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# The Critical Constants of Long-Chain Normal Paraffins

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Because of the recent availability of the critical constants of normal alkanes up to octadecane, some modifications in the estimation procedures for the critical constants have become necessary. It has been shown that the equation of Ambrose for the critical temperature of normal alkanes leads to the result that as $n \to \infty$, the limiting value for the critical temperature is equal to the limiting value for the normal boiling point and the limiting value for the critical pressure is 1 atm. Currently, the $CH_2$ increment for the critical volume is considered constant. The recent data of Teja have shown that the $CH_2$ increment increases indefinitely in a homologous series until the critical volume reaches its limiting value. This has made the current procedure for estimating the critical volume obsolete. Taking into account the new measurements of Teja, we have now developed new equations for estimating the critical constants. The limiting values for an infinitely long alkyl chain for $T_b$, $T_c$, $P_c$, and $V_c$ have been found to be 1021 K, 1021 K, 1.01325 bar, and 18618 $cm^3 \cdot mol^{-1}$, respectively. These new concepts have been applied to the estimation of various properties other than the critical constants.

**KEY WORDS:** boiling point; critical temperature; critical pressure; critical volume; enthalpy of vaporization; second virial coefficient; surface tension.

## 1. CURRENT PROCEDURES FOR ESTIMATING CRITICAL CONSTANTS

We have recently reviewed various procedures for estimation of critical constants and proposed modified procedures [1]. Among various procedures for estimating critical temperatures, the procedure of Ambrose [2]

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appears to be the best. For normal alkanes, the Ambrose equation for critical temperature is[2]

$$T_b/(T_c - T_b) = a + bn \qquad (1)$$

Another equation of interest is due to Kreglewski and Zwolinski [3]:

$$\ln(T_c^{\infty *} - T_c^*) = a - bn^{2/3} \qquad (2)$$

The above equation is particularly useful for estimating the critical temperatures of long-chain paraffins.

Ambrose [4] has proposed the following equation for the critical pressure:

$$(M^*/P_c^*)^{1/2} = a + bn \qquad (3)$$

The following is the equation for critical pressure due to Kreglewski and Zwolinski [3]:

$$\log P_c^* = a - bn^{2/3} \qquad (4)$$

Teja et al. [5] have recently proposed the following equation for the critical pressure:

$$\ln(P_c^* - P_c^{\infty *}) = a - bn^c \qquad (5)$$

For the critical volume Kreglewski and Zwolinski have proposed:

$$V_c^* = a + b(n + n^{2/3}) \qquad (6)$$

Currently [1], the critical volume is estimated from

$$V_c^* = a + bn \qquad (7)$$

The recent work of Anselme et al. [6] has shown that the $CH_2$ increment is not constant but increases indefinitely for normal alkanes and normal alkanols. According to Teja et al. [5], the critical volume of the alkanes is given by

$$V_c^* = 61.7193 + 38.3386n^{1.16535} \qquad (8)$$

## 2. RECOMMENDED PROCEDURES

### 2.1. Estimation Procedures for the Critical Temperature

Equation (1) may be rewritten as

$$T_c = T_b[1 + 1/(a + bn)] \qquad (9)$$

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

As $n \to \infty$, according to Eq. (9),

$$T_c^\infty = T_b^\infty \tag{10}$$

Unfortunately, the normal boiling points are known accurately up to octadecane only. We need, therefore, an auxiliary equation such as the one proposed by Kreglewski and Zwolinski [3] for calculating the normal boiling points above octadecane. The equation proposed for the normal boiling point is

$$\ln(T_b^{\infty}{}^* - T_b^*) = a - bn^{2/3} \tag{11}$$

Thus with the help of such an auxiliary equation and Eq. (1), one can determine the critical temperatures above octadecane and thereby $T_c^\infty$. For a better representation of the normal boiling points for $C_2$ to $C_{18}$, we have modified the Kreglewski equation as

$$\ln(T_b^{\infty}{}^* - T_b^*) = a - bn^{2/3} - cn - dp \tag{12}$$

where $p$ is the Platt number [7, 8], which represents the number of C–C–C–C structural features in the molecule and is equal to $n-3$ in the case of normal alkanes above propane. The Platt numbers of methane, ethane, and propane are zero. According to the Kreglewski equation, the limiting value for the normal boiling point is 1080 K, whereas according to Eq. (12) it is only 1021 K. Now by using the normal boiling points determined by substituting Eq. (12) in Eq. (1), one can calculate the critical temperatures. The critical temperatures calculated in this way go to a maximum value exceeding $T_c^\infty$ around the carbon number 200 and fall gradually to $T_c^\infty$ with increasing $n$. In Fig. 1 we have plotted the normal boiling points and the critical temperatures versus the carbon number. This peculiar behavior cannot be represented by Kreglewski's equation for the critical temperature, as the Kreglewski equation limits the critical temperature to a maximum value of $T_c^\infty$. It is worthwhile to point out that Ambrose never inteded his equation to be applied to high molecular weight alkanes. We have used the critical temperatures recently determined by Anselme et al. [6] in arriving at the constants of Eq. (1). A somewhat better representation of the $T_c$ for ethane to octadecane is possible, if we modify Eq. (1) as

$$T_b/(T_c - T_b) = a + bn + cp + dn^{1/3} \tag{13}$$

The differences in the $T_c$ values calculated from Eqs. (1) and (13) are not significant in the range above octadecane. We therefore prefer to use

Eq. (1) for determining the critical temperatures. This will also be consistent with our current procedures [1] for estimating the critical temperatures.

## 2.2. Estimation Procedures for the Critical Pressures

An implication of Eq. (1) is that as $n \to \infty$, $P_c^\infty$ becomes equal to $P_b$, which is 1.01325 bar. The equations of Ambrose and Kreglewski both predict $P_c^\infty$ to be zero. Equation (5) of Teja et al. [5] leads to a value of 8.4 bars for the limiting critical pressure. We consider this value to be too high. We also consider that $P_c^\infty$ should not be zero since the limiting melting point, $T_m^\infty$ of a long-chain normal alkane is 414.6 K [9], which is far below the limiting value for the $T_c^\infty$ arrived at by any procedure. We, therefore, modify Eq. (3) as follows:

$$[M^*/(P_c^* - P_b^*)]^{1/2} = a + bn \tag{14}$$

Equation (14) applies to normal alkanes. It can be applied to the isomeric alkanes and other compounds using the procedures outlined by Ambrose [4] and by us previously [1]. Critical pressures are now available up to octadecane. A somewhat better representation of the critical pressures is possible if we modify Eq. (14) as

$$[M^*/(P_c^* - P_b^*)]^{1/2} = a + bn + cp + dn^{1/2} \tag{15}$$

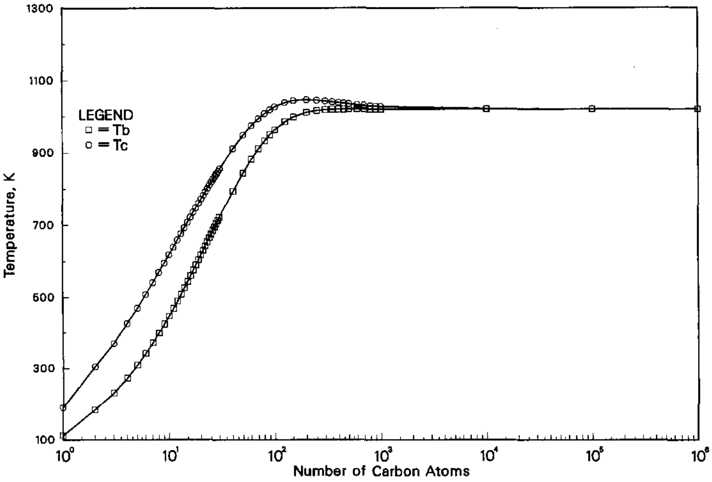

**Fig. 1.** Plots of the critical temperature and the normal boiling points of the normal alkanes versus the number of carbon atoms. The numbers of carbon atoms are plotted on a logarithmic scale.

The following equation, which is independent of the carbon number, has been found to represent the critical pressure much more satisfactorily than Eq. (15) but the differences occur largely for alkanes with high carbon numbers.

$$\ln(P_b/P_c) = aX + bX^2 + cX^3 + dX^4 + eX^5 \tag{16}$$

where $X = (T_c - T_b)/T_c$. According to Eq. (16) when $T_c = T_b$, $P_c$ equals $P_b$. Equation (16) applies not only to normal alkanes but also to the isomeric alkanes. The constants are, however, different for different homologous series. For the sake of simplicity and to avoid introducing major changes in our current estimation procedure for the critical pressure, we recommend Eq. (14) for calculating critical pressure above octadecane. If we adopt Eq. (14) in preference to Eq. (3), our current procedures for estimating critical pressures may require a very minor revision.

**Table I.** Comparison of Observed[a] and Calculated Normal Boiling Points of the Alkanes

| $n$ | $T_b$(obsd) (K) | Eq. (11)[b] (K) | Dev. (K) | Eq. (12)[b] (K) | Dev. (K) |
|---|---|---|---|---|---|
| 1 | 111.66 | 115.10 | −3.44 | 125.71 | −14.05 |
| 2 | 184.55 | 179.93 | 4.62 | 184.55 | 0.00 |
| 3 | 231.05 | 230.72 | 0.33 | 231.08 | −0.03 |
| 4 | 272.65 | 273.46 | −0.81 | 272.65 | 0.00 |
| 5 | 309.21 | 310.70 | −1.49 | 309.17 | 0.04 |
| 6 | 341.88 | 343.84 | −1.96 | 341.88 | 0.00 |
| 7 | 371.58 | 373.75 | −2.17 | 371.58 | 0.00 |
| 8 | 398.82 | 401.04 | −2.22 | 398.81 | 0.01 |
| 9 | 423.97 | 426.12 | −2.15 | 423.95 | 0.02 |
| 10 | 447.30 | 449.34 | −2.04 | 447.30 | 0.00 |
| 11 | 469.08 | 470.93 | −1.85 | 469.09 | −0.01 |
| 12 | 489.47 | 491.09 | −1.62 | 489.51 | −0.04 |
| 13 | 508.62 | 509.99 | −1.37 | 508.70 | −0.08 |
| 14 | 526.73 | 527.76 | −1.03 | 526.78 | −0.05 |
| 15 | 543.83 | 544.52 | −0.69 | 543.88 | −0.05 |
| 16 | 560.01 | 560.36 | −0.35 | 560.06 | −0.05 |
| 17 | 575.47 | 575.36 | 0.11 | 575.42 | 0.05 |
| 18 | 590.00 | 589.60 | 0.40 | 590.02 | −0.02 |

[a] The observed normal boiling points are taken from Ref. 5 and the *TRC Thermodynamic Tables* [14]. The normal boiling point of methane is from Ref. 15.

[b] The limiting temperature of $T_b = 1021$ K.

**Table II.** Comparison of Observed[a] and Calculated Critical Temperatures of the Alkanes

| $n$ | $T_b$ (K) | $T_c$(obsd) (K) | Eq. (1) (K) | Dev. (K) | Eq. (13) (K) | Dev. (K) |
|---|---|---|---|---|---|---|
| 1 | 111.66 | 190.55 | 192.36 | −1.81 | 191.13 | −0.58 |
| 2 | 184.55 | 305.24 | 305.89 | −0.65 | 305.24 | 0.00 |
| 3 | 231.05 | 369.82 | 370.35 | −0.53 | 370.27 | −0.45 |
| 4 | 272.65 | 425.16 | 424.42 | 0.74 | 424.66 | 0.50 |
| 5 | 309.21 | 469.70 | 469.07 | 0.63 | 469.48 | 0.22 |
| 6 | 341.88 | 507.50 | 506.87 | 0.63 | 507.35 | 0.15 |
| 7 | 371.58 | 540.30 | 539.73 | 0.57 | 540.19 | 0.11 |
| 8 | 398.82 | 568.83 | 568.70 | 0.13 | 569.11 | −0.28 |
| 9 | 423.97 | 594.70 | 594.55 | 0.15 | 594.87 | −0.17 |
| 10 | 447.30 | 617.70 | 617.81 | −0.11 | 618.02 | −0.32 |
| 11 | 469.08 | 638.80 | 638.97 | −0.17 | 639.05 | −0.25 |
| 12 | 489.47 | 658.40 | 658.32 | 0.08 | 658.28 | 0.12 |
| 13 | 508.62 | 676.00 | 676.11 | −0.11 | 675.94 | 0.06 |
| 14 | 526.73 | 692.30 | 692.66 | −0.36 | 692.36 | −0.06 |
| 15 | 543.83 | 707.80 | 708.02 | −0.22 | 707.60 | 0.20 |
| 16 | 560.01 | 722.20 | 722.33 | −0.13 | 721.79 | 0.41 |
| 17 | 575.47 | 735.60 | 735.87 | −0.27 | 735.22 | 0.38 |
| 18 | 590.00 | 747.70 | 748.36 | −0.66 | 747.61 | 0.09 |
| 19 | 603.95 |  | 760.15 |  | 759.29 |  |
| 20 | 617.15 |  | 771.32 |  | 770.36 |  |
| 21 | 629.65 |  | 781.87 |  | 780.83 |  |
| 22 | 641.75 |  | 791.88 |  | 790.75 |  |
| 23 | 653.35 |  | 801.37 |  | 800.17 |  |
| 24 | 664.45 |  | 810.38 |  | 809.11 |  |
| 25 | 674.95 |  | 818.98 |  | 817.64 |  |
| 26 | 685.35 |  | 827.13 |  | 825.73 |  |
| 27 | 695.10 |  | 834.93 |  | 833.48 |  |
| 28 | 704.49 |  | 842.37 |  | 840.86 |  |
| 29 | 713.52 |  | 849.50 |  | 847.94 |  |
| 30 | 722.20 |  | 856.30 |  | 854.70 |  |
| 40 | 793.68 |  | 910.93 |  | 909.03 |  |
| 50 | 844.78 |  | 948.40 |  | 946.38 |  |
| 60 | 882.50 |  | 975.02 |  | 972.99 |  |
| 70 | 910.95 |  | 994.36 |  | 992.36 |  |
| 80 | 932.80 |  | 1008.59 |  | 1006.64 |  |
| 90 | 949.78 |  | 1019.16 |  | 1017.28 |  |
| 100 | 963.13 |  | 1027.03 |  | 1025.22 |  |
| 125 | 985.78 |  | 1038.98 |  | 1037.35 |  |
| 150 | 999.02 |  | 1044.47 |  | 1042.99 |  |
| 200 | 1011.94 |  | 1046.99 |  | 1045.76 |  |
| 250 | 1017.06 |  | 1045.50 |  | 1044.46 |  |

[a] The observed values are from Refs. 5, 6, 14, and 15. The values of $T_b$ for alkanes above octadecane are those calculated using Eq. (12).

Table II. (*Continued*)

| $n$ | $T_b$(obsd) (K) | Eq. (11)[b] (K) | Dev. (K) | Eq. (12)[b] (K) | Dev. (K) |
|---|---|---|---|---|---|
| 300 | 1019.21 | 1043.12 | | 1042.22 | |
| 350 | 1020.16 | 1040.77 | | 1039.97 | |
| 400 | 1020.60 | 1038.70 | | 1037.98 | |
| 450 | 1020.80 | 1036.94 | | 1036.29 | |
| 500 | 1020.90 | 1035.45 | | 1034.86 | |
| 600 | 1020.98 | 1033.14 | | 1032.63 | |
| 700 | 1020.99 | 1031.44 | | 1031.00 | |
| 800 | 1021.00 | 1030.16 | | 1029.77 | |
| 900 | 1021.00 | 1029.15 | | 1028.80 | |
| 1,000 | 1021.00 | 1028.34 | | 1028.03 | |
| 10,000 | 1021.00 | 1021.74 | | 1021.71 | |
| 100,000 | 1021.00 | 1021.07 | | 1021.07 | |
| 1,000,000 | 1021.00 | 1021.01 | | 1021.01 | |
| 2,000,000 | 1021.00 | 1021.00 | | 1021.00 | |

## 2.3. Estimation Procedures for the Critical Volume

Our recommended equation for the critical volume is

$$1/V_c^* = aY^* + bY^{*2} + cY^{*3} + dY^{*4} + eY^{*5} \qquad (17)$$

where $Y = P_c/RT_c$. According to Eq. (17), as $P_c$ and $T_c$ approach their limiting values, $V_c$ approaches its limiting value.

An alternative procedure for determining the critical volume lies first in the determination of the compressibility factor as follows:

$$\ln(Z_c - Z_c^{\infty}) = a - bn^{2/3} - cn - dp \qquad (18)$$

We have found that Eq. (17) and Eq. (18) yield almost the same values for the critical volume. We recommend Eq. (17) for the determination of the critical volumes of alkanes and their homologues.

## 2.4. Extension of These New Concepts to Other Properties

The molar volume at the normal boiling point may be calculated from

$$\ln(V_b/V_c) = aX + bX^2 + cX^3 + dX^4 + eX^5 \qquad (19)$$

**Table III.** Comparison of Observed[a] and Calculated Critical Pressures of the Alkanes

| $n$ | $P_c$(obsd) (bar) | Eq. (14) (bar) | Dev. (bar) | Eq. (15) (bar) | Dev. (bar) | Eq. (16) (bar) | Dev. (bar) |
|---|---|---|---|---|---|---|---|
| 1 | 45.99 | 55.45 | −9.46 | 49.78 | −3.79 | 55.72 | −9.73 |
| 2 | 48.80 | 50.32 | −1.52 | 48.80 | 0.00 | 48.81 | −0.01 |
| 3 | 42.47 | 43.48 | −1.01 | 42.23 | 0.24 | 42.47 | 0.00 |
| 4 | 37.97 | 37.79 | 0.18 | 37.98 | −0.01 | 37.93 | 0.04 |
| 5 | 33.69 | 33.29 | 0.40 | 33.92 | −0.23 | 33.72 | −0.03 |
| 6 | 30.12 | 29.70 | 0.42 | 30.40 | −0.28 | 30.29 | −0.17 |
| 7 | 27.36 | 26.80 | 0.56 | 27.42 | −0.06 | 27.40 | −0.04 |
| 8 | 24.87 | 24.41 | 0.46 | 24.91 | −0.04 | 24.87 | 0.00 |
| 9 | 22.80 | 22.42 | 0.38 | 22.78 | 0.02 | 22.81 | −0.01 |
| 10 | 20.99 | 20.74 | 0.25 | 20.96 | 0.03 | 20.97 | 0.02 |
| 11 | 19.48 | 19.30 | 0.18 | 19.40 | 0.08 | 19.42 | 0.06 |
| 12 | 18.10 | 18.05 | 0.05 | 18.05 | 0.05 | 18.11 | −0.01 |
| 13 | 16.79 | 16.96 | −0.17 | 16.87 | −0.08 | 16.90 | −0.11 |
| 14 | 15.73 | 16.00 | −0.27 | 15.84 | −0.11 | 15.82 | −0.09 |
| 15 | 14.79 | 15.15 | −0.36 | 14.92 | −0.13 | 14.91 | −0.12 |
| 16 | 14.01 | 14.39 | −0.38 | 14.10 | −0.09 | 14.09 | −0.08 |
| 17 | 13.42 | 13.71 | −0.29 | 13.37 | 0.05 | 13.33 | 0.08 |
| 18 | 12.69 | 13.09 | −0.40 | 12.72 | −0.03 | 12.62 | 0.07 |
| 19 |  | 12.53 |  | 12.12 |  | 12.00 |  |
| 20 |  | 12.02 |  | 11.58 |  | 11.45 |  |
| 21 |  | 11.55 |  | 11.09 |  | 10.94 |  |
| 22 |  | 11.13 |  | 10.64 |  | 10.48 |  |
| 23 |  | 10.73 |  | 10.23 |  | 10.06 |  |
| 24 |  | 10.362 |  | 9.844 |  | 9.669 |  |
| 25 |  | 10.023 |  | 9.493 |  | 9.310 |  |
| 26 |  | 9.707 |  | 9.167 |  | 8.979 |  |
| 27 |  | 9.412 |  | 8.864 |  | 8.671 |  |
| 28 |  | 9.137 |  | 8.582 |  | 8.385 |  |
| 29 |  | 8.879 |  | 8.319 |  | 8.118 |  |
| 30 |  | 8.637 |  | 8.073 |  | 7.869 |  |
| 40 |  | 6.843 |  | 6.278 |  | 6.064 |  |
| 50 |  | 5.732 |  | 5.196 |  | 4.984 |  |
| 60 |  | 4.977 |  | 4.476 |  | 4.268 |  |
| 70 |  | 4.430 |  | 3.963 |  | 3.761 |  |
| 80 |  | 4.015 |  | 3.580 |  | 3.384 |  |
| 90 |  | 3.691 |  | 3.284 |  | 3.095 |  |
| 100 |  | 3.429 |  | 3.048 |  | 2.865 |  |
| 125 |  | 2.955 |  | 2.626 |  | 2.459 |  |
| 150 |  | 2.637 |  | 2.347 |  | 2.195 |  |
| 200 |  | 2.236 |  | 2.003 |  | 1.875 |  |
| 250 |  | 1.994 |  | 1.798 |  | 1.689 |  |
| 300 |  | 1.832 |  | 1.663 |  | 1.568 |  |

[a] The observed values up to octadecane are from Refs. 5, 6, 14, and 15.

**Table III** (*Continued*)

| $n$ | $P_c$(obsd) (bar) | Eq. (14) (bar) | Dev. (bar) | Eq. (15) (bar) | Dev. (bar) | Eq. (16) (bar) | Dev. (bar) |
|---|---|---|---|---|---|---|---|
| 350 | | 1.715 | | 1.568 | | 1.483 | |
| 400 | | 1.628 | | 1.496 | | 1.421 | |
| 450 | | 1.560 | | 1.441 | | 1.373 | |
| 500 | | 1.506 | | 1.397 | | 1.336 | |
| 600 | | 1.424 | | 1.332 | | 1.279 | |
| 700 | | 1.366 | | 1.285 | | 1.240 | |
| 800 | | 1.322 | | 1.250 | | 1.211 | |
| 900 | | 1.287 | | 1.223 | | 1.188 | |
| 1,000 | | 1.260 | | 1.202 | | 1.170 | |
| 10,000 | | 1.038 | | 1.032 | | 1.029 | |
| 100,000 | | 1.016 | | 1.015 | | 1.015 | |
| 1,000,000 | | 1.01325 | | 1.01325 | | 1.01325 | |
| 2,000,000 | | 1.01325 | | 1.01325 | | 1.01325 | |

According to Eq. (19), the limiting values of both $V_b$ and $V_c$ should be the same. Equation (19) applies to the molar volumes of the liquid as well as of the vapor at the normal boiling point. The molar volume of the saturated liquid at the normal boiling point used in Eq. (19) is determined from

$$\ln(V_l/V_c) = aX_1^{1/3} + bX_1^{2/3} + cX_1^{5/3} \tag{20}$$

where $X_1 = (T_c - T)/T_c$.

The surface tension at the normal boiling point may be calculated from

$$\gamma_b^* = aX + bX^2 + cX^3 + dX^4 \tag{21}$$

According to Eq. (21), the limiting values of both $\gamma_b$ and $\gamma_c$ should be the same and should be zero since $\gamma_c = 0$.

The enthalpy of vaporization at the normal boiling point may be calculated using the following equation:

$$\Delta H_{vb}^* = aX + bX^2 + cX^3 + dX^4 \tag{22}$$

According to Eq. (22), the limiting value of $\Delta H_{vb}$ should be zero and is in agreement with the fact that $\Delta H_{vb} = 0$ at the critical temperature.

**Table IV.** Comparison of Observed[a] and Calculated Critical Volumes of the Alkanes

| $n$ | $V_c$(obsd) ($cm^3 \cdot mol^{-1}$) | Eq. (17) ($cm^3 \cdot mol^{-1}$) | Dev. ($cm^3 \cdot mol^{-1}$) | Eq. (18) ($cm^3 \cdot mol^{-1}$) | Dev. ($cm^3 \cdot mol^{-1}$) |
|---|---|---|---|---|---|
| 1 | 98.6 | 98.6 | 0.0 | 99.7 | −1.1 |
| 2 | 147.0 | 147.0 | 0.0 | 146.8 | 0.1 |
| 3 | 200.0 | 200.1 | −0.1 | 200.0 | 0.0 |
| 4 | 255.0 | 254.8 | 0.2 | 255.2 | −0.2 |
| 5 | 313.7 | 313.7 | 0.0 | 312.9 | 0.8 |
| 6 | 370.0 | 374.2 | −4.2 | 372.8 | −2.8 |
| 7 | 432.0 | 432.8 | −0.8 | 431.4 | 0.6 |
| 8 | 492.0 | 494.7 | −2.7 | 493.7 | −1.7 |
| 9 | 555.3 | 557.3 | −2.0 | 556.9 | −1.6 |
| 10 | 624.1 | 621.7 | 2.4 | 622.0 | 2.1 |
| 11 | 688.6 | 685.9 | 2.7 | 686.6 | 2.0 |
| 12 | 753.0 | 753.8 | −0.8 | 755.0 | −2.0 |
| 13 | 822.0 | 827.0 | −5.0 | 829.0 | −7.0 |
| 14 | 892.0 | 897.3 | −5.3 | 899.4 | −7.4 |
| 15 | 965.5 | 969.2 | −3.7 | 971.3 | −5.8 |
| 16 | 1034.0 | 1,038.0 | −4.0 | 1,039.5 | −5.5 |
| 17 | 1103.0 | 1,098.7 | 4.3 | 1,098.7 | 4.3 |
| 18 | 1189.0 | 1,175.0 | 14.0 | 1,174.7 | 14.3 |
| 19 |  | 1,207.2 |  | 1,202.8 |  |
| 20 |  | 1,272.2 |  | 1,266.2 |  |
| 21 |  | 1,337.2 |  | 1,329.5 |  |
| 22 |  | 1,402.2 |  | 1,392.6 |  |
| 23 |  | 1,467.1 |  | 1,455.7 |  |
| 24 |  | 1,532.1 |  | 1,518.7 |  |
| 25 |  | 1,596.8 |  | 1,581.4 |  |
| 26 |  | 1,661.4 |  | 1,644.0 |  |
| 27 |  | 1,726.0 |  | 1,706.5 |  |
| 28 |  | 1,790.3 |  | 1,768.7 |  |
| 29 |  | 1,854.5 |  | 1,830.9 |  |
| 30 |  | 1,918.5 |  | 1,892.8 |  |
| 40 |  | 2,544.4 |  | 2,500.3 |  |
| 50 |  | 3,139.5 |  | 3,082.6 |  |
| 60 |  | 3,699.5 |  | 3,635.0 |  |
| 70 |  | 4,224.6 |  | 4,156.2 |  |
| 80 |  | 4,716.3 |  | 4,646.6 |  |
| 90 |  | 5,174.3 |  | 5,104.7 |  |
| 100 |  | 5,535.6 |  | 5,604.3 |  |
| 125 |  | 6,561.7 |  | 6,496.7 |  |
| 150 |  | 7,379.2 |  | 7,318.3 |  |
| 200 |  | 8,705.3 |  | 8,651.5 |  |
| 250 |  | 9,735.9 |  | 9,687.6 |  |
| 300 |  | 10,564.1 |  | 10,520.3 |  |

[a] The observed values are from Ref. 5, 6, 14, and 15.

Table IV. (*Continued*)

| $n$ | $V_c$(obsd) ($\mathrm{cm^3 \cdot mol^{-1}}$) | Eq. (17) ($\mathrm{cm^3 \cdot mol^{-1}}$) | Dev. ($\mathrm{cm^3 \cdot mol^{-1}}$) | Eq. (18) ($\mathrm{cm^3 \cdot mol^{-1}}$) | Dev. ($\mathrm{cm^3 \cdot mol^{-1}}$) |
|---|---|---|---|---|---|
| 350 | | 11,252.7 | | 11,212.7 | |
| 400 | | 11,825.3 | | 11,788.4 | |
| 450 | | 12,315.7 | | 12,281.4 | |
| 500 | | 12,735.4 | | 12,703.5 | |
| 600 | | 13,433.2 | | 13,405.0 | |
| 700 | | 13,976.4 | | 13,951.2 | |
| 800 | | 14,420.4 | | 14,397.6 | |
| 900 | | 14,795.4 | | 14,774.7 | |
| 1,000 | | 15,098.4 | | 15,079.4 | |
| 10,000 | | 18,189.1 | | 18,187.0 | |
| 100,000 | | 18,568.6 | | 18,568.6 | |
| 1,000,000 | | 18,617.6 | | 18,617.9 | |
| 2,000,000 | | 18,617.6 | | 18,617.8 | |

The second virial coefficient $B_c$ at $T_c$ can be calculated using an equation analogous to the critical volume. Thus we have

$$1/B_c^* = aY^* + bY^{*2} + cY^{*3} + dY^{*4} + eY^{*5} \tag{23}$$

The second virial coefficient at the critical temperature is known only for a few low molecular weight alkanes. Among various correlations for the second virial coefficients, we have found the Tsonopoulos correlation [10] to yield satisfactory values for the second virial coefficient at the critical temperature. We have therefore used the Tsonopoulos correlation to obtain the second virial coefficients at the critical temperature for a number of higher alkanes. The limiting value for the second virial coefficient at $T_c$ has been determined by us to be $-30{,}463\ \mathrm{cm^3 \cdot mol^{-1}}$.

The second virial coefficient $B_b$ at the normal boiling point can be calculated from

$$\ln(B_b/B_c) = aX + bX^2 + cX^3 + dX^4 + eX^5 \tag{24}$$

According to Eq. (24), the limiting values of both $B_b$ and $B_c$ would be the same. The second virial coefficients at the normal boiling point and the critical temperature are derived from

$$B^* = aX_2 + bX_2^2 + cX_2^3 \tag{25}$$

**Table V.** Comparison of Observed[a] and Calculated Surface Tensions and Enthalpies of Vaporization of Alkanes

| $n$ | $\gamma_b$(obsd) (mN·m$^{-1}$) | Eq. (21) (mN·m$^{-1}$) | Dev. (mN·m$^{-1}$) | $\Delta H_{vb}$(obsd) (kJ·mol$^{-1}$) | Eq. (22) (kJ·mol$^{-1}$) | Dev. (kJ·mol$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 13.78 | 14.40 | −0.62 | 8.18 | 8.48 | −0.30 |
| 2 | 16.81 | 15.57 | 1.24 | 14.72 | 14.06 | 0.66 |
| 3 | 15.75 | 15.87 | −0.12 | 18.77 | 19.00 | −0.23 |
| 4 | 15.25 | 15.53 | −0.28 | 22.39 | 22.52 | −0.13 |
| 5 | 14.18 | 14.76 | −0.58 | 25.77 | 25.89 | −0.12 |
| 6 | 13.50 | 13.78 | −0.28 | 28.85 | 28.85 | 0.00 |
| 7 | 12.75 | 12.72 | 0.03 | 31.70 | 31.59 | 0.11 |
| 8 | 12.00 | 11.62 | 0.38 | 34.41 | 34.28 | 0.13 |
| 9 | 11.17 | 10.60 | 0.57 | 36.92 | 36.74 | 0.18 |
| 10 | 10.50 | 9.62 | 0.88 | 39.28 | 39.18 | 0.10 |
| 11 | 8.66 | 8.73 | −0.07 | 41.50 | 41.48 | 0.02 |
| 12 | 7.60 | 7.96 | −0.36 | 43.64 | 43.59 | 0.05 |
| 13 | 6.60 | 7.21 | −0.61 | 45.65 | 45.73 | −0.08 |
| 14 | 6.07 | 6.53 | −0.46 | 47.61 | 47.78 | −0.17 |
| 15 | 5.54 | 5.96 | −0.42 | 49.45 | 49.62 | −0.17 |
| 16 | 5.11 | 5.44 | −0.33 | 51.21 | 51.37 | −0.16 |
| 17 | 4.74 | 4.96 | −0.22 | 52.89 | 53.07 | −0.18 |
| 18 | 4.43 | 4.52 | −0.09 | 54.48 | 54.73 | −0.25 |
| 19 |  | 4.19 |  |  | 56.02 |  |
| 20 |  | 3.86 |  |  | 57.38 |  |
| 21 |  | 3.56 |  |  | 58.64 |  |
| 22 |  | 3.30 |  |  | 59.81 |  |
| 23 |  | 3.07 |  |  | 60.89 |  |
| 24 |  | 2.86 |  |  | 61.88 |  |
| 25 |  | 2.68 |  |  | 62.79 |  |
| 26 |  | 2.51 |  |  | 63.63 |  |
| 27 |  | 2.37 |  |  | 64.38 |  |
| 28 |  | 2.24 |  |  | 65.07 |  |
| 29 |  | 2.12 |  |  | 65.70 |  |
| 30 |  | 2.02 |  |  | 66.26 |  |
| 40 |  | 1.46 |  |  | 69.22 |  |
| 50 |  | 1.30 |  |  | 69.07 |  |
| 60 |  | 1.27 |  |  | 67.39 |  |
| 70 |  | 1.27 |  |  | 65.01 |  |
| 80 |  | 1.28 |  |  | 62.35 |  |
| 90 |  | 1.28 |  |  | 59.64 |  |
| 100 |  | 1.28 |  |  | 56.99 |  |
| 125 |  | 1.25 |  |  | 50.94 |  |
| 150 |  | 1.20 |  |  | 45.81 |  |
| 200 |  | 1.08 |  |  | 37.89 |  |
| 250 |  | 0.97 |  |  | 32.19 |  |

[a] The observed values of surface tension are from Refs. 14 and 18. The observed enthalpies of vaporization are from Ref. 14.

Table V. *(Continued)*

| $n$ | $\gamma_b$(obsd) (mN · m$^{-1}$) | Eq. (21) (mN · m$^{-1}$) | Dev. (mN · m$^{-1}$) | $\Delta H_{vb}$(obsd) (kJ · mol$^{-1}$) | Eq. (22) (kJ · mol$^{-1}$) | Dev. (kJ · mol$^{-1}$) |
|---|---|---|---|---|---|---|
| 300 | | 0.87 | | | 27.93 | |
| 350 | | 0.79 | | | 24.66 | |
| 400 | | 0.72 | | | 22.06 | |
| 450 | | 0.66 | | | 19.95 | |
| 500 | | 0.61 | | | 18.20 | |
| 600 | | 0.53 | | | 15.50 | |
| 700 | | 0.46 | | | 13.49 | |
| 800 | | 0.41 | | | 11.94 | |
| 900 | | 0.37 | | | 10.70 | |
| 1,000 | | 0.34 | | | 9.70 | |
| 10,000 | | 0.00 | | | 1.03 | |
| 100,000 | | 0.00 | | | 0.10 | |
| 1,000,000 | | 0.00 | | | 0.01 | |
| 20,000,000 | | 0.00 | | | 0.00 | |

where $X_2 = 1 - (T_B/T)^{5/4}$. The exponent (5/4) was selected because the second virial coefficient, according to Goodwin et al. [11], is linear in $T^{-5/4}$. According to Eq. (25), $B = 0$ when $T = T_B$. The Boyle temperatures used in Eq. (25) are those derived from the Tsonopoulos correlation.

The Boyle temperature, $T_B$, is the temperature at which the second virial coefficient is zero. It can be calculated from

$$T_B^* = aX + bX + cX^2 + dX^3 + eX^4 \tag{26}$$

As $n \to \infty$, $T_B = 2252.5$ K.

The third virial coefficient may be treated in much the same way as the second virial coefficient. For fitting the third virial coefficients over a range of temperatures, we suggest the following expression:

$$C^* = aX_3 + bX_3^2 + cX_3^3 \tag{27}$$

where $X_3 = 1 - (T_A/T)^{5/2}$ and $T_A$ is the temperature where the third virial coefficient is zero. Using the third virial coefficients reported by Dymond and Smith [12], we have found that $T_A = 0.73 T_c$ for a number of compounds. Unfortunately, the third virial coefficients are known only for methane and ethane over a wide range of temperatures. Recently, Orbey and Vera [13] developed a correlation procedure for calculating the third

**Table VI.** Comparison of Observed[a] and Calculated Second Virial Coefficients of the Alkanes

| $n$ | $B_c$(obsd) ($cm^3 \cdot mol^{-1}$) | Eq. (23) ($cm^3 \cdot mol^{-1}$) | Dev. ($cm^3 \cdot mol^{-1}$) | $B_b$(obsd) ($cm^3 \cdot mol^{-1}$) | Eq. (24) ($cm^3 \cdot mol^{-1}$) | Dev. ($cm^3 \cdot mol^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | −116.0 | −116.0 | 0.0 | −324.6 | −341.7 | 17.1 |
| 2 | −177.0 | −177.0 | 0.0 | −523.6 | −522.2 | −1.4 |
| 3 | −247.0 | −247.3 | 0.0 | −718.0 | −717.0 | −1.0 |
| 4 | −321.9 | −321.8 | −0.1 | −956.8 | −942.0 | −14.8 |
| 5 | −400.9 | −401.6 | 0.7 | −1,109.8 | −1,133.1 | 23.3 |
| 6 | −487.4 | −487.3 | −0.1 | −1,312.2 | −1,332.1 | 23.3 |
| 7 | −573.3 | −573.3 | 0.0 | −1,512.8 | −1,518.2 | 5.4 |
| 8 | −667.8 | −666.6 | −1.2 | −1,716.2 | −1,716.6 | 0.4 |
| 9 | −765.1 | −762.8 | −2.3 | −1,923.5 | −1,917.0 | −6.5 |
| 10 | −867.3 | −863.2 | −4.1 | −2,133.3 | −2,122.6 | −10.7 |
| 11 | −970.7 | −964.3 | −6.4 | −2,338.6 | −2,327.5 | −11.1 |
| 12 | −1,081.4 | −1,072.2 | −9.2 | −2,558.0 | −2,547.7 | −10.3 |
| 13 | −1,189.4 | −1,189.3 | −0.1 | −2,761.7 | −2,755.9 | −5.8 |
| 14 | −1,319.3 | −1,302.4 | −16.9 | −3,005.2 | −3,011.2 | 6.0 |
| 15 | −1,440.4 | −1,418.4 | −22.0 | −3,231.0 | −3,245.5 | 14.5 |
| 16 | −1,558.1 | −1,529.9 | −28.2 | −3.445.2 | −3,469.5 | 24.3 |
| 17 | −1,662.4 | −1,628.5 | −33.9 | −3,613.8 | −3,660.6 | 46.8 |
| 18 | −1,791.8 | −1,752.5 | −39.3 | −3,820.6 | −3,903.3 | 82.7 |
| 19 |  | −1,805.0 |  |  | −3,900.0 |  |
| 20 |  | −1,910.8 |  |  | −4,092.2 |  |
| 21 |  | −2,016.9 |  |  | −4,283.9 |  |
| 22 |  | −2,123.0 |  |  | −4,474.3 |  |
| 23 |  | −2,229.2 |  |  | −4,663.4 |  |
| 24 |  | −2,335.4 |  |  | −4,851.0 |  |
| 25 |  | −2,441.3 |  |  | −5,036.5 |  |
| 26 |  | −2,547.2 |  |  | −5,220.5 |  |
| 27 |  | −2,653.0 |  |  | −5,402.8 |  |
| 28 |  | −2,758 |  |  | −5,583 |  |
| 29 |  | −2,864 |  |  | −5,761 |  |
| 30 |  | −2,969 |  |  | −5,937 |  |
| 40 |  | −3,996 |  |  | −7,575 |  |
| 50 |  | −4,975 |  |  | −8,995 |  |
| 60 |  | −5,896 |  |  | −10,221 |  |
| 70 |  | −6,760 |  |  | −11,287 |  |
| 80 |  | −7,570 |  |  | −12,222 |  |
| 90 |  | −8,324 |  |  | −13,044 |  |
| 100 |  | −9,032 |  |  | −13,781 |  |
| 150 |  | −11,954 |  |  | −16,530 |  |
| 200 |  | −14,138 |  |  | −18,371 |  |
| 250 |  | −15,835 |  |  | −19,721 |  |
| 300 |  | −17,199 |  |  | −20,771 |  |
| 350 |  | −18,333 |  |  | −21,633 |  |

[a] The observed values are based on the Tsonopoulos correlation [10].

**Table VI** (*Continued*)

| $n$ | $B_c$(obsd) ($cm^3 \cdot mol^{-1}$) | Eq. (23) ($cm^3 \cdot mol^{-1}$) | Dev. ($cm^3 \cdot mol^{-1}$) | $B_b$(obsd) ($cm^3 \cdot mol^{-1}$) | Eq. (24) ($cm^3 \cdot mol^{-1}$) | Dev. ($cm^3 \cdot mol^{-1}$) |
|---|---|---|---|---|---|---|
| 400 | | −19,276 | | | −22,336 | |
| 450 | | −20,084 | | | −22,935 | |
| 500 | | −20,775 | | | −23,441 | |
| 600 | | −21,925 | | | −24,287 | |
| 700 | | −22,819 | | | −24,937 | |
| 800 | | −23,551 | | | −25,470 | |
| 900 | | −24,168 | | | −25,924 | |
| 1,000 | | −24,667 | | | −26,283 | |
| 10,000 | | −29,758 | | | −29,995 | |
| 100,000 | | −30,383 | | | −30,401 | |
| 1,000,000 | | −30,463 | | | −30,463 | |
| 2,000,000 | | −30,463 | | | −30,463 | |

virial coefficients. Their procedure uses $T_c$, $P_c$, and the acentric factor $\omega$ as parameters. Using their procedure, we have calculated the third virial coefficients of alkanes up to octadecane at the normal boiling point, at the critical temperature, and at the Boyle temperature. According to these results $C_b$, the third virial coefficient at the normal boiling point, is negative up to decane but becomes positive from undecane onward and becomes greater than $C_c$, the third virial coefficient at the critical temperature, from heptadecane onward. Furthermore, $C_b$ exhibits a minimum at pentane. These results also show that $T_A$ remains constant more or less at $0.73T_c$. The result that $C_b$ is far greater than $C_c$ from heptadecane onward is somewhat contradictory to our expectations. We have therefore formulated the following expression for the prediction of the third virial coefficients of alkanes:

$$C(P_c/RT_c)^2 = 0.16447X_3 - 0.20342X_3^2 + 0.04760X_3^3 \qquad (28)$$

The constants of Eq. (28) are determined by the use of the third virial coefficients of methane. The above equation is used to calculate the third virial coefficients of all other alkanes. The value of $T_A$ is set equal to $0.732T_c$ in Eq. (28). The results obtained show that $C_b$ reaches it minimum value for hexane but becomes positive from undecane onward. The $C_b$ is slightly more positive than $C_c$ from $C_{80}$ but becomes equal to $C_c$ as $n \rightarrow \infty$. This behavior is quite analogous to the behavior of $T_c$ with respect to $T_b$. As $n \rightarrow \infty$, the value of $C_c$ according to Eq. (28) is $2.6 \times 10^8\ cm^6 \cdot mol^{-2}$.

### 2.5. Extension of These New Concepts to Various Homologous Series

By adopting the limiting values for various properties of alkanes, one can easily extend these equations to various homologous series. The results of such a study will be published elsewhere.

## 3. DISCUSSION

Experimental values of the normal boiling point, critical temperature, critical pressure, and critical volume are taken from Teja et al. [5] and the *TRC Thermodynamic Tables* [14]. The critical constants and the normal boiling point of methane are from Kleinrahm et al. [15]. Second virial coefficients of alkanes up to octane are derived from the values listed by Dymond and Smith [12], the values recently recommended by Tsonopoulos et al. [16], and the values recently determined by Xueqin et al. [17]. The second virial coefficients above octane and up to octadecane are obtained on the basis of the Tsonopoulos correlation [10]. Surface tensions are obtained from Jasper [18] and the *TRC Thermodynamic Tables* [14]. Enthalpies of vaporization at the normal boiling point are taken from the *TRC Thermodynamic Tables* [14]. Molar volumes of the saturated liquid are from the *TRC Thermodynamic Tables* [14]. The weight factor is taken as $1/\sigma^2$, where $\sigma$ is the standard error in the experimental value.

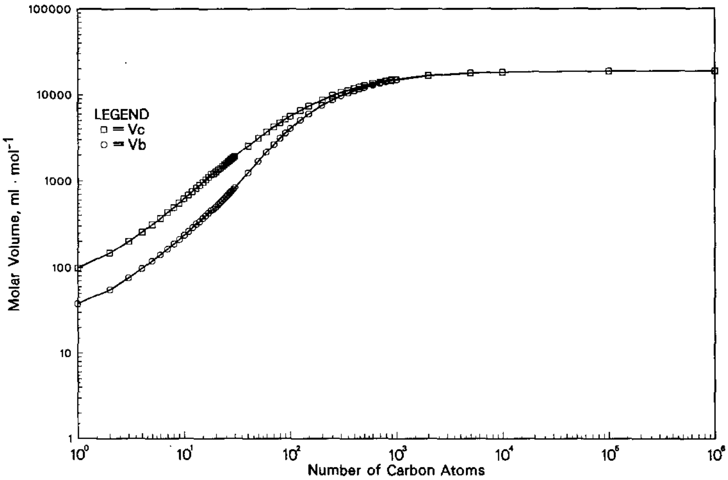

**Fig. 2.** Plots of the critical volume and the molar volume of the saturated liquid at the normal boiling point of the normal alkanes versus the number of carbon atoms. The numbers of carbon atoms as well as the molar volumes are plotted on logarithmic scales.

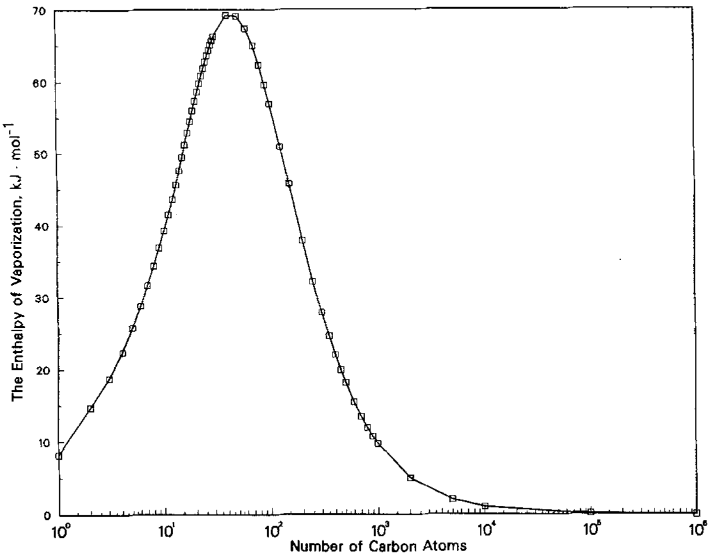

**Fig. 3.** Plot of the enthalpy of vaporization at the normal boiling points of the normal alkanes versus the number of carbon atoms. The numbers of carbon atoms are plotted on a logarithmic scale.

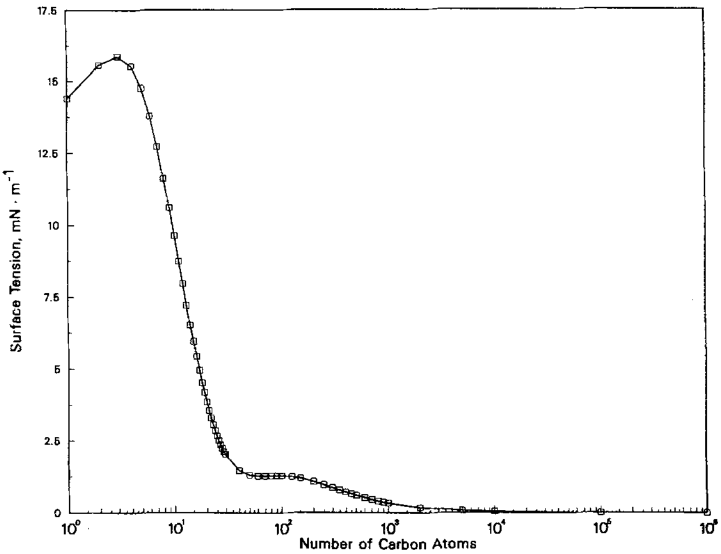

**Fig. 4.** Plot of the surface tension at the normal boiling points of the normal alkanes versus the number of carbon atoms. The numbers of carbon atoms are plotted on a logarithmic scale.

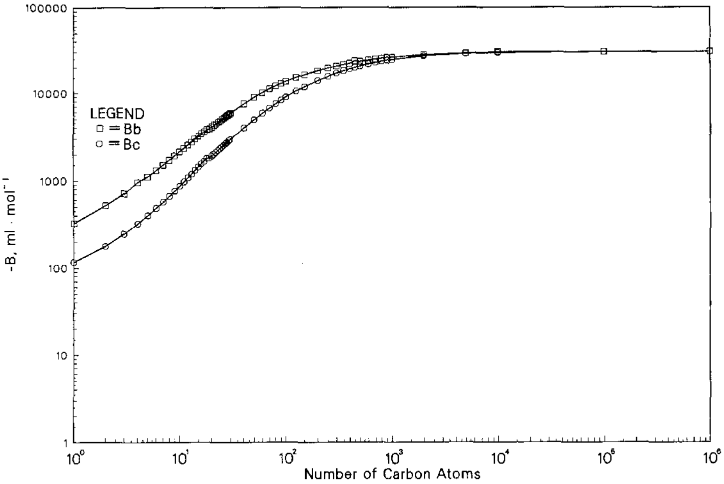

**Fig. 5.** Plots of the absolute values of the second virial coefficients at the critical temperature and at the normal boiling point of the normal alkanes versus the number of carbon atoms. The numbers of carbon atoms as well as the absolute values of the second virial coefficient are plotted on logarithmic scales.

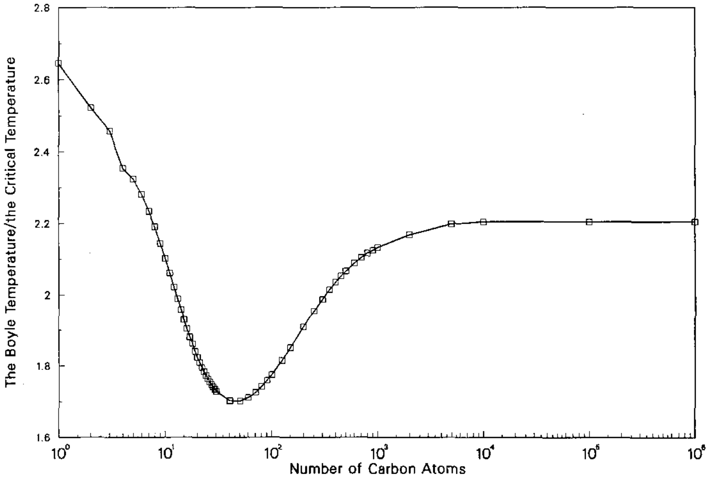

**Fig. 6.** Plot of the ratio of the Boyle temperature to the critical temperature of normal alkanes versus the number of carbon atoms. The numbers of carbon atoms are plotted on a logarithmic scale.

We have fitted the normal boiling points of alkanes in the range $C_2$ to $C_{18}$ to Eqs. (11) and (12) and compared the results in Table I. While Eq. (11) fits the data above butane, Eq. (12) fits the data even from ethane and is considered the best for determining the normal boiling points of long-chain normal paraffins. Methane forms an exception and is probably linked with its enormous stability when compared with other alkanes.

The normal boiling points calculated from Eq. (12) are then used to calculate the critical temperatures using Eqs. (1) and (13). The regresions were carried out using the critical temperatures in the range $C_2$ to $C_{18}$. The results thus obtained are given in Table II. The variation of the normal boiling point and the critical temperature with carbon number is shown in Fig. 1.

The critical pressures were calculated using Eqs. (14), (15), and (16) and are compared in Table III. Regressions for critical pressure were carried out using data in the range $C_2$ to $C_{18}$.

Critical volumes obtained from Eqs. (17) and (18) are compared in Table IV. Regressions for the critical volumes were carried out using data in the range $C_1$ to $C_{18}$. The regression for the saturated liquid volumes at the normal boiling point was carried out using data in the range $C_1$ to $C_{18}$. Results for the critical volume and the molar volume of the liquid at the normal boiling point are shown in Fig. 2.

The results for the enthalpies of vaporization are shown in Fig. 3 and in Table V. It is interesting to see from Fig. 3 that the enthalpy of vaporization reaches its maximum value around $C_{50}$. The results for the surface tension are shown in Fig. 4 and in Table V.

The results for the second virial coefficients are shown in Fig. 5 and in Table VI. The results obtained on the basis of Eq. (25) for the second virial

**Table VII.** Constants of Eq. (25) for the Second Virial Coefficients

| Alkane | $T_B$ (K)[a] | $a$ | $b$ | $c$ |
|---|---|---|---|---|
| Methane | 504.0 | $0.449716E+02$ | $-0.112282E+01$ | $0.216910E+00$ |
| Ethane | 770.0 | $0.788352E+02$ | $0.246644E+01$ | $0.155118E+01$ |
| Propane | 909.0 | $0.108262E+03$ | $-0.310147E+00$ | $0.226192E+01$ |
| Butane | 995.0 | $0.147756E+03$ | $-0.610528E+00$ | $0.503801E+01$ |
| Pentane | 1100.0 | $0.173157E+03$ | $-0.120716E+02$ | $0.435049E+01$ |
| Hexane | 1161.0 | $0.207264E+03$ | $-0.245293E+02$ | $0.498066E+01$ |
| Heptane | 1206.0 | $0.273433E+03$ | $-0.130882E+02$ | $0.118973E+02$ |
| Octane | 1243.0 | $0.343149E+03$ | $-0.425508E+01$ | $0.193351E+02$ |

[a] The Boyle temperatures are calculated using the Tsonopoulos correlation [10].

coefficients of alkanes from methane to octane are in agreement with the values obtained on the basis of the Tsonopoulos correlation. We have therefore adopted the values obtained on the basis of the Tsonopoulos correlation for these alkanes. The constants of Eq. (25) are, however, recorded in Table VII. A plot of the ratio of the Boyle temperature to the critical temperature predicts somewhat higher values for the Boyle temperature for the first three alkanes. It is interesting to note from Fig. 6 that

**Table VIII.** Third Virial Coefficients of Alkanes Calculated Using Eq. (28)

| $n$ | $T_A$ (K) | $C_b$ ($cm^6 \cdot mol^{-2}$) | $C_c$ ($cm^6 \cdot mol^{-2}$) | $C_B$ ($cm^6 \cdot mol^{-2}$) |
|---|---|---|---|---|
| 1 | 139.48 | −30,220 | 4,388 | 1,492 |
| 2 | 223.43 | −50,890 | 10,000 | 3,528 |
| 3 | 270.70 | −69,930 | 19,380 | 6,987 |
| 4 | 311.22 | −85,470 | 32,050 | 12,060 |
| 5 | 343.82 | −94,140 | 49,680 | 18,690 |
| 6 | 371.49 | −96,910 | 72,560 | 27,890 |
| 7 | 395.50 | −91,080 | 99,680 | 39,220 |
| 8 | 416.38 | −77,440 | 133,700 | 53,730 |
| 9 | 435.32 | −67,670 | 205,200 | 84,170 |
| 10 | 452.16 | −27,860 | 221,400 | 92,710 |
| 11 | 467.60 | 9,518 | 274,900 | 117,400 |
| 12 | 481.95 | 54,470 | 338,200 | 147,000 |
| 13 | 494.83 | 112,500 | 414,300 | 183,600 |
| 14 | 506.76 | 180,200 | 495,100 | 223,100 |
| 15 | 518.11 | 256,300 | 585,400 | 268,500 |
| 16 | 528.65 | 340,200 | 679,200 | 317,200 |
| 17 | 538.46 | 427,600 | 768,000 | 363,600 |
| 18 | 547.32 | 588,300 | 887,300 | 425,100 |
| 19 | 556.43 | 605,300 | 940,700 | 456,100 |
| 20 | 564.61 | 714,200 | 1,052,000 | 515,900 |
| 30 | 626.81 | 2,188,000 | 2,511,000 | 1,314,000 |
| 40 | 666.80 | 4,268,000 | 4,533,000 | 2,421,000 |
| 50 | 694.23 | 6,812,000 | 7,002,000 | 3,742,000 |
| 60 | 713.71 | 9,688,000 | 9,798,000 | 5,199,000 |
| 70 | 727.87 | 12,850,000 | 12,880,000 | 6,760,000 |
| 80 | 738.29 | 16,210,000 | 16,170,000 | 8,389,000 |
| 90 | 746.02 | 19,610,000 | 19,500,000 | 9,994,000 |
| 100 | 751.78 | 23,090,000 | 22,920,000 | 11,610,000 |
| 200 | 766.40 | 56,380,000 | 55,840,000 | 25,930,000 |
| 500 | 757.95 | 120,800,000 | 120,200,000 | 51,140,000 |
| 1,000 | 752.74 | 170,700,000 | 170,300,000 | 70,070,000 |
| 10,000 | 747.91 | 246,800,000 | 246,700,000 | 98,520,000 |
| 100,000 | 747.42 | 258,100,000 | 258,100,000 | 102,700,000 |
| 1,000,000 | 747.37 | 259,500,000 | 259,500,000 | 103,300,000 |

Table IX. Some Constants of Normal Alkanes

| Alkane | $T_B$ (K)[a] | $\omega$[b] | $V_b$(liq) ($cm^3 \cdot mol^{-1}$)[c] |
|---|---|---|---|
| Methane | 504.0 | 0.010 | 38.0 |
| Ethane | 770.0 | 0.099 | 55.3 |
| Propane | 909.0 | 0.152 | 75.9 |
| Butane | 995.0 | 0.199 | 96.7 |
| Pentane | 1100.0 | 0.251 | 119.0 |
| Hexane | 1161.0 | 0.298 | 140.7 |
| Heptane | 1206.0 | 0.350 | 163.0 |
| Octane | 1243.0 | 0.397 | 187.0 |
| Nonane | 1273.0 | 0.443 | 210.9 |
| Decane | 1296.0 | 0.489 | 235.9 |
| Undecane | 1316.0 | 0.532 | 261.2 |
| Dodecane | 1334.0 | 0.574 | 287.1 |
| Tridecane | 1346.0 | 0.617 | 316.4 |
| Tetradecane | 1358.0 | 0.656 | 339.9 |
| Pentadecane | 1367.0 | 0.697 | 369.2 |
| Hexadecane | 1373.0 | 0.739 | 396.0 |
| Heptadecane | 1382.0 | 0.773 | 424.3 |
| Octadecane | 1391.0 | 0.800 | 455.6 |

[a] The Boyle temperatures are calculated using the Tsonopoulos correlation [10].

[b] The acentric factors are taken from Ref. 19.

[c] The molar volumes of the liquid at the normal boiling point are calculated using the densities reported in Refs. 14 and 15.

the ratio of the Boyle temperature to the critical temperature reaches its minimum value around $C_{50}$. The third virial coefficients calculated on the basis of Eq. (28) are recorded in Table VIII.

The data on the molar volumes of the gases reported in the literature are insufficient for our study. The Boyle temperatures, the acentric factors, and the molar volumes of the liquid at the normal boiling point used in this work are recorded in Table IX. The acentric factors are taken from reference [19]. The constants of various equations for different properties of the normal alkanes are recorded in Table X.

**Table X.** Constants of Various Equations for Different Properties of the Alkanes

| Property | Eq. | *a* | *b* | *c* | *d* | *e* | Limiting value |
|---|---|---|---|---|---|---|---|
| $T_b$ (K) | (11) | 0.69313*E*+01 | 0.12496*E*+00 | | | | 1021 K |
| $T_b$ (K) | (12) | 0.69120*E*+01 | 0.11364*E*+00 | 0.12332*E*−02 | 0.28767*E*−02 | | 1021 K |
| $T_c$ (K) | (1) | 0.12452*E*+01 | 0.13780*E*+00 | | | | 1021 K |
| $T_c$ (K) | (13) | 0.13343*E*+01 | 0.14378*E*+00 | 0.93539*E*−03 | −0.73589*E*−01 | | 1021 K |
| $P_c$ (bar) | (14) | 0.30479*E*+00 | 0.23808*E*+00 | | | | 1.01325 bar |
| $P_c$ (bar) | (15) | 0.48405*E*+00 | 0.31179*E*+00 | −0.32636*E*−01 | −0.22230*E*+00 | | 1.01325 bar |
| $P_c$ (bar) | (16) | −0.21714*E*+02 | 0.93820*E*+02 | −0.33952*E*+03 | 0.64226*E*+03 | −0.48287*E*+03 | 1.01325 bar |
| $V_c$ ($cm^3 \cdot mol^{-1}$) | (17) | 0.45249*E*+01 | −0.21028*E*+04 | 0.19209*E*+07 | −0.79410*E*+09 | 0.11703*E*+12 | 18,617.5 $cm^3 \cdot mol^{-1}$ |
| $Z_c$ | (18) | −0.27668*E*+01 | 0.73255*E*−01 | −0.15941*E*−01 | 0.70630*E*−01 | | 0.22222 |
| $V_b$ ($cm^3 \cdot mol^{-1}$) | (19) | −0.24714*E*+01 | −0.71740*E*+02 | 0.51430*E*+03 | −0.12700*E*+04 | 0.10836*E*+04 | 18,617.5 $cm^3 \cdot mol^{-1}$ |
| $\gamma_b$ ($mN \cdot m^{-1}$) | (21) | 0.52958*E*+02 | −0.74754*E*+03 | 0.40150*E*+04 | −0.55925*E*+04 | | 0 |
| $\Delta H_{vb}$ ($kJ \cdot mol^{-1}$) | (22) | 0.14262*E*+04 | −0.96329*E*+04 | 0.23991*E*+05 | −0.21157*E*+05 | | 0 |
| $B_c$ ($cm^3 \cdot mol^{-1}$) | (23) | −0.27472*E*+01 | −0.25675*E*+03 | 0.97346*E*+05 | 0.18761*E*+08 | −0.41891*E*+10 | −30,463.5 $cm^3 \cdot mol^{-1}$ |
| $B_b$ ($cm^3 \cdot mol^{-1}$) | (24) | 0.92055*E*+01 | −0.44904*E*+02 | 0.95067*E*+02 | 0.18613*E*+01 | −0.14636*E*+03 | −30,463.5 $cm^3 \cdot mol^{-1}$ |
| $T_B$ (K) | (26) | 0.22526*E*+04 | −0.83179*E*+04 | 0.23686*E*+05 | −0.47397*E*+03 | −0.78114*E*+05 | 2252.5 K |

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## NOMENCLATURE

$M$ = Molar mass, kg · mol$^{-1}$
$V_c$ = Critical volume, cm$^3$ · mol$^{-1}$
$V_l$ = Saturated liquid volume, cm$^3$ · mol$^{-1}$
$P_c$ = Critical Pressure, bar
$T_c$ = Critical temperature, K
$T_b$ = Normal boiling point, K
$T_B$ = Boyle temperature, K
$T_A$ = Temperature at which the third virial coefficient is zero, K
$V_c^\infty$ = Limiting value of critical volume = 18,618 cm$^3$ · mol$^{-1}$
$P_c^\infty$ = Limiting value of critical pressure = 1.01325 bar
$T_c^\infty$ = Limiting value of critical temperature = 1021 K
$T_b^\infty$ = Limiting value of normal boiling point = 1021 K
$P_b$ = Pressure at the normal boiling point, 1 atm
$Z_c$ = Critical compressibility factor
$Z_c^\infty$ = Limiting value for the critical compressibility factor = 0.22222
$R$ = Gas constant, $83.1448 \times 10^{-6}$ m$^3$ · bar · K$^{-1}$ · mol$^{-1}$
$\omega$ = Acentric factor
$X = (T_c - T_b)/T_c$
$X_1 = (T_c - T)/T_c$
$X_2 = 1 - (T_B/T)^{5/4}$
$X_3 = 1 - (T_A/T)^{5/2}$
$Y = P_c/RT_c$
$\gamma$ = Surface tension, mN · m$^{-1}$
$B$ = Second virial coefficient, cm$^3$ · mol$^{-1}$
$B^\infty$ = Limiting value for the second virial coefficient = −30,463 cm$^3$ · mol$^{-1}$
$C$ = Third virial coefficient, cm$^6$ · mol$^{-2}$
$C_b$ = Third virial coefficient at the normal boiling point, cm$^6$ · mol$^{-2}$
$C_c$ = Third virial coefficient at the critical temperature, cm$^6$ · mol$^{-2}$
$C_B$ = Third virial coefficient at the Boyle temperature, cm$^6$ · mol$^{-2}$

$\Delta H_{vb}$ = Enthalpy of vaporization at the normal boiling point, $kJ \cdot mol^{-1}$

$n$ = Number of carbon atoms in a homologous series

$p$ = Platt number, number of C–C–C–C structural elements

$a, b, c, d, e$, etc. = Constants associated with the specific equation

$T_c^*, T_b^*, P_c^*, V_c^*$, etc. = Dimensionless variables

Variables such as $T_c$ are made dimensionless by dividing them by the units in which they are expressed. For example, $T_c^* = T_c/K$.

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