

cally with time; G , Q , and S , dimensionless variables that determine the velocity, strain and shear stress perturbations respectively; D , M , B , and W , dimensionless parameters that determine the values of the bulk elasticity, the dilatational viscosity, the shear viscosity, and the relaxation time respectively; $\Delta = \partial^2/\partial y^2_k$, Laplacian; $f^{(n,\ell)}$, eigenfunctions of the Laplacian; $h_{n,\ell}$, eigenvalues of the Laplacian determined from the boundary conditions (n is an index which numbers the values of h in increasing order, ℓ is the spherical harmonic index); $J_\nu(z)$, Bessel function of the first kind; $Y_\ell(\vartheta, \varphi)$, surface spherical harmonic; $P_\ell^m(\cos \vartheta)$, an associated Legendre function of the first kind; $g(n,\ell)$, $q(n,\ell)$, $s(n,\ell)$, time parts of the harmonics of the G , Q , S , value spectrum; z_1 , z_2 , and z_3 , auxiliary dimensionless parameter; A , amplitude of the velocity perturbation fluctuations; ψ , phase of the fluctuations; A_0 and ψ_0 , initial values of the amplitude and phase; $C(\beta)$, a variable corresponding to a monotonic mode; $\Omega(T)$, a variable that plays the part of frequency in the "generating" solution.

LITERATURE CITED

1. S. B. Ainbinder, É. L. Tyunina, and K. I. Tsirule, Properties of Polymers in Various States of Stress [in Russian], Moscow (1981).
2. A. Ya. Gol'dman, Volume Deformation of Plastics [in Russian], Leningrad (1984).
3. G. I. Burdé and T. M. Burdé, Zh. Prikl. Mekh. Fiz., No. 6, 114-123 (1982).
4. A. M. Hull and R. R. A. Pearson, J. Non-Newtonian Fluid Mech., 14, No. 2, 219-247 (1984).
5. V. A. Gorodtsov and A. I. Leonov, Prikl. Mat. Mekh., 32, No. 1, 70-94 (1968).
6. A. I. Leonov, Rheol. Acta, 15, No. 2, 85-98 (1976).
7. N. N. Lebedev, Special Functions and Their Applications [in Russian], Moscow-Leningrad (1963).
8. N. N. Bogolyubov and Yu. A. Mitropol'skii, Asymptotic Methods in Nonlinear Oscillation Theory [in Russian], Moscow (1974).
9. E. A. Grebennikov and Yu. A. Ryabov, Constructional Methods of Analysis of Nonlinear Systems [in Russian], Moscow (1979).
10. M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions [Russian translation], Moscow (1979).
11. E. W. Hobson, Theory of Spherical and Ellipsoidal Functions [Russian translation], Moscow (1952).
12. C. J. S. Petrie and M. M. Denn, AIChE J., 22, No. 2, 209-236 (1976).
13. I. Ya. Dorfman, A. N. Kryuchkov, É. V. Prut, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 278, No. 1, 141-144 (1984).

RELAXATION OF CONCENTRATION INHOMOGENEITIES IN NONIDEAL SOLUTIONS

P. P. Bezverkhii, M. Ya. Golota,
V. S. Gurvich, and É. V. Matizen

UDC 532.72

Numerical solutions of the nonlinear diffusion equation are obtained for nonideal solutions satisfying an equation of state of the Van der Waals-Landau average field type. The results are compared with experiment.

The study of the processes of relaxation of concentration inhomogeneities in binary gaseous solutions in the region of states in which significant nonideality has a pronounced influence on the diffusion owing to the proximity of the critical line of the mixture is a complex problem involving the nonlinearity of the equations describing these processes. Particularly difficult to solve experimentally is the inverse problem of regenerating the interdiffusion coefficient from data on the dependence of the concentration on time and the coordinates. Further obstacles arise as a result of the limited accuracy of measurement of

Institute of Inorganic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 54, No. 1, pp. 55-65, January 1988. Original article submitted July 22, 1986.

TABLE 1. Constants of the Equations of State (2), (3), and (4)

Ar-CO ₂	(2)	(3)	Ne-CO ₂	(4)
Ar $\left\{ \begin{array}{l} a_1, \text{MPa} \cdot \text{m}^6 (\text{kmole})^{-3} \\ b_1, \text{m}^3 (\text{kmole})^{-1} \end{array} \right.$	$1,062 \cdot 10^{-1}$ $25,11 \cdot 10^{-3}$	81,36 $25,11 \cdot 10^{-3}$	A_N A_τ	6,1045 7,0397
CO ₂ $\left\{ \begin{array}{l} a_2, \text{MPa} \cdot \text{m}^6 (\text{kmole})^{-1} \\ b_2, \text{m}^3 (\text{kmole})^{-1} \\ k, \text{dimensionless} \end{array} \right.$	$3,195 \cdot 10^{-1}$ $35,9 \cdot 10^{-3}$ —	79,44 $30,3 \cdot 10^{-3}$ 0,7318	A_{Nv} $A_{\tau v}$ A_{vvv}	-10,802 -6,969 -0,32015
$a_{12}, \text{MPa} \cdot \text{m}^6 (\text{kmole})^{-3}$ $b_{12}, \text{m}^3 (\text{kmole})^{-1}$	$1,769 \cdot 10^{-1}$ $31,0 \cdot 10^{-3}$	12,33 $18,5 \cdot 10^{-3}$		

the small concentration changes for which it is possible to disregard the nonlinear terms in the diffusion equation. Thus, for example, differences in N of 3-5%, which are fairly small away from the critical point and permit the accurate use of the linear diffusion equation in compressed gases, may prove large when $\tau \sim 10^{-3}$ - 10^{-2} . With further decrease in the N differentials we are faced with the problem of sharply increasing the accuracy of the concentration difference measurements for all process times.

The average field theory has been used to work out many problems of the application of the linear diffusion model to solutions in a highly nonideal state. In this article, on the basis of the theory we extend the description of the characteristics of diffusion processes near the critical line with the aid of a nonlinear equation. We did not set ourselves the task of obtaining the closest possible agreement between the calculations and actual experiments, since our attention was concentrated on the important features of the diffusion process. We therefore made certain simplifications, in particular, by considering only the one-dimensional case; as the equations of state we chose equations of the Van der Waals-Landau type. In accordance with the results of our experiments, it was assumed that the component mobility b_1^W in a mixture with a concentration of up to several mole percent behaves in the same way as in an ideal gas mixture. We studied solutions with small N , since it is precisely in these that the characteristics associated with nonideality are most strongly expressed near the critical vaporization point.

The results of diffusion measurements in Ar-CO₂, Ne-CO₂, and ⁴He-D₂ [1-4] have shown that over a fairly broad region of the nonideal state of the gas solution the decisive influence on the diffusion processes is that of the thermodynamic factor $(\partial\mu_1/\partial N)_{p,T}$ and the function $n(N)$ for regular behavior of b_1^W , when the relative change in b_1^W is small compared with the change in $(\partial\mu_1/\partial N)_{p,T}$ (D^W and b_1^W have been written in the reference system moving with the number-average velocity W).

The region of values of the parameters of the equation of state in which this approach is not applicable was estimated in [2-4]. It is primarily the region of the liquid state ($n/n_c > 1.5$) and, moreover, the region in the immediate vicinity of the critical point of vaporization of binary solutions, where it is no longer possible to consider that the Onsager coefficient varies only slightly. Thus, in the general case D^W can be represented by two terms [4]:

$$D^W = b_1^W N \left(\frac{\partial\mu_1}{\partial N} \right)_{p,T} + \frac{RT}{6\pi\eta r_c}, \quad (1)$$

where $r_c = r_0 \tau^{-\nu}$.

In regions remote from the critical point the dominant term in expression (1) is the first term, but in a region fairly close to the critical point the second term predominates and determines the diffusion rate. Estimates [2, 5] based on accurate data on the equation of state in the critical region show that for Ar-CO₂ and Ne-CO₂ solutions the influence of the second term in expression (1) is significant only at $\tau < 10^{-3}$, when $N \lesssim 0.03$ mole fraction. The experiments were carried out at $\tau \gtrsim 10^{-3}$ - 10^{-2} ($N \approx 0.03$ - 0.05 mole fraction), which made it possible to take into account only the first term in (1).

In view of the almost total lack of accurate experimental p - v - T - N data for binary mixtures near the critical point and lines of phase separation we also lack the equations of the mixtures in that region, with a few exceptions such as the Leontovich-Rozen equations [6, 7] for Ar-CO₂ [8], Ne-CO₂ [9] and C₃H₈-C₂H₆ [10], and the scaling equations for ³He-⁴He [11], Ne-CO₂ [12] and Ar-CO₂ [13]. The scaling equations are complex and using them to obtain the necessary thermodynamic derivatives calls for rather complicated numerical calculations. However, for exploring the behavior, in nonideal mixtures, of thermodynamic

derivatives with strong singularities, such as $\left(\frac{\partial\mu_1}{\partial N}\right)_{p,T}$, $\left(\frac{\partial v}{\partial N}\right)_{p,T}$, and $\left(\frac{\partial^2 v}{\partial N^2}\right)_{p,T}$, it is suffi-

cient to use simpler equations of state of the Van der Waals-Landau type, since for our purposes the values of the critical susceptibility index of the fluctuation theory and average-field type theory differ unimportantly, as 1.2 and 1 respectively. In this study we have used the Van der Waals equation of state

$$p = RT(v - b) - a/v^2 \quad (2)$$

or the modified Berthelot equation

$$p = k[RT/(v - b) - a/(Tv^2)], \quad (3)$$

which make it possible to obtain the exact form of μ_1 and μ_2 . Here, k is a matching constant, $a = a_1N^2 + 2a_{12}N(1 - N) + a_2(1 - N)^2$; $b = b_1N^2 + 2b_{12}N(1 - N) + b_2(1 - N)^2$.

For the same purposes we also used an equation of state, more accurate in the critical region adjacent to the critical point of the pure component (CO_2), in the form of a Landau expansion for the mixtures Ar- CO_2 [8] and Ne- CO_2 [9]

$$\frac{p - p_c}{p_c} = A'_N N + A'_T \tau + A'_{Nv} N \Delta v + A'_{Tv} \tau \Delta v + A'_{vvv} \Delta v^3, \quad (4)$$

where $\Delta v = (v - v_c)/v_c$, $p_c = 7.386$ MPa, $T_c = 304.15$ K, $v_c = 9.40406 \times 10^{-2}$ m³/kmole are the critical parameters of the CO_2 [9]. The constants of the equations (2) and (3) were obtained from the data on Ar- CO_2 [8]. These constants are given in Table 1. For Eqs. (2) and (3) they were determined by a least squares analysis [14], while for Eq. (4) they were so selected that the critical curve for the mixture Ne- CO_2 , calculated using (4), coincided with the experimental curve [2].

The rms error of approximation of the Ar- CO_2 data by Eq. (2) is 1.5 bar, the corresponding figure for Eq. (3) being 0.28 bar. For comparison we note that approximation by a broader, as compared with (4), expansion with 11 matching parameters gives an error of 0.09 bar [8]. Using Eqs. (2), (3), and (4), it is possible to obtain expressions for μ_1 and μ_2 and to determine the surface of the phase separation region and the critical line of the mixture [14].

Taking into account the fact that in the region of applicability of these equations of state $D^W = b_1^W N (\partial\mu_1/\partial N)_{p,T}$, where $b_1^W = D_0/RT$, and D_0 is the diffusion coefficient of the ideal gas mixture, which can be calculated from the Enskog-Chapman equation or measured [4], we obtain

$$D^W/D_0 = (N/RT) (\partial\mu_1/\partial N)_{p,T}. \quad (5)$$

In order to enable the results of analyzing the behavior of $n(N)$ and $\left(\frac{\partial\mu_1}{\partial N}\right)_{p,T}$ for $p, T = \text{const}$ to be applied to different binary gas systems, we use the law of corresponding states and reduce Eq. (2), which reflects with qualitative accuracy the behavior of a nonideal Ar- CO_2 mixture, to the dimensionless form:

$$p^* = 8T^*/z - 3a^*/v^{*2}; \quad z = 3v^* - b^*, \quad (6)$$

where $a^* = a/a_2$; $b^* = b/b_2$; $p^* = p/p_c$, $T^* = T/T_c$; $v^* = v/(3b_2)$; $p_c = a_2(27b_2^2)$; $T_c = 8a_2/(27Rb_2)$, and the index 2 relates to the CO_2 . Then the dependence of $(\partial\mu_1/\partial N)_{p,N}$ on N , v^* , and T^* takes the form [4]:

$$\frac{N}{RT} \left(\frac{\partial\mu_1}{\partial N}\right)_{p,T} = 1 - \frac{N(1-N)^2}{T^{*2}} \left\{ \frac{(\partial p^*/\partial N)_{T,v}^2}{-(\partial p^*/\partial v^*)_{T,N}} - \frac{8T^*}{z} \left(b^{*''} + \frac{(b^{*'})^2}{z} \right) + \frac{9a^{*''}}{v^*} \right\}. \quad (7)$$

Here $b^{*'} = db^*/dN$; $b^{*''} = d^2b^*/dN^2$; $a^{*''} = d^2a^*/dN^2$.

For Eq. (4) $(\partial\mu_1/\partial N)_{p,T}$, in accordance with [6], may be represented in the form:

$$\frac{N}{RT} \left(\frac{\partial\mu_1}{\partial N}\right)_{p,T} = 1 + \frac{NA_N'^2 (p_c v_c / RT_c)}{A'_{Nv} N + A'_{Tv} \tau + 3A'_{vvv} \Delta v^2}. \quad (8)$$

Comparing the behavior of curves 1 and 2 in Fig. 1, we note the existence of a minimum of $(\partial\mu_1/\partial N)_{p,T}$ for both models and a sharp increase in the density of the mixture at values

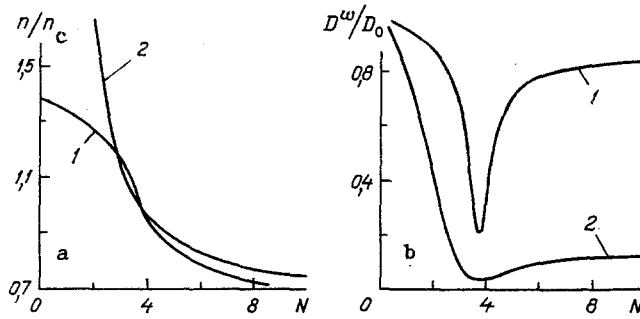


Fig. 1. Density n/n_c (a) and diffusion coefficient $D^w/D_0 = N/RT(\partial\mu_1/\partial N)_{p,T}$ (b) as functions of the concentration (mole %): 1) calculation for a Ar-CO₂ mixture from Eqs. (6) and (7) for $T^* = 0.99$ and $p^* = 1.04$; 2) calculation for a Ne-CO₂ mixture from Eqs. (4) and (8) for $p - p_c = 1.625$ MPa; $T - T_c = -0.3$ K.

of N corresponding to the region of that minimum. An analogous minimum in the region of the critical point of the mixture is also observed in the density dependence of D^w/D_0 when $N = \text{const}$, $T = \text{const}$ [4, 14]. Attention is drawn to the experimental detection of minima in the dependence of the product ρD^w on ρ in a Ar-CO₂ solution in the critical region [1] and the decrease in D^w as the boundary curve is approached along the isobars in the system ⁴He-D₂ [3], which also corresponds to the behavior of $(\partial\mu_1/\partial N)_{p,T}$ according to the model.

In order to use Eqs. (7) and (8) correctly, it is necessary to find the phase separation region. The boundary curve is determined from the equations $\mu_1^l = \mu_1^n$, $\mu_2^l = \mu_2^n$, where μ_1 and μ_2 are calculated, for example, from equations taken from [4]. Calculation of the phase separation boundary for $T^* = 0.99$ and equation of state (6) and for $T - T_c = -0.3$ K and Eq. (4) showed that the curves in Fig. 1 pass through the single-phase region.

A system of nonlinear equations describing the relaxation of an initial concentration inhomogeneity under the conditions $\nabla p = 0$ and $\nabla T = 0$ in a binary mixture was first proposed in [6] for an essentially nonideal state of the gas mixture in the critical region of vaporization:

$$n \frac{\partial N}{\partial t} + nW \frac{\partial N}{\partial x} = \frac{\partial}{\partial x} \left(nD^w \frac{\partial N}{\partial x} \right), \quad \frac{\partial n}{\partial t} + \frac{\partial}{\partial x} (nW) = 0, \quad (9)$$

$$n = n(N, p = \text{const}, T = \text{const}), \quad D^w = Nb_1^w (\partial\mu_1/\partial N)_{p,T}.$$

For investigating diffusion in Ne-CO₂, Ar-CO₂, and ⁴He-D₂ solutions in the nonideal state in the neighborhood of the critical points of CO₂ and D₂ we used a capillary opening at one end into a large reservoir containing a solution at constant concentration. The model problem corresponding to this method consists of solving system (9) for the following initial and boundary conditions: capillary of length L closed at one end (x axis directed towards the open end) and full, at the initial instant $t = 0$, of a mixture of uniform concentration N_0 . At the open end of the capillary the mixture concentration $N(L, t) = N_1$ is kept constant. Experimentally, this corresponds to the connecting of the end of the capillary ($x = L$) at time $t = 0$ to a reservoir containing a mixture of composition N_1 , whose volume is much greater than that of the capillary. The pressure and temperature in the reservoir and the capillary are the same. With the passage of time the initial concentration step is eroded, and in the experiments we measured either the average composition of the mixture in the capillary $\bar{N}(t)$ (after disconnecting it from the reservoir for time t) or the change of concentration at the closed end of the capillary $N(0, t)$. Thus, for the capillary method the boundary conditions are written in the form:

$$N(x, 0) = N_0 \text{ when } t = 0, \quad N(L, t) = N_1 \text{ when } x = L, \quad (10)$$

$$\partial N(0, t)/\partial x = 0 \text{ and } W(0, t) = 0 \text{ when } x = 0.$$

As the initial difference $N_0 - N_1$ tends to zero and as $\partial N/\partial x \rightarrow 0$ in the diffusion process for a real mixture it is possible to assume that n and D^w are practically independent

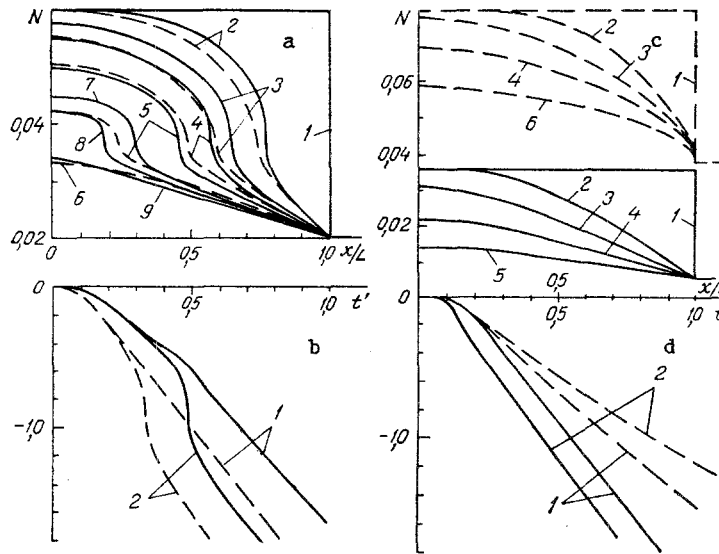


Fig. 2. Solutions of Eq. (17) using the Van der Waals equation of state (6) and D^W/D_0 from (7) for $T^* = 0.99$ and $p^* = 1.04$: a, b) solutions on the interval $0.02 \leq N \leq 0.06$ mole fraction. Broken curves - solutions obtained using (6) and $D^W/D_0 \equiv 1$; continuing curves - solutions obtained using (6) and (7) (see Fig. 1, curves 1); a) concentration distribution along capillary for the following values of t' : 1) 0.0; 2) 0.06; 3) 0.14; 4) 0.20; 5) 0.30; 6) 0.35; 7) 0.40; 8) 0.45; 9) 0.50; b) dependence of $\ln u(0, t') - u_1/(u_0 - u_1)$ (1) and $\ln N(0, t') - N_1/(N_0 - N_1)$ (2) on t' at $x' = 0$; c, d) solutions on the intervals of N : broken curves - $0.038 \leq N \leq 0.08$ mole fraction; continuous curves - $0.005 \leq N \leq 0.036$ mole fraction; c) concentration distribution along capillary for the following values of t' : 1) 0.0; 2) 0.06; 3) 0.14; 4) 0.30; 5) 0.55; 6) 0.60; d) dependence of $\ln u(0, t') - u_1/(u_0 - u)$ (1) and $\ln N(0, t') - N_1/(N_0 - N_1)$ (2) on t' at the closed end of the capillary.

of N . For real mixtures in the region of states remote from the phase equilibrium surface and the critical line of the mixture the functions $n(N)$ and $D^W(N)$ are smooth and vary only slightly, which makes it possible to consider a small difference $N_0 - N_1$ of the order of 10-20 mole %. In this case Eqs. (9) are linearized and the problem reduces to the solution of the Fick equation, valid for diffusion in a rarefied mixture:

$$\frac{\partial N}{\partial t} = D^W \frac{\partial^2 N}{\partial x^2}. \quad (11)$$

In the region of essentially nonideal behavior of the solution (see Fig. 1) $n(N)$ and $D^W(N)$ vary sharply; here only an initial difference of the order of 0.1 mole % can be considered small enough to permit the use of Eq. (11). In this case, however, to obtain D^W with the same error it is necessary considerably to improve the accuracy of measurement of N in the experiments, which is not easy. Therefore the initial differences in N of 3-5 mole % created in our measurements were sometimes found to be rather large, which made it necessary to employ the nonlinear system (9).

Solving system (9) for boundary conditions (10) is fairly complicated, even by numerical methods, owing to its nonlinearity and the complex form of the functions $D^W(N)$ and $n(N)$ even for the simplest equations of state (2) and (4). Accordingly, we first transform Eqs. (9), reducing them to dimensionless form by means of the change of variables $x' = x/L$, $t' = D_0 t/L^2$, $n^* = n/n_c$, $W^* = WL/D_0$ and eliminating from the first two equations the derivatives with respect to t' . We obtain the equation for the velocity

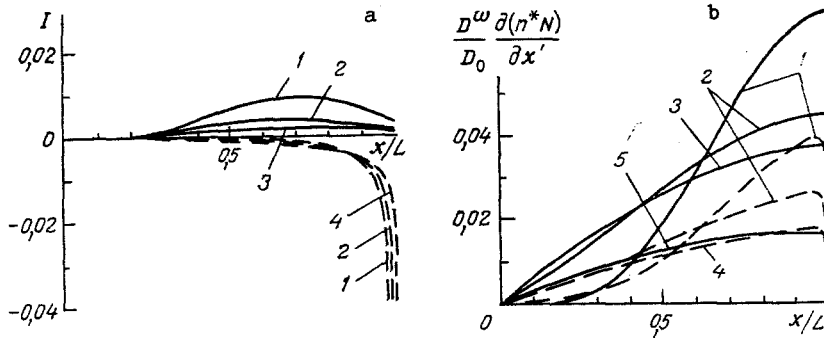


Fig. 3. Results of calculating the integral I (14) from the solutions of Eq. (17) in the case of Fig. 2c (notation same as in Fig. 2c) (a) and the calculated dependence of $D^W/D_0 \frac{\partial(n^*N)}{\partial x'}$ (15) on x' for the values of t' : 1) 0.06; 2) 0.14; 3) 0.20; 4) 0.30; 5) 0.55 (b).

$$\frac{\partial W^*}{\partial x'} = -\frac{1}{n^{*2}} \left(\frac{\partial n^*}{\partial N} \right)_{p,T} \frac{\partial}{\partial x'} \left(n^* \frac{D^W}{D_0} \frac{\partial N}{\partial x'} \right). \quad (12)$$

Taking into account the boundary condition $W^*(0, t') = 0$, we can write (12) in the form:

$$W^*(x', t') = -\frac{D^W}{D_0} \frac{1}{n^*} \left(\frac{\partial n^*}{\partial N} \right)_{p,T} \frac{\partial N}{\partial x'} - \frac{1}{n^*N} I, \quad (13)$$

where the integral I is given by the expression

$$I = n^*N \int_0^{x'} n^*(N) \frac{D^W(N)}{D_0} \left(\frac{\partial^2 (1/n^*)}{\partial N^2} \right)_{p,T} \left(\frac{\partial N}{\partial x'} \right)^2 dx'. \quad (14)$$

Substituting the number-average velocity W^* from (13) in system (9) and transforming it using (5), we obtain the nonlinear equation for the function $u = n^*N$ (number of moles of first component per unit volume)

$$\frac{\partial u}{\partial t'} = \frac{\partial}{\partial x'} \left[\frac{N}{RT} \left(\frac{\partial \mu_1}{\partial N} \right)_{p,T} \frac{\partial u}{\partial x'} + I \right], \quad (15)$$

a complex integrodifferential equation of the diffusion process in a nonideal solution which in the general case we could not solve, even numerically. We will therefore assume that in (13) the first term on the right is much greater than the second. Evaluating the integral in (13) by the mean value theorem, we find that this is possible provided that

$$\left| \Delta N \frac{\partial}{\partial N} \left[\ln \left(\frac{\partial \mu_1}{\partial N} \right)_{p,T} \right] \right| \ll 1, \quad (16)$$

where ΔN is the change in N on the interval $(0, x')$. For fairly small ΔN this condition can be satisfied if the derivative $(\partial^2 \mu_1 / \partial N^2)_{p,T}$ does not have a singularity.

Satisfaction of inequality (16) or the smallness of the integral I in the expression for the number-average velocity (13) means that the laboratory coordinate system in which the capillary is at rest coincides with the volume-average frame of reference. If I in (13) cannot be neglected, then in the case of a nonideal mixture none of the reference systems used can be made to coincide with the laboratory coordinate system. However, if condition (16) is satisfied, Eq. (15) can be written in the form:

$$\frac{\partial u}{\partial t'} = \frac{\partial}{\partial x'} \left(\frac{D^W}{D_0} \frac{\partial u}{\partial x'} \right), \quad (17)$$

which is suitable for solution by ordinary numerical methods on a computer.

The nonlinear diffusion equation (17) with initial and boundary conditions (10) was in fact solved for the density of the first component $u = Nn^*$ by the sweep method [15]. In the calculations we used $D^W(N)/D_0$ and $n^*(N)$ in accordance with Eqs. (6), (7), and (4), (8) with values of p^* and T^* that corresponded to the values of p and T in the experiments. The form of these relations is shown in Fig. 1 for specific p and T . The sweep method was used in

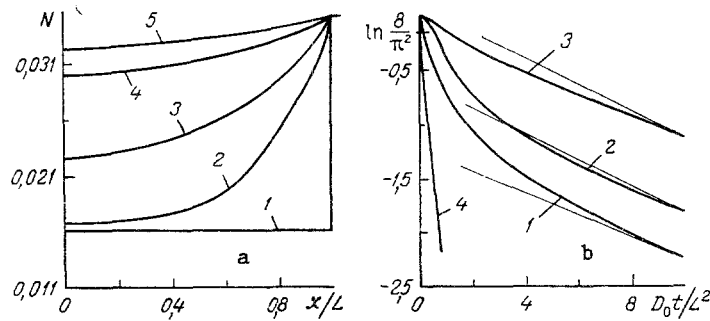


Fig. 4. Solutions of Eq. (17) using relations (4) and (8) from Fig. 1 (curves 2): a) distribution of N (mole fraction) along the capillary for the values of t' : 1) 0.0; 2) 0.26; 3) 1.02; 4) 5.1; 5) 10.2; b) dependence on time t' of the quantities: 1) $\ln N(t') - N_1/(N_0 - N_1)$; 2) $\ln N(0, t') - N_1/(N_0 - N_1)$; 3) $\ln u(0, t') - u_1/(u_0 - u_1)$; 4) solution of the linear equation (11) for $D^W/D_0 \equiv 1$ and large times (for $N(t')$).

two variants: one for solving Eq. (17) with relations (6) and (7), the other for solving it with relations (4) and (8). In the first case Eq. (17) was solved in accordance with an implicit six-point scheme with an improved order of accuracy [16], whose algorithm was adapted to the singularities of (17). For a difference grid with 40 nodes on the interval $0 \leq x' \leq 1$ the scheme was stable at values of the grid parameter $\Delta t'/(\Delta x')^2 \leq 3.2$. In solving the problem, signs of instability of the difference scheme appeared only at $\Delta t'/(\Delta x')^2 \geq 16$ (waves). When model equations (4) and (8) were employed, Eq. (17) was solved in accordance with an implicit six-point scheme [15] with 20 nodes on the interval $0 \leq x' \leq 1$ at values of $\Delta t'/(\Delta x')^2 \leq 0.4$. By means of (6) or (4) the solution $u = N(x', t') n^*(N(x', t'))$ for given p^* and T^* was reduced at $x' = 0$ to the form $\ln N(0, t') - N_1/(N_0 - N_1)$ versus t' or to the form $\ln \bar{N}(t') - N_1/(N_0 - N_1)$ versus t' , which was used for analyzing the experimental curves for the purpose of determining the values of D^W from their slope. In order to check the efficiency of the program, we solved a control problem of concentration relaxation on the interval from $N_0 = 0.06$ to $N_1 = 0.02$ mole fraction ($T^* = 0.99$, $p^* = 1.04$) under the condition $D^W/D_0 \equiv 1$ (see Fig. 2a, b, broken curves). In this case Eq. (17) becomes the linear equation (11) (but for the function $u = n^*N$), for which the form of the solution for diffusion in a capillary is well known [3] (broken curve 1, Fig. 2b). The function $\ln N(0, t') - N_1/(N_0 - N_1)$ (broken curve 2) was obtained by conversion from $u(0, t')$ using the dependence $n^*(N)$ (6) (see Fig. 1a, curve 1). Thus, the effect of nonideality on the relaxation of N was taken into account solely in terms of the dependence of the density on the concentration. The continuous curves in Figs. 2a, represent the solutions of Eq. (17) for the same conditions, but with allowance for the dependence of D^W/D_0 on N in accordance with (7) (see Fig. 1b, curve 1). A comparison of the broken and continuous curves in Fig. 2a, b reveals their similarity, though the latter reflect a slower process. The behavior of the continuous curve 1 (Fig. 2b) is influenced only by $D^W(N)$; the other continuous curves are influenced both by $D^W(N)$ and by $n^*(N)$, the latter having a more pronounced effect. D^W can be correctly determined from the slope of experimental curves of type 2 if the behavior of $n(N)$ in nonideal solutions is known.

The results of a numerical calculation of the diffusion process in a capillary for the same conditions and the same D^W/D_0 and $n^*(N)$ as in Fig. 2a, b, but on other intervals of N such that the variations of n^* and D^W/D_0 on them are monotonic, are shown in Fig. 2c, d. The broken curves represent the solutions on the interval from $N_0 = 0.08$ to $N_1 = 0.038$ mole fraction (D^W falls as N decreases, see Fig. 1b), the continuous curves the solutions on the interval from $N_0 = 0.036$ to $N_1 = 0.005$ mole fraction (D^W grows as N decreases, Fig. 1b). Despite the same p^* and T^* , curves 2 in Fig. 2d differ sharply from each other owing to the different intervals of variation of N . It should be noted that if an attempt is made to regenerate the values of D^W/D_0 used in solving Eq. (17) from the slope of curves 2 (at large times $t' \sim 1$), as in the case of dilute solutions, erroneous values of D^W/D_0 are obtained (e.g., for the continuous curve 2, Fig. 2d, $D^W \sim 1.02$ whereas the real variation is $0.2 < D^W/D_0 < 0.95$; see Fig. 1b, curve 1).

TABLE 2. Experimental Diffusion Data for a Ne-CO₂ Mixture and Values of D^W Calculated from the Solutions of Eqs. (17), (4), and (8)

No.	$T-T_c$, K	$p-p_c$, MPa	N_0 , mole%	N_1 , mole %	ρ_1 , kg/m ³	t_{expt} , 10 ³ sec	D^W_{expt} , 10 ⁻⁸ m ² /sec	t_{calc} , 10 ³ sec	D^W_{calc} , 10 ⁻⁸ m ² /sec
1	19	5,239	0	3,56	490	5	5,6	10	5,1
2	14	4,335	0	3,57	490	8	4,0	8	4,5
3	9	3,688	1,4	3,9	500	8	3,12	8	3,5
4	4	2,847	1,2	4,2	490	15	2,0	50	1,9
5	1,5	2,003	2,3	3,57	480	25	1,08	50	1,2
6	0,1	1,809	2,3	3,57	490	80	0,48	50	0,48
7	-0,3	1,625	1,6	3,57	470	150	0,31	50	0,40
8	-0,3	1,625	3,1	3,57	470	150	0,31	50	0,36

In order to check the validity of neglecting the integral (14) in Eq. (15) from the solutions in Fig. 2c, d we obtained a numerical estimate of I, for which the derivative $(\partial^2 v^* / \partial N^2)_{p,T}$ was found from Eq. (6) with the same p^* and T^* as for D^W/D_0 . As the calculations showed, this derivative fluctuates sharply with a change of sign at values of N in the region of the minimum of D^W/D_0 .

The results of the numerical estimate of I (Fig. 3a) as compared with the principal term $(D^W/D_0)\partial u/\partial x'$ (Fig. 3b) of Eq. (15) on intervals of N with a monotonic variation of D^W/D_0 show that both in magnitude and in rate of variation along the capillary the integral I is considerably less important than the principal term of (15), so that in this case neglecting the integral is justified. When calculating the diffusion process on an interval of N containing a minimum of D^W (see Fig. 1b, curve 1), it is not possible to obtain a numerical estimate of I (with a difference grid having 40 nodes with respect to the coordinate) with sufficient accuracy owing to the sharp variation of $(\partial^2 v^* / \partial N^2)_{p,T}$ with N along the capillary. The same also applies to the calculation of the contributions to I as $x' \rightarrow 1$ (Fig. 3a, broken curves) for $0.08 \geq N \geq 0.036$ mole fraction, when at the open end of the capillary a large gradient $\partial N/\partial x'$ is maintained (see Fig. 2c). In this case in order to achieve satisfactory accuracy in the calculation of I, in solving (17) the number of nodes of the difference grid on the interval $0 \leq x' \leq 1$ must be substantially increased.

The results of calculating the relaxation of the initial difference in N in the capillary from Eq. (17) using relations (4) and (8) for n^* and $(\partial \mu_1 / \partial N)_{p,T}$ (Fig. 4) relate to the parameters of experiment No. 7 in Table 2 (for $N_0 < N_1$). With respect to time the process was calculated up to a value of t' an order greater than in the case of a Van der Waals mixture (see Fig. 2). The calculated curves 1 ($N(t')$), 2 ($N(0, t')$), 3 ($u(0, t')$) (Fig. 4b) have been plotted in the same semilogarithmic coordinates as in Fig. 2b, d. The straight lines drawn to the curves 1, 2, and 3 have a slope corresponding to the values of D^W/D_0 in Fig. 1b (curve 2) for the values of $N(t')$ or $N(0, t')$ reached at the time $t' = 10$. We note that for these process times the regenerated (from the slopes of curves 1, 2, and 3) values of D^W/D_0 , obtained within the limits of experimental error, are fairly close to the values of D^W/D_0 used in the calculations, although small systematic deviations are still observed. In the same way, by means of Eqs. (17), (4), and (8) we calculated the diffusion processes in a Ne-CO₂ mixture with the parameters p , T , N_0 , and N_1 for which the experimental data on D^W were obtained. The calculations were made for $D_0 = 9.2 \cdot 10^{-8}$ m²/sec. The results are summarized in Table 2. As may be seen from the table, the agreement between the experimental values of D^W and those calculated from the slope of the curves at large times is quite satisfactory. We also note that the behavior of the curves in Fig. 2b, d and Fig. 4b is observed when investigating the capillary diffusion processes in Ar-CO₂ [5], Ne-CO₂ [2], and ⁴He-D₂ [3] mixtures.

Thus, the use, for these solutions, of equations of state (4) and (6) made it possible to reproduce with qualitative accuracy the principal features of the concentration relaxation process in a nonideal solution above the phase surface and within a fairly wide neighborhood of the critical point, where an equation of state of the average field type is applicable. An analysis of the numerical solution of Eq. (17) for the boundary conditions of the capillary method on various intervals of variation of N made it possible to establish the important influence of the behavior of $n^*(N)$ on the curves obtained in the experiments. If this dependence is not taken into account, obtaining D^W from the slope of the curve in semilogarithmic coordinates may lead to incorrect values or to a substantial systematic error in the determination of D^W .

In conclusion, we stress that these difficulties in describing diffusion in nonideal gases and the methods of overcoming them are not peculiar to the capillary method alone, i.e., to the case considered above. To some extent or another, they apply to all the known experimental methods, whatever the diffusion cell employed. We note that the method based on a capillary closed at one end and opening into a large volume of solution at constant concentration, temperature and pressure is the simplest for investigating the important aspects of nonlinear isothermal diffusion.

NOTATION

N , concentration of the first component, mole fractions; p , pressure; T , temperature; n , molar density of the mixture; $v = 1/n$, molar volume of the mixture; $\tau = (T - T_C, T^* = T/T_C, p^* = p/p_C, n^* = n/n_C, v^* = v/v_C, \text{ the index "c" denotes the values of the quantities at the critical point of the second component (CO}_2\text{)}; \mu_i$, chemical potential of the i -th component ($i = 1, 2$); D^W , interdiffusion coefficient; b_1^W , mobility of the first component, determined relative to the reference system moving with the number-average velocity of the solution W ; r_C , correlation radius; ν , critical exponent of the temperature dependence of r_C ; η , viscosity; D_0 , interdiffusion coefficient calculated from the Ènskog-Chapman theory for the values of n and T in the real gas mixture; x , a coordinate; t , time; $x' = x/L$; $t' = D_0 t/L^2$; L , length of the capillary; $u = n^*N$; $W^* = WL/D_0$; $\bar{N}(t')$, average concentration of the solution in the capillary; $N(0, t')$, concentration at the closed end of the capillary at time t' ; N_0 , composition of the mixture in the capillary at $t' = 0$; N_1 , concentration of the solution in the reservoir; ρ_1 , mass density of the mixture in the reservoir; $D^{W_{\text{calc}}}$, interdiffusion coefficient determined at large times from the slope of the $\ln N(t') - N_1/(N_0 - N_1)$ versus t' curves for solutions of (17).

LITERATURE CITED

1. V. S. Gurvich and È. V. Matizen, Zh. Èksp. Teor. Fiz., 60, No. 4, 1379-1386 (1971).
2. V. S. Gurvich and È. V. Matizen, Zh. Èksp. Teor. Fiz., 87, No. 4 (10), 1254-1261 (1984).
3. P. P. Bezverkhii and È. V. Matizen, in: Thermophysical Properties of Substances and Materials [in Russian], GSSSD, Moscow, No. 17 (1982), pp. 64-75.
4. P. P. Bezverkhii, V. G. Martynets, and È. V. Matizen, Zh. Èksp. Teor. Fiz., 73, No. 2 (8), 671-680 (1977).
5. V. S. Gurvich, L. P. Lukin, and È. V. Matizen, Zh. Èksp. Teor. Fiz., 73, No. 2(8), 671-680 (1977).
6. M. A. Leontovich, Zh. Èksp. Teor. Fiz., 49, No. 5, 1624-1630 (1965).
7. A. M. Rozen, Zh. Èksp. Teor. Fiz., 56, No. 3, 914-927 (1969).
8. V. G. Martynets and È. V. Matizen, Zh. Èksp. Teor. Fiz., 67, 1023-1026 (1974).
9. N. V. Kuskova, V. G. Martynets, È. V. Matizen, and A. G. Sartakov, Zh. Fiz. Khim., 57, No. 12, 2971-2976 (1983).
10. V. M. Miniovich and G. A. Sorina, "P-V-T-N relations in dilute solutions of propane in ethane near the ethane critical point," State Institute of the Nitrogen Industry. Deposited with the All-Union Institute of Scientific and Technical Information (1973), No. 5325-72.
11. S. S. Leung and R. B. Griffiths, Phys. Rev. A, 8, No. 5, 2670-2683 (1973).
12. V. F. Kukarin, N. V. Kuskova, V. G. Martynets, et al., Inzh.-Fiz. Zh., 50, No. 1, 71-76 (1986).
13. S. B. Kiselev, "Investigation of the isomorphous equation of state of pure components and binary mixtures in the neighborhood of the liquid-gas critical line," Thesis for the degree of Candidate of Physico-Mathematical Sciences, Moscow (1980).
14. P. P. Bezverkhii, V. G. Martynets, and È. V. Matizen, Third All-Union Symposium on "The Use of Mathematical Methods for Describing and Studying Physicochemical Equilibria," Abstr. Proc. Pt. II [in Russian], Novosibirsk (1980), pp. 196-200.
15. A. N. Tikhonov and A. A. Samarskii, Equations of Mathematical Physics [in Russian], Moscow (1972).
16. V. F. Guk, in: Machines for Engineering Calculations (Mathematical Security), No. 5 [in Russian], Kiev (1972), pp. 72-77.