UNIQUE FEATURES ENCOUNTERED IN THE SOLUTION OF EQUATIONS FOR THE DIFFUSION TRANSFER OF MASS IN THE TWO-PHASE ZONE OF A TRIPLE SYSTEM

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We employ numerical methods to study the equations of diffusion mass transfer in a two-phase zone, these equations derived from the general principles of nonequilibrium thermodynamics. We examine the case of a quasiequilibrium diffusion process in which the concentration, in grossly approximate terms, is a function exclusively of the single space variable and of time. The solutions of these equations proved to be unstable with respect to disruptions of the diffusions paths at the conoids.

INTRODUCTION

One of the basic differences between the diffusion mass transfer in triple and multicomponent systems from the case of binary systems is the possibility of forming two-phase zones in the diffusion process. The most familiar example of this kind of process is the internal oxidation of alloys [1, 2]. At the same time, the study of the mutual diffusion in two-phase zones has so far been limited to special particular cases, with the exception of [3], where an attempt was made to formulate the problem in more general form. In this communication we propose equations which describe the quasiequilibrium process of mutual diffusion (derived on the basis of general statements from nonequilibrium thermodynamics), and we will present the nontrivial results from a numerical solution of these equations.

We will subsequently utilize the hypothesis of local quasiequilibrium in the diffusion process, when the equalization of the chemopotentials μ_i for all three components in this "physically small volume," (both between grains of various phases and within the grains themselves) proceed more rapidly than the change in these chemopotentials due to divergence of macroflows (in this case, the "physically small volume" includes at least several grains from each of the phases). According to the Gibbs phase rule, in a triple two-phase system, given fixed T and p, there remains yet another thermodynamic degree of freedom which must change along the diffusion path which passes through the two-phase region. Local equilibrium for the phases α and β (see Fig. 1) is determined from the following three equations:

$$\mu_i^\alpha (c_1^\alpha,\ c_2^\alpha) = \mu_i^\beta (c_1,\ c_2^\beta), \quad i = 1,\ 2,\ 3, \tag{1}$$

where c_1^α, c_2^β, c_1^β, and c_2^β are the boundary concentrations of the phases ($c_3^\alpha = 1 - c_1^\alpha - c_2^\alpha$, $c_3^\beta = 1 - c_1^\beta - c_2^\beta$).

Conditions (1), imposed on these four quantities, leave only one of these four quantities independent. More precisely, all four boundary concentrations are defined by the single parameter k ("the conoid parameter"): $c_1(k)$, $c_2^\alpha(k)$, $c_1(k)$, $c_2^\beta(k)$. On satisfaction of the condition of local quasiequilibrium the chemopotentials of the components (equal in both phases to the average concentrations $\overline{c}_1$, $\overline{c}_2$) are defined by only the single conoid parameter k which passes through the corresponding triangle concentration point:

$$\begin{gathered} \overline{c}_1 = c_1^\alpha p_\alpha + c_1^\beta p_\beta, \\ \overline{c}_2 = c_2^\alpha p_\alpha + c_2^\beta p_\beta, \qquad \mu_i^{\alpha,\beta} (\overline{c}_1,\ \overline{c}_2) = \mu_i^{\alpha,\beta} (k), \end{gathered} \tag{2}$$

$p_\beta = 1 - p_\alpha$ (p_α and p_β are the specific fractions of the α and β phases).

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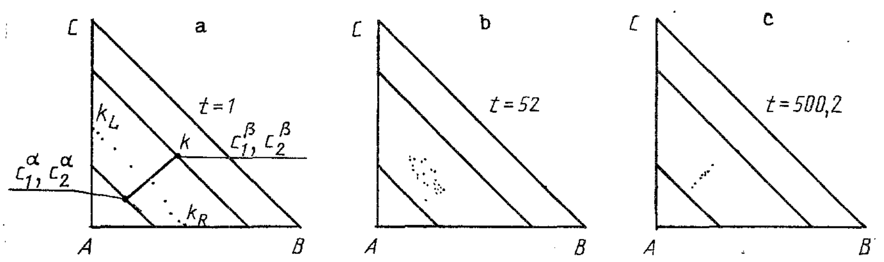

Fig. 1. Calculation of the diffusion paths in the case of strong divergence between k_L and k_R: a) at the start of the calculation; b) with the following number of grid steps over time $t = 52$, $\Delta t = 0.1$; c) diffusion path (stratified) reaches a single conoid at various points.

The chemopotentials of all regions whose concentrations lie on a single conoid are identical. The states of these regions are distinguished only by the fractions of the p_α phases. Therefore, all regions with concentrations on a single conoid are in equilibrium relative to each other and there is no diffusion between them.

According to the general phenomenological equations of nonequilibrium thermodynamics, in a laboratory reckoning system ($I_1 + I_2 + I_3 = 0$) the independent flows of components 1 and 2 (3 is the solvent) are given by the following expressions [4, 5]:

$$I_m = -\sum_{n=1}^{2}\tilde{L}_{mn}\frac{\partial(\mu_n-\mu_3)}{\partial x}\ (\tilde{L}_{mn}\ \text{Onsager coefficients}),\ m = 1,2.$$

If we take into consideration that μ_i depends only on k, we obtain an analogy of the first Fick law:

$$\begin{aligned} I_1 &= -\tilde{M}_1\frac{\partial k}{\partial x}, \\ I_2 &= -\tilde{M}_2\frac{\partial k}{\partial x}, \end{aligned} \tag{3}$$

where

$$\begin{aligned} \tilde{M}_1 &= \tilde{L}_{11}\frac{\partial(\mu_1-\mu_3)}{\partial k}+\tilde{L}_{12}\frac{\partial(\mu_2-\mu_3)}{\partial k}; \\ \tilde{M}_2 &= \tilde{L}_{21}\frac{\partial(\mu_1-\mu_3)}{\partial k}+\tilde{L}_{22}\frac{\partial(\mu_2-\mu_3)}{\partial k}. \end{aligned} \tag{4}$$

Let us make use of the continuity conditions

$$\begin{aligned} \frac{\partial\bar{c}_1}{\partial t} &= -\frac{\partial I_1}{\partial x} = \frac{\partial}{\partial x}\left(\tilde{M}_1\frac{\partial k}{\partial x}\right), \\ \frac{\partial\bar{c}_2}{\partial t} &= -\frac{\partial I_2}{\partial x} = \frac{\partial}{\partial x}\left(\tilde{M}_2\frac{\partial k}{\partial x}\right). \end{aligned} \tag{5}$$

When we take into consideration relationship (2) we obtain a system of two equations for the two functions k(t, x) and p_α(t, x) (in analogy to the second Fick law):

$$\begin{aligned} &\left\{(c_2^\alpha-c_2^\beta)\left(p_\alpha\frac{\partial c_1^\alpha}{\partial k}+p_\beta\frac{\partial c_1^\beta}{\partial k}\right)-(c_1^\alpha-c_1^\beta)\left(p_\alpha\frac{\partial c_2^\alpha}{\partial k}+p_\beta\frac{\partial c_2^\beta}{\partial k}\right)\right\}\times \\ &\times\frac{\partial k}{\partial t} = (c_2^\alpha-c_2^\beta)\frac{\partial}{\partial x}\left(\tilde{M}_1\frac{\partial k}{\partial x}\right)-(c_1^\alpha-c_1^\beta)\frac{\partial}{\partial x}\left(\tilde{M}_2\frac{\partial k}{\partial x}\right), \\ &\left\{(c_1^\alpha-c_1^\beta)\left(p_\alpha\frac{\partial c_2^\alpha}{\partial k}+p_\beta\frac{\partial c_2^\beta}{\partial k}\right)-(c_2^\alpha-c_2^\beta)\left(p_\alpha\frac{\partial c_1^\alpha}{\partial k}+p_\beta\frac{\partial c_1^\beta}{\partial k}\right)\right\}\frac{\partial p_\alpha}{\partial t} = \\ &= \left(p_\alpha\frac{\partial c_2^\alpha}{\partial k}+p_\beta\frac{\partial c_2^\beta}{\partial k}\right)\frac{\partial}{\partial x}\left(\tilde{M}_1\frac{\partial k}{\partial x}\right)-\left(p_\alpha\frac{\partial c_1^\alpha}{\partial k}+p_\beta\frac{\partial c_1^\beta}{\partial k}\right)\frac{\partial}{\partial x}\left(\tilde{M}_2\frac{\partial k}{\partial x}\right). \end{aligned} \tag{6}$$

We can predict certain of the unique features encountered in the solutions of Eqs. (5) or (6) from general thermodynamic considerations.

If in the diffusion in a single-phase alloy, in the initial stage exhibiting two regions with volumes V_L and V_R and independent concentrations (c_1^L, c_2^L) and (c_1^R, c_2^R), it is possible uniquely and independent of the specific form of the equations to predict that in the final state a homogeneous alloy of composition F will be formed:

$$c_i^{(F)} = (V_L c_i^L + V_R c_i^R)/(V_L + V_R), \quad i = 1,2, \tag{7}$$

and that in the case of two-phase alloys the situation becomes one that is no longer uniquely defined.

Let the points c^L and c^R be situated in a two-phase region of the concentration triangle. In the final state the concentration $\overline{c}_{(F)} \equiv (\overline{c}_1, \overline{c}_2)$ averaged over the entire volume is uniquely defined by Eqs. (7), but in this case the system, in the final state, must no longer be homogeneous. For example, it may consist of two regions 1 and 2, in equilibrium with each other, and whose concentrations lie on a single conoid with the point of average composition, while the volumetric fractions are associated by the relationships

$$p(F) = \Big(\sum_{i=1}^{n=2} V_i\, p(i)\Big)/(V_L + V_R). \tag{8}$$

Stratification in the final stage is a priori permissible in an arbitrary number of regions on a single conoid, provided that the normalization conditions (8) for arbitrary n are observed.

All of these final stages are in equilibrium and correspond to identical concentrations, averaged over the entire volume, and to that extent they are equally valid. It is in this lack of unique definition that we find the basic difference from a single-phase region. Naturally, it might be expected that this lack of unique definition for the final equilibrium state might make itself apparent in the features of the solutions for the equations of diffusion in the two-phase region, said equations describing relaxation of the system to equilibrium.

An analytical study of the equations of diffusion in a two-phase zone, i.e., Eqs. (5) and (6), for the time being is impossible in the general case. In order to ascertain the qualitative features of the process, we obtained numerical solutions for differential equations (5) and (6), replacing them by finite-difference equations and varying the magnitudes of the diffusion parameters. In order to describe the effective transfer parameters with respect to a locally nonuniform system we employ a variety of approaches (see, for example, [6, 7]). However, in numerous cases, if the diffusion permeability of the phases α and β exhibits no marked differences, the "model of parallel combination" serves as a rather good approximation [7]. Within the framework of this model we can assume

$$\tilde{M}_i = M_i^{\alpha} p_{\alpha} + M_i^{\beta} p_{\beta}, \tag{9}$$

where M_i^α and M_i^β are specified by the boundary conditions of conjugacy with pure phases. As was demonstrated in [8], the quantities M_i^α and M_i^β are associated with the diffusion coefficients of the phase α and β by the following relationships:

$$M_1^{\alpha,\beta} = D_{11}^{\alpha,\beta} \frac{dc_1^{\alpha,\beta}}{dk} + D_{12}^{\alpha,\beta} \frac{dc_2^{\alpha,\beta}}{\partial k}, \tag{10}$$

$$M_2^{\alpha,\beta} = D_{21}^{\alpha,\beta} \frac{dc_1^{\alpha,\beta}}{dk} + D_{22}^{\alpha,\beta} \frac{\partial c_2^{\alpha,\beta}}{\partial k}. \tag{11}$$

We will vary the quantities D_{ij}^α and D_{ij}^β.

The shape of the two-phase region in the concentration triangle and the position of the conoids are of no fundamental significance in our effort to ascertain the qualitative features of the solutions. The boundaries of the phases α and β in the concentration triangle are therefore specified as straight lines parallel to the sides 1-2: $c_1^\alpha + c_2^\alpha = e_\alpha$, $c_1^\beta + c_2^\beta = 1 - e_\beta > e_\alpha$.

We assume that all of the conoids converge as they are extended at apex 3 of the concentration triangle, so that for the points on the phase boundaries in equilibrium with each other (lying on a single conoid) the following equations are satisfied:

$$c_1^\alpha/e_\alpha = c_1^\beta/(1 - e_\beta), \quad c_2^\alpha/e_\alpha = c_2^\beta/(1 - e_\beta).$$

For the conoid parameter k we choose c_1^β, so that

$$c_1^\alpha(k) = \frac{e_\alpha}{1-e_\beta}\,k, \quad c_1^\beta(k) = k,$$
$$c_2^\alpha(k) = \left(1 - \frac{k}{1-e_\beta}\right) e_\alpha, \quad c_2^\beta(k) = 1 - e_\beta - k.$$

To calculate the diffusion paths, we apply the finite-difference method to the profiles $c_1(x)$ and $c_2(x)$. The finite-difference scheme has the form

$$c_i(j) = c_i(j) + \frac{\Delta t}{h^2}\left(\tilde{M}_i(j+1)(k(j+1) - k(j)) - \tilde{M}_i(j-1)(k(j) - k(j-1))\right), \quad i = 1{,}2. \tag{12}$$

In this case the initial conditions are specified by a discontinuous function. Under these conditions, the grid approximations, failing to account for the unique nature of the changes in the solutions, may result in considerable error. Therefore, in the place of the separation point we have introduced a narrow transition zone which is comprised of several grid intervals [9]. This boundary-layer correction factor was sought in the steady analog of system (5):

$$\begin{matrix}\nabla(\tilde{M}_1 \nabla k) = 0 \\ \nabla(\tilde{M}_2 \nabla k) = 0\end{matrix} \Rightarrow \begin{cases}\tilde{M}_1 \nabla k = \text{const}, \\ \tilde{M}_2 \nabla k = \text{const}.\end{cases}$$

Thus, in our case the boundary-layer correction factor is reduced to functions connecting the points to the left and to the right of the discontinuity.

Numerical calculations of the diffusion paths and the concentration profiles were undertaken for various forms of the diffusion-coefficient matrices in the α- and β-phases. Here all of the parameters were reduced to dimensionless form. The following represents characteristic examples of parameter selection:

$$D_{11}^\alpha = 3;\ D_{12}^\alpha = -2{,}4;\ D_{21}^\alpha = 1{,}6;\ D_{22}^\alpha = 2;\ e_\alpha = 0{,}3;$$
$$D_{11}^\beta = 0{,}5;\ D_{12}^\beta = 0{,}4;\ D_{21}^\beta = -1{,}2;\ D_{22}^\beta = 1{,}5;\ e_\beta = 0{,}25;$$
$$^{L}_{1} = e_\alpha \cdot 10^{-2};\ c_2^L = e_\alpha \cdot 1{,}6;\ c_1^R = (1 - e_\beta)\cdot 0{,}6;\ c_2^R = (1 - e_\beta)\cdot 10^{-2}.$$

As a result of these calculations we determined that the solution of the given system of equations depends significantly on the setting of the initial conditions and depends only little on the grid spacing, which suggests that the finite-difference scheme has been properly chosen. Moreover, it turned out that the nature of the behavior of these solutions is identical for all of the tested sets of diffusion parameters and differs only in the speed with which the process takes place. Thus, if k_L and k_R (see Fig. 1) of the original diffusion pair differs markedly, the solution initially exhibits a smooth nature, but over time both the functions $c_1(x)$ and $c_2(x)$ and, correspondingly, the diffusion path in the concentration triangle, become discontinuous. A second important case is observed if the initial conditions are specified by k_L and k_R close to each other, but with substantially different phase fractions (see Fig. 2). The diffusion path will then immediately reach a single conoid at various points. Let us note once again that the possibility of stratification in the final stage is independent of the specific form of the equations.

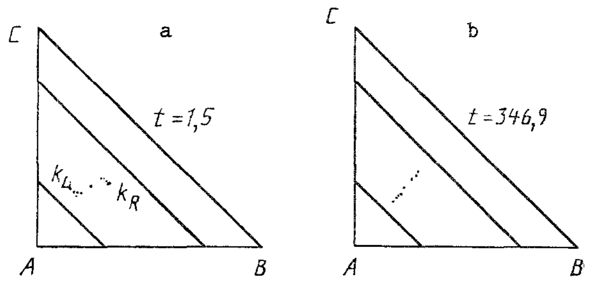

Fig. 2. Calculation of the diffusion path for k_L and k_R close in value, but with essentially different phase fractions: a) at the start of the calculation; b) the diffusion path reaching a single conoid at various points.

Let us describe the presence of discontinuities p, using the equations of flow balance in discontinuity coordinates y:

$$\Delta c_1 \frac{dy}{dt} = \Delta I_1, \quad \Delta c_2 \frac{dy}{dt} = \Delta I_2. \tag{13}$$

Using (2), we obtain

$$\Delta c_1 = (c_1^\alpha - c_1^\beta)\,\Delta p_\alpha,$$
$$\Delta c_2 = (c_2^\alpha - c_2^\beta)\,\Delta p_\alpha$$

and

$$(c_1^\alpha - c_1^\beta)\,\Delta p_\alpha \frac{dy}{dt} = \Delta I_1 = -\Delta\left(\tilde{M}_1 \frac{\partial k}{\partial x}\right),$$

$$(c_2^\alpha - c_2^\beta)\,\Delta p_\alpha \frac{dy}{dt} = \Delta I_2 = -\Delta\left(\tilde{M}_2 \frac{\partial k}{\partial x}\right).$$

Let us examine the case $\tilde{M}_1$, $\tilde{M}_2$ = const (undergoing no discontinuity in the case of discontinuity p). In this case, for comparability of Eqs. (14) and (15) it is essential that $dy/dt = 0$ (and correspondingly that $\Delta\partial k/\partial x = 0$), since otherwise, having divided (14) by (15), we obtain the equation $(c_1^\alpha - c_1^\beta)/(c_2^\alpha - c_2^\beta) = \tilde{M}_1/\tilde{M}_2$, "entry" into which is extremely unlikely. Thus, in the given case the discontinuity p is possible, while the derivative $\partial k/\partial x$ undergoes no discontinuity. If M_1 and $\tilde{M}_2$ are independent of p [for example, in the model of parallel combination (9)], the following flows are noncontinuous: $\Delta(M_i \partial k/\partial x) = 0$, and the derivative $\partial k/\partial x$ by itself is discontinuous.

The number of such discontinuities in the diffusion path (and in the concentration profiles) is entirely arbitrary. Also acceptable is a situation in which the function p(t, x), discontinuous at each point, serves as a formal solution of system of equations (6), and the function k(t, x) is discontinuous, but has a derivative $\partial k/\partial x$ that is discontinuous at each point.

This result ("stochastization" of the diffusion paths in the concentration space) is unusual and calls for some interpretation. We noted earlier that this is associated with the nonunique definition of the final equilibrium state of the two-phase alloy. We offer yet another curious analogy: in formal terms it is possible to describe the mutual diffusion in the two-phase zone of a triple system by an ordinary system of Fick equations with a 2 × 2 matrix of diffusion coefficients D_{ij} (i, j = 1, 2). However, in this case the coefficients D_{ij} are not independent (this is reflected by the fact that in the two-phase region we have only a single thermodynamic degree of freedom for fixed values of T and p) [8]. Here $\det D_{ij} = 0$, i.e., the matrix is degenerate. Let us note that the property of $\det d_{ij} = 0$ (or $\tilde{D} = 0$ for a binary alloy) is characteristic for the disintegration point of the alloy, which, as is well known, is also characterized by the "stochastization" of the system and the nonunique definition of the final state.

CONCLUSION

The solution for the equation of diffusion mass transfer in the two-phase zone of a triple system proved it to be unstable with respect to discontinuities in the diffusion paths at the conoids. In this case, the solution of the given system of equations depends substantially on the specification of the initial conditions. In principle, this property of instability may lead to nonreproducibility in the concentration profiles of the two-phase region under repeating initial conditions.

NOTATION

$\mu_i^{\alpha,\beta}$, chemopotentials of the components; $c_i^{\alpha,\beta}$, boundary concentrations of phases α and β; $\bar{c}_i$, average concentration in the two-phase zone; k, "the parameter" of the conoid; $p_{\alpha,\beta}$, specific fractions of phases α and β; I_i, component flows; $\tilde{L}_{mn}$, Onsager coefficients; $\tilde{M}_i$, phenomenological coefficients of mutual diffusion in the two-phase zone; $\tilde{M}_i^{\alpha,\beta}$, values of these coefficients at the boundaries of the two-phase zone; $V_{L,R}$, volumes of the initial regions of the diffusion pair; $c_i^{L,R}$, concentrations of components in these regions; V_i, volumes of the regions in the final state; F, composition of homogeneous alloy in final state; $D_{B,C}^{\alpha,\beta}$, coefficient of diffusion in α and β phases; Δt and h, intervals of the grid approximation over time and the coordinate x; y, coordinate of the interphase boundary.

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A COMPUTER MATHEMATICAL MODEL OF A PERCOLATION GRID

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We propose a mathematical model of two- and three-dimensional percolation grids, on the basis of which we determine certain critical indices and the fractal dimensionality of an infinite cluster.

INTRODUCTION

Recently, in the description of the structure of various micrononuniform systems and their properties intensive use has been made of various percolation models [1-3]. In most of the cases, percolation models are produced by means of finite grids whose dimensions are limited by the memory volume of the computer. Results obtained in such grids must be extrapolated to grids of infinite size and serve as the basis from which to ascertain the qualitative behavior in the properties of percolation systems. In the following we describe a mathematical model which exhibits a fractal asymptote and which allows us to calculate the precise values of the critical indices and properties of percolation systems.

In these grid models we distinguish between linkage and node problems. In the linkage (node) problem we study the properties of the grid on a change in the concentration of whole linkages (nodes) v from 1-0.

The critical concentration v_c at which an infinite cluster (IC) arises is referred to as the penetration threshold and for the linkage problem this is denoted as $v_{c,s}^{(d)}$, while for the node problem this is denoted at $v_{c,b}^{(d)}$, where the superscript indicates the dimensionality of the grid.

The critical behavior of the quantities characterizing the percolation grid is described in the following form [1]:

the relative number of nodes belonging to the IC:

$$P(v) \sim (v - v_c)^{\beta}, \quad v > v_c, \tag{1}$$

the average number of nodes in the finite cluster

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