THE EQUATION OF ISOTHERMAL DIFFUSION IN THE CRITICAL REGION

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Abstract

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THE EQUATION OF ISOTHERMAL DIFFUSION IN THE CRITICAL REGION

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In papers ($^{1-3}$) it was established for the first time that, in the critical region of a binary system, the diffusion rate falls practically to zero even with a considerable concentration gradient of one of the components. This extremely important fact showed the inapplicability of the usual Fick equation for describing diffusion in the critical region. The derivation of the correct equation of isothermal diffusion must proceed from the fact that the rate of change of the concentration of one of the components is determined by the gradient of its chemical potential

$$dm_2 = -\frac{D_0}{RT} c_2 \operatorname{grad}_n \mu_2 \, ds \, dt, \tag{1}$$

where dm_2 is the amount of component that has diffused through the area ds in the time dt in the direction of the unit vector $\mathbf{n}$, normal to ds; c_2 and μ_2 are, respectively, the concentration and the chemical potential of the second component; T is the temperature; R is the gas constant; D_0 is a proportionality coefficient, which in what follows we shall assume to be constant.

By the usual transformations from equation (1) one can obtain the equation

$$\frac{\partial c_3}{\partial t} = -\frac{D_0}{RT} \operatorname{div}(c_2 \operatorname{grad} \mu_2). \tag{2}$$

At the critical point of a binary system the conditions must be satisfied

$$\left(\frac{\partial \mu_2}{\partial N_2}\right)_{P,T} = 0, \qquad \left(\frac{\partial^2 \mu_2}{\partial N_2^2}\right)_{P,T} = 0, \tag{3}$$

where N_2 is the mole fraction of the second component.

It follows from this that, in the expansion of the chemical potential μ_2 in a series in $N_2 - N_{2,k}$ ($N_{2,k}$ is the value of the mole fraction at the critical point), the first- and second-degree terms will not enter. Restricting ourselves to the first two terms of the expansion, we may write

$$\mu_2 = \text{const} + \beta (N_2 - N_{2,k})^3. \tag{4}$$

Let us consider the diffusion equation for systems in which the partial specific and partial molar volumes in the region of the critical concentration depend only very weakly on the composition of the solution. Such a system was investigated, for example, in paper (^{3}). Taking into account that

$$V = \bar{v}_0 N_1 + \bar{v}_2 N_2, \qquad c_2 = \frac{N_2}{V} \tag{5}$$

(where V is the volume of the solution; $\bar{v}_1$ and $\bar{v}_2$ are the partial molar volumes of the components), and also conditions (3), we write equation (2) in the case of one-dimensional diffusion in the form

$$\frac{\partial N_2}{\partial t} = -\frac{3\beta D_0}{RT}(N_2 - N_{2,k}) \left\{ \left(\frac{\partial N_2}{\partial x} \right)^2 \left[N_2 - N_{2,k} + \frac{2N_2}{1 - \frac{N_2}{V}(\bar{v}_2 - \bar{v}_1)} \right] + \frac{N_2 (N_2 - N_{2,k})}{1 - \frac{N_2}{V}(\bar{v}_2 - \bar{v}_1)} \frac{\partial^2 N_2}{\partial x^2} \right\}. \tag{6}$$

For a number of systems the condition

$$\frac{N_2}{V}(\bar{v}_2 - \bar{v}_1) \ll 1, \tag{7}$$

is valid; using it, equation (6) can be simplified:

$$\frac{\partial N_2}{\partial t} = 2aN_2(N_2 - N_{2,k}) \left(\frac{\partial N_2}{\partial x} \right)^2 + a(N_2 - N_{2,k})^2 \left[\left(\frac{\partial N_2}{\partial x} \right)^2 + N_2 \frac{\partial^2 N_2}{\partial x^2} \right], \qquad a = -\frac{3\beta D_0}{RT}. \tag{8}$$

Since the solution is considered in the neighborhood of the critical point ($N_2 \to N_{2,k}$), by making the transformation

$$N_2 = N_{2,k} e^{\varphi} \tag{9}$$

and taking into account that $|\varphi| \ll 1$, we obtain the approximate equation of one-dimensional isothermal diffusion in the neighborhood of the critical point:

$$\frac{\partial \varphi}{\partial t} = A\varphi \left(\frac{\partial \varphi}{\partial x} \right)^2, \tag{10}$$

where $A = 2aN_{2,k}^3$.

The solution of equation (10) is

$$N_2 = N_{2,k} \exp \left\{ \frac{\sqrt{\dfrac{c_1}{A}}\, x + c_2}{\sqrt{2(-c_1 t + 1)}} \right\}, \tag{11}$$

where c_1 and c_2 are constants determined from the initial and boundary conditions.

In accordance with Onsager' s hypothesis in the thermodynamics of irreversible processes (^{4}), the average rate of decay of concentration fluctuations should be linearly related to the diffusion flux. It follows from this that, in the critical region, concentration equilibrium should be established slowly. In this connection it is of interest to consider the change in the mole fraction (concentration) of the second component in comparatively small volumes, say over the length of a light wavelength, which is essential for substantiating the indicated hypothesis.

If at $t = 0$ and $x = 0$, $N_2 = \alpha_1 N_{2,k}$, and at $x = l$, $N_2 = \alpha_2 N_{2,k}$ ($\alpha_2 < \alpha_1 < 1$), then

$$c_1 = \frac{2A}{l^2} \left[\ln \frac{\alpha_2}{\alpha_1} \right]^2, \qquad c_2 = \sqrt{2} \ln \alpha_1. \tag{12}$$

The coefficient β entering into (4) is, for a number of liquids, of the order of 10^2 cal $\cdot$ (mole fraction)$^{-3} \cdot$ mol^{-1}; if $D_0 \sim 10^{-6}$–10^{-7} cm$^2 \cdot$ sec^{-1}, $N_{2,k} \sim 0.2$–0.3, then for room temperatures $A \sim -(10^{-9}$–$10^{-10})$ cm$^2 \cdot$ sec^{-1}. Then for a length l equal to the wavelength of visible light, for example, 6000 Å, and $\ln(\alpha_2/\alpha_1) \sim 10^{-1}$ ($\alpha_1, \alpha_2 \to 1$),

$$c_1 \sim -10^{-3} \text{ sec}^{-1}.$$

According to solution (11), a noticeable change in the mole fraction of the component will occur when $-c_1 t$ becomes comparable with unity, i.e., after $t \sim 10^3$ sec. (Fig. 1 for $\alpha_1 = 0.95$ and $\alpha_2 = 0.9$).

The long relaxation time interval makes it possible to use optical methods for investigating diffusion processes in the critical region. In works^5, using examples of pure substances, it was established that in the critical region, after mixing, a vertical equilibrium distribution of concentration is slowly established. The authors explain this by the fact that compacted associations (clusters) of molecules form at the top of the column, which then, under the action of gravity, slowly settle downward. The calculations presented above show that the long relaxation time interval is not at all connected with the indicated model concepts. Moreover, compacted groups of molecules need not necessarily descend downward, but may disperse upward and form below.

Fig. 1. 1 $-t = 0$; 2–10^3 sec.; 3–10^4 sec.; 4–10^5 sec.

The diffusion equation (10) can be reduced to the form of the usual Fick equation

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c_2}{\partial x}\right), \tag{13}$$

for which it is necessary to determine the function $D(N_2)$, which we shall interpret as the diffusion coefficient in the critical region.

Assuming $V = \text{const}$, we obtain the determining equation for the required function D

$$\frac{\partial D}{\partial x} + f(t)D = \Phi(x,t), \tag{14}$$

where

$$f(t) = \frac{\partial}{\partial x}\frac{N_2}{N_{2,k}}, \qquad \Phi(x,t) = \frac{c_1(x+c_2)}{2(-c_1 t+1)}. \tag{15}$$

For $c_2 = 0$ (the latter corresponds to the condition that at $t = 0$ and $x = 0$, $N_2 = N_{2,k}$)

$$\Phi(x,t) = A[f(t)]^2 x. \tag{16}$$

The solution of equation (14), if (15) and (16) are used and $D(N_{2,k}) = 0$ is set, is written in the form

$$D(N_2) = A\left(\frac{N_{2,k}}{N_2} + \ln\frac{N_2}{N_{2,k}} - 1\right). \tag{17}$$

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CITED LITERATURE

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