30		344.03			
31	347.65	346.07	1.58	1.0	42
32		349.81			

[a] Results are shown from methyl icosanoate.
[b] Calculated using Eq. (6) with $a = 26.62865$; $b = 19.52636$.

melting points of methanoates with carbon numbers 30, 31, and 32 to derive the melting point equation for this series.

22. n-*Alkyl Ethanoates.* The TRC Thermodynamic Tables list the experimental melting points for all the first 20 members of this series. We collected from the literature [41] the melting points of two more

Table VIII. Comparison of the Calculated and Observed Melting Points of Ethyl Alkanoates[a]

n_C	T_m (obs.) (K)	T_m (cal.)[b] (K)	Dev. (K)	Weight	Ref. No.
22	314.55	313.26	1.29	0.0	40
23	319.15	317.74	1.41	0.0	40
24	323.15	321.85	1.30	1.0	40
25	324.35	325.63	−1.28	1.0	40
26	329.15	329.13	0.02	1.0	42
27		332.37			
28		335.35			
29		338.18			
30	340.15	340.80	−0.65	1.0	42
31		343.25			
32	346.15	345.55	0.60	1.0	42

[a] Results are shown from ethyl icosanoate.
[b] Calculated using Eq. (6) with $a = 30.02291$; $b = 22.44980$.

ethanoates. We used the melting points of nonadecyl acetate, icosyl acetate, hexacosanyl acetate, and hentriacontanyl acetate to derive the constants reported in Table II. The even–odd effect vanishes in this series from carbon number 15 itself. The calculated and observed melting points are compared in Table IX beginning from nonadecyl ethanoate.

23. Dialkyl Ethers. The melting points of ethers are difficult to determine. They are available only for a few of the methyl ethers. Fortunately we have the melting points available for eight of the dialkyl ethers. Even then we had to use graphically extrapolated melting points of ethers with carbon numbers 28, 30, and 32 to establish the melting point equation for this series.

24. 1-Alkanethiols. The TRC Thermodynamic Tables list the melting points of the first 20 members of the 1-alkanethiols. The melting points of 11 of them are based on experiment. We used the graphically extrapolated melting points of thiols with carbon numbers 30, 31, and 32 in deriving the melting point equation for this series.

25. 2-Alkanethiols. The TRC Thermodynamic Tables lists the melting points of the first 18 members of the 2-alkanethiols, but the melting points are based on experiment only for 5 of them. We used the graphically

Table IX. Comparison of the Calculated and Observed Melting Points of *n*-Alkyl Ethanoates[a]

n_C	T_m (obs.) (K)	T_m (cal.)[b] (K)	Dev. (K)	Weight	Ref. No.
21	310.75	310.28	0.47	1.0	40
22	313.15	314.66	−1.51	1.0	40
23		318.69			
24		322.40			
25		325.83			
26		329.01			
27		331.97			
28	336.65	334.72	1.93	1.0	42
29		337.30			
30		339.71			
31		341.98			
32		344.11			
33	345.15	346.11	−0.96	1.0	42

[a] Results are shown from nonadecyl ethanoate.

[b] Calculated using Eq. (6) with $a = 27.71664$; $b = 20.42408$.

extrapolated melting points of thiols with carbon numbers 30, 31, and 32 in deriving the melting point equation for this series.

26. 2-Thiaalkanes. The TRC Thermodynamic Tables list the melting points of all the first 19 members of this series but the values are experimental only for the first four members. We used the graphically extrapolated melting points of thiols with carbon numbers 30, 31, and 32 in deriving the melting point equation for this series.

27. 1-Alkanamines. The TRC Thermodynamics Tables list the melting points in this series for the first 40 members, of which the values are based on experiment for the first 20 members and for 1-dodecylamine. We therefore used the graphically extrapolated melting points for compounds with carbon numbers 30, 31, and 32 and derived the constants reported in Table II. The agreement is quite good for several of the lower members.

28. Dialkyl Amines. The TRC Thermodynamics Tables list the melting points of 10 dialkyl amines up to the carbon number 40. We used the melting points of dialkyl amines with carbon numbers 30, 32, and 36 and derived the melting point equation for this series.

29. Trialkyl Amines. The TRC Thermodynamic Tables list the experimental melting of 11 compounds of this series. We used the compounds with carbon numbers 36, 42, 48, 54, and 60 to determine the melting point equation for this series. Our results are very satisfactory for this series.

30. 1-Alkanenitriles. The TRC Thermodynamics Tables list the melting points only for the first 20 members of this series. They are all based on experiment. We used the graphically extrapolated melting points of alkanenitriles with carbon numbers 30, 31, and 32 to derive the melting point equation for this series.

3. CONCLUSIONS

Judging from the results obtained on the basis of Eq. (6), we consider the procedure extremely useful and also reliable for determining the melting points above a certain carbon number in any of the homologous series. It is particularly useful for hydrocarbon series. Its use may be somewhat limited in compounds containing oxygen, since most of the high molecular weight oxygen compounds decompose on heating up to the melting point. We recommend our equations for calculating the melting points of high molecular weight compounds of various homologous series. The standard deviation listed in Table II may not have much bearing on the value of our estimation procedure since they were calculated using three data points in most cases. Furthermore, assuming that the limiting melting point may change in future, even then the values predicted by our procedure for the lower members of several homologous series will not change appreciably.

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NOMENCLATURE

a	A constant to be determined
b	A constant to be determined
m	Number of methylene groups in the molecule
n	Number of carbon atoms in the molecule
n^*	Number of carbon atom above which Eq. (6) is applicable
T_0	Temperature constant, K
T_c	Critical temperature, K
T_c^{∞}	Critical temperature of an ultralong normal paraffin, K
T_b	Normal boiling point, K
T_b^{∞}	Normal boiling point of an ultralong normal paraffin, K
T_m	Melting point, K
T_m^{∞}	Melting point of an ultralong paraffin, K
Standard deviation	$\{\sum[(T_m(\text{obsd}) - T_m(\text{calc})]^2/(\text{No. points} - \text{No. parameters})\}^{0.5}$

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