Critical Constants of Normal Alkanes from Methane to Polyethylene

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Critical constants are the key parameters in most corresponding-states correlations for the properties of defined compounds. In addition to the critical temperature T_c and critical pressure P_c, many corresponding-states correlations use the acentric factor. This is not discussed here because its rigorous calculation involves the vapor pressure, which will be considered separately. An alternative to the acentric factor is the critical compressibility factor, $Z_c = P_c v_c / RT_c = P_c (M/d_c)/RT_c$, where R is the gas constant, v_c the critical molar volume, M the molecular weight, and d_c the critical density.

Experimental critical constants are generally not available for heavy organic liquids ($T_c > 700$ K), because most organic compounds become thermally unstable above 700 K. Therefore, if we are to predict the properties of heavy liquids with corresponding-states correlations based on critical constants, we will need to extrapolate available data for lighter liquids to higher carbon numbers. Such extrapolations are possible, at least empirically, because critical constants apparently approach limiting values as the carbon number goes to infinity. These limits are investigated here for normal alkanes, the simplest and most extensively studied organic compounds.

Our interest in bridging the gap between methane and polyethylene is twofold. First, we want to present the evidence on the limiting behavior of certain properties of normal alkanes as the carbon number goes to infinity. Second, we want to use this information as a basis for characterizing heavy petroleum and synthetic liquids.

Dependence of Properties on Carbon Number

The critical temperature, pressure, and density of normal alkanes apparently approach limiting values as the carbon number goes to infinity. The functional dependence on carbon number, n_C, was proposed by Kreglewski and Zwolinski (1961):

$$\log_{10}(y_\infty - y) = a - b n_C^{2/3} \tag{1}$$

In Eq. 1, y is a property such as T_b, T_c, or P_c, while y_∞ is the value of the property in the limit as $n_C \rightarrow \infty$. Kreglewski and Zwolinski found that Eq. 1 represented satisfactorily the properties of n-alkanes with $n_C \geqq 3$. [They used data up to $n_C = 18$ reported in the 1960 edition of the API Research Project 44 tables; these are now called "TRC Thermodynamic Tables—Hydrocarbons" (TRC, 1986).]

Kreglewski and Zwolinski recommended for the normal boiling point

$$\log_{10}(1{,}078 - T_b) = 3.03191 - 0.0499901\, n_C^{2/3} \tag{2}$$

but cautioned that 1,078 K and the other y_∞ values "should be considered pure numbers without any physical significance." The two reasons they gave for that caution were:

1. dy/dn_C "cannot be expected to become equal to zero"
2. There is no proof that the dependence on $n_C^{2/3}$, proposed by Kurata and Isida (1955), holds for $n_C > 20$

In spite of the cautious remarks of Kreglewski and Zwolinski, Kudchadker and Zwolinski (1966) used Eq. 1 to predict vapor pressures and boiling points for n-alkanes up to $n_C = 100$, after confirming that it works reasonably well up to $n_C = 36$. These predictions are included in the current version of the API Research Project 44 tables (TRC, 1986).

We determined a slightly different form of Eq. 2 by regressing the normal boiling data of C_3–C_{20} n-alkanes given in Table 1:

$$\log_{10}(1{,}071.28 - T_b) = 3.02962 - 0.0505115\, n_C^{2/3} \tag{3a}$$

or

$$\ln(1{,}071.28 - T_b) = 6.97596 - 0.116307\, n_C^{2/3} \tag{3b}$$

The maximum deviation from the data (for $n_C \geqq 4$) was 0.089% (or 0.54 K) for C_{19}.

Critical Constants

Table 1 also lists experimental data for the critical temperature, pressure, and density. Although it is generally accepted that we know the most about the critical temperature and the least about the critical density, the following discussion shows

Table 1. Normal Boiling Point and Critical Constants of Normal Alkanes

Carbon No.	T_b K	T_c K	P_c MPa	d_c g · cm^{-3}
1	$111.63^{a,f}$	$190.55^{a,f}$	$4.595^{a,f}$	$0.162^{b,f}$
2	$184.55^{a,g,j}$	305.33^{a}	$4.871^{a,g}$	$0.203^{b,g}$
3	$231.07^{a,h}$	369.85^{a}	$4.247^{a,h}$	$0.217^{b,h}$
4	$272.64^{a,i}$	425.16^{a}	3.796^{a}	$0.228^{b,i}$
5	$309.21^{a,j}$	469.7^{a}	3.369^{a}	0.237^{b}; 0.232^{k}
6	$341.89^{a,j}$	507.4^{a}	3.012^{a}	0.233^{b}
7	$371.57^{a,j}$	540.2^{a}	2.736^{a}	0.232^{b}
8	$398.82^{a,j}$	568.83^{a}; 568.65^{c}	2.487^{a}	0.232^{b}
9	$423.97^{a,j}$	594.64^{a}; 594.65^{c}	2.288^{a}	—
10	$447.30^{a,j}$	617.6^{a}; 617.86^{c}	2.104^{a}	—
11	469.08^{b}	638.8^{b}; 637.07^{c}	1.966^{b}	—
12	489.47^{b}	658.2^{b}; $657.3\underline{2}^{c}$	1.824^{b}	—
13	508.62^{b}	676^{b}; 673.99^{c}	1.72^{b}	—
14	526.73^{b}	693^{b}; $691.1\underline{7}^{c}$	1.44^{b}	—
15	543.835^{e}	$706.3\underline{3}^{c}$	—	—
16	560.01^{b}	722^{b}; $721.6\underline{8}^{c}$	—	—
17	575.17^{e}	736^{d}	—	—
18	$589.4\underline{5}^{b,j}$	748^{b}	—	—
19	$603.0\underline{5}^{e}$	—	—	—
20	$616.9\underline{5}^{e}$	—	—	—

[a] GPA (1986)
[b] Ambrose (1980)
[c] Smith et al. (1985)
[d] Mogollon et al. (1982)
[e] TRC (1986)
[f] Goodwin (1974): $T_b = 111.632$ K, Eq. 3; $T_c = 190.555$ K; $P_c = 4.598825$ MPa; $d_c = 0.1604$ g · cm^{-3}
[g] Goodwin et al. (1976): $T_b = 184.547$ K; $P_c = 4.871\underline{4}$ MPa; $d_c = 0.204\underline{5}$ g · cm^{-3}
[h] Goodwin and Haynes (1982): $T_b = 231.068$ K; $P_c = 4.24746$ MPa; $d_c = 0.2205$ g · cm^{-3}
[i] Haynes and Goodwin (1982): $T_b = 272.638$ K; $P_c = 3.7960$ MPa; $d_c = 0.22785$ g · cm^{-3}
[j] TRC (1986): T_b (K) = 184.570 (C_2), 309.215 (C_5), 341.886 (C_6), 371.574 (C_7), 398.823 (C_8), 423.968 (C_9), 447.305 (C_{10}), 589.4$\underline{5}$ (C_{18})
[k] Kratzke (1985) demonstrated that $d_c = 0.232$ g · cm^{-3}

that it is the limiting value of the critical density that we know with the most certainty.

Critical temperature

The critical temperature data extend up to C_{18}, but there is considerable scatter between old and new values for $n_C > 10$.

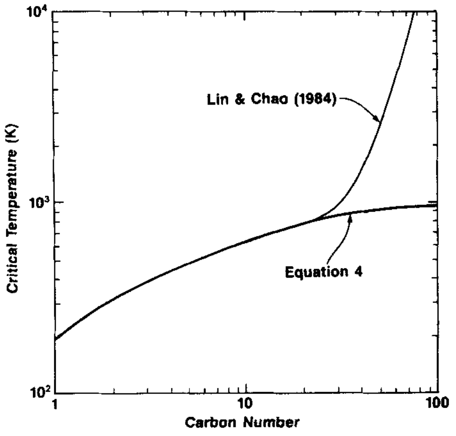

Figure 1. Critical temperature of normal alkanes.

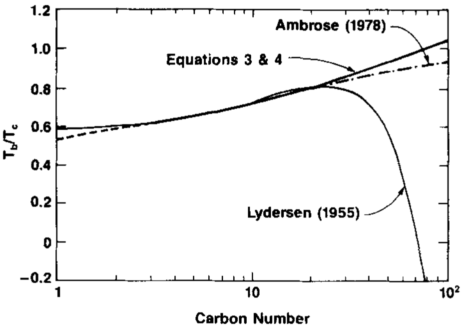

Figure 2. Ratio of normal boiling point to critical temperature for normal alkanes.

When all the values in Table 1 for $n_C \gtrless 3$ were used, the resulting equation:

$$\ln (959.98 - T_c) = 6.81536 - 0.211145\, n_C^{2/3} \tag{4}$$

gave an excellent fit of the data and was statistically indistinguishable from the equation published by Bolotin et al. (1979). The maximum deviation between Eq. 4 and the data (for $n_C \geq 4$) was 0.337% (or 2.27 K) for C_{13} (value reported by Smith et al., 1985).

Equation 4 has been plotted in Figure 1 and has been extrapolated to $n_C = 100$. It is not claimed that this extrapolation represents the "truth," but the dependence on $n_C^{2/3}$ has been tested up to C_{36} for subatmospheric boiling points (Kudchadker and Zwolinski, 1966). Equation 4 certainly is much more reasonable than the extrapolation of the Lin and Chao (1984) correlation. This correlation gives a very good fit of the experimental data, but "explodes" for $n_c > 20$: it predicts $T_c = 2{,}377$ K for $n_C = 50$, and $T_c = 23{,}761$ K for $n_C = 100$.

An experimental determination for $n_C \gtrsim 30$ would be most helpful in establishing whether Eq. 4 is reasonable at such high carbon numbers. Perhaps the approach of Smith et al. (1985) may provide the answer.

Boiling point/critical temperature ratio

Most critical temperature correlations require the normal boiling point. For example, Lydersen's (1955) well-known T_c correlation assumes the following form for normal alkanes:

$$T_b/T_c = 0.567 + 0.02\, n_C - (0.02\, n_C)^2 \tag{5}$$

Equation 5 correlates satisfactorily available data for the T_b/T_c ratio, but has the inherent limitation that it does not allow T_b to exceed T_c. Indeed, as shown in Figure 2, Eq. 5 reaches a maximum value of 0.817 at $n_C = 25$ and decreases to zero at $n_C = 70$. At $n_C = 76.5$, where Eqs. 3 and 4 cross, Eq. 5 gives a negative value for T_b/T_c.

Figure 2 also includes the line calculated with Ambrose's (1978) correlation:

$$\frac{T_b}{T_c} = \frac{1.242 + 0.138\, n_C}{2.242 + 0.138\, n_C} \tag{6}$$

Equation 6 is in excellent agreement with the ratio of Eqs. 3 and 4 up to $n_C = 30$, but is less satisfactory for $n_C > 30$ because it approaches 1 ($T_b = T_c$) in the limit as $n_C \rightarrow \infty$. However, the limit $T_b \rightarrow T_c$ has no physical significance. As shown in the next section, $P_c \ll 101.325$ kPa in the limit as $n_C \rightarrow \infty$.

Critical pressure

The experimental data extend only to C_{14} (for which the value is suspect). Bolotin et al. (1979) recommended that $P_{c\infty} = 0$. We used this limit in regressing the data for $n_C \geqq 3$ in Table 1, with the following results (P in MPa):

$$\ln P_c = 2.01718 - 0.274281\, n_C^{2/3} \tag{7}$$

This is a less satisfactory fit than in the case of T_b and T_c (the maximum deviation was 6.11% or 0.088 MPa for C_{14}), but this is primarily due to the more limited database and the lower quality of the data (especially for C_{14}, and even for C_{11}–C_{13}). Another unsatisfactory aspect of Eq. 7 is that it predicts $P_c = 0.101325$ MPa at $n_C = 62.2$ rather than 76.5 (from Eqs. 3 and 4).

As shown in Figure 3, Eq. 7 is in reasonable agreement with the correlation of Lin and Chao, which approaches zero even more rapidly than Eq. 7. On the other hand, Lydersen's method, or the nearly identical correlation of Ambrose, extrapolates to much higher P_c values and approaches zero much more slowly than Eq. 7:

$$P_c(\text{MPa}) = \frac{0.101325\, M}{(0.34 + 0.227\, n_C)^2} \tag{8}$$

Critical density

The very limited critical density data given in Table 1 have been plotted in Figure 4. What is striking is that the critical density appears to reach a limiting value by $n_C = 8$.

Because the d_c database is so limited, the dependence of liquid density on carbon number was tested with data up to C_{30} for the liquid density at the triple (or melting) point (TRC, 1986; Doss, 1943). These data support the limiting value $d_{t\infty} = 0.78\underline{4}$ $\text{g} \cdot \text{cm}^{-3}$. This is in excellent agreement with the value of $0.78\underline{8}$ $\text{g} \cdot \text{cm}^{-3}$ for the liquid density of linear polyethylene at its melting point (Maloney and Prausnitz, 1974). Furthermore, the d_t of n-alkanes is very close to the limiting value for $n_C \gtrsim 10$ ($d_t \gtrsim 0.77$).

The limiting value for d_c is assumed to be $\underline{d_{c\infty} = 0.3\, d_{t\infty}} = 0.23\underline{5}$ $\text{g} \cdot \text{cm}^{-3}$. It may be as high as 0.24 or as low as 0.232 $\text{g} \cdot \text{cm}^{-3}$.

Figure 4 includes the curve predicted with Lydersen's (1955) correlation

$$d_c = \frac{M}{40 + 55\, n_C} \tag{9}$$

which leads to $d_{c\infty} = 0.255$ $\text{g} \cdot \text{cm}^{-3}$. On the other hand, the correlation of Lin and Chao (1984), although it fits the data well, reaches a maximum and then decreases fairly rapidly, which is contrary to the expected behavior. Thus, Lydersen's assumption that the critical volume increases linearly with carbon number gives a limiting value for d_c that is only 8.5% higher than the recommendation made here. A modification of Eq. 9 that is consistent with the recommended $d_{c\infty}$ and emphasizes the data for C_4–C_8 is

$$d_c = \frac{M}{14 + 59.7\, n_C} \tag{10}$$

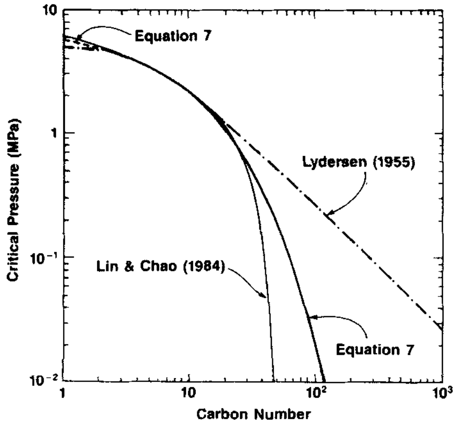

Figure 3. Critical pressure of normal alkanes.

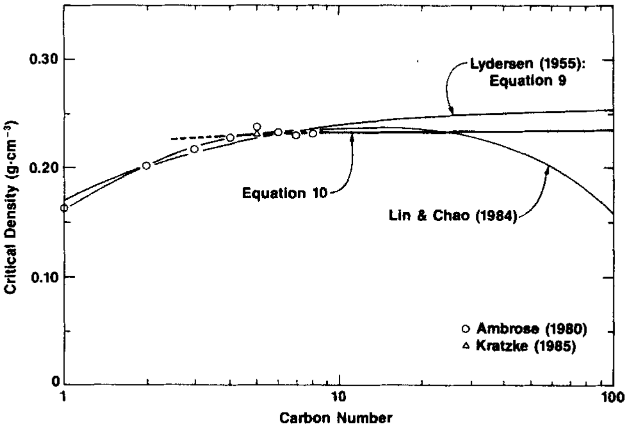

Figure 4. Critical density of normal alkanes.

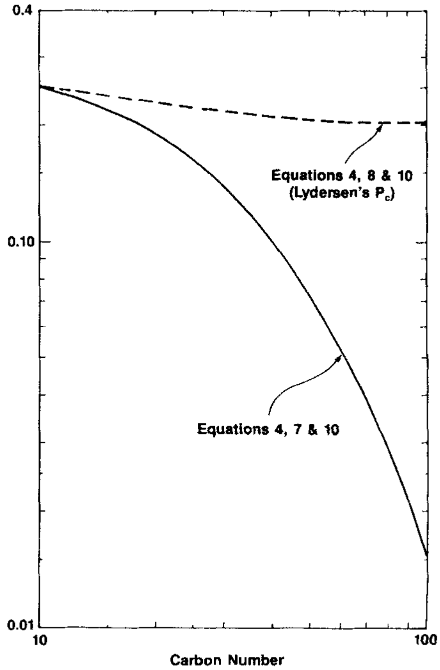

Figure 5. Critical compressibility factor of normal alkanes.

Equation 10 is plotted in Figure 4. The predicted d_c for C_{10} is within 1% of the limiting value, $d_{c\infty} = 0.235\ \mathrm{g \cdot cm^{-3}}$.

Critical compressibility factor

The Z_c calculated with Eqs. 4, 7, and 10, along with $R = 8.3145\ \mathrm{J \cdot gmol^{-1} \cdot K^{-1}}$, is given by the solid curve in Figure 5. It decreases very rapidly with increasing n_C and the limiting value is $Z_{c\infty} = 0$. However, if P_c is calculated with Lydersen's correlation, Eq. 8, then Z_c has a very weak dependence on carbon number, as shown by the dashed curve in Figure 5.

Figure 3 illustrates the difference between Eqs. 7 and 8. Both have the same limit, $P_{c\infty} = 0$, but the approach to that limit differs greatly. Indeed, the use of Eq. 8, Lydersen's correlation, leads to $Z_{c\infty} = 0.206$. Recommendations on dZ_c/dn_C and $Z_{c\infty}$ will have to wait for the resolution of the proper dependence of P_c on n_C.

Conclusions

The limits as $n_C \rightarrow \infty$:

$$T_{c\infty} = 960\ \mathrm{K}$$

$$P_{c\infty} = 0\ \mathrm{MPa}$$

$$d_{c\infty} = 0.235\ \mathrm{g \cdot cm^{-3}}$$

are offered as useful values in guiding extrapolations of available data for normal alkanes to high carbon numbers. Perhaps surprisingly, the most reliable limiting value is for the critical density. Furthermore, this limit is approached by $n_C \gtrsim 8$. On the other hand, although $P_{c\infty} = 0$ is reasonable (and consistent with the expectation that an infinite chain cannot exist as a vapor), dP_c/dn_C is uncertain, and that also makes dZ_c/dn_C, as well as $Z_{c\infty}$, uncertain. Apparently, the dependence on $n_C^{2/3}$ is less satisfactory for P_c than it is for T_b and T_c.

The value $T_{c\infty} = 960$ K is intriguingly low. However, even if it is incorrect, it should be clear from Figures 1 and 2 that the Lin and Chao (1984) and Lydersen (1955) correlations break down for $n_C > 25$, while Ambrose's (1978) correlation, Eq. 6, has the incorrect limit $T_{b\infty} = T_{c\infty}$, which implies the similarly incorrect limit $P_{c\infty} = 101.325$ kPa.

If the values for $T_{c\infty}$ and dT_c/dn_C are firmed up, then it may be possible to use a reliable vapor pressure equation to predict P_c for normal alkanes up to $n_C = 36$ by extrapolating available subatmospheric vapor pressure data to T_c. This will be considered in a future paper.

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Notation

d = density (mass)
M = molecular weight
n_C = carbon number
P = pressure
R = gas constant
T = temperature (absolute)
v = molar volume
Z = compressibility factor

Subscripts

b = boiling-point property
c = critical property
t = triple-point property
∞ = infinite carbon number property

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