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Critical behavior of binary gaseous mixtures

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The behavior of the kinetic coefficients of binary gaseous mixtures has been studied in a vicinity of the gas-liquid critical line. It is shown experimentally by the diffusion equalization of concentration that the mutual diffusion coefficient D depends on the reduced temperature $\tau[\tau=(T-T_c)/T_c$, where T_c is the critical temperature] as a power function with exponent $\gamma\sim 1.2$ up to $\tau\sim 10^{-3}-10^{-4}$ at the approach to the critical point. The dependence $D\sim\tau^{0.6}$ predicted by the scaling theory should be observed in closest proximity of the critical point. It is shown that the diffusion equalization of the isotope concentration does not have any peculiarity near the critical point. Equations of state are proposed for both pure substance and binary mixtures, based on up-to-date theories. They may be used to calculate the required thermodynamic derivatives for describing the temperature dependences of kinetic coefficients. The crossover temperatures have been determined. The experiments performed are in good agreement with our theoretical calculations. [S1063-651X(99)13402-0]

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I. INTRODUCTION

The description of diffusion in nonideal solutions at the level of molecular interaction involves considerable problems which are so far unsolved. Moreover, the means to solve them are unknown due to substantial mathematical difficulties caused by, e.g., the considerable nonlinearity of the problem [1,2]. These difficulties are similar to those observed upon calculation of the thermodynamic properties (thermodynamic potentials) of equilibrium nonideal systems. More difficult is the situation with describing systems near the critical points of solutions, which are points of second-order phase transitions. As has been shown, theories such as mean field theories (e.g., the virial equation of state) are unsuitable in this case, because the introduction of a minor parameter is impossible here [3]. A phenomenological approach, lacking the advantages of a microscopic description, may be used to describe, in general terms, the main features of the behavior of nonideal systems.

The present paper gives the main phenomenological equations to describe the relation between the thermodynamic properties and the diffusion processes in nonideal systems, reveals the role of the mobility of components, and proposes the equations of state for these systems. Particular attention is paid to the experiments performed in the region adjacent to the gas-liquid critical line in which the nonideality of solutions is quite substantial and is manifested in the range of solution parameters (pressure p, mass density ρ, concentration c, temperature T), which is narrowing with approach to the critical point of a pure solvent. Experimentally, this choice is convenient because changing slightly the solution parameters, we may study the entire region beginning with the ideal state up to substantially nonideal ones. The main goal of the study is to describe the relaxation process in a nonideal solution (for simplicity, in a two-component one) when its minor part is taken from the equilibrium state and left free to its own (external fields being zero including the gravitational field although it may have a great effect on the properties of solutions near the critical points and upon phase stratification). (We further consider one-phase systems unless otherwise specified.) This relaxation process is described in terms of a two-component system using the following differential equations [4]. The equation of continuity is

$$\frac{\partial\rho}{\partial t}+\vec{\nabla}\cdot(\rho\vec{v})=0, \tag{1.1}$$

the Navier-Stokes equation is

$$\rho\left[\frac{\partial\vec{v}}{\partial t}+(\vec{v}\cdot\vec{\nabla})\vec{v}\right]=-\vec{\nabla}p+\eta\Delta\vec{v}+(\zeta+\eta/3)\vec{\nabla}(\vec{\nabla}\cdot\vec{v}), \tag{1.2}$$

The equation of continuity for the 2nd component with concentration c_2 is

$$\frac{\partial(\rho c_2)}{\partial t}=-\vec{\nabla}\cdot[\rho c_2\vec{v}+\vec{J}_2^{(m,v)}], \tag{1.3}$$

the equation for entropy production is

$$\rho T\left(\frac{\partial s^{(m)}}{\partial t}+\vec{v}\cdot\vec{\nabla}s^{(m)}\right)=\sigma^{ik}\frac{\partial(\vec{v})_i}{\partial x_k}+\vec{\nabla}\cdot(\overrightarrow{q_T}-\mu^{(m)}\vec{J}_2^{(m,v)})-\vec{J}_2^{(m,v)}\cdot\vec{\nabla}\mu^{(m)},\quad i,k=1,2,3 \tag{1.4}$$

the equation for the second component flow is

$$J_2^{(m,v)}=-\rho D^{v,c}\left(\nabla c_2+\frac{k_T}{T}\nabla T+\frac{k_p}{p}\nabla p\right), \tag{1.5}$$

the equation of state is

$$p=f(c_2,\rho,T), \tag{1.6}$$

and the equation for thermal flux is

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$$\vec{q}_T=\left[k_T\left(\frac{\partial\mu^{(m)}}{\partial c_2}\right)_{p,T}-T\left(\frac{\partial\mu^{(m)}}{\partial T}\right)_{p,c}+\mu^{(m)}\right]\cdot\vec{J}_2^{(m,v)}+\lambda\vec{\nabla}T. \tag{1.7}$$

In this case, t is the time; $\vec{v}$ is the velocity as a momentum of solution unit mass (mean-mass rate); $c_2=\rho_2/\rho$, $c_1=1-c_2=\rho_1/\rho$, where c_1 and c_2 are the mass fractions of the first and second components; ρ_1 and ρ_2 are their mass densities; η is the shear viscosity; ζ is the bulk viscosity; σ^{ik} is the viscous stress tensor; $\vec{J}_2^{(m,v)}$ is the density of diffusion mass flow of the second component relative to the coordinate system, moving with velocity $\vec{v}$; s is the entropy of unit mass; $D^{v,c}$ is the coefficient of mutual diffusion; k_T is the thermal diffusion factor; k_p is the barodiffusion ratio; λ is the coefficient of thermal conductivity; T is the absolute temperature; and $\mu^{(m)}$ is the chemical potential ($\mu^{(m)}=\mu_2/m_2-\mu_1/m_1$, where m_i is the particle mass of the ith component; μ_i is the chemical potential of the ith component per one particle).

The system of equations (1.1)–(1.7) seems rather complex and cannot be simplified for describing a solution over the entire critical region because with approach to the critical point its coefficients display some singularities ($\eta,\zeta,k_T,k_p\to\infty$, $D^{v,c}\to 0$). However, when experiments are performed outside of the asymptotic vicinity of this particular point, according to our investigations, some substantial simplifications are quite possible for a more concrete problem, namely, for studying concentration relaxation (diffusion). We assume that the relaxation of temperature and pressure occurs with a much higher rate than that of the concentration inhomogeneity. In any case, this is the way to perform the experiment, e.g., in capillaries whose walls are kept at constant temperature. Thus, it is assumed that the one-dimensional case is realized and diffusion occurs at a constant temperature ($T=\text{const}$) and pressure ($p=\text{const}$). To avoid misunderstanding, note that the conditions $p=\text{const}$ and $\nabla p=0$ do not mean that we may neglect the hydrodynamic velocity $\vec{v}$. The condition $\nabla p=0$ assumes that the system is in the mechanical equilibrium, that the acceleration ($\partial\vec{v}/\partial t$) and the viscous stress tensor σ^{ik} are so small that they are insignificant. Taking into account the above conditions, we simplify the system of equations (1.1)–(1.7):

$$\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial x}(\rho v_x)=0,\qquad \frac{\partial(\rho c_2)}{\partial t}+\frac{\partial}{\partial x}[\rho c_2 v_x+J_{2x}^{(m,v)}]=0,$$

$$J_{2x}^{(m,v)}=-\rho D^{v,c}\frac{\partial c_2}{\partial x},$$

$$\rho T\left(\frac{\partial s^{(m)}}{\partial t}+v_x\nabla s^{(m)}\right)=\mu^{(m)}\nabla J_{2x}^{(m,v)},$$

$$\rho=f(c_2),\qquad T=\text{const},\qquad p=\text{const}. \tag{1.8}$$

Solving the system (1.8) for the given initial and boundary conditions, one can determine the unknown functions $\rho=\rho(x,t)$, $c_2=c_2(x,t)$, $v_x=v_x(x,t)$, and $s^{(m)}=s^{(m)}(x,t)$ if one knows the coefficients in Eqs. (1.8). Of most interest in this paper is the inverse problem, i.e., the problem of determining the coefficients of mutual diffusion from these experimentally found functions.

The existence of a mechanical equilibrium allows one to prove an important theorem concerning the rules of replacement in the diffusion equations of hydrodynamic (mean-mass) velocity $\vec{v}$ by other velocities [5]. Using this, it is convenient to pass to other velocities, namely, to consider the component particle currents relative to the mean-numerical velocity $w=(N_1v_1+N_2v_2)$ where N_i are the mole concentrations of components and v_i are the mean velocities of components relative to the laboratory system of coordinates (capillary). Besides, we are not interested in the behavior of entropy. In this case, the system of equations (1.8) takes the form (index x is omitted for brevity)

$$\frac{\partial n}{\partial t}+\frac{\partial}{\partial x}(nw)=0,\qquad n\frac{\partial N_2}{\partial t}+nw\frac{\partial N_2}{\partial x}=\frac{\partial}{\partial x}nD^{wN}\frac{\partial N_2}{\partial x},$$

$$n=f(N_2,T=\text{const},\ p=\text{const}),$$

$$J_2^{nw}=nN_2(v_2-w)=-nD^{wN}\frac{\partial N_2}{\partial x},\qquad J_2^{nw}+J_1^{nw}=0. \tag{1.9}$$

This system of equations was first proposed by [6]. The relationship between the new and old quantities has the form $\rho=\rho_1+\rho_2$, $n=n_1+n_2$, $\rho_i=m_in_i$, $c_i=N_im_i/(N_1m_1+N_2m_2)$, and $D^{wN}=D^{v,c}=D$, where n_i is the numerical density of particles of the ith component; n is the total numerical density of particles. In subsequent studies, we shall use the concept of the macroscopic mobility of solution components, b^w. This mobility is defined as the mean velocity of the component, considered as a continuous medium (gas, liquid) relative to some system of coordinates (moving, in this case, with velocity w) under the action of a unit force. Thus, the component flow and the diffusion coefficient in Eqs. (1.9) may be expressed in terms of the mobility b^w and the chemical potential gradient:

$$J_2^{wN}=n_2b_2^w\nabla\mu_2, \tag{1.10}$$

$$D=b_2^wN_2\left(\frac{\partial\mu_2}{\partial N_2}\right)_{p,T}. \tag{1.11}$$

As follows from Eq. (1.10), b_2^w is one of the Onsager coefficients [5]. When $N_2\to 0$ we have $(\partial\mu_2/\partial N_2)_{p,T}\to k_BT/N_2$, $b_2^w\to b_{20}^w$ [7], and we get the known Einstein relation $D=b_{20}^wk_BT$ where b_{20}^w is the mobility of a single-component molecule, considered as the Brownian particle. With approach to the gas-liquid critical point of the solution, $b_2^w\to\infty$, whereas $(\partial\mu_2/\partial N_2)_{p,T}\to 0$. Thus, in nonideal solutions the mobility loses its clear physical meaning and usually the term ''macroscopic mobility'' is used. Let us now study the system (1.9) which describes the relaxation of the concentration inhomogeneity in a capillary with definite boundary and initial conditions. Our purpose is to derive an expression for the experimentally observed values of $J_2^{wN}=nN_2(v_2-w)$ (the mean flow of the number of particles of the second component relative to the capillary) and of w (the mean numerical velocity) in terms of the concentration gradient). Integrating Eqs. (1.9) over the capillary length from 0 to x with boundary conditions $(\partial N_2/\partial x)_{t,x=0}=0$ and $w(0)=0$, we have

$$w(x)=-\frac{1}{n}\left(\frac{\partial n}{\partial N_2}\right)_{p,T}\left(D\frac{\partial N_2}{\partial x}\right)-\int_0^x nD\left(\frac{\partial N_2}{\partial x}\right)^2\left(\frac{\partial^2 v}{\partial N_2^2}\right)_{p,T}dx, \tag{1.12}$$

where $v=1/n$ is the specific volume,

$$J_2^N(x)=-nD\left[1+\frac{N_2}{n}\left(\frac{\partial n}{\partial N_2}\right)_{p,T}\right]\left(\frac{\partial N_2}{\partial x}\right)-nN_2\int_0^x nD\left(\frac{\partial N_2}{\partial x}\right)^2\left(\frac{\partial^2 v}{\partial N_2^2}\right)_{p,T}dx. \tag{1.13}$$

Equations (1.12) and (1.13) show that the velocity $w(x)$ and flow $J_2^N(x)$ are the nonlocal quantities and are determined by the values of D, N_2, and n over the entire length x. Note also that besides the peculiarities observed in the behavior of D with approach to the critical point of the solution, the derivatives of n with respect to concentrations are also divergent. Obviously, to understand the behavior of the diffusion process (the equalization of concentration) in nonideal solutions, it is necessary not only to know the purely kinetic coefficients (mobilities) but also the equilibrium properties of these solutions. Therefore we have studied experimentally both the thermal equation of state and the diffusion processes in strongly nonideal solutions.

II. EQUILIBRIUM THERMODYNAMIC PROPERTIES AND DIFFUSION NEAR THE GAS-LIQUID CRITICAL LINE OF BINARY SOLUTIONS

Since the driving force of diffusion is the chemical potential gradient, let us consider the methods of its calculation for various cases, i.e., the methods of determination of the chemical potential derivative with respect to the component concentration as well as the dependences of the mixture density on its composition. We consider first the weakly nonideal binary gaseous solution. According to [7], its thermodynamic potential Ω is expressed as the partition function with the terms determined by the system energy levels to within the second-order terms in series expansion in powers of density:

$$\Omega=-k_BT\ln\left[1+\xi_1 v+\xi_2 v+\frac{\xi_1\xi_2}{2!}v^2I_{12}+\frac{\xi_1^2}{2!}v^2I_{11}+\frac{\xi_2^2}{2!}v^2I_{22}\right], \tag{2.1}$$

where $\xi_1=[m_1k_BT/(2\pi\hbar^2)]^{3/2}\exp\{\mu_1/k_BT\}$, $\xi_2=[m_2k_BT/(2\pi\hbar^2)]^{3/2}\exp\{\mu_2/k_BT\}$, $I_{12}=\int dv[\exp\{-U_{12}/k_BT\}-1]$, $I_{11}=\int dv[\exp\{-U_{11}/k_BT\}-1]$, and $I_{22}=\int dv[\exp\{-U_{22}/k_BT\}-1]$.

U_{12}, U_{11}, and U_{22} are the energies of the interaction between the molecules of the first and second components, among the molecules of the first component and among the molecules of the second component, respectively. The I_{ij} integrals for various interaction types are shown, e.g., by [2]. For the pressure and chemical potentials we may get the expressions $p=-(\Omega/v)$. The mean values of the densities of component molecules are determined by simple differentiation $\langle n_1\rangle=(d\Omega/d\mu_1)_{T,v}$, $\langle n_2\rangle=(d\Omega/d\mu_2)_{T,v}$. To determine the chemical potentials, we give ξ_1 and ξ_2 in terms of $\langle n_1\rangle$ and $\langle n_2\rangle$ and pass to the concentrations $N_1=\langle n_1\rangle/[\langle n_1\rangle+\langle n_2\rangle], N_2=1-N_1$. Hence,

$$\mu_1=k_BT\left(\ln\frac{N_1}{v}-I_{11}\frac{N_1}{v}-\frac{1}{2}I_{12}\frac{1-N_1}{v}\right)-k_BT\frac{3}{2}\ln\left(\frac{m_1k_BT}{2\pi\hbar^2}\right),$$

$$\mu_2=k_BT\left(\ln\frac{N_2}{v}-I_{22}\frac{N_2}{v}-\frac{1}{2}I_{12}\frac{1-N_2}{v}\right)-k_BT\frac{3}{2}\ln\left(\frac{m_2k_BT}{2\pi\hbar^2}\right). \tag{2.2}$$

The equation of the state of a weakly nonideal gaseous solution, expressed in terms of concentrations and specific volume, has the form

$$\frac{p}{k_BT}=\frac{1}{v}+\frac{I_{11}}{2}\left(\frac{N_1}{v}\right)^2+\frac{I_{22}}{2}\left(\frac{1-N_1}{v}\right)^2+\frac{I_{12}}{2}\frac{N_1(1-N_1)}{v^2}. \tag{2.3}$$

Using these equations, we may derive the derivatives of the chemical potential and specific volume:

$$\left(\frac{\partial\mu_2}{\partial N_2}\right)_{p,T}=\frac{k_BT}{N_2}\left[1-\frac{N_2(1-N_2)}{v}(I_{11}+I_{22}+I_{12})\right], \tag{2.4}$$

$$\left(\frac{\partial v}{\partial N_2}\right)_{p,T}=\left[I_{11}(1-N_2)+I_{22}N_2+\frac{I_{12}}{2}N_2(1-N_2)\right]\times\left[1+I_{11}\frac{(1-N_2)^2}{v}+I_{22}\frac{N_2^2}{v}+I_{12}\frac{N_2(1-N_2)}{v}\right]. \tag{2.5}$$

Now we consider the limiting case of a strongly nonideal system, namely, the two-component solution near the gas-liquid critical point of the solvent. By definition, the critical line of a binary solution is described by the equations [7,8]

$$(\partial\mu_1/\partial N_1)_{p,T}=(\partial\mu_2/\partial N_2)_{p,T}=0,$$

$$(\partial^2\mu_1/\partial N_1^2)_{p,T}=(\partial^2\mu_2/\partial N_2^2)_{p,T}=0. \tag{2.6}$$

Two coexisting phases become identical in this line. As is known [7], in the vicinity of the critical line an increase in system susceptibility $[(\partial N/\partial\mu)_{p,T}\to\infty]$ causes an increase in fluctuations of the order parameter (for our case, a combination of density and concentration; see [9]). In this case, the fluctuations are considered as interacting [3,10]. This leads to a singular behavior of equilibrium and kinetic values which cannot be described either by the theory of perturbations or by the theory of mean field, e.g., by the van der Waals theory [11] or by the Landau theory of second-order phase transitions [7]. However, the description of the critical behavior of such a theory is rather useful. It is simple enough and there is a region which is not too close to the critical point in which this theory may be used in some approximation. Let us use it to describe the phenomena occurring near the gas-liquid critical point of the solvent; later we will pass to a more general theory.

In the theory of mean fields, the expression for the derivative of chemical potential with respect to concentration with allowance for Eqs. (2.6) may be expanded in a power series of solution parameters deviations from the critical values:

$$\left(\frac{\partial\mu_2(p,T,N_2)}{\partial N_2}\right)_{p,T}=A'_{NN}(N_2-N_{2c})^2+A'_T(T-T_c)+A'_p(p-p_c). \qquad (2.7)$$

However, this expansion is inconvenient for an analysis. Therefore, if we know the equation of state $p=p(v,T,N_2)$, it may be derived in a different form [6]. The free energy of the unit volume $F(v,T,N_2)$ is the homogeneous function of particle number:

$$F=nf(T,v,N_2)=n[k_BTN_2\ln N_2+f^*(T,v,N_2)].$$

Hence,

$$\mu_2=\left(\frac{\partial F}{\partial n_2}\right)_{T,v,n_1}=f-v(\partial f/\partial v)_{T,N}+(1-N_2)(\partial f/\partial N_2)_{T,v}. \qquad (2.8)$$

Differentiating Eq. (2.8) with respect to N_2, we get the expression for $(\partial\mu_2/\partial N_2)_{p,T}$ in the general form

$$\left(\frac{\partial\mu_2}{\partial N_2}\right)_{p,T}=\frac{1-N_2}{N_2}k_BT\left\{1-\frac{N_2}{k_BT}\left[\frac{(\partial p/\partial N_2)^2_{v,T}}{-(\partial p/\partial v)_{N,T}}+f^*_{NN}(v,T,N_2)\right]\right\}. \qquad (2.9)$$

In this case $f^*(v,T,N_2)$ is the free energy per one particle, and $f^*_{NN}=(\partial^2f^*/\partial N_2^2)_{v,T}$. When we know the equation of state, the chemical potential may also be found using the formula [12]

$$\frac{\mu_2(p,T)-\mu_2^0(p=1,T)}{RT}=\ln(pN_2)+\frac{1}{RT}\int_0^p\left[v+N_1\left(\frac{\partial v}{\partial N_2}\right)_{p,T}-\frac{RT}{p}\right]dp. \qquad (2.10)$$

For instance, for the van der Waals equation

$$p=\frac{RT}{v-b}-\frac{a}{v^2} \qquad (2.11)$$

or, in the dimensionless form,

$$p^*=8T^*/(3v^*-b^*)-3a^*/v^{*2}, \qquad (2.12)$$

$a^*=a/a_1$, $b^*=b/b_1$, $p^*=p/p_c$, $T^*=T/T_c$, $v^*=v/v_c$, $p_c=a_1/(27b_1^2)$, $T_c=8a_1/(27Rb_1)$, and $v_c=3b_1$, where

$$a=a_1N_1^2+2a_{12}N_1(1-N_1)+a_2(1-N_1)^2,$$

$$b=b_1N_1^2+2b_{12}N_1(1-N_1)+b_2(1-N_1)^2, \qquad (2.13)$$

the derivative $(\partial\mu_2/\partial N_2)_{p,T}$ has the form

$$\frac{N_2N_1}{RT}\left(\frac{\partial\mu_2}{\partial N_2}\right)_{p,T}=1-\frac{N_2N_1^2}{T^{*2}}\left\{\frac{\left(\frac{\partial p^*}{\partial N_2}\right)_{T,v}}{-\left(\frac{\partial p^*}{\partial v^*}\right)_{T,N}}-\frac{8T^*}{3v^*-b^*}\times\left[\frac{d^2b^*}{dN_2^2}+\frac{(db^*/dN_2)^2}{3v^*-b^*}+\frac{9d^2a^*/dN_2^2}{v^*}\right]\right\}. \qquad (2.14)$$

If the equation of state is given as the expansion into a Rozen series [13] (see also [6]) ($N_2\equiv N$),

$$\Delta p=(p-p_c)=A_NN+A_T\Delta T+A_{N\rho}N\Delta\rho+A_{T\rho}\Delta T\Delta\rho+A_{\rho^3}\Delta\rho^3+A_{N^2}N^2+A_{T^2}\Delta T^2+A_{NT}N\Delta T+A_{T\rho^2}\Delta T\Delta\rho^2+A_{N\rho^2}N\Delta\rho^2+A_{\rho^4}\Delta\rho^4, \qquad (2.15)$$

then we have

$$\left(\frac{\partial\mu_2}{\partial N}\right)_{p,T}=\frac{1-N}{N}k_BT\left[1-\frac{N}{k_BT}\left(\frac{A_N^2+2A_NA_{Nv}\Delta v}{-A_{Nv}N-A_{Tv}\Delta T-3A_{v^3}\Delta v^2}\right)\right], \qquad (2.16)$$

$$\left(\frac{\partial v}{\partial N}\right)_{p,T}=\frac{A_N+2A_{Nv}\Delta v}{-A_{Nv}N-A_{Tv}\Delta T-3A_{v^3}\Delta v^2}. \qquad (2.17)$$

Deriving Eqs. (2.14)–(2.17), we neglected the terms of the fourth order and the derivative f^*_{NN} which near the gas-liquid critical point of the solvent is small compared with other terms of Eq. (2.9).

According to numerous investigations (see, e.g., the review in [10]; also see [14–19] and our papers [20–25]), equations of the type (2.11),(2.15), belonging to some of the so-called mean field theories, are inadequate for experimental results in close vicinity of the critical point. We propose more complex equations of state to describe the singular behavior of thermodynamic quantities near the gas-liquid critical point of the solvent. These equations are based on the hypotheses of scaling invariance, isomorphism, and conformal invariance of fluctuating quantities [3,26,27]; see also [28,29].

For a pure solvent with allowance for nonasymptotic corrections our equation of state has the form [30]

$$\Delta\rho=(\rho-\rho_c)/\rho_c=A_1+bA_2,$$

$$\tau=(T-T_c)/T_c=(1-ab)^{-1}(h_2-bh_1),$$

$$\sigma=(S/v-S_c/v_c)T_c/p_c=aA_1+A_2,$$

$$\Delta\mu=(\mu-\mu_c)/p_cv_c=(1-ab)^{-1}(h_1-ah_2). \quad (2.18)$$

In this case, $\Delta\rho$, τ, σ, and $\Delta\mu$ are the reduced mass density, temperature, entropy, and chemical potential of the system; a and b are constants; A_1, A_2, h_1, and h_2 are the quantities, corresponding to magnetic moment, reduced entropy, magnetic field, and reduced temperature of this Ising lattice, respectively; the subscript c is the critical value. The expressions for these quantities in terms of parameters r and θ, introduced by [31] for a ‘‘linear model,’’ which solves conveniently the problem of equation analyticity at a critical point, have the form (with nonasymptotic correction first introduced by [32] and [33] and modified by us)

$$A_1=gr^{\beta}\theta-\frac{Eg}{A}r^{\beta+\Delta}\varphi(\theta),$$

$$A_2=Agr^{1-\alpha}(s_0-s_2\theta^2)+Egr^{1-\alpha+\Delta}Q_0,$$

$$h_1=Ar^{\gamma+\beta}(\theta-\theta^3), \quad h_2=r(1-B^2\theta^2), \quad (2.19)$$

where γ, β, and α are the critical indices of compressibility, boundary curve (binodal), and thermal capacity, respectively; Δ is the index of nonasymptotic corrections; the coefficients A,g,E are the fitting quantities; $s_0=\gamma(\gamma-1)/2B^2\alpha(1-\alpha)$, $s_2=-\gamma(1-2\beta)/2\alpha$, $Q_0=-(\gamma+\Delta)/2B^2(1-\alpha+\Delta)$, and $B^2=(\gamma-2\beta)/\gamma(1-2\beta)$,

$$\varphi(\theta)=\frac{\theta[1-B^2\theta^2(1-2\beta)]}{1+\theta^2[B^2(2\gamma+2\beta-1)-3]+\theta^4B^2(3-2\gamma+2\beta)}.$$

The areas of changing parameters are $0\leqslant r\leqslant\infty, -1\leqslant\theta\leqslant+1$. For the one-component order parameter, which holds for the critical points of liquids, $\alpha=0.11$, $\beta=0.325$, $\gamma=1.24$, and $\Delta=0.45$. These values of the critical indices were theoretically obtained by [26] and were confirmed by numerous measurements (see, e.g., [10]). Note that only two of these are independent because are related via $\alpha+2\beta+\gamma=2$.

The pressure is expressed in terms of these parameters as

$$\Delta p=(p-p_c)/p_c=(S_cT_c/p_cv_c-a)\tau+Ar^{\gamma+\beta}(\theta-\theta^3)$$
$$+Er^{\gamma+\beta+\Delta}+Agr^{2-\alpha}(z_0+z_2\theta^2+z_4\theta^4)$$
$$+Egr^{2-\alpha+\Delta}(p_0+p_2\theta^2).$$

In this case $z_0=(\gamma-2\beta-\gamma\alpha B^2)/2B^2\alpha(1-\alpha)(2-\alpha)$, $z_2=[\alpha B^2(2\gamma+2\beta-1)-\gamma+2\beta]/2B^2\alpha(1-\alpha)$, $z_4=(\gamma+\beta-3/2)/\alpha$, $p_0=-(\gamma+\Delta)/2B^2(1-\alpha+\Delta)(2-\alpha+\Delta)$, and $p_2=(1-2\beta)/2(1-\alpha+\Delta)$.

To derive the equation of state of the binary solution, the quantities defining of the system state are convenient to express in terms of some parameters ζ, $\tilde{\tau}$, and h which include the regular parts (the Leung-Griffiths equation) [34]. This parametric equation of state is written as

$$\mu_1-\mu_2=RT\ln\{[\zeta/(1-\zeta)]K_2/K_1\},$$

$$p=\omega(\zeta,h,\tilde{\tau})RT,$$

$$\rho=\omega_h^{\mathrm{reg}}+\Delta\rho,$$

$$T=[R(a_0+a_1\zeta-a_0\tilde{\tau})]^{-1},$$

$$N=\zeta+\zeta(1-\zeta)[\omega_\zeta+a_1\omega_\tau)/\rho-v_1]. \quad (2.20)$$

The subscript denotes differentiation with respect to a corresponding variable; μ_1 and μ_2 are the chemical potentials of the first and second components; and K_1 and K_2 are the dimensionless constants, determined by the critical values of entropy for pure components [34]. Unlike the Leung-Griffiths equation we have written down [35] $\omega=\omega^{\mathrm{reg}}+\omega^{\mathrm{sing}}$, $\omega^{\mathrm{reg}}=c(\zeta)+d_0\tilde{\tau}+l_0\tilde{\tau}^2+f(\zeta)h$, $\Delta\rho=f(\zeta)(A_1+bA_2)$, $A_1=\partial\pi/\partial h_1$, $A_2=\partial\pi/\partial h_2$, $c(\zeta)=c_0+c_1\zeta$, $f(\zeta)=f_0+f_1\zeta$, and $\omega^{\mathrm{sing}}=f(\zeta)\pi(h,\tilde{\tau})$. A_1 and A_2 are the same as in Eqs. (2.18) and the thermodynamic potential π as a function of the variables of the ‘‘linear model’’ has the form

$$\pi=Agr^{2-\alpha}(z_0+z_2\theta^2+z_4\theta^4)+Egr^{2-\alpha+\Delta}(p_0+p_2\theta^2).$$

Parameters $\tilde{\tau}$ and ζ display a clear physical meaning: $\tilde{\tau}=1/(RT_c)-1/(RT)$, $\zeta=K_1\exp(\mu_1/RT)/[K_1\exp(\mu_1/RT)+K_2\exp(\mu_2/RT)]$. Parameter h is more complex:

$$h=\ln[K_1\exp(\mu_1/RT)+K_2\exp(\mu_2/RT)]$$
$$-b_0+b_1\zeta+b_2\zeta(1-\zeta)+g_0\tilde{\tau}.$$

Expressing $\tilde{\tau}$ and h in terms of parameters r and θ, we get

$$\tilde{\tau}=a_0[r(1-B^2\theta^2)-bAr^{\gamma+\beta}(\theta-\theta^3)],$$

$$h=Ar^{\gamma+2\beta}(\theta-\theta^3). \quad (2.21)$$

Hence,

$$\rho=f(\zeta)\left[1+gr^{\beta}\theta-\frac{Eg}{A}r^{\beta+\Delta}\varphi(\theta)+bAgr^{1-\alpha}(s_0+s_2\theta^2)\right],$$

where $\varphi(\theta)$ is the same as in Eqs. (2.19). The coefficients a_i, A, g, E, b, b_i, c_i, K_i, d_0, g_0, l_0, f_i, and v_1 are the fitting constants. The quantities of T_c, ρ_c, and p_c are determined by the vanishing of the singular terms of equations. The ranges of the parameters variation are $0\leqslant r\leqslant\infty$, $-1\leqslant\theta\leqslant+1$, and $0\leqslant\zeta\leqslant1$. Our equation differs from Leung-Griffiths equation by the introduction of additional terms in the expressions for π and $\tilde{\tau}$. The nonasymptotic correction is taken into account by terms containing the constant E and index Δ, and the conformal invariance of fluctuating quantities is taken into consideration by terms with a constant b.

The resulting equations are difficult to analyze. Their advantage, however, is in the fact that they are based on the fundamental principles of the up-to-date theory of second-order phase transitions, hold for any vicinity of the critical point, and may be sewed (matched smoothly) with the virial equation of state at a sufficient amount of terms in regular functions. Simplifications are possible in studying real systems. In this case, however, the degree of errors, arising from

TABLE I. The piezometer characteristics.

	Measured interval	Absolute error	Parameter's sensibility
P (MPa)	0-10	± 0.01	$4\times10^{-5}-4\times10^{-4}$
T (K)	275-330	± 0.001	2×10^{-4}
V (cm^3)	14-20	$\pm 4\times10^{-4}$	2×10^{-4}
m (g)	200	$\pm 1\times10^{-4}$	1×10^{-4}

these simplifications, is always clear. An important peculiarity of these equations is that they give expressions for the thermodynamic potentials (chemical potentials) of components and, thus, we may simultaneously determine many properties to characterize the system (the diagrams of state p-T-N, the behavior of boundary curve diameter, thermal capacity, compressibility depending on three variables, determining the system state $\rho,\ T,\ N$ or $p,\ \rho,\ N$).

The above theory needed verification or, more precisely, determination of the physical meaning of the corollaries of its equations. With the accumulation of experimental data, the theory improved. The experimental investigations near the gas-liquid critical point of the solvent had two main purposes. The first one was to study the dependence of pressure on the temperature, volume, and concentration of binary solutions (p,ρ,T,N dependences). The second one was to study diffusion in order to determine the constants of equations, to establish the regions of the applicability of these equations, and to explain the peculiarities of the behavior of nonideal solutions.

For the first purpose the original apparatus was created to obtain the p,v,T,N data. One of these [36] is a piezometer with variable volume in the form of a cylinder with a plunger located horizontally in a thermostat. It contained windows to observe phase stratification and critical opalescence. The pressure was measured using a standard dead weight gauge and a pressure detector, based on the measurement of sapphirine membrane deformation determined by the resistance of a doping semiconductor strip, deposited on the membrane [37]. Variations in volume were measured using a microscopic screw which moved the plunger. The temperature was determined by means of a high-precision platinum resistance thermometer. A magnetic mixer was used to establish equilibrium in the piezometer. The piezometer characteristics are listed in Table I. This apparatus was used to study pure CO_2 [20,21] and the solutions CO_2-^4He [38,39], CO_2-Ne [40,41,35], CO_2-Ar [36], CO_2-Kr [42], and CO_2-Xe [43] near the gas-liquid critical point of CO_2.

Another low-temperature setup [44] was employed to measure the p-v-T dependences of ^4He near the gas-liquid critical point. In this setup the density was measured by the dielectric permeability of helium using the capacity method. The pressure was measured by means of a mercury manometer and the temperature was measured by a semiconductor model resistance thermometer. The gas density was determined to within $\pm 2\times10^{-3}\%$. The mercury manometer with a sensitivity of 0.05 Torr allowed us to measure pressure over the range of 1530–2030 Torr with an absolute error of ± 0.1 Torr. The temperature in a measuring cell was controlled to within $\pm 10^{-4}$ K.

Using the data obtained, we determined the coefficients of thermal equations of state (2.18) and (2.20). Besides, the data on ^4He were also used to determine the coefficients of the caloric equation of state, derived by us using the same hypotheses [23]. As an example, we give the results of data approximation for the CO_2-Ne solution [40,41,35] by the method of minimization of quadratic functional with respect to pressure. The data were obtained within the ranges $302.15\ \mathrm{K} \leqslant T \leqslant 309.65\ \mathrm{K}$, $392\ \mathrm{kg/m^3} \leqslant \rho \leqslant 568\ \mathrm{kg/m^3}$, $0 \leqslant N \leqslant 5.076$ mol % Ne, and $7.2\ \mathrm{MPa} \leqslant p \leqslant 9.4$ MPa. These results are $a_0 = 3.95445\times10^{-4}$ kmol/kJ, $m_0 = 2.920\,30$ kmol/m^3, $f_0 = 10.6346$ kmol/m^3, $g = 1.193 \pm 0.04$, $A = 6.26 \pm 0.6$, $E = 2.1 \pm 4.6$, $b = -0.050 \pm 0.076$, $v_1 = 2.29 \pm 0.90$, $a_1 = (6.82 \pm 4.6)\times10^{-5}$ kmol/kJ, $c_1 = 34.7 \pm 24$ kmol/m^3, $d_0 = (44.24 \pm 0.3)\times10^3$ kPa, $l_0 = (-4.9 \pm 1.0)\times10^8$ kJ^2/kmol/m^3, $f_1 = 23.7 \pm 16$ kmol/m^3, $\alpha = 0.11$, $\beta = 0.325$, $\gamma = 1.24$, and $\Delta = 0.45$. The mean-square errors in the approximation of pressure, density, temperature, and concentration were $\delta p = 0.0015$ MPa, $\delta\rho = 0.005$ kmol/m^3 (≈ 0.2 kg/m^3), $\delta T = 0.0031$ K, and $\delta N = 0.02$ mol % Ne. The errors were calculated for a confidence coefficient of 0.68.

The given accuracy of approximation by this scaling equation is higher than that by the equation of state (2.15) and is close to the accuracy of the experimental data.

To reach the second purpose, we have mainly studied the temperature dependences of diffusion coefficients for the densities close to the critical ones with approach to the critical temperature as well as their dependences on concentration and density.

The diffusion coefficients were measured in the systems CO_2-^{40}Ar [45–47], CO_2-^{40}Ar-^{36}Ar [48], CO_2-Ne [49–51], ^4He-D_2 [52–54], and ^3He-^4He [24,25]. To obtain data on the first four solutions, we used the method of capillaries. Diffusion in the ^3He-^4He solution has been studied using the method of the measurement of horizontal solution layer capacity. The first method is used to measure the mean solution concentration in a capillary, depending on the time when one of the capillary ends is closed, and the other is connected to a large volume with different concentration. The valves, located at capillary ends, were used to fill the diffusion cell with gases, to create the concentration difference, and to pass the mixture to mass spectrometer for analysis. A large cell volume with a magnetic mixer contained enough gas to maintain constant pressure and concentration at the open end of the capillary during the diffusion. Thus, diffusion occurred under constant boundary conditions. The cell was thermostated at the required experimental temperature. In the second method [55,56] the diffusion cell consisted of a copper block with a cylindrical cavity with a minor height/diameter ratio. In the upper section of the cell there was a flat capacitor to measure variations in the solution density and concentration. The concentration gradient in the cell was initially produced by fast heating from the temperature at which the solution separates into liquid and vapor phases to the experimental temperature, corresponding to the one-phase state region [56,25].

As has been mentioned, diffusion near the critical point is described by a set of nonlinear equations. It is rather difficult to solve these equations, i.e., to determine the dependences of concentration in the capillary on the time and coordinate. More difficult is the problem of the determination of the

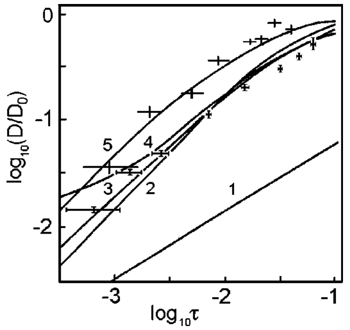

FIG. 1. Temperature dependences of the coefficients of mutual diffusion in CO_2-Ne ($N_2=0.036$) and CO_2-Ar ($N_2=0.043$) solutions near the gas-liquid critical point of CO_2. CO_2-Ne: special crosses, experiment. (1) D/D_0 where D is described by Eq. (3.5), and $D_0=9.3\times10^{-3}\ \mathrm{m^2\,s^{-1}}$; (2) Eq. (3.6); (3) $D/D_0=(\partial\mu/\partial N)_{p,T}$ where $(\partial\mu/\partial N)_{p,T}$ is given on the critical isochore according to Eq. (2.16); (4) on the isochore close to the critical one. CO_2-Ar: simple crosses, experiment; (5) calculation similar to that for curve 3.

diffusion coefficient by experimental dependences $N_2=f(x,t)$ [47,49–51]. However, at sufficiently small concentration differences Eqs. (1.8) and (1.9) may be linearized and the diffusion coefficient may be determined using the Fick law [45,46]. Obviously, the closer the binary solution is to the critical point, the smaller is the concentration differential. Therefore, in these experiments one should carefully choose the maximum value of the difference, basing the choice on the required measurement accuracy and on the estimation of terms by the known equations of state.

For large times the solution to Fick's equation

$$\frac{\partial N_2}{\partial t}=D\frac{\partial^2 N_2}{\partial x^2}\quad (T=\mathrm{const},\ \ p=\mathrm{const}) \tag{2.22}$$

is well known,

$$N_2(t)-N_2^v=A\exp(-t/t_p), \tag{2.23}$$

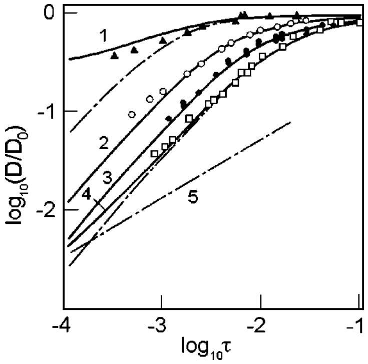

FIG. 2. The dependence of the coefficient of mutual diffusion in the solutions of He isotopes on the reduced temperature at the various densities and concentrations. Circles, experiment; solid lines, the results obtained by using Eq. (3.3). (1) For molar fraction of ^{3}He, $N=0.007$, the deviation of density from the critical one, $\Delta n/n_c=0.05$; (2) $N=0.046$, $n=n_c$; (3) $N=0.108$, $\Delta n/n_c=0.02$; (4) $N=0.205$, $n=n_c$. The dot-dashed continuation of curves 1 and 4, the calculated behavior of D for $n=n_c$. (5) The results obtained by using $D=k_BT/6\pi r_c\eta$.

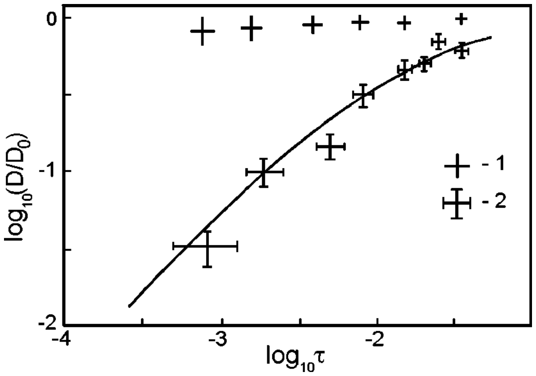

FIG. 3. The temperature dependences of the reduced diffusion coefficient (D/D_0) which determine the times of the equalization of isotopic Ar content (1), the times of the equalization of Ar concentration in CO_2(2), and near the gas-liquid critical point of CO_2-Ar with $N=4.8$ mol % of Ar. The curve shows calculations by formula $D/D_0=(\partial\mu/\partial N)_{p,T}N/kT$ where $(\partial\mu/\partial N)_{p,T}$ was calculated by using Eq. (2.16).

where $t_p=4l^2/\pi^2D$; $N_2(t)$ is the mean concentration in the capillary; N_2^v is the equilibrium concentration in the volume and, initially, at the open end of the capillary; and l is the capillary length. The diffusion coefficient D involved in Eq. (2.23) is calculated in the system of coordinates, moving with mean numerical velocity w. Experimentally, the determination of D as D^{wN} in terms of Eq. (2.23) is preferable.

III. INTERPRETATION OF RESULTS

The main experimental data on the study of kinetic coefficients are shown in Fig. 1–5. Figures 1 and 2 demonstrate that with approach to the critical point the diffusion coefficient D tends to zero. This diffusion behavior was first observed by [8] (see also [57]) in binary liquid solutions near the critical points of mixing. Let us consider experiments on the CO_2-^{40}Ar system [48], performed using the method of capillary, to understand the physical meaning of this phenomenon, i.e., the problem of the relationship between the macroscopic mobility and the mobility of separate molecules. For this aim, the different concentrations of isotopes relative to each other and to CO_2 were produced in the capillary and in the cell volume. When the capillary was opened

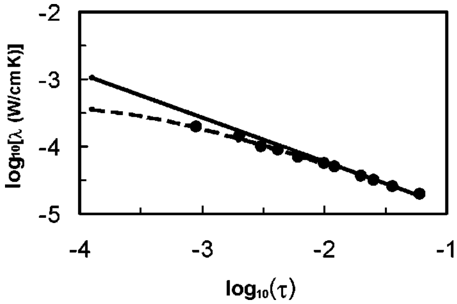

FIG. 4. The dependence of thermal conductivity of ^{3}He-^{4}He solution on the reduced temperature near the gas-liquid critical point. The solid line corresponds to Eqs. (3.8) for λ in which the terms, decaying with approach to the critical point, are neglected. The dotted line corresponds to the passage to the limiting behavior (λ ~ const). The circles denote the experimental data [61].

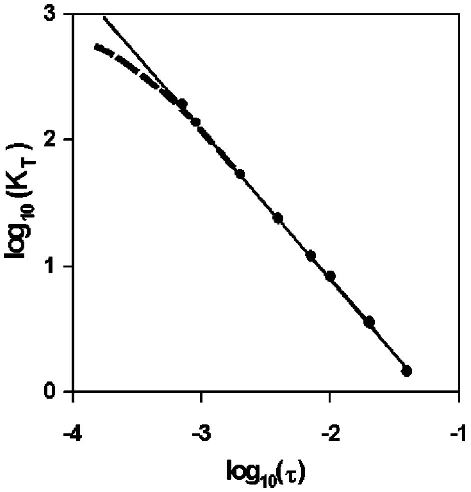

FIG. 5. The dependence of thermal diffusion factor k_T of ^{3}He-^{4}He solution on the reduced temperature. The solid line corresponds to the calculation according to formula (3.8) for k_T. The dotted line corresponds to the passage to the limiting behavior ($k_T \sim \tau^{\nu}$). The circles correspond to experimental data [61].

(connected to the cell), the mutual diffusion of argon and CO_2 proceeded parallel to the equalization of argon isotope concentration. Figure 3 depicts the dependence of a reduced diffusion coefficient D/D_0 on temperature $\tau=(T-T_c)/T_c$ where

$$D_0=\frac{0.1496}{\sigma_{12}^2\Omega^{(1,1)}n}\left[\frac{(m_1+m_2)k_BT}{m_1m_2}\right]^{1/2}. \tag{3.1}$$

For Eq. (3.1) the σ_{12}^2, $\Omega^{(1,1)}$, m_1, and m_2 quantities were taken from [2] for argon and CO_2; the mean molar fraction of Ar was $N_2=0.048$ with $n=n_c=6.5\times10^{27}$ m^{-3}. As follows from Fig. 3, the diffusion coefficients of argon and CO_2 decrease many times whereas that responsible for the equalization of the isotopic concentration of argon in CO_2 is temperature independent and equal to D_0, corresponding the limit of rarefied gases but with a density equal to the critical density. Thus, it is assumed that $D_0=b_0k_BT$, where b_0 is the mobility of separate molecules and has the form [2]

$$b_0=\frac{0.1496}{\sigma_{12}^2\Omega^{(1,1)}n}\left[\frac{(m_1+m_2)}{m_1m_2}\right]^{1/2}(k_BT)^{-1/2} \tag{3.2}$$

and no peculiarities in any vicinity of the critical point. Thus, for the region studied ($\tau>10^{-3}$), the component mobility is assumed to have no peculiarities and to be equal to the quantity calculated by the theory of rarefied gases with density almost equal to the critical value. This is of fundamental importance because either a decrease in the diffusion coefficient near the critical point or an increase in the relaxation time of the inhomogeneities of the concentration of solution components is caused not by the slowing down Brownian motion of molecules but by a decrease in the thermodynamic force due to some mean field which prevents the equalization of concentration. This mean field is similar in its action to the gravitational field which also prevents from the vertical equalization of the concentration gradient in the solution.

Thus, calculating the thermodynamic force, i.e., the $(\partial\mu_2/\partial N_2)_{p,T}$ derivative, using one of the equations of state, the data obtained may be approximated by the expression

$$D=N_2b_0(\partial\mu_2/\partial N_2)_{p,T}, \tag{3.3}$$

where b_0 is calculated by Eq. (3.2). Equation (3.3) was verified by experimental investigations of the solutions CO_2-Ar (Fig. 3), CO_2-Ne (Fig. 1), ^{3}He-^{4}He (Fig. 2), and D_2-^{4}He. Note that the above results are valid only for the region that is not too close to the gas-liquid critical point of the solvent. The studies indicate (see [10]) that over the entire region of the critical state of solutions, the macroscopic mobility (the Onzager coefficient) has a important peculiarity which has no relation to the mobility of separate molecules. In the general case, the diffusion coefficient may be given as follows:

$$D=\frac{k_BT(b^{\text{sing}}+b^{\text{reg}})}{\dfrac{k_BT}{N_2}\left(\dfrac{\partial N_2}{\partial\mu_2}\right)_{p,T}^{\text{sing}}+\dfrac{k_BT}{N_2}\left(\dfrac{\partial N_2}{\partial\mu_2}\right)_{p,T}^{\text{reg}}}. \tag{3.4}$$

The superscripts denote the singular and regular parts of the values. According to the theory of critical phenomena [10], on the critical isochores we have $(\partial N/\partial\mu)_{p,T}^{\text{sing}}\sim\tau^{-\gamma}$, $b^{\text{sing}}\sim\tau^{-\gamma+\nu}$, where γ and ν are the critical indices of both the compressibility and correlation radius, respectively ($\gamma=1.24$, $\nu=0.62$). With approach to the critical point, $b^{\text{sing}}\to\infty$, $(\partial\mu_2/\partial N_2)_{p,T}^{\text{sing}}\to0$ and in the limit

$$D\to N_2b^{\text{sing}}(\partial\mu_2/\partial N_2)_{p,T}^{\text{sing}}\sim\tau^{\gamma-\gamma+\nu}\sim\tau^{0.62}. \tag{3.5}$$

This relation determines the limiting behavior of the diffusion coefficient with approach to the critical point. It was verified in many experiments, mainly, by measuring the width of the Rayleigh line in liquid solutions [10]. However, according to present-day investigations, near the gas-liquid critical point of the solvent within a temperature range of the states ($10^{-3}<\tau\leqslant1$), excluding the closest vicinity of the critical point, we may neglect the term $b^{\text{sing}}(b^{\text{sing}}\ll b^{\text{reg}})$. In a particular case, which may be of use to us in subsequent estimations, on the isochore at a critical concentration of solution, it is assumed that

$$(\partial N_2/\partial\mu_2)_{p,T}^{\text{reg}}=N_2/k_BT,$$

$$(\partial N_2/\partial\mu_2)_{p,T}^{\text{sing}}=a'(N_1N_2)^{\epsilon}\tau^{-\gamma},$$

$$D=b^{\text{reg}}k_BT/(1+a'(N_1N_2)^{\epsilon}\tau^{-\gamma}); \tag{3.6}$$

here a',ϵ were found from the state equation ($\epsilon\sim1$).

Using our experimental results on diffusion, we estimate the behavior of other critical coefficients within this region. The fluxes of components, J^m, and of heat, q, are determined using the gradients $\nabla\mu$ and ∇T [4]:

$$J^{(m,v)}=-L_{j\mu}\nabla\mu^{(m)}-L_{jT}\nabla T,$$

$$q-\mu J^{(m,v)}=-L_{q\mu}\nabla\mu^{(m)}-L_{qT}\nabla T,$$

where the Onzager coefficient $L_{j\mu}$ is related to the component mobility in the mean-numerical reference system via the equation $b^w=L_{j\mu}\rho^2/[n^3(m_1m_2)^2N_1N_2]$. According to the scaling theory of critical phenomena [58,59], the kinetic coefficients near the critical point have the form

$$\begin{aligned} L_{j\mu}&=\alpha^{\rm sing}+\alpha^{\rm reg}=\frac{k_BT_c}{6\pi\eta r_c}\rho(\partial c_2/\partial\mu^{(m)})_{p,T}+\alpha^{\rm reg},\\ L_{jT}&=L_{q\mu}/T=\beta^{\rm sing}+\beta^{\rm reg}=\frac{k_BT_c}{6\pi\eta r_c}\rho\left(\frac{\partial c_2}{\partial T}\right)_{p,\mu}+\beta^{\rm reg}\\ &=-(\partial\mu^{(m)}/\partial T)_{p,c}\alpha^{\rm sing}+\beta^{\rm reg},\\ L_{qT}&=\gamma^{\rm sing}+\gamma^{\rm reg}=\frac{k_BT_c}{6\pi\eta r_c}\rho T(\partial s^{(m)}/\partial T)_{\mu,p}+\gamma^{\rm reg}\\ &=T(\partial\mu^{(m)}/\partial c_2)_{p,T}(\partial s^{(m)}/\partial T)_{\mu,p}\alpha^{\rm sing}+\gamma^{\rm reg}, \end{aligned}\qquad(3.7)$$

where r_c is the correlation radius, η is the shear viscosity, and $s^{(m)}$ is the entropy of unit mass. Equations (3.7) show that the singular parts of transfer coefficients may be expressed in terms of $\alpha^{\rm sing}$. Thus, the transfer coefficients, involved in the basic hydrodynamic equations, have the form

$$\begin{aligned} \lambda&=(L_{qT}L_{j\mu}-L_{jT}^2T)/L_{j\mu}\\ &=\frac{\alpha^{\rm sing}}{\alpha^{\rm sing}+\alpha^{\rm reg}}\left\{\alpha^{\rm sing}C_{p,c}\left(\frac{\partial\mu^{(m)}}{\partial c_2}\right)_{p,T}\right.\\ &\quad+T\alpha^{\rm reg}\left(\frac{\partial\mu^{(m)}}{\partial T}\right)_{p,c}^2+2T\beta^{\rm reg}\left(\frac{\partial\mu^{(m)}}{\partial T}\right)_{p,c}\\ &\quad+\alpha^{\rm reg}C_{p,c}\left(\frac{\partial\mu^{(m)}}{\partial c_2}\right)_{p,T}\\ &\quad\left.+\gamma^{\rm reg}+(\gamma^{\rm reg}\alpha^{\rm reg}-T\beta^{\rm reg^2})/\alpha^{\rm sing}\right\},\\ k_T&=\frac{T(\partial c_2/\partial\mu^{(m)})_{p,T}}{\alpha^{\rm sing}+\alpha^{\rm reg}}[\beta^{\rm reg}+\alpha^{\rm reg}(\partial\mu^{(m)}/\partial T)_{p,c}],\\ D&=(\alpha^{\rm sing}+\alpha^{\rm reg})(\partial\mu^{(m)}/\partial c_2)_{p,T}/\rho,\\ k_p&=p\left(\frac{\partial(1/\rho)}{\partial\mu^{(m)}}\right)_{p,T}=-p\left(\frac{\partial(1/\rho)}{\partial T}\right)_{p,\mu}\left(\frac{\partial T}{\partial\mu^{(m)}}\right)_{p,\rho},\\ \kappa&=(L_{qT}L_{j\mu}-L_{jT}^2T)/L_{j\mu}C_{p,c}\rho=\lambda/(\alpha^{\rm sing}+\alpha^{\rm reg})\rho C_{p,c}, \end{aligned}\qquad(3.8)$$

where $C_{p,c}$ is the heat capacity and κ is the coefficient of thermal diffusivity. As has been shown above, near the critical point of a pure solvent within the region studied, we may neglect the term $b^{\rm sing}$ and, hence, $\alpha^{\rm sing}$. As a result, the expressions for, e.g., k_T and λ will be the power laws $\lambda\sim\tau^{-\nu}$, $k_T\sim\tau^{-\gamma}$. The dependences obtained for k_T and λ may be compared with the available experimental data on the thermodiffusion relation and thermal conductivity for the ^{3}He-^{4}He solutions [60,61]. A comparison of the results is shown in Figs. 4 and 5.

As follows from the figures, there is fair agreement between our results and the experimental data of [60] and [61] within experimental error and the above estimations. Thus, our notion about the behavior of kinetic coefficients has been confirmed experimentally. We may also obtain the functional dependences for other kinetic coefficients within the studied temperature range , taking into account their interrelation. Thus, in this temperature range the kinetic coefficients are of the form

$$\begin{gathered} D\sim\tau^{\gamma},\quad \lambda\sim\tau^{-\nu},\quad \kappa\sim\tau^{-\nu},\\ k_T\sim\tau^{-\gamma},\quad k_p\sim\tau^{-\gamma},\quad b\sim\text{const}. \end{gathered}\qquad(3.9)$$

According to the scaling theory, the limiting (asymptotic) critical behavior of these coefficients is determined as [10]

$$\begin{gathered} D\sim\tau^{\nu},\quad \lambda\sim\text{const},\quad \kappa\sim\tau^{\nu},\\ k_T\sim\tau^{-\nu},\quad k_p\sim\tau^{-\gamma},\quad b\sim\tau^{-\nu}. \end{gathered}\qquad(3.10)$$

Taking into account the fact that the critical index $\gamma\simeq1.2$ and $\nu\simeq0.6$, then the temperature dependences of these coefficients differ dramatically in these two regions.

Now let us estimate the temperature regions in which the kinetic coefficients must display the dependences (3.9) and (3.10) on the critical isochore in the solution with concentration N_2. We perform estimations for the dependence $D=f(\tau)$ which is sure to hold for other critical coefficients. As follows from Eqs. (3.4) and (3.8) there are two crossover temperatures τ_1 and τ_2 at which D changes its behavior (critical index). Experimentally, these crossover temperatures $[\tau=(T-T_c)/T_c]$ differ by orders of magnitude.

The first temperature range up to temperature τ_1 determines by the inequality

$$(\partial N_2/\partial\mu_2)^{\rm sing}\ll(\partial N_2/\partial\mu_2)^{\rm reg}.\qquad(3.11)$$

Thus, τ_1 is determined by the equality (3.11). Taking into account Eqs. (3.6), we have

$$\tau_1=\{a[(1-N_2)N_2]^{\epsilon}\}^{1/\gamma}.\qquad(3.12)$$

The crossover temperature τ_2 may be obtained taking into account the fact that the second change in the behavior of D occurs for $b^{\rm sing}\approx b^{\rm reg}$ (or $\alpha^{\rm sing}=\alpha^{\rm reg}$). The value of $b^{\rm reg}$ may be estimated as

$$b^{\rm reg}=1/6\pi\eta r_0\qquad(3.13)$$

where r_0 is of the order of a molecule size. Thus, according to Eqs. (3.6), we get

$$\frac{r_0k_BT}{r_cN_2}(\partial N_2/\partial\mu_2)_{p,T}^{\rm sing}\approx1.\qquad(3.14)$$

It is usually assumed [10] that $r_c\approx r_0\tau^{-\nu}$. Hence,

$$\tau_2=\{a[(1-N_2)N_2]^{\epsilon}\}^{1/(\gamma-\nu)}.\qquad(3.15)$$

Equations (3.12) and (3.15) show that τ_1 and τ_2 are determined using the coefficient of proportionality (''amplitude'') of the scaling dependence of compressibility on temperature. For instance, for the ^{3}He-^{4}He solutions the crossover temperatures τ_1 and τ_2, calculated using the equation of state by [34], are

$$N_2(^3\mathrm{He}) = 0.01,\ 0.10,\ 0.50,\ 0.80,$$

$$\tau_1 = 3.0\times10^{-6},\ 1.4\times10^{-4},\ 8.5\times10^{-4},\ 3.9\times10^{-4},$$

$$\tau_2 = 1.0\times10^{-3},\ 8.8\times10^{-3},\ 2.5\times10^{-2},\ 1.6\times10^{-2},$$

which is in agreement with our measurements of the diffusion coefficient D. Note that as follows from Figs. 4 and 5, in the region $\tau < 10^{-4}$, i.e., where $\alpha^{\mathrm{sing}} > \alpha^{\mathrm{reg}}$, there is a tendency to the limiting asymptotic dependences at a critical point (3.10).

Note that according to the known equations of state in our region we may determine not only the temperature dependences of these kinetic coefficients but also their dependences on volume and concentration.

IV. WIDTH OF THE RAYLEIGH LINE

It is interesting to use our concepts obtained to interpret experiments on the determination of the width of the Rayleigh line in the ^{3}He-^{4}He solution. The normalized autocorrelation function of the scattered light intensity near the gas-liquid critical point of the binary solution, measured experimentally, is written as [62]

$$g^{(2)}(t) = 1 + [g^{(1)}(t)]^2. \tag{4.1}$$

According to [63], the first-order autocorrelation function for binary solutions has the form

$$g^{(1)}(t) = \frac{\dfrac{S_1\pi}{\Gamma_+}\exp(-\Gamma_+ t) + \dfrac{S_2\pi}{\Gamma_-}\exp(-\Gamma_- t)}{S_1\pi/\Gamma_+ + S_2\pi/\Gamma_-}, \tag{4.2}$$

where S_1 and S_2 are the functions of equilibrium thermodynamic properties and of kinetic coefficients; $\Gamma_\pm$ is the inverse time of the relaxation of critical fluctuations and is related to the width of the Rayleigh line:

$$\Gamma_\pm = \frac{1}{2}k^2(\kappa + D(1+A_R) \pm \{[\kappa + D(1-A_R)]^2 - 4\kappa D\}^{1/2}), \tag{4.3}$$

where k is the change in the wave vector upon scattering, and $A_R = (k_T^2/TC_{p,c})(\partial\mu^{(m)}/\partial c_2)_{p,T}$. Knowing the values of κ, D, and A_R, we may calculate the values of Γ_+ and Γ_- and compare them with the experimental data in Table I of [65] on the ^{3}He-^{4}He solution. The quantities of k_T and λ were taken from [61] and the quantities of the heat capacity $C_{p,c} - C_{v,c}$ were obtained using the caloric equation of state which was derived by using the same hypothesis as for Eqs. (2.18). The experimental values of $C_{v,c}$ were taken from [64]. The diffusion coefficient was estimated using the formula taking into account only the regular component mobility:

$$D/D_0 = 1 \bigg/ \left[1 + \frac{RT}{c_2}(\partial c_2/\partial\mu^{(m)})_{p,T}\right]. \tag{4.4}$$

The $(\partial c_2/\partial\mu^{(m)})_{p,T}$ quantity was determined using the equation of state by [34]. Figure 6 shows the calculated temperature dependences of the Γ_+ and Γ_- values (the solid lines).

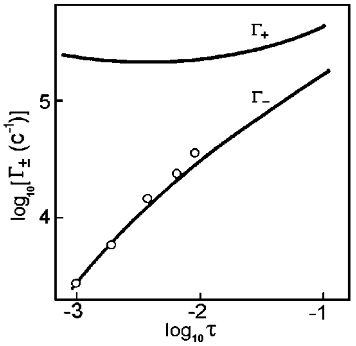

FIG. 6. The width of the Lorentzian components of the Rayleigh line depending on the reduced temperature for the ^{3}He-^{4}He solution with ^{3}He concentration $N_2 = 0.79$. The solid line corresponds to the result obtained by formula (4.3). The circles correspond to experimental values by [65].

It is seen that $\Gamma_+ \gg \Gamma_-$ with $\tau < 10^{-2}$. The calculations performed for S_1 and S_2 show that within the same temperature range they are almost the same. Thus, the second term in square brackets of expression (4.2) is more important than the first. Experimentally, this is manifested in the existence of the only time of the relaxation of critical fluctuations. This conclusion coincides with the results obtained by [65]. The experimental data on the Γ_- values used from Table I of [65] (open circles, Fig. 6). Figure 6 shows that the curve calculated for Γ_- by taking into account our measurements of the coefficient of mutual diffusion and the experimental data given by [65] are in fair agreement and their behavior do not correspond to the limiting critical behavior. Nevertheless, the conclusion about the practical independence of the diffusion coefficients of helium isotope solutions on composition, drawn by [65], contradicts our measurements shown in Fig. 1. The fact is that according to [65], the width of the Rayleigh line does not coincide with the diffusion coefficient. The width of this line depends not only on D but also on κ and A_R. Thus, in a given case, the competition between these quantities in expression (4.3) leads to this independence of the Rayleigh line on concentration although the diffusion coefficient depends on concentration. This assumption has been verified numerically [25]. Figure 7 shows the temperature dependences of D obtained with allowance for our measurements using Eq. (3.3) and for the estimations

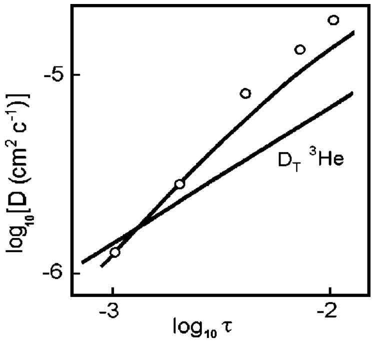

FIG. 7. The dependence of the coefficient of mutual diffusion for ^{3}He-^{4}He solution with ^{3}He concentration $N_2 = 0.79$ on the reduced temperature. The straight line corresponds to the coefficient of thermal diffusivity of ^{3}He. The circles are the experimental data by [65].

obtained by [65]. The open circles were taken from Table I of [65]. The solid line is the result of our calculations performed by Eq. (4.4) for $N_2=0.79$, taking into account D_0^{vc} obtained from our measurements [25]. For comparison Fig. 7 shows the dependence of the coefficient of thermal diffusivity κ for pure ^{3}He [66] (the straight line in the figure). Figure 7 shows agreement between the solid line and the circles which indicates again the consistency between our data on the determination of D and the experimental data by [65]. Note that the quantity D for the solution with $N_2=0.79$ and the quantity κ for pure ^{3}He [66] are close to each other in the region of comparison, but exhibit different temperature dependences.

The interpretation of dynamic light scattering experiments is not simple near the critical points of mixtures. It was shown recently in the theoretical work of [67] that the physical meaning of the prevalent coefficients in expression (4.3) changes as one considers states in the vicinity of different points on the critical locus.

V. CONCLUSION

Our investigation indicates that the isothermal process, occurring in nonideal gaseous solutions, is mainly determined by the peculiarities of the thermodynamic force rather than by those of the Onzager coefficient (mobility). Even in the vicinity of the gas-liquid critical point of the solution, at least for the low concentrations of one of the components, the behavior of D^{wN} depends on $(\partial\mu_2/\partial N_2)_{p,T}$. The mobility, in this case, may be calculated assuming the gaseous solution to be ideal. Thus, the Mayer formula is a good approximation [68],

$$D=(N_2/k_BT)(N_2D_1+N_1D_2)(\partial\mu_2/\partial N_2)_{p,T},$$

where we assume $D_1\approx k_BT/r_1\eta$, $D_2\approx k_BT/r_2\eta$; r_i is the effective radii of the molecules, and η is the solution shear viscosity. Note that this formula holds for the entire experimental region up to the gas-liquid critical line of the solution. Near the gas-liquid critical point of the solution, the other kinetic coefficients may be expressed in terms of both the singular part of the mobility and the corresponding regular parts which weakly depend on the reduced temperature so that this dependence may be neglected. To calculate the $(\partial\mu_2/\partial N_2)_{p,T}$ derivative for the general case, one should know the equation of the solution state. Some types of equations are given in Sec. II. The crossover temperatures are determined at which the form of the power law dependences of the kinetic coefficients vary in the critical region. Using the concepts developed in this paper, we explain the temperature dependences of the kinetic coefficients observed experimentally. Thus, the present paper develops concepts of the behavior of the kinetic coefficients in nonideal binary gaseous solutions, including the region located near the gas-liquid critical point. These concepts are based on the fundamental principles of the theory of second-order phase transitions.

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