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CONVECTIVE DIFFUSION TO A SOLID PARTICLE IN THE CASE OF NONLINEAR KINETICS OF HETEROGENEOUS CHEMICAL REACTION

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Abstract—An approximate solution is obtained for a stationary problem of mass transfer between a moving solid spherical particle and a laminar gas flow at low finite Peclet and Reynolds numbers. The case of a chemical surface reaction which depends arbitrarily on reagent concentration at the particle surface is considered. The results obtained may be used, in particular, to determine the rate of mass transfer between a particle and a flow for the integral- and fractional-order reactions. The solution of the problem has been found by the method of matching outer and inner asymptotic expansions in the Peclet number. The concentration field has been determined. The dependence of the total reagent flow at the particle surface on the reaction kinetics, rate constant and the Peclet number has been obtained.

NOMENCLATURE

a,	particle radius;
U,	particle velocity;
D,	diffusivity;
ν,	kinematic viscosity of liquid;
k',	reaction rate constant;
κ,	reaction index;
w,	reaction rate;
f,	$= f(c)$, reaction law;
Pe,	$= aUD^{-1}$, Peclet number;
Re,	$= aU\nu^{-1}$, Reynolds number;
$c(\xi)$,	concentration (nondimensional);
c_0,	concentration of the incident flux;
Sc,	Schmidt number;
Sh,	Sherwood number;
I,	total diffusion flux;
ψ,	stream function;
r, θ,	spherical coordinates;
$\partial(\psi, \xi)/\partial(\tau, \mu)$,	Jacobian of the functions ψ and ξ;
ρ,	$= Pr$, external coordinate;
q,	root of equations (8), (24);
a_n, b_n, A_n,	constants;
Δ,	Laplacian operator;
q^*,	coefficient determined in (17).

INTRODUCTION

INVESTIGATION of convective diffusion to the surface of a reacting particle in a homogeneous flow of viscous fluid was the concern of a number of publications [1, 2] which considered the case of complete absorption of reagent by the particle surface as well as of the chemical first-order surface reaction [3, 4]. It is of interest to study the diffusion of reagent to a moving particle at the surface of which there is a chemical reaction the rate of which depends on the reagent concentration near the particle surface in a more complex, generally speaking arbitrary way. This type of problem occurs, for example, when studying reagent diffusion to a particle under the conditions of the reaction at the particle surface proceeding according to the Langmuir kinetics with mean filling of the surface [5]. Examples of the integral-order reactions are also generally known.

The paper considers stationary convective diffusion of a reacting substance to a solid spherical particle moving in a viscous gas. The particle is assumed to be small enough so that the Reynolds and Peclet numbers are low. Arbitrary conditions of the diffusing substance absorption are prescribed at the surface allowing an arbitrary-order chemical reaction on the surface to be considered as a special case.

For low finite (of the order of unity and smaller) Reynolds and Peclet numbers, the dependence of the total influx of reagent to a particle on the reaction rate constant, its order and the Reynolds and Peclet numbers is determined in a closed form. Several specific examples are considered.

STATEMENT OF THE PROBLEM

Consideration is given to convective diffusion of a reagent, dissolved in the flow, to the surface of a moving spherical particle. It is assumed that the Reynolds, $Re = aU\nu^{-1}$, and Peclet, $Pe = aUD^{-1}$, numbers are small [the Schmidt number for a gas $Sc = Pe/Re = O(1)$]. Here, a is the particle radius, U is its velocity, ν the kinematic velocity of the gas, and D is the diffusivity. The chemical reaction proceeds on its surface with the rate $w = k'f'(c_1)$, where k' is the reaction rate constant and c_1 is the reagent concentration near the surface. The function f' is determined by a mechanism of the surface reaction. Thus, for the κ-order reactions, $f'(c) = c^\kappa$. Of considerable interest are the fractional-order reactions. This kind of problem appears, for example, in the studies of reagent diffusion in the case when reaction on the particle surface proceeds according to the Langmuir kinetics with mean filling of the catalyst surface [5]. In this case κ is some effective order of reaction. As a practically important example we could cite a catalytic reaction between carbon and oxygen. In this case the order of the reaction is between a third and a half [6, 7].

The process of reagent transfer is governed by the convective diffusion equation and the boundary conditions which, in terms of the nondimensional variables, in the spherical coordinate system connected with the particle, have the form

$$\frac{Pe}{r^2}\frac{\partial(\psi,\xi)}{\partial(r,\mu)} = \Delta\xi,\ \xi = \frac{c_0-c}{c_0},\ \mu = \cos\theta;$$
$$r \to \infty,\ \xi \to 0;\ r = 1,\ \partial\xi/\partial r = kf(\xi-1);$$
$$f(\xi-1) = -f'(c). \qquad (1)$$

Here c_0 is the concentration far from the particle; the particle radius and gas velocity in the incident flux stand for the scales of the nondimensional variables; ψ is the dimensionless stream function determined at $Re < O(1)$ in [8]; $k' = kaD^{-1}$.

Let us examine the boundary-value problem (1) by the method of matched asymptotic expansions in terms of the Peclet number. For the limiting case of complete absorption an analogous analysis has been made in [2], while for the linear absorption law, in [3].

For the analysis to be performed, introduce the external coordinate $\rho = Pr$ and seek the solution in the form of inner and outer expansions

$$\xi_* = \sum_{n=0}^{\infty} \alpha_n(Pe)\xi_n(r,\mu),\ 1 \leqslant r < O(Pe^{-1}), \qquad (2)$$

$$\xi^* = \sum_{n=0}^{\infty} \alpha^{(n)}(Pe)\xi^{(n)}(r,\mu),\ O(Pe^{-1}) < r,$$

$$\alpha_0 = 1,\ \lim_{Pe\to 0}(\alpha_{n+1}/\alpha_n) = \lim_{Pe\to 0}(\alpha^{(n+1)}/\alpha^{(n)}) = 0. \qquad (3)$$

The inner expansion terms are determined successively by solving equation (1) with the boundary condition on the particle surface, the stream function being prescribed [8] by the expression

$$\psi_* = \tfrac{1}{4}(r-1)^2(1-\mu^2)$$
$$\times\left[\left(1+\frac{3}{8Sc}Pe+\frac{9}{40Sc^2}Pe^2\ln Pe\right)\times\left(2+\frac{1}{r}\right)\right.$$
$$\left.-\frac{3}{8Sc}Pe\left(2+\frac{1}{r}+\frac{1}{r^2}\right)\mu\right]+O(Pe^2). \qquad (4)$$

To determine the outer expansion terms, we have the problem

$$\Delta^*\xi^* = \frac{1}{\rho^2}\frac{\partial(\psi^*,\xi^*)}{\partial(\rho,\mu)};\ \xi^* \to 0,\ \rho \to \infty \qquad (5)$$

$$\psi^* = \tfrac{1}{2}\rho^2(1-\mu^2)-\tfrac{3}{2}ScPe(1+\mu)$$
$$\times\left[1-\exp\left(-\rho\frac{1-\mu}{2Sc}\right)\right]+O(Pe^2), \qquad (6)$$

where Δ^* is the Laplacian operator with respect to the variables ρ and μ. The unknown constants appearing in the process of solution are determined by matching solutions (2) and (3).

CONCENTRATION FIELD

We shall start the solution of problem (1) with determining the zero term of the outer expansion. It is evident that the trivial solution $\xi^{(0)} = 0$ satisfies equation (5).

To find the zero term of the inner expansion, it is necessary to solve equation (1) at $Pe = 0$ with the boundary condition at the particle surface and the condition of matching with the zero term of the outer expansion at $r \to \infty$. The solution of this problem is

$$\xi_0 = qr^{-1}, \qquad (7)$$

where q is the root of the equation

$$F(q) = kf(q-1)+q = 0. \qquad (8)$$

Henceforth it is assumed that equation (8) has a single root over the interval $(0, +\infty)$. For this to be the case, it is sufficient to impose the requirement, for example, that $f'_x \geqslant 0$, $x \geqslant -1$. In a particular case, for the linear law of absorption, $q = k/(k+1)$ [3].

Rewriting (7) in terms of the external variables yields $\alpha^{(1)} = Pe$. Taking this into account and substituting (2) into equations (5)–(6) we obtain the following problem to determine the first term of the outer expansion

$$\Delta^*\xi^{(1)} - \left(\mu\frac{\partial}{\partial\rho}+\frac{1-\mu^2}{\rho}\frac{\partial}{\partial\mu}\right)\xi^{(1)} = 0;$$
$$\xi^{(1)} \to 0,\quad \rho \to \infty. \qquad (9)$$

The general solution of equation (9) has the form

$$\xi^{(1)} = \exp(\tfrac{1}{2}\rho\mu)\left(\frac{\pi}{\rho}\right)^{1/2}\sum_{n=0}^{\infty} A_n K_{n+1/2}\left(\frac{\rho}{2}\right)Pe_n(\mu), \qquad (10)$$

where A_n are arbitrary constants, $Pe_n(\mu)$ the Legendre polynomials and

$$K_{n+1/2}\left(\frac{\rho}{2}\right) = \left(\frac{\pi}{\rho}\right)^{1/2}\exp\left(-\frac{\rho}{2}\right)\sum_{m=0}^{n}\frac{(n+m)!}{(n-m)!m!\rho^m} \qquad (11)$$

are the modified Bessel functions of the second kind.

The coefficients A_n are determined from the condition of matching the expression for $\xi^{(1)}$ with the first term of the inner expansion of (7). Letting ρ approach zero in (10), we obtain that the condition

$\lim_{r\to\infty}\xi_0(r,\mu) = \lim_{\rho\to 0}\xi^{(1)}(\rho,\mu)$ is satisfied at

$$A_0 = q/\pi,\quad A_n = 0;\quad n = 1, 2, \ldots.$$

Hence

$$\xi^{(1)} = \frac{q}{\rho}\exp[\tfrac{1}{2}\rho(\mu-1)]. \qquad (12)$$

Expression (12) written in internal variables shows that $\alpha_1 = Pe$. Therefore the first term of the inner expansion is described by

$$\Delta\xi_1 = -\frac{q}{r^2}\left(1-\frac{3}{2r}+\frac{1}{2r^3}\right)\mu \tag{13}$$

with the boundary condition at the surface of the particle

$$r = 1,\ \partial\xi_1/\partial r = k\lambda\xi_1;\ \lambda = [\partial f/\partial x]_{x=q-1}. \tag{14}$$

The general solution of the problem (13)–(14) has the form

$$\xi_1 = q\left(\frac{1}{2}-\frac{3}{4r}-\frac{1}{8r^3}\right)\mu + \sum_{n=0}^{\infty}(a_n r^n + b_n r^{-n-1})Pe_n(\mu), \tag{15}$$

where the constants a_n and b_n are determined respectively from

$$(1-k\lambda)a_1 + 3/8q(k\lambda+3) = (k\lambda+2)b_1;$$

$$(n-k\lambda)a_n = (k\lambda+n+1)b_n;\ n = 0,2,3,\ldots. \tag{16}$$

The final expression for the coefficients a_n and b_n is determined from the condition of matching the first terms of the inner (14) and outer (12) expansions. The matching yields

$$a_0 = -\frac{q}{2},\ b_0 = \frac{qq^*}{2},\ a_1 = 0,\ b_1 = \frac{3q}{8(k\lambda+2)},$$

$$a_n = b_n = 0,\ n = 2,3,\ldots;\ q^* = k\lambda(1+k\lambda)^{-1}. \tag{17}$$

Hence

$$\xi_1 = -\frac{q}{2}+\frac{qq^*}{2r}+q\left(\frac{1}{2}-\frac{3}{4r}+\frac{3}{8r}\frac{k\lambda+3}{k\lambda+2}-\frac{1}{8r^3}\right)\mu. \tag{18}$$

The second terms of the outer and inner expansions may be obtained in an analogous way [2–3], which leads to the following expression for the second term of the inner expansion

$$\xi_2 = \tfrac{1}{2}q(q^* r^{-1}-1). \tag{19}$$

DIFFUSION FLUX TO THE PARTICLE SURFACE

We shall characterize the influx of reagent to a particle by the mean Sherwood number

$$Sh = \frac{I}{4\pi a D c_0} = -\frac{1}{2}\int_{-1}^{+1}\left(\frac{\partial\xi_*}{\partial r}\right)_{r=1} d\mu. \tag{20}$$

Here I is the total diffusion flux. Substituting into (20) the available terms of the inner expansion, we obtain

$$Sh = q+\tfrac{1}{2}qq^*(Pe+Pe^2\ln Pe), \tag{21}$$

where q is the root of equation (8) and q^* is determined in (17).

Let us now specify the form of the function f and consider a particular case of the κ-order reaction

$$f(x) = -[-x]^{\kappa}. \tag{22}$$

This corresponds to the following boundary condition on the particle surface

$$r = 1,\ \partial\xi/\partial r = k(\xi^{\kappa}-1). \tag{23}$$

The equation for q in the case of the reaction law (22) acquires the form

$$F(q) = -k(1-q)^{\kappa}+q = 0. \tag{24}$$

Since $F(k,\kappa,0) < 0$ and $F(k,\kappa,1) > 0$, then the root always exists over the interval $(0,1)$, i.e. $0 < q(k,\kappa) < 1$, $F[k,\kappa,q(k,\kappa)] = 0$.

Let $\kappa_1 < \kappa_2$, while q_1 and q_2 are the roots of equation (24) respectively at κ_1 and κ_2 and at a fixed k. Then $q_2 < q_1$. This is proved by the inequality

$$F(k,\kappa_2,q_1) = -k(1-q_1)^{\kappa_2} + q_1 > -k(1-q_1)^{\kappa_1}+q_1 > 0.$$

From this it follows that with increase of the reaction law index, the Sherwood number will decrease.

Let now $k_1 < k_2$, while q_1 and q_2 be the roots of equation (24) respectively at k_1 and k_2 with κ being fixed. Then $q_1 < q_2$. This is proved with the aid of the inequality

$$F(k_2,\kappa,q_1) = -k_2(1-q_1)^{\kappa} + q_1 < -k_1(1-q_1)^{\kappa}+q_1 = 0.$$

Therefore, with increase in the reaction rate constant k, the Sherwood number increases. At $k \gg 1$, for the root of (24) we have

$$q(k) \approx 1-k^{-1/\kappa}.$$

For the linear law of absorption ($\kappa = 1$), $\lambda = 1$ and $q^* = q$, which leads to the result obtained in [3].

For the reaction law (22) the following formula holds for the total Sherwood number

$$Sh = q+\tfrac{1}{2}\frac{\kappa q^2}{1-q+\kappa q}(Pe+Pe^2\ln Pe). \tag{25}$$

Now, consider several examples.

For the second-order reaction the function $q(k)$ is represented by curve 1 in Fig. 1. For a heterogeneous reaction between carbon and oxygen proceeding on the carbon particle surface, we have $1/3 \leqslant \kappa \leqslant 1/2$ [6, 7]. Curves 2 and 3 illustrate the function $q(k)$ for $\kappa = 1/2$ and $\kappa = 1/3$, respectively. The dashed curve is given for the case of the first-order reaction [3].

The results obtained may be compared with those available for the large Peclet numbers [4]. The comparison shows the possibility for the results to be interpolated into the region of intermediate values of the Peclet number.

CONCLUSIONS

The results obtained in the present work make it possible to determine the total influx of substance to a particle moving in a gas for a wide class of surface reactions. In the case of the κ-order reaction, expression (25) has been obtained for the total Sherwood number. The diffusion flux is shown to decrease with increase in the order of reaction.

It should be noted that the results obtained are applicable for the analysis of heat and mass transfer of spherical particles moving in a gas only at small Peclet and Reynolds numbers. The solution may be used to calculate the heat flux to a moving particle in the fluid at low Reynolds numbers when the Prandtl

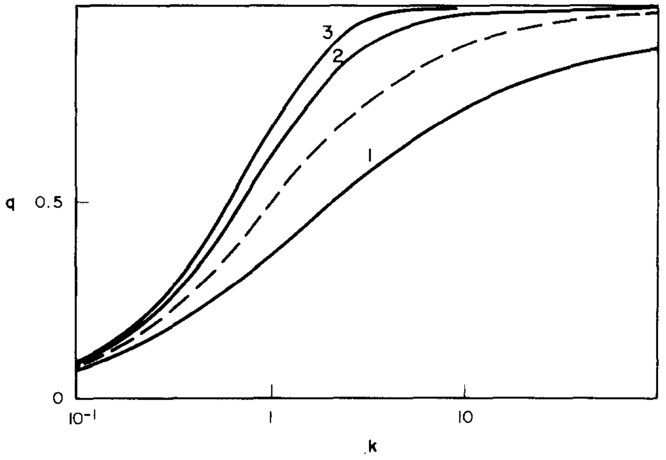

Fig. 1.

number is not large. In the analysis of heat transfer between a particle and the flow the results do not change on the diffusion coefficient being replaced by thermal diffusivity and the Sherwood number by the Nusselt number. The results retain their validity if the thermal effect of the surface reaction does not cause substantial expansion of a gas and considerable variations in thermal diffusivity.

REFERENCES

1. V. G. Levich, *Physicochemical Hydrodynamics*. Prentice Hall, Englewood Cliffs (1962).
2. P. L. Rimmer, Heat transfer from a sphere in a stream of small Reynolds number, *J. Fluid Mech.* **32**(1), 1–7 (1968).
3. Yu. P. Gupalo and Yu. S. Ryazantsev, Mass and heat transfer from a sphere in a laminar flow, *Chem. Engng Sci.* **27**(1), 61–68 (1972).
4. A. D. Polyanin and Yu. A. Sergeev, On diffusion to an absorbing particle with mixed kinetics, *Prikl. Mat. Mekh.* **41**(4), 667–677 (1977).
5. D. A. Frank-Kamenetsky, *Diffusion and Heat Conduction in Chemical Kinetics*. Nauka Press, Moscow (1967).
6. Z. Klibanova and D. Frank-Kamenetsky, Ignition of carbon and kinetics of its reaction with oxygen, *Acta Physicochim. U.S.S.R.* **18**(5), 387–405 (1943).
7. A. F. Semechkova and D. A. Frank-Kamenetsky, Recovering of dioxide by carbon, *Zh. Fiz. Khim.* **14**(3), 291–304 (1940).
8. I. Proudman and J. R. A. Pearson, Expansions at small Reynolds numbers for the flow past a sphere and a circular cylinder, *J. Fluid Mech.* **2**(3), 237–269 (1957).

CONVECTION PAR UNE PARTICULE SOLIDE DANS LE CAS D'UNE CINETIQUE NON LINEAIRE DE REACTION CHIMIQUE HETEROGENE

Résumé—Une solution approchée est obtenue pour le problème permanent du transfert de masse entre une particule solide et sphérique et un gaz en écoulement laminaire à faibles nombres de Péclet et de Reynolds. On considère le cas d'une réaction chimique en surface qui dépend arbitrairement de la concentration de réactant à la surface de la particule. Les résultats obtenus sont utilisés, en particulier, pour déterminer le flux massique entre particule et fluide pour des réactions d'ordre intégral ou fractionnel. La solution du problème est trouvée par la méthode des développements asymptotiques, interne et externe, en nombre de Péclet. Le champ de concentration est déterminé et on obtient la dépendance du flux total de réactant sur la surface de la particule à la cinétique de la réaction et au nombre de Péclet.

KONVEKTIVER STOFFTRANSPORT AN EIN FESTSTOFFPARTIKEL BEI NICHTLINEARER KINETIK HETEROGENER CHEMISCHER REAKTIONEN

Zusammenfassung—Für das stationäre Problem des Stoffaustausches zwischen einem sphärischen Partikel und einer laminaren Gasströmung wird eine Näherungslösung für kleine Peclet- und Reynolds-Zahlen erhalten. Dabei wird der Fall einer chemischen Oberflächenreaktion betrachtet, die unmittelbar von der Konzentration des reagierenden Stoffes an der Oberfläche der Teilchen abhängig ist. Die erhaltenen Ergebnisse können insbesondere dazu benutzt werden, das Maß des Stofftransports zwischen einem Teilchen und der Strömung bei vollständiger oder teilweise ablaufender Reaktion zu bestimmen. Die Lösung des Problems wurde durch ein Verfahren gefunden, bei welchem Reihenentwicklungen der inneren und äußeren Peclet-Zahl einander angepaßt werden. Das Konzentrationsfeld wurde bestimmt. Die Abhängigkeit der Reaktionskinetik vom gesamten reagierenden Stoffstrom, die Reaktionsrate und die Peclet-Zahl wurden erhalten.

КОНВЕКТИВНАЯ ДИФФУЗИЯ К ТВЕРДОЙ ЧАСТИЦЕ ПРИ НЕЛИНЕЙНОЙ КИНЕТИКЕ ГЕТЕРОГЕННОЙ ХИМИЧЕСКОЙ РЕАКЦИИ

Аннотация — Получено приближенное решение стационарной задачи массообмена движущейся твердой сферической частицы с ламинарным потоком газа при малых конечных числах Пекле и Рейнольдса. Рассмотрен случай поверхностной химической реакции, произвольным образом зависящей от концентрации реагента у поверхности частицы. Полученные результаты могут быть использованы в частности для определения скорости массообмена частицы с потоком в случаях реакций целого и дробного порядков. Решение задачи найдено при помощи метода сращивания внешнего и внутреннего асимптотических разложений по числу Пекле. Определено поле концентрации. Получена зависимость полного потока реагента на поверхность частицы от кинетики реакции, константы скорости и числа Пекле.