# ISOCHORIC SPECIFIC HEAT IN THE METHANE–ETHANE SYSTEM AROUND THE LIQUID–GAS CRITICAL LINE

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Experimental and theoretical studies have been made on the behavior of the isochoric specific heat for binary methane–ethane mixtures in the critical region.

1. Introduction. Some progress has recently been made in describing critical phenomena for binary solutions [1-7] because of the fluctuation theory for phase transitions generally [8, 9] and from advances in describing the critical behavior for one-component liquids, as in [10-15]. However, no single closed scale equation of state has yet been derived for binary solutions, and we have no exact description of the thermodynamic parameters in the critical region. Existing equations either give only a qualitative description of the isochoric specific heat $C_{v,x}$ for a binary solution [1-3] or else are too complicated [5-7], which gives rise to mathematical difficulties in using them. Also, the measured $C_{v,x}$ for binary solutions in the critical region are very scanty. There are virtually no reliable and systematic measurements on $C_{v,x}$ for binary mixtures around the liquid–gas critical line, although such measurements would not merely increase the accuracy in existing calculation methods but would also provide essentially new methods and equations.

Here we present a combined experimental and theoretical study on the isochoric specific heat for methane–ethane mixtures near the liquid–gas line. The measurements were made with molar fractions of ethane x = 0.0986, 0.3995, and 0.8400 over wide ranges in density and temperature. A new form of isomorphous gauge equation of state is used. The results confirm that a universal description can be given for these binary solutions near that line.

2. The isochoric specific heat was measured for this system in the critical region. The adiabatic calorimeter [16, 17] we used met the requirements for critical-region measurements. The equipment design and manufacture ensured that the method was reliable.

The calorimetric suspension is a major unit, which consists of the calorimeter and an insulating system: two cylindrical screens around the calorimeter, cold finger, and ring. The calorimeter was suspended on a capillary along an axis common to all the objects. The suspension was placed in a vacuum chamber, which in turn was immersed in a nitrogen bath.

The heaters for the insulating objects were used with ART-1D temperature regulators and R-341 amplifiers providing control; the system provided automatic control of the set temperature difference between the calorimeter and the insulating objects. The temperature-difference sensors were copper–constantan thermocouple banks.

Adiabatic measurements were provided by the control and continuous-pumping systems. The stability in the adiabatic state was improved by dividing the screen heaters into sections, while the outer surface of the calorimeter was coated with a thin layer of copper, the isothermal shell.

The temperatures were measured with a TSPN-1 platinum resistance thermometer set in the jacket containing the heater within the calorimeter. The circuits for measuring the temperature and the power supplied to the calorimeter heater were based on an R-3003 voltage comparator, accuracy class $5 \cdot 10^{-4}$. The absolute error in measuring the temperature on the thermometer scale was not more than $5 \cdot 10^{-4}$ K. The random errors in the concentrations were not more than 0.1%, while the filling densities varied by 0.05-0.1%. A correction was applied for the effects of calorimeter deformation on the density when the $C_{v,x}$ measurements were processed.

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TABLE 1. Measured Methane–Ethane Mixture Specific Heats in the Single-Phase Region

| T, K | $C_{v,x}$, J·kg⁻¹×K⁻¹ |
|---|---|
| $x = 0{,}0986$ | |
| $\rho = 149{,}000$ kg/m³ | |
| 211,43 | 2878,93 |
| 212,61 | 2534,41 |
| 213,97 | 2393,95 |
| 215,74 | 2280,98 |
| 219,99 | 2101,33 |
| 223,02 | 2049,10 |
| 227,40 | 1962,58 |
| 241,00 | 1830,24 |
| $\rho = 171{,}839$ kg/m³ | |
| 209,02 | 3673,41 |
| 209,18 | 3281,84 |
| 210,17 | 2727,61 |
| 210,95 | 2526,77 |
| 211,90 | 2421,30 |
| 213,41 | 2310,31 |
| 214,18 | 2256,30 |
| 216,30 | 2118,14 |
| 256,42 | 1774,42 |
| $\rho = 184{,}735$ kg/m³ | |
| 207,95 | 3994,38 |
| 208,02 | 3540,51 |
| 208,24 | 3176,27 |
| 208,50 | 2982,47 |
| 210,08 | 2522,44 |
| 212,56 | 2283,02 |
| 215,25 | 2153,33 |
| 225,93 | 1948,07 |
| $\rho = 210{,}615$ kg/m³ | |
| 205,89 | 2884,78 |
| 206,69 | 2518,15 |
| 208,24 | 2311,22 |
| 209,41 | 2223,08 |
| 213,75 | 2060,0 |
| 219,60 | 1956,21 |
| 225,98 | 1892,41 |
| $x = 0{,}3995$ | |
| $\rho = 130{,}475$ kg/m³ | |
| 258,17 | 2257,82 |
| 258,52 | 2099,13 |
| 259,00 | 2077,63 |
| 260,57 | 2021,39 |
| 265,29 | 1931,99 |
| 272,53 | 1825,99 |
| $\rho = 180{,}013$ kg/m³ | |
| 254,09 | 3242,11 |
| 255,01 | 2617,90 |
| 258,52 | 2124,18 |
| 261,94 | 2012,64 |
| $\rho = 194{,}030$ kg/m³ | |
| 252,56 | 3651,54 |
| 253,98 | 2452,20 |
| 258,36 | 2113,03 |
| 261,82 | 1989,52 |
| 267,42 | 1905,95 |
| 273,85 | 1826,79 |
| 280,31 | 1832,10 |
| $\rho = 202{,}441$ kg/m³ | |
| 251,51 | 3594,12 |
| 251,64 | 3147,65 |
| 251,86 | 2872,79 |
| 251,02 | 2771,58 |
| 252,45 | 2575,55 |
| 253,00 | 2446,63 |
| 256,90 | 2114,10 |
| $\rho = 210{,}421$ kg/m³ | |
| 250,54 | 3704,11 |
| 251,33 | 2593,08 |
| 252,01 | 2436,24 |
| 253,41 | 2253,75 |
| $\rho = 210{,}421$ kg/m³ | |
| 254,07 | 2203,50 |
| 255,55 | 2102,00 |
| 258,40 | 1994,24 |
| 264,43 | 1907,90 |
| 281,22 | 1795,51 |
| 295,67 | 1832,87 |
| $\rho = 221{,}204$ kg/m³ | |
| 249,06 | 2985,68 |
| 249,43 | 2690,27 |
| 250,77 | 2321,67 |
| 251,14 | 2280,70 |
| 254,62 | 2058,25 |
| 259,31 | 1938,11 |
| $\rho = 240{,}160$ kg/m³ | |
| 246,92 | 2515,85 |
| 247,10 | 2424,25 |
| 250,04 | 2097,23 |
| 255,30 | 1938,02 |
| 262,92 | 1842,45 |
| 269,81 | 1800,80 |
| 279,46 | 1776,09 |
| $\rho = 264{,}314$ kg/m³ | |
| 243,28 | 2049,13 |
| 244,40 | 2014,79 |
| 247,48 | 1929,74 |
| 253,93 | 1828,17 |
| 271,13 | 1758,57 |
| 265,15 | 1917,82 |
| 268,92 | 1902,17 |
| 273,21 | 1845,71 |
| $x = 0{,}8400$ | |
| $\rho = 140{,}137$ kg/m³ | |
| 293,07 | 2336,53 |
| 295,33 | 2096,40 |
| 299,67 | 1997,83 |
| 311,25 | 1797,53 |
| 328,58 | 1820,29 |
| $\rho = 181{,}048$ kg/m³ | |
| 295,09 | 2710,52 |
| 298,13 | 2131,52 |
| 302,85 | 1976,54 |
| 312,18 | 1863,12 |
| 325,10 | 1797,28 |
| 335,17 | 1756,53 |
| $\rho = 198{,}667$ kg/m³ | |
| 292,99 | 3794,24 |
| 293,12 | 3184,17 |
| 293,24 | 2981,17 |
| 293,51 | 2766,22 |
| 293,72 | 2543,68 |
| 293,82 | 2572,99 |
| 293,92 | 2548,12 |
| 294,02 | 2504,60 |
| 294,22 | 2419,92 |
| 294,56 | 2429,68 |
| 295,10 | 2341,74 |
| 296,19 | 2249,44 |
| 298,46 | 2131,05 |
| 302,63 | 2024,56 |
| 209,28 | 1944,06 |
| $\rho = 225{,}215$ kg/m³ | |
| 292,07 | 2728,50 |
| 293,39 | 2337,86 |
| 295,57 | 2146,28 |
| 299,64 | 2025,50 |
| 306,38 | 1931,47 |
| 314,39 | 1872,83 |
| 322,40 | 1854,42 |
| $\rho = 278{,}031$ kg/m³ | |
| 288,45 | 2050,95 |
| 292,10 | 1930,89 |
| 297,01 | 1875,63 |
| 301,94 | 1842,27 |
| 306,87 | 1839,77 |
| 311,79 | 1786,28 |
| 319,21 | 1763,49 |

The experimental values on the isochores were determined as follows: A certain amount of heat was injected into the calorimeter containing the specimen, and the temperature increment was measured. $C_{v,x}$ was calculated from the measured quantities:

$$C_{v,x} = \frac{1}{M}\left(\frac{U_h U_s \Delta t}{R_s \Delta T} - C_c\right). \tag{1}$$

The $C_{v,x}$ data showed that the main contribution to the error $\delta C_{v,x}$ comes from $\delta(\Delta T)$. In the critical region, where the width of the calorimetric step is minimal ($\Delta T \approx 0.02$ K) and the system is sensitive even to perturbations caused by the measuring instruments, $\delta(\Delta T)$ is determined by the error in approximating the temperature drift (the calorimeter temperature T as a function of time t) before and after heating. Necessary conditions for the maximum accuracy in determining $\Delta T$ are linear and parallel T(t) curves, as these indicate thermodynamic equilibrium and stable adiabatic conditions. Linear temperature curves are favored by mixing, and parallelism by the optimum mixing conditions.

$\Delta T$ is determined as the difference in the temperatures extrapolated to the middle of $\Delta t$, which is done with linear T(t) before and after heating. The critical fillings were determined from the peak in the specific-heat anomalies on the isochores. The error in selecting $\rho_c$ was ~1%. The critical temperatures were calculated from the specific-heat steps on the critical isochores with an error of $2 \cdot 10^{-3}$ K.

Calculations on the random errors $\delta C_{v,x}$ showed that they are related to the concentrations; the maximal $\delta C_{v,x}$ varied over the range 1.4-2.5% as the ethane concentration increased, while $\delta C_{v,x}$ did not exceed 1.8% for x = 0.3995.

The methane and ethane were of 99.89 and 99.5% purity correspondingly; Table 1 gives the results.

3. Gauge Equation of State. The equation of state near the critical-point line can be derived from gauge theory [8, 9] and the isomorphism hypothesis [18-20]. Thermodynamic analysis shows [5, 7] that the isochoric specific heat for a binary solution in the critical region shows universal behavior, while the free energy F(T, ρ, x) per mole can [21] be put as

$$\rho F(T,\ \rho,\ x) = \Phi_S(\varphi)\,\Psi_{LM}(r,\ \theta) + \Psi_{NA}(r,\ \theta) + \Psi_{AS}(r,\ \theta) + \rho F_0(T,\ \rho). \tag{2}$$

Here $\Phi_S(\varphi)$ is a universal function. The gauge function $\Psi_{LM}(r,\ \theta)$ corresponds to the linear model for the equation of state for a one-component liquid [10]:

$$\Psi_{LM}(r,\ \theta) = \frac{1}{2}\,\frac{ak}{b^2}\,r^{2-\alpha}\left[\frac{2\beta(b^2-1)}{2-\alpha} + \frac{2\beta(2\gamma-1)}{\gamma(1-\alpha)}(1-b^2\theta^2) - \frac{1-2\beta}{\alpha}(1-b^2\theta^2)^2\right], \tag{3}$$

and the next term incorporates the nonasymptotic behavior for a one-component liquid [10]:

$$\Psi_{NA}(r,\ \theta) = \frac{1}{2}\,\frac{ck}{b^4}\,\frac{r^{2-\alpha+\Delta}}{1-\alpha+\Delta}\left[\frac{\gamma-\Delta}{2-\alpha+\Delta} - (1-2\beta)\,b^2\theta^2\right], \tag{4}$$

and the third term incorporates the asymmetry in a real liquid with respect to the critical isochore [11, 22]:

$$\begin{aligned}\Psi_{AS}(r,\ \theta) = k r^{2\gamma+3\beta-1}\,\theta\Big\{d + \frac{1}{3}[f - 2d(e-\beta)]\,b^2\theta^2 + \\ + \frac{1-2\beta}{5\beta-e}\left[d(e-\beta)(1-2\beta) + \frac{1}{3}[f-2d(e-\beta)](e-3\beta)\right]b^4\theta^4\Big\}.\end{aligned} \tag{5}$$

The polar coordinates r and θ are related to the dimensionless temperature $\tau(x) = T/T_c(x) - 1$ and density $\Delta\rho(x) = \rho/\rho_c(x) - 1$ by

$$\tau = r(1-b^2\theta^2), \tag{6}$$

$$\Delta\rho = kr^{\beta}\theta - B_3\tau, \tag{7}$$

in which α, β, and γ are critical parameters defined in the usual way, while Δ is the critical parameter for the nonasymptotic terms, where all the quantities are universal in accordance with gauge theory; $b^2 = (\gamma - 2\beta)/\gamma(1 - 2\beta)$, $e = 2\gamma + 3\beta - 1$ are also universal quantities, while $k = B_0(b^2 - 1)^{\beta}$ and the parameters $a$, c, d, f, $B_0$, $B_3$ are related to the individual features of the liquid and in general are analytic functions of the concentration x. The regular part of the free energy $F_0(T,\ \rho)$ is an analytic function of temperature and density:

$$F_0(T,\ \rho) = m_0/\rho_c - P_c/\rho + \sum_{i=1}^{4}(m_i/\rho_c + f_i/\rho)\,\tau^i, \tag{8}$$

where the critical pressure $P_c$ and the parameters $f_i$ and $m_i$ are also analytic concentration functions.

In [21], φ in (2) was taken as

$$\varphi_1 = r^{\alpha}(x)\,\xi_y, \tag{9}$$

and the expression obtained for $\Phi_S$ was

$$\Phi_S(\varphi_1) \equiv \Phi_{1S}(\varphi_1) = \left(\frac{\varphi_1}{1+\varphi_1}\right)^{\frac{2-\alpha}{1-\alpha}}. \tag{10}$$

It has been shown [23] that the critical behavior in a binary solution is of universal type and is governed by the dimensionless parameter $\varphi_0 = \tau(x)\xi_y^{1/\alpha}$, or by the following parameter when one replaces τ(x) by the dimensionless distance from the critical point r(x):

$$\varphi = r(x)\,\xi_y^{1/\alpha}, \tag{11}$$

TABLE 2. Parameters in (24) for Binary Methane–Ethane Mixtures

| Parameter | $x=0{,}0986$ | $x=0{,}3995$ | $x=0{,}8400$ |
|---|---|---|---|
| $T_c$, K | 208,98 | 252,53 | 292,97 |
| $\rho_c$, kg/m³ | 171,839 | 194,030 | 198,667 |
| $P_c$, MPa | 5,58 | 6,91 | 5,62 |
| $k$ | 1,0949 | 1,1148 | 1,1439 |
| $\xi_y$ MPa | 1,598 | 1,695 | 9,010 |
| $a$, MPa | 48,48 | 70,07 | 62,38 |
| $c$, MPa | —39,71 | —97,78 | 2,538 |
| $d$, MPa | —160,4 | —331,8 | — 1,181 |
| $f$, MPa | 178,2 | 514,6 | —113,1 |
| $f_2$, MPa | —96,37 | —208,3 | 17,72 |
| $f_3$, MPa | —170,0 | —155,2 | 243,9 |
| $f_4$, MPa | 148,8 | —73,87 | —899,8 |
| $m_2$, MPa | 95,86 | 221,5 | —25,57 |
| $m_3$, MPa | 238,4 | 234,2 | —228,3 |
| $m_4$, MPa | 258,6 | —149,9 | 917,7 |

and $\Phi_S(\varphi)$ is

$$\Phi_S(\varphi) = f_S(\varphi)\,[2 - f_S^{\alpha/(1-\alpha)}(\varphi)], \tag{12}$$

$$f_S(\varphi) = \frac{\varphi}{1+\varphi}. \tag{13}$$

Here

$$\xi_y = |\xi y_2|\,|y_1 y_2^{-1}|^{\alpha}, \tag{14}$$

$$\xi = \frac{(1-\alpha)\,T_c^2}{Ax(1-x)}\left(\frac{dT_c}{dx}\right)^{-2}, \tag{15}$$

$$A = \frac{\tilde{a}k\gamma(\gamma-1)}{2\alpha b^2}, \tag{16}$$

$$y_1 = 1 + 2x(1-x)\left(\frac{1}{T_c}\,\frac{dT_c}{dx}\right)^2 y(\tilde{f}_1 + w), \tag{17}$$

$$y_2 = 1 + 2x(1-x)\left(\frac{1}{T_c}\,\frac{dT_c}{dx}\right)^2 [y(\tilde{f}_1 + w) - (\tilde{m}_2 + \tilde{f}_2)], \tag{18}$$

$$y = \frac{T_c}{\rho_c}\,\frac{d\rho_c}{dx}\left(\frac{dT_c}{dx}\right)^{-1}, \tag{19}$$

$$w = T_c\left(\frac{dT_c}{dx}\right)^{-1}\frac{d\tilde{P}_c}{dx}, \tag{20}$$

and the tilde denotes a dimensionless quantity. It can be shown that $\Phi_{1S}(\varphi_1)$ is a particular case of the general (12) and that it is equivalent to $\Phi_S(\varphi)$ in the asymptotic behavior. There is a major difference between $\Phi_S(\varphi)$ and $\Phi_{1S}(\varphi_1)$ in that transfer from $\varphi$ to $\varphi_1 = \varphi^{\alpha}$ leads to temperature broadening in the transition region as well as to sign change for the singular part of the isochoric specific heat $[C_{v,x}]_{\text{sing}} = -T(\partial^2 F_S/\partial T^2)_{\rho,x}$ at small $\varphi$. For $\varphi \ll 1$, we have from (2) and (12) that

$$[C_{v,x}]_{\text{sing}} \sim \text{const} - \tau^{\alpha/(1-\alpha)}(x), \tag{21}$$

while using (10) gives

$$[C_{v,x}]_{\text{sing}} \sim \tau^{\alpha/(1-\alpha)}(x). \tag{22}$$

For $\varphi \gg 1$, the two functions are equivalent, and the specific heat behaves as for a pure substance:

$$[C_{v,x}]_{\text{sing}} \sim \tau^{-\alpha}(x) \tag{23}$$

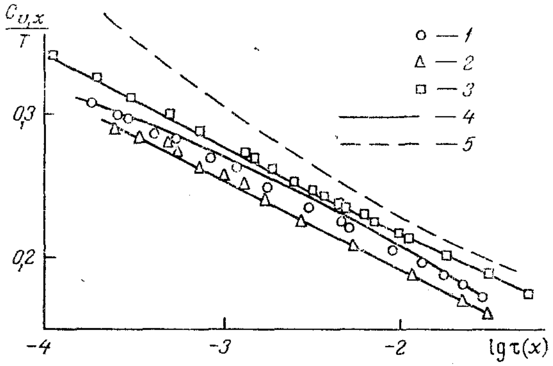

Fig. 1. Comparison of measured and calculated $C_{v,x}/T$ for the methane–ethane system on the critical isochore: 1) x = 0.0986; 2) 0.3995; 3) 0.8400; 4) calculation from (24); 5) pure ethane. $C_{v,x}/T$ in J/mole·K², log τ(x) dimensionless.

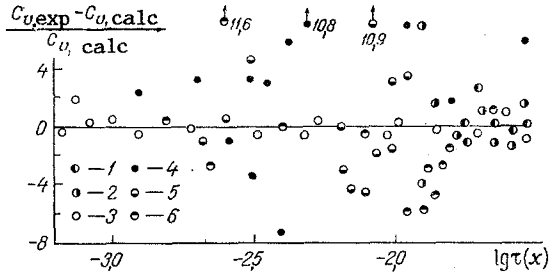

Fig. 2. Deviations of measured $C_{v,x}$ from those calculated from (24) for the methane–ethane system having x = 0.0986 on the isochores: 1, 2, 3, 4, 5, 6) $\rho/\rho_c$ = 0.662; 0.867; 1.0; 1.075; 1.167; 1.226. $(C_{v,calc} - C_{v,exp})/C_{v,calc}$, %.

and preference can be given to either of them only after exact comparison with measurements. The final expression for $C_{v,x}$ on the basis of (2)-(8) with (12) and (13) is

$$\frac{\rho C_{v,x}}{T} = \Phi_S(\varphi)\, r^{-\alpha}\Bigg\{-r^{\alpha}\left(\frac{\partial^2\Psi_{LM}}{\partial T^2}\right)_{\rho,x} - \frac{\alpha}{(1-\alpha)(1+\varphi)}\Bigg\{2r^{-(1-\alpha)} \times \\ \times \left(\frac{\partial\Psi_{LM}}{\partial T}\right)_{\rho,x}\left(\frac{\partial r}{\partial T}\right)_{\rho,x}\left[2-\alpha-\frac{2}{2-f_S^{\alpha/(1-\alpha)}}\right] + \\ + r^{-(2-\alpha)}\Psi_{LM}\left(\frac{\partial r}{\partial T}\right)^2_{\rho,x}\left[(2-\alpha)F_{2S}-\frac{F_{2S}+2\alpha/(1+\varphi)}{2-f_S^{\alpha/(1-\alpha)}}\right]\Bigg\}\Bigg\} - \\ - \left(\frac{\partial^2\Psi_{NA}}{\partial T^2}\right)_{\rho,x} - \left(\frac{\partial^2\Psi_{AS}}{\partial T^2}\right)_{\rho,x} - \rho\left(\frac{\partial^2 F_0}{\partial T^2}\right)_{\rho,x}, \tag{24}$$

where

$$F_{2S} = \left[\frac{\alpha(2-\alpha)}{1-\alpha} - 1\right]\frac{1}{1+\varphi} - 2f_S + r\left(\frac{\partial r}{\partial T}\right)^{-2}_{\rho,x}\left(\frac{\partial^2 r}{\partial T^2}\right)_{\rho,x}, \tag{25}$$

where the regular part $F_0(T, \rho, x)$, the derivative $(\partial^2F_0/\partial T^2)$, and the derivatives $(\partial\psi_{LM}/\partial T)$, $(\partial^2\psi_{L,M}/\partial T^2)$, $(\partial^2\psi_{NA}/\partial T^2)$, $(\partial^2\psi_{AS}/\partial T^2)$ coincide with the corresponding functions for one-component liquids [24].

4. Data Processing. These equations were used to describe our measurements, where the processing included ones for the range $0.65\rho_c \le \rho \le 1.45\rho_c$ and temperatures from the saturation line up to $T \le 1.2T_c$. The calculations were performed with $\Phi_S(\varphi)$ and $\Phi_{1S}(\varphi_1)$, where

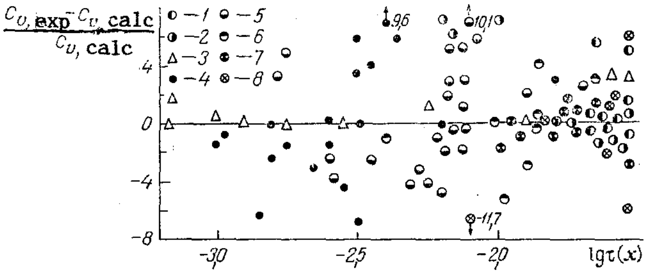

Fig. 3. Deviations of measured $C_{v,x}$ from those calculated from (24) for the methane–ethane system having x = 0.0986 on the isochores: 1, 2, 3, 4, 5, 6) $\rho/\rho_c$ = 0.673; 0.928; 1.0; 1.043; 1.084; 1.140; 1.238; 1.362.

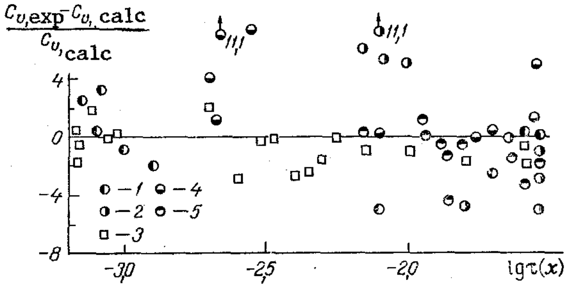

Fig. 4. Deviations of measured $C_{v,x}$ from those calculated from (24) for the methane–ethane system having x = 0.8400 on the isochores: 1, 2, 3, 4, 5) $\rho/\rho_c$ = 0.705; 0.911; 1.0; 1.134; 1.399.

the measurements were described substantially better in terms of $\varphi$ than $\varphi_1$, so (24) was used in the subsequent analysis.

We calculated $\xi_y$ for each concentration from (14)-(20); the $a$, k, $f_1$, and $f_2$ for the various concentrations were calculated from additive relations:

$$a(x)=a_1(1-x)+a_2x,\qquad k(x)=k_1(1-x)+k_2x \tag{26}$$

where the subscript 1 corresponds to pure methane and subscript 2 to pure ethane. The constants for the pure components were taken from [24], while $T_c(x)$ and $\rho_c(x)$ together with their derivatives $dT_c/dx$ and $d\rho_c/dx$ were determined from our measurements, as they are required to calculate $\xi$ and $\xi_y$. $P_c(x)$ and $dP_c/dx$ were interpolated from the data of [25]. The critical parameters were derived on $\alpha$ = 0.11, $\beta$ = 0.325, and $\Delta$ = 0.5 following from theoretical estimates [26-28].

Table 2 gives the resulting k and $\xi_y$. The other parameters there have been derived by least squares from the entire data set. Small values of $\xi_y$ for the first two concentrations (1.6 for x = 0.0986 and 1.7 for x = 0.3995) indicate a renormalization region for $\tau \ll 10^{-4}$-$10^{-3}$ [$\varphi \ll 1$, see (21)], which can be observed from the specific-heat depression on the critical isochores (Fig. 1). The $\xi_y$ for the third concentration is large (9.0 for x = 0.8400), and the renormalization region is not accessible to experiment ($\tau \ll 10^{-9}$), but even here the behavior of the isochoric specific heat differs from that for a pure substance.

Calculations and comparison with experiment on other isochores are given in Figs. 2-4. The mean deviation in the measurements from the calculated values for $|\Delta\rho| \le 0.4$ and $10^{-3} \le \tau \le 10^{-1,5}$ are random and are in the range 2-4%, which corresponds approximately to the experimental accuracy. However, when the transition line is approached closely, $\tau_S \le (10^{-3}$-$10^{-4})$ ($\tau_S = T/T_S - 1$, where $T_S$ is the transition temperature), there is an increase of up to 10-15% in the calculation error because here one cannot simply replace $\tau(x)$ by $r(x)$ in (11) in order to pass to noncritical densities, strictly speaking. Theoretical analysis shows that (7) must here be replaced by the equivalent

$$\Delta\rho = k\left(\frac{\varphi_2}{1+\varphi_2}\right)^{\nu/2} r^{\beta}\theta - B_3\tau, \tag{27}$$

where $\varphi_2 = r\xi_2^{1/\gamma}$ and $\xi_2$ is a new nonuniversal parameter. This instead of (7) is used in (2)-(6) together with P, ρ, T, and x data to determine all the nonuniversal constants, which we consider should improve the accuracy in the equations and extend them to the entire critical region.

## NOTATION

$C_{V,x}$, isochoric specific heat, J/kg·K; $T_c$, critical temperature, K; $\rho_c$, critical density, kg/m³; x, concentration, molar fraction; $P_c$, critical pressure, MPa; V, volume, m³; R, gas constant; F, free energy of solution, J/kg; τ and Δρ, temperature and density deviations from critical value, r and θ, Schofield's radial and angular variables; ψ, gauge functions; $a$, c, d, f, $B_0$, $B_3$, $m_i$, $f_i$, nonuniversal constants in the free-energy expression; $\Phi_S$, universal function; φ, argument in universal function; $\xi_y$, renormalization parameter; critical subscripts: α, specific heat; γ, compressibility; β, boundary curve; Δ, nonasymptotic terms; M, specimen mass, kg; $U_h$ and $U_s$, potential differences across calorimeter heater and standard coil, V; Δt, heating time, sec; $R_s$, standard coil resistance, Ω; $C_c$, calorimeter heat capacity, J/kg·K; ΔT, calorimetric step, K.

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# PHASE TRANSITIONS IN SLOT SYSTEMS FOR SMALL Kn NUMBERS

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The combined problems of sublimation of a thin deposit on the walls of a narrow slot and of freezing-on of a desublimate layer on the walls are considered.

Weakly nonequilibrium phase transitions on the surfaces of parallel plates forming slot devices with the process rate depending substantially on the phase resistance were investigated in [1] by using the methods of molecular kinetics. Our aim is to analyze the processes whose rate is determined almost entirely by the hydraulic resistance of the slot system and the thermal resistance of the walls, as the effect of phase resistance is negligible.

In considering viscous and molecular-viscous sublimate flows, which correspond roughly to the Kn ≪ 0.01 and 0.01 < Kn < 0.1 ranges, we can use with an accuracy sufficient for technological purposes the ordinary Navier–Stokes equations. However, corrections for slippage, thermal slip (creep), and the temperature jump must be introduced in the boundary conditions. If the height of the slot device is small in comparison with its plane dimensions ($\gamma \ll 1$), the continuity and momentum equations can be conveniently represented in dimensionless form:

$$\frac{\partial}{\partial\zeta}\left(\frac{\Pi}{\Theta}w\right) = -\nabla\left(\frac{\Pi}{\Theta}\bar{\mathbf{u}}\right), \tag{1}$$

$$\begin{aligned}\frac{\partial\Pi}{\partial\zeta} = \gamma^2\bar{\mu}\frac{\partial^2 w}{\partial\zeta^2} - \gamma^2\mathrm{Re}_*\frac{\Pi}{\Pi_*\Theta}\left[(\bar{\mathbf{u}}\nabla)w + w\frac{\partial w}{\partial\zeta}\right] + {}\\ + \gamma^4\bar{\mu}\nabla^2 w - \left(\frac{\bar{\mu}}{3} + \bar{\mu}'\right)\gamma^3\frac{\partial}{\partial\zeta}\left[\frac{\bar{\mathbf{u}}\nabla(\Pi/\Theta) + w\partial(\Pi/\Theta)/\partial\zeta}{\Pi/\Theta}\right],\end{aligned} \tag{2}$$

$$\frac{\partial^2\bar{\mathbf{u}}}{\partial\zeta^2} = \frac{1}{\bar{\mu}}\nabla\Pi + \frac{\mathrm{Re}_*\Pi}{\Pi_*\Theta\bar{\mu}}\left[(\bar{\mathbf{u}}\nabla)\bar{\mathbf{u}} + w\frac{\partial\bar{\mathbf{u}}}{\partial\zeta}\right] - \gamma^2\nabla^2\bar{\mathbf{u}} + \left(\frac{1}{3} + \frac{\bar{\mu}'}{\bar{\mu}}\right)\gamma^2\nabla\left[\frac{\bar{\mathbf{u}}\nabla(\Pi/\Theta) + w\partial(\Pi/\Theta)/\partial\zeta}{\Pi/\Theta}\right]. \tag{3}$$

The energy equation will be needed only to demonstrate that, in these processes, the variation of the sublimate temperature occurs almost exclusively along the walls of the slot device. However, in order to avoid the impression that some of the neglected caloric effects

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*Deceased.

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