INVESTIGATIONS OF THE SHAPE OF THE COEXISTENCE CURVE FOR A BINARY CH$_4$-CF$_4$ SOLUTION

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The coexistence curve of the binary solution CH$_4$-CF$_4$ in the vicinity of the liquid-liquid critical point is studied by measuring the displacement of the phase interface. The equation for the coexistence curve is $X' - X'' = A|t|^\beta$, where X' and X'' are the concentrations of the coexisting phases, A and β are constants, and $t \equiv (T - T_c)/T_c$. The value for the critical exponent is found to be $\beta = 0.355 \pm 0.01$. Study of the problem concerning existence of the hydrostatical effect near the critical dissolution temperature is continued. It is demonstrated that in the temperature range studied, $T - T_c > 0.001°$ ($T_c = 94.72°$K), the effect is not very appreciable in the solution.

$\mathbf{I}$N spite of the large number of both theoretical and experimental investigations of the shape of the coexistence curve near critical points, this question is not yet completely clear. Most experimental investigations, in accordance with the conclusions of the phenomenological similarity theory,[1] give an approximately cubic equation for this curve both near the liquid-vapor value of T_c, and for the critical dissolution point.[2-4] There are, besides, investigations in which other results were obtained.[5,6] The discrepancies between the experimental data, and also the absence of a microscopic theory of critical phenomena, preclude any theoretical predictions.

The lack of reliable results is due to well known difficulties in the study of critical phenomena: the large times of equilibrium establishment and the need for high accuracy in the thermostatic control and in the measurements. In addition, the shape of the boundary curve near the critical liquid-vapor point is greatly influenced by the presence of the hydrostatic effect, which leads to a flattening of the top of the coexistence curve.[7,8] For the critical solution-mixing point, the existence of the hydrostatic effect was predicted theoretically.[9] However, attempts to investigate the hydrostatic effect experimentally at this point[10,11] did not yield sufficiently reliable results, a fact that will be discussed later. Obviously, the solution of this question is of great importance for the study of critical properties of liquids, including the determination of the shape of the critical curve.

As already reported,[12] we have observed the appearance of a concentration gradient near the lamination line of the system CH$_4$-CF$_4$ at temperatures below T_c, and formation of a considerable concentration gradient in the layers adjacent to the liquid-vapor interface. It was assumed that the cause of formation of these concentration inhomogeneities near the interface is the hydrostatic effect, since the obtained concentration distribution was in qualitative agreement with the theoretical calculation.[9] The nature of formation of a concentration gradient in the liquid-vapor surface at $T > T_c$ is not completely clear. In the absence of a vapor phase in the temperature interval above the critical temperature,

no inhomogeneities of concentration were observed along the height of the liquid column. It turned out subsequently that diffusion on the liquid-liquid interface at $T < T_c$ leads to a similar distribution of the concentration gradient.[13] A possible cause of the observed concentration inhomogeneities could be also the thermal diffusion due to the temperature gradients. To obtain a final solution to this problem, additional investigations were performed.

The system CH$_4$-CF$_4$ has an upper critical dissolution point at $T_c = 94.72°$K and $x_c = 43.5$ mol.% CF$_4$. The purity of the investigated components was not worse than 99.98%. The determination of T_c (in degrees K) was effected in several stages in a solution with critical concentrations. The lamination temperature of the solution was first determined roughly. The system was then gradually cooled in temperature steps of 0.01°. Following thorough mixing and thermostatic control of the solution for approximately 1-2 hours, the instant of lamination of the solution, which was registered visually upon cooling, determined T_c with accuracy ±0.01°. This was followed by stepwise heating of the solution and determination of the temperature at which complete mixing of the solution took place. Similar operations were repeated with stepwise cooling and heating of the solutions in temperature steps of 0.001° and finally in steps of 0.0005°. The difference in the determination of the transition temperature in cooling and in heating of the solution reached ±0.001°. The critical temperature was determined in repeated experiments and was also reproducible with accuracy ±0.001°.

The chosen system is characterized by a rather large difference of the component densities, ρCF$_4$/ρCH$_4$ ~ 5, making it advantageous from the point of view of observing the hydrostatic effect. We used the well-known Toepler shadow method for the investigation.[14] The procedure used to measure the concentration gradient is described in detail in [12,15]. The experimental setup of [16] was modernized somewhat to improve the accuracy of thermostatic control and to eliminate the temperature gradient. To this end, the chamber for the investigations 1 (see Fig. 1) was surrounded by a quasi-adiabatic shell 2 and was connected with the latter
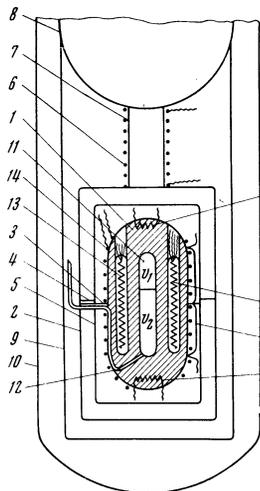
FIG. 1. Diagram of cryostat. 1—Chamber for investigations, 2—quasiadiabatic shell, 3, 4—cold ducts, 5—intermediate frame, 6—heater, 7—cold duct, 8—nitrogen container, 9—nitrogen screen, 10—vacuum sheath, 11—working cavity, 12—capillary, 13—thermal-regulator pickup, 14—temperature-regulator heater, 15—thermometer, 16—differential thermocouple, 17, 18—heaters.

through ducts 3 and 4 and through an intermediate frame 5. The temperature of the quasiadiabatic shell was set with the aid of a heater 6, placed on the surface of tubular cold duct 7. The latter communicated with the nitrogen container 8. To prevent heat influx from the outside, the quasiadiabatic shell was surrounded by a nitrogen screen 9.

The chamber constituted a copper block with vertical cavity 11, having a height ~5 cm and a cross section 8 × 16 mm, and was filled with the investigated liquid through the capillary 12. The thermostatic control was with the aid of an automatic electronic circuit and had an accuracy ±0.0005°. The pickup of the thermal regulator was a copper resistance thermometer 13. The heater 14, uniformly wound around the contour of the chamber, was intended to maintain a definite temperature regime. The temperature was measured with a standard platinum resistance thermometer 15 and a potentiometer circuit (potentiometer R309), with accuracy ±0.001°.

To monitor and eliminate vertical temperature gradients, the chamber was equipped with a differential thermocouple 16 of copper and an alloy of gold with cobalt; heaters 17 and 18, located in the upper and lower parts of the chamber, made it possible to produce artificial vertical temperature gradients. The temperature gradient was measured with sensitivity ~0.0001 deg-cm^{-1} with the aid of an R306 potentiometer and an F-116/1 microvolt-microammeter.

As a result of investigations performed at $|\Delta T|$ > 10^{-3}°K, it turned out that the presence of a vertical temperature gradient of ~0.002 deg-cm^{-1} leads to formation of a concentration gradient in the layers adjacent to the liquid-vapor interface. The presence of a temperature gradient also explains the occurrence of the concentration gradients near the lamination line. In this case the mixing leads to equalization of the temperature over the height of the chamber. After the mixing stops, the subsequent redistribution of the temperature causes the lamination line to be displaced as a result of the diffusion of the components, leading at a diffusion coefficient D → 0 near T_C to the occurrence of a stable concentration gradient.

If there are no temperature gradients along the height h of the liquid column, no inhomogeneities of the

concentration x are observed either above or below T_C at $|\Delta T|$ > 10^{-3}°K and a measurement sensitivity dx/dh close to 0.01 mol.%-cm^{-1}. Thus, in this approach to the critical point, the gravitational effect in the solution near the dissolution point T_C does not attain a noticeable value (dx/dh < 10^{-2} mol.%-cm^{-1}).

It is therefore quite probable that the results of [10, 11], where observation of this effect was reported for solutions, are also due to temperature-distribution inhomogeneities due to the insufficient accuracy of the thermostatic control. This pertains in particular to [11], where the thermostatic-control was ±0.05°, which is much higher than the values at which the concentration gradients occurred in our experiments.

As is known from thermodynamics of nonequilibrium processes, [17] the connection between the concentration and temperature gradients in the equilibrium state are given by the equation

$$\frac{D_\tau}{D} = -\frac{1}{x_1 x_2}\frac{\partial x/\partial h}{\partial T/\partial h}, \tag{1}$$

where D_T is the thermal diffusion coefficient, D is the coefficient of mutual diffusion, h is the height of the chamber, and x_1 and x_2 are the molar concentrations of the components. In place of the coefficient D_T one uses more frequently the dimensionless thermal diffusion factor

$$\alpha \equiv D_\tau / D. \tag{2}$$

The behavior of the thermal diffusion factor α near the critical dissolution point was investigated in [18, 19] for the systems n-butane-methane and nitrobenzene-n hexane, and it was shown that $\alpha \to \infty$ on approaching T_C of the solution.

Thus, rather appreciable concentration gradients can appear even at small temperature gradients. The times of establishment of equilibrium in our experiments (tens and hundreds of hours) also agree with the characteristic times of thermal diffusion processes.

The solution of this important problem has made it possible to investigate the shape of the coexistence curve of the aforementioned solution. The main method for determining the shape of the boundary curve is to this day the method of directly measuring the densities of the coexisting phases in the pure substance or the concentrations in the solution, as functions of the temperature. In both cases, additional difficulties arise, due to measurements of the density and concentration of the coexisting phases, and lead accordingly to an increase in the errors.

We used a relatively simple method of investigating the coexistence curve for laminating solutions, consisting of measuring the displacement of the meniscus with changing temperature. The idea of this method was proposed by I. R. Krichevskiĭ, and the calculations for the case of the liquid-vapor critical point of a pure substance were carried out in [20]. The procedure reduces to measuring the ratio of the amounts of matter in the coexisting phases as a function of the temperature. Usually the interface constitutes near T_C a distinct flat surface, the level of which can readily be measured with the highest accuracy.

Let us consider the process of lamination in terms of the coordinates

$$t \equiv (T - T_c) / T_c, \quad X = x - x_c. \tag{3}$$

In these coordinates, the coexistence curve near the critical point can be approximated by a relation of the type

$$|X' - X''| = A|t|^\beta, \tag{4}$$

where X' and X'' are the concentrations of the coexisting phases, and A and β are constants. If X_0 is the average concentration of the solution (the concentration in the homogeneous region), then for a laminating solution the lever rule holds true:

$$(X' - X_0) / (X_0 - X'') = n' / n'' \equiv \eta, \tag{5}$$

or $X' + X''\eta = X_0(1 + \eta)$, where n' and n'' are the numbers of moles of substance in the two coexisting phases. For a coexistence curve that is symmetrical with respect to the critical concentration ($X' = -X''$) we obtain

$$X' = X_0(1 + \eta) / (1 - \eta) \tag{6}$$

and taking (4) into account we get

$$\left| \frac{1 + \eta}{1 - \eta} \right| = \frac{A}{2|X_0|} t^\beta. \tag{7}$$

It is obvious that to determine β it suffices to measure the dependence of η on t for one solution with arbitrary concentration $X_0 \neq 0$. In order to come as close to T_c as possible, it is necessary to have minimal values of $|X_0|$, but this increases the errors due to the very strong dependence of η on t. It therefore becomes necessary to choose optimal values of X_0.

In the more general case of an asymmetrical curve ($X' \neq X''$), its form can be determined by measurements made at least for solutions of two concentrations. Writing down Eq. (5) for solutions with concentrations X_{01} and X_{02} (corresponding to the functions $\eta_1(t)$ and $\eta_2(t)$), and X' and X'' from the system of two equations, we obtain ultimately for the coexistence curve

$$\frac{(1 + \eta_1)(1 + \eta_2)}{|\eta_1 - \eta_2|}|X_{01} - X_{02}| = At^\beta. \tag{8}$$

The value of β can be determined from the measurement data for two solutions with arbitrarily different concentrations. It is also obvious that the value of $|X_{01} - X_{02}|$ is of no importance for the determination of β, but from accuracy considerations it should not be too small.

In the experiment it is usually convenient to determine not the ratio of the number of moles of substance η in the corresponding phases, but the ratio of the volumes of the phases. To change over from volume to molar ratios it is necessary to know the molar volumes V' and V'' on the saturation line. The simplest situation corresponds to equality of V' and V''. In many cases these quantities do not differ appreciably, and the correction for the difference in the volumes can be taken into account with sufficient accuracy if one knows the excess mixing volumes for the investigated solutions and the approximate form of the lamination curve.

For the investigated CH_4–CF_4 system, the $\eta(t)$ dependence was measured for solutions with three concentrations x_0, namely 38.5, 44.5 and 48.5 mol.% CF_4, making it possible to determine β from three pairs of curves. Measurements at different temperatures were

performed after thorough mixing of the solution and storing it subsequently for the time needed for complete separation of the phases. This time was determined in separate experiments and depended on the degree of approach to the critical lamination temperature. Below T_c, owing to the strong dispersion of the system, this time was exceedingly large and reached several dozen hours.

Establishment of equilibrium was monitored against the absence, on the shadow picture, of concentration inhomogeneities in adjacent layers of the coexisting phases, which indicated establishment of their equilibrium composition values. The result was the establishment of a constant interphase boundary, and the thickness of the layers adjacent to this boundary on either side did not exceed 0.1–0.2 mm, i.e., it stayed within the limits of the permissible experimental error. On moving away from the critical point, the time of establishment of equilibrium decreased rapidly and at $\Delta T \sim 0.1°K$ it amounted to several minutes. The place of appearance of the lamination line was determined both by the degree of deviation of the solution concentration from the critical value, and by the sign of X_0. Enrichment of the solution with the heavier component caused the appearance of a separation line in the upper part of the chamber. This line shifted towards the center when the critical temperature was approached. To the contrary, enrichment with the lighter component (CH_4 in this case) shifted the separation line from the lower point of the chamber to its middle on approaching T_c.

The measurement results were used to calculate and plot $\eta(t)$ on a logarithmic scale (Fig. 2). η was calculated from the formula

$$\eta = \frac{V'}{V''} \frac{v_2}{v_1}, \tag{9}$$

where v_1 and v_2 are the volumes of the coexisting phases (see Fig. 1) and V'/V'' is a correction that takes into account the difference between the molar volumes. The latter was determined from the data of [21] from the following relation

$$\frac{V'}{V''} = \frac{X_1'V_1 + (1 - X_1')V_2 + V^E(X')}{X_1''V_1 + (1 - X_1'')V_2 + V^E(X'')}, \tag{10}$$

where V_1 and V_2 are the molar volumes of the first and second components, and V^E is the excess mixing volume. It should be noted that on approaching T_c the correction due to the difference between the molar volumes becomes insignificant and changes from unity at $t = 0$ to ~ 0.9 at $t \sim 10^{-2}$.
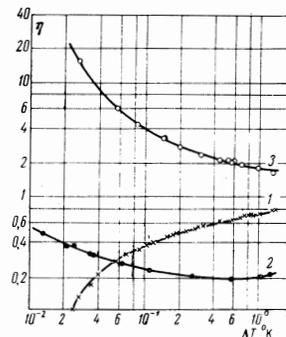
The results shown in Fig. 2 were processed in ac-

FIG. 2. Dependence of the ratios of the numbers of moles of matter in the upper and in the lower phases of the CH_4-CF_4 solution on ΔT for solutions with different initial concentrations of the CF_4 component: curve 1—η_1, $X_{01} = 38.5$ mol.%; curve 2—$\eta_2 - 1$, $X_{02} = 44.5$ mol.%; curve 3—η_3, $X_{03} = 48.5$ mol.%.
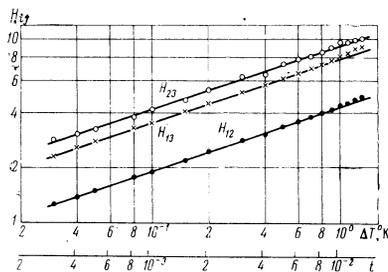
FIG. 3. Dependence of the quantity H_{ij} (11) on ΔT for different pairs of solutions with ratios η_1, η_2, and η_3 of the numbers of moles in the upper and lower phases (see Fig. 2).

cordance with (8) for each pair of investigated solutions. The obtained data are shown in Fig. 3 in a log-log scale in the coordinates H_{ij} and t, where

$$H_{ij} = \frac{(\eta_i + 1)(\eta_j + 1)}{\eta_i - \eta_j}. \tag{11}$$

Within the limit of experimental accuracy, all the plots are parallel straight lines whose slope determines the value of the exponent β of the coexistence curve.

As seen from the figure, the values of β for the three pairs of investigated solutions are 0.352, 0.355, and 0.357, respectively. It should be noted that the accuracy of the result increases when T_c is approached, since the correction for the molar volumes becomes insignificant and the error in the determination of the ratio of the volumes of the coexisting phases also decreases.

Thus, the results of the measurements have shown that the coexistence curve near the critical point of lamination of the solution CH_4-CF_4 is described by a power-law dependence (4) with exponent $\beta = 0.355 \pm 0.01$.

This result, and also the data of previously performed measurements of the temperature dependence of the coefficient of mutual diffusion in this system[15] make it possible, by using the relations of similarity theory,[1] to determine the values of all the critical exponents, namely, α, β, γ, δ, and ν, which are connected by the equations

$$d\nu = 2 - \alpha = \gamma + 2\beta = \beta \, (\delta + 1),$$

where d is the dimensionality of the space, in this case equal to three. According to measurements of D(T), we have $\nu = 0.67 \pm 0.02$, for which, at $\beta = 0.355 \pm 0.01$, we obtain $\alpha \approx 0$, $\gamma = 1.3 \pm 0.08$ and $\delta = 4.65 \pm 0.35$. Most values of these exponents are in good agreement with the corresponding values for pure substances near the critical liquid-vapor point[22] and with estimates based on the three-dimensional Ising model.[1]

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237