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CROSSOVER EQUATION OF STATE OF NORMAL HEXANE IN THE CRITICAL REGION

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The coefficients of the basic crossover equation of state of n-hexane are determined in the critical region from experimental P, ρ, T and C_p, P, T data. In the reduced density and temperature ranges $0.35 \leq \rho/\rho_c \leq 1.65$ and $0.982 \leq T/T_c \leq 1.23$ the root mean square errors of the calculated pressure, isobaric heat capacity, and isochoric heat capacity were 0.115%, 4.87%, and 3.04%, respectively.

Experimental studies of thermodynamic characteristics of n-hexane in a wide vicinity of the critical point were reported in [1-6], where the P, ρ, T-curve [1, 2] and the isochoric C_v [3] and isobaric C_p [4-6] heat capacities were investigated. Equations of state (ES) for calculating thermodynamic characteristics in the critical region were also derived. The equation of state obtained using the "pseudospinodal" hypothesis was presented in [7]. Its coefficients were determined from C_c, ρ, T and P, ρ, T data. The root mean square error was $\sigma P = 0.15\%$ for the pressure, $\sigma C_v = 1.5\%$ for the isochoric heat capacity, and $\sigma C_p = 7.8\%$ for the isobaric heat capacity. In this case the isobars closest to the critical point were not analyzed. It should be noted that the isochoric heat capacity of n-hexane was not studied in the immediate vicinity of the critical point in the single-phase region. Therefore there is no reliable description of the caloric properties in the critical region using this equation of state. In [8] a scale ES was obtained in the form of a linear model taking into account nonasymptotic expansion terms and the asymmetry of a real liquid [9]. The coefficients in the thermial part of the ES were determined from P, ρ, T data [1, 2] and the coefficients in the caloric part were found from C_p, P, T data obtained by the present authors. The range of state parameters and the calculation errors for thermal and caloric properties are given in Table 1. It can be seen from the table that the errors in the description of heat capacities C_v and C_p are far from experimental errors [3-6], and the ES is applicable in a rather narrow density range. Thus, the problem of reliable description of the thermal and caloric properties of normal hexane in a wide vicinity of the critical point remains to be solved.

The range of validity of the ES in the critical region may be expanded out correctly, using the notion of a crossover function [10, 12]. Omitting the details of the theoretical aspects of the problem, we emphasize that at present the best practical results are obtained by Kisilev [11, 12] and Sengers et al. [13, 14]. Comparison of their equations leads to the conclusion that the crossover ES developed in [14] applies to a much wider density range than Kiselev's does [11]. Furthermore, in our opinion, the ES of [14] has a more profound theoretical basis. Therefore we developed the ES for n-hexane, using results obtained in [13, 14].

The equation of state was obtained by introducing a crossover function into the sexanomial Landau expansion for the Helmholtz free energy per unit volume. The asymmetry of a real liquid was included by going from the model variables (order parameter M and field t) to the physical variables (dimensionless density $\Delta\rho^*$ and dimensionless temperature ΔT^*). The transition rules are determined by the system of equations

$$M = c_\rho(\Delta\rho^* - B_3\Delta T^*) + c\left(\frac{\partial \Delta As^*}{\partial t}\right)_M, \tag{1}$$

$$t = c_t\Delta T^* + c\left(\frac{\partial \Delta As^*}{\partial M}\right)_t, \tag{2}$$

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TABLE 1. Comparison of the Equations of State for n-Hexane in the Critical Region

Parameters compared	Equation from [8]	Equations (1)-(5)
Temperature range of validity:		
ΔT, K, at $\rho = \rho_c$	503.15 ... 623.15	498.15 ... 623.15
$\Delta(T/T_c)$, at $\rho = \rho_c$	0.992 ... 1.23	0.982 ... 1.23
Density range of validity:		
$\Delta\rho$, kg/m^3, at $T = T_c$	149 ... 325	82 ... 385
$\Delta(\rho/\rho_c)$ at $T = T_c$	0.64 ... 1.39	0.35 ... 1.65
rms error, %		
pressure	0.114	0.115
C_p	9.20	4.87
C_v	10.40	3.04

TABLE 2. Parameters of the Crossover Equation of State for n-Hexane

Parameter	Notation	Numerical value
Critical parameters	T_c	507.20 K
	P_c	3.025 MPa
	ρ_c	233.5 kg/m^3
Crossover function parameters	u	0.448
	Λ	1.301
Parameters taking into account the assymmetry of a real liquid	c	-0.0150
	c_t	2.189
	c_ρ	2.360
	B_3	-0.320
Landau expansion coefficients	a_{05}	-0.412673
	a_{06}	1.476329
	a_{14}	0.446138
	a_{22}	0.359876
Regular thermal function coefficients $A_0(\Delta T^*)$	A_0	-1
	A_1	-6.524805
	A_2	2.324301
	A_3	16.758295
	A_4	-50.842695
Regular caloric function coefficients $\mu_0(\Delta T^*)$	m_0	-104.093
	m_1	-84.527
	m_2	-55.0411
	m_3	-46.1598
	m_4	-29.8779

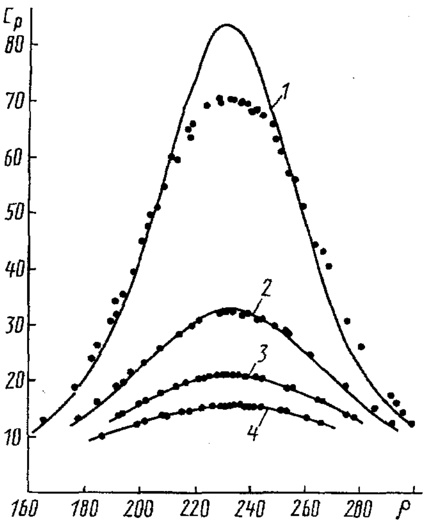
$$\Delta A^* = \Delta A_s^* - c\left(\frac{\partial \Delta A_s^*}{\partial M}\right)_t \left(\frac{\partial \Delta A_s^*}{\partial t}\right)_M, \tag{3}$$

where ΔA^*s is the singular part of the Helmholtz thermodynamic potential, corresponding to the Landau-Ginzburg-Wilson model Hamiltonian [13]; ΔA^* is the singular part of the Helmholtz specific free energy of a real liquid. The specific free energy A^* is defined by the relation

$$A^* = \rho^*\mu_0(\Delta T^*) + A_0(\Delta T^*) + \Delta A^*, \tag{4}$$

where $\mu_0(\Delta T^*)$, $A_0(\Delta T^*)$ are regular temperature functions.

The expression for the dimensionless pressure has the form



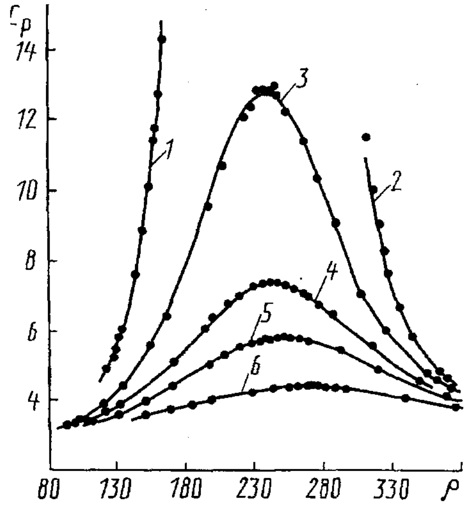


Fig. 1. Isobaric heat capacity of n-hexane in the critical region: 1) P = 3.103 MPa; 2) 3.202; 3) 3.302; 4) 3.402 MPa; points) experimental data [6]; curves) calculation using the crossover ES. C_p, kJ/(kg·K); ρ, kg/m^3.

Fig. 2. Isobaric heat capacity of n-hexane in the critical region: 1) P = 3.004 MPa, gas phase; 2) 3.003, liquid phase; 3) 3.503; 4) 4.003; 5) 4.503; 6) P=5.002 MPa; points) experimental data [4, 5]; curves) calculation using the crossover ES.

$$P^* = [c_p(1 + B_3\Delta T^*) + M]\left(\frac{\partial \Delta \overset{*}{A_s}}{\partial M}\right)_t - A_0(\Delta T^*). \qquad (5)$$

Details of the mathematics and the notation are given in the Appendix.

In developing a basic ES describing both the thermal and caloric properties, the problem of thermodynamic correlation of dissimilar experimental data arises. As was indicated in [6, 8], there are systematic discrepancies between P, ρ, T data [1, 2] and C_p, P, T data [4-6], which should be taken into account although they are within the limits of the systematic errors of temperature and pressure measurements in these studies. Our analysis has shown that for correlation of the data, it is necessary to decrease the pressure in the isochors by 0.005 MPa. It is characteristic here that P, ρ, T data [2] obtained from experimental isotherms need no correction.

The coefficients in the thermal part of the ES were determined from experimental P, ρ, T data [1, 2] and the coefficients m_2, m_3, m_4 in the caloric part of the ES from the authors' experimental C_p, P, T data [4-6]. The coefficients m_0 and m_1 were calculated using tabulated enthalpies and entropies in the critical region [15]. The numerical values of the critical indices were assumed equal to their theoretical estimates obtained by the renorm-group method and are given in Appendix.

The coefficients of the crossover ES for n-hexane are given in Table 2, and the precision parameters and the approximation range for temperature and density are given in Table 1. It can be seen from Table 1 that the root mean square errors of the calculated pressures using the equation from [8] and the crossover equation (5) are equal with a wider approximation range for density for equation (5). In the density range $0.64 \le \rho/\rho_c \le 1.39$ we have $\sigma P = 0.083\%$. The results for heat capacities C_p and C_v calculated from the relations $C_p = (H_2 - H_1)/(T_2 - T_1)$, $C_v = (u_2 - u_1)/(T_2 - T_1)$ are shown in Figs. 1 to 3. It is seen from Table 1 and Figs. 1-3 that the error in the calculation of C_p is half the value obtained in [8] and the isochoric heat capacity is calculated with an error one-third that in [8]. The calculation errors are close to the estimated measurement errors for C_p and C_v in [3, 4-6], excluding the isobar P = 3.103 MPa, closest to the critical point. With this isobar neglected, the root mean square error of the calculated C_p is 2.10%.

The sharp increase in the of deviations of the isobar P = 3.103 MPa nearest to the critical point may be explained by the increasing effect of various kinds of perturbations: temperature and pressure gradients, impurities. Without completely neglecting these factors, it seems important to pay attention to one more fact revealed when

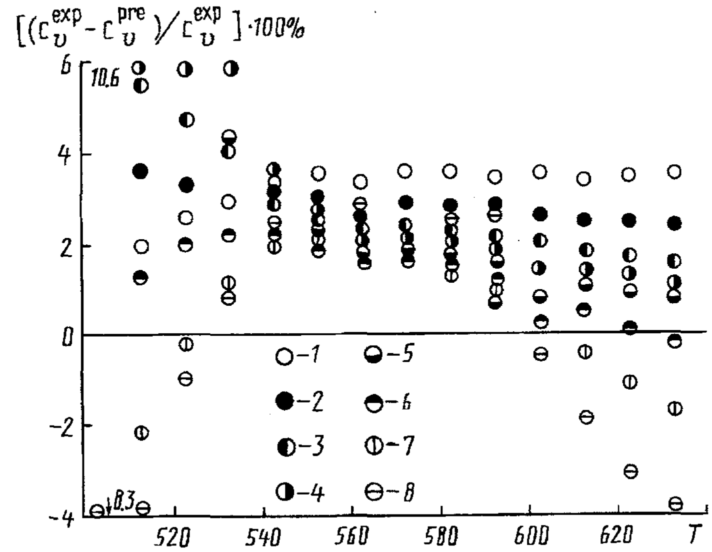


Fig. 3. Deviation of the experimental C_v [3] from those predicted by the crossover ES: 1) $\rho = 332.9\ \mathrm{kg/m^3}$; 2) 285.7; 3) 250.0; 4) 234.1; 5) 222.2; 6) 186.9; 7) 142.9; 8) $\rho = 100.0\ \mathrm{kg/m^3}$. T, K.

investigating C_p of the n-hexane series from n-C_5 to n-C_9. These studies have shown that the "anomaly distortion" range is substantially narrower for pentane than for hexane and especially heptane although the purity of the samples and the temperature and pressure gradients were practically identical in the experiments. This may possibly be explained by the fact that all n-alkanes starting from ethane are not truly pure substances but an equilibrium mixture of conformers and the longer the hydrocarbon chain, the larger the number of conformers that exist with these parameters. However, any attempts to obtain quantitative estimates of the effect of conformers on the thermodynamic properties in the critical region failed.

Analyzing the coefficients in the basic ES presented in Table 2, we must emphasize one result that seems important. In [8, 16-18] the coefficients in the asymmetric scale ES for the series of n-alkanes from n-C_5 to n-C_9 were obtained. For all the alkanes the coefficient B_3 taking into account the slope of the rectilinear diameter of the coexistence curve was found to be zero. The coefficient B_3 in equation (1) has the same meaning. The present calculations carried out with the same experimental P, ρ, T data [1, 2] indicate a clearly nonzero negative value for this coefficient, which largely agrees with results of the study of the n-hexane coexistence curve [19].

The basic ES for n-hexane presented in this article allows all the thermodynamic properties to be calculated in a wide vicinity of the critical point. The reliability of the calculations is confirmed not only by comparison with experimental data but also by the fact that we have developed a generalized crossover ES for hydrocarbons on the basis of this ES.

APPENDIX

1. The notation for dimensionless thermodynamic quantities:

$$\begin{gathered}
T^* = -\frac{T_c}{T}, \quad \Delta T^* = 1 - \frac{T_c}{T}, \quad \rho^* = \frac{\rho}{\rho_c}, \quad \Delta\rho^* = \frac{\rho}{\rho_c} - 1, \\
\mu^* = \frac{\mu\rho_c T_c}{TP_c}, \quad \Delta\mu^* = \mu^* - \mu_0(\Delta T^*), \quad P^* = \frac{PT_c}{PT_c}, \\
A^* = \frac{\rho A T_c}{TP_c}, \quad U^* = \frac{\rho U}{P_c}, \quad S^* = \frac{\rho S T_c}{P_c}, \quad H^* = \frac{\rho H T_c}{TP_c}, \\
\chi^* = \left(\frac{\partial\rho^*}{\partial\mu^*}\right)_T, \quad C_v^* = \frac{\rho C_v T_c}{P_c}, \quad C_p^* = \frac{\rho C_p T_c}{P_c}, \quad W^* = W\left(\frac{\rho_c T_c}{P_c T}\right)^{1/2},
\end{gathered} \tag{A.1}$$

where T is the temperature; ρ is the density; μ is the chemical potential; P is the pressure; A is the Helmholtz free energy; U is the internal energy; H is the enthalpy; C_v is the isochoric heat capacity; C_p is the isobaric heat capacity; W is the velocity of sound.

2. The basic equation of state:

$$A^* = \rho^* \mu_0 (\Delta T^*) + A_0 (\Delta T^*) + \Delta A^*, \tag{A.2}$$

where

$$A_0 (\Delta T^*) = -1 + \sum_{j=1}^{4} A_j (\Delta T^*)^j, \tag{A.3}$$

$$\mu_0 (\Delta T^*) = \sum_{j=0}^{4} m_j (\Delta T^*)^j. \tag{A.4}$$

3. The thermodynamic derivatives:

$$\Delta\mu^* = \left(\frac{\partial \Delta A^*}{\partial \Delta \rho^*} \right)_{\Delta T^*}, \tag{A.5}$$

$$(\chi^*)^{-1} = \left(\frac{\partial^2 \Delta A^*}{\partial (\Delta \rho^*)^2} \right)_{\Delta T^*}, \tag{A.6}$$

$$U^* = -\frac{dA_0 (\Delta T^*)}{d\Delta T^*} - \rho^* \frac{d\mu_0 (\Delta T^*)}{\partial \Delta T^*} - \left(\frac{\partial \Delta A^*}{\partial \Delta T^*} \right)_{\Delta \rho^*}, \tag{A.7}$$

$$W^* = \left(\frac{\rho^* C_p^*}{\chi^* C_v^*} \right)^{1/2}. \tag{A.8}$$

4. The basic crossover equation of state:

$$M = c_\rho (\Delta \rho^* - B_3 \Delta T^*) + c \left(\frac{\partial \Delta A\overset{*}{s}}{\partial t} \right)_M, \tag{A.9}$$

$$t = c_t \Delta T^* + c \left(\frac{\partial \Delta A\overset{*}{s}}{\partial M} \right)_t, \tag{A.10}$$

$$\Delta A^* = \Delta A\overset{*}{s} - c \left(\frac{\partial \Delta A\overset{*}{s}}{\partial M} \right)_t \left(\frac{\partial \Delta A\overset{*}{s}}{\partial t} \right)_M, \tag{A.11}$$

$$\begin{aligned} \Delta As = {} & \frac{1}{2} t M^2 T_k D_k + \frac{1}{4!} u \Lambda M^4 D_k^2 U_k + \frac{1}{5!} a_{05} M^5 D_k^{5/2} V_k U_k + \\ & + \frac{1}{6!} a_{06} M^6 D_k^3 U_k^{3/2} + \frac{1}{4!} a_{14} t M^4 T_k D_k^2 U_k^{1/2} + \\ & + \frac{1}{2!2!} a_{22} t^2 M^2 T_k^2 D_k U_k^{-1/2} - \frac{1}{2} t^2 K_k, \end{aligned} \tag{A.12}$$

$$T_k = Y^{(2-1/\nu)/\omega}, \tag{A.13}$$

$$D_k = Y^{-\eta/\omega}, \tag{A.14}$$

$$V_k = Y^{(2\omega_a - 1)/2\omega}, \tag{A.15}$$

$$U_k = Y^{1/\omega}, \tag{A.16}$$

$$K_k = \frac{\nu}{\alpha u \Lambda} (Y^{-\alpha/\nu\omega} - 1). \tag{A.17}$$

The crossover function Y is determined from the relation

$$(1-\bar{u})Y=\bar{u}[1+(\Lambda/k)^2]^{1/2}Y^{1/\omega}, \tag{A.18}$$

where

$$k^2=tT_k+\frac{1}{2}u\Lambda U_kM^2D_k, \tag{A.19}$$

$$\bar{u}=u/u^*. \tag{A.20}$$

5. The first thermodynamic derivatives:

$$\left(\frac{\partial\Delta A^*}{\partial\Delta\rho^*}\right)_{\Delta T^*}=c_\rho\left(\frac{\partial\Delta\overset{*}{A}s}{\partial M}\right)_t, \tag{A.21}$$

$$\left(\frac{\partial\Delta A^*}{\partial\Delta T^*}\right)_{\Delta\rho^*}=c_t\left(\frac{\partial\Delta\overset{*}{A}s}{\partial t}\right)_M-c_\rho B_3\left(\frac{\partial\Delta\overset{*}{A}s}{\partial M}\right)_t. \tag{A.22}$$

6. The derivatives of the crossover function:

$$\left(\frac{\partial k^2}{\partial t}\right)_M=F_1(t,\ M)T_k, \tag{A.23}$$

$$\left(\frac{\partial k^2}{\partial M}\right)_t=F_1(t,\ M)u\Lambda MU_kD_k, \tag{A.24}$$

$$\left(\frac{\partial Y}{\partial t}\right)_M=F_2(t,\ M)T_k, \tag{A.25}$$

$$\left(\frac{\partial Y}{\partial M}\right)_t=F_2(t,\ M)u\Lambda M_kU_kD_k, \tag{A.26}$$

where

$$F_1=(1+f_1f_2)^{-1}, \tag{A.27}$$

$$F_2=f_1YF_1, \tag{A.28}$$

$$f_1=\frac{\Lambda}{2k^4}\left(1+\frac{\Lambda^2}{k^2}\right)^{-1}\left[\frac{1}{\omega}+\frac{(1-\bar{u})Y}{1-(1-\bar{u})Y}\right]^{-1}, \tag{A.29}$$

$$f_2=-\left[\left(\frac{2-\nu^{-1}}{\omega}\right)tT_k+\left(\frac{1-\eta}{2\omega}\right)u\Lambda M^2U_kD_k\right]. \tag{A.30}$$

7. The values of critical indices and constants: $\nu = 0.630$; $\eta = 0.0333$; $\alpha = 2 - 3\nu = 0.110$; $\Delta = 0.51$; $\omega = \Delta/\nu = 0.80952$; $\omega_a = 2.1$; $u^* = 0.472$.

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