MUTUAL DIFFUSION AND MOBILITY IN A CO_2–^{40}Ar–^{36}Ar MIXTURE NEAR THE CRITICAL POINT OF VAPORIZATION OF CO_2

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Experiments have revealed that the relaxation of the chemical composition is strongly retarded, while the equalization of the isotopic composition has no singularities near the critical line of vaporization of the mixture.

One of the important problems in the study of mass exchange in nonideal mixtures is to reveal the role of macroscopic mobility and that of the derivative of the chemical potential with respect to the concentration in the mechanism of the slowing of diffusion near the critical point. According to conditions of nonequilibrium thermodyanmics [1], it is precisely these factors that determine the coefficient of mutual diffusion

$$\mathscr{D} = Nb\,(\partial\mu/\partial N)_{p,T}. \tag{1}$$

It is known that the mobility of an isolated molecule has no singularities near the critical point of vaporization of a pure liquid or near the critical point of mixing of mixtures [2]. However, it has been established that the mobility related to the Onsager coefficient has such a singularity: namely, as the critical point is approached, it diverges as the correlation radius of fluctuations of concentration [3] and, since $(\partial N/\partial\mu)_{p,T} \sim \xi^2$, $\mathscr{D}$ should decrease as ξ^{-1}. This relationship has been confirmed experimentally near the critical point of mixing of liquid solutions [4]. However, near the critical point of vaporization of solutions, experiments have revealed the relationship $\mathscr{D} \sim (\partial\mu/\partial N)_{p,T}$ [5], without singularities in the macroscopic mobility, a result that is in agreement with the Enskog–Chapman theory for dilute gases [6]. Such behavior can be explained by the fact that in mixtures a singularity in the mobility arises near the critical point in a region, previously inaccessible for observations, located nearer to the critical point of the region than in the case of the critical point for mixing [3]. In connection with this, it is of interest to check the assumption of the regular nature of the macroscopic mobility by its direct measurement [7]. A mass spectrometer used as a gas analyzer allows us to simultaneously measure the coefficient of mutual diffusion and the mobility by measuring the time rate of change of the chemical and isotopic compositions of the diffusing gases. We studied diffusion in the CO_2–^{40}Ar–^{36}Ar mixture near the critical point of vaporization of CO_2 with the help of this apparatus.

The diffusion cell used in our experiments consisted of a capillary connected to a relatively large cavity filled with a gaseous mixture; the state of this mixture did not change during diffusion, thus providing for the constancy in concentration and pressure of the gas at the open end of the capillary. Before starting the experiment, the capillary was filled with a dilute mixture containing argon with an excess of the stable isotope ^{36}Ar. When the experiment began, the concentration of argon in the inner cavity of the diffusion cell had a natural isotopic composition and exceeded the argon concentration in the mixture contained in the capillary. The diffusion coefficients were calculated from the data obtained by measuring the average chemical and isotopic compositions of the components as functions of time. The measurement method was presented in more detail in [5].

Generally, in nonideal mixtures, flows of the entire mixture arise as a result of the mixing of the components and related changes in density. Therefore, strictly speaking, the process of diffusion must be described by a nonlinear equation. However, if changes in the concentration of the components in a closed space are sufficiently small, the diffusion equation can be linearized and reduced to the Fick equation. This condition has been met in our experiment. The diffusion coefficient for the isotopic mass exchange has been calculated

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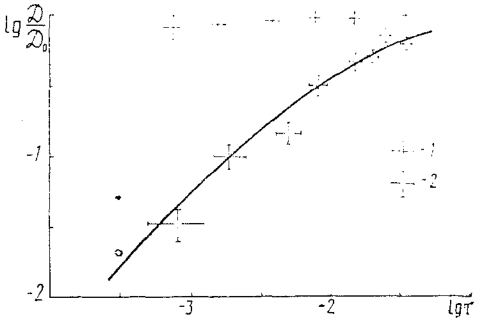

Fig. 1. Temperature dependences of the reduced coefficients of diffusion ($\mathcal{D}/\mathcal{D}_0$) determining the equalization times for the isotopic composition of argon (1) and equalization times for the argon concentration in CO_2 (2) near the critical point of vaporization of a CO_2–Ar mixture with an Ar concentration of N = 0.048 mol. fractions.

over relatively long periods of time throughout the experiment from the solution of the Fick equation

$$\mathcal{D} = \frac{1}{t}\left(\frac{2l}{\pi}\right)^2 \ln\left(\frac{\pi^2}{8}\,\frac{c_0 - c(t)}{c_0 - c(0)}\right). \tag{2}$$

The coefficient of mutual diffusion has been determined from the tangent of the angle of inclination of the linear region of the time-dependent plot $\ln(N_0 - N(t))$ for even longer periods of time from the same experiment.

Figure 1 illustrates the temperature dependences of these coefficients, on a logarithmic scale, referred to the coefficient of mutual diffusion. This coefficient of mutual diffusion has been calculated for the given gas density from the Enskog–Chapman formula

$$\mathcal{D}_0 = bkT = \frac{0.1496}{\sigma_{12}^2 \Omega^{(1,1)} n}\left[\frac{(m_1 + m_2)kT}{m_1 m_2}\right]^{1/2}, \tag{3}$$

for the following values: $m_1 N_A = 44.01$ kg $(\text{kmole})^{-1}$, $m_2 N_A = 39.91$ kg $(\text{kmole})^{-1}$, $\sigma_{12} = 3.71 \cdot 10^{-10}$ m, $\varepsilon_{12}/k = 153$°K, $n = n_k = 6.5 \cdot 10^{27}$ m^{-3}, taken from [6] (values for σ_{12} and ε_{12}/k have been calculated using the combination rules). The vertical segments of the experimental data correspond to the magnitudes of the experimental errors, while the horizontal segments determine the change of the critical temperature of the mixture during diffusion. Figure 1 shows that the coefficient of mutual diffusion decreases as the critical point is approached, owing to a decrease of a thermodynamic factor for constant b. Actually, the curve in Fig. 1 represents the value of $(\partial\mu/\partial N)_{p,T} N/kT = \mathcal{D}/\mathcal{D}_0$, which has been calculated from the Leontovich–Rozen equation of state [2, 8] with coefficients determined in [9].

It follows from Fig. 1 that the diffusion coefficient for the isotopic exchange is equal to the coefficient $\mathcal{D}_0$. Since $\mathcal{D}_0$ has been calculated for ideal mixtures with the thermodynamic factor equal to kT/N, the corresponding mobility of argon atoms is proportional to n^{-1} and $T^{-\frac{1}{2}}(\Omega^{(1,1)})^{-1}$, i.e., there are no singularities at the critical point.

In order to explain the observed effect, we use the Fokker–Planck equation of diffusion with the average field of interaction [10]

$$\frac{\partial \mathcal{P}}{\partial t} = \frac{\partial}{\partial x}\, b\left(\mathcal{P}\frac{\partial U}{\partial x} + kT\frac{\partial \mathcal{P}}{\partial x}\right). \tag{4}$$

It is natural to assume that the average field in the nonideal mixture being considered depends on its chemical composition. We expand the field in a power series in small deviations from the equilibrium concentration and restrict ourselves to the first term of the expansion:

$$U = U_0 + U_1 \delta N. \tag{5}$$

Taking into consideration that $\mathcal{P} \sim N$, and substituting Eq. (5) into (4), we obtain the nonlinear diffusion equation

$$\frac{\partial N}{\partial t} + w\frac{\partial N}{\partial x} = \mathcal{D}\frac{\partial^2 N}{\partial x^2}, \tag{6}$$

where $\mathcal{D} = Nb(\partial\mu/\partial N)_{p,T}$, $w = -bU_1(\partial N/\partial x)$, $(\partial\mu/\partial N)_{p,T} = U_1 + kT/N$. When the concentration differential is small, the nonlinear term proportional to the differential squared vanishes, and Eq. (6) is reduced to the equation of Fick's second law

$$\frac{\partial N}{\partial t} = \mathscr{D}\frac{\partial^2 N}{\partial x^2}. \qquad (7)$$

As the critical point is approached, the interaction between particles increases, so that $U_1 \to -kT/N$; therefore, the coefficient of mutual diffusion decreases, $\mathscr{D} \to 0$ provided that b is well-behaved. It is also clear that the interaction is independent of the isotopic composition while the concentration of the chemical component is constant; therefore, the isotopic mass exchange does not change the probability of diffusion, i.e., isotopes can be mixed by ordinary Brownian motion. In other words, the equalization time for the isotopic concentration is independent of the self-consistent field and the distance to the critical point, which is confirmed by the present experiment.

NOTATION

p, pressure; T, temperature; T_c, critical temperature of the gaseous mixture; $\tau = (T - T_c)/T_c$, reduced temperature; n, number density; n_e, critical number density of the CO_2 particles; μ, chemical potential (here, of argon in the mixture); N, fraction of chemical component (here, argon); c, fraction of the ^{36}Ar isotope in this chemical component; m_1 and m_2, the mean masses of diffusing molecules or atoms; t, diffusion time; x, coordinate along the axis of a capillary; ℓ, the capillary length; c(0), c(t), and c_0, the mean isotope concentrations of ^{36}Ar at the initial moment of diffusion in the capillary, at time t in the capillary, and at the open end of the capillary, respectively; N(0), N(t), and N_0, the same for the mean concentrations of a chemical component (argon); $\mathscr{D}$, the coefficient of mutual diffusion defined by the relation $N(v - w) = -\mathscr{D}\nabla N$; v, velocity of the component; w, mean number velocity; $\mathscr{D}_0 = bkt$, diffusion coefficient calculated from Eq. (3); b, macroscopic mobility; k, Boltzmann constant; σ_{12}, diameter of the scattering cross section of diffusing molecules; $\Omega^{(1.1)}$, reduced temperature-dependent collision integral [6]; ξ, correlation radius of concentration fluctuations; $\mathscr{P}$, probability of finding a particle at a point x at time t; U, average field of interaction; $U_1 = (\partial U/\partial N)_{p,T}$; N_A, Avogadro's number.

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