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MASS TRANSFER FROM A MOVING BUBBLE DURING A SLOW CHEMICAL REACTION

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A previously proposed method for solving inhomogeneous problems in the theory of heat and mass transfer is refined. As an illustration, the stationary mass transfer from a moving bubble during a slow chemical reaction of first or second order is examined.

We shall examine the problem

$$\frac{\partial C}{\partial \tau}-\frac{\partial^2 C}{\partial \xi^2}=Q(\xi,\ \tau),\quad 0\leqslant\xi<\infty,\ 0<\tau<\infty, \tag{1}$$

$$C|_{\xi=0}=C_s(\tau);\quad C|_{\xi=\infty}=0;\quad C|_{\tau=0}=0, \tag{2}$$

which describes mass transfer in a semiinfinite region under the action of a source. It is necessary to find the quantity $q_s = (\partial C/\partial \xi)_{\xi=0}$, which determines the mass flux through the boundary of the region.

As in [1], we shall represent Eq. (1) in the form

$$\left(D^{1/2}-\frac{\partial}{\partial\xi}\right)\left(D^{1/2}+\frac{\partial}{\partial\xi}\right)C=Q(\xi,\ \tau), \tag{3}$$

where the fractional differentiation operators are defined by the expressions

$$D^{\nu}f(\tau)=\frac{1}{\Gamma(1-\nu)}\frac{d}{d\tau}\int\limits_0^{\tau}(\tau-z)^{-\nu}f(z)\,dz,\quad -\infty<\nu<1.$$

The concentration gradient sought at the boundary is obtained as follows [1]. We apply the operator inverse to $D-\partial/\partial\xi$ on the left side of Eq. (3). For $(D-\partial/\partial\xi)^{-1}$, we previously found an expression in the form of an infinite series. It turns out that the inverse operator can also be written in the form

$$\left(D^{1/2}-\frac{\partial}{\partial\xi}\right)^{-1}f(\xi,\ \tau)=\int\limits_{\xi}^{\infty}e^{-(\eta-\xi)D^{1/2}}f(\eta,\ \tau)\,d\eta. \tag{4}$$

The following expression, defined in [2], enters into the operator in the integrand:

$$e^{-aD^{1/2}}f(\xi,\ \tau)=\frac{d}{d\tau}\int\limits_0^{\tau}\operatorname{erfc}\left(\frac{a}{2\sqrt{\tau-z}}\right)f(\xi,\ z)\,dz. \tag{5}$$

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Its basic properties are also given in [2] and the usefulness of the notation adopted is explained.

By direct verification, using the properties of the operation (5), it can be shown that (4) is indeed the inverse operator relative to $D^{1/2} - \partial/\partial\xi$.

Operating on Eq. (3) by operator (5), writing the expression obtained for $\xi = 0$ and for convenience rewriting the integration variable as $\eta \to \xi$, we find the gradient sought at the boundary in the form

$$-q_s = D^{1/2}C_s - \int_0^\infty e^{-\xi D^{1/2}} Q(\xi, \tau)\, d\xi. \tag{6}$$

Expression (6) does not require specifying a concentration field to find q_s.

We shall examine one of the basic problems in the theory of mass transfer, describing in the quasistationary approximation the process of mass transfer from a spherical bubble moving with a constant velocity U in a large fluid volume. The substance 1, whose concentration on the surface of the sphere is assumed to be constant and equal to A, diffuses into the surrounding medium, containing substance 2, which has an initial concentration B, not penetrating through the phase separation boundary. Substances 1 and 2 enter into a second-order chemical reaction.

The transfer equations for substance 1 and the system of conditions are written in the form

$$u_r \frac{\partial C}{\partial r} + u_\theta \frac{1}{r}\frac{\partial C}{\partial \theta} - D\Delta C + kCC' = 0, \quad R \leqslant r < \infty, \quad 0 \leqslant \theta \leqslant \pi, \tag{7}$$

$$C|_{r=R} = A, \quad C|_{r=\infty} = 0, \quad \left.\frac{\partial C'}{\partial r}\right|_{r=R} = 0, \quad C'|_{r=\infty} = B, \quad C|_{\theta=0} < \infty,$$
$$C'|_{\theta=0} < \infty. \tag{8}$$

The reason that we do not present the transfer equation for substance 2 is explained in what follows.

The velocity field for Re > 80 is well described by a potential flow [3] (at least up to the separation point of the boundary layer)

$$u_r = -U\left(1 - \frac{R^3}{r^3}\right)\cos\theta, \quad u_\theta = U\left(1 + \frac{R^3}{2r^3}\right)\sin\theta. \tag{9}$$

It is necessary to determine the mass flow through the bubble surface.

Using the generally accepted boundary layer approximation, we shall neglect the diffusion transport in the direction of flow, the contribution to radial transport due to the term $(2/r)\partial C/\partial r$. In expressions (9), we shall retain only the first terms in the expansion in powers of $r - R$, setting

$$u_r = -\frac{3(r-R)}{R} U\cos\theta, \quad u_\theta = \frac{3}{2} U\sin\theta. \tag{10}$$

Let us introduce the following dimensionless variables:

$$\delta = \frac{r-R}{R}\sqrt{\frac{\mathrm{Pe}}{2}}, \quad \sigma = \frac{C}{B}, \quad \sigma' = \frac{C'}{B}, \quad \mathrm{Pe} = \frac{Ud}{\mathcal{D}},$$
$$\varkappa = \frac{Bkd^2}{4\mathcal{D}}. \tag{11}$$

Then, after a well-known substitution,

$$\xi = \delta\sin^2\theta, \quad \tau = \frac{4}{9} - \frac{2}{3}\cos\theta + \frac{2}{9}\cos^3\theta, \tag{12}$$

the problem (7), (8), and (10) is written in the form

$$\frac{\partial\sigma}{\partial\tau} - \frac{\partial^2\sigma}{\partial\xi^2} + \frac{\lambda}{\sin^4\theta}\sigma\sigma' = 0, \quad 0 \leqslant \xi < \infty, \quad 0 < \tau < 8/9, \tag{13}$$

$$\sigma|_{\xi=0} = \frac{A}{B}, \quad \sigma|_{\xi=\infty} = 0, \quad \left.\frac{\partial\sigma'}{\partial\xi}\right|_{\xi=0} = 0, \quad \sigma'|_{\xi=\infty} = 1,$$
$$\sigma|_{\tau=0} = 0, \quad \sigma'|_{\tau=0} = 1, \quad \lambda = 2\varkappa/\mathrm{Pe}. \tag{14}$$

Here θ is expressed in terms of τ with the help of Eqs. (12):

$$\sigma = \sigma_0 + \lambda\sigma_1 + \lambda^2\sigma_2 + \dots, \quad \sigma' = \sigma_0' + \lambda\sigma_1' + \lambda^2\sigma_2' + \dots,$$
$$q_s = q_0 + \lambda q_1 + \lambda^2 q_2 + \dots \tag{15}$$

In what follows, we will limit ourselves to determining the mass flux for the case of a slow reaction, when terms containing higher powers of λ, beginning with the second, can be neglected. Substituting (15) into (13) and (14) and equating the expressions for like powers of λ, we find

$$\sigma_0 = \frac{A}{B}\operatorname{erfc}\left(\frac{\xi}{2\sqrt{\tau}}\right), \quad -q_0 = D^{1/2}\frac{A}{B} = \frac{1}{\sqrt{\pi\tau}}\frac{A}{B}. \tag{16}$$

For σ_1, we have the problem

$$\frac{\partial\sigma_1}{\partial\tau} - \frac{\partial^2\sigma_1}{\partial\xi^2} + \frac{A}{B}\frac{1}{\sin^4\theta}\operatorname{erfc}\left(\frac{\xi}{2\sqrt{\tau}}\right), \quad 0 \leqslant \xi < \infty,\ 0 < \tau < 8/9, \tag{17}$$
$$\sigma_1|_{\xi=0} = 0, \quad \sigma_1|_{\xi=\infty} = 0, \quad \sigma_1|_{\tau=0} = 0.$$

It is evident that in order to find σ_1 it is not necessary to solve the diffusion equation for component 2, which would be necessary for determining σ_n, $n \geq 2$.

Calculating σ_1 from (17) with the help of the generally used methods is a very cumbersome operation. However, with the help of Eq. (6), it is easy to complete the solution. For q_1, we have the expresion

$$-q_1 = \frac{A}{B}\int_0^\infty \left[\frac{d}{d\tau}\int_0^\tau \frac{1}{\sin^4\vartheta}\operatorname{erfc}\left(\frac{\xi}{2\sqrt{\tau - z}}\right)\operatorname{erfc}\left(\frac{\xi}{2\sqrt{z}}\right)dz\right]d\xi.$$

Here, ϑ is a function of z, defined by Eq. (12), where it is necessary to carry out the formal substitution $\theta \to \vartheta$, $\tau \to z$.

Changing the order of integration and noting that

$$\int_0^\infty \operatorname{erfc}\alpha\xi\operatorname{erfc}\beta\xi\, d\xi = \frac{1}{\sqrt{\pi}}\,\frac{\alpha + \beta - \sqrt{\alpha^2 + \beta^2}}{\alpha\beta},$$

we obtain

$$-q_1 = \frac{A}{B}\frac{2}{\sqrt{\pi}}\frac{d}{d\tau}\int_0^\tau \frac{1}{\sin^4\vartheta}\left(\sqrt{z} + \sqrt{\tau - z} - \sqrt{\tau}\right)dz. \tag{18}$$

We find the total flux of matter through the bubble surface (integrating expressions (16) and (18) along the surface of the sphere taking into account $dz = (2/3)\sin^3\vartheta d\vartheta$), resulting from Eqs. (12) in the form

$$\mathrm{Sh} = \frac{3}{\sqrt{2\pi}}\sqrt{\mathrm{Pe}}\,[I(\varphi) + J(\varphi)\cdot\varkappa/\mathrm{Pe}],$$
$$I(\varphi) = \sqrt{\frac{4}{9} - \frac{2}{3}\cos\varphi + \frac{2}{9}\cos^3\varphi}, \tag{19}$$
$$J(\varphi) = \frac{4}{3}\int_0^\varphi \frac{1}{\sin^4\vartheta}\left[\left(\frac{4}{9} - \frac{2}{3}\cos\vartheta + \frac{2}{9}\cos^3\vartheta\right)^{1/2}\right.$$
$$\left. + \left(\frac{2}{3}\cos\vartheta - \frac{2}{3}\cos\varphi - \frac{2}{9}\cos^3\vartheta + \frac{2}{9}\cos^3\varphi\right)^{1/2} + \left(\frac{4}{9} - \frac{2}{3}\cos\varphi + \frac{2}{9}\cos^3\varphi\right)^{1/2}\right]d\vartheta.$$

Here $\mathrm{Sh} = F/2\pi R\mathcal{D}A$, $F = -2\pi R^2\mathcal{D}\int_0^\varphi (\partial C/\partial r)_{r=R}\sin\theta d\theta$.

We determined numerically the values $J(7\pi/12) \approx 0.56$; $J(2\pi/3) \approx 0.70$; $J(3\pi/4) \approx 0.88$. For a separationless flow ($\varphi = \pi$), the integral, after the substitution $\operatorname{tg}\vartheta/2 = z$ and subsequent elementary substitutions, can be computed exactly:

$$J(\pi) = \frac{16\sqrt{2}}{3\sqrt{3}}\left[1 - \frac{1}{\sqrt{3}} - \frac{1}{2\sqrt{3}}\ln\frac{\sqrt{3}+1}{2(\sqrt{3}-1)}\right] \approx 1.06.$$

For $\varkappa = 0$, we obtain from (19) the well-known expression in ([4], p. 69).

Equation (19) is useful for practical calculations, if $\lambda = 2\varkappa/\mathrm{Pe} = (d/2U)/(1/Bk) = t_{reg}/2t_{diem} < 0.3$.

For typical organic synthesis processes, where bubbling is used, $t_{reg} \approx 0.02$ sec and the condition of applicability is satisfied for $t_{diem} > 0.03$ sec.

From an analysis of the problem (13), it follows that for slow reactions, when only the linear term in the expansion with respect to λ is taken into account, Eq. (19) has the same form for a first-order reaction. It is only necessary to carry out the formal substitution for the quantity $\varkappa$, setting $Bk \to k'$ and $\varkappa \to k'd^2/4\mathcal{D}$.

NOTATION

Here a is a constant; A, concentration of substance 1 on the bubble surface; B, concentration of substance 2 far away from the bubble; C, concentration of substance 1; C', concentration of substance 2; D^{ν}, symbol for fractional differentiation; d, diameter of the bubble; F, total mass flux through the bubble surface; f, arbitrary function; I, J, functions of the angles of separation of the flow, entering into the solution; k, rate constant of the second-order reaction; k', rate constant of the first-order reaction; Q, source function of the substance; q_s, gradient of the dimensionless concentration at the boundary of the region; R, bubble radius; r, radial coordinate; t_{chem}, characteristic time of the chemical reaction; t_{reg}, characteristic time for regenerating the bubble surface; u_r, u_θ, radial and angular components of the fluid velocity; z, an integration variable; α, β, constants; δ, variable related linearly to the coordinate; η, integration variable; θ, ϑ, polar coordinates; $\varkappa$, dimensionless rate constant of the chemical reaction; σ, σ', dimensionless concentrations of components 1 and 2; ξ, τ, dimensionless coordinates; φ, angle of separation of the flow; Pe, Peclet number; Sh, Sherwood number; Re, Reynolds number. Indices: s, surface.

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DETERMINATION OF COEFFICIENT OF EXTERNAL MASS TRANSFER IN DRYING PROCESSES

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A method is proposed for determining the coefficient of external mass transfer from experimental curves of drying kinetics in porous materials. A comparison of results obtained by this method and by the method of moisture content measurements indicates a close agreement.

Important aspects of studying the mass transfer in systems with a solid phase are gathering of experimental data on the mass transfer coefficients, and related with it, development of methods of determining their dependence on the concentration of fluid substance in the porous body. The coefficient of external mass transfer, referred to the motive force in the solid phase, determines the intensity of transfer of the bounded substance from the surface of a capillary-porous body to the ambient medium during a drying process, and can be calculated from the relation

$$j = \beta_{\bar{u}} (u_s - u_e), \tag{1}$$

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