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EXPERIMENTAL VERIFICATION OF THE ISOMORPHISM HYPOTHESIS OF CRITICAL PHENOMENA

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An experimental investigation of the isochoric specific heat near the liquid-gas critical points is carried out for two binary mixtures, for ethane + carbon dioxide and for ethane + heptane. The results of the measurements as a whole are in accordance with theoretical calculations based on the concept of isomorphism of critical phenomena. Renormalization of the critical specific heat index (α) near the liquid-gas critical points on going from a pure substance to a mixture is observed for the first time. Two types of renormalization, $-\alpha \rightarrow \alpha/(1-\alpha)$ and $-\alpha \rightarrow \alpha/\beta$, are found. The renormalization of the second type is peculiar to liquid systems and may be observed when the critical density depends on the solution concentration much more than the critical temperature does. Results of calculation of the specific heat in various thermodynamic regions are presented

1. INTRODUCTION

THE concept of isomorphism of second-order phase transitions in different systems is used in a recent paper to describe these transitions in the language of a certain "ideal" system in which the character of the singularity is known. This approach was first formulated by Fisher[1]. The main result of[1] is the renormalization of the critical exponents on going from an "ideal" system to a "real" system, and agrees with the results of an investigation of "decorated" lattice models[2-5]. Fisher has proposed that in a "real" system the definition of the ordering field (a quantity conjugate to the ordering parameter) is the same as in the "ideal" system, and therefore his results are applicable only to objects similar to an Ising paramagnet with impurity. In this model, only the critical temperature depends on the impurity concentration, while the magnetic field remains unchanged.

Saam[6] considered the thermodynamics of binary mixtures near the critical liquid-gas points by the method proposed by Fisher. He took into account the change of the "ordering field" in the solution in comparison with the pure substance. The result of[6] is that the isochore specific heat at constant concentration is finite on the critical line (with the exception of the singular points), and that its critical exponent is renormalized in accordance with[1], while the coefficient of the isothermal compressibility and the isobar specific heat at constant concentration have weak singularities. Griffiths and Wheeler[7], analyzing the conditions of the thermodynamic stability in solutions, reached analogous conclusions.

In the most general form, the hypothesis of isomorphism of critical phenomena was formulated in[8]. It is assumed that in the case of correctly chosen (isomorphic) thermodynamic variables the singularities of the principal quantities near transition points of different nature have the same form. The choice of the isomorphic variables is determined by the condition that the stability of the system against changes of the corresponding ordering parameter is lost.

Real experimental conditions, however, impose limitations on the choice of the thermodynamic variables. If the connection between the experimental and isomorphic variables is not analytic, then the character of the singularity changes, and renormalization of the critical exponents takes place. In[8], special attention was paid to an analysis of the possibility of observing renormalization of the critical exponents in a real experiment, and the obtained relations, which contain the measured characteristics of the system, can be quantitatively verified.

To check experimentally on the isomorphism hypothesis, we investigated the isochore specific heat (at constant concentration) in the vicinity of the liquid-gas critical points of two systems, ethane + carbon dioxide and ethane + heptane. The different dependence of the critical parameters of these solutions on their composition makes it possible to observe both asymptotic and transition regions of critical-exponent renormalization, and also to investigate the singular points of the critical lines.

The experimental results agree in the main with the theoretical calculations. One of the most interesting results, in our opinion, is the unusual character of the renormalization of the critical exponent of the specific heat in the ethane-heptane system, which is apparently connected with the fact that there exists a region in which the deviation from the critical temperature at constant concentration is equivalent to the deviation from the critical density in isomorphic thermodynamic space. In connection with this possibility, which is peculiar to the critical phenomena in liquid solutions, we also had to analyze in greater detail than in[8] the dependence of the chemical potential on the density and temperature in different thermodynamic regions.

2. CALCULATION OF THE SPECIFIC HEAT IN DIFFERENT THERMODYNAMIC REGIONS NEAR CRITICAL POINTS OF A BINARY SOLUTION

If we assume the expression that results from scaling theory (see[8]) for the free energy as a function of the temperature T and volume V in the vicinity of the critical liquid-gas point of the pure substance, then the isomorphic thermodynamic potential per mole of binary solution is given by[8]

$$F(T, V, \mu) = F_s\{\tau(\mu), v(\mu)\} + F_0(T, V, \mu), \tag{1}$$

where $F_s = \tau(\mu)^{2-\alpha} f\{v(\mu)/\tau(\mu)^\beta\}$ is the singular part of the potential $F(T, V, \mu)$, $F_0(T, V, \mu)$ is the regular function, μ is the chemical potential of the solution (the difference between the chemical potentials of the components, $\mu = \mu_2 - \mu_1$), $\tau(\mu) = |T - T_c(\mu)|/T_c(\mu)$ ($T_c(\mu)$ is the critical temperature of the solution), $v(\mu) = |V - V_c(\mu)|/V_c(\mu)$ ($V_c(\mu)$ is the critical molar volume of the solution and the condition $v(\mu) \neq 0$ corresponds to the presence of an "ordering field"), α and β are the critical exponents of the isomorphic specific heat ($C_{V,\mu}/T = A\tau(\mu)^{-\alpha} + B$) and of the phase-coexistence curve in the isomorphic variables, and $f\{z(\mu)\}$ is a function with known asymptotic behavior.

To calculate the singularities of the actually measured thermodynamic quantities (at a fixed concentration $x = -\partial F/\partial \mu$), we use the equation $x(T, V, \mu) - x_c = 0$ [8], which determines the physical potential as a function of the temperature and of the density

$$x - x_s = \frac{1}{T_c}\frac{dT_c}{d\mu}\left\{\frac{\partial F_s}{\partial \tau} - B\tau(\mu) + \frac{\partial^2 F_0}{\partial \tau\, \partial v} v(\mu)\right\}$$
$$+ \frac{1}{V_c}\frac{dV_c}{d\mu}\left\{\frac{\partial F_s}{\partial v} + \frac{\partial^2 F_0}{\partial v\, \partial \tau}\tau(\mu)\right\} - \frac{\partial^2 F_0}{\partial \mu\, \partial v} v(x) - \frac{\partial^2 F_0}{\partial \mu\, \partial \tau}\tau(x) + \frac{dx}{d\mu}\Delta\mu = 0. \tag{2}$$

Here

$$\tau(\mu) = \tau(x) - \frac{1}{T_c}\frac{dT_c}{d\mu}\Delta\mu, \tag{3}$$

$$v(\mu) = v(x) - \frac{1}{V_c}\frac{dV_c}{d\mu}\Delta\mu \tag{4}$$

(the total differentials denote throughout differentiation along the critical line $V_c(\mu)$ or $T_c(\mu)$).

To calculate the specific heat $C_{V,x} = T(\partial S/\partial T)_{V,x}$ we separate from Eq. (2) the terms connected with the entropy $S = -(\partial F/\partial T)_{V,\mu}$:

$$S - S_c = \left(\frac{dT_\kappa}{d\mu}\right)^{-1}\left\{\left(\frac{dx}{d\mu} - \frac{1}{V_c}\frac{dV_c}{d\mu}\frac{\partial^2 F_0}{\partial \tau\, \partial v}\frac{1}{T_c}\frac{dT_c}{d\mu}\right)\Delta\mu\right.$$
$$\left. + \left(\frac{1}{V_c}\frac{dV_c}{d\mu}\frac{\partial^2 F_0}{\partial \tau\, \partial v} + \frac{\partial^2 F_0}{\partial \mu\, \partial \tau}\right)\tau(x) - \frac{\partial^2 F_0}{\partial \mu\, \partial v} v(x)\right\}. \tag{5}$$

We consider the solution of equation (2) on the isochore $v(x) \ll \tau(x)$.

In the case $z(\mu) \equiv v(\mu)/\tau(\mu)^\beta \ll 1$ [8] at

$$\tau(x)^\alpha \ll \xi^{-1} \tag{6}$$

we have

$$\Delta\mu = \left(\frac{1}{T_\kappa^c}\frac{dT_c}{d\mu}\right)^{-1}\{1 - [\xi^{1/\alpha}\tau(x)]^{\alpha/(1-\alpha)}\}\tau(x), \tag{7}$$

where

$$\xi = \frac{1-\alpha}{A(dx/d\mu)(dT_c/dx)^2}(1-\theta),$$
$$\theta = \frac{\partial^2 F_0}{\partial \mu\, \partial T}\frac{dT_c}{dx} - \frac{\partial^2 F_0}{\partial V\, \partial T}\frac{dV_c}{dT_c}\left(\frac{dT_c}{dx}\right)^2\frac{dx}{d\mu}. \tag{8}$$

In dilute solutions ($x \ll 1$) we have $dx/d\mu = x/RT_c$ [8] and $\xi^{-1} \sim x$. We note that we have previously[8] not taken into account the second term in θ, which is proportional to dV_c/dT_c. Substituting (7) and (8) in (5) and differentiating the obtained expression with respect to temperature, we get

$$C_{v,x}/T = A^*\tau(x)^\varkappa + B^*, \tag{9}$$

where $\kappa = \alpha/(1-\alpha) > 0$,

$$A^* = -\frac{1}{1-\alpha}B^*(1-\theta)\xi^{1/(1-\alpha)} < 0, \tag{10}$$

$$B^* = \left(1 - \frac{\partial^2 F_0}{\partial \mu\, \partial T}\frac{dT_c}{dx}\right)\Big/\left(\frac{dT_c}{dx}\right)^2\frac{dx}{d\mu} > 0. \tag{11}$$

In the region $\tau(x)^\alpha \gg \xi^{-1}$, a similar calculation leads to the result

$$\Delta\mu = \frac{A}{1-\alpha}\{1 - o(x)\}\tau(x)^{1-\alpha} + B\{1 - o(x)\}\tau(x), \tag{12}$$

$$C_{v,x}/T = A\{1 - o(x)\}\tau(x)^{-\alpha} + B\{1 - o(x)\}. \tag{13}$$

The increments to the coefficients A and B in the region $\tau(x)^\alpha \gg \xi^{-1}$ are estimated to be of the order of θ and can change the coefficients by several dozen per cent in some cases[9]. The singularities of the remaining thermodynamic derivatives near the critical points of the solution can be obtained in similar fashion (see[8]).

It was emphasized in[8] that although in the asymptotic sense the specific heat $C_{V,x}$ in the solution is always finite, in a real experiment the region $\tau(x)^\alpha \ll \xi^{-1}$ may turn out to be unattainable. In exactly the same way, it is necessary to ascertain what limitations are imposed by the properties of different systems on the satisfaction of the condition $v(\mu)/\tau(\mu)^\beta \ll 1$ at $v(x) = 0$.

Substituting (7) and (12) in (3) and (4) and introducing the notation $y = (T_c/V_c)|dV_c/dT_c|$, we obtain at $\tau(x)^\alpha \ll \xi^{-1}$ and $v(x) = 0$

$$\frac{v(\mu)}{\tau(\mu)^\beta} = \xi^{-\beta/(1-\alpha-\beta)}y^{(1-\alpha)/(1-\alpha-\beta)}\tau(x), \tag{14}$$

and at $\tau(x)^\alpha \gg \xi^{-1}$ and $v(x) = 0$

$$\frac{v(\mu)}{\tau(\mu)^\beta} = \xi^{-1}y^{1/(1-\alpha-\beta)}\tau(x). \tag{15}$$

Thus, the condition $v(\mu) \ll \tau(\mu)^\beta$ on the isochore $v(x)$ is satisfied (in the region of a positive exponent of the specific heat) only if

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

and in the region of a negative exponent if

$$\tau(x) \ll (\xi^{-1}y)^{1/(1-\alpha-\beta)}. \tag{17}$$

Consequently, a case that is usual at first glance is possible in solutions in principle, namely, the isochore at a fixed concentration turns out to be close to the "isotherm" at a fixed chemical potential ($v(\mu) \gg \tau(\mu)^\beta$ at $v(x) \ll \tau(x)$). Let us therefore find the dependence of μ on T and V at $v(\mu)/\tau(\mu)^\beta \gg 1$.

2. $v(\mu)/\tau(\mu)^\beta \gg 1$ at $v(x) \ll \tau(x)$. In this case it is convenient to represent the singular part of the thermodynamic potential in the form

$$F_s\{\tau(\mu), v(\mu)\} = v(\mu)^{(2-\alpha)/\beta}\tilde{f}\{\tau(\mu)/v(\mu)^{1/\beta}\}, \tag{18}$$

$$\lim_{\tilde{z}\to 0}\tilde{f}(\tilde{z}) = -{}^1/_2\tilde{A}T_c^{\tilde{2}}\tilde{z}^2 + \text{const}. \tag{19}$$

Then

$$C_{v,x}/T=\tilde{A}v(\mu)^{-\alpha/\beta}+\tilde{B}. \tag{20}$$

Substituting (18) in (2) and solving (2) at $\tilde{z}\ll 1$, we obtain in the region

$$\tilde{\xi}^{\beta/(1-\alpha-\beta)}y^{-(1-\alpha)/(1-\alpha-\beta)}\ll\tau(x)\ll\tilde{\xi}^{-\beta/\alpha}y^{-1} \tag{21}$$

the result[1)]

$$\Delta\mu=\left(\frac{1}{T_c}\frac{dT_c}{d\mu}\right)^{-1}\{1-[\tilde{\xi}^{\beta/\alpha}y\tau(x)]^{\alpha/\beta}\}\tau(x), \tag{22}$$

where $\tilde{\xi}=\xi A/\tilde{A}(1-\alpha)$ (we assume henceforth that $\tilde{\xi}=\xi$). Subsituting (22) in (5) we obtain for the specific heat an expression equivalent to (9), with $\kappa=\alpha/\beta$:

$$\frac{C_{v,x}}{T}=B^{*}\left\{1-\left(1+\frac{\alpha}{\beta}\right)(1-\theta)\tilde{\xi}[y\tau(x)]^{\alpha/\beta}\right\}, \tag{23}$$

where B^* is determined by (11).

In the region $\tau(x)\gg\tilde{\xi}^{-\alpha/\beta}y^{-1}$ we can obtain similarly

$$\frac{C_{v,x}}{T}=\left\{\frac{\beta}{\alpha+\beta}\tilde{A}(y\tilde{\xi}^{-1}\tau(x))^{-\alpha/(\alpha+\beta)}+\frac{dV_c}{dx}\frac{\partial^2F_0}{\partial T\,\partial V}\right\}(1-o(x)). \tag{24}$$

Thus, the character of the renormalization of the critical exponent of the specific heat in the region $v(\mu)\gg\tau(\mu)^{\beta}$ differs significantly from the result for $v(\mu)\ll\tau(\mu)^{\beta}$ obtained in[1,8]. Such a situation is peculiar to phase transitions of the type of stratification into two coexisting phases, where the ordering parameter (or the "ordering field") changes when an impurity is added.

To be able to observe a renormalization of the type (23) in experiment, the parameter y should be large enough (10–100 at $\xi\sim 1$), i.e., the critical density should depend more strongly on the concentration than the critical temperature. The characteristic thermodynamic regions defined by inequalities (6), (16), (17), and (21) are shown in Fig. 1a. In region 1 we have $z(\mu)<1$ and the specific heat behaves in analogy with the specific heat in pure matter (formula (13)). In region 2, the condition $z(\mu)<1$ remains in force, but the exponent of the specific heat is renormalized in accordance with (9), where $\kappa=\alpha/(1-\alpha)$. The width of the renormalization region is determined here by the consition $\tau(x)^{\alpha}=\xi^{-1}$. Violation of the condition $z(\mu)<1$ leads to the appearance of regions 3 and 4. In region 3, the specific heat is described by formula (23) with a "large" positive exponent, and in region 4 it is described by formula (24), with a "large" negative exponent. Simultaneous solution of the equations of the boundaries of the two regions leads to the following coordinates of the "node":

$$\tau_0=y^{-1/(1-\beta)},\qquad\xi_0=y^{\alpha/(1-\beta)}. \tag{25}$$

Naturally, in the region close to $\{\tau_0,\xi_0\}$, the approximation of the experimental results by power-law dependences with definite values of the exponents is not reliable.

We present the main results for the case $\tau(x)$

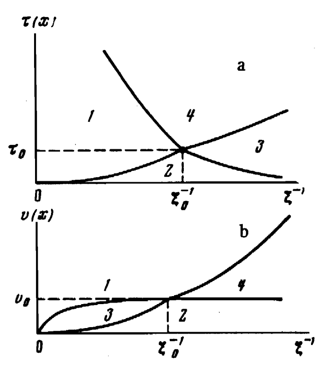

FIG. 1. Thermodynamic region of renormalizations of the critical exponent of the specific heat at $v(x)=0$ (a) and at $\tau(x)=0$ (b); $\xi^{-1}\sim x$.

$\ll v(x)$. It can be shown by the methods used above that in the region

$$\{\sigma v(x)\}^{\alpha/(1-\alpha)}<\xi^{-1}$$
$$\left(\sigma=\frac{T_cV_c(\partial^2F_0/\partial\mu\,\partial V)}{A(dT_c/d\mu)}\right)$$

and under the condition

$$z(\mu)\equiv v(\mu)/\tau(\mu)^{\beta}=\sigma^{-\beta/(1-\alpha)}v(x)^{(1-\alpha-\beta)/(1-\alpha)}<1$$
$$(v(x)<v_0=\sigma^{\beta/(1-\alpha-\beta)})$$

the singular part of the specific heat behaves like $\Delta C_{V,x}\sim -v(x)^{\alpha/(1-\alpha)}$ (region 2 in Fig. 1b). Sufficiently close to the critical point, the condition $z(\mu)\ll 1$ is always satisfied both on the isochore $v(x)=0$ and on the isotherm $\tau(x)=0$.

In region 1 (Fig. 1b), where

$$v(x)>(\sigma\xi^{-1})^{\beta/(1-\beta)}\quad\text{if}\quad\xi<\xi_0=\sigma^{-\alpha/(1-\alpha-\beta)},$$
$$v(x)>\xi^{-\beta/\alpha}\quad\text{if}\quad\xi>\xi_0,$$

there is no renormalization of the critical exponents ($\Delta C_{V,x}\sim v(x)^{-\alpha/\beta}$), and the condition $z(\mu)>1$ is satisfied. Regions 3 and 4 are intermediate, namely, on the 1–3 boundary the condition $z(\mu)>1$ is violated and $\Delta C_{V,x}\sim v(x)^{-\alpha}$, and in region 4 we have $\Delta C_{V,x}\sim -v(x)^{\alpha/\beta}$ (renormalization under the condition $z(\mu)>1$). In addition to the regions in which the critical exponents become renormalized (Fig. 1), there exist in liquids regions that are more extensive in terms of $\tau(x)$ and $v(x)$ ($\tau\lesssim x^{1/\gamma}$ at $v(x)=0$ and $v\lesssim x^{1/(\delta-1)}$ at $\tau(x)=0$), where the singularity of the compressibility $(\partial V/\partial P)_{T,x}$ is depressed and the quantity $(\partial x/\partial\mu)_{P,T}$ begins to increase[8,10] ($(\partial V/\partial P)_{T,x=0}\sim\tau^{-\gamma}$ at $v=0$; $(\partial V/\partial P)_{T,x=0}\sim v^{-(\delta-1)}$ at $\tau=0$).

We note finally that we have used the thermodynamic potential as a function $\tau(\mu)$ and $v(\mu)$ (the "order parameter").

As the "order parameter" for solutions we can choose the quantity $\Delta x(P)=|x-x_c(P)|$. The variables $\tau(P)$ and $\Delta x(P)$ are convenient for the description of the properties of a solution near the critical liquid-liquid equilibrium points [8,9].

When describing the critical point of a single-component system, one uses frequently the thermodynamic potential $\Omega=-PV$, with independent variables τ and $\Delta\mu_0$ (μ_0 is the chemical potential of the pure substance) which are isomorphic to the variables T and h (h is the magnetic field) in a ferromagnet[11]. In binary solutions, such a description corresponds to the use of the variables $\tau(\mu_2)$ and $\Delta\mu_1(\mu_2)$, where μ_1 is the chemical potential of the solvent ($\mu_1\to\mu_0$ as $x\to 0$). It can be shown that this approach leads to results that are equivalent to ours.

[1)] Equation (2) was solved, just as in [8], by a perturbation-theory method, i.e., $\Delta\mu$ was represented in the form $\Delta\mu=\Delta\mu_0+\Delta\mu_1(\Delta\mu_1\ll\Delta\mu_0)$ and the condition $\Delta\mu_1/\Delta\mu_0\lesssim 1$ determined the upper limit of the region of applicability ($\tau(x)\lesssim\tilde{\xi}^{-\beta/\alpha}y^{1}$) of the solution (22).

In conclusion of this section we discuss the possibility of experimentally verifying the concepts of isomorphism of critical phenomena. It has been noted many times[8,9] that binary liquid solutions are the optimal objects for such a verification. Many studies were devoted to the "susceptibility" $(\partial x/\partial\mu)_{P,T}$ near liquid-liquid critical equilibrium points with the aid of molecular scattering of light (see, for example,[12]). The experiment is performed in the presence of saturated vapor (the pressure changes little) and $(\partial x/\partial\mu)_{P,T}$ behaves isomorphically to $(\partial V/\partial P)_T$ near the critical point of the pure substance: $(\partial x/\partial\mu)_{P,T} \sim \tau(P)^{-\gamma}$, where $\gamma \approx 1.2$–1.3.

An investigation of the isobaric and isochoric specific heats ($C_{P,x}$, $C_{V,x}$) near the critical liquid-liquid equilibrium line of the methanol-cyclohexane system[9] has shown that $C_{P,x} \sim \tau(P)^{-\alpha}$ $(0 < \alpha < 0.2)$, i.e., it behaves in analogy with C_V in pure matter. The exponent of the isochoric specific heat $C_{V,x}$ should be renormalized in accordance with formula (9), but for the system investigated in[9] the renormalization region cannot be reached in experiment ($\tau \lesssim 10^{-10}$). In[13] they investigated the specific heat of C_P near the λ transitions of the He^3—He^4 mixture. In this case, the singularity of the ideal system is possessed by the quantity $C_{P,\mu}$ (see[8]), while $C_{P,x}$ remains finite. Experiment[13] has confirmed this conclusion, although an attempt to describe the obtained results by means of different functional relations leads to ambiguous results. In[14], a renormalization of the exponent $\gamma \to \gamma^* = \gamma/(1-\alpha)$ was observed in an investigation of the intensity of scattered light near the critical equilibrium point of a ternary liquid-liquid system ($\gamma^* = 1.50 \pm 0.08$). On the other hand, an investigation of the intensity of scattered light near the liquid-vapor critical point of the n-pentane + cyclopentane system is experimentally unattainable. Estimates by means of formulas (8) and (6) yield $\xi \approx 10^{-2}$, and accordingly $\tau \lesssim 10^{-16}$. In order for the normalization region to become experimentally accessible, it is necessary to choose objects with $\xi \approx 1$–3, i.e., with a sufficiently strong $T_c(x)$ and $V_c(x)$ dependences.

3. INVESTIGATION OF THE BEHAVIOR OF THE ISOCHORIC SPECIFIC HEAT NEAR THE CRITICAL LIQUID-GAS LINE OF THE ETHANE-CARBON DIOXIDE SYSTEM

Of particular importance to the experimental verification of the isomorphism hypothesis is the ethane + carbon dioxide system, the critical line of which reveals two singular points, at the minimum of the $P_c(x)$ dependence and at the point of intersection of the critical line with the azeotrope lines (Fig. 2). Figure 3 shows the results of the measurements of the isochoric specific heat near the point of the minimum of $T_c(x)$ (56.4% mol. CO_2), of the critical azeotrope (71.9% mol. CO_2), and also the critical point of a solution containing 28.8% mol. CO_2, for which the values of dT_c/dx and dV_c/dx are close to the corresponding parameters of the critical azeotropic mixture2).

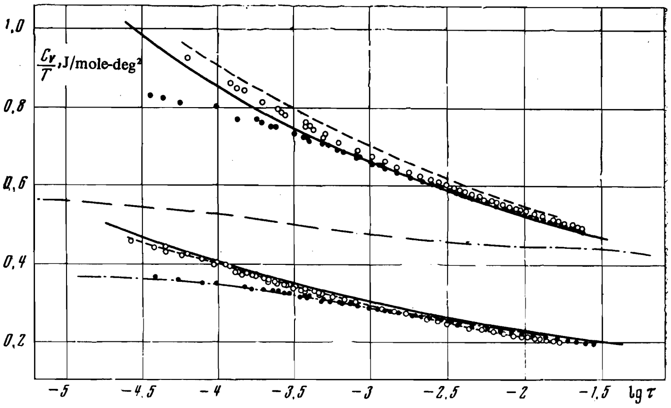

FIG. 3. Dependence of $C_{V,x}/T$ on log τ in the ethane + carbon dioxide system ($\tau = |(T-T_c)/T_c|$): ○—solution with composition corresponding to the minimum of $T_c(x)$ (56.4% CO_2), ●—solution containing 28.2% CO_2, solid line—pure ethane, dashed line—azeotropic mixture, dash-dot line—100% solution of heptane in ethane (here and in Figs. 4, 7, and 9 the upper branches of the curves pertain to the region $T < T_c$, and the lower ones to $T > T_c$).

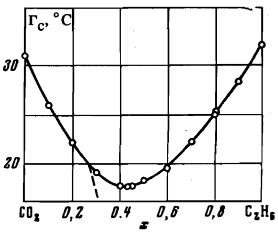

FIG. 2. Dependence of the critical temperature on the composition of the ethane + carbon dioxide system (the dashed line is the azeotrope line).

At the minimum of $T_c(x)$ we have $\xi^{-1} = 0$, and according to the condition (6) we should expect a singularity in the behavior of $C_{V,x}$, similar to that observed for pure matter (region 1 on Fig. 1). An analysis of the experimental data has confirmed this conclusion of the theory. At $T > T_c$ we have $\alpha = 0.13 \pm 0.01$ in the experimentally most reliable interval $10^{-4} \lesssim \tau\ 10^{-2}$[16]. In pure ethane[16], a value $\alpha = 0.14 \pm 0.02$ was obtained both above and below T_c. The increased accuracy in comparison with pure ethane is apparently connected with the decrease of the distorting influence of the mixing, which is important in real matter as a result of the infinite growth of the compressibility3) [16].

We call attention to the agreement between the obtained value of α and the results of the approximate solution of the three-dimensional model of lattice gas ($\alpha = 0.125$ [11]) and with the value of the exponent α obtained in[17] for carbon dioxide ($\alpha = 0.125 \pm 0.02$). In the region $T < T_c$ we have obtained for the interval

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2) The measurement procedure and the construction of the calorimeter were described in [16], which cites the results of the measurement of the isochoric specific heat in the vicinity of the critical point of pure ethane. The measurement results were processed with a computer. Tables of the experimental data will be published in Issue No. 7 of the GSSD collection of "Thermophysical Properties of Substances." The use of C_V/T in place of C_V extends the region of applicability of the power-law dependences of the type (13) by almost one order of magnitude with respect to τ. Within the framework of scale transformations, however, such an operation cannot be rigorously justified. Therefore, in the analysis of renormalization effects, when the anomaly of $C_{V,x}$ is small, we confine the approximation to the region $\tau \lesssim 2 \times 10^{-3}$, where replacement of T by T_c in the left-hand side of (9) does not exceed the error in the measurement of $C_{V,x}$.

3) In the case of the critical point of an azeotropic mixture, the level of the random error is again higher (an infinite increase of compressibility), which leads to a decrease in the accuracy of the determination of α.

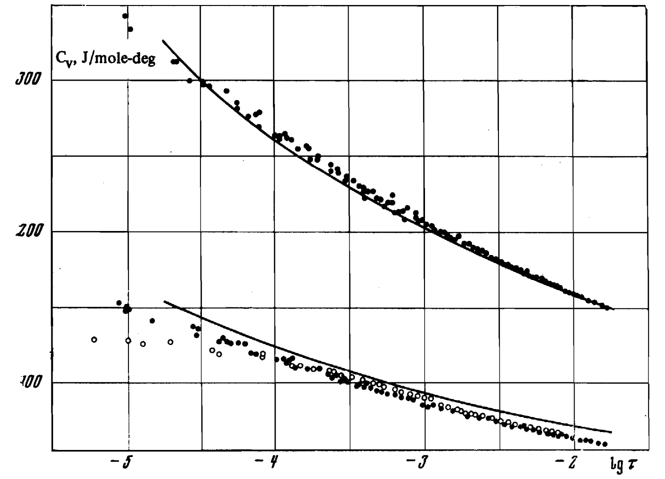

FIG. 4. Dependence of the specific heat $C_{V,x}$ on log τ near the critical point of an azeotropic mixture. ●—our last experiment, ○—experiment of [18] ($T > T_c$), solid line—pure ethane.

$10^{-4} \lesssim \tau \lesssim 10^{-2}$ an unexpectedly high value of the critical exponent, $\alpha = 0.16 \pm 0.01$. This fact will be discussed later on, since in almost all the investigated cases we encountered considerable difficulties in the interpretation of the behavior of the specific heat in the region of the heterogeneous states of the systems.

For a critical azeotropic mixture, just as for the minimum of $T_c(x)$, the specific heat $C_{V,x}$ increases in the entire investigated temperature interval in accordance with a power law, in analogy with C_V of pure matter. In the region $10^{-4} \lesssim \tau \lesssim 10^{-2}$, we have $\alpha = 0.13 \pm 0.02$ both for $T > T_c$ and for $T < T_c$. In comparison with the results of earlier measurements[18], the character of the singularity has become sharper: the $C_{V,x}(\tau)$ has come closer to the dependence of C_V of pure ethane on τ (see Fig. 4). This shows that the depression of the singularity observed in[18] at $\tau < 5 \times 10^{-4}$ was due to methodological factors (temperature gradients, which were eliminated after improving the procedure, see[16]).

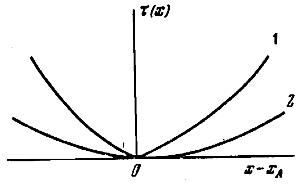

FIG. 5. Characteristic thermodynamic regions of the vicinity of the critical point of an azeotropic mixture: $1-\tau(x) \sim (x-x_A)^{2/\gamma}$, $2-\tau(x) \sim (x-x_A)^{2/\alpha}$.

There were many discussions of the character of the singularity of the isochoric specific heat near the critical point of an azeotropic mixture. In[19] it was proposed that $C_{V,x}$ increases without limit at this point, on the basis of the fact that the compressibility and the isobaric specific heat behave in analogy with the quantities in the pure substance. An opposite conclusion was drawn subsequently[8], that $C_{V,x}$ at the critical point of an azeotropic mixture is finite and the results of the experiments in[18] can be attributed to the fact that $T_c^{-1}dT_c/dx$ is relatively small in this case (~0.1) and the region of the expected renormalization is $\tau \lesssim 10^{-12}$. Since the estimates of α based on the formulas of dilute solutions are not reliable at $x \approx 0.3$, we measured the specific heat of $C_{V,x}$ in a solution that is symmetrical to the azeotropic solution (71.8% ethane + 28.2% CO_2). In both cases, dT_c/dx and dV_c/dx practically coincide. As seen from Fig. 3, a noticeable depression of the singularity of the specific heat it is observed here, starting with $\tau \approx 10^{-3}$, in contrast to the azeotropic mixture. This shows that the interpretation proposed in[6-8] is incorrect. The conclusion of[6-8] that $C_{V,x}$ is finite is based on the assumption that at the critical point of an azeotropic mixture we have $dx/d\mu = \text{const}$, and then $dT_c/d\mu = (dT_c/dx)(dx/d\mu) \neq 0$, and, as can be seen formula (1),

$$\left(\frac{\partial x}{\partial \mu}\right)_{P,T} \sim \left(\frac{\partial x}{\partial \mu}\right)_{V,T} = A\left(\frac{dT_c}{d\mu}\right)^2 [\xi\tau(x)]^{-\alpha/(1-\alpha)} + \text{const} \; [^8].$$

In order for the specific heat $C_{V,x}$ in an azeotropic critical point to become infinite (in accord with experiment), it is necessary to satisfy at this point the condition $dx/d\mu = 0$. Then

$$\xi^{-1} = 0, \quad \frac{dT_c}{d\mu} = 0, \quad \left(\frac{\partial x}{\partial \mu}\right)_{P,T} \sim \left(\frac{\partial x}{\partial \mu}\right)_{V,T} = \text{const},$$

$$C_{V,x} \sim C_{V,\mu} \sim \tau(x)^{-\alpha}.$$

These conditions mean that $(\partial P/\partial V)_{T,x} \sim \partial P/\partial x)_{T,V}{}^{2}$[10]. If it is assumed that $(\partial P/\partial x)_{T,V} \sim x - x_A$ (when moving toward the azeotropic composition x_A along the critical line), then $dT_c/d\mu \sim x - x_A$, and the behavior of the thermodynamic quantities is determined by the presence of two "cones": $\tau^\gamma \sim (x - x_A)^2$ and $\tau^\alpha \sim (x - x_A)^2$ (Fig. 5).

Inside the region $(x - x_A)^{2/\alpha} < \tau < (x - x_A)^{2/\gamma}$ we have

$$(\partial x/\partial \mu)_{P,T} \sim (x - x_A)^2 \tau(x)^{-\gamma},$$

and only at $\tau^\alpha \ll (x - x_A)^2$ do we have

$$\left(\frac{\partial x}{\partial \mu}\right)_{P,T} \sim (x - x_A)^2 \tau(x)^{-\gamma/(1-\alpha)}, \quad \left(\frac{\partial x}{\partial \mu}\right)_{V,T} \sim (x - x_A)^2 \tau(x)^{-\alpha/(1-\alpha)},$$

and $C_{V,x}$ remains finite.

An analysis of the temperature dependence of the specific heat in a solution containing 28.2% CO_2 has shown that at $T > T_c$ in an interval $10^{-4} \lesssim \tau \lesssim 5 \times 10^{-3}$ the specific heat $C_{V,x}$ is described by formula (9) with parameters $\kappa = 0.15 \pm 0.05$, $A^* = -0.63$ J/mole-deg², and $B^* = 0.51$ J/mole-deg² (at $\kappa = 0.15$). Using the experimental values[20] $T_c^{-1}dT_c/dx \approx 0.1$ and $(T_c/V_c)dV_c/dT_c \approx 5$, and assuming $\partial^2 F_0/\partial T \partial V \approx -dP_c/dT_c \sim 0.5$ atm/deg, we obtain in accordance with formulas (8), (10), and (11)

$$\frac{dx}{d\mu} \approx 20\frac{x}{RT_c} \approx 0.2\,\frac{\text{mole}}{1-\text{atm}},$$

$$\theta \approx 0.3 - 0.4, \quad \xi \approx 2.$$

We note that the value of $dx/d\mu$ differs by an approximate factor 20 from the estimates based on the dilute-solution formulas, and the term in θ, proportional to dV_c/dx and unaccounted for in[8], changes the value of ξ by ~1.5 times. An estimate of the width of the region $\tau = \xi^{-1/\alpha} \approx 5 \times 10^{-3}$, in which the depression of the singularity of $C_{V,x}$ should be observed, agrees well with experiment.

We now consider the heterogeneous-state regions. We note that even in the interpretation of the experiment in the region $T < T_c$ of the pure substance there arise definite difficulties[16] connected with the asym-

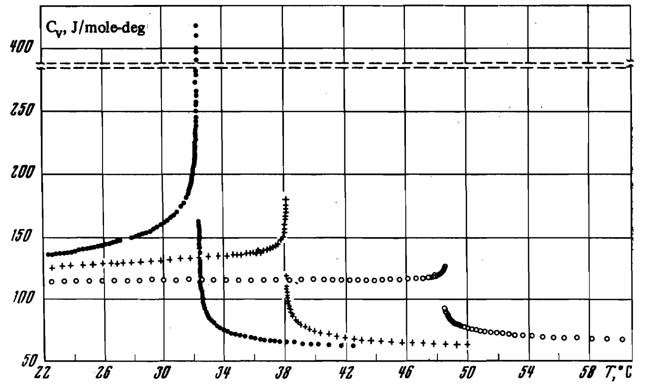

FIG. 6. Temperature dependence of the isochoric specific heat in the ethane-heptane system: ●—pure ethane; +—1% solution of heptane in ethane; O—3% solution of heptane in ethane (ρ = 0.248 g/cm^3).

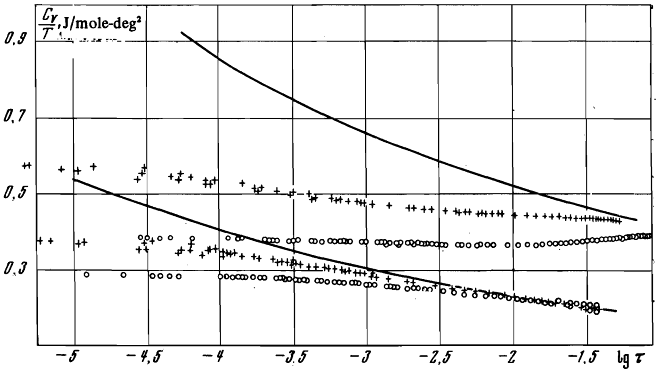

FIG. 7. Dependence of $C_{V,x}/T$ on log τ in the ethane-heptane system: solid line -pure ethane; the remaining symbols are the same as in Fig. 6.

metry of the liquid-gas coexistence curve. In solutions, this asymmetry becomes important much closer to T_c and the thermodynamic behavior that is isomorphic to the "ideal" system (for example, lattice gas) can differ strongly from the experimental isochore. This may be the reason for the extra large exponent $\alpha = 0.16$ at $T < T_c$ at the point of the minimum of $T_c(x)$, and in a solution containing 28.2% CO_2, the same circumstance can lead to a shift towards smaller τ in the transition region of the renormalization of the exponents (see Fig. 3).

Near the critical point of an azeotropic mixture, up to $\tau \lesssim 10^{-2}$, the boundary T – V liquid-gas curve remains the same as in the pure substance, and we see no difference in the behavior of $C_{V,x}$ in the regions $T < T_c$ and $T > T_c$.

4. RENORMALIZATION OF THE CRITICAL EXPONENT OF THE SPECIFIC HEAT IN THE ETHANE-HEPTANE SYSTEM

The measured specific heats C_V of pure ethane and $C_{V,x}$ of two solutions (0.94 and 3.16% mol) of heptane in ethane are shown in Figs. 6 and 7. The sharp decrease of the anomaly of the specific heat following the addition of heptane is clearly seen. A quantitative interpretation presupposes a maximum possible correspondence of the density (ρ) of the calorimeter content

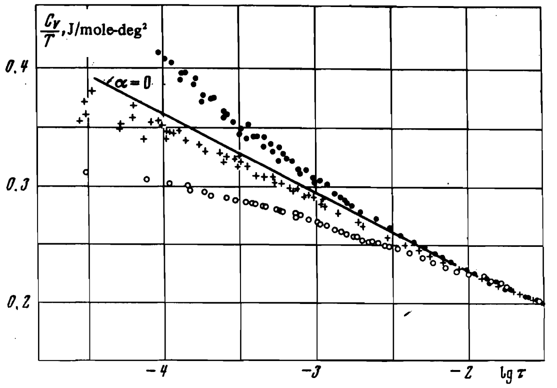

FIG. 8. Dependence of $C_{V,x}/T$ on log τ in the region of the homogeneous state ($T > T_c$) of the ethane-heptane system (the notation is the same as in Fig. 6), in a 3% solution with ρ = 0.240 g/cm^3.

to the critical value. At the same time, data on the $\rho_c(x)$ dependence[21] are not reliable (for example, the value of ρ_c of pure ethane is 10% too high). We have therefore investigated the specific heat of a 3% solution of heptane in ethane at three values of the density. The concentration at which the anomaly $C_{V,x}$ was maximal (ρ = 0.240 g/cm^3) was assumed to be critical (accurate to ±1%).

Just as in the preceding case, we discuss first the region of the homogeneous state ($T > T_c$). A comparison of the experimental curves for ethane and for 1 and 3% solutions of heptane in ethane in a semilogarithmic scale (Fig. 8) shows that whereas for pure ethane only a negative exponent is possible ($\alpha = 0.14 \pm 0.02$ [16]), the curves 2 and 3 have regions in which the dependence of $C_{V,x}$ on τ can be approximated by formula (9) with a positive exponent κ.

For the 1% solution we obtained $\kappa = 0.1 \pm 0.1$ in the interval $3 \times 10^{-5} \lesssim \tau \lesssim 10^{-3}$. The low accuracy with which κ is determined is due here principally to the decrease in the amplitude of the anomaly of the specific heat at a sufficiently large random error (up to 2% at $\tau \lesssim 10^{-4}$). Formula (9) with $\kappa = 0.15$ can be used to describe the temperature dependence of $C_{V,x}$ only in a narrow and methodologically unreliable vicinity ($\tau \lesssim 10^{-4}$) of the critical point, and the interval $10^{-4} \lesssim \tau \lesssim 5 \times 10^{-3}$ pertains to the intermediate region. Therefore the comparison with theory can be only qualitative in this case. Approximation of the curve by formula (9) with $\kappa = 0.15$ yields

$$A^* = -0.6 \ \text{J/mole-deg}^2 \quad B^* = 0.5 \ \text{J/mole-deg}^2$$

Assuming

$$\frac{1}{V_c}\frac{dV_c}{dx} = -(3 \div 6), \quad \frac{1}{T_c}\frac{dT_c}{dx} \approx 2,$$

$$-\frac{\partial^2 F_0}{\partial T\,\partial V} \approx \frac{dP_c}{dT_c} \approx 1\,\frac{\text{atm}}{\text{deg}}\,[21], \quad \frac{dx}{d\mu} \approx \frac{x}{RT_c}$$

and neglecting in B^* and θ the term containing $\partial^2 F_0/\partial\mu\,\partial T \sim x \ln x$, we find from (10) and (11) that $\xi \approx 2$–3. The estimate of ξ by formula (7) yields the close value $\xi \approx 4$, which does not contradict the width of the renormalization region observed by us.

In the 3% solution, the scatter of the points turned out to be smaller by almost one order of magnitude, making it possible to determine the parameters of the function (9) with greater accuracy. Attention is called to the existence of the dependence of the exponent κ on the τ interval for which the approximation was carried out. At $2 \times 10^{-4} \lesssim \tau \lesssim 2 \times 10^{-3}$ we have $\kappa = 0.37 \pm 0.08$, and an attempt to expand this interval both towards larger and smaller τ leads to a decrease of the exponent κ. Thus, for $10^{-4} \lesssim \tau \lesssim 10^{-2}$ we have $\kappa = 0.15 \pm 0.08$, and allowance for points $10^{-5} \lesssim \tau \lesssim 2 \times 10^{-3}$ closer to T_c yields $\kappa = 0.18 \pm 0.08$.

A large value of the renormalized index in the experimentally reliable region could denote violation of the condition $v(\mu)/\tau(\mu)^{\beta} \ll 1$ at $v(x) = 0$. Assuming $\alpha = 0.13$ and $\beta = 0.34$[16], we obtain in accordance with (24) $\kappa = \alpha/\beta = 0.38$. Then, at sufficiently small τ, the condition $v(\mu)/\tau(\mu)^{\beta} \ll 1$ should again be satisfied (see Fig. 1a) and $\kappa = \alpha/(1 - \alpha) = 0.15$. This can explain the decrease of the exponent κ, observed when account is taken of points close to T_c. In exactly the same manner, at large τ we should go over into a region of negative exponents and allowance for the remote points again decreases κ.

In the interval $2 \times 10^{-4} \lesssim \tau \lesssim 2 \times 10^{-3}$ we have at $\kappa = 0.38$

$$A^{\bullet} = -0.70\ \text{J/mole-deg}^2 \quad B^{\bullet} = 0.32\ \text{J/mole-deg}^2$$

and in the interval $10^{-5} \lesssim \tau \lesssim 5 \times 10^{-4}$ at $\kappa = 0.15$

$$A^{\bullet} = -0.34\ \text{J/mole-deg}^2 \quad B^{\bullet} = 0.39\ \text{J/mole-deg}^2$$

According to formulas (11) and (24) we have in both cases

$$B^{\bullet} = \frac{RT_c}{x(dT_c/dx)^2} = 0.32 \pm 0.08$$

(we have assumed $T_c^{-1} dT_c/dx = 1.6 \pm 0.1$[21], $dx/d\mu \approx x/RT_c$, and neglected the term containing $\partial^2 F_0/\partial x \partial T \sim x \ln x$). From (24) and (11) we obtain $\xi = 1.4 \pm 0.4$, $y = 10 \pm 5$, $\theta = 0.5 \pm 0.1$ (this corresponds to the estimate $-\partial^2 F_0/\partial T \partial V \approx dP_c/dT_c \approx 0.5$ atm/deg), which does not contradict the experimental data. The limits of the corresponding regions are

$$\tau_{4-3} \approx 10^{-1}, \quad \tau_{3-2} \approx 10^{-2}, \quad \tau_0 \approx 5 \cdot 10^{-2}, \quad \xi_0 \approx 1.6,$$

i.e., the concentration $x \approx 3 \times 10^{-2}$ is only slightly larger than x_0 ($x/x_0 \approx \xi_0/\xi$).

A "large" renormalized exponent $\kappa = \alpha/\beta$ is observed in the interval of τ to 5×10^{-4}, which differs from the foregoing estimate of τ_{3-2} by a factor 1.5. This means that all the experimental points lie in the region of transition from the exponent $\kappa = \alpha/\beta$ to the exponent $\kappa = \alpha/(1 - \alpha)$. It is interesting, however, that an attempt to approximate the dependence of $C_{V,x}$ on τ by formula (9) with one exponent κ in a wide interval $10^{-5} \lesssim \tau \lesssim 10^{-2}$ leads to $\kappa = 0.2 \pm 0.1$, which is close to the value $\alpha/(1 - \alpha) = 0.15$. The estimates of the parameters ξ, θ, and y turn out to be the same as before. One can therefore not exclude the possibility that the "large" exponent obtained in the narrow interval is connected with some distorting factors which we did not take into account.

The deviation of the density from the critical value leads to additional depression of the specific heat in the region $T > T_c$ (Fig. 9). The ethane-heptane system is characterized by a particularly strongly pronounced asymmetry of the liquid-gas boundary curve, which increases with increasing heptane concentration. One can therefore expect in the region $T < T_c$ the asymptotic renormalization of the exponent should shift into the direct vicinity of the critical point. The dependence of $C_{V,x}$ on τ is therefore quite complicated in almost the entire experimental region. Thus, a slight change in the density (~2%) of the 3% solutions leads in the interval $10^{-4} \lesssim \tau \lesssim 3 \times 10^{-3}$ to a qualitative change in the character of this dependence, the exponent approximated by formula (9) reverses sign, and becomes negative for the critical density (Fig. 9).

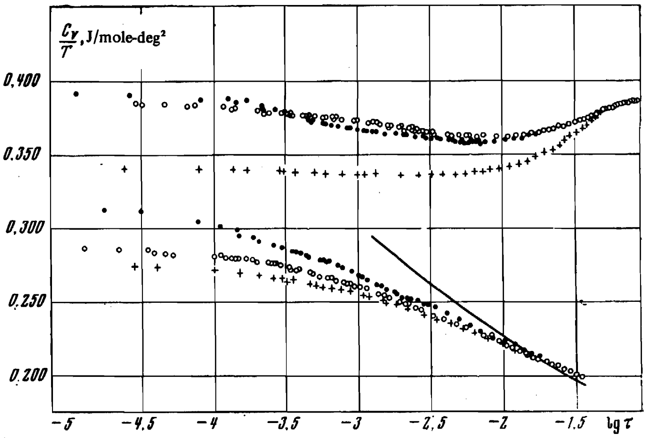

FIG. 9. Dependence of $C_{V,x}/T$ on $\log \tau$ in the ethane-heptane system for different densities: ●—$\rho = 0.248$, ○—$\rho = 0.240$ (critical), +—$\rho = 0.281$ g/cm³; solid line—pure ethane.

What is characteristic in this respect is the comparison of the specific-heat curves of the 1% ethane-heptane solution and a solution containing 28.2% of CO_2 in ethane (Fig. 5). Whereas the high-temperature branches (in the homogeneous regions) practically coincide (estimates yield large values of ξ), the low-temperature branches differ strongly. If we disregard the complicated character of the behavior of $C_{V,x}$ as a function of τ in the transition region, then on the whole the distorting influence of the impurities appears at $T < T_c$ at an instant τ which is approximately two orders of magnitude earlier than at $T > T_c$, as is indeed expected from the estimate of ξ (the coefficients A at $T > T_c$ and $T < T_c$ differ by a factor of two).

5. CONCLUSION

Our foregoing analysis of the experimental investigation of the specific heat near the critical points of the binary solutions has shown that the character of the phase transitions in different systems is sufficiently universal to be able to describe them from a unified point of view. At the same time, the individual properties of the objects determines the coefficients of the singular parts of the thermodynamic quantities and the regions of applicability of the asymptotic regularities.

Is this the only manifestation of the individuality of the object in the description of the phase transition, or are the very values of the critical exponents no longer universal for different liquids?

Further increase of the experimental accuracy and an increase in the number of investigated systems will make it possible to answer this theoretically and practically important question.

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