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Scaled Equation for the Isochoric Heat Capacity of Methane–Ethane Mixtures in the Critical Region

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Results of an experimental study of the isochotic heat capacity of methane–ethane mixtures in a wide region around the liquid–gas critical line are presented. The data are represented by a universal scaled equation for critical mixtures.

KEY WORDS: critical phenomena; ethane; heat capacity; methane; mixtures.

1. INTRODUCTION

Comprehensive studies of the critical behavior of one-component fluids have resulted in a universal description of thermodynamic properties of substances in a wide vicinity of a critical point [1–5]. As for critical mixtures, it is too early to say that the problem of a quantitative description of the thermodynamic properties has been solved. The equations, proposed earlier for binary mixtures near their liquid–gas critical lines, were qualitative rather than quantitative, or in terms of the experimental variables (temperature, density, and concentration), they were too sophisticated and cumbrous for an application.

Furthermore, one should note that liquid–gas critical mixtures have been insufficiently investigated experimentally. For example, reliable and systematic experimental data for the heat capacity at a constant volume in a wide region near the liquid–gas critical line are practically lacking.

In this paper the results of a study of the heat capacity at a constant volume in a wide region around the liquid–gas critical line of the methane–ethane mixture are presented. Measurements were carried out at three

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concentrations ($x = 0.0986$, 0.3995, and 0.8348 mole fraction of ethane) over a wide range of densities and temperatures. A new form of a universal scaled equation of state is introduced to represent the experimental data.

2. HEAT CAPACITY OF METHANE–ETHANE MIXTURES

High-resolution adiabatic calorimetry [6–8] was used for the measurements of the isochoric heat capacity at different densities for three concentrations of the methane–ethane mixture. The technique will be described in detail elsewhere [9]. Analysis of experimental errors has shown that the error in the determination of the "calorimetric step" ΔT is the dominant contribution of the error in the heat capacity. In the critical region our minimum calorimetric step was about 0.02 K and the error in

Table I. Heat Capacity of the Methane–Ethane Mixture in the One-Phase Region

T (K), 1	$C_{V,x}$ ($\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$), 2	T (K), 3	$C_{V,x}$ ($\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$), 4
	$x = 0.09686$ mole fraction of ethane		
	$T_c = 208.98$ K, $\rho_c = 171.839\ \mathrm{kg \cdot m^{-3}}$, $P_c = 5.58$ MPa		
	$\rho = 149.000\ \mathrm{kg \cdot m^{-3}}$		$\rho = 171.830\ \mathrm{kg \cdot m^{-3}}$
211.43	2878.93	209.02	3673.41
211.59	2761.69	209.18	3281.84
211.89	2658.91	209.71	2853.13
212.61	2534.41	210.17	2727.61
213.97	2393.95	210.95	2526.77
215.74	2280.98	211.90	2421.30
219.99	2101.33	213.41	2310.31
223.02	2049.10	214.18	2256.30
227.40	1962.58	216.30	2118.14
241.00	1830.24	256.42	1774.42
	$\rho = 184.735$		$\rho = 210.615$
207.95	3994.38	205.89	2884.78
208.02	3540.51	206.06	2722.99
208.24	3176.27	206.69	2518.15
208.50	2982.47	208.24	2311.22
210.08	2522.44	209.41	2223.08
212.56	2283.02	213.75	2060.00
215.25	1215.33	219.60	1956.21
225.93	1948.07	225.98	1892.41

Table I. *(Continued)*

T (K), 1	$C_{V,x}$ (J · kg^{-1} · K^{-1}), 2	T (K), 3	$C_{V,x}$ (J · kg^{-1} · K^{-1}), 4
	$x = 0.3995$		
	$T_c = 252.53$ K, $\rho_c = 194.030$ kg · m^{-3},		$P_c = 6.91$ MPa
	$\rho = 130.475$		$\rho = 180.013$
258.17	2257.82	254.09	3242.11
258.26	2117.32	255.01	2617.90
258.52	2099.13	258.52	2124.18
258.00	2077.63	261.94	2012.64
260.57	2021.39	265.15	1917.82
265.29	1931.99	268.92	1902.17
272.52	1825.99	273.21	1845.71
	$\rho = 194.030$		$\rho = 202.441$
252.56	3651.54	251.51	3594.12
252.61	3110.25	251.56	3379.89
252.71	3061.34	256.60	3288.27
252.86	2899.06	251.64	3147.65
253.98	2452.20	251.72	3212.63
258.36	2113.03	251.86	2872.79
261.82	1989.52	252.02	2771.58
267.42	1905.95	252.45	2575.55
273.85	1826.79	253.00	2446.63
280.31	1832.10	256.90	2114.10
	$\rho = 210.421$		$\rho = 221.204$
250.54	3704.11	249.06	2985.68
250.55	3604.69	249.16	2871.61
250.57	3498.10	249.43	2690.27
250.61	3212.15	250.77	2321.67
250.67	3171.15	251.14	2280.70
250.71	3055.33	254.62	2058.25
250.72	2996.91	259.31	1938.11
250.79	2859.57		$\rho = 240.10$
250.88	2845.22	246.92	2515.85
251.00	2720.19	247.10	2424.25
251.14	2674.05	250.04	2097.23
251.33	2593.08	255.30	1938.02
251.64	2513.12	262.92	1842.45
252.01	2436.24	269.81	1800.80
253.41	2253.75	279.46	1776.09
254.07	2203.50		$\rho = 264.314$
255.55	2102.00	243.28	2049.13
258.40	1994.24	244.40	2014.79
264.43	1907.90	247.48	1929.74
281.22	1795.51	253.93	1828.17
295.67	1832.87	271.13	1758.57

Table I. *(Continued)*

T(K), 1	$C_{V,x}$ (J · kg^{-1} · K^{-1}), 2	T(K), 3	$C_{V,x}$ (J · kg^{-1} · K^{-1}), 4
	$x = 0.8400$		
	$T_c = 292.97$ K, $\rho_c = 198.667$ kg · m^{-3},		$P_c = 5.62$ MPa
	$\rho = 140.137$		$\rho = 181.048$
293.07	2336.53	295.09	2710.52
293.16	2274.97	295.27	2574.72
293.23	2239.57	298.13	2131.52
295.33	2096.40	302.85	1976.54
299.67	1997.83	312.18	1863.12
311.25	1797.53	325.10	1797.28
328.58	1820.29	335.17	1756.53
	$\rho = 198.667$		$\rho = 225.215$
292.99	3794.24	295.07	2728.50
293.03	3420.82	292.19	2667.30
293.07	3298.15	293.39	2337.86
293.12	3184.17	295.57	2146.28
293.18	3053.90	299.64	2025.50
293.24	2981.17	306.38	1931.47
293.51	2766.22	314.39	1872.83
293.72	2543.68	322.40	1854.42
293.82	2572.99		$\rho = 278.031$
293.92	2548.12	288.45	2050.95
294.02	2504.60	288.67	2033.88
294.22	2419.92	288.99	2031.54
294.56	2429.68	292.10	1930.89
292.10	2341.74	297.01	1875.63
296.19	2249.44	301.94	1842.27
298.46	2131.05	206.87	1839.77
302.63	2024.56	311.70	1786.28
209.28	1944.06	319.21	1763.49

the temperature did not exceed 3×10^{-4} K, which amounts to an error of about 1 %. To compare the experimental data with those calculated by the equation of state, an accurate determination of the critical parameters is essential. The critical densities $\rho_c\ (x)$ were identified, with the densities corresponding to the maximum of the heat capacity as a function of density. The error in the determination of ρ_c was about 1 %. The critical temperatures were determined from the heat capacity jumps at the critical isochore with an accuracy of 10^{-2} K.

The error in the heat capacity increases with increasing ethane concentration. The maximum errors ranged from 1.5 to 2.5%. Purity of methane and ethane used in the experiment was 99.89 and 99.5%, respectively. The experimental data are presented in Table I. The values of the temperatures corresponding to the values of $C_{v,x}$ are those at the middle of the calorimetric steps.

3. SCALED EQUATION OF STATE FOR A BINARY CRITICAL MIXTURE

An equation of state for the isochoric heat capacity of a binary mixture in the vicinity of its liquid–gas critical line can be obtained on the basis of the scaled equation of state for a one-component fluid [5, 10–12] and the isomorphism hypothesis [13–15] (see also Refs. 8, 16, and 17).

According to this hypothesis, the free energy per unit volume of a critical one-component fluid and that of a binary mixture are the same functions of density and temperature when taken at the constant "field" $\Delta = \mu_2 - \mu_1$ (μ_2 and μ_1 are the chemical potentials of the components), which is conjugate to concentration x of a second component. This principle allows one to obtain various explicit forms of the equation of state for a critical binary mixture using various thermodynamic potentials. Thus in the work of Leung and Griffiths [18] the density of the thermodynamic potential $\Omega = -PV$ was used:

$$\frac{\Omega}{V} = -P(T, \mu_1, \Delta) \tag{1}$$

where P is the pressure and V is the volume. The isomorphic way is determined by the condition

$$\tilde{x} = \frac{\exp(\Delta/RT)}{1+\exp(\Delta/RT)} = \text{const} \tag{2}$$

where R is the gas constant. All the coefficients of the equation of state can be represented as series of powers of $\tilde{x}$. The equation proposed in Ref. 18 qualitatively describes the isochoric heat capacity behavior in some critical mixtures [19, 20]. However, the discrepancies between the calculated values and the experimental data are essential. In Ref. 21, a modification of the Leung–Griffiths equation with an account of the liquid–gas asymmetric and nonasymptotic correction terms was proposed. The resulting correlation of the carbon dioxide-neon P, V, T, x data in Ref. 21 was good, but it did not yield a representation of heat capacities.

Use of the isomorphic Helmholtz free energy density, proposed in Refs. 13 and 14, appeared to be more natural for the description of the isochoric heat capacity of critical mixtures [15, 22]. This free energy has the following form:

$$\tilde{F}^*(T, \rho, \Delta) = \psi(T, \rho, \Delta) + F_0^*(T, \rho, \Delta) \tag{3}$$

where

$$\tilde{F}^* = \frac{F^*}{V}, \qquad F^*(T, V, \Delta) = F(R, V, x) - Nx\Delta$$

$F(T, V, x)$ is the Helmholtz free energy, $x = (N_2/N)$, $N = N_1 + N_2$ is the number of molecules, $\psi(T, p, \Delta)$ is the scaling function, which at $\Delta = \text{const}$ has the same form as for a one-component fluid, and $F_0^*(T. \rho, \Delta)$ is an analytic background. Use of the activity $\tilde{x}$ instead of Δ in Eq. (3) appears to be more practical because $\Delta \to \pm\infty$ at $x \to 0$ and $x \to 1$, while $\tilde{x}$ coincides with x on the critical line.

Experiments are usually performed at constant concentration x. This means that Δ and, hence, $\tilde{x}$ are not constant. In this case one should transform the free energy $\tilde{F}^*$ to the Helmholtz free energy density $\tilde{F} = (F/V)$:

$$\tilde{F}(T. \rho, x) = \frac{F}{V} = \tilde{F}^* + \rho x \Delta \tag{4}$$

It was shown in Ref. 22 that the Helmholtz free energy density for the binary critical mixture, expressed with the experimental variables T, ρ, and x, can be represented in the following form:

$$\tilde{F}(T, \rho, x) = \Phi(\phi)\, \Psi_{\mathrm{LM}}(r, \theta) + \Psi_{\mathrm{NA}}(r, \theta) + \Psi_{\mathrm{AS}}(r, \theta) + F_0(T, \rho) \tag{5}$$

where the scaling function Ψ_{LM} corresponds to the linear model of the asymptotic scaled equation of state for a one-component critical fluid [12]:

$$\psi_{\mathrm{LM}}(r, \theta) = \frac{1}{2}\frac{ak}{b^2} r^{2-\alpha} \left[\frac{2\beta(b^2-1)}{2-\alpha} + \frac{2\beta(2\gamma-1)}{\gamma(1-\alpha)}(1-b^2\theta^2) - \frac{1-2\beta}{\alpha}(1-b^2\theta^2)\right] \tag{6}$$

Here Ψ_{NA} accounts for the nonasymptotic corrections and has the form

$$\psi_{\mathrm{NA}}(r, \theta) = \frac{1}{2}\frac{ck}{b^2}\frac{r^{2-\alpha+\Delta}}{1-\alpha+\Delta}\left[\frac{\gamma-\Delta}{2-\alpha+\Delta} - (1-2\beta)b^2\theta^2\right] \tag{7}$$

while Ψ_{AS} accounts for the asymmetry of a fluid with respect to the critical isochore:

$$\Psi_{\mathrm{AS}}(r, \theta) = kr^{2\gamma+3\beta-1}\theta\left\{d + \frac{1}{3}[f - 2d(e-\beta)]\, b^2\theta^2 + \frac{1-2\beta}{5\beta - e}\left[d(e-\beta)(1-2\beta) + \frac{1}{3}[f-2d(e-\beta)](e-3\beta)\right] b^4\theta^4\right\} \tag{8}$$

The parametric variables r and θ are related to the deviations of temperature and density from their critical vales by the transformation:

$$\tau = r(1 - b^2\theta^2) \tag{9}$$

$$\Delta\rho = kr^{\beta} - B\tau \tag{10}$$

where $\tau = [T - T_c(x)]/T_c(x)$ and $\Delta\rho = [\rho - \rho_c(x)]/\rho_c(x)$. According to the modern theory of critical phenomena the critical exponents α, β, and Δ are universal for fluids and fluid mixtures [23]. The constants

$$b^2 = \frac{\gamma - 2\beta}{\gamma(1-2\beta)}$$

and

$$e = 2\gamma + 3\beta - 1$$

are also universal. The nonuniversal parameters $k = B_0(b^2-1)^{\beta}$, a, c, d, f, and B are analytic functions of concentration. The regular part of the free energy is also an analytic function:

$$F_0(T, \rho, x) = -P_c + f_1\tau + f_2\tau^2 + f_3\tau^3 - \frac{\rho}{P_c}(m_0 + m_1\tau + m_2\tau^2 + m_3\tau^3) \tag{11}$$

where the critical pressure P_c and all the coefficients are analytic functions of the concentration.

The universal function $\Phi(\phi)$ has the following form [4]:

$$\Phi(\phi) = \left(\frac{\phi}{1+\phi}\right)^{\alpha}\left[2 - \left(\frac{\phi}{1+\phi}\right)^{\alpha/(1-\alpha)}\right] \tag{12}$$

where

$$\phi = r(x)\,\xi^{1/\alpha} \tag{13}$$

The parameter $\tilde{\xi}$ in Eq. (13) depends on the shape of a critical line and the concentration of a mixture:

$$\tilde{\xi} = \xi \, |y_2| \left(\frac{y_1}{y_2}\right)^{\alpha} \tag{14}$$

with

$$\xi = \frac{(1-\alpha)\, RT_{\mathrm{c}}^2}{Ax(1-x)} \left(\frac{dT_{\mathrm{c}}}{dx}\right)^{-2}$$

$$y_1 = 1 + yx(1-x)\left(\frac{1}{T_{\mathrm{c}}}\frac{dT_{\mathrm{c}}}{dx}\right)^2 (\tilde{f}_1 + w)$$

$$y_2 = 1 + 2x(1-x)\left(\frac{1}{T_{\mathrm{c}}}\frac{dT_{\mathrm{c}}}{dx}\right)^2 [y(\tilde{f}_1 + w) - (\tilde{m}_2 + \tilde{f}_2)]$$

$$y = \frac{T_{\mathrm{c}}}{\rho_{\mathrm{c}}}\frac{d\rho_{\mathrm{c}}}{dT_{\mathrm{c}}}, \qquad \tilde{f}_i = \frac{f_i}{\rho_{\mathrm{c}} RT_{\mathrm{c}}}, \qquad \tilde{m}_2 = \frac{m_2}{\rho_{\mathrm{c}} RT_{\mathrm{c}}}$$

$$w = \frac{1}{\rho_{\mathrm{c}} R}\frac{dP_{\mathrm{c}}}{dT_{\mathrm{c}}}$$

The critical amplitude of the unmeasurable isomorphic heat capacity $C_{V,\Delta}$ can be determined by the formula which follows from the linear model:

$$A = \frac{ak\gamma(\gamma-1)}{2\alpha b^2 \rho_{\mathrm{c}} T_{\mathrm{c}}} \tag{15}$$

Upon differentiating Eq. (5) twice with respect to temperature at a constant density and concentration, one obtains the expression for the isochoric heat capacity $C_{V,x} = -(T/\rho)(\partial^2 \tilde{F}/\Delta T^2)_{\rho,x}$:

$$\begin{aligned}\frac{\rho C_{V,x}}{T} = {} & -\Phi(\phi)\, r^{-\alpha} \Bigg\{ r^{\alpha} \left(\frac{\partial^2 \Psi_{\mathrm{LM}}}{\partial T^2}\right) \\ & + \frac{\alpha}{(1-\alpha)(1+\phi)} \Bigg[2r^{-1+\alpha} \frac{\partial \Psi_{\mathrm{LM}}}{\partial T} \frac{\partial r}{\partial T} \left\{ 2 - \alpha - \frac{2}{2 - [\phi/(1+\phi)]^{\alpha/(1-\alpha)}} \right\} \\ & + (2-\alpha)\, r^{-2+\alpha} \Psi_{\mathrm{LM}} \left(\frac{\partial r}{\partial T}\right)^2 \left(\zeta - \frac{[1/(2-\alpha)]\{\zeta + [2\alpha/(1+\phi)]\}}{2 - [\phi/(1+\phi)]^{2/(1-\alpha)}} \right) \Bigg] \Bigg\} \\ & - \frac{\partial^2 \Psi_{\mathrm{NA}}}{\partial T^2} - \frac{\partial^2 \Psi_{\mathrm{AS}}}{\partial T^2} - \frac{\partial^2 F_0}{\partial T^2} \end{aligned} \tag{16}$$

with

$$\zeta = \left[\frac{\alpha(2-\alpha)-1+\alpha}{1-\alpha}\right]\frac{1}{1+\phi} - 2\frac{\phi}{1+\phi} + r\left(\frac{\partial r}{\partial T}\right)^{-2}\left(\frac{\partial^2 r}{\partial T^2}\right) \qquad (17)$$

At the critical isochore $[\tau(x) = r(x)]$, when $\tau(x) \gg \tilde{\xi}^{1/\alpha}$, the experimental and isomorphic thermodynamic ways practically coincide,

$$\tau(\tilde{x}) = \tau(x)\left|\frac{y_1}{y_2}\right|$$

and the heat capacity $C_{V,x}$, measured experimentally, has the same singularity as C_v in a one-component critical fluid:

$$C_{V,x} \simeq A\tau(x)^{-\alpha} + \text{background} \qquad (18)$$

When $\tau(x) \ll \tilde{\xi}^{1/\alpha}$ the heat capacity $C_{V,x}$ is renormalized and tends to a finite value at a critical point:

$$C_{V,x} \simeq -A\tilde{\xi}[\tilde{\xi}(\tau\tilde{\xi})^{\alpha/(1-\alpha)} - 1] + \text{background} \qquad (19)$$

In Ref. 22 the argument of the renormalization function Φ in Eq. (5) had the form

$$\phi^* = \phi^\alpha = r(x)^\alpha \tilde{\xi} \qquad (20)$$

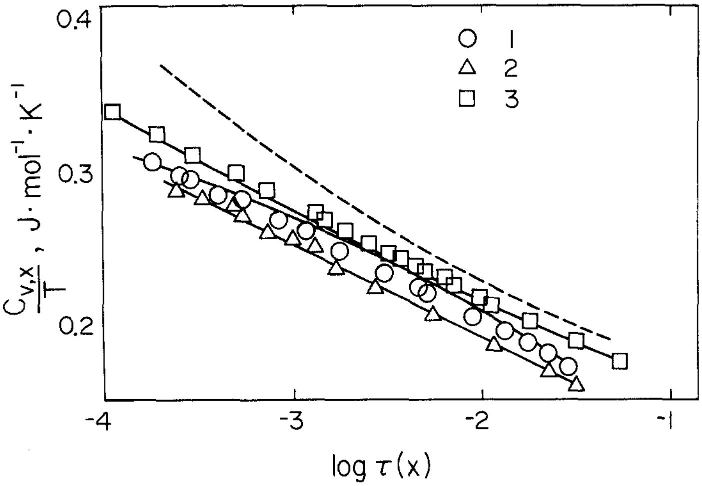

Fig. 1. Comparison between the experimental and the calculated values of $C_{V,x}/T$ in the methane–ethane mixture on the critical isochore in the one-phase region: x = mole fraction of ethane: 0.3995 (1); 0.0986 (2); 0.8400 (3). Solid curves represent Eq. (16); dashed curve is for pure ethane [14].

Using ϕ instead of ϕ^* appears to be more practical, because the small value of the exponent α ($\alpha = 0.11$) leads to a very small variation of ϕ^* at a comparatively large variation of $r(x)$ (see also Ref. 24).

4. COMPARISON WITH THE EXPERIMENTAL DATA

The equations were used to represent our experimental data for the isochoric heat capacity at three concentrations of the methane–ethane mixture ($x = 0.0986$, 0.3995, and 0.9400 mole fractions of ethane). Experimental data at densities in the range $0.65 \leqslant \rho/\rho_c(x) \leqslant 1.45$ and at temperatures from the saturation line to $T \leqslant 1.2T_c(x)$ were included in the fit. The values of the nonuniversal parameters a, k, c, d, and f_i were related to those for the individual components as

$$a(x) = a_1(1 - x) + a_2 x, \text{ etc...}$$

where the indexes "1" and "2" refer to methane and ethane, respectively. The values of the constants for the pure components were taken from Ref. 25. The function $T_c(x)$ and $\rho_c(x)$ were determined experimentally. The function $P_c(x)$ was interpolated from the data in Ref. 26. The universal critical exponents were fixed at the theoretical values: $\alpha = 0.11$, $\beta = 0.325$, and $\Delta = 0.5$ (see Refs. 1 and 8).

5. DISCUSSION

A comparison of the experimental results with the calculations is presented in Figs. 1–4. One sees that the standard error in the range of

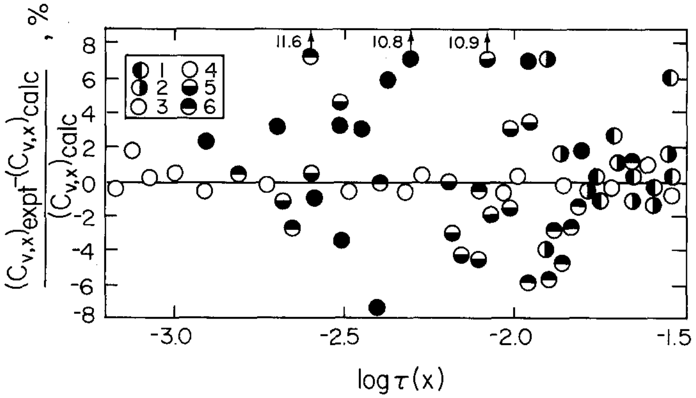

Fig. 2. Deviations of the experimental values of $C_{V,x}$ from the calculated values for the methane–ethane mixture ($x = 0.0986$ mole fraction of ethane) on the isochores: $\rho/\rho_c = 0.662$ (1); 0.867 (2); 1.0 (3); 1.075 (4); 1.167 (5); 1.226 (6).

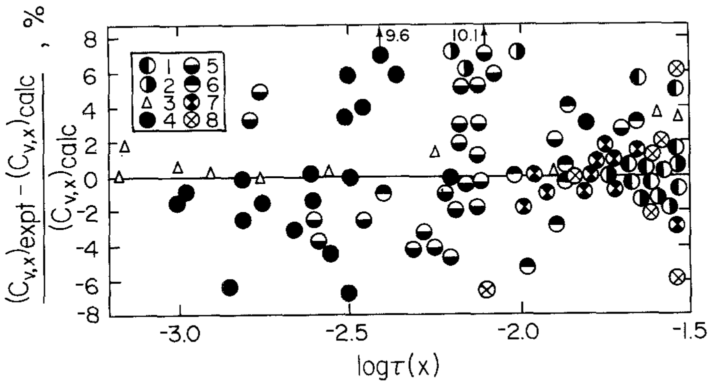

Fig. 3. Deviations of the experimental values of $C_{V,x}$ from the calculated values for the methane–ethane mixture ($x = 0.3995$ mole fraction of ethane) on the isochores: $\rho/\rho_c = 0.673$ (1); 0.928 (2); 1.0 (3); 1.043 (4); 1.140 (5); 1.238 (6); 1.362 (7); 1.399 (8).

$|\Delta\rho| \leqslant 0.4$ and $10^{-3} \leqslant \tau \leqslant 10^{-1.5}$ varies from 2 to 4%, which does not differ much from the experimental accuracy. However, in the immediate vicinity of the saturated line the error increases considerably (up to 10–15%). Physically, it implies a failure of Eq. (10), because this equation (at $x = \text{const}$) does not take into account the deformation of the P, V, T surface of a mixture at a constant concentration. Modification of Eq. (10) (see Ref. 24) and involvement of P, V, T, x data in the fit should increase the accuracy of the description of heat capacity data for critical mixtures [24].

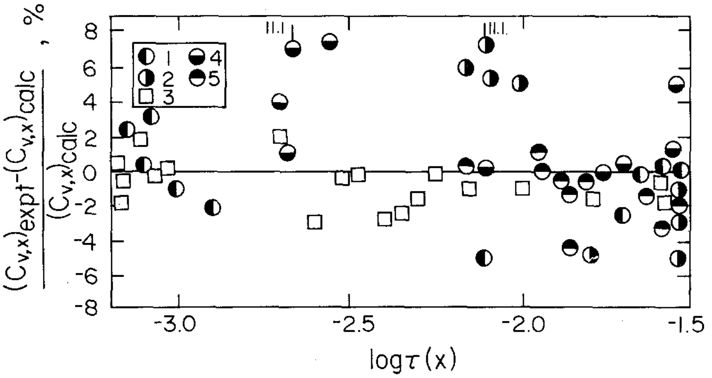

Fig. 4. Deviations of the experimental values of $C_{V,x}$ from the calculated values for the methane–ethane mixture ($x = 0.8400$ mole fraction of ethane) on the isochores: $\rho/\rho_c = 0.705$ (1); 0.911 (2); 1.0 (3); 1.134 (4); 1.399 (5).

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