MASS TRANSFER IN A SOLID DISPERSE MEDIUM
WITH A PHASE TRANSFORMATION

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Mass transfer in a solid material with a phase transformation is examined with the change in size and diffusion displacement of the new phase particles taken into account. A closed system of equations is obtained in a quasistationary approximation to describe these processes.

1. Mass transfer processes in heterogeneous media are often accompanied by phase and chemical transformations proceeding on surfaces distributed in a continuous matrix of foreign particles of the dispersed phase. The physical nonlinearity is essential here that consists of the effective transfer characteristics being dependent on the properties of the medium and, particularly, on the particle size and concentration that the transformation affects, and the kinetics of this latter depends on the rate of diffusion exchange between the matrix and the particles.

The processes mentioned are ordinary for metastable heterogeneous media in which condensation or crystallization, evaporation, dissolution, reconstruction of the crystal lattice or the formation of new chemical compounds on the particle surfaces occurs. In applied respects they are apparently especially important for the chemicothermal treatment of metals and other solid materials with a heterogeneous structure whose singularities determine their structural properties to a considerable extent [1, 2].

The presence of a heterogeneous transformation on particle surfaces changes the physical pattern of the diffusion process radically as compared with diffusion in the same medium with particles inert with respect to the diffusing substance, which is related to spoilage of the continuity of the concentration and the normal component of the flux of this substance on the mentioned surfaces and, respectively, to the appearance of sources and sinks on them, as well as to the influence of changes in the particle size and their diffusion motion due to the transformation [3]. The general principles for describing mass transfer with surface discontinuities and sources taken into account were examined in [4] and applied to an analysis of diffusion in the gaps between nonconducting particles in [5]. The presence of surface sources or sinks specifies the appearance of certain effects that are also specific for heat transfer processes [6]. However, the dependence of the particle size on time and the diffusion displacement of the dispersed phase are generally neglected in these investigations. This is allowable say, for an analysis of transport in granular systems with adsorption or by heterogeneous catalytic reactions but can result in errors in important problems on the transfer and kinetics of phase transformations in the diffusion zone [1-3].

For definiteness, solid disperse systems with a fixed matrix are examined in this paper. However, the particles can undergo diffusion displacement, whose influence on the kinetics of mass transfer and heterogeneous transformation is comparable to the influence of a change in the particle size in the general case. As in [4-6], the analysis is performed within the framework of a model of a moderately concentrated system, which corresponds to neglecting non-overlappability and correlations in the arrangement of adjacent particles generally. Utilization of this model for system of high concentration is justified to a definite extent by the possibility of a real merger of particles growing out of closely arranged seeds [7]. For simplification the particles are considered spherical while the dispersed phase is locally monodisperse, characterized by a constant numerical concentration of particles n within the limits of the whole volume under consideration. It is also assumed that there are no chemical reactions, and therefore, no distributed sources or sinks, while the diffusion and heterogeneous transformation processes proceed under isothermal−isobaric conditions.

In conformity with the method in [4], the equations for the mean concentrations c_0 and c_1 in the continuous and dispersed phases are obtained as a result of taking the average over an ensemble of configurations of particle systems of a detailed mass conservation equation

$$\partial C/\partial t + \nabla (\mathbf{V}C) = -\nabla \mathbf{Q}, \quad \mathbf{Q} = -\mathscr{D}\nabla C,$$

multiplied by θ_0 and $1 - \theta_1$, where the structural functions are

$$\begin{Bmatrix} \theta_0 \\ \theta_1 \end{Bmatrix} = 1 - \Sigma \eta \left(a_j + \begin{Bmatrix} \delta_0 \\ -\delta_1 \end{Bmatrix} - |\mathbf{R} - \mathbf{R}_j| \right), \ \delta_i > 0,$$

with subsequent passage to the limit $\delta_0 \backsim \delta_1 \to 0$. Summation here is over all particles with radii a_j and centers at the points $\mathbf{R}_j$, $\eta(x)$ is the Heaviside function, and C, $\mathbf{V}$, $\mathbf{Q}$ and $\mathscr{D}$ are understood to be generalized functions, continuous in both phases but having discontinuities on the particle surfaces.

Averaging of the detailed equation is performed completely analogously to that in [4] with utilization of the relationships

$$\frac{\partial}{\partial t} \begin{Bmatrix} \theta_0 \\ \theta_1 \end{Bmatrix} = -\Sigma \left(\mathbf{n}_j \mathbf{w}_j + \frac{da_j}{dt} \right) \delta \left(a_j + \begin{Bmatrix} \delta_0 \\ -\delta_1 \end{Bmatrix} - |\mathbf{R} - \mathbf{R}_j| \right),$$

$$\nabla \begin{Bmatrix} \theta_0 \\ \theta_1 \end{Bmatrix} = \Sigma \mathbf{n}_j \delta \left(a_j + \begin{Bmatrix} \delta_0 \\ -\delta_1 \end{Bmatrix} - |\mathbf{R} - \mathbf{R}_j| \right), \ \mathbf{n}_j = \frac{\mathbf{R} - \mathbf{R}_j}{|\mathbf{R} - \mathbf{R}_j|}, \ \mathbf{w}_j = \frac{d\mathbf{R}_j}{dt},$$

where $\delta(x) = d\eta(x)/dx$ is the Dirac delta function. It should be taken into account during the averaging that the detailed velocity $\mathbf{V}$ is identically zero in the gaps between the particles, and within each particle should be considered as a homogeneous vector equal to the velocity $\mathbf{w}_j$ of the diffusion motion of this particle. From the assumption n = const and the evident conservation equation $\partial n/\partial t + \nabla(\mathbf{w}n) = 0$ there follows that the vector field $\mathbf{w}(t, \mathbf{R})$ of the mean velocity of the dispersed phase should be solenoidal $\nabla \mathbf{w} = 0$. After taking the average we arrive at the equations

$$\partial (\varepsilon c_0)/\partial t + m + g_0 = -\nabla \mathbf{q} + u + h,$$

$$\partial (\rho c_1)/\partial t + \mathbf{w}\nabla (\rho c_1) - g_1 = -u, \ \rho + \varepsilon = 1, \tag{1}$$

where we introduced the notation

$$m = n \int\limits_{|\mathbf{R}'-\mathbf{R}|=a} \mathbf{w}'\mathbf{n}'\overset{*}{c_0}d\mathbf{R}', \ g_{0,1} = n \int\limits_{|\mathbf{R}'-\mathbf{R}|=a} \frac{da'}{\partial t} \overset{*}{c}_{0,1}d\mathbf{R}',$$

$$u = n \int\limits_{|\mathbf{R}'-\mathbf{R}|<a} \nabla \overset{*}{\mathbf{q}_1}d\mathbf{R}',$$

$$\mathbf{q} = -D_0\nabla (\varepsilon c_0 + \rho c_1) - (D_1 - D_0) n \int\limits_{|\mathbf{R}'-\mathbf{R}|<a} \nabla \overset{*}{c_1}d\mathbf{R}' + \tag{2}$$

$$+ D_0 n \int\limits_{|\mathbf{R}'-\mathbf{R}|=a} (\overset{*}{c_0} - \overset{*}{c_1})\mathbf{n}'d\mathbf{R}', \ h = n \int\limits_{|\mathbf{R}'-\mathbf{R}|=a} (\mathbf{q}^* - \overset{*}{\mathbf{q}_1})\mathbf{n}'d\mathbf{R}'.$$

The integration here is over the positions $\mathbf{R}'$ of the center of the extracted (trial) particle such that the point $\mathbf{R}$ lies on its surface or within it, $\mathbf{n}'$ is the unit vector of the external normal on this surface and the superscript asterisk denotes the conditional mean obtained by taking the average over the ensemble of configurations in which the position of the center of the trial particle is given a priori at the point $\mathbf{R}'$. The quantities a and $\mathbf{w}$ as well as $\rho = (4\pi/3)a^3 n$ and ε are considered as fields, i.e., as functions of t and $\mathbf{R}$ and the primes in the notation show that the corresponding quantities are evaluated at the point $\mathbf{R}'$. The constancy of n was taken into account in writing (2). Taking account of the diffusion motion and changes in the particle sizes due to the heterogeneous transformation results therefore in the appearance of original new convective terms in the left sides of (1).

To close the system (1), the quantities (2) must be expressed in the form of certain functions (or functionals) of the unknowns c_0 and c_1 of this system. Naturally such expressions should be found in strict conformity with the relationships following from the repre-

sentations (2), which comprises the content of the necessary condition for the self-consistency of the theory. To obtain such relationships it is necessary to find the conditional means c_0*, c_1* as well as the appropriate diffusion fluxes $\mathbf{q}*$ and $\mathbf{q}_1*$, i.e., to solve the problem of perturbations induced in the mean concentration field of the trial particle under consideration [4-6].

2. Within the framework of the model of a moderately concentrated system used here, the equation for the field c_0* outside the trial particle is assumed to agree with the first equation in (1) in formula while within it the ordinary diffusion equation is considered valid [4]. Correspondingly, c_1* and $\mathbf{q}_1* = D_1 \nabla c_1*$ have the meaning of mean concentration and diffusion flux in this particle. In a coordinate system connected with the center of the trial particle these equations are written thus

$$\varepsilon \partial c_0^*/\partial t = -\nabla \mathbf{q}^* + p^*, \quad p = u + h - g_0 - m - c_0 \partial \varepsilon/\partial t - \varepsilon \mathbf{w}' \nabla c_0,$$

$$\partial c_1^*/\partial t = D_1 \Delta c_1^* - \mathbf{w}' \nabla c_1^*, \quad \mathbf{w}' = d\mathbf{R}'/dt, \tag{3}$$

where the quantities with the asterisk depend on the conditional means exactly as do the analogous quantities without the asterisks depend on the appropriate condition-free means. Here $\mathbf{w}'$, da/dt are considered as parameters. Differentiation in (3) is realized with respect to $\mathbf{r} = \mathbf{R} - \mathbf{R}'$.

The fundamental difficulties occurring in the solution of the problem of a trial particle and in subsequent calculations are associated with the complex form of the first equation in (3) upon substitution of the necessary representations for the terms in the right side. A substantial simplification can be achieved by using the strong inequality $a \ll \ell$ that is the necessary condition for applicability of continual methods to the description of transfer in heterogeneous media, and assuming in addition that the time scale of the function $a(t, \mathbf{R})$ is much greater than the characteristic relaxation times of the diffusion and phase transformation processes under consideration.

The change in the fields c_0*, c_1* that have the linear scale a as time elapses is associated firstly with the variability of the field c_0 characterized by the scale ℓ, and secondly with the motion of the surface $a(t, \mathbf{R}')$ of the trial particle. If this surface were fixed then the order equalities $|\partial c_0*/\partial t| \sim |\partial c_1*/\partial t| \sim |\partial c_0/\partial t|$ would be satisfied. Now $|\partial c_0/\partial t| \sim Dc/\ell^2$ follows from the first equation of (1), where D and c are the characteristic values of the diffusion and concentration coefficients. At the same time $|\nabla \mathbf{q}*| \sim Dc/a^2$. Therefore

$$\frac{\varepsilon |\partial c_0^*/\partial t|}{|\nabla \mathbf{q}^*|} \sim \frac{a^2}{l^2}, \quad \frac{|\partial c_1^*/\partial t|}{D_1|\Delta c_1^*|} \sim \frac{D}{D_1} \frac{a^2}{l^2},$$

from which it follows that a change of the conditional fields related to the variability of the condition-free fields with time cannot be taken into account if infinitesimals of the order of a^2/ℓ^2 are neglected in the analysis.

The diffusion relaxation times of the concentration near and in the trial particle are of the order of the quantities a^2/D, a^2/D_1 and the relaxation times characterizing the phase transformation can be written as a/k_0, a/k_1, where k_0 and k_1 are constants of the exchange process rates on the interphasal separation surfaces introduced rigorously below. Let

$$\frac{1}{\tau_a} = \left| \frac{d \ln a}{dt} \right| \ll \frac{1}{\tau} = \max \left\{ \frac{D}{a^2}, \frac{D_1}{a^2}, \frac{k_0}{a}, \frac{k_1}{a} \right\},$$

i.e., $\tau/\tau_a \ll 1$. It is clear than by neglecting terms on the order of τ^2/τ_a^2 the change in the conditional fields due to motion of the trial particle surface is described by the relationships

$$\varepsilon \frac{\partial c_0^*}{\partial t} = \varepsilon \frac{\partial a}{\partial t} \frac{\partial c_0^*}{\partial a}, \quad \frac{\partial c_1^*}{\partial t} = \frac{\partial a}{\partial t} \frac{\partial c_1^*}{\partial a}, \tag{4}$$

where c_0* and c_1* are considered dependent on a as a parameter. These expressions determine the left side in (3) in the approximation under consideration.

The terms in the right sides of the first equations in (1) and (3) can be considered in the same approximation as algebraic quantities and not functionals. As follows from general considerations of the kind utilized in [4-6] and is also confirmed by results obtained below, the following structural formulas are valid

$$\mathbf{q} = -D\nabla c_0 - G(c^{(1)} - c_0)\nabla\rho, \quad p = K(c^{(2)} - c_0) - Fw\nabla c_0 - Hc^{(3)}w\nabla\rho. \tag{5}$$

where $c^{(j)}$, quantities independent of c_0 to be identified later, and D, G, K, F and H are certain coefficients dependent on ρ, which should be evaluated a posteriori from (5) expressing the self-consistency condition in the case when expressions for $\mathbf{q}$ and p determined in conformity with (2) and (3) are used in their left sides. Neglecting infinitesimals of order a^2/ℓ^2, we obtain from (5)

$$-\nabla\mathbf{q}^* = D(1 + v_D\mathbf{r}\nabla\rho)\Delta c_0^* + Db\nabla\rho\nabla c_0^*,$$

$$p^* = s^2 D(1 + v_K\mathbf{r}\nabla\rho)(c^{(2)} - c_0^*) - Fw'\nabla c_0^* - Hc^{(3)}w'\nabla\rho, \tag{6}$$

$$v_D = \frac{\partial \ln D}{\partial \rho}, \quad v_K = \frac{\partial \ln K}{\partial \rho}, \quad b = -\frac{G}{K} + v_D, \quad s^2 = \frac{K}{D},$$

where all the coefficients of c_0^* and its derivatives introduced in the expressions for $\nabla\mathbf{q}^*$ and p^* as well as $\mathbf{w}'$ are determined at the point $\mathbf{R}'$ occupied by the center of the trial particle, and should be considered as constant parameters in solving the problem of the perturbations it induces (for simplification, the primes in the notation for these quantities as well as for a', da'/dt are omitted).

At a distance from the trial particle the field $c_0^*(t, \mathbf{t}|\mathbf{R}')$ should approach the field $c_0(t, \mathbf{R})$ asymptotically, from which we obtain the accuracy assumed

$$c_0^*\big|_{r \to \infty} \to c_0' + \mathbf{E}'\mathbf{r}, \quad c_0' = c_0 - \mathbf{E}\mathbf{r}, \quad \mathbf{E}' = \mathbf{E},$$

$$\begin{Bmatrix} c_0 \\ c_0' \end{Bmatrix} = \begin{Bmatrix} c_0(t, \mathbf{R}) \\ c_0(t, \mathbf{R}') \end{Bmatrix}, \quad \begin{Bmatrix} \mathbf{E} \\ \mathbf{E}' \end{Bmatrix} = \begin{Bmatrix} \nabla c_0(t, \mathbf{R}) \\ \nabla c_0(t, \mathbf{R}') \end{Bmatrix}, \tag{7}$$

where c_0' and $\mathbf{E}'$ are also considered constants in the trial particle problem.

Boundary conditions connecting the external and internal solutions whose mode is dictated by the transformation proceeding in it should be satisfied on the trial particle surface. If there are no chemical reactions resulting in absorption or emission of diffusing atoms or molecules on the surface, and their exchange kinetics between the phase volumes and the surface layer separating these phases and being simulated by the surface mentioned corresponds to first order reactions, then the boundary conditions can be written in the form

$$Dn'\nabla c_0^* + (wn' + da/dt)c_0^* = k_0 c_0^* - k_{s0}\Gamma,$$

$$-D_1 n'\nabla c_1^* - (wn' + da/dt)c_1^* = k_1 c_1^* - k_{s1}\Gamma, \tag{8}$$

$$a^{-2}d(a^2\Gamma)/dt = k_0 c_0^* + k_1 c_1^* - (k_{s0} + k_{s1})\Gamma, \quad r = a$$

(for the particular case of a fixed surface these conditions, that are obvious balance relationships, were discussed in [8]).

The characteristic microscopic build-up time for local thermodynamic equilibrium in the surface layer and directly nearby should be much less than the macroscopic time scales of the mass transfer and phase transformation processes. Then the quantity $d\Gamma/dt$ in (8) can be neglected while the surface concentration Γ can be considered as a physical characteristic of the system under investigation that depends on the temperature and the pressure. Consequently, under isothermal-isobaric conditions this quantity as well as the equilibrium concentrations of the substance in the phase volumes, introduced formally by the relationships

$$c_{*j} = (k_{sj}/k_j)\Gamma, \quad j = 0, 1, \tag{9}$$

can also be considered as constants. The quantities (9) are connected by the relationship $c_{*1} = \alpha c_{*0}$ to the distribution coefficient $\alpha = k_0 k_{s1}/k_1 k_{s0}$.

The relationships presented are sufficient for a correct formulation of the trial particle problem in the approximation under consideration, where it is easy to see that this problem is actually split into two, whose successive solution permits finding first c_1^* and then c_0^*. We have from (3), (4), (8), and (9)

$$\Delta c_1^* - \frac{\mathbf{w}}{D_1} \nabla c_1^* - \frac{1}{D_1} \frac{\partial a}{\partial t} \frac{\partial c_1^*}{\partial a} = 0, \ 0 \leqslant r < a; \ c_1^* < \infty, \ r = 0;$$

$$D_1 \mathbf{n}' \nabla c_1^* + (\mathbf{w}\mathbf{n}' + da/dt) c_1^* - k_1 (c_{*1} - c_1^*) = 0, \ r = a. \tag{10}$$

Introducing the new unknown function

$$\varphi(t, \ \mathbf{r}|\mathbf{R}') = c_0^*(t, \ \mathbf{r}|\mathbf{R}') - c_0(t, \ \mathbf{R}), \tag{11}$$

we obtain from (3), (4) and (6)-(9) by taking account of the smallness of $v_D \mathbf{r} \nabla \rho$ (at $r = a$) as compared with one:

$$\Delta \varphi + \left(b \nabla \rho - \frac{F}{D} \mathbf{w} \right) \nabla \varphi - s^2 (1 + v r \nabla \rho) \varphi - \frac{\varepsilon}{D} \frac{da}{dt} \frac{\partial \varphi}{\partial a} = 0,$$

$$v = v_K - v_D, \ r > a; \ \varphi \to 0, \ r \to \infty; \tag{12}$$

$$\varphi = c_{*0} - c_0' - \mathbf{E}' \mathbf{r} + \sigma (c_{*1} - c_1^*) + \frac{2\gamma}{ak_0} \frac{da}{dt} c_{*1},$$

$$\sigma = \frac{k_1}{k_0}, \ \gamma = \frac{k_1}{k_{s1}}, \ r = a.$$

The remaining unused boundary condition (the first in (8)) takes the following form when (9) is taken into account

$$D \mathbf{n}' \nabla (c_0' + \mathbf{E}' \mathbf{r} + \varphi) + (\mathbf{w}\mathbf{n}' + da/dt)(c_0' + \mathbf{E}' \mathbf{r} + \varphi) + k_0 (c_{*0} - c_0' - \mathbf{E}' \mathbf{r} - \varphi) = 0, \ r = a \tag{13}$$

and determines the rate of change of the radius and velocity of diffusion motion of the particle.

It is convenient to solve the equations in (10) and (12) by the small parameter method by using the fact that the relative order of the terms with gradients therein equals a/ℓ while the terms containing da/dt are of order τ/τ_a. Consequently, the solutions are expressed in the form of series in powers of the mentioned small parameters, where in connection with the assumptions made in deriving the equations, only terms containing these parameters in the zeroth or first degree have physical meaning. Special linear problems that are easily solved in quadratures follow for the coefficients of these terms from (10) and (12). However, appropriate formulas turn out to be quite awkward, consequently, for simplification we here limit ourselves to the solution of the problem for just the first terms of the series mentioned. Consequently, we obtain from (10) to the accuracy assumed

$$c_1^* = A + B\mathbf{w}\mathbf{r}, \ A = \frac{k_1 c_{*1}}{k_1 + da/dt} \approx \left(1 - \frac{1}{k_1} \frac{da}{dt} \right) c_{*1},$$

$$B = -\frac{A}{D_1 + a(k_1 + da/dt)} \approx -\frac{c_{*1}}{(1 + \beta_1) D_1}, \ \beta_1 = \frac{ak_1}{D_1}. \tag{14}$$

Analogously we have from (12)

$$\varphi = \left[c_{*0} - c_0' + \frac{c_{*1}}{k_0} \left(1 + \frac{2\gamma}{a} \right) \frac{da}{dt} \right] \left(\frac{a}{r} \right)^{1/2} \frac{K_{1/2}(sr)}{K_{1/2}(sa)} + a\mathbf{n}' \left[-\mathbf{E}' + \frac{\sigma c_{*1}}{(1 + \beta_1) D_1} \mathbf{w} \right] \left(\frac{a}{r} \right)^{1/2} \frac{K_{3/2}(sr)}{K_{3/2}(sa)} \tag{15}$$

where $K_j(x)$ is the Macdonald function.

Let us first examine the corollary of (13). Substituting φ from (15) therein, we see that in the approximation under consideration the left and right sides are the sum of components proportional to the first two spherical harmonics. Separating these harmonics, we obtain two equations governing the rate of change of the radius and velocity of diffusion motion of a particle with center at the point $\mathbf{R}'$. Omitting the primes in the notation c_0', $\mathbf{E}'$ and $\mathbf{n}'$ we arrive at analogous relationships for the quantities mentioned that refer to a particle with center at the point $\mathbf{R}$. The solution of the first equation yields with the accuracy taken here

$$\frac{da}{dt} = k_0 D \frac{(1 + sa)(c_{*0} - c_0)}{ak_0 (c_{*0} - c_{*1}^\circ) - (1 + sa) Dc_{*1}^\circ}, \ c_{*1}^\circ = \left(1 + \frac{2\gamma}{a} \right) c_{*1}. \tag{16}$$

Hence, conditions can be obtained at once that should be imposed on the physical characteristics of the system in order to assure satisfaction of the inequality $\tau_a \gg \tau$ needed for the quasistationary theory being developed. For instance, in the limit diffusion mode when $D \ll ak_0$, required for this is $|c_{*0} - c_0| \ll |c_{*0} - c_{*1}|$, while in the limit kinetic mode ($D \gg ak_0$) there is necessary $|c_{*0} - c_0| \ll c_{*1}$. For the majority of solid metal dispersions these inequalities are satisfied [1, 2].

We obtain by analogous means for the rate of particle diffusion motion from (13) and (15)

$$\mathbf{w} = -W\mathbf{E}, \quad W = \left(3 + \frac{s^2 a^2}{1 + sa}\right)\left\{c_{*0} - \frac{\sigma c_{*1}}{(1 + \beta_1)D_1} \left[\left(2 + \frac{s^2 a^2}{1 + sa}\right)D + ak_0\right]\right\}^{-1} D \qquad (17)$$

(within the framework of the approximation being realized here the quadratic terms in α and $d\mathbf{w}/dt$ are neglected). Let us note that (16) and (17) depend only on the two coefficients D and K ($s^2 = K/D$) introduced in (6).

3. In conformity with the noted program let us now utilize the results obtained to calculate the integrals figuring in (2). In connection with the approximateness of the calculation of the fields ϕ, c_1^* here it is meaningful to take account just of the principal terms of the representations for the integrals mentioned. In particular, as can be shown, the coefficient in the integrands to be determined at the point $\mathbf{R}'$ must be replaced by their values at the point $\mathbf{R}$, which permits extracting these coefficients outside the integral sign. The quantities c_0', $\mathbf{E}'$ in the determination of ϕ according to (15) are expressed in terms of c_0 and $\mathbf{E}$ in conformity with (7). As a result of the calculations we first obtain by neglecting quadratic terms in $\mathbf{w}$ and $d\alpha/dt$:

$$g_0 = c_{*0} \frac{d\rho}{dt}, \quad g_1 = c_{*1} \frac{d\rho}{dt}, \quad m = u = 0,$$

$$h = (c_{*0} - c_{*1}) \frac{d\rho}{dt}, \quad n \int_{|\mathbf{R}'-\mathbf{R}|<a} \nabla c_1^* d\mathbf{R}' = -\frac{\rho c_{*1}}{(1 + \beta_1)D_1}\mathbf{w}, \qquad (18)$$

$$n \int_{|\mathbf{R}'-\mathbf{R}|=a} (c_0^* - c_1^*)\mathbf{n}' d\mathbf{R}' = \rho \frac{(1 + \sigma)c_{*1}}{(1 + \beta_1)D_1}\mathbf{w}, \quad \frac{d\rho}{dt} = 4\pi a^2 \frac{da}{dt} n,$$

where $d\alpha/dt$ and $\mathbf{w}$ are expressed in terms of c_0 and $\mathbf{E} = /\nabla c_0$ in conformity with (16) and (17). On the basis of (2) and (18), we have for the flux $\mathbf{q}$

$$\mathbf{q} = -\left[\varepsilon D_0 + \frac{\rho c_{*1} W}{(1 + \beta_1)D_1}(\sigma D_0 + D_1)\right]\nabla c_0 - D_0 \left[\left(1 - \frac{1}{k_1}\frac{da}{dt}\right)c_{*1} - c_0\right]\nabla\rho \qquad (19)$$

(here the expression for c_1 obtained by taking the average of c_1^* in (14) over the volume of the trial particle), W is defined in (17).

From (2) and (18) we obtain for the quantity p introduced in (3)

$$p = -(c_{*1} - c_0)d\rho/dt - c_0 \mathbf{w}\nabla\rho - \varepsilon\mathbf{w}\nabla c_0. \qquad (20)$$

As has been remarked above in connection with (16), the concentration c_0 should differ from its equilibrium value c_{*0} by a quantity whose ratio to $|c_{*0} - c_{*1}|$ or c_{*1} has the order of the infinitesimal τ/τ_a. Consequently, within the limits of the accuracy under consideration c_0 in (20) can be replaced by c_{*0}. Expression $-(c_{*1} - c_{*0})d\rho/dt$ in conformity with (16) and (18), we finally obtain

$$p = \frac{3\rho(1 + sa)a^{-1}k_0}{\nu\beta - (1 + sa)\mu}(c_{*0} - c_0) - c_{*0}\mathbf{w}\nabla\rho - \varepsilon\mathbf{w}\nabla c_0, \qquad (21)$$

where we have introduced the parameters

$$\beta = \frac{ak_0}{D}, \quad \nu = 1 - \frac{2\gamma\omega}{a}, \quad \mu = \left(1 + \frac{2\gamma}{a}\right)\omega, \quad \omega = \frac{c_{*1}}{c_{*0} - c_{*1}}. \qquad (22)$$

Comparison of the expressions for q and p in (19) and (21) with the representations for these quantities introduced in (5), results in the equalities

$$c^{(1)} = c_1 = \left(1 - \frac{1}{k_1}\frac{da}{dt}\right)c_{*1}, \quad c^{(2)} = c^{(3)} = c_{*0}, \quad G = D_0, \quad F = \varepsilon, \quad H = 1 \qquad (23)$$

and

$$D = xD_0, \quad K = y^2(D/a^2) = xy^2(D_0/a^2). \qquad (24)$$

Let us write these equations in the form

$$x - \frac{\rho(\sigma + \varkappa)}{\varkappa(1+\beta_1)}\left(3 + \frac{y^2}{1+y}\right)\left\{\frac{1+\omega}{\omega} - \frac{\sigma}{\varkappa(1+\beta_1)}\left[\left(2 + \frac{y^2}{1+y}\right)x + \beta_0\right]\right\}^{-1} x = 1 - \rho,$$

$$xy^2 = \frac{3\rho\beta_0(1+y)^1}{\nu\beta_0/x - \mu(1+y)}, \quad \beta_0 = \frac{ak_0}{D_0}, \quad \varkappa = \frac{D_1}{D_0}. \tag{25}$$

The expression for W from (17) and the definitions of the different physical parameters introduced above were taken into account here.

The results obtained are completely adequate for the formulation of a closed system of equations which, in the continual approximation, simultaneously describe the kinetics of the phase transformation and the mass transfer in solid dispersions with the accuracy taken here. Let us note first that the second equation of (1) is transformed into an identity; it must evidently be replaced by an equation for c_1 that follows directly from (14). The two other equations are obtained from the first equation of (1) and from (17) by using the formulas obtained above. Consequently, we have the following closed system of continual equations for the unknowns c_0, c_1, and ρ:

$$(1 - \rho)\frac{\partial c_0}{\partial t} - (c_{*0} - c_{*1})\frac{\partial \rho}{\partial t} + c_{*1}\mathbf{w}\nabla\rho = \nabla\left[D\nabla c_0 + D_0(c_1 - c_0)\nabla\rho\right],$$

$$c_1 = \left(1 - \frac{aK}{3\rho k_1}\frac{c_{*0} - c_0}{c_{*0} - c_{*1}}\right)c_{*1}, \quad \frac{\partial \rho}{\partial t} + \mathbf{w}\nabla\rho = K\frac{c_{*0} - c_0}{c_{*0} - c_{*1}}, \tag{26}$$

where D and K are functions of ρ to be determined from the solution of (25), while the rate **w** of particle diffusion motion is expressed in (17). It was taken into account in the left side of the first equation in (26) that the quantity c_0 in the coefficient for $\partial\rho/\partial t$ can be replaced by c_{*0} without loss of accuracy of the theory.

Equations (26) that are linear in c_0 and c_1 but substantially nonlinear in ρ can be utilized to solve a broad circle of mass transfer problems in solid dispersions that accompany phase transformations. A macroscopic inhomogeneity of the dispersion, due to an inhomogeneity in the particle radius is allowed here, where the vector $\nabla\rho \sim \nabla a$ is not absolutely collinear to $\nabla c_0 \sim$ **w.** the inhomogeneity results, in particular, in the occurrence of an additional component of the effective diffusion flux directed along $\nabla\rho$.

Because of the appearance of a significant number of diverse physical parameters in the theory and the possibility, in principle, of realizing substantially different modes in practice, a detailed investigation of the equations and relationships obtained must be considered as an independent problem. Nevertheless, a number of important deductions concerning the determination of domains of approximate validity and clarification of the disadvantages of existing models even at the stage of the investigation achieved in this paper. For instance, in the overwhelming majority of models traditionally being proposed for the analysis of phase transformations in metallic disperse systems, it is assumed a priori that the concentration of the diffusing substance within inclusions agrees with the equilibrium value [1-3]. From (14) and (23) it is easy to consider that this assumption results in inaccuracies on the order of magnitude of da/dt whose evaluation is one of the fundamental final aims of the models mentioned.

The most substantial disadvantage of the developed theory is utilization of a sufficiently rough approximation to solve the trial particle problem. It can be expected that taking account of the next corrections to this approximation, and a correspondingly more accurate calculation of the integrals in (2) will result in the long run in a certain correction of the formulas and equations obtained above. Consequently, determination of such corrections and the refinements associated therewith of the domain of validity in the space of physical and modal parameters should be considered one of the nearest aims of further investigation.

NOTATION

a, particle radius; c, concentration; D, diffusion coefficient; **E**, concentration gradient; k, exchange reaction rate constants; ℓ, linear scale of the mean fields; n, numerical particle concentration; **n, n'**, unit vectors of the normals; **Q, q**, detailed and mean fluxes;

R, spatial coordinates; R', radius vector of the center of the trial particle; V, detailed velocity; t, time; w, particle diffusion motion velocity; α, distribution factor; β, $\alpha k_0/D$; β_i, $\alpha k_i/D_i$; Γ, surface concentration; δ_i, infinitesimals introduced in the definition of the structural functions θ_i; ε = 1 − ρ; ρ, particle volume concentration; τ, τ_α, time scales; φ, concentration perturbation near the trial particle; the asterisk superscript denotes conditional means, and the subscript denotes equilibrium values of the concentration; the prime refers to quantities to be determined at the point R', while the subscripts 0 and 1 refer to the continuous and disperse phases, respectively.

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HETEROGENEOUS MASS-TRANSFER KINETICS UNDER

DIFFUSION-CONTROLLED CONDITIONS

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Calculations have been performed on nonisothermal mass transfer with transport characteristics dependent on temperature: velocity, concentration, temperature, and mass-transfer coefficient distributions.

Topics in hydrodynamics and in heat and mass transfer are frequently handled on the assumption that the parameters representing the physical properties are constant, whereas in fact they are often dependent on temperature, so that assumption is justified only when the system is completely or nearly isothermal. If the system is essentially non isothermal, parameters characterizing the physical properties such as the viscosity may vary by substantial factors, and it is essential to incorporate the temperature dependence. However, then there can be considerable computational difficulties, whereas the corresponding isothermal treatment involves a simple analytic formula. Therefore, engineering calculations are commonly based on correcting for the nonisothermal situation by formal substitution into the theoretical formula for the isothermal case of an effective temperature, which is chosen either from rather arbitrary assumptions or from the condition that the numerical result agrees with experiment [1].

That technique sometimes gives useful results, but it has the essential disadvantage of lacking a physical basis. A basis can be provided only by solving the nonisothermal case for a sufficiently wide range of external conditions, which is considered here.

We consider the convective mass transfer from a certain substance (reagent) to a solid surface, at which there is a reaction involving the absorption of it, with the reagent dissolved in the surrounding liquid. The flow is taken as laminar and stationary, while the transport mechanism is diffusion-limited, so the concentration at the surface can be taken as zero. An example is provided by a rotating disk as commonly used in electrochemistry [2].