INVESTIGATION OF DIFFUSION IN A SOLUTION NEAR THE CRITICAL MIXING POINT

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The temperature and concentration dependences of the diffusion coefficient D in a Ch_4-CF_4 system are studied in the vicinity of the critical lamination point. Measurements of D are performed by the Matano–Boltzman technique, the concentration gradient being measured by the shadow method. The temperature and concentration dependences can be described by a power function of the form (5).

AT the present time it has been reliably established that diffusion in a solution in the vicinity of the critical lamination point is sharply slowed down, and at the critical point itself the diffusion coefficient D is close to zero.[1] However, the results of existing investigations are contradictory with respect to the form of the temperature and concentration dependences in the vicinity of T_c. The most reliable data of recent years, obtained by the light-scattering method,[2,3] give for the temperature dependence $D \propto \Delta T^{2/3}$ ($\Delta T = T - T_c$), which agrees with calculations performed within the framework of similarity theory.[4] However, the value of the microscopic coefficient D determined in this manner and connected with the growth and fading away of the fluctuations, can in principle differ from the macroscopic values characterizing the diffusion in large volumes. This difference may be due to the fact that when the characteristic dimensions of the concentration inhomogeneity are much larger than the fluctuation correlation radius, new mass-transport mechanisms may come into play. Other types of D(T) dependences are also cited in the literature. Thus, for example, Lorentzzen and Hansen[5] obtained $D \propto \Delta T$.

In connection with the foregoing, we have investigated the coefficient of mutual diffusion D by a new method near the critical lamination point of the solution CH_4-CF_4 ($T_c = 94.72°K$, $x_c = 43.5\%$ CF_4). Our aim was to determine the character of the D(T) and D(x) dependences at $T > T_c$. The difficulty in the investigation of the diffusion near the critical point lies not only in the very low value of D, but also in its strong dependence on x and T, which makes the use of several simple and reliable methods impossible. We used the Matano–Boltzmann method for the measurements.[6] This method is based on a solution of the second Fick equation with allowance for the dependence of the diffusion coefficient on the concentration at T = const. If two layers of a solution with different compositions are placed in contact, then in the course of time the concentration will vary along the height h. Knowing the dependence of x on h and of dx/dh on h after a certain time interval τ, it is possible to determine the value of the diffusion coefficient D at a point with arbitrary concentration x_1 by means of the formula

$$D = -\frac{1}{2\tau}\frac{dh}{dr}\int_0^{x_1} h\,dx. \tag{1}$$

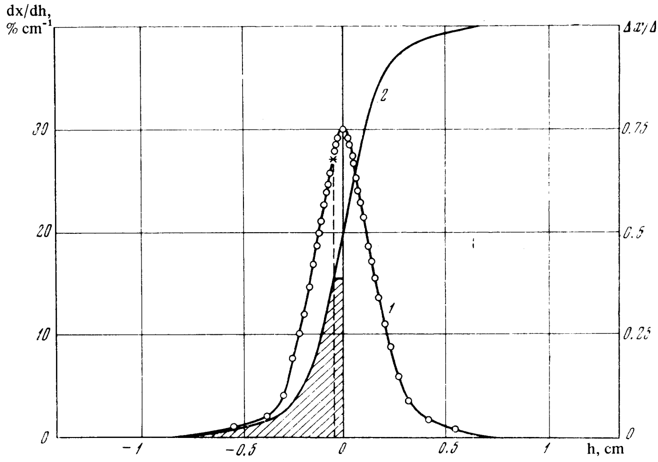

FIG. 1. Distribution of the concentration gradient (curve 1) and of the concentration (curve 2) over the height of the diffusion layer at $\Delta T = 0.086°$, $\Delta x_0 = 12.9\%$, $\tau = 27$ h.

The gist of the calculations by this method can be explained using as an example Fig. 1, which shows the distributions of the concentration gradient (curve 1) and of the concentration (curve 2) along the height of the diffusion layer for the investigated solution at $\Delta T = 0.086°$ and $\tau = 27$ h. The value of the integral in (1) corresponds to the shaded area under curve 2 in this figure, and the value of dh/dx is determined at the point denoted by the asterisk on curve 1.

For a real solution, at different partial volumes of the components, macroscopic displacements of matter are possible during the course of the diffusion process. These are not taken into account by (1), and lead to a displacement of the layer with average concentration (h = 0, Fig. 1). In our case, however, these displacements are of little importance, in view of the relatively small concentration drop Δx in the diffusion region. The maximum values of Δx did not exceed ±(5–6) mol.%, and the average changes of the concentration in the upper and in the lower halves of the diffusion layer were approximately ±(2–3)%. At a diffusion-layer thickness ~ 1 cm and at a relative difference of the molar volumes of the components ~ 40%, such a change in the composition corresponded to a shift of the center of the layer by 0.05–0.1 mm. In addition, this shift was automatically taken into account during the course of the experiment, since in each measurement of the concentration distribution we determined the position of the surface corresponding to $h = 0$. The position of this surface (the so-called Matano surface), was chosen from the condition that the areas on the left and on the right of the line $h = 0$ on Fig. 1, bounded by curve 2 and this line, be equal. In most cases the position of this surface coincided with the maximum gradient of the concentration, as shown in the figure.

The measurements were made with the setup previously employed for the investigation of the gravitational effect[7] in the same solution, with a determination of the concentration gradient by the Toepler shadow method.[8] The sensitivity of the method with respect to the concentration gradient, using the standard IAB-451 instrument, reached ~0.01% cm^{-1}. Since the instrument is designed for the measurement of small gradients of the refractive index, compensating glass wedges were used to extend the measurement range. An assortment of such wedges has made it possible to carry out measurements up to values $dn/dh \sim 0.03\,\text{cm}^{-1}$ or $dx/dh \sim 50\%\ \text{cm}^{-1}$.

The critical mixture was condensed into a chamber of height 50 mm with a rectangular horizontal cross section 8 × 16 mm, until it was completely filled, and a temperature somewhat lower than the critical point was established. After a careful preliminary mixing, the solution became laminated into two phases with a concentration difference Δx_0. Then, relatively rapidly but not fast enough to cause convective mixing of the solution, the chamber was heated to a certain calculated temperature T (in degrees K) above T_c, at which the diffusion coefficient was measured. The time of heating ranged from 5 minutes at $\Delta T = T - T_c = 0.013°$ to 30 minutes at $\Delta T = 5.381°$. The shadow method employed made it possible to monitor continuously the distribution of the concentration and the absence of convection both during the heating and during the subsequent measurements. The system was thermostatically controlled for a certain time τ, after which the diffusion zone became sufficiently wide for measurement and at the same time still did not reach the edges of the chamber, making it possible to regard the diffusion as occurring in a semi-infinite space (one of the conditions of the theory of the method), after which we measured the distribution of the concentration gradient.

Such a measurement was repeated in fact several times at definite time intervals for each diffusion experiment, making it possible to monitor the process of diffusion in time, and to increase the reliability and accuracy of the measurements. The initial time of the experiment was taken to be the time of establishment of the calculated temperature. At $\Delta T \sim 0.2°$, the time of one diffusion experiment usually amounted to 60 hours, and with increasing distance from T_c, it decreased to 40–20 hours. Individual measurements of the distribution of the concentration gradient were made at intervals of 6–8 hours.

As is well known, in the shadow method one determines the gradient of the refractive index dn/dh directly.[8] For the connection between dn/dh and the concentration gradient dx/dh we used the Lorenz–Lorentz formula

$$\frac{n^2-1}{n^2+2}\frac{M}{\rho} = R.$$

The possibility of using this equation at the critical point was verified by Larsen et al.,[9] who estimated the correction to the Lorenz–Lorentz equation due to the presence of long-wave density fluctuations at the critical point. According to the estimate of [9], it does not exceed 10^{-4} for argon. In addition, the behavior of the refraction near the critical point was investigated by Mishels[10] for CO_2 and by Shimanskiĭ and coworkers[11] for benzene and propyl alcohol, and satisfaction of the Lorenz–Lorentz equation at the critical liquid-vapor point was also demonstrated. There are no grounds for assuming that the correction to this equation will be much larger for the critical lamination point of the solution.

After differentiating with respect to h and performing certain transformations, the Lorenz-Lorentz equation leads to the following expression:

$$\frac{6n}{(n^2+2)^2}\frac{dn}{dh} = \frac{R_1V_2 - R_2V_1 + (R_1 - R_2)V^E}{V^2}\frac{dx}{dh}, \tag{2}$$

where $n = n_1x_1 + n_2x_2$, $V = V_1x_1 + V_2x_2 + V^E$, and x_1 is the molar concentration of CF_4. The values of the molar refractions and refractive indices of the components were taken from the work of Abbiss et al.[12] ($n_1 = 1.2369$, $n_2 = 1.2915$, $R_1 = 7.072\ \text{cm}^3/\text{mole}$, $R_2 = 6.512\ \text{cm}^3/\text{mole}$ at $T = 94.78°\text{K}$). The excess mixing volume V^E was measured for the given system in a separate investigation.[13] In the derivation of (2) we assumed also additivity of the molar refraction of the solution in the absence of an essential singularity for V^E at the critical point.

The assumption of additivity of refraction for solutions of spherically-symmetrical nonpolar molecules follows from the satisfaction of the Lorenz-Lorentz formula and is confirmed by the results of numerous experimental investigations.[14] The assumed additivity of molar refraction of the solution near the critical liquid-vapor point was used by Shimanskiĭ and co-workers[11] and the results obtained thereby were subsequently confirmed by another method.[15]

Since the concentration in the diffusion layers changed by not more than 10%, and the difference between n_1 and n_2 or V_1 and V_2 were small, calculations based on (2) could be carried out by successive approximations, taking as the first approximations the values of n, V, and V^E for the critical concentration. The second approximation turned out to be adequate with a high degree of accuracy.

After obtaining the dependence of dx/dh on h, the dependence of Δx on h was calculated by graphical integration (curve 2, Fig. 1), after which D was calculated as a function of x. The height h was measured with a micrometer.

Particular attention was paid to the accuracy of the thermostat control, which amounted to $\pm 5 \times 10^{-4}$ deg in the investigated temperature region. The error in the determination of the change of temperature with the aid of a standard platinum resistance thermometer and a potentiometer circuit (R-309 potentiometer) did not exceed 0.001°. The position of the critical point was determined in each diffusion experiment, and the scatter of the values did not exceed ±0.001°. The absence of con-

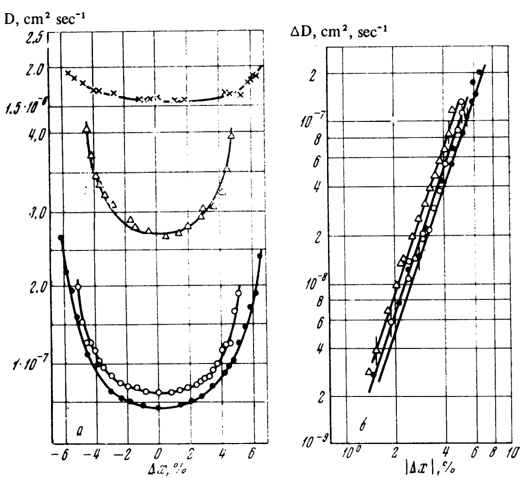

FIG. 2. Concentration dependence of the diffusion coefficient: ●–ΔT = 0.013°, O–ΔT = 0.026°, Δ–ΔT = 0.224°, X–ΔT - 2.831°.

vection was ensured by the high thermostatic accuracy and by maintenance of a minimum temperature gradient over the height of the chamber. The temperature gradient was measured with the aid of an R-306 potentiometer and an F-116/1 microvoltmeter/microammeter. The pickup was a differential copper-gold-cobalt alloy thermocouple. During the time of the experiment, the temperature gradient over the height of the chamber did not exceed $\pm 5 \times 10^{-4}$ deg-cm^{-1}; this was attained with the aid of an automatic control circuit including heaters placed in the upper and lower points of the chamber. In addition, as already indicated, there was constant visual monitoring by means of the shadow picture. The relative error in the determination of D_0 was ±3% at $\Delta T < 1°$ and increased to ±5% at $\Delta T \sim 4$–$5°$. The measurements were made in the temperature interval ΔT from 0.013° to 5.381° and $\Delta x = x - x_c \sim \pm 8\%$.

One of the main advantages of the method, compared with many others, is the possibility of investigating the concentration dependence of the diffusion coefficient in a single diffusion experiment. Figure 2a shows plots of D against Δx for four temperatures. We see that all curves have a parabolic form with a minimum lying near the center of the diffusion layer, i.e., at a concentration close to critical. Attention is called to the approximate identical growth of D with increasing $|\Delta x|$ at all temperatures. Analogous curves were also obtained for other temperatures. The concentration dependence can be described by a power-law function, by representing the diffusion coefficient in the form

$$D(x, T) = D_0(T) + b|\Delta x|^m, \tag{3}$$

where b is a weak function of T.

Figure 2b shows, in a logarithmic scale, the dependence of $\Delta D = D(x, T) - D_0(T)$ on Δx for the curves shown in Fig. 2a, with the exception of the isotherm corresponding to $\Delta T = 2.831°$. The latter is not represented because the error in the determination of ΔD increases at high temperatures because of the increase of D_0, and this leads to an appreciable scatter of the points and makes the character of the concentration dependence less definite. For the same reason, the isotherm $\Delta T = 0.224°$ was plotted on the basis of the smoothed curve of Fig. 2a. As seen from the figure, the exponent m for the presented curves, as well as for most other isotherms investigated in the present study, is equal to $m = 3 \pm 0.2$. To obtain a more accurate value of m it is necessary to increase the measurement accuracy as well as to increase the intervals Δx.

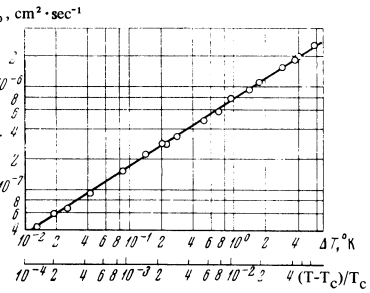

FIG. 3. Temperature dependence of the diffusion coefficient.

The concentration-curve minima corresponding to the critical composition also depend quite strongly on the temperature.

In the investigated region of ΔT, the value of D_0 changes by almost two orders of magnitude. Figure 3 shows plots of $D_0(T)$ in a log-log scale. As seen from the figure, the change of $D_0(T)$ can be approximated in the entire temperature interval by a power-law function

$$D_0(T) = a(\Delta T)^\nu \tag{4}$$

with exponent $\nu = 0.67 \pm 0.02$. Such a dependence agrees well with the conclusions of similarity theory[4] and with the results obtained by the method of light scattering.[2,3] At small τ, however, i.e., at large concentration gradients in the diffusion layer, somewhat exaggerated values of D_0 were observed in all the experiments. This result is possibly due to the additional mechanism of nonlinear diffusion,[16] the occurrence of which can be expected at very small ΔT and appreciable concentration gradients. At the same time, we did not observe a layered gradient structure of the diffusion flux, likewise predicted by Fisher's theory of nonlinear diffusion[16] and observed by Smirnov.[17] Such a structure arose only at large temperature gradients, for example in the case of fast heating or cooling, and did not depend on the concentration gradients. In all the experiments, when good thermostatic control was employed, there was no stratification. Probably, just as in [17], this effect is due to inhomogeneities of the temperature and calls for an additional explanation.

Thus, the final dependence of D on T and on x at $T > T_c$ can be represented by the equation

$$D = a(\Delta T)^\nu + b(T)|\Delta x|^m, \tag{5}$$

where $m = 3 \pm 0.2$ and $\nu = 0.67 \pm 0.02$. It should be noted that a concentration and temperature dependence of D similar to (5) was observed by Lorentzen and Hansen,[5] but with an exponent $\nu = 1$.

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