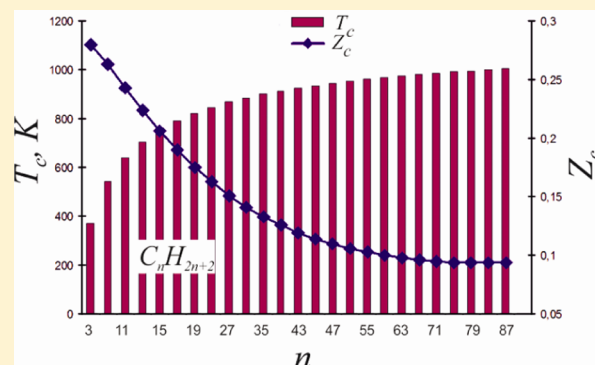


Methods for Calculating the Critical Constants of Hydrocarbons (Using the *n*-Alkane Series as an Example)

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ABSTRACT: This paper presents the calculation method allowing one to obtain the matched magnitudes of critical parameters of hydrocarbon gases with an accuracy comparable to the errors of the experimental methods. The ratios obtained allow an assessment of the values of the critical temperature, critical pressure, critical volume, acentric factor, and compressibility in the homologous series of alkanes up to C_{100} . The critical parameters for alkanes $4 < n_C < 40$ calculated using formulas presented in the article demonstrated good consistency with the experimental data. The proposed values of critical constants for normal alkanes can be used to calculate the physiochemical properties of the compounds, while the calculation methods can be used to determine the critical constants of hydrocarbon components of other homologous series.



INTRODUCTION

Currently, very few correlations of thermodynamic properties used to determine the properties of a mixture contain their actual parameters. The critical constants of pure substances are used instead, based on which the physicochemical characteristics of complex fluids are calculated using such variables as temperature, pressure, and composition. Despite extensive experimental studies and an arsenal of methods for calculating critical properties of liquid and gaseous hydrocarbons, in 2002, the IUPAC Commission on Thermodynamics recommended continuation of work on systematization of the available data and methods of their calculation and matching. However, data on physicochemical properties of individual groups of hydrocarbons are limited as research has focused on solving other problems. The limitations in the available values of critical constants create difficulties in selecting reliable values; thus, a calculation method that generates consistent values of critical parameters of hydrocarbons with an accuracy comparable to the errors of experiment is required.

Various functions and their characteristic constants allow one to forecast the values of various properties of substances and their mixtures with some stated accuracy. This is particularly important when the determination of physiochemical properties using direct experimental methods is associated with technical difficulties. Critical constants are important not by themselves but as parameters included in the equation for determining other thermodynamic properties of substances. If there is lack of accuracy in their values for phase transitions as an example, inconsistent equations may be obtained, up to the emergence of relationships resulting in violation of the laws of thermodynamics.

CURRENT STATE OF THE PROBLEM

The calculation of the physiochemical equilibria of systems under pressures other than the standard ones which are based on the corresponding states theory are in better agreement with the experimental data than those based on special equations of state.¹ Therefore, the use of the provisions of the corresponding states theory that have been reliably substantiated using the methods of statistical thermodynamics^{2,3} is the optimal method for calculating the “liquid – vapor” equilibria with allowance for nonideality of the gas phase components.

The Lee–Kesler equation^{4,5} enables one to accurately describe the relationships between the *PTV* parameters of real gases using the following parameters: the normal boiling point, critical temperature, pressure, and volume. On the basis of these parameters the following are calculated:

- (1) Critical compressibility factor of a gas:³

$$z_c = \frac{P_c V_c}{RT_c} \quad (1)$$

where T_c is the critical temperature, K; P_c is the critical pressure, bar; V_c is the critical volume, cm^3/mol ; and R is the universal gas constant, $R = 83.144 \text{ bar} \cdot \text{cm}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

- (2) The acentric factor of a gas molecule (Pitzer factor):⁴

$$\omega = \frac{-\ln P_c - 5.92714 + 6.09648\theta^{-1} + 1.28862 \ln \theta - 0.169347\theta^6}{15.2518 - 15.6875\theta^{-1} - 13.4721 \ln \theta + 0.43577\theta^6} \quad (2)$$

where $\theta = T_{\text{boil}}/T_c$; T_{boil} is the normal boiling point, K.

In certain cases, the simplified relationship is used:³

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$$\omega = \frac{3}{7} \frac{\theta}{1 - \theta} \log P_c - 1. \quad (3)$$

The use of critical constants of hydrocarbons in thermodynamic calculations requires matching them with their normal boiling point, since a number of experimental variables that were determined for low-purity substances require clarification. The experimental data obtained for heavy hydrocarbons with a large number of isomers (including the conformational ones) and their poorly separable mixtures require careful processing.⁶

The determination of critical constants and the normal boiling points of higher homologues is based on estimations, since they dissociate at lower temperatures and do not exist at a “hypothetical” critical point.⁷ Therefore, the critical constants and normal boiling points of higher homologues are the criteria for thermodynamic similarity, which enable the comparison of these compounds with the lighter representatives of the homologous series.⁸

Numerous studies^{6,9} demonstrate that the enthalpy increment, heat capacity, entropy, temperature, and enthalpy of fusion and boiling, as well as the critical constants of the substances in a homologous series correlate well with the contribution of structural components. Methods for assessing the values of critical constants in homologous series have been developed using these correlations. These methods can be divided into two groups: (1) Additive methods, which are based on calculating the contribution of structural components to the numerical value of a certain property.^{3,10–14} and (2) Approximation methods that establish mathematical relationships between properties of substances in a homological series and changes in the number of structural components.^{8,15–22}

As shown in ref 14, the additive methods for assessing critical property data of substances in a homologous series of higher homologues can be characterized by extremely low accuracy. The selection of approximation methods for matching and assessing the thermodynamic properties is based on accuracy of description of the experimental data and the feasibility of using asymptotes when extrapolating these properties for higher homologues. The asymptotes of thermodynamic properties can be assigned based on the mathematical and thermodynamic conditions.

The approach consisting in mutual coordination of the critical parameters using a single equation is being elaborated in this study. The acentric factor has physical meaning only under a certain combination of the boiling point, critical pressure, and critical temperature. The inverse problem of refining and coordinating the boiling point, critical pressure, and critical temperature values is solved with allowance for this restriction. It has been demonstrated that even small divergence from the “reliable” values of boiling point, critical pressure, and critical temperature cause abrupt changes in the dependence between the acentric factor and the hydrocarbon number, which contradicts the physical meaning of the acentric factor.

RESEARCH METHODS

The critical properties of temperature, pressure, and volume, and the normal boiling points of homologous series of hydrocarbons are characterized by a high degree of correlation with the number of carbon atoms (n_c).⁸ Consider these correlations for the members of the homological series of normal alkanes, for which the problem of matching the values of the critical constants is most illustrative. The regularities of

changes in properties will be considered using the first “full-fledged” member of the homologous series, propane, which is characterized by a number of structural characteristics pertaining to all heavier alkanes.

The experimental and estimated normal boiling temperatures provided in refs 3, 9, 21, 23, and 24 are shown in Figure 1 as a function of n_c , since the oscillation of the values in these aforementioned sources is rather low. The exponential form $T_{\text{boil}} = f(n_c)$ can be clearly seen.

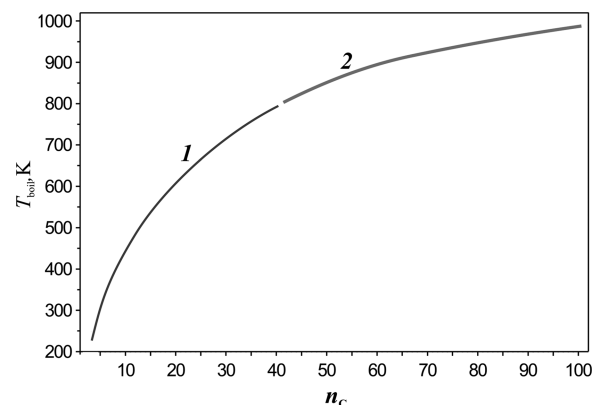


Figure 1. The normal boiling point as function of the number of carbon atoms in the n -alkanes series: (1) experimental data,^{3,9,23,24} and (2) estimated values.^{21,24}

The data on critical temperature (Figure 2) and pressure (Figure 3) of a series of n -alkanes were obtained from the experimental studies;^{25–29} estimated values have also been taken into consideration.^{12,17–21,30,31}

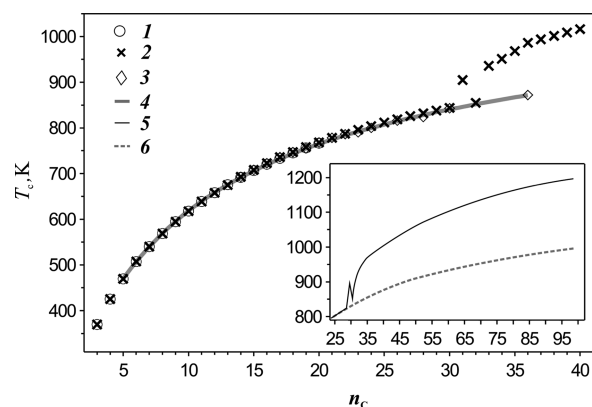


Figure 2. The critical temperature as function of the number of carbon atoms in the n -alkane series: (1) ref 9; (2) ref 24; (3) ref 26; (4) ref 3. The insert demonstrates (5) the estimated relationship for higher homologues²⁴ and (6) extrapolation using eq 4.

The most reliable experimental data on critical temperature and pressure of n -alkanes are presented in refs 25 and 26. The results of processing and fitting the experimental values were reported in ref 26 in the form of equations:

$$T_c = 1258.73 - 2654.38n_c^{-1/2} + 1992n_c^{-1} \text{ K}; \quad n_c = 5 \dots 36 \quad (4)$$

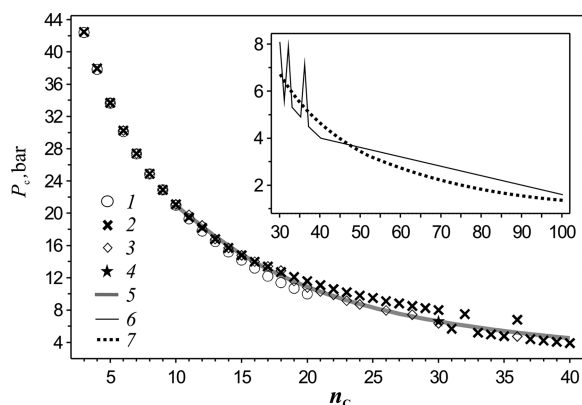


Figure 3. The critical pressure as function of the number of carbon atoms in the n -alkane series: (1) experimental data from ref 9; (2) ref 24; (3) ref 26; (4) n -triacontane from ref 29; (5) eq 5. The insert demonstrates (6) the estimated relationship for higher homologues²⁴ and (7) extrapolation using eq 5.

$$P_c = 138.775n_c^{-3/2} - 78.5279n_c^{-2} - 476.45n_c^{-5/2} \text{ MPa};$$

$$n_c = 10 \dots 36 \quad (5)$$

The results of the studies summarized in ref 3 demonstrate that there is a linear relationship between the critical volume and n_c in the homological series. The following equation was obtained on the basis of the combined approximation of the data:^{3,31}

$$V_c = 57.142n_c + 29.778 \text{ cm}^3/\text{mol}; \quad n_c \geq 2 \quad (6)$$

Equation 6 allows extrapolations of the critical volume to higher homologues of the n -alkanes series.

The variation and oscillation of the critical compressibility values of n -alkanes provided in different literature sources are rather high (Figure 4). This can be attributed to variation and oscillation of the critical temperature and pressure values (see Figures 2, 3), which are used to calculate the values of the critical compressibility factor using eq 1.

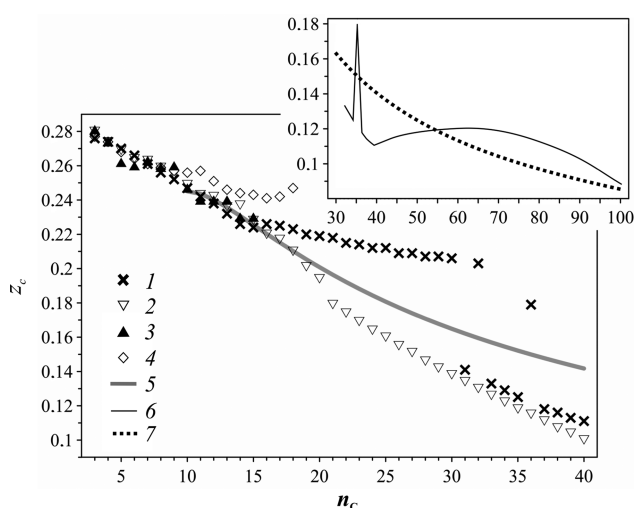


Figure 4. The critical compressibility factor as function of the number of carbon atoms in the n -alkanes series. (1) ref 24; (2) ref 23; (3) ref 3; (4) ref 31; (5) calculation according to eq 3 based on the data from ref 26; (6) the estimated relationship for higher homologues according to ref 24; (7) calculation according to eq 3 based on the data presented in ref 26.

The relationship between the acentric factor of a molecule and n_c (Figure 5), which is calculated according to eq 3, is not

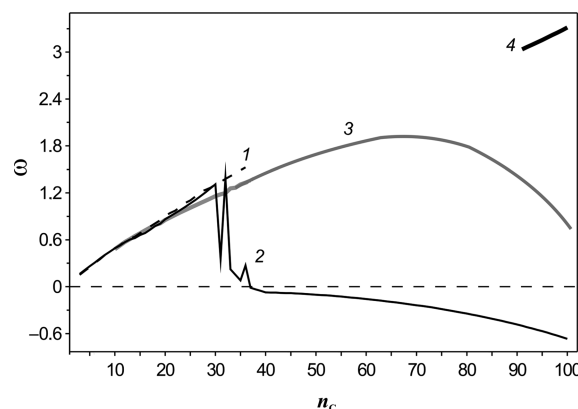


Figure 5. The acentric factor of a molecule as function of the number of carbon atoms in the n -alkanes series: (1) ref 24; (2) calculation according to eq 3 based on T_{boil} , T_c and P_c ;²⁴ (3) calculation based on T_c and P_c obtained using the eqs 4, 5, and T_{boil} ;²⁴ (4) ref 21.

correct for higher homologues. This can be attributed to poor thermodynamic validity of extrapolating the normal boiling point, critical temperature, and pressure to the range of higher homologues.

Thus, as one can observe in Figures 2–5, oscillation and the incorrect form $T_c = f(n_c)$ and $P_c = f(n_c)$ results in oscillations similarly for $Z_c = f(n_c)$ and $\omega = f(n_c)$. Note that even an insignificant oscillation in $T_{\text{boil}} = f(n_c)$ causes a noticeable oscillation in the acentric factor calculated on the basis of the former (see Figure 5).

Incorrect extrapolations of T_c , P_c and T_{boil} for the higher homologues gives values of z_c and ω that are significantly different from the experimental data when used in thermodynamic calculations; in certain cases these results may even contradict the laws of thermodynamics. The matching of experimentally studied values and the correctness of the extrapolated evaluation values of T_c , P_c and T_{boil} can be evaluated by analyzing the forms of $Z_c = f(n_c)$ and $\omega = f(n_c)$.

Since the contribution of each additional structural unit to the properties of substances of the homologous series has a smaller “weight”, there are no physical and thermodynamic reasons for oscillations of the relationships between these properties and n_c . Oscillation of the evenness–oddness affects the heat capacity⁹ but does not affect the relationship between the values of critical constants and n_c . Moreover, there are no reasons for relationships which are observed in Figure 2 (curve 5) or in Figure 3 (curve 6). It is logical to assume that the contribution of each additional structural unit on the coefficients z_c and ω will also decrease with increasing n_c in the homologous series. Therefore, the form $Z_c = f(n_c)$ shown in Figure 4 (insert, curve 6) is inappropriate. Correct extrapolations of the critical constants of higher homologues should not provide the types of $\omega = f(n_c)$ shown in Figure 6 (curves 2, 3).

The relationships $T_{\text{boil}} = f(n_c)$, $T_c = f(n_c)$, and $P_c = f(n_c)$ in the homologous series were found to be exponential.^{9,13,15,16,22} The following forms of equations are used for approximation and extrapolation of $T_{\text{boil}} = f(n_c)$ and $T_c = f(n_c)$ of homologous series:

$$T_{\text{boil}} = a_1 - \exp(a_2 - a_3 n_c^4) \quad (7)$$

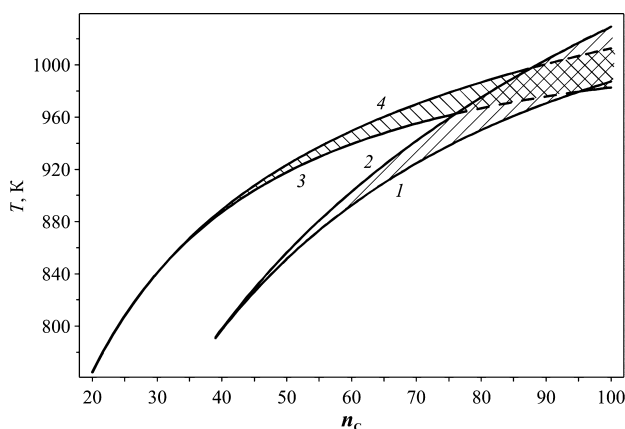


Figure 6. Extrapolation of the dependence of the normal boiling point and the critical temperature on the number of carbon atoms in the n -alkanes series to the range of higher homologues. The calculation of the normal boiling point was carried out according to (1) eq 7 and (2) eq 8. Calculation of the critical temperature was carried out according to (3) eq 9 and (4) eq 10.

$$T_{\text{boil}} = a_1 + \exp(a_2 - a_3 n^{a_4}) \quad (8)$$

$$T_c = a_1 - \exp(a_2 - a_3 n^{a_4}) \quad (9)$$

$$T_c = a_1 + \exp(a_2 - a_3 n^{a_4}) \quad (10)$$

In eqs 7 and 9, coefficients a_1 are an asymptote of T_{boil} and T_c provided that $n \rightarrow \infty$, since in this case the exponential summand tends to approach zero. The values of these asymptotes obtained by approximation and extrapolation using various types of equations and reported by different workers differ rather significantly. Thus, the value of 959.98 K was proposed for the limiting critical temperature of n -alkanes in ref 22, 1143.8 K in ref 16, and 1217 K in ref 32. The ratio between the asymptotes of the normal boiling point and the critical temperature is often contradictory. Thus, the values $T_{\text{boil}}(\infty) = 1076$ K and $T_c(\infty) = 1050$ K are provided in ref 8.

The coefficients a_1 in eqs 8 and 10 are the values approaching T_{boil} and T_c of the first substance of the homologous series taken for used in the approximation. The asymptotes of temperatures obtained in these equations provided that the exponential summand tends to zero will obviously differ significantly from those obtained in eqs 7 and 9. The extrapolation performed according to the eqs 7, 9 and 8, 10 will also be significantly different.

Figure 6 shows the results of extrapolation of T_{boil} and T_c using eqs 7 to 10 with coefficients obtained in the approximation of the data $(T_{\text{boil}})^9$ and $(T_c)^{25,26}$. The extrapolation of T_c values using eq 4 borrowed from²⁶ yields a result that is close to that obtained using eq 10. The ratios T_{boil}/T_c shown in Figure 6 are close to those obtained using equations recommended in refs 8, 16, 22, and 32.

The limit of the T_{boil} value obtained during the approximation of the experimental data using eq 8 is approximately 1800 K, which is considered to be an overestimated value. The asymptote of T_{boil} obtained using eq 7 is 1080 K. This value, which is in close agreement with the data presented in many articles, was obtained based on approximation of the experimentally studied range n_c (3...40). Hence, it is reasonable to use the T_{boil} values obtained using eq 7 as the "reference" ones in further calculations.

The intersection of $T_{\text{boil}} = f(n_c)$ and $T_c = f(n_c)$ misrepresents the physical meaning of the relationship between these values and gives 1/0 uncertainty when using eq 2 and 3 to calculate ω . Furthermore, the form of functions eq 2 and 3 for the ratio $T_{\text{boil}}/T_c > 1$ yields negative ω values for large hydrocarbons, which contradicts the physical sense of this parameter. Therefore, it is reasonable to assume temperature $T_c = f(n_c)$ obtained using eq 10 (which does not intersect $T_{\text{boil}} = f(n_c)$) obtained using the eq 7 in the interval n_c 3...100 as the reference temperature for further calculations.

Since the correctness criteria for the extrapolation of T_c into the range of larger homologues have not been developed, the "reference" relationship $T_c = f(n_c)$ may result in unsatisfactory results of the evaluation of the critical constants (see Figures 4, 5) calculated based on T_c . The function $\omega = f(n_c)$ can be the universal criterion for correctness of extrapolation of $T_c = f(n_c)$. It is obvious that when $T_{\text{boil}} = f(n_c)$ and $P_c = f(n_c)$ are considered to be adequate, the form of $\omega = f(n_c)$ is determined by the form of $T_c = f(n_c)$. For example, the forms $\omega = f(n_c)$ presented in Figure 5 contradict the physical meaning of relationships $f(n_c)$, since it is unlikely that the contribution of several new methylene groups in the interval of n_c 70...80 will abruptly change the properties of the parent substance in the homologous series. In this case, there is a mathematical problem, since functions (2) and (3) are highly sensitive to the T_{boil}/T_c ratio. Having determined the correct form of $\omega = f(n_c)$, one can solve the problem of finding the correct form of $T_c = f(n_c)$ using functions (2) and (3). For eq 3, the inverse relationship has the following form:

$$T_c = \frac{T_{\text{boil}}}{\left(\frac{7}{3} \frac{\omega + 1}{\log P_c}\right) / \left(1 + \left(\frac{7}{3} \frac{\omega + 1}{\log P_c}\right)\right)} \quad (11)$$

The use of eq 11 for adjusting the extrapolation of $T_c = f(n_c)$ to larger homologues requires the extrapolation of $P_c = f(n_c)$ to be unambiguously determined.

Despite the fact that there is a criterion in the homologous series for assessing the validity of extrapolation ($P_c > 1$ bar) for $P_c = f(n_c)$, when performing the extrapolation to the region of larger homologues, the problem of compliance of the asymptotic value of $P_c(\infty)$ and the forms of the extrapolation curve affecting the form of $Z_c = f(n_c)$ arises (see inserts in Figures 3 and 4).

The polynomial eq 5 recommended in ref 26 has as an asymptote value tending to zero. If an n -alkane consists of 118 carbon atoms, the critical pressure calculated according to eq 5 becomes less than 1 bar. In refs 16 and 22 eq 12 is used for the approximation and extrapolation of the relationship $P_c = f(n_c)$; hence, a_1 must be > 1 in order to comply with the condition $P_c > 1$ bar.

$$P_c = a_1 + \exp(a_2 - a_3 n^{a_4}) \quad (12)$$

Fitting of the experimental data^{9,26} yields the following equation:

$$P_c = 1.0078 + \exp(4.4375 - 0.3746 n^{0.5822}) \text{ bar} \quad (13)$$

which provides satisfactory results of extrapolation of $P_c = f(n_c)$ into the region of large n -alkanes. For example, P_c for n -heptane ($C_{100}H_{202}$) is 1.364 bar.

As noted above, the form of $\omega = f(n_c)$ (Figure 7, curve 1) calculated using eq 3 based on the "reference" extrapolations of $T_{\text{boil}} = f(n_c)$, $T_c = f(n_c)$, and $P_c = f(n_c)$ contradicts the physical

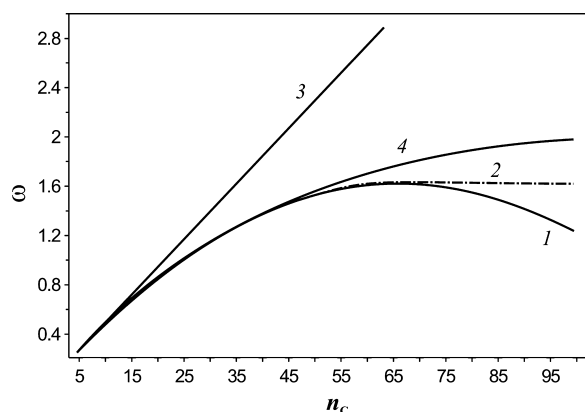


Figure 7. Extrapolation of the dependence of the acentric factor of a molecule on the number of carbon atoms in the n -alkanes series to the range of higher homologues: (1) calculation on the basis of the accepted "reference" relationships $T_{\text{boil}} = f(n_c)$, $T_c = f(n_c)$, and $P_c = f(n_c)$; (2) for the condition $\omega = \text{const}$; (3) linear extrapolation of ω (C_5H_{12} ; C_6H_{14}); (4) using eq 15.

meaning of the functions $f(n_c)$. Line 2 in Figure 7 shows the "lower boundary" of the acentric factor values, which is associated with the fact that the acentric factor cannot decrease as the hydrocarbon number increases, while line 3 specifies the "upper boundary" of the acentric factor values, which is determined on the basis of the postulate that the contribution of each new methyl group to the magnitude of a property under consideration decreases (or remains constant in line 3) with increasing hydrocarbon number. Hence, the interval where the acentric values have physical meaning is being considered. Figure 8 (curves 1, 2) presents the results of calculating T_c using eq 11 performed on the basis of these extrapolations; curve 4 in the inset shows the previously adopted $T_c = f(n_c)$.

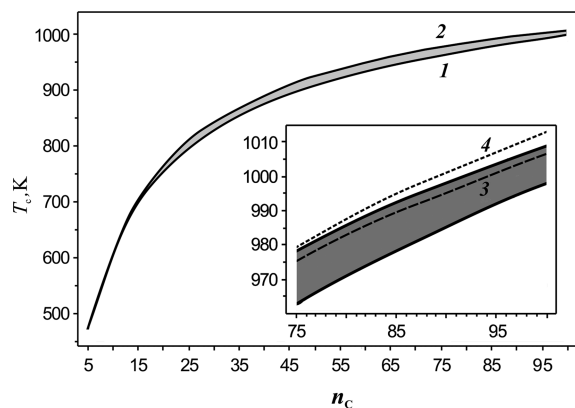


Figure 8. Dependences of the critical temperature on the number of carbon atoms in the n -alkanes series obtained by solving the inverse problem using eq 11 on the basis of extrapolation: (1) linear ω (C_5H_{12} ; C_6H_{14}); (2) for the condition $\omega = \text{const}$; (3) according to eq 15; (4) basic relationship $T_c = f(n_c)$.

The range of variations of $T_c = f(n_c)$ is narrow (see Figure 8); therefore, relatively significant variations of ω result in considerably smaller variations in T_c . Thus, at $n_c = 100$, a 2.77-fold change in ω results in a ~ 6 -fold change in T_c . The inverse statement has practical sense: small variations in T_c lead to the relatively considerable variations in ω . Therefore, it is important to match the critical constants of the substances in the

homologous series in order to ensure their correct relationships.

The choice of the correct $\omega = f(n_c)$ can be accomplished using recurrent relations of the properties of organic compounds³³ developed by I. G. Zenkevich; these relations are based on using the ω values calculated with respect to the properties of n -alkanes from the $C_{10}H_{22}$... $C_{36}H_{74}$ series.

Similar results are obtained by the approximation using the equation:

$$\omega = a_1 - \exp(a_2 - a_3 n_c^{a_4}) \quad (14)$$

for the ω values of this series, which assume the form

$$\omega = 2.1112 - \exp(0.7128 - 0.01709 n_c^{1.1182}) \quad (15)$$

The extrapolation of ω using eq 15 is shown in Figure 7 (curve 4); the result of solving the inverse problem using eq 11 is presented in Figure 8 (insert, curve 3). The corrected $T_c = f(n_c)$ differs insignificantly from the reference temperature; however, the effect of this difference can be seen in Figure 7, which demonstrates the relationship between the acentric factor of a molecule and the number of carbon atoms in the n -alkanes series.

The ratios obtained enable one to assess the values of the critical temperature, critical pressure, critical volume, acentric factor, and compressibility in the homologous series of alkanes up to C_{100} (Table 1). The critical parameters for alkanes $4 < n_c < 40$ calculated using the formulas 3, 5, and 7 have shown a close agreement with the data in ref 9. The proposed values of the critical constants for normal alkanes can be used to calculate the physiochemical properties of mixtures; the calculating methods presented in this paper can be used to determine the critical constants in hydrocarbon components of other homologous series.

CONCLUSIONS

The comparison of the experimentally determined critical constants of hydrocarbons with the data obtained using the proposed methods show a rather good agreement. The emergence of correlations more perfect than eqs 2 and 3 will allow one to provide the better-verified and more accurate assessment of the calculated values.

Unlike the scattered sets of data pertaining to critical parameters, provided in a variety of sources, the method proposed in this article has enabled one to achieve the internal consistency of the critical constants and thereby ensure the reliability of the thermodynamic calculations of the equilibria in heterogeneous hydrocarbon systems using computer programs based on the minimization of thermodynamic potentials. The correctness of the method proposed consists in the fact that mutually coordinated and noncontradictory values of the critical parameters have been obtained using the well-proven correlations (eqs 1 to 3) with allowance for the physical meaning of all the data under consideration (e.g., the boiling point is not higher than the critical temperature).

The method presented enables one to adjust the dependences between the critical constants and the number of carbon atoms in other homologous series, and, hence, makes it possible to create a database of thermodynamic properties of gaseous and liquid hydrocarbons (including those of high molecular weight).

The analytical equations for the critical properties of substances presented in this paper and statistical processing

Table 1. Critical Constants of Normal Alkanes (Estimated Data)

name	formula	T_{boil}	T_c	P_c	V_c	z_c	ω
		K	K	bar	cm ³ /mol		
methane	CH ₄	111.64 ^a	190.55 ^a	45.99 ^a	99.2 ^b	0.288	0.011
ethane	C ₂ H ₆	184.57 ^a	305.42 ^a	48.80 ^a	148.3 ^b	0.285	0.098
propane	C ₃ H ₈	231.08 ^a	369.80 ^a	42.40 ^a	203.0 ^b	0.280	0.153
<i>n</i> -butane	C ₄ H ₁₀	272.66 ^a	425.14 ^a	37.84 ^a	255.0 ^b	0.273	0.200
<i>n</i> -pentane	C ₅ H ₁₂	309.44	468.68	33.562	315.5	0.272	0.263
<i>n</i> -hexane	C ₆ H ₁₄	342.22	507.26	30.262	372.6	0.267	0.310
<i>n</i> -heptane	C ₇ H ₁₆	371.91	540.76	27.487	429.8	0.263	0.355
<i>n</i> -octane	C ₈ H ₁₈	399.07	569.74	25.114	486.9	0.258	0.403
<i>n</i> -nonane	C ₉ H ₂₀	424.12	595.74	23.060	544.1	0.253	0.447
<i>n</i> -decane	C ₁₀ H ₂₂	447.37	619.08	21.262	601.2	0.248	0.491
<i>n</i> -undecane	C ₁₁ H ₂₄	469.06	639.84	19.676	658.3	0.243	0.536
<i>n</i> -dodecane	C ₁₂ H ₂₆	489.38	658.65	18.267	715.5	0.239	0.581
<i>n</i> -tridecane	C ₁₃ H ₂₈	508.48	675.81	17.007	772.6	0.234	0.626
<i>n</i> -tetradecane	C ₁₄ H ₃₀	526.50	691.54	15.874	829.8	0.229	0.670
<i>n</i> -pentadecane	C ₁₅ H ₃₂	543.53	706.03	14.852	886.9	0.224	0.714
<i>n</i> -hexadecane	C ₁₆ H ₃₄	559.68	719.45	13.925	944.1	0.220	0.757
<i>n</i> -heptadecane	C ₁₇ H ₃₆	575.02	731.91	13.082	1001.2	0.215	0.799
<i>n</i> -octadecane	C ₁₈ H ₃₈	589.61	743.52	12.312	1058.3	0.211	0.841
<i>n</i> -nonadecane	C ₁₉ H ₄₀	603.52	754.39	11.608	1115.5	0.206	0.881
π -eicosane	C ₂₀ H ₄₂	616.81	764.58	10.961	1172.6	0.202	0.921
<i>n</i> -heneicosane	C ₂₁ H ₄₄	629.50	774.17	10.366	1229.8	0.198	0.961
<i>n</i> -docosane	C ₂₂ H ₄₆	641.66	783.20	9.817	1286.9	0.194	0.999
<i>n</i> -tricosane	C ₂₃ H ₄₈	653.30	791.74	9.310	1344.0	0.190	1.037
<i>n</i> -tetracosane	C ₂₄ H ₅₀	664.48	799.82	8.840	1401.2	0.186	1.073
<i>n</i> -pentacosane	C ₂₅ H ₅₂	675.20	807.49	8.405	1458.3	0.183	1.109
<i>n</i> -hexacosane	C ₂₆ H ₅₄	685.52	814.77	8.000	1515.5	0.179	1.144
<i>n</i> -heptacosane	C ₂₇ H ₅₆	695.44	821.69	7.623	1572.6	0.175	1.178
<i>n</i> -octacosane	C ₂₈ H ₅₈	704.99	828.30	7.272	1629.8	0.172	1.212
<i>n</i> -nonacosane	C ₂₉ H ₆₀	714.20	834.60	6.945	1686.9	0.169	1.244
<i>n</i> -triacontane	C ₃₀ H ₆₂	723.07	840.62	6.639	1744.0	0.166	1.276
<i>n</i> -hentriacontane	C ₃₁ H ₆₄	731.64	846.37	6.352	1801.2	0.163	1.307
π -dotriacontane	C ₃₂ H ₆₆	739.91	851.89	6.084	1858.3	0.160	1.336
<i>n</i> -tritriacontane	C ₃₃ H ₆₈	747.89	857.18	5.832	1915.5	0.157	1.366
<i>n</i> -tetratetracontane	C ₃₄ H ₇₀	755.61	862.25	5.596	1972.6	0.154	1.394
<i>n</i> -pentatriacontane	C ₃₅ H ₇₂	763.08	867.12	5.374	2029.7	0.151	1.422
<i>n</i> -hexatriacontane	C ₃₆ H ₇₄	770.31	871.81	5.165	2086.9	0.149	1.448
<i>n</i> -heptatriacontane	C ₃₇ H ₇₆	777.31	876.31	4.968	2144.0	0.146	1.475
<i>n</i> -octatriacontane	C ₃₈ H ₇₈	784.08	880.66	4.783	2201.2	0.144	1.500
<i>n</i> -nonatriacontane	C ₃₉ H ₈₀	790.65	884.84	4.608	2258.3	0.141	1.524
<i>n</i> -tetracontane	C ₄₀ H ₈₂	797.01	888.87	4.444	2315.5	0.139	1.548
<i>n</i> -hentetracontane	C ₄₁ H ₈₄	803.19	892.77	4.288	2372.6	0.137	1.572
<i>n</i> -dotetracontane	C ₄₂ H ₈₆	809.18	896.53	4.141	2429.7	0.135	1.594
<i>n</i> -tritetracontane	C ₄₃ H ₈₈	814.99	900.16	4.001	2486.9	0.133	1.616
<i>n</i> -tetratetracontane	C ₄₄ H ₉₀	820.63	903.67	3.870	2544.0	0.131	1.637
<i>n</i> -pentatetracontane	C ₄₅ H ₉₂	826.12	907.07	3.745	2601.2	0.129	1.658
<i>n</i> -hexatetracontane	C ₄₆ H ₉₄	831.44	910.37	3.627	2658.3	0.127	1.678
<i>n</i> -heptatetracontane	C ₄₇ H ₉₆	836.62	913.55	3.514	2715.5	0.126	1.697
<i>n</i> -octatetracontane	C ₄₈ H ₉₈	841.65	916.64	3.408	2772.6	0.124	1.716
<i>n</i> -nonatetracontane	C ₄₉ H ₁₀₀	846.54	919.64	3.307	2829.7	0.122	1.734
<i>n</i> -pentacontane	C ₅₀ H ₁₀₂	851.31	922.55	3.211	2886.9	0.121	1.752
<i>n</i> -henpentacontane	C ₅₁ H ₁₀₄	855.94	925.37	3.120	2944.0	0.119	1.769
<i>n</i> -dopentacontane	C ₅₂ H ₁₀₆	860.45	928.11	3.033	3001.2	0.118	1.786
<i>n</i> -tripentacontane	C ₅₃ H ₁₀₈	864.84	930.78	2.950	3058.3	0.117	1.802
<i>n</i> -tetrapentacontane	C ₅₄ H ₁₁₀	869.11	933.37	2.872	3115.4	0.115	1.818
<i>n</i> -pentapentacontane	C ₅₅ H ₁₁₂	873.28	935.89	2.797	3172.6	0.114	1.833
<i>n</i> -hexapentacontane	C ₅₆ H ₁₁₄	877.33	938.34	2.726	3229.7	0.113	1.848
<i>n</i> -heptapentacontane	C ₅₇ H ₁₁₆	881.29	940.72	2.658	3286.9	0.112	1.862
<i>n</i> -octapentacontane	C ₅₈ H ₁₁₈	885.14	943.05	2.593	3344.0	0.111	1.876
<i>n</i> -nonapentacontane	C ₅₉ H ₁₂₀	888.90	945.31	2.531	3401.2	0.110	1.889

Table 1. continued

name	formula	T_{boil}	T_c	P_c	V_c	z_c	ω
		K	K	bar	cm ³ /mol		
<i>n</i> -hexacosane	C ₆₀ H ₁₂₂	892.56	947.52	2.472	3458.3	0.109	1.902
<i>n</i> -henhexacontane.	C ₆₁ H ₁₂₄	896.13	949.67	2.416	3515.4	0.108	1.915
<i>n</i> -dohexacontane	C ₆₂ H ₁₂₆	899.62	951.77	2.362	3572.6	0.107	1.927
<i>n</i> -trihexacontane	C ₆₃ H ₁₂₈	903.02	953.82	2.311	3629.7	0.106	1.938
<i>n</i> -tetrahexacontane	C ₆₄ H ₁₃₀	906.34	955.82	2.261	3686.9	0.105	1.950
<i>n</i> -pentaheptacontane	C ₆₅ H ₁₃₂	909.58	957.77	2.214	3744.0	0.104	1.961
<i>n</i> -hexaheptacontane	C ₆₆ H ₁₃₄	912.74	959.68	2.170	3801.2	0.103	1.972
<i>n</i> -heptaheptacontane	C ₆₇ H ₁₃₆	915.83	961.54	2.127	3858.3	0.103	1.982
<i>n</i> -octaheptacontane	C ₆₈ H ₁₃₈	918.85	963.37	2.085	3915.4	0.102	1.992
<i>n</i> -nonaheptacontane	C ₆₉ H ₁₄₀	921.79	965.15	2.046	3972.6	0.101	2.002
<i>n</i> -heptacosane	C ₇₀ H ₁₄₂	924.67	966.89	2.008	4029.7	0.101	2.011
<i>n</i> -henheptacontane	C ₇₁ H ₁₄₄	927.48	968.60	1.972	4086.9	0.100	2.020
<i>n</i> -doheptacontane	C ₇₂ H ₁₄₆	930.23	970.27	1.938	4144.0	0.100	2.029
<i>n</i> -triheptacontane	C ₇₃ H ₁₄₈	932.92	971.91	1.904	4201.1	0.099	2.038
<i>n</i> -tetraheptacontane	C ₇₄ H ₁₅₀	935.55	973.51	1.872	4258.3	0.099	2.046
<i>n</i> -pentaheptacontane	C ₇₅ H ₁₅₂	938.11	975.08	1.842	4315.4	0.098	2.054
<i>n</i> -hexaheptacontane	C ₇₆ H ₁₅₄	940.62	976.62	1.813	4372.6	0.098	2.062
<i>n</i> -heptaheptacontane	C ₇₇ H ₁₅₆	943.08	978.13	1.785	4429.7	0.097	2.069
<i>n</i> -octaheptacontane	C ₇₈ H ₁₅₈	945.48	979.61	1.758	4486.9	0.097	2.077
<i>n</i> -nonaheptacontane	C ₇₉ H ₁₆₀	947.83	981.06	1.732	4544.0	0.096	2.084
<i>n</i> -octacosane	C ₈₀ H ₁₆₂	950.13	982.48	1.707	4601.1	0.096	2.091
<i>n</i> -henoctacontane	C ₈₁ H ₁₆₄	952.38	983.88	1.683	4658.3	0.096	2.097
<i>n</i> -dooctacontane	C ₈₂ H ₁₆₆	954.58	985.25	1.660	4715.4	0.096	2.104
<i>n</i> -trioctacontane	C ₈₃ H ₁₆₈	956.73	986.59	1.638	4772.6	0.095	2.110
<i>n</i> -tetraoctacontane	C ₈₄ H ₁₇₀	958.84	987.92	1.617	4829.7	0.095	2.116
<i>n</i> -pentaoctacontane	C ₈₅ H ₁₇₂	960.90	989.21	1.596	4886.8	0.095	2.122
<i>n</i> -hexaoctacontane	C ₈₆ H ₁₇₄	962.93	990.49	1.576	4944.0	0.095	2.127
<i>n</i> -heptaoctacontane	C ₈₇ H ₁₇₆	964.90	991.74	1.558	5001.1	0.094	2.133
<i>n</i> -octaoctacontane	C ₈₈ H ₁₇₈	966.84	992.97	1.539	5058.3	0.094	2.138
<i>n</i> -nonaoctacontane	C ₈₉ H ₁₈₀	968.74	994.18	1.522	5115.4	0.094	2.143
<i>n</i> -nonacontane	C ₉₀ H ₁₈₂	970.60	995.37	1.505	5172.6	0.094	2.148
<i>n</i> -hennonacontane	C ₉₁ H ₁₈₄	972.42	996.54	1.489	5229.7	0.094	2.153
<i>n</i> -Dononacontane	C ₉₂ H ₁₈₆	974.20	997.69	1.473	5286.8	0.094	2.158
<i>n</i> -trinonacontane	C ₉₃ H ₁₈₈	975.95	998.82	1.458	5344.0	0.094	2.162
<i>n</i> -tetranonacontane	C ₉₄ H ₁₉₀	977.67	999.94	1.444	5401.1	0.094	2.167
<i>n</i> -pantanonacontane	C ₉₅ H ₁₉₂	979.35	1001.03	1.430	5458.3	0.094	2.171
<i>n</i> -hexanonacontane	C ₉₆ H ₁₉₄	980.99	1002.11	1.416	5515.4	0.094	2.175
<i>n</i> -heptanonacontane	C ₉₇ H ₁₉₆	982.60	1003.17	1.403	5572.6	0.094	2.179
<i>n</i> -octanonacontane	C ₉₈ H ₁₉₈	984.19	1004.21	1.391	5629.7	0.094	2.183
<i>n</i> -nonanonacontane	C ₉₉ H ₂₀₀	985.74	1005.24	1.379	5686.8	0.094	2.187
<i>n</i> -hectane	C ₁₀₀ H ₂₀₂	987.26	1006.25	1.367	5744.0	0.094	2.190

^aReference ⁹. ^bReference ³.

of the experimental data allow one not only to calculate the critical constants, but also to inter- and extrapolate the available thermodynamic data.

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