MACROKINETICS OF SURFACE REACTIONS IN A LIQUID OR GAS FLOW AND AN APPROXIMATE METHOD OF CALCULATING THE MASS-TRANSFER RATE OF THE REACTING PARTICLES

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A simple approximate formula is proposed for calculating the mass-transfer coefficient for a moving reactive particle, the surface of which is the site of a heterogeneous chemical reaction with arbitrary kinetics.

The most important mass-transfer characteristic in a chemically active disperse phase is the integral flow of the dispersion medium to a particle (drop) of the disperse phase averaged over the surface of the particle — the Sherwood number [1-12]. Here, it is assumed that the particle is reacting with the homogeneous phase. It turns out to be considerably simpler to calculate the integral flow of the reactant to the particle surface in limiting cases of purely diffusional and kinetic surface chemical reactions — when the concentration on the surface assumes a constant value — than in the general case of arbitrary kinetics. Such calculations have been performed for a whole series of special cases of hydrodynamic flow about a particle (e.g., [1-3, 13, 14]).

Proposed below is an approximate formula for calculating the mean value of the Sherwood number (integral flow) on the surface of a reacting particle in the case of arbitrary kinetics of the heterogeneous chemical reaction from the known value of integral flow corresponding to a diffusional reaction regime.

In an isothermal process, the distribution of concentration C in the flow of liquid (or gas) is determined by solving the equation of steady-state convective diffusion, with the boundary condition of constant concentration away from the particle and the following boundary condition on the active surface

$$(\mathbf{v}\nabla)\, c = \mathrm{Pe}^{-1}\Delta c; \quad c|_{r\to\infty} \to 1; \tag{1}$$

$$\left[\frac{\partial c}{\partial n} - kf(c)\right]_{r} = 0, \quad k = k' a D^{-1} C_{\infty}^{-1} \quad (f(0) = 0).$$

The equation and boundary conditions (1) are written in dimensionless form. It is assumed that the distribution of the velocity of the liquid **v** is known from the solution of the corresponding hydrodynamic problem of flow about a particle.

Many works (see [1-15], for example) previously examined the solution of problem (1) for certain specific types of surface-reaction kinetics, defined by the function f (in the general case or for the diffusional regime), or for particles of different shapes with different flow fields. However, the analysis of problem (1) turned out to be fairly complex even in the simplest limiting cases of large and small Peclét numbers [1-15], so that it is more expedient if approximate methods are used.

Certain methods of obtaining an approximate solution of problem (1) were proposed in [1]. The applicability of these methods was discussed in [1-4] in regard to specific examples. It was shown [1, 3] that the method of local equal access to the surface gives satisfactory results in certain cases. This method makes it possible to approximately determine the concentration on the particle surface by solving a certain transcendental equation.

In problems of the type being discussed, the characteristics that are usually of the most interest are the integral mass-transfer characteristics of mean Sherwood number Sh or

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dimensionless total diffusional flow I to the particle surface:

$$\mathrm{Sh} = IS^{-1}, \quad I = \int_{\Gamma} \frac{\partial c}{\partial n}\, d\Gamma, \quad S = \int_{\Gamma} d\Gamma. \tag{2}$$

Here S is the total (dimensionless) surface area of the particle Γ.

The (local) equal-surface-access method [1] does not offer a convenient algorithm for calculating the mean Sherwood number (or integral flow) (2). We therefore need simple formulas which will make it possible to approximately determine the integral characteristics (2) without resort to this approach.

It is proposed here that, as such an approximate method, the mean Sherwood number be calculated from the following algebraic equation:

$$\mathrm{Sh} = kf\left(1 - \frac{\mathrm{Sh}}{\mathrm{Sh}_d}\right), \tag{3}$$

where Sh_d is the mean Sherwood number for a particle reacting in the diffusional regime (i.e., under the condition of complete absorption of the dispersion medium on its surface: $c|_\Gamma = 0$). Further, it is assumed that Eq. (3) has a unique positive solution.

The origin of Eq. (3) can be explained on the basis of the following simple considerations. It follows from determination of the mean Sherwood number that

$$\mathrm{Sh} = kf(\langle c_s \rangle), \tag{4}$$

where $\langle c_s \rangle$ is a certain mean value of surface concentration. On the other hand, the relationship between the numbers Sh and Sh_d and the mean surface concentration $\langle c_s \rangle$ has the following obvious physical properties: the ratio $\mathrm{Sh}/\mathrm{Sh}_d$ monotonically decreases with an increase in $\langle c_s \rangle$; $\mathrm{Sh}/\mathrm{Sh}_d = 1$ when $\langle c_s \rangle = 0$ (diffusional regime); $\mathrm{Sh}/\mathrm{Sh}_d = 0$ when $\langle c_s \rangle = 1$ (kinetic regime). The simplest interpolational relation satisfying these conditions has the form

$$\mathrm{Sh} = (1 - \langle c_s \rangle)\, \mathrm{Sh}_d. \tag{5}$$

Excluding the unknown $\langle c_s \rangle$ from Eqs. (4) and (5), we obtain Eq. (3).

It should be noted that, in the special case of a first-order reaction, Eq. (3) reduces to the form

$$\frac{1}{\mathrm{Sh}} = \frac{1}{k} + \frac{1}{\mathrm{Sh}_d}, \tag{6}$$

i.e., it yields the rule of addition of the kinetic and diffusion resistances.

We checked the applicability of Eq. (4) in approximately determining the mean Sherwood number for several special characteristic cases for which exact or asymptotic solutions are available. Let us examine some of these cases.

1. With small Peclét numbers $\mathrm{Pe} \ll 1$ and small Reynolds numbers $\mathrm{Re} \ll 1$, the trinomial expression obtained by the method of combining asymptotic expansions in small Peclét numbers to find the mean Sherwood number in the case of a diffusion reaction on the surface of a solid spherical particle has the form [13]

$$\mathrm{Sh}_d = 1 + \frac{1}{2}\mathrm{Pe} + \frac{1}{2}\mathrm{Pe}^2 \ln \mathrm{Pe}.$$

Substituting this expression in Eq. (3) and expanding into a series in small Pe, we obtain

$$\mathrm{Sh} = q + \frac{1}{2} qq^* (\mathrm{Pe} + \mathrm{Pe}^2 \ln \mathrm{Pe}), \tag{7}$$

where q is the root of the equation

$$kf(1 - q) - q = 0; \quad q^* = k\lambda(1 + k\lambda)^{-1}, \quad \lambda = [\partial f/\partial c]_{c=1-q}.$$

A comparison of (7) with the formula from [8], obtained from analytic solution of problem (1) by the method of combining asymptotic expansions, shows that Eq. (3) gives the correct result for at least the first three terms of the asymptotic expansion of Sherwood numbers in small Peclét numbers for any values of the rate constant k and an arbitrary form of the function f [6, 8, 15].

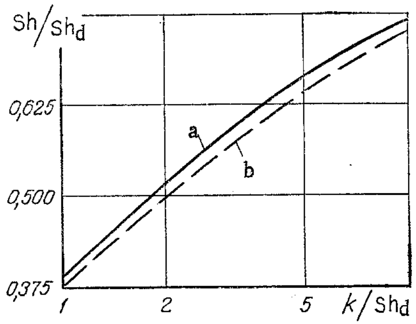

Fig. 1

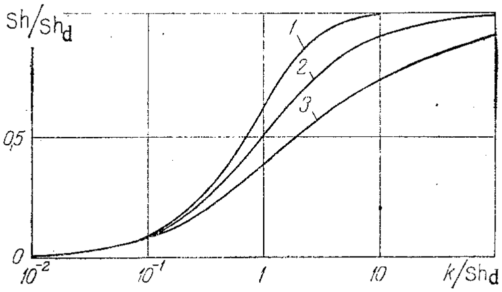

Fig. 2

Fig. 1. Comparison of exact [9-12] (a) and approximate (calculated in accordance with Eq. (3)) (b) values of the Sherwood number for a sample second-order reaction.

Fig. 2. Dependence of mean Sherwood number on reaction-rate constant: 1, 2, 3 correspond to surface reactions of orders 1/2, 1, and 2.

2. Given an arbitrary function f, Eq. (3) gives the correct asymptotic result in the limiting cases of large and small reaction-rate constants ($k \to 0$ and $k \to \infty$) for arbitrary Peclét numbers (see [8-11], for example).

3. In approximating the diffusion boundary layer for finite values of the rate constant k with a power law for the reaction $f(c) = c^n$ ($n = 1/2$, 1, 2), we checked the applicability of Eq. (3) by comparing its root Sh with exact results obtained for the Sherwood number by numerical solution of the corresponding integral equations with Stokes flow about a sphere [10, 11], drop (bubble) [12], and circular cylinder [9]. In these cases, the particle radius was chosen for the characteristic length scale a and the flow velocity away from the particle U for the characteristic flow velocity (for the drop and bubble, the characteristic velocity was the quantity $U(1+\beta)^{-1}$, where β is the ratio of the viscosities of the drop and surrounding liquid; $\beta = 0$ corresponds to a gas bubble). Figure 1 shows the results of the comparison of the exact [9-12] and approximate (3) Sherwood number values using the example of a second-order reaction. The maximum deviation of the root of Eq. (3) from the mean Sherwood number in [9-12] is seen at $k/\mathrm{Sh_d} \approx 1\text{-}10$ and does not exceed 6%.

4. To check the applicability of Eq. (3) for finite Peclét numbers, we used the numerical solutions obtained in [3] for the problem of mass transfer of a spherical particle in the case of a heterogeneous first-order chemical reaction on its surface ($f(c) = c$). It follows from the table on page 130 in [3] that in this case Eq. (4) ensures an accuracy to within 5%.

5. Equation (3) can also be used to calculate the convective heat and mass transfer of nonspherical particles. To this end, we first introduce the dimensionless form factor ξ in the following manner. As before, let a be a characteristic dimension of the particle (such as the radius of an equivalent sphere). Keeping the quantity a as a length scale while we determine the Sherwood number, we introduce the new scale $a\xi$ in determining the dimensionless rate constant of the chemical reaction, having needed to satisfy Eq. (3) for a particle at rest, i.e. (the corresponding quantities have been indicated with a zero subscript)

$$\mathrm{Sh}_0 = kf\left(1 - \frac{\mathrm{Sh}_0}{\mathrm{Sh}_{0d}}\right). \tag{8}$$

Taking Eq. (8) into account, we reduce Eq. (3) to the form

$$\mathrm{Sh} = \left[\mathrm{Sh}_0 \Big/ f\left(1 - \frac{\mathrm{Sh}_0}{\mathrm{Sh}_{0d}}\right)\right] f\left(1 - \frac{\mathrm{Sh}}{\mathrm{Sh_d}}\right). \tag{9}$$

Equation (9) allows us to easily calculate the Sherwood number for a moving reactive particle from known Sherwood numbers for a particle reacting in the diffusion regime ($\mathrm{Sh_d}$), for a stationary particle with assigned kinetics (Sh_0), and for a stationary particle in the diffusion regime (Sh_{0d}).

In particular, we obtain the following from (9) for a first-order reaction

$$\frac{1}{\mathrm{Sh}}=\frac{1}{\mathrm{Sh}_0}+\frac{1}{\mathrm{Sh}_d}-\frac{1}{\mathrm{Sh}_{0d}}. \tag{10}$$

To check the above procedure for calculating the convective mass transfer of particles of arbitrary form, let us examine an analytical solution of the problem in the case of a first-order surface reaction at small Peclét numbers obtained in [7] by the method of combining asymptotic expansions:

$$\mathrm{Sh}=\mathrm{Sh}_0+\frac{1}{2}\mathrm{Sh}_0^2\,\mathrm{Pe}+\frac{1}{2}\mathrm{Sh}_0^2 F\,\mathrm{Pe}^2\ln\mathrm{Pe}+O(\mathrm{Pe}^2). \tag{11}$$

Here F is the dimensionless drag associated with the particle at a given orientation in the flow (it is equal to the dimensional drag divided by the Stokes drag associated with a sphere of radius a, i.e., $6\pi\mu Ua$).

Using Eq. (11), we have the following, accurate to within terms of the order Pe^2

$$\frac{1}{\mathrm{Sh}}=\frac{1}{\mathrm{Sh}_0}-\frac{1}{2}\mathrm{Pe}-\frac{1}{2}F\,\mathrm{Pe}^2\ln\mathrm{Pe}=\frac{1}{\mathrm{Sh}_0}+\frac{1}{\mathrm{Sh}_d}-\frac{1}{\mathrm{Sh}_{0d}},$$

which agrees with (10).

Equation (4) is relatively simple in form and allows us to determine the Sherwood number from assigned reaction kinetics f. Equation (3) includes the auxiliary Sherwood number Sh_d, which has already been calculated by numerical or analytical methods for a large number of problems concerning the heat and mass transfer of isolated bodies (see [1-3], for example). Equation (3) can be used to calculate the heat and mass transfer of both solid and liquid particles enveloped by a liquid flow of arbitrary structure (either nonviscous or viscous, particularly Newtonian). When the value of Sh_d is unknown, it can be determined by solving the simpler corresponding problem (1) with a zero boundary condition on the particle surface: $c|_\Gamma=0$. A value of Sh_d obtained experimentally can also be used in Eq. (3).

If the principal terms of the asymptotic expansions for the auxiliary problem at small and large Peclét numbers $\mathrm{Sh}_d(0)$ (see [6-8, 13], for example) and $\mathrm{Sh}_d(\infty)$ [1-3] are known, then, in view of the properties $\mathrm{Sh}_d(0)\sim 1$ and $\mathrm{Sh}_d(\infty)\sim \mathrm{Pe}^{1/(n+1)}$ ($n=1$ for liquid particles and $n=2$ for solid particles), use of the following interpolational formula may be proposed for the auxiliary Sherwood number Sh_d in Eq. (3):

$$\mathrm{Sh}_d=\mathrm{Sh}_d(0)+\mathrm{Sh}_d(\infty). \tag{12}$$

As an example of the practical application of Eq. (3), we will use the results from [14] for a diffusion flow on the surface of a cylinder and sphere Sh_d, obtained on the assumption of large Reynolds and Peclét numbers. Separation of the hydrodynamic boundary layer occurs in both cases, the point of separation being approximately given by the same value of the angle $\theta_*\approx 1.83$ (105°) in each instance (the angle θ is reckoned from the point of inflow). We use Eq. (3) in these cases to obtain the mean Sherwood number in the region of intact (unseparated) flow $0\le\theta\le\theta_*$.

The auxiliary Sherwood number has the form [14]

$$\mathrm{Sh}_d=\lambda_\alpha\mathrm{Re}^{1/2}\mathrm{Pe}^{1/3},\quad \lambda_1=0.605,\quad \lambda_2=0.588, \tag{13}$$

where $\alpha=1$ corresponds to the cylinder and $\alpha=2$ corresponds to the sphere.

Substitution of (13) into Eq. (3) with an assigned reaction-rate constant k and surface-reaction kinetics f gives us the equation for the Sherwood number Sh. Figure 2 shows the dependence of the mean Sherwood number on the parameter k/Sh_d with a power relation for the surface-reaction rate $f(c)=c^n$.

The approximate equation (3), for a single concentration component, can be generalized to the case of a complex chemical reaction with an arbitrary number of components.

NOTATION

c, relative concentration; c_s, surface concentration; C_∞, concentration at infinity; D, diffusion coefficient; U, characteristic flow velocity; a, characteristic dimension of body; Γ, surface area of body; k', reaction-rate constant; $k = k' a D^{-1} C_\infty^{-1}$, dimensionless rate constant; $f = f(c)$, dependence of rate of chemical reaction on concentration of reactant close to surface; Re, Reynolds number; Pe, Peclét number; Sh, mean Sherwood number; Sh_d, mean Sherwood number under the condition of complete absorption; Sh_0, mean Sherwood number for a quiescent medium; n, normal to the particle surface Γ.

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