

## **A Generalized Scaled Equation of State for *n*-Alkanes (Methane to *n*-Nonane) in the Critical Region**

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A generalized scaled equation of state has been developed to calculate thermodynamic properties of *n*-alkanes from methane (CH<sub>4</sub>) to *n*-nonane (C<sub>9</sub>H<sub>20</sub>) in the critical region. The equation is valid in the reduced density range  $0.7 \leq \rho_c \leq 1.3$  at  $T = T_c$  and up to  $1.2T_c$  at  $\rho = \rho_c$ .

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**KEY WORDS:** critical parameters; critical phenomena; equation of state; methane, ethane; *n*-alkanes; specific heat; sound velocity.

### **1. INTRODUCTION**

Interesting work on the improvement of nonanalytic equations of state for the thermodynamic properties of fluids in a wide vicinity around the critical point has been pursued in a number of research centers [1, 2]. In these approaches crossover functions are introduced into the equations to connect the "mean-field" or "Van der Waals" region with the fluctuation region [1] or, conversely, from the fluctuation region to the mean-field region [2]. Both approaches yield a description of the thermodynamic surface of pure liquids with sufficient reliability in a wide region of parameters of state. In recent years, the Thermophysical Laboratory of the Grozny Petroleum Institute has obtained experimental density and isobaric heat capacity data in the critical region of *n*-alkanes from C<sub>5</sub>H<sub>12</sub> to C<sub>9</sub>H<sub>20</sub>. Moreover, the literature provides a number of quite reliable experimental data for the thermodynamic properties of the *n*-alkanes from CH<sub>4</sub> to C<sub>4</sub>H<sub>10</sub>. Hence, we believed it desirable to test the applicability of the approaches mentioned above to a group of substances and also to study the possibility of developing a generalized scaled equation of state for *n*-alkanes.

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Table I. Experimental Information

Sub- stance (1)	Pro- perty (2)	Refe- rence (3)	Investigated interval of state parameters				Date used in the work				
			$T$ (K) (4)	$P$ (MPa) (5)	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ ) (6)	Region <sup>a</sup> (7)	Isotherms (K) (8)	Isochores (9)	Isobars (MPa) (10)		
Methane	PVT	7, 8	90.68–193.00	0.01–6.70	60.0–260.0	1, v	189.50	189.80			
							190.00	190.10			
							190.20	190.30			
							190.40	190.45			
							190.50	190.55			
			193.00								
Ethane	PVT	9, 10	163.15–423.15	1.77–275.42	16.33–232.41	1, v	190.63	190.85			
							191.45	193.05			
							195.15	200.15			
							210.15	223.15			
						200.92	246.65				
Propane	PVT	11	273.15–423.15	1.88–21.76	25.66–246.45	v					
						200.92	246.65				
<i>n</i> -Butane	PVT	12	249.15–623.15	1.17–40.0	22.55–481.11	v					
						165.39	180.42				
<i>n</i> -Butane	PVT	13	288.87–328.17	27.14–33.70	47.66–628.91	1, v					
						225.53	240.56				
<i>n</i> -Butane	PVT	14	283.15–473.15	0.1–10.0	0.0–360.84	1, v					
						141.22	177.02				
<i>n</i> -Butane	PVT	15	292.65–448.15	0.1–11.77	1.23–314.23	1, v					
						200.92	246.65				
<i>n</i> -Butane	PVT	16	100.00–325.02	5.61–26.89	77.48–322.53	1, v					
						252.6	259.7				
<i>n</i> -Butane	PVT	17	79.55–374.80	159.0–306.0	159.0–306.0	1, v					
						229.0	306.0				
<i>n</i> -Butane	PVT	18	311.0–589.0	0.2–8.3	5.0–513.0	1, v					
						177.98	200.23				
						213.58	288.84				
						266.98	320.37				

<i>n</i> -Pentane	PVT	19	173.15–658.15	0.1–150.0	3.97–769.07	1, v	469.65	473.15	332.9	302.0
							498.15	523.15	300.9	262.1
							548.15	573.15	243.4	242.7
							598.15		231.4	231.4
	$C_p$	20	293.15–623.15	0.1–60.0	1, v			221.4	220.3	
							186.8	165.5		
							124.0	123.2		
							3.40	3.45		
								3.50	3.70	
								4.00	4.50	
								5.00	4.50	
<i>n</i> -Hexane	PVT	21	223.15–623.15	0.1–150.0	1, v	507.85	508.15	198.8	207.1	
						505.15	506.15	216.3	226.0	
						523.15	548.15	232.9	236.9	
						573.15	598.15	248.9	262.0	
	$C_p$	22	293.15–623.15	0.1–60.0	1, v	623.15		272.4	293.0	
								3.103	3.203	
								3.302	3.402	
								3.503	4.003	
								4.503		
<i>n</i> -Heptane	PVT	19	188.15–623.15	0.1–150.0	1, v	148.3		178.3		
						199.5		219.6		
						232.3		249.3		
						269.5		288.2		
	$C_p$	23	293.15–625.52	0.1–60.0	1, v	319.5		349.4		
								4.5	5.0	
								6.0	7.0	
<i>n</i> -Octane	PVT	24	223.15–598.15	0.1–100.0	1, v	568.15	568.77	166.6	193.5	
						569.15	569.35	225.0	233.3	
						573.15	598.15	256.6	295.8	
								330.4		
	$C_p$	23	293.15–632.24	0.1–60.0	1, v					
								2.70	3.00	
								3.50	4.00	
								4.50		
<i>n</i> -Nonane	PVT	25	253.0–623.15	0.1–100.0	1, v	592.15	593.55			
						594.57	596.00			
						596.15	623.15			
	$C_p$	23	293.15–623.77	0.1–60.0	1, v					
								2.5	3.0	

*a* l, liquid region; v, vapor region.

## 2. EXPERIMENTAL DATA BASE

To analyze the application of the existing nonanalytic descriptions of the thermodynamic properties in the critical region, experimental  $P$ ,  $\rho$ ,  $T$ ,  $C_v$ ,  $C_p$ , and  $C_s$  data were used. Table I reviews the information. References 7–13 give the techniques of measuring the density  $\rho$ , the heat capacity at constant volume  $C_v$ , the heat capacity at constant pressure  $C_p$ , and the sound velocity  $C_s$  of methane, ethane, propane, and  $n$ -butane and also the accuracy of the measurements.

The measurements of the density and the isobaric heat capacity of  $n$ -pentane,  $n$ -hexane,  $n$ -heptane,  $n$ -octane, and  $n$ -nonane have been obtained in the Thermophysical Laboratory of the Grozny Petroleum Institute at temperatures from the triple point to the dissociation temperatures and at pressures from 0.1 to 150 MPa for  $\rho$  and to 60 MPa for  $C_p$  [19–23]. The investigations covered the liquid and gaseous regions, the two-phase region, and the critical region.

The density was obtained with a constant-volume piezometer with an error of 0.05–0.07% at  $\rho > 2\rho_c$ , 0.07–0.1% at  $2\rho_c > \rho > 0.8\rho_c$ , and 0.1–0.2% at  $\rho < 0.8\rho_c$ . The error of the pressure measurements is 0.05%; that of the temperature measurements is 0.02 K. The heat capacity at constant pressure was measured with an adiabatic flow calorimeter with an error of  $\pm 0.35\%$  in the liquid state (far from the critical region) and with an error from 5 to 15% in the critical region; the temperatures differences varied from 0.3 to 0.6 mK and the absolute temperatures were measured with an error of 0.02 K. Pressures were measured with an error in the range from 0.06 to 0.1%. References 19–23 contain detailed descriptions of experimental apparatus and measurement techniques.

## 3. THE EQUATION OF STATE

A tentative analysis of the experimental data on the thermodynamic properties of the homological series of  $n$ -alkanes showed that it is not yet expedient to use a crossover scaled equation of state [1, 2], which is rather complicated, but a simpler asymptotic scaled parametric equation of state [4, 5]. These equations incorporate the leading nonasymptotic and asymmetric corrections and, in addition, contain fewer nonuniversal parameters. At the same time, the region of validity remains sufficiently large:  $0.65 \leq \rho/\rho_c \leq 1.4$  and  $T_\sigma \leq T \leq 1.1T_c$  for the equation used by Levelt Sengers et al. [4] and  $0.65 \leq \rho/\rho_c \leq 1.4$  and  $T_\sigma \leq T \leq 1.2T_c$  for the equation used by Kiselev [5], where  $T_\sigma$  is the liquid–vapor coexistence temperature. After a tentative analysis, we have selected the equation of Kiselev [5].

It is a parametric equation of the form

$$\Delta\mu(r, \theta) = ar^{\beta\delta}\theta(1 - \theta^2) + cr^{\beta\delta + A}\theta + r^{2\gamma + 2\beta - 1}[d(1 + e_1 b^4 \theta^4) + fb^2 \theta^2(1 + e_2 b^2 \theta^2)] \quad (1)$$

with

$$\tau = r(1 - b^2 \cdot \theta^2) \quad (2)$$

and

$$\Delta\rho = kr^\beta\theta - B_3\tau \quad (3)$$

Here  $\Delta\mu = [\mu(\rho, T) - M_0(T)] \rho_c / P_c$  is a reduced chemical potential difference;  $\tau = T/T_c - 1$  and  $\Delta\rho = \rho/\rho_c - 1$  are reduced deviations of temperature and density from their critical values;  $T_c$ ,  $P_c$ , and  $\rho_c$  are the critical temperature, pressure, and density;  $r$  and  $\theta$  are parametric variables specifying the thermodynamic state; and  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $A$ , and  $\gamma$  are universal critical exponents. The values adopted for the critical exponents are  $\alpha = 0.11$ ,  $\beta = 0.325$ , and  $A = 0.5$  in agreement with the literature [4–6];  $\delta = 4.815$  and  $\gamma = 1.24$  were calculated from formulas:

$$\alpha + 2\beta + \gamma = 2 \quad (4)$$

$$\beta(\delta - 1) = \gamma \quad (5)$$

The constants  $b^2$ ,  $e$ ,  $e_1$ , and  $e_2$  are given by [5]

$$b^2 = (\gamma - 2\beta)/\gamma(1 - 2\beta) \quad (6)$$

$$e = 2\gamma + 3\beta - 1 \quad (7)$$

$$e_1 = (5 - 2e)(e - \beta)(3 - 2e)/3(5\beta - e) \quad (8)$$

$$e_2 = (5 - 2e)(e - 3\beta)/3(5\beta - e) \quad (9)$$

$B_3$ ,  $k$ ,  $a$ ,  $c$ ,  $d$ , and  $f$  are nonuniversal constants to be determined from a fit to the experimental data.

In accordance with Eqs. (1)–(3) the specific free energy, i.e., the free energy per unit mass, becomes

$$F = \frac{P_c}{\rho_c} [\Psi(r, \theta) + \Phi_0(\tau) + (\Delta\rho + 1) M_0(\tau)] \quad (10)$$

where the regular background parts  $\Phi_0(\tau)$  and  $M_0(\tau)$  are approximated by polynomials

$$\Phi_0(\tau) = -1 + \sum_{i=1}^4 f_i \tau^i \quad (11)$$

$$M_0(\tau) = \sum_{i=0}^3 m_i \tau^i \quad (12)$$

The singular part of the specific free energy consists of three parts:

$$\Psi(r, \theta) = \Psi_{\text{lm}}(r, \theta) + \Psi_{\text{na}}(r, \theta) + \Psi_{\text{as}}(r, \theta) \quad (13)$$

where  $\Psi_{\text{lm}}$ ,  $\Psi_{\text{na}}$ , and  $\Psi_{\text{as}}$  represent asymptotic, nonasymptotic, and asymmetric terms:

$$\Psi_{\text{lm}} = \frac{1}{2} \frac{akr^{2-\alpha}}{b^4} \left[ \frac{2\beta(h^2-1)}{2-\alpha} + \frac{2\beta(2\gamma-1)(1-b^2\theta^2)}{\gamma(1-\alpha)} + \frac{(2\beta-1)(1-b^2\theta^2)^2}{\alpha} \right] \quad (14)$$

$$\Psi_{\text{na}} = \frac{1}{2} \frac{ckr^{2-\alpha+\Delta}}{b^2(1-\alpha+\Delta)} \left[ \frac{\gamma+\Delta}{2-\alpha+\Delta} - (1-2\beta)b^2\theta^2 \right] \quad (15)$$

$$\Psi_{\text{as}} = kr^{2\gamma+3\beta-1}\theta \left\{ d + \frac{1}{3} [f - 2d(e-\beta)] b^2\theta^2 + \frac{1-2\beta}{5-2e} [de_1 + fe_2] b^4\theta^4 \right\} \quad (16)$$

The resulting expressions for the pressure, the isochoric and isobaric specific heat capacity, and the sound velocity are

$$P = -\rho^2 \left( \frac{\partial F}{\partial \rho} \right)_T = p_c [(\Delta\rho + 1) \Delta\mu(r, \theta) - \Psi(r, \theta) - \Phi_0(\tau)] \quad (17)$$

$$c_v = -\frac{p_c T}{T_c^2 \rho} \left[ \left( \frac{\partial^2 \Psi}{\partial \tau^2} \right)_{\Delta\rho} + 2B_3 \left( \frac{\partial \Delta\mu}{\partial \tau} \right)_{\Delta\rho} + B_3^2 \left( \frac{\partial \Delta\mu}{\partial \Delta\rho} \right)_\tau + \frac{\rho}{\rho_c} \left( \frac{d^2 Mo}{dt^2} \right) - \left( \frac{d^2 \Phi_0}{dt^2} \right) \right] \quad (18)$$

$$c_p = c_v + \frac{T}{\rho} k_T \left( \frac{\partial p}{\partial T} \right)_\rho^2 \quad (19)$$

$$c_s = \sqrt{\left( \frac{\partial p}{\partial \rho} \right)_s} = \sqrt{(\rho K_T)^{-1} + \frac{T}{2} \left( \frac{\partial p}{\partial T} \right)_\rho^2} \quad (20)$$

Here  $K_T$  is the isothermal compressibility determined by

$$K_T = \frac{\rho_c}{P_c \rho^2} \left( \frac{\partial \Delta\mu}{\partial \Delta\rho} \right)_T^{-1} \quad (21)$$

#### 4. CONSTRUCTION OF A GENERALIZED EQUATION OF STATE

An essential point is the selection of the critical parameters. Table II presents the values adopted for the critical temperature  $T_c$ , the critical pressure  $P_c$ , and the critical density  $\rho_c$ . The table also gives values of the acentric factor  $\omega$ , used to correlate the nonuniversal coefficients of the *n*-alkanes.

The construction of a generalized scaled equation of state for the *n*-alkanes has been done as follows. First, the nonuniversal system-dependent coefficients  $B_3$ ,  $k$ ,  $a$ ,  $c$ ,  $d$ ,  $f$ ,  $f_1$ ,  $f_2$ ,  $f_3$ , and  $f_4$  were determined for each hydrocarbon with the use of Eq. (17) to approximate experimental  $P$ ,  $\rho$ ,  $T$  data. Then a correlation analysis was performed to find the dependence of these coefficients on the individual properties of the hydrocarbons such as acentric factor, molecular mass, etc. A reasonable correlation was determined to be observed only for the coefficients  $k$ ,  $a$ ,  $f_1$ , and  $f_2$ . For the remaining coefficients no systematic correlation was observed. The reason lies probably in the fact, in practice, data in different temperature intervals were used for different hydrocarbons. For instance, the  $P$ ,  $\rho$ ,  $T$  data, used for methane, *n*-octane, and *n*-nonane, correspond to a narrow temperature interval from  $T_\sigma$  to  $1.06T_c$ . In this case, the coefficients  $B_3$ ,  $d$ ,  $f$ ,  $f_3$ , and  $f_4$  become statistically insignificant and it is expedient to take these coefficients to be zero. As a consequence, the equation of state then becomes simpler, although the region of validity becomes slightly smaller, in density to  $0.7 \leq \rho/\rho_c \leq 1.3$  and in temperature to  $T_\sigma \leq T \leq 1.2T_c$ . With this simplified equation of state the coefficients  $k$ ,  $a$ ,  $c$ ,  $f_1$ , and  $f_2$  were determined once again for each hydrocarbon. Figures 1, 2, and 3 show the coefficients  $k$ ,  $a$ , and  $f_1$  as a function of the acentric factor  $\omega$  of the *n*-alkanes.

Table II. Critical Parameters and Acentricity Factors for *n*-Alkanes

Substance	$T_c$ (K)	$P_c$ (MPa)	$\rho_c$ ( $\text{kg} \cdot \text{m}^{-3}$ )	Reference	Acentric factor, $\omega$
Methane	190.55	4.5992	162.66	8	0.008
Ethane	305.33	4.8714	204.48	26	0.098
Propane	369.85	4.2460	218.50	27	0.152
<i>n</i> -Butane	425.16	3.7960	227.85	28	0.193
<i>n</i> -Pentane	469.55	3.3530	232.00	19	0.251
<i>n</i> -Hexane	507.20	3.0282	233.60	21	0.296
<i>n</i> -Heptane	540.10	2.7320	234.00	19	0.351
<i>n</i> -Octane	568.77	2.4850	234.00	24	0.394
<i>n</i> -Nonane	594.40	2.2954	234.00	25	0.444

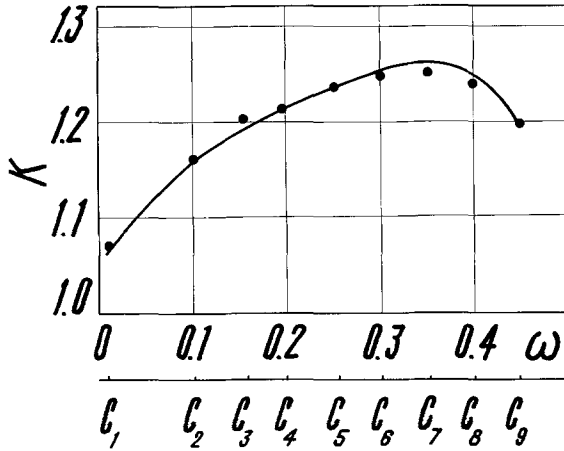


Fig. 1. The coefficient  $k$  as a function of the acentric factor  $\omega$  for  $n$ -alkanes.  $C_1$ , methane;  $C_2$ , ethane;  $C_3$ , propane, etc.

Initially, an attempt was made to construct a generalized equation of state with the help of polynomials for all coefficients  $k$ ,  $a$ ,  $f_1$ ,  $c$ , and  $f_2$  as a function of  $\omega$ . However, the resulting generalized equation of state has too small a range of applicability. Therefore, another approach was adopted. The coefficients  $k$ ,  $a$ ,  $c$ ,  $f_1$ , and  $f_2$  were investigated according to

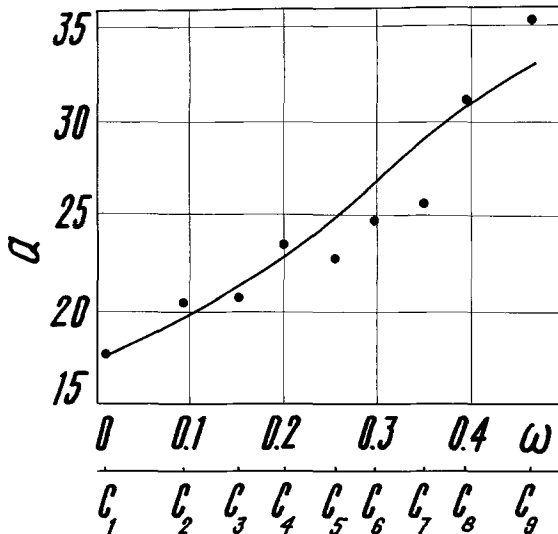


Fig. 2. The coefficient  $a$  as a function of the acentric factor  $\omega$  for  $n$ -alkanes.  $C_i$  ( $i=1-9$ ) as in the legend to Fig. 1.



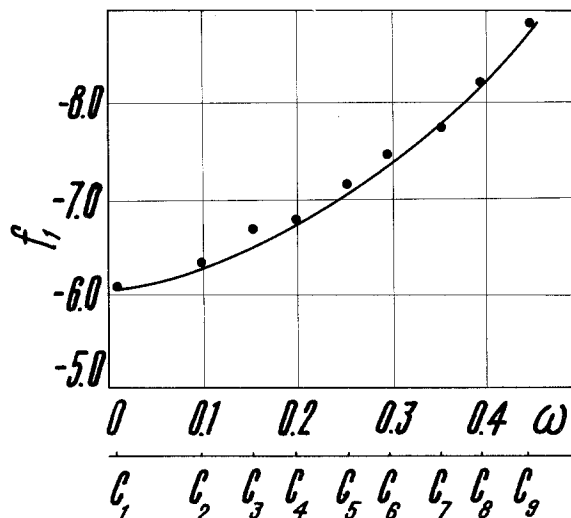


Fig. 3. The coefficient  $f_1$  as a function of the acentric factor  $\omega$  for *n*-alkanes.  $C_i$  ( $i=1-9$ ) as in the legend to Fig. 1.

their significance. As Figs. 1–3 show, the values of the coefficient  $f_1$  are the most correlated. This coefficient was approximated by

$$f_1 = -6.0081 - 2.7291\omega - 7.3922\omega^2 \quad (22)$$

Then the values of  $f_1$  calculated from Eq. (22) were substituted into Eq. (17) and fixed. After that, the values  $k$ ,  $a$ ,  $c$ , and  $f_2$  were again calculated by fitting to the experimental  $P$ ,  $\rho$ ,  $T$  data for each hydrocarbon. Then new coefficients  $a$  were represented by a polynomial

$$a = 17.285 + 15.811\omega + 81.4882\omega^2 - 85.9680\omega^3 \quad (23)$$

Calculated values  $a = a(\omega)$  were then introduced into Eq. (17), fixed, and the other coefficients,  $k$ ,  $c$ , and  $f_2$ , were determined once again from the experimental  $P$ ,  $\rho$ ,  $T$  data. After that the same procedure was repeated in succession for the coefficients  $k$ ,  $c$ , and  $f_2$ :

$$k = 1.0532 + 1.8705\omega - 10.7976\omega^2 + 35.6773\omega^3 - 43.1991\omega^4 \quad (24)$$

$$c = -7.621 - 14.4329\omega + 126.7435\omega^2 - 485.1483\omega^3 \quad (25)$$

$$f_2 = 19.2387 - 96.7404\omega + 790.6185\omega^2 - 2075.92\omega^3 + 2218.417\omega^4 \quad (26)$$

To determine the caloric coefficients  $m_2$  and  $m_3$  of the scaled equation of state, it is necessary to represent heat capacity data or sound velocity

data with the aid of Eq. (18), (19), or (20). In the process of determining the coefficients  $m_2$  and  $m_3$ , the values of the coefficients  $k$ ,  $a$ ,  $c$ ,  $f_1$ , and  $f_2$  remained unchanged, being equal to their calculated values from Eqs. (22)–(26). It is also necessary to note that to gain the best results in representing the experimental  $c_p$  data, the experimental isobars were corrected for some substances by a “shift” of the pressure values within the range of total error of the  $P$ ,  $\rho$ ,  $T$  and  $C_p$  measurements. The value of “shift” was  $-0.007$  MPa for  $n$ -pentane,  $0.004$  MPa for  $n$ -hexane,  $0.005$  MPa for  $n$ -heptane, and  $0.009$  MPa for  $n$ -nonane. The values  $m_2$  and  $m_3$  were represented by polynomials:

$$m_2 = -13.927 + 214.781\omega - 1661.369\omega^2 - 3832.47\omega^3 + 28583.96\omega^4 - 34802.45\omega^5 \quad (27)$$

$$m_3 = 18.697 - 1878.966\omega + 30047.21\omega^2 - 160402.8\omega^3 + 371983\omega^4 - 330023\omega^5 \quad (28)$$

That concluded the construction of the generalized equation of state.

**Table III.** Comparison Between Experimental and Calculated Data for  $n$ -Alkanes

Substance	Property	Reference	Number of experimental points	Range of parameters		SD, $\sigma(\%)$
				Density, $\rho/\rho_c$	Temperature	
Methane	PVT	7, 8	144	0.7–1.4	$T_c-1.06T_c$	0.008
	$C_s$	9, 10	51	0.7–1.3	$T_c-1.17T_c$	6.00
Ethane	PVT	11	6	0.8–1.21	$T_c-1.14T_c$	0.100
	PVT	12	23	0.7–1.3	$T_c-1.22T_c$	0.195
	$C_v$	13	13	0.8–1.16	$(1.0-1.08)T_c$	11.24
	$C_p$	14	14	0.7–1.3	$(1.0-1.06)T_c$	1.92
	$C_s$	15	10	0.8–1.3	$(1.0-1.08)T_c$	7.46
Propane	PVT	16	20	0.78–1.2	$(1.0-1.12)T_c$	0.222
	$C_v$	17	24	0.78–1.05	$(1.0-1.10)T_c$	8.34
$n$ -Butane	PVT	18	38	0.7–1.2	$(1.0-1.20)T_c$	0.263
$n$ -Pentane	PVT	19	89	0.7–1.3	$T_c-1.2T_c$	0.237
	$C_p$	20	109	0.7–1.3	$(1.0-1.11)T_c$	8.71
$n$ -Hexane	PVT	21	172	0.7–1.3	$T_c-1.2T_c$	0.201
	$C_p$	22	163	0.7–1.3	$(1.0-1.20)T_c$	6.51
$n$ -Heptane	PVT	19	38	0.75–1.25	$T_c-1.06T_c$	0.257
	$C_p$	23	53	0.7–1.3	$(1.0-1.16)T_c$	6.12
$n$ -Octane	PVT	24	95	0.7–1.3	$T_c-1.06T_c$	0.222
	$C_p$	25	20	0.7–1.3	$(1.0-1.06)T_c$	4.26
$n$ -Nonane	PVT	25	33	0.7–1.3	$T_c-1.005T_c$	0.314
	$C_p$	23	20	0.7–1.3	$(1.0-1.05)T_c$	6.45

## 5. DISCUSSION

Table III presents the results of the calculation of all thermodynamic data used from the generalized scaled equation of state, with the coefficients  $k$ ,  $a$ ,  $c$ ,  $f_1$ ,  $f_2$ ,  $m_2$ , and  $m_3$  represented by the polynomials (22) to (28). As Table III shows, the standard deviation  $\sigma$  of the experimental  $P$ ,  $\rho$ ,  $T$  data is in the range from 0.008 to 0.26%. The deviation of the caloric properties is in the range from 6 to 8% with the exception of  $\sigma = 11.24\%$  for the  $c_v$  of ethane. Noting that the deviations of the sound velocity for ethane are 7.5% and the deviations for the heat capacity are 1.9%, we conclude that there is some inconsistency between the  $c_v$  data [13] and the  $C_s$  and  $c_p$  data [14, 15].

As a result of the analysis we arrive at the following conclusions.

(i) A scaled equation of state describes the thermodynamic surface of homological series of *n*-alkanes from  $\text{CH}_4$  to  $\text{C}_9\text{H}_{20}$  with errors approaching the experimental error. Testing a generalized scaled equation of state for higher *n*-alkanes is problematic, since even for *n*-decane the experimental investigations in the critical and supercritical regions are affected by thermal dissociations.

(ii) The range of validity of the generalized equation of state for *n*-alkanes is  $0.7 < \rho/\rho_c < 1.3$  in density and  $T_c$  to  $1.2T_c$  in temperature. Figure shows this range of validity in terms of reduced variables  $T/T_c$  and  $\rho/\rho_c$ .

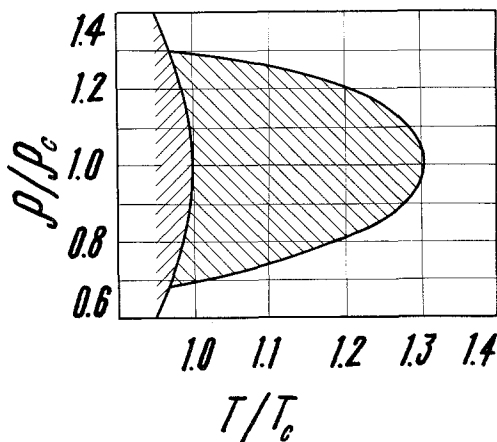


Fig. 4. The range of validity of the generalized scaled equation of state for *n*-alkanes in the terms of reduced variables  $T/T_c$  and  $\rho/\rho_c$ .



According to the modern theory of critical phenomena the behavior of substances with different molecular structures in the critical region should be universal. The analysis carried out confirms this theory for a group of fluids with regular structure. It is interesting to use the obtained generalized equation for the description of thermodynamic properties of other classes of hydrocarbons. This analysis is difficult to do due to the absence of experimental data for the separate homological series. Besides *n*-alkanes, the thermodynamic properties of aromatic hydrocarbons have been investigated in detail [30, 31]. We have tested the application of the obtained generalized equation for the description of the thermodynamic properties of benzene, toluene, metha-, ortho-, and para-xylenes, and ethylbenzene in the critical region using the same equations [(22) to (28)] for the system-dependent coefficients as a function of  $\omega$ . Table IV presents the basic information for these hydrocarbons and the results of comparison of the calculated values with experimental values. Table IV shows that the error of description of  $P$ ,  $\rho$ ,  $T$  data is about 0.2% as for the *n*-alkanes, while the error in the heat capacity  $c_v$  is even lower. The exception is ortho-xylene, for which  $\sigma = 13\%$ . The obtained representation of the properties of aromatic hydrocarbons is rather satisfactory.

We can say in conclusion that the analysis carried out in this work confirmed the validity of a universal generalized scaled equation of state and showed the fundamental possibility to construct a generalized equation of state which is valid for various homological series of hydrocarbons.

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