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DISSOLUTION OF A POLYDISPERSE SYSTEM OF PARTICLES SHAPED LIKE A PARALLELEPIPED IN A NONFLOWING SYSTEM

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The process of mass dissolution has been investigated on the basis of the crystal-size distribution function in the case where the crystal faces traveled in accordance with the power law and the dissolution proceeded in a periodic regime. It has been proposed to reduce the dissolution problem to a system of equations that could be solved analytically in certain cases that are of interest in practice. The notion of dissolution efficiency has been introduced.

Processes of dissolution are abundant in nature and have found wide use in industry. They are similar in physical essence to crystallization. Dissolution formally differs from crystallization in the sign of the velocity of travel of crystal faces. Both crystallization and dissolution, as mass-exchange processes, occur with a number of physicochemical effects that can be revealed experimentally but are very difficult to theoretically describe with the use of existing models of these processes. For example, it is known, that crystals can break or stick together in the process of growth (dissolution); their faces can travel with different velocities, with the result that some of them disappear; the rates of transformation of crystal faces can fluctuate, etc. [1–3]. Because of this, it is difficult to theoretically describe the effects observed in experiments; moreover, there is not a sufficient number of mathematical models of the above-mentioned processes and the calculations by the available equations are very complex. As a rule, only a small number of factors influencing the course of these process are taken into account in calculations, and researchers are forced to introduce simplifying assumptions. For example, the crystal is traditionally characterized by a single parameter — the equivalent radius of the sphere equal to the crystal in volume. At the same time, any crystals taken from an apparatus (or loaded into it) clearly demonstrate the discrepancy between this representation and the experimental facts. Furthermore, every so often the habit of a crystal changes in the process of growth (dissolution). Up to now, attempts to theoretically describe the transformation of a crystal whose shape differs from a sphere and the changes in its habit in the process of mass crystallization have been episodical in character [4–7] as compared to the enormous number of works devoted to this theme. The author has no information on works in which the mass dissolution of crystals of nonspherical shape was analyzed.

Below, we will consider the dissolution of crystals shaped as a parallelepiped in the case where the crystal faces travel in accordance with the power (with respect to the dimension parameters) law. This circumstance brings the theory closer to the real processes of dissolution of particles occurring in practice; however, the description of the phenomenon becomes more complex in this case. First and foremost, in the case where a crystal has a complex shape, the dimensionality of the problem increases, since an individual law of velocity of travel should be introduced for each crystal face. Analysis of the mass dissolution of crystals shaped as a parallelepiped is evidently the most simple, except for that of spherical crystals.

Formulation of the Problem. The process is modeled on the basis of the crystal-size distribution density function (CSDDF) — $F(X_1, X_2, X_3, t)$, where the parameters X_1, X_2, and X_3 determine the size of a crystal in the direction of the corresponding axis $X_i \in [0, \infty)$ ($i = 1$–3). This function multiplied by the "volume" element $dX_1dX_2dX_3$ gives the number of crystals with sizes falling in the ranges (X_1, $X_1 + dX_1$), (X_2, $X_2 + dX_2$), and (X_3, $X_3 + dX_3$) at small values of dX_i ($i = 1$–3). The approach proposed gives an exhaustive description of the process since it determines the granulometric composition of a disperse system. Let us assume that each crystal face travels in accordance with the power law relative to the corresponding dimension (coordinate) with its own parameters

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$$dX_i/dt = V_i\,(C^* - C)\,X_i^{1-\alpha_i}\,,\quad i = 1-3\,,\quad C^* > C\,, \tag{1}$$

where C^* is the equilibrium (at a given, constant temperature) concentration of the object substance (saturation concentration). The functions V_i of the undersaturation $C^*- C$ are usually almost linear, and $V_i(0) = 0$ ($i = 1–3$). In the case of dissolution of crystals, the values of these functions are negative. If the functions $V_i(C^*- C) = U_i(C^*- C)$ are linear, the multipliers U_i ($i = 1–3$) are functions of definite physicochemical constants, examples of which (functions) for spherical particles are given, in particular, in [8–10]. The functional dependences of the rate of dissolution of particles with a more complex shape have an analogous form. Thus, the dissolution of crystals depends on the undersaturation $C^*- C$ of the solution ($C < C^*$), considered as the main variable, and on the physicochemical characteristics (density, viscosity, etc., accounted for by the quantities U_i), considered as parameters. Note that formula (1) defines the rate of change, for example, in the first "coordinate" X_1, whereas the corresponding face X_2X_3 travels with a two times lower velocity since a parallelepiped has two opposite faces transformed in accordance with the change in X_1.

It is usually assumed that the functional dependences dX_i/dt have the same form in the case of growth of particles and in the case of their dissolution. The determination of the velocity of travel of crystal faces represents an independent problem, the numerous aspects of which are topical at present [1, 11, 12]. The point is that there are several justified theories on the mechanism of growth (dissolution) of crystals, for example, "thermodynamic theories," "dislocation theories," and others [1, 11–13]. It is also known [11, 12] that impurities markedly influence the velocity of travel of a crystal face and certain substances (impurities) act differently on different faces of one and the same crystal. Therefore, in practice, in deciding on the law of the velocity of travel of crystal faces, it is necessary to determine the mechanism of growth (dissolution) of crystals that corresponds better to experimental data and then select the coefficients of theoretical models such that they are in agreement with experimental data on condition that the difficultly controlled "nonidealities" of the process are taken into account. Both the theory and experiment [12] give different values of the rate of growth of different faces of a crystal, and these differences can be very large in certain cases. For example, in [14] it has been established that the rates of growth of two types of faces of calcium sulfate crystals (gypsum) differ approximately by a factor of 10^2 and analytical dependences have been proposed for their determination.

Let us now consider the influence of the sizes of crystals on the rate of their transformation. In the "single-parameter" case of particles shaped as a sphere, three values of the parameter α have a practical value and can be theoretically substantiated. This parameter determines the character of the dissolution process that proceeds in a kinetic regime at $\alpha = 1$, in a diffusion regime at $\alpha = 2$, and, at $\alpha = 3/2$, in one of the intermediate regimes realized in accordance with the power law in flow-through apparatus at Reynolds numbers higher than 500 [2, 3, 8, 9]. Thus, the most interesting, from the practical standpoint, regimes of dissolution of particles are realized at $\alpha \in [1, 2]$ and relation (1) involves the greater part of dependences used in practice for description of the dissolution of particles in an undersaturated solution [3, 8, 9, 15]. For particles having a more complex shape (for example, particles shaped as a parallelepiped), similar dependences of the rate of their dissolution on the parameters determining particle size are expected. The particle sizes play no part in the kinetic regime of dissolution that is realized at very large Reynolds numbers. In the diffusion regime ($\alpha = 2$), a plane face grows with time by the same law $x \sim t^{1/2}$ as a spherical one, $r \sim t^{1/2}$. On differentiation, we have $dx/dt \sim 1/x$ and $dr/dt \sim 1/r$. It is probable that the regime $\alpha = 3/2$ for spherical particles is analogous to this regime for particles shaped as a parallelepiped in the same range of Reynolds numbers. In any event, the power law used in [16, 17] for the rate of growth of spherical particles depending on their sizes in the process of crystallization can be true for dissolution of particles having a complex shape.

We will also assume that the regime of ideal mixing of a suspension is realized in the system; therefore, the CSDDF and the concentration of the object substance in a solution will insignificantly depend on the space coordinates. The basic equations will be constructed without regard for fluctuations of the rate of dissolution of crystals and the influence of the aggregation and cleavage of crystals on the process. The travel of crystal faces will be considered as the main factor influencing the CSDDF, so that the other above-mentioned factors and the factors indicated in [1–3] that determine the form of the equation for the CSDDF will be neglected.

We derive an equation for the crystal-size distribution density function $F(X_1, X_2, X_3, t)$ representing the number of particles ΔN with sizes ΔX_1, ΔX_2, and ΔX_3 in an apparatus (i.e., $\Delta N = F(X_1, X_2, X_3, t)\Delta X_1\Delta X_2\Delta X_3$ at small values of ΔX_i ($i = 1–3$)). Let us write the material balance on the object substance in the solid phase. The change in the number of particles with sizes (X_1, $X_1 + \Delta X_1$), (X_2, $X_2 + \Delta X_2$), and (X_3, $X_3 + \Delta X_3$) for a small time interval Δt is described with an accuracy of up to small values of the first order with respect to ΔX_i (i = 1–3) and Δt as $(\partial F/\partial t)\Delta X_1 \Delta X_2 \Delta X_3 \Delta t$. This change is caused, first of all, by the appearance of new particles with sizes larger than $X_i + \Delta X_i$ (i = 1–3) due to the dissolution (the decrease in the size $(\partial X_i/\partial t)\Delta t$ (i = 1–3)). For the first "coordinate," we have $(dX_1/dt)\Delta t F(X_1 + \Delta X_1, X_2, X_3, t)\Delta X_2 \Delta X_3$. Similar relations can be written for the other "coordinates." Second, N changes due to the disappearance of particles with sizes (X_i, $X_i + \Delta X_i$) (i = 1–3) because of the decrease in the sizes of particles as a result of their dissolution. For example, for the X_1 "coordinate" this change is described as $(\Delta X_1/dt)\Delta t F(X_1, X_2, X_3, t)\Delta X_2 \Delta X_3$. Similar relations can be written for the other X_i.

Using Eq. (1), we write the balance on the number of crystals in the following form:

$$\frac{\partial F}{\partial t} \Delta X_1 \Delta X_2 \Delta X_3 \Delta t + \Big\{ V_1 (C^* - C) \, [(X_1 + \Delta X_1)^{1-\alpha_1} F (X_1 + \Delta X_1, X_2, X_3, t) -$$

$$- X_1^{1-\alpha_1} F (X_1, X_2, X_3, t)] \, \Delta X_2 \Delta X_3 + V_2 (C^* - C) \, [(X_2 + \Delta X_2)^{1-\alpha_2} \times$$

$$\times F (X_1, X_2 + \Delta X_2, X_3, t) - X_2^{1-\alpha_2} F (X_1, X_2, X_3, t)] \, \Delta X_1 \Delta X_3 + V_3 (C^* - C) \times$$

$$\times [(X_3 + \Delta X_3)^{1-\alpha_3} F (X_1, X_2, X_3 + \Delta X_3, t) - X_3^{1-\alpha_3} F (X_1, X_2, X_3, t)] \, \Delta X_1 \Delta X_3 \Big\} \Delta t = 0 \, ,$$

Having divided this equality by $\Delta X_1 \Delta X_2 \Delta X_3 \Delta t$, we obtain, in the limit $\Delta X_i \to 0$ (i = 1–3), the equation

$$\frac{\partial F}{\partial t} + \sum_{i=1}^{3} \left[V_i (C^* - C) \left(\frac{\partial (F X_i^{1-\alpha_i})}{\partial X_i} \right) \right] = 0 \, . \tag{2}$$

Equation (2) is inadequate to describe the dissolution. It is necessary to additionally write the balance on the object substance in a solution, i.e., the equation of evolution in the case of undersaturation. Let us consider the transition of the object substance into solution as a result of the dissolution of crystals in the case where the change in the mass of the substance for the time Δt (at small Δt) is $Q \Delta t dC/dt$ everywhere over the volume of the apparatus. For a crystal with sizes X_1, X_2, X_3 and a volume $X_1 X_2 X_3$, the change in the volume for the time Δt is $(dX_1/dt)X_2 X_3 = V_i(C^* - C)X_2 X_3 X_1^{1-\alpha_1}$ in the case where only the increment of the parameter X_1 is taken into account, i.e., the "area" of the $X_2 X_3$ face is multiplied by the rate of change in the X_1 "coordinate" normal to it. The increment of the volume, which is due to the change in the parameters X_2 and X_3, is estimated in a similar way. Multiplication of the sum of the indicated increments of the crystal volume by the solid-phase density gives the mass of the substance, and additional division by the volume of the apparatus Q gives its concentration. Since, in certain cases, it is appropriate to consider particles with a shape differing from a parallelepiped (but "three-parametric), we introduce the shape factor β to take into account this circumstance. The shape factor will represent the ratio between the density of the particles (multiplier) and the volume of the apparatus (divisor). The main aim of the shape factor is to correctly take into account the mass transition of the substance from crystals into solution. To take into account the effect of all crystals, it is necessary to use the CSDDF, having summed (integrated) the effect of a single crystal over the effects of all crystals with sizes falling in the range studied. Thus, the increment of the mass that is due to the dissolution of particles is

$$\beta \Delta t \left[V_1 \int_W X_2 X_3 X_1^{1-\alpha_1} F dW + V_2 \int_W X_1 X_3 X_2^{1-\alpha_2} F dW + V_3 \int_W X_1 X_2 X_3^{1-\alpha_3} F dW \right] .$$

Having related this quantity to the rate of change in the concentration of the object substance in a solution $\Delta t dC/dt$ and having performed division by Δt, we obtain the desired equation

$$\frac{dC}{dt} + \beta \left[V_1 \int_W X_2 X_3 X_1^{1-\alpha_1} F dW + V_2 \int_W X_1 X_3 X_2^{1-\alpha_2} F dW + V_3 \int_W X_1 X_2 X_3^{1-\alpha_3} F dW \right] = 0 \, , \tag{3}$$

defining the dependence of the CSDDF on the undersaturation of the solution. Here, $dW = dX_1dX_2dX_3$ and the lower limit of integration W in (3) means that integration is done over all the coordinates X_i (i = 1–3) from zero to infinity. The factor β characterizes the shape of a crystal or, more precisely, the relation between the crystal volume and the product of its sizes X_1, X_2, X_3. We will not concretize this coefficient since it can be used for investigating the dissolution of crystals having a more complex shape, for example, the shape of an oblique prism, etc. A single important requirement is that the volume of a crystal is to be expressed in terms of its sizes in the form of the function $X_1X_2X_3$ with any multiplier and its faces are not to disappear. Examples of determination of the factor β are given, for example, in [17, 18].

Equations (2) and (3) should be supplemented with the initial and boundary conditions. The initial conditions

$$F\big|_{t=0} = F_0\,(X_1, X_2, X_3)\,, \quad C\big|_{t=0} = C_0\,, \quad C^* > C_0 \tag{4}$$

determine, respectively, the granulometric composition and concentration (undersaturation) of the solution at the onset of the process. The boundary conditions should provide a fairly rapid decrease in the CSDDF at X_1, X_2, and $X_3 \to \infty$. In actual practice the CSDDF becomes zero once the increasing X_i intersects any surface in the first quadrant of the coordinate system X_1, X_2, X_3. This is also true for the function F_0. As for the boundary conditions at X_i = 0 (i = 1–3), they are not essential for problems of the mass dissolution (unlike the related problems of the mass crystallization from solutions). This is explained by the fact that, in the problems on the dissolution, the sign of the rate of growth (dissolution) is such that the characteristics of Eq. (2) [19] pass through the planes X_1 = 0, X_2 = 0, and X_3 = 0 (in the general case, a concrete characteristic intersects only one of these planes). Therefore, we cannot formulate definite conditions for the given planes X_i = 0 (i = 1–3) that would bound the region of change in the parameters X_i [19]. Actually, the characteristics of (2) represent solutions of the system of equations (1) and, since $V_i < 0$ (i = 1–3), all the coordinates X_i decrease in value. Consequently, the characteristic lines tend to go out from the region $X_1 > 0$, $X_2 > 0$, $X_3 > 0$, where the physical meaning of the initial condition F_0 is determined.

The absence of boundary conditions for the planes X_i = 0 (i = 1–3) in problems on the dissolution introduces significant corrections to the analysis of the problem as compared to the problem on the mass crystallization, even though in the basic equations only the signs of the rates of increase in the sizes change.

Analysis of the Problem. We introduce the moment characteristics of any function ψ by the formula

$$M_{ijk}\,(\psi) = \int\limits_W X_1^i X_2^j X_3^k\, \psi(X_1, X_2, X_3, t)\, dW\,,$$

where the time argument of the function ψ can be absent under the integral or be replaced by other parameters. The moments of the CSDDF reflect important characteristics of a collection of crystals. For example, the moment $N = M_{000}$ determines the number of crystals and the moment M_{100} determines the average size of a crystal in the direction of the X_1 axis (the moments M_{010} and M_{001} have an analogous meaning). The moments M_{110}, M_{011}, and M_{101} determine the average areas of the face surfaces perpendicular to the axes specified by subscript 0. The total volume of the crystals is determined by the moment M_{111}. In certain heat-mass-exchange processes, of importance is the specific surface of particles, which represents an integral characteristic of their collection. It is easy to verify that, in the case of a crystal shaped as a parallelepiped, its specific surface S_* is determined by the formula [20]

$$S_* = 2\,[M_{011} + M_{101} + M_{110}]/M_{111}\,,$$

representing the ratio between the total area of the parallelepiped (crystal) faces and the total volume of the crystal.

A definite integral equality follows from Eqs. (2) and (3). Multiplying Eq. (2) by $\beta X_1X_2X_3$ and integrating the expression obtained over all X_i (i = 1–3) from 0 to ∞, we obtain, with the use of (3), the following relation:

$$d\,[C + \beta M_{111}\,(F)]/dt = 0\,. \tag{5}$$

This relation defines the balance on the total amount of the substance in a solution and in solid particles. Equation (5) is easily solved with the use of the initial conditions (4) in the following form:

$$C + \beta M_{111}(F) = q = \mathrm{const} = C_0 + \beta M_{111}(F_0)\,, \tag{6}$$

Dependence (6) can be used instead of Eq. (3). Thus, Eqs. (2) and (6) make it possible to determine the unknown functions F and C in the case where initial condition (4) is used for the function F (the initial condition for the function C has already been used in deriving expression (6) and will not be used hereinafter).

In solving problem (2), (6), and (4) it makes sense, instead of F, to determine the new function g defined by the equality

$$F(X_1, X_2, X_3, t) = g(\zeta_1, \zeta_2, \zeta_3, t) \prod_{j=1}^{3} X_j^{\alpha_j - 1}\,, \quad \zeta_j = X_j^{\alpha_j}/\alpha_j\,. \tag{7}$$

The moments of the function F expressed in terms of the variables X_j are related to the moments of the function g by the easily verified relation

$$M_{ijk}(F) = \alpha_1^{i/\alpha_1}\alpha_2^{j/\alpha_2}\alpha_3^{k/\alpha_3} M_{i/\alpha_1, j/\alpha_2, k/\alpha_3}(g)\,. \tag{8}$$

Having done the necessary calculations, we obtain, instead of (2), the following equation:

$$\frac{\partial g}{\partial t} + \sum_{i=1}^{3} \left[V_i(C^* - C) \frac{\partial g}{\partial \zeta_i} \right] = 0\,. \tag{9}$$

The initial condition for the CSDDF in the new coordinates has the form

$$g\big|_{t=0} = g_0(\zeta_1, \zeta_2, \zeta_3) = F_0(X_1, X_2, X_3) \prod_{j=1}^{3} X_j^{1-\alpha_j}\,, \quad X_j = (\alpha_j \zeta_j)^{1/\alpha_j}\,. \tag{10}$$

Now only the function g can be considered as unknown since the undersaturation is expressed in its terms with the use of expressions (6) and (8) at $i = j = k = 1$. This makes the problem on the determination of the function g nonlinear, which presents the main difficulties for its analysis and analytical solution. However, under certain conditions realized in practice, this problem can be solved in quadratures. To do this, it is convenient to describe the problem by a system of ordinary differential equations supplemented with an integral equality.

We will assume for a while that the dependence $C = C(t)$ is known. In such an event, the functions $V_i(C)$ are also known. In accordance with the equations

$$d\lambda_j/dt = -V_j(C)\,, \quad \lambda_j(0) = 0 \quad (j = 1-3)\,, \tag{11}$$

we introduce the new functions $\lambda_j(t)$ (j = 1–3). For brevity, in relations (11) and sometimes in other relations, where this will not cause any misunderstanding, we will write the argument C instead of $(C^* - C)$ under the sign of the function V_i.

We will solve the problem with the use of the method of characteristics [19]. It is easy to verify by direct calculation with the use of relations (10) and (11) that Eq. (9) has the following solution:

$$g = g_0[\zeta_1 + \lambda_1(t), \zeta_2 + \lambda_2(t), \zeta_3 + \lambda_3(t)]\,. \tag{12}$$

Now, to close the problem (the function $C(t)$ is not known in fact) we will use dependences (6) and (8). Let us write a common expression for the moments of the function g that, with needed values of the indices, will lead to a desired relation. It can easily be obtained from formula (12):

$$M_{ijk}(g) = \int_W \zeta_1^i \zeta_2^j \zeta_3^k g_0[\zeta_1 + \lambda_1(t), \zeta_2 + \lambda_2(t), \zeta_3 + \lambda_3(t)]\, d\zeta_1 d\zeta_2 d\zeta_3\,. \tag{13}$$

Thus, the integral expression supplementing (11) and representing, in combination with it, a complete system of equations for determining the unknown functions C and λ_j (j = 1–3) has the form

$$C + \beta_* M_{1/\alpha_1, 1/\alpha_2, 1/\alpha_3}(g) = q\,, \quad \beta_* = \beta \prod_{j=1}^{3} \alpha_j^{1/\alpha_j}\,. \tag{14}$$

In the general case, the four equations of (11) and (14) can easily be reduced to three equations, on solution of which one quadrature (instead of the fourth equation) remains to be done. Actually, having divided expressions (11) at j = 2 and j = 3 by the equation at j = 1, we obtain

$$\frac{d\lambda_2}{d\lambda_1} = \frac{V_2(C)}{V_1(C)}\,, \quad \frac{d\lambda_3}{d\lambda_1} = \frac{V_3(C)}{V_1(C)}\,, \quad \lambda_2\Big|_{\lambda_1=0} = 0\,, \quad \lambda_3\Big|_{\lambda_1=0} = 0\,. \tag{15}$$

Thus, expression (14) with two equations (15) should be integrated to obtain the functions $C = C(\lambda_1)$, $\lambda_2 = \lambda_2(\lambda_1)$, and $\lambda_3 = \lambda_3(\lambda_1)$, and then it is necessary to find the relation between the time t and the parameter λ_1 from (11) at j = 1. Thus, Eq. (11) transforms into the simple quadrature

$$t = \int_0^{\lambda_1} V_1^{-1}\,[C(\zeta)]\, d\zeta\,. \tag{16}$$

In this case, depending on the form of the functions $V_j(C)$ (j = 1–3), we may separate not only λ_1 (in the manner described above, (15)) but also other parameters (λ_2 or λ_3) if this will simplify the equations considered.

Common Properties of Solutions of the Dissolution Problem. In the process of dissolution, the concentration C will monotonically increase with time to the equilibrium value C^*. This follows from Eq. (2) and the physically acceptable (in sign) values of the parameters and functions in (2). Likewise, from (11) it follows that the function $\lambda_j(t)$ (j = 1–3) monotonically increases with time. However, two different variants of the behavior of these functions at $t \to \infty$ are possible: all $\lambda_j(t)$ (j = 1–3) tend to infinity or they do not exceed certain ultimate (stationary) values of λ_j^{s}. The first variant is realized if

$$C^* \geq C_0 + \beta M_{111}(F_0)\,. \tag{17}$$

In this case, the concentration C does not reach the equilibrium value even if the entire substance is dissolved, i.e., any stationary concentration C_{s} falling in the range $C \in [C_0, C^*]$ is attained. The undersaturation $C^* - C_{\mathrm{s}}$ is positive, and it follows from relations (11) that $\lambda_j \sim t$ at $t \to \infty$. This is also explained by the fact that only at $\lambda_j \to \infty$ (j = 1–3) does the CSDDF calculated by (12) tend to zero (complete dissolution), which follows from the properties of the CSDDF at larger values of the argument. The value of C_{s} can be determined from relation (6) at $M_{111}(F_{\mathrm{s}}) = 0$, i.e.,

$$C_{\mathrm{s}} = q = C_0 + \beta M_{111}(F_0)\,. \tag{18}$$

In the case where inequality (17) has the opposite sign (<) and $t \to \infty$, only a part of the loaded product, with which the equilibrium concentration $C_{\mathrm{s}} = C^*$ is attained, is dissolved (the moving force of the process disappears). This is possible only at any finite values of λ_j^{s} (j = 1–3) in the case of material balance (6). In this variant, a nonzero, steady-state CSDDF is realized:

$$g_{\mathrm{s}}(\zeta_1, \zeta_2, \zeta_3) = g_0(\zeta_1 + \lambda_1^{\mathrm{s}}, \zeta_2 + \lambda_2^{\mathrm{s}}, \zeta_3 + \lambda_3^{\mathrm{s}})\,. \tag{19}$$

It is significant that a steady-state solution of (19) cannot be obtained from the steady-state equations of dissolution (2) and (3) in the case of a periodic process since at $\partial/\partial t = 0$ and $C = C^*$ these equations completely degenerate (are reduced to the identity $0 \equiv 0$). Therefore, the quantities λ_j^{s} (j = 1–3) should be determined in the process of calculation of unsteady equations. We may also use one relation (which is insufficient for the three unknowns λ_j^s) — the steady-state form of Eq. (6)

$$M_{111}(F_s) = (C^* - C_0)/\beta + M_{111}(F_0) . \tag{20}$$

In the case of a nonzero steady-state CSDDF, it makes sense to introduce the dissolution efficiency coefficient μ by the formula, following from (20),

$$\mu = 1 - M_{111}(F_s)/M_{111}(F_0) = (C^* - C_0)/[\beta M_{111}(F_0)] . \tag{21}$$

At $F_s = 0$, the right side of dependence (21) gives $\mu = 1$ (complete dissolution). From Eq. (2) it follows, in the case of "calculation" of the moment $M_{111}(F)$ for the positive CSDDF, that $dM_{111}/dt < 0$, i.e., $M_{111}(F_s) \le M_{111}(F_0)$. This allows us to suggest that the inequality $0 \le \mu \le 1$ is always true. Below are given examples illustrating the conclusions drawn in this section.

Simplified Form of System (11), (14). The greatest simplifications can be made in the particular case where the rates of growth of crystal faces are proportional:

$$V_2 = \kappa_2 V_1 , \quad V_3 = \kappa_3 V_1 , \quad \kappa_2, \kappa_3 = \text{const} . \tag{22}$$

It should be noted that such a situation is of great practical importance since, as the theoretical and experimental data show, the rate of growth (dissolution) is proportional or nearly proportional to the oversaturation (undersaturation), which makes it possible to use the relation $V = U(C - C^*)$ (U = const) for the description of the travel of each crystal face with corrections calculated, if necessary, by the perturbation method. The functional relations between the rate of growth of crystals and the oversaturation as well as the differences between them and the law $V = U(C - C^*)$ have been considered in [8–11] on the basis of experimental data. The functions $V_j(C)$ proportional to the undersaturation lead to dependences (22), with which we find two integrals of system (11):

$$\lambda_2 = \kappa_2 \lambda_1 , \quad \lambda_3 = \kappa_3 \lambda_1 . \tag{23}$$

On substitution of these expressions into (14), the problem is reduced to the integral relation between the variables C and λ_1:

$$C(\lambda_1) = q - \beta_* \int_W g_0(\zeta_1 + \lambda_1, \zeta_2 + \lambda_2 \kappa_2, \zeta_3 + \lambda_3 \kappa_3)\, d\zeta_1 d\zeta_2 d\zeta_3 \prod_{j=1}^{3} \zeta_j^{1/\alpha_j} . \tag{24}$$

In actual fact, formula (24) gives the functional dependence $C(\lambda_1)$; therefore, the solution of the problem leads to quadrature (16) relating the parameter λ_1 (and consequently, according to (23), the parameters λ_2 and λ_3) with time. The analogy between the "three-dimensional" approach involving conditions (22) and the one-dimensional approach used in [21, 22] has engaged our attention.

Since the form of Eq. (24) is similar to the form of the equation used in the "one-dimensional" description of the dissolution and only the characteristic variable λ_1 is significant for the calculation, the question arises of whether the dissolution problem considered can be reduced to a one-parameter (with respect to the particle size) problem or, more precisely, whether the crystal-size distribution density function F can be related to a new CSDDF that would depend only on one variable characterizing the particle size. In certain cases, such reduction of the problem can be done in an exhausting way. In other cases, this leads to unnatural laws of dissolution of an introduced one-parameter particle, since in order that the particle size be described by one parameter, the initial shape of the particle (in our case, the ratio between the parallelepiped sides) must remain practically unchanged in the process of dissolution. However, a particle shaped as a parallelepiped with finite sizes can disappear at any instant of time, for example, when only one of the three "coordinates" X_j turns into zero (the particle is shaped as a rectangular plate at the instant it disappears), i.e., the ratio between the given size and any of the other two sizes is equal to zero, which was not observed at earlier instants of time. In this variant, we do not obtain a simple (power) law of the change in the rate of dissolution of a crystal depending on its equivalent size (introduced in the natural way).

Let us consider an example of the above-described "transformation" of the CSDDF. Let the function g_0 have the form

$$g_0(\zeta_1, \zeta_2, \zeta_3) = G_0(\zeta_1)\, \delta(\zeta_2 - \kappa_2\zeta_1)\, \delta(\zeta_3 - \kappa_3\zeta_1)\,, \tag{25}$$

where $\delta(z)$ is the Dirac delta function. This means that at the initial instant of time the size ratios of any particle are $\zeta_2/\zeta_1 = \kappa_2$ and $\zeta_3/\zeta_1 = \kappa_3$. In the case where equality (22) is fulfilled, from formula (12), derived for solving the dissolution problem, it follows that these ratios will be retained at any instant of time. It can be shown using expression (7) that the ratios between different X_j will also be retained in the coordinates X_j ($j = 1$–3).

It can be verified by direct calculation that the one-dimensional crystal-size distribution density function $G(\zeta_1, t)$ satisfies the "one-dimensional" equation

$$\partial G/\partial t + V_1(C)\, \partial G/\partial \zeta_1 = 0 \tag{26}$$

at the initial condition

$$G|_{t=0} = G_0(\zeta_1)\,. \tag{27}$$

However, the variables g and ζ_j (as well as G and ζ_1) play an auxiliary role. It is more important to obtain the main relations for description of the dissolution problem in the physical variables F and X_j. This can be done using Eq. (24), which makes it possible to determine the dependence of the rate of dissolution on the coordinate X_1. On substitution of (12) into (24) with account for (25) and integration with respect to the variables ζ_2 and ζ_3, we obtain

$$C(\lambda_1) = q - \beta_* \prod_{j=1}^{3} \kappa_j^{1/\alpha_j} \int_0^\infty \zeta_1^{1/\alpha_*} G_0(\zeta_1 + \lambda_1)\, d\zeta_1\,, \quad \alpha_*^{-1} = \frac{1}{3}\sum_{j=1}^{3} \alpha_j^{-1}\,, \tag{28}$$

where $\kappa_1 = 1$. This corresponds to the "one-dimensional" variant of dissolution of crystals where the variables X_1 and ζ_1 are related by the power law. Comparison of these expressions with an analogous expression for spherical particles leads to the following relations relating the "three-dimensional" and "one-dimensional" cases of dissolution:

$$\beta_1 = \frac{3\beta}{\alpha_*^{3\alpha_*}} \prod_{j=1}^{3} (\alpha_j\kappa_j)^{1/\alpha_j}\,, \quad \frac{dX_1}{dt} = V_1(C^* - C)\, X_1^{1-\alpha_*}\,, \tag{29}$$

here, β_1 is the effective shape factor. It is seen from dependences (29) that the dissolution of particles shaped as a parallelepiped under the above-indicated conditions proceeds in the same way as the dissolution of spherical crystals with an effective shape parameter β_1 and a parameter α_* in the law of dissolution of crystals.

It is interesting to note that the parameter α_* is the mean harmonic parameter α_j for the three faces of a crystal. We also note that the result obtained is dependent on the special ratios between the crystal sizes selected from a continual set of possible variants. It is very important here that the characteristic of the three-dimensional system pass through the origin of the coordinates ζ_1, ζ_2, ζ_3 (X_1, X_2, X_3). In other cases, such simple results are not obtained, even though it is known [23] that the equations for the moments of the CSDDF in the "three-dimensional" problem on the crystallization in a kinetic regime of growth of crystals ($\alpha_j = 1$, $j = 1$–3) can be reduced to a "one-dimensional" momentum system.

Example. We will exemplify the aforesaid using, as the initial condition, the exponential function

$$F_0(X_1, X_2, X_3) = \hat{f} \exp\left(- \sum_{j=1}^{3} X_j/\hat{X}_j\right), \tag{30}$$

where $\hat{f}$ and $\hat{X}_j$ (j = 1–3) are constants. Our consideration will be restricted to the case of a kinetic regime of dissolution. It will be assumed that $\alpha_i = 1$ in formula (1) and the functions V_i are linear: $V_i = U_i\ (C^* - C)$ and U_i (i = 1–3) are constants. Having calculated the integrals in (14) (or, more precisely, in (6) since at $\alpha_j = 1$ (j = 1–3) the variables X_j and ζ_j are analyzed in the same way), we find

$$C - C_0 = \hat{C}\,[1 - \exp\,(-\,\lambda/\hat{r})]\ , \tag{31}$$

$\left(\hat{C} = \beta\hat{f}\prod_{j=1}^{3}\hat{X}_j^2\ ;\ \hat{r}^{-1} = \sum_{j=1}^{3}\kappa_j/\hat{X}_j\ ,\ \lambda = \lambda_1\right)$. The relation (31) was derived with the use of formulas (22) and (23). It follows from the proportionality of the rates of dissolution of crystal faces that $\kappa_1 = 1$, $\kappa_2 = U_2/U_1$, and $\kappa_3 = U_3/U_1$. The parameter $\hat{C}$ in (31) is equal to $\beta M_{111}(F_0)$ in inequality (17). Let us introduce the dimensionless parameters $\vartheta = (C^* - C_0)/\hat{C}$. Inequality (17) corresponds to the case where $\vartheta \geq 1$. In any variant ($\vartheta < 1$, $\vartheta > 1$), substitution of (31) into formula (11) at j = 1 and integration of the expression obtained give

$$\frac{\lambda}{\hat{r}} = \ln\left[\frac{\vartheta\exp\,[(\vartheta - 1)\,U\hat{C}t] - 1}{\vartheta - 1}\right], \tag{32}$$

where $U = U_1$. Substituting (32) into formula (31) and the CSDDF into (12) and using (30) and (23), we obtain the expression for the change in the concentration C with time:

$$F\,(X_1, X_2, X_3, t) = \frac{\hat{f}\,(\vartheta - 1)}{\vartheta\exp\,[(\vartheta - 1)\,U\hat{C}t] - 1}\exp\left(-\sum_{j=1}^{3}X_j/\hat{X}_j\right),$$
$$\frac{C - C_0}{\hat{C}} = \frac{\vartheta\left\{\exp\,[(\vartheta - 1)\,U\hat{C}t] - 1\right\}}{\vartheta\exp\,[(\vartheta - 1)\,U\hat{C}t] - 1}\,. \tag{33}$$

At $\vartheta < 1$, for $t \to \infty$ we find from (32) that $\lambda_s/\hat{r} = -\ln\,(1 - \vartheta)$. At $\vartheta = 1$, from (32) it follows in the limit $\vartheta \to 1$ that $\lambda/\hat{r} = \ln\,(1 + U\hat{C}t)$. At $\vartheta \geq 1$ and $t \to \infty$, from (31) we obtain that $C_s = C_0 + \hat{C}$.

CONCLUSIONS

1. Equations for description of the process of mass dissolution of crystals shaped as a parallelepiped in the two-phase medium "liquid–solid phase" have been derived and additional conditions for them have been formulated. A number of useful consequences of these equations have been obtained.

2. The problem has been reduced to a system of ordinary differential equations supplemented with an integral relation.

3. An example of solution of the problem is presented.

NOTATION

C^*, equilibrium concentration; C, current concentration; C_0, initial concentration; G, modified crystal-size distribution density function; $G_0(\zeta_1)$, initial value of G; g, auxiliary crystal-size distribution density function; g_0, initial value of g; t, time; V_j (j = 1–3), undersaturation functions determining the laws of dissolution of crystal faces; X_1, X_2, X_3, parameters determining the crystal sizes; $F(X_1, X_2, X_3, t)$, crystal-size distribution density function; $F_0(X_1, X_2, X_3)$, initial value of F; $M_{ijk}(\psi)$, moments of the function ψ of the ith, jth, and kth order; N, number of crystals; q, constant in the law of conservation of substance (6) and in other relations; α, α_*, parameters of the power law of dissolution of spherical particles; α_j (j = 1–3), parameters in the power laws of dissolution of crystals shaped as a parallelepiped; β, shape factor; β_*, β_1, modified shape factors; ζ_1, ζ_2, and ζ_3, auxiliary parameters replacing X_1, X_2, and X_3; $\lambda_j(t)$ (j = 1–3), auxiliary functions. Subscripts: s, steady-state solution; $\hat{\ }$, constant parameters in the example.

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