

MASS TRANSFER ACCOMPANIED BY A CHEMICAL
REACTION TAKING PLACE RAPIDLY INSIDE A
MOVING SPHERICAL DROP

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The article deals with the problem of convective mass exchange between a liquid drop and a continuous medium, accompanied by an irreversible chemical reaction of second order at high Pe and K values. A numerical solution of the transfer equations is given. The limits of applicability of the resulting solutions are defined.

Mass exchange within a moving spherical drop in the presence of an irreversible second-order chemical reaction under conditions such that the resistance to the transfer was concentrated in the volume of the dispersed phase was dealt with in [1, 2]. Calculations were carried out for $Re < 1$ for finite values of Pe and of the reaction-rate constant.

In the present article we shall investigate the transfer process again for $Re < 1$ but for comparable phase resistances and the limiting case $Pe \rightarrow \infty$ and $K \rightarrow \infty$. Without loss of generality, we shall consider the case which occurs most frequently in practice, namely, the case in which at the initial instant of time the concentration of the chemisorbent inside the drop, C_{20} , is constant throughout its volume. The concentration of the extracting agent in the continuous phase, y_0 , is taken to be constant with respect to the height of the column and independent of time; this will be true for the condition $U_d(C_{20} + C_{10}) \ll Ucy_0$. It is assumed, as usual, that there is phase equilibrium at the surface of the drop.

For small values of the velocity constant K the reaction between the extracting agent and the chemisorbent takes place throughout the volume of the drop. As K increases, the thickness of the reaction zone is reduced, and for sufficiently large values of K this thickness is much smaller than the radius of the drop. As $K \rightarrow \infty$, the thickness of the reaction zone approaches zero, and the zone itself may be approximately replaced by a surface front. As time increases, the reaction front moves from the surface to the interior of the drop, separating the volume of the drop into two regions, with the extracting agent in one region and the chemisorbent in the other. Thus, the problem of mass transfer in a moving spherical drop with a rapid chemical reaction reduces to the solution of a set of equations of convective diffusion for the extracting agent and the chemisorbent, which are related to each other by conditions of conjugacy at the front of the chemical reaction.

For sufficiently large values of Pe, when $Re < 1$, the equations of convective diffusion for the extracting agent and the chemisorbent can be approximately described by the equations of Kronig and Brink [3, 4]:

$$\frac{\partial}{\partial x} \left[p(x) \frac{\partial C_1}{\partial x} \right] = \frac{q(x)}{16} \frac{\partial C_1}{\partial \tau}, \quad (1)$$

$$\frac{\partial}{\partial x} \left[p(x) \frac{\partial C_2}{\partial x} \right] = \frac{q(x)}{16n} \frac{\partial C_2}{\partial \tau}, \quad (2)$$

where $x = 4r^2(1-r^2) \sin^2 \theta$; $q(x)$, $p(x)$ are defined in [3] as functions of elliptic integrals.

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Equation (1) was obtained in [3] on the assumption that the concentrations along a streamline are constant; this assumption is satisfied as $Pe \rightarrow \infty$. In this case the equation of convective diffusion reduces to an equation of nonstationary molecular diffusion (1) in a direction perpendicular to the streamlines. As $K \rightarrow \infty$, the condition of constant extracting-agent and chemisorbent concentrations along the streamlines is satisfied at surfaces arbitrarily close to the reaction front. Therefore the reaction front also coincides with the streamlines. At the reaction front the concentrations of the reactants are equal to zero, and their flow rates are equal in magnitude and opposite in direction:

$$(C_1)_{x=l} = (C_2)_{x=l} = 0, \quad (3)$$

$$\left(\frac{\partial C_1}{\partial x} \right)_{x=l} = -n \left(\frac{\partial C_2}{\partial x} \right)_{x=l}, \quad (4)$$

where l is the moving position of the reaction front. In the case where the extracting agent and the chemisorbent have different valences, the concentration of the chemisorbent should be multiplied by a stoichiometric coefficient.

On the surface of the drop the boundary condition for the extracting agent has the same form as in the case of mass transfer not complicated by a chemical reaction, for comparable phase resistances and constant extracting-agent concentration in the continuous phase [5, 6]:

$$\left(\frac{\partial C_1}{\partial x} \right)_{x=0} = \frac{3}{32\beta} [(C_1)_{x=0} - 1], \quad (5)$$

where

$$\beta = \frac{D_1 \psi^*}{K_C d}.$$

Within the drop the concentrations of the reactants are bounded.

The initial conditions for this case have the form

$$C_1|_{\tau=0} = 0, \quad C_2|_{\tau=0} = 1. \quad (6)$$

For small values of τ the reaction takes place at the surface of the drop, and the boundary conditions (3)-(5) are not satisfied. In the present case the concentration of the extracting agent at the surface of the drop is zero, and instead of the boundary conditions (4), (5), we have

$$\left(\frac{\partial C_2}{\partial x} \right)_{x=0} = \frac{3}{32\beta mn}. \quad (7)$$

For $0 < \tau \leq \tau_1$ we solve Eq. (2) for a boundary condition of the second kind, (7). The time τ_1 is determined from the condition $C_2(\tau_1)|_{x=0} = 0$. For $\tau > \tau_1$ we solve Eqs. (1)-(6).

For the average chemisorbent concentration \bar{C}_2 , when $\tau \leq \tau_1$, we can obtain an analytic expression:

$$\bar{C}_2 = 1 - \frac{3}{2} \frac{\tau}{\beta m}. \quad (8)$$

Starting at time $\tau = \tau_2$, corresponding to the value $\bar{C}_2 = 0$ (the position of the reaction front is determined by the value $x = 1$), the process of mass transfer is described by Eq. (1). The boundary conditions for C_1 remain the same as before, and the initial condition is determined by the value of C_1 obtained when we solve the problem in the interval $0 < \tau \leq \tau_2$ at time $\tau = \tau_2$.

The solution of the problem was carried out on a BESM-4 computer by the finite-difference method. The difference scheme for Eqs. (1), (2) was written in the form

$$\frac{2}{h_i + h_{i+1}} \left[p_j \left(x_i + \frac{h_{i+1}}{2} \right) \frac{u_{i+1}^j - u_i^j}{h_{i+1}} - p_j \left(x_{i-1} + \frac{h_i}{2} \right) \frac{u_i^j - u_{i-1}^j}{h_i} \right] = \frac{q(x_i)}{16} \frac{u_i^j - u_{i-1}^{j-1}}{h_i}, \quad (9)$$

where $h_i = x_i - x_{i-1}$, x_i is a point of subdivision of the interval $[0, 1]$,

$$u = \begin{cases} -C_1, & 0 \leq x \leq l, \\ C_2, & l < x \leq 1, \end{cases} \quad (10)$$

* In [6], pp. 115 and 299-306 the notation $\beta = D_1 \psi / K_C R$ is incorrectly used instead of $\beta = D_1 \psi / K_C d$.

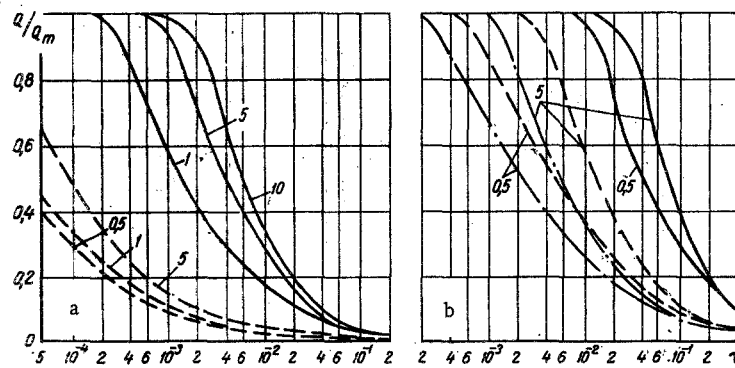


Fig. 1. Q/Q_m as a function of τ : a) for $\beta = 0.0005$ (solid curves: $m = 10$; $n = 1, 5, 10$; dashed curves: $m = 1$; $n = 0.5, 1, 5$) and b) for $\beta = 0.005$ (solid curves: $m = 10$; $n = 0.5, 5$; dashed curves: $m = 2$; $n = 0.5, 5$; dot-and-dash curves: $m = 1$; $n = 0.5, 5$).

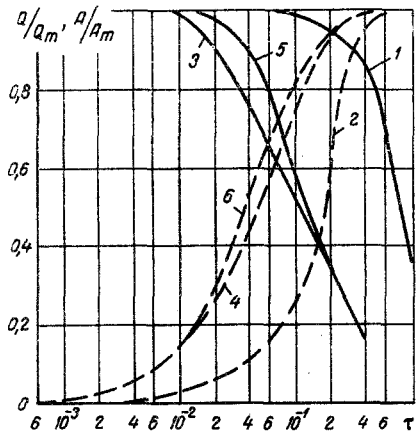


Fig. 2. Variation of Q/Q_m (solid curves) and A/A_m (dashed curves) as functions of τ for $\beta = 0.05$; curves 1, 2: $n = 0.5, 5$; $m = 10$; curves 3, 4: 0.5 and 1, respectively; curves 5, 6: 5 and 1.

$$p_j \left(x_i + \frac{h_{i+1}}{2} \right) = \begin{cases} np \left(x_i + \frac{h_{i+1}}{2} \right), & \text{if } u_i^+ \geq 0 \text{ and } u_{i+1}^+ \geq 0, \\ p \left(x_i + \frac{h_{i+1}}{2} \right), & \text{if } u_i^+ < 0 \text{ and } u_{i+1}^+ < 0, \\ np \left(x_i + \frac{h_{i+1}}{2} \right) \frac{|u^+| + |u^-|}{n|u^-| + |u^+|}, & \text{if } u_i^+ \text{ and } u_{i+1}^+ \text{ differ in sign.} \end{cases} \quad (11)$$

By u^+ and u^- we denote the positive and negative values, respectively, of the function u^j at the point (x_i, τ_j) or (x_{i+1}, τ_j) .

The scheme is obviously nonlinear. To solve it, we use the usual method of successive approximations: from the value of u_i^{j+1} we construct the coefficients $p_j^0(x_i + h_{i+1}/2)$ on layer τ_j , after which the resulting linear scheme is solved by the trial-and-error method, so that we find the values $u_i^{j(i)}$; using these, we construct $p_j^{(1)}(x_i + h_{i+1}/2)$, and so on, until the values $u_i^{j(k)}$ for two successive iterations are found to be sufficiently close to each other. It should also be noted that the system of linear algebraic equations obtained at each iteration includes a number of equations equal to the number of unknowns, which is obtained by writing the scheme at the node $x = 1$ (for more details on such approximations, see [7, 8]).

In the calculation process we determined τ_1, l , the concentration values for the reactants averaged over the volume, and their derivatives. The calculations were carried out for the following values of the parameters: $m = 1, 2, 10$; $n = 0.1, 0.5, 1, 5, 10$; $\beta = 0.0005, 0.005, 0.05$.

For the calculated values of \bar{C}_1 and \bar{C}_2 we found the average value of the flow rate for the extracting agent

$$Q = C_{10} \frac{\pi d^3}{6t} [\bar{C}_1 + m(1 - \bar{C}_2)] \quad (12)$$

and its ratio to the maximum flow rate $Q_m = \pi d^2 K_{CY} y_0$,

$$\frac{Q}{Q_m} = \frac{2\beta}{3\tau} [\bar{C}_1 + m(1 - \bar{C}_2)], \quad (13)$$

as well as the value A/A_m , which characterizes the ratio of the extracting agent absorbed by the drop to the maximum possible absorption in the case of chemisorption,

$$\frac{A}{A_m} = \frac{\bar{C}_1 + m(1 - \bar{C}_2)}{1 + m}. \quad (14)$$

Some examples of numerical calculations are shown in Figs. 1 and 2 for Q/Q_m and A/A_m as functions of τ and of the parameters of the problem. From the value of the parameter β we can judge which of the phases limits the transfer process [4]. It should be noted that for any value of β an increase in the parameters m and n brings an increase in the rate of transport of the chemisorbent to the surface of the drop, and, in addition, an increase in m leads to an increase in chemical capacity, which leads to an increase in the value of time τ_1 that determines the initial time interval in which the reaction takes place at the surface of the drop.

In Fig. 1a we show how Q/Q_m varies with τ for a limiting resistance of the dispersed phase ($\beta = 0.0005$) and various values of the parameters m and n . As can be seen from the curve, the reaction front for $m = 10$, for an appreciable period of time $\tau_1 \approx 10^{-3}$, is practically at the surface of the drop; when $m = 1$, it moves very rapidly to the interior. Even for very small values of τ ($\tau \approx 5 \cdot 10^{-5}$) the concentrations of extracting agents and chemisorbent in the drop are changed considerably in relation to their original values, and the value of the mass flow rate is much less than the maximum value attained for $\tau = 0$.

In Fig. 1b the transfer process is considered for comparable phase resistances ($\beta = 0.005$), and in Fig. 2 we show how Q/Q_m and A/A_m vary with τ for the case in which the resistance to transfer is concentrated, to a significant extent, in the continuous phase ($\beta = 0.05$). From the curves in Fig. 2 it can be seen that during most of the time the reactions take place at the surface of the drop (τ_1 is very large). The value of τ_1 is most significantly influenced by the parameter m . As m increases, the influence of the parameter n on the nature of the process is very much reduced. Thus, when $m = 10$, the curves for $n = 0.5$ and $n = 5$ coincide.

Let us estimate what will be the values of the parameters Pe , K , and Re for which the results obtained will be usable. The applicability of the solutions with respect to Pe is due to the possibility of using the Kronig-Brink equations [3] for describing the mechanism of transfer inside the drop. As was shown in [4], these equations can be used for $Pe' > 100$.

Now let us estimate the value of the reaction-rate constant for which it may be assumed that the thickness of the reaction front is much less than the radius of the drop. We define the characteristic time of the chemical reaction as the time it takes for the concentration of extracting agent at $m = 1$ to decrease by a factor of e . We assume that when $t = 0$, $C_1 = C_2 = C_{10}$ throughout the volume of the drop. This is the characteristic time $t_x \approx (e-1)/kC_{10}$. The characteristic time of diffusion in the presence of liquid circulation in the drop can be found from the Kronig-Brink solution. A decrease by a factor of e in the concentration of the extracting agent corresponds to a degree of extraction of $A_0 \approx 0.63$, which is achieved for $\tau \approx 0.022$ (see Table 1 on p. 299 of [6]). Consequently, $t_d \approx 0.022R^2/D_1$, and from the condition $t_x \ll t_d$ we find that $K \gg 100$.

The solution given above was obtained for $Re < 1$. However, as was shown in [4], for spherical drops with $\mu < 2$, in the description of the mechanism of transfer within the drop Eq. (1) (and consequently the solution obtained here for mass exchange with a chemical reaction) can be used for $Re \approx 100$.

NOTATION

r	is the radial coordinate;
θ	is the polar angle;
R	is the radius of the drop;
u	is the velocity of the steady-state motion of the drop;
ρ	is the density;
$\mu = \mu_d/\mu_c$	is the ratio of the dynamic viscosities of the dispersed and continuous phases;
D	is the diffusion coefficient;
C_{10} and C_{20}	are the initial concentrations of extracting agent and chemisorbent, respectively;
$C_1 = C_1/C_{10}$ and $C_2 = C_2/C_{20}$	are the dimensionless coordinates;
k	is the constant for the rate of the second-order chemical reaction;
$K = kR^2C_{20}/D_1$;	
$m = C_{20}/C_{10}$;	
$n = D_2/D_1$;	
$\beta = D_1\psi/k_c d$, where k_c is the average coefficient of mass transfer for the continuous phase;	

d	is the diameter of the drop;
ψ	is the distribution coefficient;
$Re = ud\rho_c/\mu_c$	is the Reynolds number;
$\tau = D_1t/R^2$	is the Fourier number;
$Pe = ud/D_1$	is the Peclet number;
$Pe' = Pe/4(1 + \mu)$.	

Subscripts

- 1 denotes the extracting agent;
- 2 denotes the chemisorbent;
- d denotes the dispersed phase;
- c denotes the continuous phase.

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