SOVIET PHYSICS JETP VOLUME 33, NUMBER 4 OCTOBER 1971

# *DIFFUSION EXPERIMENTS NEAR THE CRITICAL POINT OF VAPORIZATION OF SOLVENTS*

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Submitted July 15, 1970

Zh. Eksp. Teor. Fiz. 60, 1379–1386 (April, 1971)

The kinetics of mass transfer at constant pressure and temperature near the vaporization critical point of a mixture is studied on the basis of the diffusion of argon in a capillary tube filled with carbon dioxide and open at one end. The dependence of the diffusion coefficient on the density and the concentration was determined near the critical point of carbon dioxide at various temperatures. Transfer effects connected with the dependence of the density on the concentration are also investigated.

## 1. FORMULATION OF PROBLEM

NEAR the critical point of vaporization of a solvent, in the case of diffusion mixing of the components, macroscopic streams resulting from the significant dependence of the density on the concentration are observed.[1] In this connection, there is a certain leeway in the choice of the diffusion coefficients.[2] We shall therefore determine first the diffusion coefficient and present the necessary relations for the description of our diffusion experiments.

Let us consider the flux density $J_i$ of the particles of the i-th component single-phase system at a constant temperature in the absence of external fields and chemical reactions:

$$\mathbf{J}_i = nc_i\mathbf{w}_i = -nD\,\mathrm{grad}\,c_i + nc_i\mathbf{w}, \tag{1}$$

$$c_i = n_i / n, \quad i = 1, 2, \tag{2}$$

$$\mathbf{w} = c_1\mathbf{w}_1 + c_2\mathbf{w}_2, \tag{3}$$

where D is the diffusion coefficient, $n_i$ the number of particles of the i-th component per unit volume, $n_i + n_2 = n$ the density, $\mathbf{w}_i$ the velocity of the i-th component, and $\mathbf{w}$ the numerical average velocity.

The diffusion coefficient D defined in (1) characterizes the diffusion fluxes of the solvent and solute through a unit area moving with the numerical average velocity.

The system under consideration is in mechanical equilibrium.[2] This means that we neglect the acceleration of the fluxes, and also those terms of the equation of motion which describe the viscous flow. Obviously, in such a system the pressure drops are much smaller than the pressure itself, and if the mixing of the components occurs in a small volume, one can expect p = const. Physically the condition of equilibrium denotes that the time of spreading of the pressure gradients in a system where there is no diffusion is much smaller than the time of establishment of these gradients as a result of diffusion at $\mathbf{w} = 0$.

Since p = const and T = const, the density depends only on the concentration:

$$n = f(c_i). \tag{4}$$

We write down the continuity equation:

$$\begin{gathered} \partial c_i n / \partial\tau + \mathrm{div}\, nc_i\mathbf{w}_i = 0, \\ \partial n / \partial\tau + \mathrm{div}\, n\mathbf{w} = 0. \end{gathered} \tag{5}$$

Equations (1), (4), and (5) serve for the determination of five functions of the coordinates and the time:

$$c_i = c_i(\bar{\mathbf{r}}, \tau), \quad \mathbf{w}_i = \mathbf{w}_i(\overline{\mathbf{r}, \tau}), \quad n = n(\mathbf{r}, \tau). \tag{7}$$

According to [2], the diffusion flux is given by the expression

$$-nD\,\mathrm{grad}\,c_i = nc_i(\mathbf{w}_i - \mathbf{w}) = -L_i(\mathrm{grad}\,\mu_i)_{p,T}. \tag{8}$$

Here $\mu_i$ is the chemical potential of the i-th component and $L_i$ is a phenomenological coefficient.

From (8) we obtain

$$nD = (\partial\mu_i / \partial c_i)_{p,T} L_i. \tag{9}$$

In the case of a weak solution ($c_i \to 0$) there follows from [3,4]

$$\mu_i = kT \ln c_i + \psi_i(p, T), \tag{10}$$

$$D = b^* kT, \quad D = b_i(1 - c_i)kT, \tag{11}$$

where $b^*$ is the mobility of the molecules relative to the coordinate system moving with velocity $\mathbf{w}$, and $b_i$ is the mobility of the molecules of the i-th component relative to a system of coordinates the velocity of which is $\mathbf{w}_j (j \neq i)$. Thus, in weak solutions

$$L_i = nb^* c_i = nb_i(1 - c_i)c_i. \tag{12}$$

If $b_i$ does not depend on $c_i$, but depends only on the pressure and the temperature, then the diffusion coefficient of the two-component system, just as in [5], is equal to

$$D = b_i(1 - c_i)c_i(\partial\mu_i / \partial c_i)_{p,T}. \tag{13}$$

The experimental diffusion coefficient was calculated from the experimentally determined functions c, $\mathbf{w}$, and n.

Let us write down the necessary relations for our experiments on diffusion in a capillary with one end closed. We assume that at the open end there is maintained a constant concentration $c_{0i}$, and in the capillary at the initial instant of time the components are uniformly distributed with concentration $c^0_{ci}$. From relations (1)–(6) we obtain

$$J_{ix} = nc_i w_{ix} = -nD\left[1 + \frac{c_i}{n}\left(\frac{\partial n}{\partial c_i}\right)_{P,T}\right]\frac{\partial c_i}{\partial x}$$

$$+\int_x^l nD\left(\frac{\partial c_i}{\partial x}\right)^2\left(\frac{\partial^2(1/n)}{\partial c_i^2}\right)_{p,T}dx. \tag{14}$$

Here the x axis is directed along the capillary from its open end, and $l$ is the length of the capillary. It follows from (14) that the flux of the i-th component in the capillary at $c \neq 0$ is not determined at all by the coefficient D alone, and depends significantly on the derivative $(\partial n/\partial c_i)_{p,T}$ and on the value of the integral.

The flux of the component in the capillary can increase or decrease, depending on the sign of the concentration gradient, since the integral is an even function of this gradient, and the first term of Eq. (14) is an odd function. Obviously, at small drops, when $\Delta c_i \ll c_i(c_{0i} - c_{ci}^0 \ll c_{0i})$, we can use for the determination of $c_i = f(x, \tau)$ the equation[5]

$$\partial c_i / \partial\tau = D\partial^2 c_i / \partial x^2. \tag{15}$$

In our case the solution of Eq. (15) is known:[6]

$$\frac{c_{0i} - c_{ci}^{\tau}}{c_{0i} - c_{ci}^{0}} = \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left\{-\left[\frac{\pi(2m+1)}{2l}\right]^2 D\tau\right\}, \tag{16}$$

where $c_{ci}^{\tau}$ is the average concentration established in the capillary after the lapse of a time $\tau$.

When the diffusion occurs in a system that is close to the critical point of vaporization of the solvent, the diffusion coefficient is expressed, in accordance with [5], by the relation

$$D = bkT\frac{\Delta v^2 + \alpha\Delta T + (\beta - \gamma)c}{\Delta v^2 + \alpha\Delta T + \beta c}, \tag{17}$$

where $v = (1/n)$, $\alpha$, $\beta$, and $\gamma$ are the corresponding limiting values of the ratios

$$-2(\partial^2 p / \partial v\,\partial T)_{\text{cr}} / (\partial^3 p / \partial v^3)_{\text{cr}};\quad -2(\partial^2 p / \partial v\,\partial c)_{\text{cr}} / (\partial^3 p / \partial v^3)_{\text{cr}};$$
$$2(\partial p / \partial c)_{\text{cr}}{}^2 / kT(\partial^3 p / \partial v^3)_{\text{cr}},$$

at the critical point of the solvent and $\Delta T$ and $\Delta v$ are the deviations of the temperature and of the specific volume from their critical values. Equation (17) is valid assuming that the free energy of the system can be expanded in powers of $\Delta T$ and $\Delta v$ near the critical point of the solvent. In Eq. (17) and in the sequel we omit the index i. It is understood that the flux density, the concentration, the chemical potential, and the mobility pertain to the dissolved substance (argon).

In the present paper, with $CO_2$-Ar as an example, we investigate the diffusion for the purpose of an experimental verification of certain consequences that follow from relations (14) and (17), and determine those concentration, density, and temperature intervals in which these relations are valid.

## 2. EXPERIMENT

The carbon dioxide–argon system was chosen from considerations of convenience in the performance of the experiment, and the use of the capillary method[7] gave the most complete realization of the condition of mechanical equilibrium at T = const.

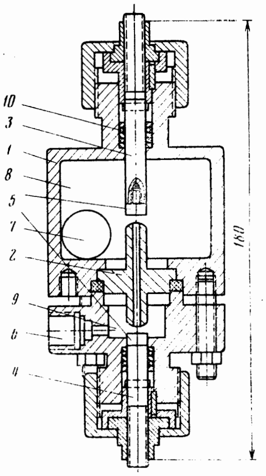

FIG. 1. Measuring cell. 1–high-pressure bomb, 2–capillary, 3–internal valve, 4–external valve, 5–silver end pieces, 6–socket of screw for connecting the cell with the inlet and filling systems, 7–steel ball for mixing the gas mixture, 8–closed volume of bomb, 9–external volume of bomb, 10–teflon packing gland.

The diffusion cell (see Fig. 1) was a thick-walled capillary (2) of 1 mm diameter and length 75 mm, one end of which was inserted in the closed volume (8) of the bomb (1). The ends of the capillary were covered with internal (3) and external (4) valves. In the presence of a concentration drop, the diffusion from the capillary into the closed volume of the bomb was initiated by opening the internal value (3), and was terminated by closing this valve. The construction of the bomb made it possible to perform experiments at pressures up to 100 atm. The heat released upon mixing of the gases in the capillary was diverted during the diffusion time by the metallic walls of the capillary, and the bomb itself was placed in a water thermostat whose temperature was maintained constant to ± 0.005 °C.

Since the ratio of the volume of the cavity of the bomb to the volume of the capillary was $3 \times 10^3$, the diffusion occurred under constant pressure at all possible concentration drops between the capillary and the bomb. For the same reason, during the process of diffusion, the concentration in the bomb remained almost unchanged and the weak mixing ensured satisfaction of the boundary condition $c_0$ = const at the open end of the capillary.

The capillary-method variant employed by us is described in greater detail in [8].

The measurements were made near the critical point, but not too close to it, so that the conditions of mechanical equilibrium in the system, as shown by estimates, were also satisfied. The component concentrations were determined with the aid of an MI-1305 mass spectrometer. The mass spectrometer was graduated against standard calibrated gas mixtures.[9]

To estimate the numerical average velocity **w** we measured the average density of the system in the capillary as a function of the diffusion time. The density was calculated from the pressure of gas let out from the capillary into a sufficiently large external vessel (of capacity 1 liter) and from the known volume of the capillary. The density of the gas mixture in the bomb was determined from the weight of the bomb, the internal volume of which was known.

Before the start of the experiment, the capillary was usually filled with pure carbon dioxide, the bomb with a mixture of carbon dioxide and argon. The diffusion cell was oriented in the thermostat in such a way as to exclude simple pouring of the denser gas out of the capillary at the start of the diffusion. Before the start of the experiment, the pressures in the bomb and in the capillary were equalized.

To determine D = D(n, T, c) we investigated the dependence of the average concentration of the argon in the capillary $c_c^\tau$ on the time $\tau$ at the different n, T, and c. Since after a sufficiently long diffusion time the concentration difference between the bomb and the capillary becomes small, the diffusion begins to proceed in accordance with Eq. (15). If it is recognized that in the course of time the influence of the initial distribution of the concentration on the function $c_0 = c_c^\tau = f(\tau)$ becomes smaller and smaller, then at $\tau \to \infty$ the following relation holds true:

$$c_0 - c_c^\tau = \text{const}\cdot\exp\left(-\frac{\pi^2}{4l^2}D\tau\right) \qquad (18)$$

The determination of the diffusion coefficient D was based on the angle of inclination of the experimental plot of ln $(c_0 - c_c^\tau)$ against $\tau$ at times when the relation (18) was satisfied.

In addition, experiments were also performed in which the concentrations of the argon $c_0$ and $c_c^0$ differed little at the very beginning, and the diffusion proceeded in accordance with Eq. (15) from the very start of the experiment. The first and second methods gave more nearly equal values for the diffusion coefficients.

The error in the determination of the diffusion coefficient was approximately 5%.[8] The measurement accuracy in our experiments was limited by the error with which the argon concentration was determined. The concentration was measured with a relative error of 1%. At large diffusion times or small concentration differences, the error in the measurement of D increases, since it is necessary to measure a small difference $(c_0 - c_c^\tau)$. A considerable increase of the concentration differences in order to increase the measurement accuracy of $(c_0 - c_c^\tau)$ is impossible. The reason is that on approaching the critical point the integral term in (14) increases for a given concentration difference, and the diffusion can no longer be described by Eq. (15). We were therefore unable to approach close enough to the critical point to be able to measure correctly (within 5%) an appreciable decrease (by whole orders of magnitude) of the diffusion coefficient D, although a sharp decrease of the flow of argon in the capillary could be easily observed.

## 3. EXPERIMENTAL DATA AND THEIR DISCUSSION

The measured values of the diffusion coefficient D as functions of the density $\rho$, the temperature T, and the concentration c of the dissolved argon in carbon dioxide are shown in Figs. 2 and 3. For the purpose of comparison of the experimental data with relation (17), the ordinates in these figures represent the values of $D/b^0kT) = (D\rho/D_0\rho_0)$, and not the diffusion coefficients themselves. The quantity that we call the ideal mobility $b^0$ is defined as the mobility of the argon atoms relative to the molecules of carbon dioxide under conditions when the diffusion occurs in accordance with the theory of rarefied gases, i.e., $b^0 \sim (1/\rho)$.[10] For convenience in interpretation, we shall henceforth consider in these figures not n but the mass density of the system $\rho$. This substitution does not affect the character of the relations, for in our case the fraction of the argon is small and the mass of the atom of its basic isotope $Ar^{40}$ differs little from the mass of the molecule of the main isotopic combination of carbon dioxide $C^{12}O_2^{16}$. It is understood here that the diffusion coefficient and the relations for the fluxes are determined as before in terms of the particle density n.

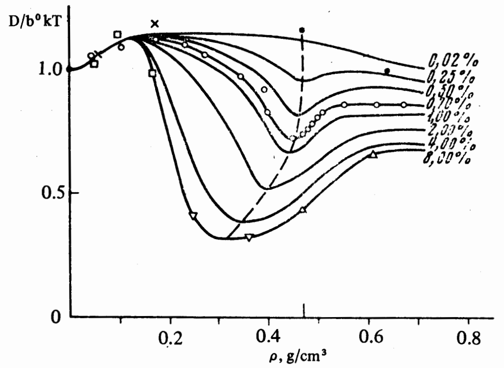

FIG. 2. Plot of $D/b^0kT$ against the density at T = 35°C for different argon concentrations; the solid lines represent interpolation curves. The experimental points correspond to the following argon concentrations: ●–0.02%, X–0.1%, ○–0.7%, □–7.0%, △–7.9%, ▽–9.4%.

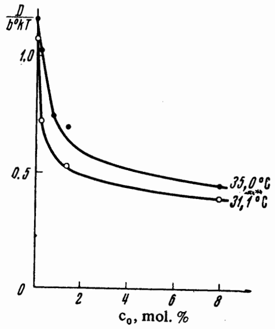

FIG. 3

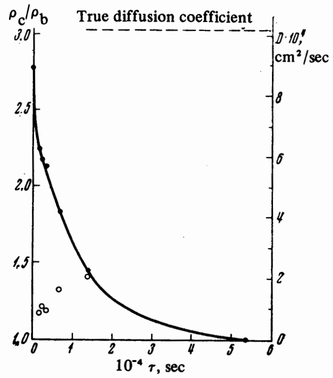

FIG. 4

FIG. 3. Dependence of $D/b^0kT$ on the argon concentration at 31.1 and 35°C for $\rho = 0.47$ g/cm³.

FIG. 4. Dependence of the density of the argon–carbon dioxide system in the capillary on the diffusion time for mixing of the gases, and the effective diffusion coefficient in the presence of hydrodynamic streams connected with the change of the density upon mixing of the components. T = 31.1°C, $c_0 = 8.5\%$. ●–Experimental values of the ratio of the density in the capillary $\rho_c$ and of the density in the bomb $\rho_b$. ○–Values of the diffusion coefficient, formally calculated in accordance with Eq. (16).

The upper curve of Fig. 2, in accordance with Eq. (11), represents the density dependence of the ratio of the true and ideal mobilities $b/b^0)$ at 35°C, since these data were obtained at a sufficiently low argon concentration, when the system was a weak solution. The solid lines of Fig. 2 represent interpolation curves of the relation $D = f(\rho)$ at 35°C and at different concentrations, with allowance for the experimental points of Figs. 2 and 3.

It is seen from Figs. 2 and 3 that at small c, ΔT, and $\Delta v = (-\Delta\rho/\rho_{cr}^2)$ the experimental relations confirm the relation (17) (for pure carbon dioxide $T_{cr} = 31.04$°C, $\rho_{cr} = 0.468$ g/cm³, and $p_{cr} = 72.87$ atm).

Indeed, at ΔT = const, c = const, and $\Delta\rho \to 0$, it follows from (17) that

$$\frac{D}{b^0kT}=\frac{\alpha\Delta T+(\beta-\gamma)c}{\alpha\Delta T+\beta c}+\frac{\gamma c}{(\alpha\Delta T+\beta c)\rho^4}\Delta\rho^2. \qquad (19)$$

The curves (19) represent a family of parabolas of second degree, which degenerate into a straight line as $c \to 0$. The real curves differ from the curves (19) in the entire investigated density interval. However, at $|\Delta\rho| < 0.1$ g/cm$^3$ and $c < 1\%$ mol. Ar, i.e., at small deviations from the critical point of the solvent, the real curves correspond to the character of the curve (19).

At $\Delta\rho = 0$, $\Delta T = \text{const}$, and low concentrations, it follows from (17) that

$$\frac{D}{b^0kT}=1-\frac{\gamma}{\alpha\Delta T}c. \qquad (20)$$

The real relations shown in Fig. 3 have a linear section corresponding to Eq. (20) at $c < 1\%$ mol. Ar, and the smaller $\Delta T$ the larger is the inclination of the lines to the c axis. The value of the limiting ratio $D/b^0kT$ at $\Delta\rho = 0$, $\Delta T = \text{const}$ and $c \to 0$ differs little from unity. The reason is that the abscissas represent, as already mentioned, the ratio of the true and ideal mobilities, which do not differ in the theory of [5].

The experimental dependence of the diffusion coefficient on the temperature will not be presented here, since our data are incomplete. We only indicate that at $\Delta\rho = \rho_m - \rho_{cr}$, where $\rho_m$ is the fixed density of the mixture and $c = \text{const}$, we have

$$\frac{D}{b^0kT}=A+B\Delta T, \qquad (21)$$

where A and B are certain constants. In the case of the $CO_2$–Ar system we have $A > 0$ and $B > 0$, and consequently $D = 0$ when $\Delta T > 0$. This means that the critical temperature of the $CO_2$–Ar system is lower than the critical temperature of pure carbon dioxide.

Thus, the experimental data on at least the dependence of the diffusion coefficient on c and $\rho$ confirm the relation (17) in the concentration interval $0 < c < 1\%$, the density interval $0.4 < \rho < 0.55$ g/cm$^3$, and the temperature $31.1 < T < 35\,°C$, with an approximate error of 5%.

Figure 4 shows the change of the average density of the gas in the capillary near the critical point upon mixing of the carbon dioxide and the argon in the capillary during the diffusion process. The same figure shows the accompanying change of the effective diffusion coefficient, if the latter is calculated formally in accordance with (16). It is seen from Fig. 4 that at the start of the diffusion process the density of the argon flow in the capillary is quite low because of the strong general counterflow due to the decreased density upon mixing of the gases in the capillary in accordance with Eq. (14).

Special experiments have shown that when the sign of the concentration difference between the mixtures in the capillary and the internal volume of the bomb is reversed, the flow density of the argon in the capillary is strongly increased at the start of the experiment, owing to the integral term in (14), decreasing in the course of time to the value

$$J_x=-nD\left(1+\frac{c}{n}\frac{\partial n}{\partial c}\right)\frac{\partial c}{\partial x}.$$

Of course, in these experiments, to avoid simple filling with the denser gas, the capillary was oriented with the closed end upward.

An appreciable decrease of the flow of the dissolved gas in the capillary as a result of $(\partial\mu/\partial c)_{p,T} \to 0$ and of the increase in the absolute magnitude of $(\partial n/\partial c)_{p,T}$ was first observed in [11, 12]. However, a study of the diffusion of the isotopes $Ar^{36}$ and $Ar^{40}$ near their critical points [13] revealed no noticeable deviation from the relation $D \sim 1/\rho$, i.e., from the result predicted by the theory of rarefied gases. The latter is probably due to the small difference between the critical parameters of the argon isotopes and consequently is connected with the fact that the experiments were performed sufficiently far from the critical points, where $(\partial n/\partial c) = 0$ and the solution can be regarded as weak: $(\partial\mu/\partial c)_{p,T} = (kT/c)$.

In conclusion, we note that measurements of the diffusion coefficients as functions of $\rho$, T, and c can yield information on the behavior of the chemical potential of the components in the solution and concerning the second derivatives that enter in relation (17). Unfortunately, our data are insufficiently complete for reliable calculation of these derivatives and insufficiently accurate to bring out the deviations from the classical theory of the critical point of Van der Waals and Landau, on which the relation (17) is based.

We are grateful to M. A. Leontovich for interest in the work and to I. R. Krichevskiĭ for a fruitful discussion.

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Translated by J. G. Adashko
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