UNSTEADY INTERNAL DIFFUSION IN DISPERSIONS

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The two parameter functional model of mass transfer is formulated between the dispersed and continuous phases without chemical reaction taking place in the dispersion and with negligible diffusion resistances in the continuous phase. The model takes into consideration polydispersity of the system and non-linearity of the equilibrium relation. The parameters of the model can be either estimated on basis of the theory of unsteady diffusion in solid particles or determined experimentally.

In mass transfer studies in the two-phase heterogeneous system, it is usually necessary to know the distribution of the transported "active component" (AC) between both phases. As simple is considered the case when the concentration equilibrium between the continuous phase (index F) and the dispersed phase (index S) is reached, characterized by the equilibrium distribution

$$\bar{c}_S = E(c_F) \, . \tag{1}$$

At the given total concentration AC in the dispersion, c_D, it is then possible to determine the distribution AC between both phases according to Eq. (1) and according to total balance AC in the dispersion which gives

$$\phi \bar{c}_S + (1 - \phi) c_F = c_D \, . \tag{2}$$

The most important stages of such operations as is leaching of ores, dissolving of gases in the stirred suspension, drying of materials in the fluidized bed *etc.*, the concentration equilibrium between the continuous and dispersed phases is not reached. Distribution AC between both phases at the given instant is conditioned by the initial distribution and by the dynamics of processes at which the dispersion approaches the concentration equilibrium.

In this study is determined the time dependence of concentration AC in both phases $\bar{c}_S(t)$, $c_F(t)$, at conditions when it is not possible, even approximately, to assume equilibrium distribution. We limit ourselves to cases when the compound AC is not participating on the chemical reaction and when it is possible to neglect resistances

to mass transfer of AC both in the continuous phase and at the interface. The material of the dispersed phase can be taken as the medium whose permeability to spreading of AC due to concentration differences can be quantitatively characterized by the diffusivity D_S which is independent of concentration. The resulting theory applicable *e.g.* for description of mass transfer of AC in the intensively stirred liquid dispersion at relatively fast concentration changes supplies a simple model of the considered operations for polydisperse systems with the solid dispersed phase and for non-linear equilibrium relation (*1*).

FORMULATION OF THE PROBLEM

At the assumptions given in the introduction, the surface concentration AC on any part of the surface of the dispersed phase is equal as it is determined by the equilibrium relation (*1*) and the instantaneous concentration AC in the continuous phase which is considered to be perfectly stirred *i.e.* perfectly permeable. If we know the shape of all particles and diffusivity AC in the bulk of the dispersed phase we can propose a detailed description of the time-dependent distribution of concentration AC in individual particles $c(t, \mathbf{r})$, at the given course of concentration AC in the continuous phase $c_F(s)$, $s \leqq t$. In the next part we will limit ourselves to the special case which includes the majority of industrially interesting situations. We assume that in time $t = 0$, the dispersed and continuous phases are in the concentration equilibrium characterized by the constant concentration c_F^e or c_S^e in the continuous or dispersed phase and that the relation holds $c_S^e = E(c_F^e)$. The concentration field $c(t, \mathbf{r})$ in an individual particle of the given volume V and surface A and diffusivity D_S is, according to the given assumptions, determined the mathematical model

$$\partial_t c = D_S \nabla^2 c ; \qquad \mathbf{r} \in V, t \geqq 0 , \qquad (3a)$$

$$c = E(c_F^e) ; \qquad \mathbf{r} \in V, t = 0 , \qquad (3b)$$

$$c = c_A = E(c_F(t)) ; \quad \mathbf{r} \in A, t > 0 . \qquad (3c)$$

Dependence of mean concentration AC in the particle

$$\bar{c}_S(t) = V^{-1} \int_V c(\mathbf{r}, t) \, dV \qquad (4)$$

is thus uniquely determined by the corresponding changes of concentration AC in the continuous phase $c_F = c_F(s)$, $0 \leqq s \leqq t$.

Though, this problem is nonlinear to c_F, it is possible to apply known solutions[1−3] for its solution which correspond to the linear boundary problem at the given surface

concentration $c_A = E(c_F)$. According to the general theory[1,2] of this linear boundary problem it is possible to express the mean concentration AC in the particle c_S by use of the linear response functional[3] $\mathfrak{F}$,

$$\bar{c}_S(t) = \mathfrak{F}[c_A(s)]_0^t . \tag{5}$$

In our case can be thus introduced the corresponding nonlinear response function by the relations

$$\bar{c}_S(t) = \mathfrak{R}[c_F(s)]_0^t = \mathfrak{F}[E(c_F(s))]_0^t , \tag{6}$$

where $c_F(t)$ is the time dependence of concentration AC in the continuous phase surrounding the particle.

If the dispersed phase consists of identical particles then $\bar{c}_S$ for a single particle is identical with $\bar{c}_S$ for the whole dispersed phase. But if the dispersed phase consists of fractions of different sizes, different shapes and different diffusivities then the time dependences of the mean concentration in individual fractions $\bar{c}_{S,i}(t)$, $i = 1, 2, \ldots$ are different and are determined by the response functional $\mathfrak{R}_i$ or $\mathfrak{F}_i$ for the given i-th fraction. The mean concentration $\bar{c}_S$ in the dispersion as the whole is then given by the average, weighed volume fractions of individual fractions

$$\bar{c}_S = \sum_i \phi_i^* \, \bar{c}_{S,i} \tag{7}$$

or

$$\bar{c}_S(t) = \mathfrak{R}[c_F(s)]_0^t = \mathfrak{F}[E(c_F(s))]_0^t , \tag{8}$$

where

$$\mathfrak{R}[c_F(s)]_0^t = \sum_i \phi_i^* \, \mathfrak{R}_i[c_F(s)]_0^t , \tag{9a}$$

$$\mathfrak{F}[c_A(s)]_0^t = \sum_i \phi_i^* \, \mathfrak{F}_i[c_A(s)]_0^t . \tag{9b}$$

The total material balance AC in the dispersion can be now expressed according to Eqs (2) and (8) in the form

$$\phi \, \mathfrak{F}[E(c_F(s))]_0^t + (1 - \phi) \, c_F(t) = c_D(t) . \tag{10}$$

In some cases it is possible *a priori* to fix the time dependence of c_F. But more usual is the case where the total amount AC transferred from outside into the dispersion is given as a whole. In such case the function $c_D(t)$ is *a priori* determined and for determination of $c_F(t)$ it is necessary to solve the non-linear functional equation (10).

In the following part of this study we will deal with two questions. First is the question of the suitable approximative expression of the response functional $\mathfrak{F}$, suitable for practical computations. As we will see such expression can be found in the

form of a single integral operator which includes three adjustable parameters ϕ, λ_0, ξ by which it is possible to characterize each dispersion system. To this topics is devoted the first part of this study. The second question is determination of the mentioned three adjustable parameters. From the approximative theory results for them some expression on basis of other characteristics of the dispersion (diffusivity AC in the dispersed phase and the granulometric compositon of dispersion), but more interesting is the possibility of determination of these parameters by evaluation of corresponding experiments. The approximative theory of such experiment is given in the second part of this study. In the last part is considered the possibility to include the effect of diffusion resistances in the surrounding of particles of the dispersed phase into the mentioned approximative description.

APPROXIMATIVE REPRESENTATION OF THE RESPONSE FUNCTIONAL IN POLYDISPERSION SYSTEMS

We have demonstrated in our recent studies[3] that for individual particle of an arbitrary shape, it is possible for an arbitrary dependence of the surface concentration $c_A(t)$ to approximate the response functional

$$\bar{c}_S(t) = \mathfrak{F}[c_A(s)]_0^t$$

by asymptotic series in diferintegrals[3,4]

$$\mathfrak{F}[c_A(s)]_0^t \approx c_A(O_-) + (\lambda_S^{-1/2} d_t^{-1/2} - \beta_\infty \lambda_S^{-1} d_t^{-1}) [c_A(t) - c_A(O_-)] ;\quad \text{De} \gg 1 \tag{11a}$$

or

$$\mathfrak{F}[c_A(s)]_0^t \approx (1 + \beta_0 \lambda_S d_t) c_A(t) ;\quad \text{De} \ll 1 . \tag{11b}$$

The dynamic criterion $\text{De} = \lambda_S/t_0$ is the relative size of the rate of concentration changes on the surface of particle with respect to its ability to respond to these changes[3]. For $\text{De} \gg 1$ we consider the fast and for $D \ll 1$ the slow operations.

Let us consider cases when all fractions of the considered dispersed phase which are of significance for balance are represented by so large (or small) values λ_S that the concentration operations for each of these fractions can be considered as sufficiently "fast" (or sufficiently "slow") in the sense of approximative representations (11a, b). Then it is possible to approximae the response functional $\mathfrak{F}$ for the dispersed phase as the whole according to Eq. (9b) by relations

$$\mathfrak{F}[c_A(s)]_0^t \approx c_A(O_-) + (\overline{\lambda_S^{-1/2} d_t^{-1/2}} - \overline{\beta_\infty \lambda_S^{-1} d_t^{-1}}) (c_A(t) - c_A(O_-)) ,\quad \overline{\text{De}^{-1}} \ll 1 \tag{12a}$$

or

$$\mathfrak{F}[c_A(s)]_0^t \approx (1 + \bar{\beta}_0 \overline{\lambda_s} d_t) \, c_A(t), \quad \overline{De} \ll 1, \qquad (12b)$$

where all the considered mean values are in agreement with Eq. $(9a)$ weighed by the volume fractions of individual fractions thus $e.g.$

$$\overline{De} = \sum_i \phi_i^* \, De_i = t_0^{-1} \sum_i \phi_i^* \lambda_{s,i} = t_0^{-1} \overline{\lambda_s}, \qquad (13)$$

where $\lambda_{s,i} = V_i^2 A_i^{-2} D_{s,i}^{-1}$ for the i-th fraction of identical particles and ϕ_i^* the relative volume fraction of the i-th fraction is independent of the ratio of continuous and dispersed phases in the heterogeneous system

$$\phi_i^* = \phi_i / \sum_i \phi_i = \phi_i / \phi . \qquad (14)$$

Now, let us consider the case, when all particles of the dispersion are of the same material, $D_S = \text{const}$. Then the parameter $\overline{\lambda_s^{-1/2}}$ in Eq. $(12a)$ can be expressed as

$$\overline{\lambda_s^{-1/2}} = \sum_i \phi_i^* A_i V_i^{-1} D_s^{-1/2} = D_s^{-1/2} \psi / \phi = D_s^{-1/2} \psi^*, \qquad (15)$$

where ψ is the total macroscopic surface of all particles of the dispersed phase, related to unit volume of dispersion as a whole (so-called specific surface of the dispersion). The ratio

$$\psi^* = \psi / \phi \qquad (16)$$

is thus independent of concentration of the dispersed phase in the dispersion.

The parameters $\overline{\beta_\infty \lambda_s^{-1}}$, $\overline{\beta_0 \lambda_s}$, $\overline{\lambda_s^{-1}}$ and $\overline{\lambda_s}$ do not already have so illustrative macroscopic interpretation. Nevertheless, it is possible to express these parameters for the system of geometrically similar particles of the same material by use of the granulometric composition of the dispersed phase. But we limit ourselves here to the case of discrete distributions characterized by the relative volumetric representation ϕ_i^* of individual fractions of identical particles.

For the geometrically similar particles the ratio $A_i^{1/2} / V_i^{1/3} = \beta_A$ is independent of their dimensions. The shape factor β_A can be expressed also by use of the specific surface of dispersion, and of the granulometric composition

$$\beta_A^2 = A_i / V_i^{2/3} = \psi^* / \sum_i \phi_i^* V_i^{-1/3} . \qquad (17)$$

By application of this identity it is possible, for systems of geometrically similar particles having the same diffusivity D_S, to express the parameters $\overline{\lambda_s}$ and $\overline{\lambda_s^{-1}}$ by relations

$$\overline{\lambda_S} = \zeta_0(\overline{\lambda_S^{-1/2}})^{-2} , \quad \overline{\lambda_S^{-1}} = \zeta_\infty(\overline{\lambda_S^{-1/2}})^2 , \qquad (18a,b)$$

where ζ_0, ζ_∞ are normalized functionals of the granulometric composition of the dispersed phase

$$\zeta_0 = \left(\sum_i \phi_i^* V_i^{2/3}\right)\left(\sum_i \phi_i^* V_i^{-1/3}\right)^2 , \qquad (19a)$$

$$\zeta_\infty = \left(\sum_i \phi_i^* V_i^{-2/3}\right)\left(\sum_i \phi_i^* V_i^{-1/3}\right)^{-2} . \qquad (19b)$$

For the system of geometrically similar particles there obviously holds

$$\overline{\beta_\infty \lambda_S^{-1}} = \beta_\infty \overline{\lambda_S^{-1}} = \xi_\infty \beta_\infty (\overline{\lambda_S^{-1/2}})^2 , \qquad (20a)$$

$$\overline{\beta_0 \lambda_S} = \beta_0 \overline{\lambda_S} = \xi_0 \beta_0 (\overline{\lambda_S^{-1/2}})^{-2} . \qquad (20b)$$

The qualitatively used term "fraction significant for balancing" can have a different significance in the regime of fast operations, where the intensity of transfer AS depends first of all on the total surface of the given fraction and in the regime of slow operation it depends first of all on the volume of the given fraction. This differentiation is included in the definition of individual mean relaxation times. While in $\overline{\lambda_S}$ are significant contributions of fractions having large volume in $\overline{\lambda_S^{-1}}$ and $\overline{\lambda_S^{-1/2}}$ are of significance contributions of fractions with large surface. For example the mixture of equal volumes of two fractions of spherical particles with $D_S \approx 3 \cdot 10^{-12}$ m^2 s^{-1}, one of which consists of particles with the diameter 0·01 mm, i.e. $\lambda_{S,1} \approx 100$ s, the second consists of particles with the diameter 0·001 mm, i.e. $\lambda_{S,2} \approx 1$ s is $\overline{\lambda_S} \approx 50$ s$_\lambda (\overline{\lambda_S^{-1}})^{-1} \approx 2$ s a $(\overline{\lambda_S^{-1/2}})^{-2} \approx 3$ s. The criteria of sufficiently fast operations is according to Eq. (12a) the inequality $\overline{De^{-1}} < 1$ or $t_0 < (\overline{\lambda_S^{-1}})^{-1} \approx 2$ s and of the sufficiently slow in the sense of Eq. (12b) it is possible to consider the operations for which $t_0 > \overline{\lambda_S} \approx$ ≈ 50 s.

In comparison with monodisperse systems for which the regions of "fast" and "slow" operations (11a, b) are in close vicinity, the use of asymptotic representations (12a, b) for polydisperse systems is thus rather limited.

From the given example it is also obvious that the detailed considerations on the effect of "shape" factors on the concentrations in dispersed systems[5] have only an academic significance as the concentration responses in actual heterogeneous systems will be sensitive first of all to details in granulometric composition of the dispersed phase.

FAST ASYMPTOTE AS THE PHENOMENOLOGIC MODEL

In sufficiently slow processes for which $\overline{De} < 1$ it is possible with relatively small errors as to $\overline{c_S}(t)$ to neglect in the asymptotic representation $(12b)$ the "kinetic" term $\overline{\beta_0 \lambda_S} d_t c_A(t)$ and thus to assume the equilibrium distribution AC between the continuous and dispersed phases. The situation is different with the approximative description of fast operations $\overline{De^{-1}} < 1$, where the negligence of "kinetic" terms would mean neglecting the whole mass transfer between the continuous and dispersed phases. In the next part we will limit ourselves to the study of properties of the approximative model $(12a)$ which can have interesting practical applications in the region of fast or short processes of mass transfer in heterogeneous systems.

In the approximative functional relation $(12a)$ there appear two kinetic parameters $\overline{\lambda_S^{-1/2}}$, $\overline{\beta_\infty \lambda_S^{-1}}$ which can be expressed on basis of properties of individual particles by Eqs (15) and $(20a)$. But there appears as more realistic such an approach in which the mentioned kinetic parameters are considered as adjustable material constants of the given dispersion which must be determined by evaluation of the corresponding experimental data.

The considered experiment is performed so that into the intensively stirred dispersion which is in time $t = 0$ in the internal concentration equilibrium, characterized by the corresponding distribution AC between the continuous and dispersed phases, which is given by relation

$$\phi E(c_F^e) + (1 - \phi) c_F^e = c_D(O_-) \qquad (21a)$$

to which is in time $t = 0$ suddenly added a final amount AC which step changes the original balance concentration $c_D(O_-)$ to another value $c_D(O_+)$ to which there corresponds the step change $c_F(t)$ from the value $c_F(O_-) = c_F^e$ to the value

$$c_F(O_+) = c_F^0 = c_F^e + (c_D(O_+) - c_D(O_-))/(1 - \phi) . \qquad (21b)$$

We assume that with some sufficiently fast reacting sensor (conductivity cell, potenciometric electrode) it is possible to follow the time dependence of concentration AC in the continuous phase $c_F(t)$ which in time $t = 0$ is step changing from c_F^e to c_F^0 and then it is approaching a new equilibrium value c_F^∞ between both limiting values c_F^e and c_F^0 and is according to Eqs (1) and (2) the solution of equation

$$\phi E(c_F^\infty) + (1 - \phi) c_F^\infty = \phi E(c_F^e) + (1 - \phi) c_F^0 . \qquad (22)$$

We will now be interested in a theoretical forecast of the dependence $c_F(t)$ in this experiment on basis of the approximative model $(12a)$, which can be arranged ac-

cording to Eqs (10) and (21a, b) into the balance relation in the form

$$(\lambda_0^{-1/2} d_t^{-1/2} + \xi \lambda_0^{-1/2} d_t^{-1}) \left[c_A(t) - c_A(O_-) \right] + c_F(t) - c_F^0 = 0, \quad (23a)$$

where there is

$$c_A(t) - c_A(O_-) = E(c_F(t)) - E(c_F^e) \quad (23b)$$

and where the quantities λ_0 and ξ, given by relations

$$\lambda_0 = (1 - \phi)^2 \, \phi^{-2} \, \overline{(\lambda_S^{-1/2})}^{-2}, \quad (24a)$$

$$\xi = (1 - \phi) \, \phi^{-1} \, \overline{(\lambda_S^{-1/2})}^{-2} \, \overline{(\beta_\infty \lambda_S^{-1})} \quad (24b)$$

are considered to be the primary material constants of the given mixed fluid dispersion.

To be able to solve generally the functional Eq. (23) we must choose some modified representation of the equilibrium relation $E(c_F)$. We know that c_F can reach at the given conditions only values from the interval (c_F^0, c_F^∞) where c_F^0 is the given initial condition and c_F^∞ is the solution of Eq. (22). On this interval (or on the interval (c_F^∞, c_F^0) in the case $c_F^\infty < c_F^0$), we choose the polynomial representation $E(c_F)$ e.g. but not necessarily — as the Taylor expansion in the environement of the point c_F^0

$$E(c_F) - E(c_F^e) = \Delta E \left(1 + \sum_k (-1)^k A_k C^k \right), \quad (25)$$

where we have introduced the dimensionless concentration variable by relations

$$C = (c_F^0 - c_F(t))/\Delta c, \quad (26)$$

$$\Delta c = c_F^0 - c_F^e, \quad (27)$$

$$\Delta E = E(c_F^0) - E(c_F^e) \quad (28)$$

and (e.g.)

$$A_k = \frac{(\Delta c)^k}{k! \, \Delta E} \left(\frac{d^k}{dc^k} \, E(c) \right) \Bigg|_{c \, = \, c_F^0}. \quad (29)$$

On introduction of the dimensionless time variable by the relation

$$T = \left(\frac{\Delta E}{\Delta c} \right)^2 \frac{t}{\lambda_0} \quad (30)$$

and by substitution of new variables according to Eqs (25)–(30) into (23) it is possible to obtain the suitably normalized formulation of the problem by the equation

$$(d_T^{-1/2} - \gamma d_T^{-1}) \left[1 + \sum_{k=1}^{\infty} (-1)^k A_k C^k(T) \right] = C(T), \qquad (31)$$

where

$$\gamma = \frac{\Delta c}{\Delta E} \xi \ll 1 \qquad (32)$$

is characterizing the size of secondary effect of the second kinetic term d_T^{-1}.

At first let us look up the solution for the case when in the range of values c_F^e and c_F^0 it is possible to approximate the equilibrium relation linearly $E(c_F) - E(c_F^e) \approx$ $\approx (c_F - c_F^e) \Delta E/\Delta c$. In this case $A_1 = 1$, $A_k = 0$ for $k = 2, 3, \ldots$ and the functional relation (31) becomes linear

$$(d_T^{-1/2} - \gamma d_T^{-1})(1 - C) = C. \qquad (33)$$

The solution can be found e.g. by use of the Laplace transformation in the closed form

$$C(T) = 1 - \omega^{-1} \left[\frac{\omega + 1}{2} \text{ eerfc} \left(\frac{\omega + 1}{2} T^{1/2} \right) + \right.$$

$$\left. + \frac{\omega - 1}{2} \text{ eerfc} \left(-\frac{\omega - 1}{2} T^{1/2} \right) \right], \qquad (34)$$

where

$$\text{eerfc} (\pm z) = \exp (z^2)(1 - \text{Erf} (\pm z)) \qquad (35)$$

and

$$\omega = (1 + 4\gamma)^{1/2} . \qquad (36)$$

This solution of the linear problem (33) is known[6,7] as the asymptote of the corresponding exact solution of the problem on unsteady diffusion AC from the final volume of the mixed liquid into the spherical particle. By suitable approximations of function (34) the power expansion with respect to $T^{1/2}$ are obtained in the form

$$C(T) \approx \frac{2}{\sqrt{\pi}} T^{1/2} - T(1 + \gamma) + \frac{4}{3\sqrt{\pi}} T^{3/2}(1 + 2\gamma) - \tfrac{1}{2} T^2(1 + 3\gamma + \gamma^2) \quad (37)$$

and the asymptote for $\gamma \to 0$ at the arbitrary final T, by relation

$$C(T) \approx 1 - \text{eerfc} (T^{1/2}) + 0(\gamma) . \qquad (38)$$

The approximative results according to Eqs (34), (37) and (38) were compared with the exact solution of the problem for unsteady diffusion AC from the finite volu-

me of the fluid into the system of identical spherical particles when there holds $\gamma = (1 - \phi)(3\phi \, \Delta E/\Delta c)^{-1}$. For graphical plot of concentration changes it seems advantageous to introduce new reduced variables $Z = (1 + 3\gamma)^{-2} T$, $C^*(Z) = C(T)/C(\infty) = (1 + 3\gamma) C$. These variables were introduced so that C^* is changing in the range from 0 to 1 and the function $C^*(Z)$ has for all values of γ a common initial shape

$$C^*(Z) \approx 2/\sqrt{\pi} \, Z^{1/2}, \quad Z \ll 1. \tag{39}$$

The exact dependence[7] of $C^*(Z)$ and the approximative dependences according to Eq. (34) differ in the region where $C^* < 0.8$ less than by 1% and thus in Fig. 1 they merge. In Fig. 1 is also demonstrated the accuracy with which the exact dependences C^* are approximated by the four-term polynomial according to Eq. (37). Even in the less favourable case $\gamma \to 0$ is this polynomial approximation applicable with a good accuracy in the region $C^* \leqq 0.4$ i.e. still at the 40% saturation of particles.

Solution of the non-linear functional equation (31) cannot be found in a closed form. But as already the own formulation of Eq. (31) is limited by the assumption of fast and short time existing operations with $T \to 0$, it is possible to consider the power expansion

$$C(T) = \frac{2}{\sqrt{\pi}} \, T^{1/2} - T(A_1 + \gamma) + \frac{4}{3\sqrt{\pi}} \, T^{3/2} \left(A_1^2 + 2A_1 + \frac{4}{\pi} A_2 \right) - $$

$$- \tfrac{1}{2} T^2 \left(A_1^3 + 3A_1^2\gamma + A_1\gamma^2 + \left(\frac{4}{\pi} + 3 \right) A_2(A_1 + \gamma) + \frac{6}{\pi} A_3 \right) - \ldots \tag{40}$$

as adequate approximative solution of the general non-linear problem (31). From the analogy with the corresponding power expansion (37) for the linear equilibrium relation can be expected that the approximative solution in the form (40) i.e. with the first four terms of the power expansion in $T^{1/2}$ represents the unknown exact
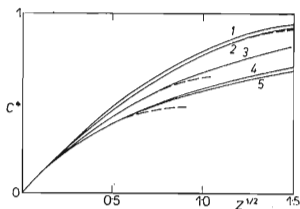

Fig. 1

Time Dependence of Concentration AC in the Stirred Continuous Phase After Sudden Addition of AC

Solid curves represent exact dependences of the reduced concentration or of their approximations according to Eq. (34), dashed lines are approximations according to Eq. (37). Numbers 1 to 5 denote dependences for γ ∞, 3, 1/3, 1/27, 0.

solution with the accuracy better than 1% from the value $\left(c_F^\infty - c_F^0\right)$ roughly in the region $C/C(\infty) \leqq 0{\cdot}4$ or $T \leqq 0{\cdot}8$. In this region Eq. (40) is suitable as the theoretical basis for evaluation of parameters λ_0, ξ at the known equilibrium relation. For an adequate representation of $E(c_F)$ in the range of the considered approximation suffices its dependence in the region $c_F \in < c_F^e, c_F^e + 0{\cdot}4(c_F^\infty - c_F^e) >$ by the polynomial of second degree.

EFFECT OF EXTERNAL DIFFUSION RESISTANCES

We would like to demonstrate here how it is possible to make use of the formalism of response functionals at modelling more complex transport problems. Under the term "external diffusion resistance" we understand the resistances to transfer AC between the dispersed and continuous phases concentrated in a thin layer of fluid adhering to the surface of the particle. These resistances are dependent on the flow kinematics of the fluid in vicinity of the particles and on development of the concentration field in the fluid and in the particle. To an estimate of the order of magnitude of the effect of external diffusion resistances it is usual to base the model on an empirical film mass transfer coefficient in fluid h_F which we define for the system of identical particles by the relation

$$R_S d_t \bar{c}_S = R_S^{-1} h_F\left(c_F - c_A^*\right), \qquad (41)$$

where c_A^* is the concentration AC in the fluid in close vicinity of the surface of the particle and c_F is the concentration AC in the perfectly mixed core (bulk) of fluid, so that there holds

$$E(c_A^*) = c_A \quad \text{resp.} \quad c_A^* = E^*(c_A). \qquad (42a, b)$$

The relation $R_S d_t \bar{c}_S = V/A d_t \bar{c}_S$ obviously gives the mean intensity of flow AC across the interface.

The mean concentration $\bar{c}_S$ in the dispersed phase consisting of identical particles can be expressed as the response to the corresponding time changes of concentration $c_A^*(t)$. By application of the balance relation

$$\bar{c}_S + \left(1 - \phi\right) c_F = c_D \qquad (43)$$

and Eq. (41) it is possible to express $c_A^*(t)$ in the terms of c_F and c_D and to obtain the formulation of the problem in the form

$$\phi \, \mathfrak{F}\big[E\{c_F(s) + R_S^2 h_F^{-1} \phi^{-1}((1 - \phi)\,dc_F(s) - dc_D(s))\}\big]_{s=0}^t + (1 - \phi)\,c_F = c_D, \qquad (44)$$

where $c_D(t)$ is given and $c_F(t)$ is the wanted function of time.

For the asymptotic representation of the response functional according to Eq. (12a) and at the assumption of linear equilibrium relation it is possible to simplify Eq. (44) and to arrange it into the form of linear differintegral equation. In the special case when for the problem considered in the last paragraph the relation holds

$$c_D(t) = c_D(O_+) = \phi E(c_F^e) + (1 - \phi) c_F^0 , \tag{45}$$

it is possible, after the mentioned simplification, to express Eq. (44) in the form

$$\left(\eta d^{1/2} + (1 + \eta \gamma) + d_T^{-1/2} + \gamma d_T^{-1}\right) C = \left(d_T^{-1/2} + \gamma d_T^{-1}\right) 1 , \tag{46}$$

where

$$\eta = \frac{\phi}{1 - \phi} \frac{D_S}{h_F} . \tag{47}$$

We limit ourselves to the case $\gamma = 0$, when the solution of this differintegral equation can be expressed explicitly in the form

$$C(T) = 1 - (2\varkappa)^{-1} \left((1 + \varkappa) \operatorname{eerfc} \left(\frac{1 - \varkappa}{2\eta} T^{1/2} \right) - \right.$$

$$\left. - (1 - \varkappa) \operatorname{eerfc} \left(\frac{1 + \varkappa}{2\eta} T^{1/2} \right) \right), \tag{48}$$

where

$$\varkappa = (1 - 4\eta)^{1/2} . \tag{49}$$

In the estimate of region of relevent values η it is possible to start from the assumption that the film resistance is represented by the fluid film whose thickness δ is a certain multiple of the particle diameter $\delta = \xi_F . R_S$.
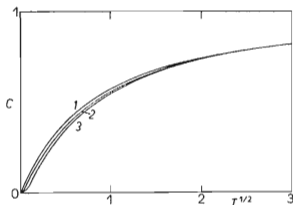

FIG. 2

Effect of External Resistances on Time Dependence of Concentration AC in the Stirred Continous Phase After Sudden Addition of AC, $\gamma = 0$ according to Eq. (48)

Numbers 1 to 3 denote the dependences of $C(T)$ for $\eta = 0$, 0·05, 0·01.

The parameter η can be then expressed in the form

$$\eta \approx \frac{\phi}{1 - \phi} \frac{D_S \zeta_F}{D_F}. \tag{50}$$

Even at the extreme assumption $\xi_F \phi/(1 - \phi) \approx 1$ is $\eta \approx D_S/D_F \ll 1$. In this region of values of the parameter η there holds for $T^{1/2} > \eta$ a simple empirical approximation

$$C(T, \eta) \approx 1 - \text{eerfc}\left(T^{1/2} - \eta\right), \tag{51}$$

as is obvious also from Fig. 2.

There is no reason why to discuss the effect of external resistances in the intensively mixed dispersion as there are no available data which would enable more accurate estimate of values of the parameter η especially of its dependence on ϕ and R_S under the mixing conditions. Let us only note that in the case when h_F is independent of the particle dimensions it is also possible to obtain for the polydisperse system the description of the considered process by the relation (46) with the difference that η is then given by relation

$$\eta = \frac{\phi}{1 - \phi} \frac{D_S}{h_F} \overline{\left(\lambda_S^{1/2}\right)} \overline{\left(\lambda_S^{-1/2}\right)}. \tag{52}$$

CONCLUSIONS

In this paper is studied the unsteady mass transfer between the well stirred fluid and particles of the solid phase dispersed in it. The basical simplification considered is the assumption that the diffusion resistances in the liquid can be neglected and that the rate of the whole operation is controlled by unsteady diffusion in particles of the dispersed solid phase. The main result is in the formulation of the functional model (12a) for fast concentration operations. This model includes both the parameters ϕ, $E(c_F)$ for whose determination suffices to perform equilibrium experiments and two "kinetic" parameters $\overline{\lambda_S^{-1/2}}$, $\overline{\beta_\infty \lambda_S^{-1}}$. A method is proposed for experimental determination of these kinetic parameters which is based on measurement of decrease in concentration of the active component in the liquid phase after sudden (momentous) addition of this component into the dispersion.

The proposed model seems to be an adequate approximation of real operations even in the case when all diffusion resistances in the liquid phase cannot be completely neglected, when the flow in the liquid phase is turbulent and the ratio of diffusivities AC in the solid and liquid phase is smaller than 0.1 i.e. $D_S/D_F < 0.1$. This is proved by the approximate analysis of the model with included resistance in the thin film of stagnant fluid around the particle.

In the proposed model are not, however, included effects related to the resistance to spreading of the active component across the dispersion which are of significance in the case where the liquid dispersion is stagnant or in laminar flow. These effects will be considered in our next study[8], see also[9].

LIST OF SYMBOLS

A	surface area of the particle
A_i	surface area of the i-th fraction of identical particles
c	concentration field AC in individual particle, Eq. (4)
c_A	surface concentration AC in particles of the dispersed phase
c_A^*	surface concentration AC in the stagnant film of the continuous phase, Eq. (42)
c_F	concentration AC in the core of continuous phase
$c_F^e - c_F(O_-)$	initial equilibrium concentration
$c_F^0 = c_F(O_+)$	initial concentration after momentous addition of AC into dispersion
c_F^∞	limiting equilibrium concentration AC for $t \to \infty$
$\bar{c}_S$	mean concentration AC in the particle or in dispersed phase, Eq. (4) or (7)
$\bar{c}_{S,i}$	mean concentration AC in the i-th fraction (i.e. in the system of identical particles)
C	normalized concentration, Eq. (26)
Δc	characteristic concentration difference in the continuous phase, Eq. (27)
$d_t^{-1/2}, d_t^{-1}, d_t^1$	difintegral operators[3,4]
$De = \lambda_S/t_0$	diffusion Deborah number
D_S, D_F	diffusivity AC in the dispersed or continuous phase
ΔE	characteristic concentration difference in the dispersed phase, Eq. (28)
h_F	film coefficient of mass transfer, Eq. (41)
$R_S = A/V$	characteristic dimension of the particle[5]
r	coordinate
s	supporting time variable
t	time
t_0	characteristic time interval of the concentration operation
T	dimensionless time variable, Eq. (31)
V	volume of particle
V_i	volume of the i-th fraction of identical particles
β_0, β_∞	shape coefficients in asymptotic representations of the response functional[3] $\mathfrak{F}$, Eq. (11a, b)
γ	parameter of model (31), defined by Eq. (32)
η	parameter of model (46), defined by Eq. (47)

ξ_0, ξ_∞	parameters characterizing the granulometric composition of the dispersed phase
$\lambda_s = R_s^2/D_s$	relaxation time of individual particle
$(\overline{\lambda_s^{-1/2}})^{-2}$	characteristic relaxation time of fast concentration operations in polydisperse system, Eq. (15)
$\overline{\lambda_s}$	characteristic relaxation time for slow concentration operations in the polydisperse system, Eq. $(18a)$
λ_0	characteristic relaxation time for dispersion as a whole at fast concentration operations, Eq. $(24a)$
ξ	parameter of the model $(23a)$, defined by Eq. $(24b)$
ϕ	volume fraction of the dispersed phase in dispersion
ϕ_i	volume fraction of the i-th fraction of the dispersed phase in dispersion
$\phi_i^* = \phi_i/\phi$	
ψ	specific surface area of the dispersed phase in dispersion
$\psi^* = \psi/\phi$	specific surface area of the dispersed phase related to the volume of dispersed phase

REFERENCES

1. Carslaw H. S., Jaeger J. C.: *Conduction of Heat in Solid*. Clarendon Press, Oxford 1946.
2. Crank J.: *Mathematics of Diffusion*. Oxford University Press, Oxford 1976.
3. Wein O.: This Journal, in press.
4. Oldham K. B., Spannier J.: *The Fractional Calculus*. Academic Press, New York 1976.
5. Aris R.: Chem. Eng. Sci. *7*, 8 (1957).
6. Amundson N. R.: Ind. Eng. Chem. *48*, 26 (1956).
7. Carman P. C., Haul R. A.: Proc. Roy. Soc. *222A*, 109 (1954).
8. Wein O.: Inzh. Fiz. Zh., in press.
9. Wein O.: Paper presented at the national CHISA 77 Conference, Bratislava, August 1977.

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