Isomorphous equation of state in a broad vicinity of the critical point of a binary mixture

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An isomorphous equation of state is obtained on the basis of an expanded scaling-theory state equation for binary mixtures near liquid–gas critical points. The equation is theoretically analyzed and numerically verified. Critical phenomena in dilute solutions and concentrated mixtures are considered in detail, and the normalization of the critical exponents in the investigated systems is made more precise. The possibility of a universal description of critical phenomena in such systems is considered.

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1. INTRODUCTION

The fluctuation theory of phase transitions (see Refs. 1 and 2) has yielded not only numerical values of critical exponents, but also the equation of state near critical points. Moreover, allowance for the non-asymptotic terms expanded greatly the region of applicability of the scaling-theory equation of state.

The scaling-theory equation of state, however, can be rigorously calculated only for systems with isolated transition points describable by two independent variables, whereas in real objects, transitions proceed mainly on critical lines or surfaces. The problem of extending scaling theory (ST) to include more complicated systems is solved on the basis of the isomorphism hypothesis,[3,4] which has been further corroborated and developed in recent years (see Refs. 5 and 6 and the literature cited therein).

In Refs. 4 and 7 they not only determined the conditions for the choice of the isomorphous variables, but also verified experimentally the isomorphism hypothesis, using as an example the isochoric heat capacity in the vicinity of liquid–gas critical points of two systems: ethane + carbon dioxide and ethane + heptane. At that time, however, the lack of an equation of state in explicit scaling form made a comparison of theory with experiment difficult, and the analysis of the experimental data in Ref. 7 was qualitative in character.

In this paper we use an expanded scaling-theory equation of state for a pure substance to obtain an isomorphous equation of state of binary mixtures near the line of liquid–gas critical points. The derived equation is theoretically analyzed and numerically verified. Critical phenomena in dilute solutions and concentrated mixtures are considered in detail, and the renormalization of the critical exponents in the investigated systems is made more precise. The influence of the asymmetry of a real liquid on the behavior of binary critical mixtures is analyzed and the possibility is considered of a universal description of critical phenomena in such system. Since the expressions are unusually cumbersome and the solution of the system of transcendental equations necessitates a change from experimental to isomorphous variables, the equation of state for mixtures cannot be represented in an explicit analytic form. Numerical methods are therefore used for the comparison with experiment and for the calculation of the thermodynamic quantities.

2. ISOMORPHOUS EQUATION OF STATE

An analysis, based on the isomorphism hypothesis, of the conditions under which the system is stable to a change of the corresponding order parameter shows[4] that the form of the thermodynamic potential does not change on going from a pure liquid to binary solutions if one fixes the chemical potential of the solution

$$\tilde{\mu}=\mu_2-\mu_1, \tag{1}$$

in which case the isomorphous thermodynamic potential is

$$F(T,\rho,\tilde{\mu})=F^*(T,\rho,x)-\tilde{\mu}x(T,\rho,\tilde{\mu}), \tag{2}$$

where F^* is the free energy of the solution per mole, and $x=N_1/(N_1+N_2)$ is the concentration of the solution.

Assuming the expression arrived at in the ST (see Refs. 8 and 9) for the free energy as a function of the temperature T and of the density ρ in the vicinity of the liquid–vapor critical point of a pure substance, the isomorphous thermodynamic potential per mole of the binary solution is of the form[1)]

$$F(T,\rho,\tilde{\mu})=\frac{1}{\rho}\Psi(r,\theta,\tilde{\mu})+F_0(T,\rho,\tilde{\mu}), \tag{3}$$

where r and θ are polar coordinates connected with the dimensionless density $\Delta\rho(\tilde{\mu})=\rho/\rho_{\text{cr}}(\tilde{\mu})-1$ and temperature $\tau(\tilde{\mu})=T/T_{\text{cr}}(\tilde{\mu})-1$ by the relations

$$\tau=r(1-b^2\theta^2),\quad \Delta\rho=kr^\beta\theta, \tag{4}$$

while the scaling function $\Psi(r,\theta)$, with account taken of the following ST approximations obtained in Ref. 10, is

$$\Psi(r,\theta)=\frac{1}{2}\frac{ak}{b^2}r^{2-\alpha}\left[\frac{2\beta(b^2-1)}{2-\alpha}+\frac{2\beta(2\gamma-1)}{\gamma(1-\alpha)}(1-b^2\theta^2)\right.$$
$$\left.+\frac{2\beta-1}{\alpha}(1-b^2\theta^2)^2\right]-\frac{1}{2}\frac{kc}{b^2}\frac{r^{2-\alpha+\Delta}}{1-\alpha+\Delta}\left[\frac{\Delta-\gamma}{2-\alpha+\Delta}+(1-2\beta)b^2\theta^2\right]. \tag{5}$$

Here γ, β, and α are respectively the critical exponents of the isomorphous coefficient of isothermal compressibility, of the coexisting-phase line in terms of the isomorphous variables, and of the isomorphous isochoric heat capacity, and Δ is the critical exponent that determines the behavior of the nonasymptotic terms

$$b^2=(\gamma-2\beta)/\gamma(1-2\beta) \text{ и } k=[(b^2-1)/z_0]^\beta$$

(z_0 is the value of the parameter $z = \tau/|\Delta\rho|^{1/\beta}$ on the coexistence curve). In Eq. (3), $F_0(T, \rho, \tilde\mu)$ is an analytic function of the temperature, density, and chemical potential, and goes over at constant into the corresponding functions for a pure substance; with this taken into account, F_0 can be represented as a series in powers of $\Delta\tilde\mu$:

$$F_0(T,\rho,\tilde\mu)=\frac{1}{\rho}(f_1\tau^2(x)+f_2\tau^3(x))$$
$$+m_1\tau^2(x)+m_2\tau^3(x)-\frac{1}{2}\frac{dx_{cr}}{d\tilde\mu}(\Delta\tilde\mu)^2-x_{cr}\frac{T}{T_{cr}}\Delta\tilde\mu, \tag{6}$$
$$\Delta\tilde\mu=\tilde\mu(T,\rho,x)-\tilde\mu(T_{cr},\rho_{cr},x),$$

where a, c, f_1, f_2, m_2, m_1 are constants, $x_{cr} = x(T_{cr}(\tilde\mu), \rho_{cr}(\tilde\mu), (\tilde\mu)$. Thus, relations (2)–(6) determine in fact the equation of state of a binary mixture in the critical region.

To calculate the singularities of the actually measured thermodynamic quantities [at a fixed concentration $x = -(\partial F/\partial\tilde\mu)_{T,\rho}$], we use a method proposed in Refs. 3 and 4. Expanding $F(T, \rho, \tilde\mu)$ in a series about the critical point $\tilde\mu = \tilde\mu_{cr}$, $T = T_{cr}(x)$, $\rho = \rho_{cr}(x)$ and representing $T_{cr}(\tilde\mu)$, $\rho_{cr}(\tilde\mu)$ in the form

$$T_{cr}(\tilde\mu)=T_{cr}(x)+\frac{dT_{cr}}{d\tilde\mu}\Delta\tilde\mu,\quad \rho_{cr}(\tilde\mu)=\rho_{cr}(x)+\frac{dT_{cr}}{d\tilde\mu}\Delta\tilde\mu, \tag{7}$$

we obtain, taking into account (6) and the condition $x - x_{cr} = 0$,

$$\frac{T}{T_{cr}^2}\frac{1}{\rho}\left(\frac{\partial\Psi}{\partial\tau}\right)_{T,\rho,\tilde\mu}\frac{dT_{cr}}{d\tilde\mu}+\frac{1}{\rho^2}\left(\frac{\partial\Psi}{\partial\Delta\rho}\right)_{T,\rho,\tilde\mu}\frac{d\rho_{cr}}{d\tilde\mu}=-\frac{\partial x_{cr}}{d\tilde\mu}\Delta\tilde\mu. \tag{8}$$

Equation (8) is basic in the analysis of critical binary solutions, since it is used for the transition from the surface $\tilde\mu$ = const to x = const at each fixed value of the density and temperature, and to calculate the singularities of the actually measured quantities. In particular, to calculate the heat capacity $C_{V,x} = T(\partial S/\partial T)_{V,x}$ we separate from (2) the terms connected with the entropy, and obtain from (3) and (8)

$$\frac{C_{V,x}}{T}=-\frac{1}{\rho}\left(\frac{\partial^2\Psi}{\partial T^2}\right)_{\rho,\mu}-\left(\frac{\partial^2F_0}{\partial T^2}\right)_{\rho,\mu}+\left(\frac{\partial^2F_0}{\partial\mu\,\partial T}\right)^2\Big/\left(\frac{\partial^2F}{\partial\mu^2}\right)_{\rho,T}. \tag{9}$$

We have taken into account here the fact indicated by Gorodetskiĭ and Mikulinskiĭ,[11] that the isomorphous path is determined by the equation $\mu = \tilde\mu + c_1T$, and not by expression (1), and this leads only to the appearance of a term $\sim x$ in the expression for the entropy

$$S=-\left(\frac{\partial F}{\partial T}\right)_{\rho,\mu}-c_1x \tag{10}$$

leaving the remaining relations unchanged. We shall therefore write simply μ in place of $\tilde\mu$, taking Eq. (10) into account.

Analysis of (9) with allowance for (3), (7), and (8) shows that at

$$\frac{\partial^2\Psi}{\partial\tau^2}\gg2\frac{\partial\Psi}{\partial\tau}+2y\frac{\partial^2\Psi}{\partial\Delta\rho\,\partial\tau}+y^2\left(\frac{\partial\Psi}{\partial\Delta\rho}+\frac{\partial^2\Psi}{\partial\Delta\rho^2}\right)+T_{cr}{}^2\rho_{cr}\left(\frac{dT_{cr}}{d\mu}\right)^{-2}\frac{\partial^2F_0}{\partial\mu^2} \tag{11}$$

the critical exponent of the heat capacity reverses sign, and the heat capacity has the asymptotic value

$$\frac{C_{V,x}}{T}=\rho T_{cr}{}^2\left(\frac{dT_{cr}}{d\mu}\right)^{-2}\left(\frac{\partial F_0}{\partial\mu\,\partial T}\right)\left[2\left(\frac{dT_{cr}}{d\mu}\right)^{-1}\frac{\partial^2F_0}{\partial\mu^2}+\frac{\partial^2F_0}{\partial\mu\,\partial T}\right]\left(\frac{\partial^2\Psi}{\partial\tau^2}\right)^{-1}$$
$$-\left[\frac{\partial^2F_0}{\partial\tau^2}+2\left(\frac{dT_{cr}}{d\mu}\right)^{-1}\frac{\partial^2F_0}{\partial\mu\,\partial T}+\left(\frac{dT_{cr}}{d\mu}\right)^{-2}\left(\frac{\partial^2F_0}{\partial\mu^2}\right)\right]+$$
$$+O(yr^{1-\alpha-\beta}+y^2r^{2-\alpha-2\beta}), \tag{12}$$
$$y=(T_{cr}/\rho_{cr})(d\rho_{cr}/dx)(dT_{cr}/dx)^{-1}.$$

3. RENORMALIZATION OF THE CRITICAL EXPONENTS

For a quantitative analysis of the renormalization effect we consider the solution of Eq. (8) on the isochor $\Delta\rho(x) = 0$. In the case $z(\mu) \gg 1(\theta(\mu) \ll 1,\ r(\mu) \approx \tau(\mu))$ and $y \lesssim 1$ Eq. (8), with allowance for (5), then takes the form

$$\tau(\mu)\left(\frac{A}{1-\alpha}-\tau^\alpha(\mu)A\xi\right)=-\rho_{cr}T_{cr}\left(\frac{dT_{cr}}{d\mu}\right)^{-1}x\tau(x)-A\xi\tau(x), \tag{13}$$

and at

$$\tau(\mu)\ll\xi^{-1/\alpha}, \tag{14}$$

which also corresponds to the condition (11), we have

$$\tau(\mu)=(\tilde\xi\tau(x))^{1/(1-\alpha)};\quad A=-\frac{ak\gamma(\gamma-1)}{2\alpha b^2}, \tag{15}$$
$$\xi=\frac{T_{cr}}{A}\rho_{cr}\left(\frac{dT_{cr}}{dx}\right)^{-1}\left(\frac{dT_{cr}}{d\mu}\right)^{-1},\quad \tilde\xi=\frac{1-\alpha}{A}\left[-\rho_{cr}T\left(\frac{dT_{cr}}{d\mu}\right)^{-1}x-A\xi\right].$$

At

$$\tau(x)\ll\xi^{-1/\alpha} \tag{16}$$

we obtain from (12), with allowance for (15),

$$\frac{C_{V,x}}{T}=A^*\tau^\varkappa(x)+B^*+O(\tau(x)); \tag{17}$$
$$\varkappa=\frac{\alpha}{1-\alpha},\quad A^*=\rho_{cr}T_{cr}\left(\frac{dT_{cr}}{d\mu}\right)^{-1}x\left[2\left(\frac{dT_{cr}}{dx}\right)^{-1}+\frac{x}{T_{cr}}\right]A^{-1}\xi^{\alpha/(1-\alpha)},$$
$$B^*=-\frac{2}{T_{cr}}\left(\frac{f_1}{\rho_{cr}}+m_1\right)+\frac{2x}{T_{cr}}\left(\frac{dT_{cr}}{d\mu}\right)^{-1}+\left(\frac{dT_{cr}}{d\mu}\right)^{-1}\left(\frac{dT_{cr}}{dx}\right)^{-1}. \tag{18}$$

This means that when condition (16) is satisfied a renormalization $-\alpha \to \alpha/(1-\alpha)$ of the critical exponent of the heat capacity takes place, and when $\tau(x)$ tends to zero the heat capacity $C_{V,x}$ of a binary solution remains finite rather than tend to infinity as does C_V in pure substances.

In the region $\tau(x) \gg \xi^{(\alpha-1)/\alpha}\tilde\xi^{-1}$ the condition (11) is not satisfied, $\tau(\mu) \approx \tau(x)$ and

$$C_{V,x}/T\sim\tau^{-\alpha}(x)+\text{const}, \tag{19}$$

i.e., there is no renormalization and the heat capacity behaves in analogy with the heat capacity in a pure substance.

The case of dilute solutions ($x \ll 1$), which is of interest from the practical point of view, can be regarded as a particular case of the equations obtained. Indeed, putting according to Ref. 4

$$dx_{cr}/d\mu=Mx/RT_{cr} \tag{20}$$

(R is the universal gas constant and M is the molecular weight), we find from (16) that at

$$\tau(x)\ll\left[\frac{AM}{RT_{cr}}\frac{dT_{cr}}{dx}x\right]^{1/\alpha} \tag{21}$$

a renormalization of the type (17) is observed, and the solution cannot be regarded as dilute at any x. In this case, taking (17) and (18) into account, we have

$$C_{V,x} \sim \tau(x)^{\alpha/(1-\alpha)}/x + 1/x + \text{const}, \tag{22}$$

i.e., as the critical point of a pure substance is approached along the critical line of the solution the heat capacity $C_{V,x}$ tends to infinite like $1/x$.

Equation (15) and all our estimates were obtained under the condition $z(\mu) \gg 1$. At $y \gg 1$, however, i.e., when the critical density has a stronger dependence on the concentration than the critical temperature, there can exist a temperature region where this condition is violated. It follows from (15) that the condition $z(\mu) \gg 1$ on the isochor $\Delta\rho(x) = 0$ is satisfied (in the region of the positive exponent) only at

$$\tau(x) \ll \tilde{\xi}^{\beta/(1-\alpha-\beta)} y^{-(1-\alpha)/(1-\alpha-\beta)}, \tag{23}$$

so that to analyze the character of the renormalization in the case of large y it is necessary to find a solution of (8) for values $z(\mu) \ll 1$. At $z(\mu) \ll 1$ ($|\theta(\mu| \approx b^{-1}$, $r \approx (b/k)^{1/\beta} |\Delta\rho|^{1/\beta}$), and $y \ll 1$ Eq. (8) with allowance for (7) takes the form

$$\Delta\rho(\mu)^{(1-\alpha)/\beta} - (1-\alpha)\xi \frac{A}{\tilde{A}} y^{-1} \Delta\rho(\mu) = [\tilde{\xi} + (1-\alpha)\xi] \frac{A}{\tilde{A}} \tau(x), \quad \tilde{A} = A \frac{2\alpha\beta}{1-\gamma} \left(\frac{b}{k}\right)^{(1-\alpha)/\beta}, \tag{24}$$

from which, under the condition

$$\xi^{\beta/(1-\alpha-\beta)} y^{-(1-\alpha)/(1-\alpha-\beta)} \ll \tau(x) \ll \xi^{-\beta/\alpha} y^{-1} \tag{25}$$

and taking (14) into account, we obtain

$$\Delta\rho(\mu) = \left[\frac{A}{\tilde{A}} (\tilde{\xi} + (1-\alpha)\xi) \tau(x)\right]^{\beta/(1-\alpha)}.$$

The renormalization of the critical exponent of the heat capacity $C_{V,x}$ has thus the same form (17) as before. This differs from the result $\varkappa' = \alpha/\beta$ of Ref. 7. It follows from (24) that the solution $\Delta\rho(\mu) = y\tau(x) \times (2-\alpha)/(1-\alpha)$ and the exponent $\varkappa = \varkappa'$ are obtained under the condition

$$\tau(x) \ll \xi^{\beta/(1-\alpha-\beta)} y^{-(1-\alpha)/(1-\alpha-\beta)},$$

which corresponds to the condition (23), and consequently contradicts the considered case $z(\mu) \ll 1$.

It is seen thus that the character of the renormalization of the critical exponent of the heat capacity $C_{V,x}$ in the region $z(\mu) \ll 1$ does not differ substantially from the result for $z(\mu) \gg 1$. The only difference is the smearing of the renormalization region and the renormalizations of the constants in (17).

A similar analysis under the condition $\tau(x) = 0$ on the critical isotherm shows that in the case $z(\mu) \gg 1$, $y \ll 1$ and under the condition

$$\Delta\rho(x) \ll (y^{-1}\xi)^{\beta/(1-\alpha-\beta)} \tag{26}$$

the heat capacity takes the asymptotic form

$$C_{V,x} \sim |\Delta\rho(x)|^{\alpha/(1-\alpha)} + \text{const} \tag{27}$$

and the renormalization is therefore of the type $-\alpha/\beta \to \alpha/(1-\alpha)$. At $z(\mu) \ll 1$ and $y \gtrsim 1$ the character of the renormalization does not change, and in the density region

$$\left(y^{-1} \frac{A}{\tilde{A}} \xi\right)^{\beta/(1-\alpha-\beta)} \ll \Delta\rho(x) \ll y\xi^{-1/\alpha} \tag{28}$$

the exponent $\varkappa$ remains the same as before.

It must be emphasized in this connection that all our conclusions are strictly speaking valid only for the region defined by the inequalities (16) and (26), inasmuch as at higher values of y, temperatures, and densities the important terms in (8), (9), and (12) are not only $\sim y r^{1-\alpha-\beta}$ and $\sim y^2 r^{2-\alpha-2\beta}$, but also the higher-order approximations of the ST, i.e., the terms $\sim r^{\Delta-\alpha}$. It is precisely the failure to take all the terms into account in the reduction of the experimental data on the heat capacity $C_{V,x}$ which led in Ref. 7 to the overestimated value $\varkappa = 0.37 \pm 0.08$. Consequently, for a rigorous quantitative check on the isomorphism hypothesis it is necessary to solve numerically the system (4)–(9) and to compare the calculation results directly with the experimental data.

4. QUANTITATIVE CHECK ON THE ISOMORPHISM HYPOTHESIS

For a quantitative check on the isomorphism hypothesis, the complete ST equation (5) together with Eqs. (7) and (8) were combined into a single parameter-optimization program. We used for this purpose the algorithm of the paper of Berestov and Malyshev,[12] which not only yields the parameters of the model and their variances and covariations, but can also check the adequacy of the employed model, using the Fisher criterion $F_{0.95}(m, n-m)$ for this purpose.

The calculation results and their comparison with the experimental data on the heat capacity $C_{V,x}$ of pure ethane and of two solutions of heptane in ethane[13] with two concentrations (0.94 and 3.16 mol.%) are shown in Fig. 1.

It must be emphasized that here and below, in accord with the main premises of the ST and the isomorphism hypothesis, the calculations were performed at fixed values $\alpha = 0.112$ and $\beta = 0.340$, obtained by reduction of precise experimental data on argon, which agree with the calculations (see Ref. 14). The correction exponent was fixed at the value $\Delta = 0.45$, which follows from the theoretical estimates. In addition, the values of a and k were set equal to the corresponding values for pure

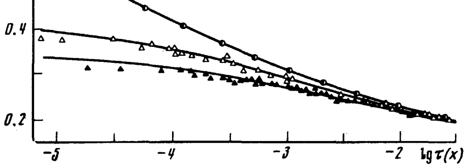

FIG. 1. Comparison of the experimental[13] and calculated values of $C_{V,x}/T$ in an ethane+heptane system on the critical isochor [△—x = 0.0093, ▲—x = 0.00315, ◐—pure ethane, solid lines—calculation in accord with Eq. (9)].

ethane. The values of dT_{cr}/dx and $d\rho_{cr}/dx$ were taken by us from Ref. 7. The parameters c, m_1, and m_2 were determined by reducing the experimental data. Analysis of the calculation result shows that in the methodologically reliable temperature range $10^{-4} \lesssim \tau(x) \lesssim 3 \cdot 10^{-2}$ the deviations of the experimental heat capacities $C_{V,x}$ from the calculated ones do not exceed the experimental error ($\Delta C_{V,x} \sim 0.5$ to 1%), and a comparison of the calculated values of $F_{0.95}$ [$F_{0.95}(7.29) = 1.081$ for $x = 0.0094$ and $F_{0.95}(6.40) = 1.613$ for $x = 0.0315$] with the tabulated ones shows that the proposed equation describes the experimental data adequately. An estimate of the width of the normalization region shows that in the case $x = 0.0094$, $\xi = 4.36$, $y = -2 \pm 1$ and in accord with (21) the boundary of the renormalization region corresponds to $\tau(x) \approx 4 \times 10^{-7}$. Consequently, all the experimental points are in some transitional temperature region closely adjacent to the normalization region, and it is this which explains the experimentally observed dip in the heat capacity. In the case $x = 0.0315$, $\xi = 2.6$, $y = 10$ and the estimate in accord with (21) yields $\tau(x) \approx 7 \cdot 10^{-5}$, and, in view of the influence of y on the smearing of the renormalization region, it can be stated that the experimental points in the temperature region $\tau(x) \lesssim 10^{-4}$ are located in the renormalization region, in good agreement with the experimental results.

For an experimental verification of the isomorphism hypothesis, particular interest attaches to the ethane + carbon dioxide system, the critical line of which has two singular points: a minimum of $T_{cr}(x)$ and the point of intersection of the critical line with the line of the azeotropes. At the minimum point of $T_{cr}(x)$ (43.6 mol.% C_2H_6, see Fig. 2) we have $\xi = 0$ and according to the condition (16) there is no renormalization. Since, however, $d\rho_{cr}/dx \neq 0$ and $dx_{cr}/d\mu \neq 0$, Eq. (8) has a nonzero solution $\Delta\mu$ whose absolute numerical value increases with increasing distance from the critical point. The increase of $\Delta\mu$ shifts the critical isochor, and this in turn should lead to a certain additional dip of the heat capacity, described by the last term of (9).

Thus, at the minimum point of $T_{cr}(x)$ the heat capacity $C_{V,x}$ of the mixture should increase more slowly than the heat capacity of the pure substance. This qualitative conclusion is confirmed both by an analysis of the experimental data and by exact numerical calculations in accord with Eq. (9). The calculation results and their comparison with experiment are shown in Fig. 2. In the calculations, the parameters dT_{cr}/dx and $d\rho_{cr}/dx$ were taken from Ref. 7, and the value of $dx_{cr}/d\mu$, found by trial and error to obtain a best fit to the experimental data, was $dx_{cr}/d\mu = 6.193 \cdot 10^{-4}$ mol/J, approximately four times larger than the estimates based on the equations (20) for dilute solutions. It is seen from the figure that within the limits of the experimental error, the deviation of the experimental $C_{V,x}$ from the calculated amounts on the average to 0.5–1% and does not exceed 2%, while a comparison of the calculated value $F_{0.95}(6.15) = 0.642$ with the tabulated one attests to the adequacy of the proposed model.

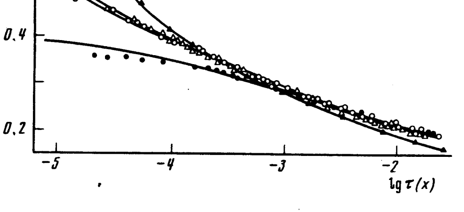

FIG. 2. Comparison of the experimental[13] and calculated values of $C_{V,x}/T$ in the ethane + carbon dioxide system on the critical isochor [○—azeotropic mixture, $x = 0.282$, △ $-x = 0.436$, ● $-x = 0.72$, ▲—pure carbon dioxide,[9] solid lines—calculation in accord with Eq. (9)].

The character of the singularity of the isochoric heat capacity near the critical point of an azeotropic mixture was considered earlier.[4,7,15] Various assumptions were made in these references concerning the value of $dx_{cr}/d\mu$ at the critical point of an azeotropic mixture. From the assumption that $dx_{cr}/d\mu \neq 0$, it follows that $C_{V,x}$ is finite at the critical point of an azeotropic mixture, but in view of the smallness of $T_{cr}^{-1} dT_{cr}/dx$ the renormalization region is experimentally unattainable ($\tau(x) \lesssim 10^{-12}$). In Ref. 7 it is proposed, on the basis of the condition $dx_{cr}/d\mu = 0$, that $C_{V,x}$ increases without limit at the azeotropic critical point. It must be stated that the available experimental data and the present-day experimental accuracy in this region cannot provide an unequivocal answer to this question. We have performed calculations for two cases: $dx_{cr}/d\mu = 0$ and $dx_{cr}/d\mu = 4.386 \cdot 10^{-4}$ mol/J (obtained, as in the preceding variant, by trial and error). Comparison of the calculated values of $F_{0.95}$ [$F_{0.95}(6.30) = 1.2$ in the first case and $F_{0.95}(6.30) = 0.32$ in the second] with the tabulated values shows that both variants are equivalent from the statistical point of view. An analysis of the obtained parameters has shown, however, that in the case $dx_{cr}/d\mu = 0$ the obtained values $a = 4043$ J • mol/cm^3 and $c = 10050$ J • mol/cm^3 are outside the range valid for pure substances (see Ref. 8). The reason may be that the isochoric heat capacity $C_{V,x}$ behaves differently in an azeotropic critical mixture than in a pure substance, it is therefore more justified to use for the calculation the complete isomorphous equation (9) with a nonzero value of $dx_{cr}/d\mu$. An analysis of the calculation results for the second case (see Fig. 2) shows that the difference between the calculation and experiment does not exceed 2%. An estimate of the renormalization region in accord with Eq. (16) with a value $\xi = 23$ determined from the calculated a and $dx_{cr}/d\mu$ yields $\tau(x) \ll 10^{-14}$, and consequently all the experimental data lie far from the renormalization region. Interest attaches in this connection to the behavior of the heat capacity $C_{V,x}$ in a solution that is symmetric to azeotropic: $x = 0.72$ (black circles in Fig. 2), for which the values of dT_{cr}/dx, $d\rho_{cr}/dx$, ξ, and consequently of the limits of the renormalization region are practically equal to the azeotropic ones. The experimentally observed dip in the heat capacity $C_{V,x}$ can likewise not be attributed to the influence of the large value $y = 9.3 \pm 1.5$, since an estimate of the limit of the smearing of the renormalization region yields, according to Eq. (25), $\tau(x) \ll 10^{-5}$ and practically coincides with the estimate for the azeotropic solution. At the same time, a numerical reduction has shown that the isomorphous equation describes adequately the experimental data. This confirms the conclusion that, even in the region far from the renormalization region, a physically rigorous and correct comparison of the experimental data with the theory calls for the use of the complete isomorphous equation of state and practically this entire region must be regarded as transitional.

From the point of view of a numerical check of the isomorphism hypothesis, an important question is the estimate of the width of the temperature interval $\tau(x)$ and density interval $\Delta\rho(x)$ in which the isomorphous equation of state can be used for an adequate description of the experimental data. We have used for this purpose the equation obtained for the description of the experimental data on the heat capacity $C_{V,x}$ for three concentrations (10.88, 18.2, and 48.85 mol.% Ar) on different isochors of an Ar–Co$_2$ mixture.[16] A preliminary analysis of the experimental data on the heat capacity $C_{V,x}$ from the point of view of renormalization (the critical isochor was assumed to be in this case the isochor with the maximum heat-capacity anomaly, the parameter a was calculated using the additive law, and $dx_{\text{cr}}/d\mu$ was determined from Eq. (20) for a dilute solution) has shown that in the case of low concentrations $\xi = 15.8$ for $x = 0.1088$ and $\xi = 7.8$ for $x = 0.182$, and consequently all the experimental points lie outside the renormalization region [the boundary of the region $\tau(x) \sim 10^{-12}$–10^{-8}]. At a concentration $x = 0.4885$ we have $\xi = 3.1$ and consequently all the points with $\tau(x) < 10^{-5}$ lie in the renormalization region, as is well seen from the dip of the heat capacity $C_{V,x}$ on the critical isochor compared with the preceding case. A numerical reduction of the experimental data has shown that for the case when there is no renormalization ($x = 0.109$) and the behavior of the heat capacity is determined mainly by the form of the singular part of the thermodynamic potential, as well as for the case when renormalization takes place and the regular part is the principal one ($x = 0.488$), only four constants (f_1, f_2, m_1, m_2) are sufficient for an adequate description of the experimental data in Eq. (6), in analogy with a pure substance. This indicates that the isomorphous equation offers a physically correct description of the character of the renormalization and of the behavior of the heat capacity $C_{V,x}$ of a binary mixture in a wide range of the state parameters [$|\Delta\rho(x)| \lesssim 0.2$ and $10^{-3} \leqslant \tau(x) \leqslant 10^{-1}$] near the line of the liquid-gas critical points. At the same time, for an adequate description of the experimental data at $x = 0.182$ in Eq. (6) it was necessary to add a polynomial of third degree in the density and temperature. In addition, the accuracy of the calculation for the mixtures turned out to be somewhat lower than the accuracy reached for individual substances.[8,9] The reason for this result is that in critical binary solutions, in contrast to pure substances, the use of the regular part of the thermodynamic potential influences strongly the calculation accuracy in the expanded model. An incorrect choice of the regular part may even make the model inadequate for use in a wide range of densities and temperatures. Experimental data in the immediate vicinity of the critical point are therefore highly desirable for a numerical check on the isomorphism hypothesis. In this sense a description of the liquid–vapor boundary curve in the vicinity of the critical point is of great interest, particularly that part of the boundary curve that lies in the temperature region where retrograde concentration is possible. We have reduced the experimental data on the equilibrium curve of Ar–CO$_2$ mixtures with three densities.[16] The calculation algorithm was the same as before, except that Eq. (9) was replaced by the equation for the coexistence curve in the isomorphous variables

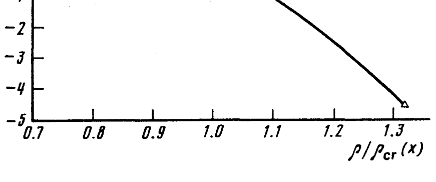

FIG. 3. Segment of the liquid–vapor equilibrium line in the Ar–CO$_2$ system: ○ $-x = 0.1088$, ● $-x = 0.182$, △ $-x = 0.4885$ [solid line—calculation in accord with Eq. (29)].

$$\Delta\rho(\tau(\mu)) = \operatorname{sign}(\Delta\rho(\mu))[A_1(\tau(\mu)^{\beta} + A_2(\tau(\mu))^{\beta+\Delta}] + \left(A_3 + \frac{dA_3}{d\mu}\right)(\tau(\mu))^{1-\alpha}. \tag{29}$$

It must be noted that in this equation, in contrast to Eqs. (4) and (5), account is taken not only of the next higher ST approximation, but also the "asymmetry" of a real liquid [the terms $\sim(\tau(\mu))^{1-\alpha}$]. The results of calculation using Eq. (29) and their comparison with the experimental data shown in Fig. 3. It is seen from the figure that some of the experimental data lie in the temperature region $T_s > T_{\text{cr}}(x)$, which is described with good accuracy by an isomorphous equation of state. This means that the isomorphism hypothesis makes it possible to describe a phenomenon such as retrograde condensation, which is important in practice and interesting physically. The calculations have also shown that the parameters A_3 and $dA_3/d\mu$ are sufficiently large statistically significant. As shown in Ref. 17, the corrections to the isomorphous equation for the heat capacity, necessitated by asymmetry, are of the order of $\sim A_3 r^{-\alpha+(\beta+\gamma-1)}$, and the equations that connect the parameters r and θ with the dimensionless temperature τ and density $\Delta\rho$ in a real asymmetrical system are of the form

$$\tau = \tau_{\text{l.g.}} - var^{\beta\delta}\theta(1-\theta^2),$$

$$\Delta\rho = \Delta\rho_{\text{l.g.}} - v\frac{A}{1-\alpha}r^{1-\alpha}\left[1 - \frac{(1-2\beta)(1-\alpha)}{\gamma-1}b^2\theta^2\right],$$

where $\tau_{\text{l.g.}}$ and $\Delta\rho_{\text{l.g.}}$ are the temperature and density of the symmetrical lattice-gas model, which are defined by Eqs. (4), and the proportionality coefficient is

$$v = -A_3\alpha(1-\alpha)b^2(b^2-1)^{1-\alpha}/ak\beta(1-2\beta).$$

As a result of this functional connection between the parameters r and θ, on one hand, and τ and $\Delta\rho$, on the other, the exponents for the correction terms due to asymmetry are substantially smaller on the critical isochor ($\Delta\rho(x) = 0$) than the non-asymmetric terms ($r \sim \tau, \theta \sim \tau^{1-\alpha-\beta}$) and are proportional to $A_3\tau^{-\alpha+(\gamma-\alpha)}$. In addition, since $\gamma - 2\alpha \approx 1$, it is difficult to distinguish them from the terms $\sim\tau(x)$ that appear when the regular part of the heat capacity is expanded in powers of the temperature. The situation is different on the critical isotherm ($\tau(x) = 0$), on which $|\theta| = 1/b, r = |\Delta\rho|^{1/\beta}$. In this case the asymmetric corrections for the heat capacity are of the order of $A_3|\Delta\rho|^{-\alpha+(\beta+\gamma-1)}$ and consequently become commensurate at $|A_3| \geqslant c$ with the non-asymptotic terms in Eqs. (5). This means that to the extend the region of description of the isomorphous state equation to include other isochore, and for a more rigorous check on the isomorphism hypothesis, it is necessary to take into account in Eqs. (5) and (9), besides the non-asymptotic terms, the corrections necessitated by the asymmetry.

5. POSSIBILITY OF A UNIVERSAL DESCRIPTION OF CRITICAL PHENOMENA IN BINARY SYSTEMS

According to Eq. (16), the behavior of all binary systems is determined by the value of the dimensionless parameter $\varphi = \tau^{\alpha}(x)\xi$. In the case of small φ ($\varphi \ll 1$) a renormalization $\tau(\mu) \sim (\tau(x))^{1/(1-\alpha)}$ is observed and the heat capacity on the critical isochor $\rho = \rho_{cr}(x)$ varies like $C_{V,x} \sim (\tau(x))^{\alpha/(1-\alpha)}$. For larger values of φ ($\varphi \gg 1$) there is no renormalization: $\tau(\mu) \sim \tau(x)$, and the heat capacity varies as in a pure substance: $C_{V,x} \sim \tau^{-\alpha}(x) + B$. It is seen thus that the character of the renormalization depends on the universal dimensionless parameter φ, and the heat capacity approaches certain asymptotic values. This means that the thermodynamic potential of such a system can be written, close enough to the critical point, in the form

$$F(T, \rho_{cr}(x)) = A_1\tau^{2-\alpha}(x)F_s(\varphi) + F_0, \tag{30}$$

where $F_s(\varphi)$ is a universal function of its argument with known asymptotic values. At the same time, the individual properties of the objects determine the coefficient A_1 of the singular part, as well as the regular part F_0. For a direct numerical check on this conclusion, we have reduced the data on the isochoric heat capacity of the investigated systems in accord with (30), using the formula

$$\frac{C_{V,x}}{T} = \bar{A}\tau^{-\alpha}(x)F_s''(\varphi) + \bar{B} + \bar{C}\tau(x), \tag{31}$$

where $\bar{A}$, $\bar{B}$, and $\bar{C}$ are fit parameters. The function $F_s(\varphi)$ was chosen in the form

$$F_s(\varphi) = \left(\frac{\varphi}{1+\varphi}\right)^{(2-\alpha)/(1-\alpha)}. \tag{32}$$

It is easy to show that this choice of the function $F_s(\varphi)$ satisfies the asymptotics indicated above. The results of the reduction by means of Eq. (31) are shown in Fig. 4. It is seen from the figure that almost all the experimental points obtained for systems with different concentrations lie on the theoretical curve calculated from Eq. (31). This confirms convincingly the conclusion drawn from the isomorphism, that the phase transitions in various binary systems have a universal (isomorphous) character.

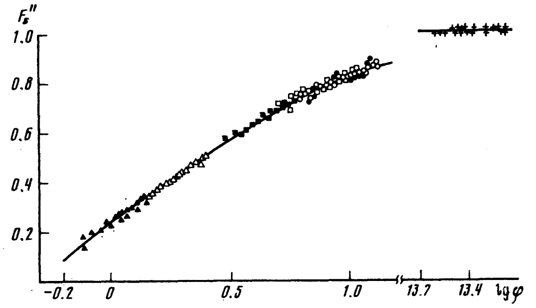

FIG. 4. Universal scaling function $F''(\tau^{\alpha}(x)\xi)$ for the heat capacity; △ – x = 0.0093, ▲ – x = 0.0315 (ethane + heptane system), ○ — azeotropic mixture x = 0.282, + – x = 0.436, ● – x = 0.72 (ethane + carbon dioxide system, see Figs. 1 and 2); solid line—calculation in accord with Eq. (21); □ (x = 0.1088), ■ (x = 0.1558)—experimental data for Ar + CO_2 mixture.[16]

6. CONCLUSION

We have thus obtained here, for the first time ever, a rigorous isomorphic equation of state for binary systems near the line of the liquid–vapor critical points, in accord with the isomorphism hypothesis and on the basis of an expanded linear model of the equation of state of a one-component liquid. A computational-theoretical analysis of the experimental results on the isochoric heat capacity and on the line of coexisting phases has demonstrated the validity of the isomorphism hypothesis and the feasibility of a universal quantitative description, on its basis, of the thermophysical properties in a broad vicinity of the critical points of the mixture. The analysis has shown at the same time that with increasing distance from the critical coexistence points the accuracy of the calculations is strongly affected by the asymmetry of the properties of a real mixture relative to $\rho_{cr}(x)$, as well as by the analytic form of the regular part of the isomorphous thermodynamic potential.

Unfortunately, for mixtures there are still no joint experimental data on the heat capacity and on the dependence of the pressure on the temperature, on the density, and on the concentration in the critical region. Such data and their reduction would make it possible to describe the thermodynamic properties of mixtures as exhaustively as those of pure substances.

1) Equation (3) was derived under the assumption that the chemical potential $\mu(\rho, T) = (\partial\rho F/\partial\rho)_T$ for a liquid has a singularity of the type

$$\mu(\rho, T) - \mu(\rho_{cr}, T) = \Delta\rho|\Delta\rho|^{\delta-1}h_0(z)P_{cr}/\rho_{cr}.$$

The validity of this assumption was investigated by us in detail earlier.[8,9]

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