

Derivation and methods of solution are given for the integrodifferential equations for heat transfer in an immobile bed of polydisperse materials with physicochemical transformations within the particles occurring in the kinetic-diffusion or kinetic-thermal regions. Examples are given of the method applied to mass-transfer processes.

We consider the quasistationary approximation for heat transfer in a polydisperse bed consisting of spherical particles whose physical properties (density, diffusion coefficients, reaction coefficient, contents of reactants in the solid, etc.) are not dependent on the size.

In such a bed of ideally mixed material, the size distribution can be represented by the differential distribution curve for particles of identical density:

$$\frac{dq}{dR} = \chi(R) \left(\int_{R_{\min}}^{R_{\max}} \chi(R) dR = 1 \right). \quad (1)$$

The response of a particle will be dependent on its size under otherwise equal conditions; on the other hand, even in the general case, the reaction in an arbitrary particle can be described by the following equation [1]:

$$\beta z_0 V_R \frac{\partial \psi}{\partial \tau} = g F_R (\Pi_x - \Pi_e). \quad (2)$$

Here, as previously [1], we restrict consideration to heterogeneous interactions in which the reaction rate proper can be approximated adequately merely by considering the transport rate either for mass or for heat, i.e., we consider processes occurring in the kinetic-thermal or kinetic-diffusion regions.

The equilibrium potential Π_e for these processes is constant during the reaction, while the total conductance is a function of particle size and degree of conversion, i.e.,

$$g = g(\psi, R). \quad (3)$$

An analog of Π_e is, for example, the temperature of an evaporating surface in drying, where the driving force of the evaporation may be taken as the temperature difference, since Lykov's [2] and Filonenko's [3] models indicate that the drying rate in the period of decreasing rate can be expressed in terms of the drying rate in the first period. In a heterogeneous isothermal mass transfer for first-order reversible reactions, the driving force is the concentration difference $c - c_e$ [4]. In the case of highly endothermic reactions, where the incoming heat is used up largely in the reaction, the temperature of the reacting solid phase remains virtually constant, and then the driving force may be taken as the difference $t - t_e$, where t_e is determined by the initial reaction rate under given conditions [5], and hence by the temperature of the reacting component.

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If (3) is derived in some way, then (2) should be supplemented to describe the mass transfer in such a bed via a balance equation (mass conservation or energy conservation, depending on the form of reaction) involving the gas flow and the reacting particles in an elementary volume. This equation can be given the form of (5) below since (1) and (2) indicate that the consumption of mass or energy from the gas flow per unit volume of the bed is

$$W = \int_{R_{\min}}^{R_{\max}} \frac{(1-m)F_R}{V_R} g(\Pi_x - \Pi_e) \chi(R) dR, \quad (4)$$

and can be given the following quasistationary approximation†:

$$\sigma_p \omega \frac{\partial \Pi_x}{\partial x} = -W, \quad (5)$$

where $\sigma_p = c_g$ if the temperature is the transport potential, while $\sigma_p = \rho_g$ if the concentration is the same; we introduce the dimensionless variables

$$\begin{aligned} \kappa &= \frac{\Pi_x - \Pi_e}{\Pi_0 - \Pi_e}, & \varepsilon &= \frac{R}{R_*}, & \eta &= \frac{3a_p(\Pi_0 - \Pi_e)\tau}{\beta z_0 R_*^2}, \\ \xi &= \frac{3(1-m)a_p x}{\sigma_p \omega R_*^2} \end{aligned} \quad (6)$$

and then write (2) and (5) in the form

$$\frac{\partial \psi}{\partial \eta} = \kappa \Phi(\psi, \varepsilon), \quad \frac{\partial \kappa}{\partial \xi} = -\kappa \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} v(\varepsilon) \Phi(\psi, \varepsilon) d\varepsilon, \quad (7)$$

where

$$\Phi = \frac{1}{\varepsilon^2} f(\psi, \varepsilon); \quad f = \frac{gR}{a_p}; \quad v = R_* \chi. \quad (8)$$

Here f is the dimensionless analog of the impedance, while R_* is expressed in some way in relation to the physical formulation of the problem. Often R_* is conveniently defined as the weighted-mean radius of the particles

$$R_* = \frac{\int_{R_{\min}}^{R_{\max}} \chi(R) R dR}{\int_{R_{\min}}^{R_{\max}} \chi(R) dR}. \quad (9)$$

Equations (7) represent a system of two nonlinear integrodifferential equations for the unknowns $\psi(\xi, \eta, \varepsilon)$ and $\kappa(\xi, \eta)$.

In what follows we assume that Φ is bounded at $\psi = 0$ and 1, together with its first derivative with respect to ψ ; then we expect that the reaction initially extends to the entire semiinfinite volume of the bed, and therefore the boundary conditions may be put in the following form [6]:

$$\kappa|_{\xi=0} = 1, \quad \psi|_{\eta=0} = 0. \quad (10)$$

The first (boundary) condition of (10) gives from the first equation of (7) with $\xi = 0$ the following relation representing the course of the reaction in particles of any size at the surface of the bed:

†We neglect in a first approximation the variation in the filtration rate over the thickness of the bed with respect to normal conditions.

$$\eta = h(\psi_0, \varepsilon), \quad \psi_0(\eta, \varepsilon) = \psi|_{\xi=0}, \quad (11)$$

where

$$h(\psi, \varepsilon) = \int_0^\psi \frac{d\psi}{\Phi(\psi, \varepsilon)}. \quad (12)$$

Our initial assumptions about the properties of Φ mean that h is a monotonically increasing function of ψ defined in the range $(0, 1)$.

We now transfer to direct integration of (7), first rewriting the first equation in (7) as

$$\frac{\partial h}{\partial \eta} = \kappa. \quad (13)$$

As κ is independent of ε , it follows from (13) that

$$\frac{\partial}{\partial \eta} \left(h \Big|_{\varepsilon_1}^{\varepsilon_2} \right) = 0, \quad (14)$$

where ε_1 and ε_2 are arbitrary numbers in the range $(\varepsilon_{\min}, \varepsilon_{\max})$; then the second (initial) condition in (10) and the definition of h in (12) imply that $h|_{\varepsilon_1}^{\varepsilon_2} = 0$, and therefore this quantity is not dependent on ε ; in other words, $\psi(\xi, \eta, \varepsilon)$ and ε appear in h in such a way that

$$h(\psi, \varepsilon) = H, \quad (15)$$

where H is dependent only on ξ and η , but not on ε . We introduce the degree of conversion of the bed material weighted with respect to particle size:

$$\Psi(\xi, \eta) = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \psi v d\varepsilon. \quad (16)$$

As (15) in essence defines $\psi(H, \varepsilon)$, (16) relates Ψ to H , i.e., unambiguously defines $H(\Psi)$; we then multiply the first equation in (7) by $v(\varepsilon)$ and then integrate with limits of ε_{\min} and ε_{\max} ; we compare the result with the second equation of (7) and use (16) to get

$$\frac{\partial \Psi}{\partial \eta} + \frac{\partial \kappa}{\partial \xi} = 0. \quad (17)$$

On the other hand, (13) with (15) gives

$$\frac{\partial H(\Psi)}{\partial \eta} = \kappa. \quad (18)$$

Equations (17) and (18) can be put as the following quasilinear system of differential equations:

$$\frac{\partial \Psi}{\partial \eta} = \kappa F(\Psi), \quad \frac{\partial \kappa}{\partial \xi} = -\kappa F(\Psi), \quad (19)$$

where

$$F(\Psi) = \frac{d\Psi}{dH} = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} v(\varepsilon) \Phi(\psi, \varepsilon) d\varepsilon. \quad (20)$$

When (19) is to be solved, (10) and (16) give the boundary conditions as

$$\chi|_{\xi=0} = 1, \quad \Psi|_{\eta=0} = 0. \quad (21)$$

Then the heat transfer in this polydisperse medium amounts essentially to a previously considered problem [6] for heat transfer in a monodisperse bed, with the degree of conversion represented by the weighted mean of (16). The solution is [6]

$$H(\Psi_0) = \eta, \quad G(\Psi_0, \Psi) = \xi, \quad \chi = \frac{\Psi}{\Psi_0}, \quad (22)$$

where

$$H = \int_0^{\Psi_0} \frac{d\Psi}{F(\Psi)}; \quad G = \int_{\Psi}^{\Psi_0} \frac{d\Psi}{\Psi F(\Psi)}; \quad \Psi_0 = \Psi|_{\xi=0}. \quad (23)$$

It is sometimes more convenient to use a modified expression for the second quadrature in (22):

$$G = \int_{H(\Psi)}^{\eta} \frac{dH}{\Psi(H)}. \quad (24)$$

This expression is obtained if in (23) we replace the variable of integration in accordance with the differential equality $d\Psi = FdH$; as regards $\psi(\xi, \eta, \epsilon)$, the degree of conversion, this can be found from (15).

The resulting solution is automatically extended to a discrete particle-size distribution; if, for instance, there are n types of particles in the bed, with the proportions of the fractions of size R_i ($i = 1, \dots, n$) equal to χ_i , it is sufficient to assume that

$$\chi(R) = \sum_{i=1}^n \chi_i \delta(R - R_i), \quad (25)$$

where $\delta(R)$ is a Dirac delta function [7]. Here, if we introduce the symbols

$$\begin{aligned} \epsilon_i &= \frac{R_i}{R_*}, \quad \psi_i(\xi, \eta) = \psi(\xi, \eta, \epsilon_i), \quad \Phi_i(\psi_i) = \Phi(\psi_i, \epsilon_i), \\ h_i(\psi_i) &= h(\psi_i, \epsilon_i), \end{aligned} \quad (26)$$

then (15) and (16) take the form

$$h_i(\psi_i) = H, \quad \Psi = \sum_{i=1}^n \chi_i \psi_i. \quad (27)$$

The general relationships of (22) are clearly unaltered in this case.

We now consider examples illustrating the scope for using this method.

1. Drying of a two-component bed of iron ore nodules of radii R_1 and R_2 ($R_1 > R_2$) with contents of 50% for both types; the theoretical method of calculating nodule drying [8] implies that the dimensionless analog of the total conductance for part of the first and second kinds is

$$f_i = \frac{1}{\frac{1}{Bi_i} + \frac{3}{k_i(b_i)(1 - \psi_i)}}, \quad i = 1, 2, \quad (28)$$

where $\psi_i = 1 - u_i/u_0$.

As R_* we take the arithmetic-mean radius, and then (25) and (26) give

$$\chi_1 = \chi_2 = \frac{1}{2}, \quad \varepsilon_1 = 1 + \Delta, \quad \varepsilon_2 = 1 - \Delta, \quad (30)$$

where

$$\Delta = \frac{R_1 - R_2}{R_1 + R_2} \quad (0 < \Delta < 1). \quad (31)$$

The first group of relations in (27) is put in the following form on the basis of (8), (12), and (26):

$$\psi_1 \frac{(1 + \Delta)^2}{Bi_1} - \frac{3(1 + \Delta)^2}{k_1(b_1)} \ln(1 - \psi_1) = H, \quad (32)$$

$$\psi_2 \frac{(1 - \Delta)^2}{Bi_2} - \frac{3(1 - \Delta)^2}{k_2(b_2)} \ln(1 - \psi_2) = H.$$

The following is the expression of (27) by virtue of (30):

$$\Psi = \frac{\psi_1 + \psi_2}{2}. \quad (33)$$

Equations (32) and (33) enable one to generate $H(\Psi)$ and $H(\psi_1)$ and thus to solve the problem completely for the drying of this bed; to check the theoretical relationships, we perform the following tests under the conditions $R_1 = 10.5$ mm, $R_2 = 5.5$ mm, $\chi_1 = \chi_2 = 1/2$, $u_0 = 0.085$ kg/kg, with a bed of thickness 250 mm, a heat-carrier gas temperature at the inlet of 250°C, a flow speed of 1.1 m/sec, and a drying time of 3.5 min. The drying parameters of the nodules were such that the method of [8] gave $Bi_1 = 3.14$, $Bi_2 = 1.4$, $k_1(b_1) = 12.8$, $k_2(b_2) = 5.4$, $\eta = 1.88$; then these were used with (22)-(24) and (28)-(33) to perform a Minsk-22 computation of $\Psi(\xi)$, $\psi_1(\xi)$, and $\psi_2(\xi)$.

Figure 1 compares the calculated curves with experiment; the agreement is satisfactory.

2. We consider heterogeneous mass transfer in a polydisperse bed with a uniform and continuous particle-size distribution (Fig. 2) subject to the condition that for particles of any size

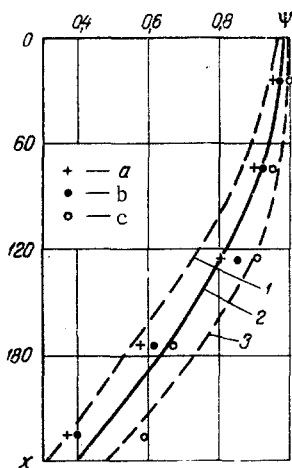


Fig. 1. Distribution of ψ in two-component nodule bed at a given instant (curves from theory, points from experiment): 1) $\psi = \psi_1$ (points a); 2) $\psi = \Psi$ (points b); 3) $\psi = \psi_2$ (points c). x , mm.

$$f_R = \frac{1}{\frac{1}{Bi_R} + \frac{3}{b_R^2(1 - \psi)}} \quad (34)$$

and $Nu \sim Re$; the latter conditions means that the Biot criterion in (34) will be proportional to R . System (15) and (16) after integration and transformation can be put as

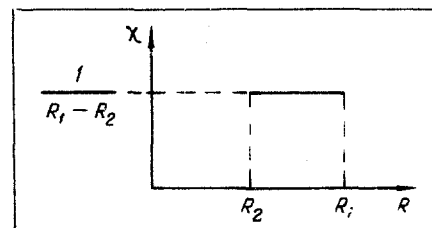


Fig. 2. Particle-size distribution in the second example.

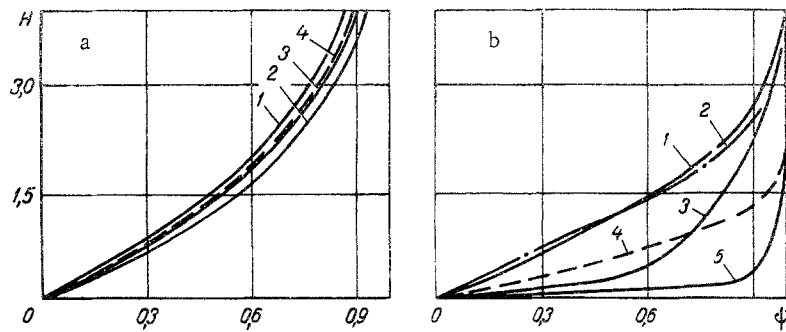


Fig. 3. Curves for $H(\psi_1)$, $H(\psi_2)$, and $H(\Psi)$ for (a) second; (b) third examples: a. 1) $H(\psi_1)$; 2) $H(\psi_2)$; 3) $H(\Psi)$; 4) $H(\Psi_M)$. b. 1) $H(\psi_1)$; 2) $H(\psi_1)$ from (41); 3) $H(\Psi)$; 4) $H(\Psi_M)$; 5) $H(\psi_2)$ (see text).

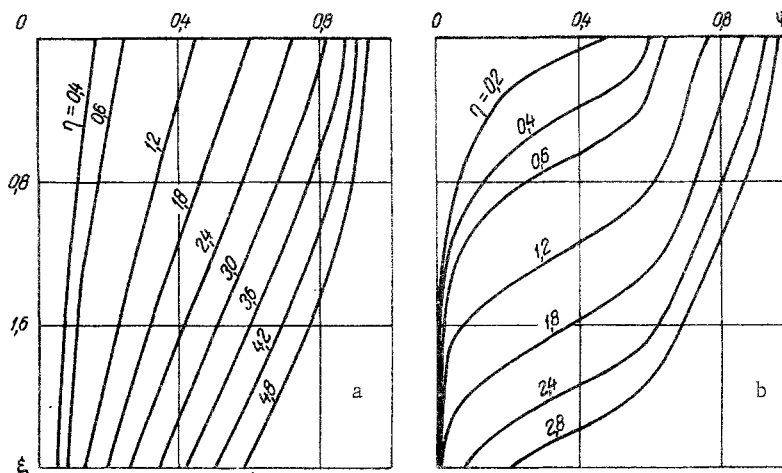


Fig. 4. Mean degree of conversion $\Psi(\xi, \eta)$ within bed for polydisperse particles in the examples: a) second; b) third.

$$\frac{\varepsilon\psi}{\text{Bi}} - \frac{3}{b^2} \ln(1-\psi) = H, \quad \Psi = \frac{1}{2\Delta} \int_{1-\Delta}^{1+\Delta} \psi d\varepsilon, \quad (35)$$

where

$$\Delta = \frac{R_{\max} - R_{\min}}{R_{\max} + R_{\min}}. \quad (36)$$

As (35) enables one to reproduce $H(\Psi)$, this formulation terminates the detailed treatment of the problem; before we transfer to the purely numerical analysis, we consider the following example.

3. Mass transfer in a two-component bed where the transfer in the particles of the first type occurs in the diffusion state, while that in the second type is in the kinetic state. Standard models for the reaction kinetics [1] give us, for particles of the first type, that

$$f_1 = \frac{1}{\frac{1}{\text{Bi}_{R_1}} + \frac{1 - (1 - \psi_1)^{1/3}}{(1 - \psi_1)^{1/3}}}, \quad (37)$$

and for particles of the second type

$$f_2 = \frac{1}{\frac{1}{\text{Bi}_{R_2}} + \frac{3}{b_{R_2}^2(1-\psi_2)}} \quad (38)$$

If now, as in the second example, we assume that $\text{Nu} \sim \text{Re}$, then (27) after integration and use of (8), (12), and (37) and (38) is put as

$$\begin{aligned} \frac{3}{2}(1+\Delta)^2 [\psi_1 - (1-\psi_1)^{2/3}] - (1+\Delta) \left(1 + \Delta - \frac{1}{\text{Bi}}\right) \psi_1 &= H, \\ \frac{1-\Delta}{\text{Bi}} \psi_2 - \frac{3}{b^2} \ln(1-\psi_2) &= H \end{aligned} \quad (39)$$

and

$$\Psi = \frac{\psi_1 + \psi_2}{2}, \quad (40)$$

where as before Bi and b are calculated for $R = R_* = 1/2(R_1 + R_2)$ and Δ is determined from (31).

When we have determined $H(\Psi)$ in accordance with (35) in the second example of (39) and (40) in the third, we can transfer to determining $\Psi(\xi, \eta)$. As in the first case, we use (22), with G , as previously, given by (24).

The calculation is carried through for the second problem for $\text{Bi} = 1$, $R_1/R_2 = 2$, and $b = 1.5$ and for the third for $\text{Bi} = 1$, $R_1/R_2 = 10$, and $b = 11$ ($b_{R_1} = 20$, $b_{R_2} = 2$). Figure 3 shows $H(\Psi)$, $H(\psi_1)$, and $H(\psi_2)$ for the second and third cases. The first relation in (22) means that Fig. 3 represents the course of the mass transfer at the surface of the bed. Here we have to put that $H = \eta$. The broken lines in the two curves

$$\eta = \frac{\Psi}{\text{Bi}} - \frac{3}{k(b)} \ln(1-\Psi) \quad (\Psi = \Psi_M), \quad (41)$$

characterize the course of the reaction at the surface of a monodisperse bed with $R = R_*$. In the first case $k(b) = b^2 = 9/4$, while in the second, where the reaction occurs in the intermediate region ($b = 11$), $k(b)$ is derived from a special empirical interpretation of the available numerical solution [1] corresponding to the heat transfer in the body of the particles [$k(b) = 24$]. In the purely diffusion-reaction region, which is defined in the same way, $k(b)$ is not dependent on b and equals 27.5; then the corresponding (41) is shown as the dot-dash curve in Fig. 3b and fairly closely reproduces the curve for ψ .

Figure 3 shows that a small spread in particle size in the second problem (Fig. 3a) means that replacing the polydisperse layer by an equivalent monodisperse one does not result in a large error, but this error increases as Bi decreases. If the particle-size spread is large (third case), this substitution results in a substantial distortion of the actual picture.

Figure 4 shows Minsk-22 patterns for $\Psi(\xi, \eta)$ for the second and third cases; it, together with Fig. 3, enables one to determine $\psi_1(\xi, \eta)$ and $\psi_2(\xi, \eta)$, while to determine $\psi(\xi, \eta, \epsilon)$ in the second case we use the first equation in (35).

NOTATION

R is the current particle size; q is the weight proportion of fractions smaller than R ; β is the stoichiometric reaction coefficient; z_0 is the initial volume concentration of reactant in particle; V_R and F_R are the current volume and external surface of particle; τ is the time; x is the distance of particle from surface; ψ is the degree of conversion averaged over current particle volume; g is the total mass-transfer

rate by reaction in current particle; Π_0 , Π_x are the transport potentials; a_p is the potential-conductivity factor for current particle volume; σ_p is the specific heat or density of gas; u is the current water content of nodules; u_0 is the initial water content; $k(b)$ is the mass-transfer coefficient; R_x is the scale dimension of particles; Bi is the Biot number; Nu is the Nusselt number; Re is the Reynolds number; b is the mass-transfer number.

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