INFLUENCE OF FREE CONVECTION ON THE DIFFUSION CURRENT TO A SPHERE IN A LAMINAR FORCED FLOW REGIME

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The formulation and solution of a boundary value problem is presented, describing the influence of the free convective diffusion on the forced one to a sphere for a wide range of Rayleigh, *Ra*, and Peclet, *Pe*, numbers. It is assumed that both the free and forced convection are oriented in the same sense. Numerical results obtained by the method of finite differences were approximated by an empirical formula based on an analytically derived asymptotic expansion for $Pe \to \infty$. The concentration gradient at the surface and the total diffusion current calculated from the empirical formula agree with those obtained from the numerical solution within the limits of the estimated errors.

Diffusion plays an important role in many physico-chemical and chemical engineering problems. Its most general case in the liquid phase is convective diffusion, *i.e.* essentially transport of a dissolved substance in a streaming solution accompanied by molecular diffusion. Streaming can be either artificial, caused by an external force, or natural, due to density gradients in a field of gravity, causing the lighter parts of the solution to move upwards and the heavier downwards. Thus, we have to deal respectively with forced and free convection, both of which may in reality proceed at the same time. This combined case has been dealt with by several authors[1–4], although mainly experimentally and with an empirical mathematical description. The present paper deals with the influence of free on forced convection to a sphere under laminar flow regime in the cocurrent case.

Mathematical Formulation of the Problem

Convective diffusion in liquid phase is described by the following system of partial differential equations

$$\mathbf{v} \cdot \nabla c = D \, \Delta c \,, \tag{1a}$$

$$(\mathbf{v} \cdot \nabla) \mathbf{v} = \mathbf{F} - \varrho^{-1} \nabla p + \nu \, \Delta \mathbf{v} \,, \tag{1b}$$

$$\nabla \cdot \mathbf{v} = 0 \tag{1c}$$

with suitable boundary conditions (see below). Here, c denotes concentration of the diffusing substance, D its diffusion coefficient, $\mathbf{v}$ solution velocity vector, ϱ density of solution, ν its viscosity, $\mathbf{F}$ vector of external force acting upon the solution, and p pressure. The diffusion flux, Q, is given by grad c at the surface of the sphere. First we shall simplify the system ($1a-c$).

We shall use the coordinate system shown in Fig. 1. Arrows denote the direction of the forced flow characterized by velocity $\mathbf{v}$. It is convenient to introduce spherical coordinates r, φ, ϑ

$$\begin{aligned} x &= r \sin \vartheta \cos \varphi \\ y &= r \sin \vartheta \sin \varphi \\ z &= r \cos \varphi \, . \end{aligned} \tag{2}$$

It is appearent from Fig. 1 and equations (2) that the solution will be independent of the angle φ.

We assume that the only force acting upon the system is due to the acceleration of gravity $\mathbf{g}$. Hence,

$$F_x = 0 \, , \quad F_y = 0 \, , \quad F_z = -kg\varrho^{-1}(c - c_0) \, , \quad k = (\partial\varrho/\partial c)_{c=c_0}$$

or in spherical coordinates

$$F_r = -kg\varrho^{-1}(c - c_0) \cos \vartheta \, , \quad F_\varphi = 0 \, , \quad F_\vartheta = kg\varrho^{-1}(c - c_0) \sin \vartheta \, ,$$

where c_0 denotes concentration for $r \to \infty$. We assume that $c_0 > 0$, $k > 0$.

The continuity equation ($1c$) enables us to lower the number of unknown functions by one: the sought velocity components v_r and v_ϑ are replaced by the stream function

$$v_r = (1/r^2 \sin \vartheta) \, \partial\psi/\partial\vartheta \, , \quad v_\vartheta = -(1/r \sin \vartheta) \, \partial\psi/\partial r \, . \tag{3}$$

It can be shown that the velocity components (3) satisfy equation ($1c$) expressed in spherical coordinates. Pressure p in equation ($1b$) can be eliminated by simple rearrangement.

Further simplification can be achieved by introducing dimensionless variables y, C, Ψ and parameters Pe (Peclet number), Sc (Schmidt number) and Gr (Grashof number)

$$y = (r - a)/a \, , \quad C = c/c_0 \, , \quad \Psi = \psi/va \, . \tag{4}$$

$$Pe = av/D \, , \quad Sc = \nu/D \, , \quad Gr = kgc_0a^3/\varrho\nu^2 \, , \tag{5}$$

where a denotes radius of the sphere. Second powers of the stream function ψ in the transformed equations may be omitted, since they have a negligible influence on the concentration gradient. (This was proved by separate calculations.) Thus,

$$Sc(1 + y)^{-2} (1/\sin \vartheta) [(\partial C/\partial y) \partial \Psi/\partial \vartheta - (\partial C/\partial \vartheta) \partial \Psi/\partial y] = \partial^2 C/\partial y^2 + + 2(1 + y)^{-1} \partial C/\partial y + (1 + y)^{-2} \partial^2 C/\partial \vartheta^2 + \text{cotg}\, \vartheta (1 + y)^{-2} \partial C/\partial \vartheta \,, \quad (6a)$$

$$\Omega_y \Omega_y \Psi = Gr[(1 + y) \sin^2 \vartheta\, \partial C/\partial y + \sin \vartheta \cos \vartheta\, \partial C/\partial \vartheta] \,, \quad (6b)$$

where

$$\Omega_y = \partial^2/\partial y^2 + (1 + y)^{-2} \partial^2/\partial \vartheta^2 - \text{cotg}\, \vartheta (1 + y)^{-2} \partial/\partial \vartheta \,.$$

Free convection is characterized by the parameter Gr. If $Gr = 0$ in equation ($6b$), then equations ($6a$) and ($6c$)

$$\Omega_y \Omega_y \Psi = 0 \quad (6c)$$

describe the case of pure forced convection.

Let us assume that the functions C_1 and Ψ_1 satisfying the system of equations ($6a$,c) are known. We introduce new functions

$$C_2 = C - C_1 \,, \quad \Psi_2 = \Psi - \Psi_1 \,, \quad (7)$$

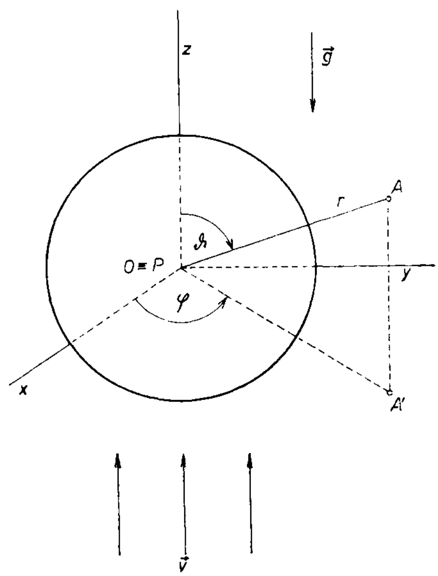

FIG. 1
Coordinate system used. Arrows denote direction of flow

which satisfy the following system of partial differential equations:

$$Sc(1+y)^{-2}(1/\sin\vartheta)\left[(\partial C_1/\partial y)\,\partial\Psi_2/\partial\vartheta + (\partial C_2/\partial y)\,\partial\Psi_1/\partial\vartheta + (\partial C_2/\partial y)\,\partial\Psi_2/\partial\vartheta - (\partial C_1/\partial\vartheta)\,\partial\Psi_2/\partial y - (\partial C_2/\partial\vartheta)\,\partial\Psi_1/\partial y - (\partial C_2/\partial\vartheta)\,\partial\Psi_2/\partial y\right] = \partial^2 C_2/\partial y^2 + 2(1+y)^{-1}\,\partial C_2/\partial y + (1+y)^{-2}\,\partial^2 C_2/\partial\vartheta^2 + \operatorname{cotg}\vartheta(1+y)^{-2}\,\partial C_2/\partial\vartheta\,, \tag{8a}$$

$$\Omega_y\Omega_y\Psi_2 - Gr\left[(1+y)\sin^2\vartheta\,\partial C_2/\partial y + \sin\vartheta\cos\vartheta\,\partial C_2/\partial\vartheta\right] = Gr\left[(1+y)\sin^2\vartheta\,\partial C_1/\partial y + \sin\vartheta\cos\vartheta\,\partial C_1/\partial\vartheta\right]. \tag{8b}$$

This system describes the influence of free convection on the forced one. We choose the following boundary conditions

$$C_2(0,\vartheta) = 0\,, \qquad \lim_{y\to\infty} C_2(y,\vartheta) = 0\,, \tag{9a}$$

$$\frac{\partial C_2}{\partial\vartheta}(y,0) = 0\,, \qquad \frac{\partial C_2}{\partial\vartheta}(y,\pi) = 0\,,$$

$$\Psi_2(0,\vartheta) = 0\,, \qquad \lim_{y\to\infty}\Psi_2(y,\vartheta) = 0\,, \tag{9b}$$

$$\Psi_2(y,0) = 0\,, \qquad \Psi_2(y,\pi) = 0\,,$$

$$\frac{\partial\Psi_2}{\partial y}(0,\vartheta) = 0\,, \qquad \lim_{y\to\infty}\frac{\partial\Psi_2}{\partial y}(y,\vartheta) = 0\,, \tag{9c}$$

$$\frac{\partial\Psi_2}{\partial\vartheta}(y,0) = 0\,, \qquad \frac{\partial\Psi_2}{\partial\vartheta}(y,\pi) = 0\,.$$

The functions C_1 and Ψ_1 were obtained by solving the problem for $Gr = 0$, *i.e.* pure forced convection[5].

For the numerical solution, it is convenient to introduce a new function Φ_2

$$\Phi_2(y,\vartheta) = Gr^{-1}(1+y)^{-2}\,\Psi_2(y,\vartheta) \tag{10}$$

and a new variable z

$$z = y/(1+y)\,, \quad \text{or} \quad y = z/(1-z)\,, \tag{11}$$

whereby the semiinfinite integration domain $(0,\infty)\times(0,\pi)$ is transformed to a finite one, $(0,1)\times(0,\pi)$. For simplicity, we shall use the following notation

$$C_2(y,\vartheta) = C_2\left(\frac{z}{1-z},\,\vartheta\right) = C(z,\vartheta)\,,$$

$$\Phi_2(y, \vartheta) = \Phi_2\left(\frac{z}{1-z}, \vartheta\right) = \Phi(z, \vartheta) .$$

Thus, we arrive at the following transformed system of partial differential equations:

$$\begin{aligned}
&(1-z)^3 \sin\vartheta\, \partial^2 C/\partial z^2 + (1-z)\sin\vartheta\, \partial^2 C/\partial\vartheta^2 + [2Pe\sin\vartheta\cos\vartheta\,.\\
&\quad .\,(\tfrac{1}{2}(1-z) - \tfrac{3}{4}(1-z)^2 + \tfrac{1}{4}(1-z)^4) - Ra(1-z)\,\partial\Phi/\partial\vartheta]\,\partial C/\partial z +\\
&\quad + [(1-z)\cos\vartheta - Pe\sin^2\vartheta(1 - \tfrac{3}{4}(1-z) - \tfrac{1}{4}(1-z)^3) + Ra(2\Phi +\\
&\quad + (1-z)\,\partial\Phi/\partial z)]\,\partial C/\partial\vartheta - Ra(1-z)\,\partial\Phi/\partial\vartheta\,\partial C_1/\partial z +\\
&\quad + Ra\,\partial C_1/\partial\vartheta(2\Phi + (1-z)\,\partial\Phi/\partial z) = 0 \qquad (12a)
\end{aligned}$$

$$\begin{aligned}
&(1-z)^6\,\partial^4\Phi/\partial z^4 + (1-z)^2\,\partial^4\Phi/\partial\vartheta^4 + 2(1-z)^4\,\partial^4\Phi/\partial z^2\,\partial\vartheta^2 -\\
&\quad - 4(1-z)^5\,\partial^3\Phi/\partial z^3 - 2\operatorname{cotg}\vartheta(1-z)^2\,\partial^3\Phi/\partial\vartheta^3 - 2\operatorname{cotg}\vartheta\,.\\
&\quad .\,(1-z)^4\,\partial^3\Phi/\partial z^2\,\partial\vartheta + (1-z)^2\,(1 + 3\sin^{-2}\vartheta)\,\partial^2\Phi/\partial\vartheta^2 -\\
&\quad - \operatorname{cotg}\vartheta(1-z)^2\,(2 + 3\sin^{-2}\vartheta)\,\partial\Phi/\partial\vartheta - (1-z)\sin^2\vartheta\,\partial C/\partial z -\\
&\quad - \sin\vartheta\cos\vartheta\,\partial C/\partial\vartheta = (1-z)\sin^2\vartheta\,\partial C_1/\partial z + \sin\vartheta\cos\vartheta\,\partial C_1/\partial\vartheta\,. \qquad (12b)
\end{aligned}$$

The boundary conditions are

$$C(0, \vartheta) = 0\,, \qquad C(1, \vartheta) = 0\,, \qquad (13a)$$
$$\frac{\partial C}{\partial\vartheta}(z, 0) = 0\,, \quad \frac{\partial C}{\partial\vartheta}(z, \pi) = 0\,,$$

$$\Phi(0, \vartheta) = 0\,, \qquad \Phi(1, \vartheta) = 0\,, \qquad (13b)$$
$$\Phi(z, 0) = 0\,, \qquad \Phi(z, \pi) = 0\,,$$

$$\frac{\partial\Phi}{\partial z}(0, \vartheta) = 0\,, \quad \frac{\partial\Phi}{\partial z}(1, \vartheta) = 0\,, \qquad (13c)$$
$$\frac{\partial\Phi}{\partial\vartheta}(z, 0) = 0\,, \quad \frac{\partial\Phi}{\partial\vartheta}(z, \pi) = 0\,.$$

The conditions (*13b,c*) are physically based on the solution of the hydrodynamic problem of a sphere in a streaming liquid[6,7].

Approximate Solution for $Pe \to \infty$

Our aim was to calculate the concentration gradient at the surface of the sphere;

the results for large values of *Pe* are of special interest in practice. Therefore, we attempted to find an asymptotical expansion for grad *C* at the surface for large *Pe* values and we have found one for $\vartheta = \pi$ (see Appendix)

$$\text{grad } C(0, \pi) = (Ra/Pe)(k_0 + k_1 Pe^{-1/3} + k_2 Ra\, Pe^{-4/3} + \ldots), \tag{14}$$

where

$$Ra = Gr\, Sc = kgc_0 a^3/(D\nu\varrho) \tag{15}$$

is the Rayleigh number. The coefficients $k_0, k_1, k_2, \ldots$ are difficult to express analytically; they were determined from numerical calculations. The first three terms of the expansion (*14*) were used in an empirical formula of the concentration gradient for $\vartheta \in \langle 0, \pi)$

$$\text{grad } C(0, \vartheta) = (Ra/Pe)\left[k_0(\vartheta) + k_1(\vartheta)\, Pe^{-1/3} + k_2(\vartheta)\, Ra\, Pe^{-4/3}\right] \tag{16}$$

leading to the total flux

$$Q = 4\pi a^2 c_0 D I, \tag{17}$$

where

$$I = \frac{1}{2}\int_0^{\pi} \text{grad } C(0, \vartheta) \sin \vartheta \, \mathrm{d}\vartheta = (Ra/Pe)\left[K_0 + K_1 Pe^{-1/3} + K_2 Ra\, Pe^{-4/3}\right]. \tag{18}$$

Numerical Solution

The system of equations (*12*) and (*13*) for functions *C* and Φ was solved by the finite-difference method. The partial differential equations (*12a,b*) with boundary conditions (*13*) thus gave a nonlinear system of difference equations which were solved by the Newton method. We arrived at a system of linear equations whose sparse matrix contained irregularly distributed nonzero elements, and it was solved by our modified method of Gupta and Tanji[8]. To keep the discretization error small, the coordinate grid was chosen rather dense, resulting in a very bulky system of equations. This could not be solved directly with regard to the capacity of the memory of the ICL 4-72 computer. Therefore, we used the following method: The solution was carried out in three stages corresponding to the domains

1) $z \in \langle 0, 1\rangle$, $\vartheta \in \langle 0, \pi\rangle$,

2) $z \in \langle 0, \frac{1}{2}\rangle$, $\vartheta \in \langle 0, \pi\rangle$,

3) $z \in \langle 0, \frac{1}{4}\rangle$, $\vartheta \in \langle 0, \pi\rangle$.

The intervals of the *z* variable were shortened as indicated to make the grid spacing gradually finer and to minimize the error in the calculation of grad C at the surface. In the second and third stages, it was necessary to determine the boundary conditions for $z = 1/2$ or $1/4$, $\vartheta \in \langle 0, \pi \rangle$. We chose them as the boundary conditions of the first order by fixing the function values at the nodes of the newly formed part of the boundary. The prescribed values of C and Φ were obtained by calculation in the preceding stages.

Each of the boundary value problems was in each stage replaced by two boundary value problems on overlapping rectangles (Fig. 2):

$$\text{Rectangle A} \quad \langle 0, z_1 \rangle \times \langle 0, \pi \rangle ,$$
$$\text{rectangle B} \quad \langle z_0 - z_1, z_0 \rangle \times \langle 0, \pi \rangle ,$$

where $z_0 = 1$ (first stage), $\frac{1}{2}$ (second stage), and $\frac{1}{4}$ (third stage). Further, we used the following "external iteration": For given approximate values of C and Φ at the nodes of the basic rectangle $\langle 0, z_0 \rangle \times \langle 0, \pi \rangle$

a) the boundary value problem is solved on rectangle A with boundary conditions (*13*) except for $z = z_1$, $\vartheta \in \langle 0, \pi \rangle$, where the boundary conditions are defined by given values which are fixed.

b) In further step, the analogous problem is solved on rectangle B and the boundary conditions on the abscissa $z = z_0 - z_1$, $\vartheta \in \langle 0, \pi \rangle$ are given by the values of the functions C and Φ calculated in the preceding step.

Thus, an iteration step of the external iteration cycle is finished. In the "internal iteration", *i.e.* in solving the boundary value problems, 4–5 steps of the Newton method were used in most cases.

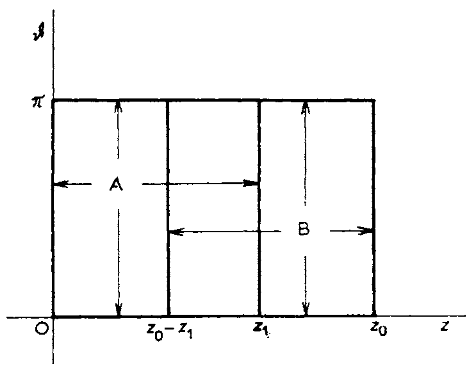

FIG. 2
Subdomains *A* and *B* for the solution of the boundary value problem

In every step of the external iteration cycle, in each of the three stages, the values calculated in the preceding step were used as starting approximation for the internal iteration on the rectangle (except for intersection A $\cap$ B in solving the problem on rectangle B). Values calculated in step *a*) were used on A $\cap$ B in step *b*). Values obtained in preceding stage were supplemented by interpolated values at new nodes when passing to the subsequent stage. At the beginning of the first stage, C and Φ were set equal to zero as starting approximation.

It would be very difficult to prove the convergence of the given iteration procedure which is based on the known principle of maximum and minimum of the solution of boundary value problems given by partial differential equations of the elliptic type. The convergence was tested numerically and the rough estimates were substantiated.

RESULTS AND DISCUSSION

Approximate values of grad C were calculated as

$$(\mathrm{grad}\ C)_j = \tfrac{1}{6}h^{-1}(-11C_{0j} + 18C_{1j} - 9C_{2j} + 2C_{3j}) + O(h^3)\,, \qquad (19)$$

where h is the grid spacing and C_{ij} denotes approximate value of the concentration at the grid point (i, j) calculated as above. The calculated values of grad C are given in Table I for selected values of ϑ, Pe and Ra. The values of Pe were chosen with respect to our preceding work[5] and Eq. (*16*), those of Ra are related to our other work[9].

The data in Table I are in accord with physical expectation. For ϑ close to 180° (Fig. 1), the diffusion flux is increased by free convection, since the rate of streaming to the surface is higher. With decreasing ϑ the influence of free convection increases up to a maximum at about 90° and then decreases so that for small values of ϑ the free convection has a negative effect on the diffusion currrent. This is because the value of grad C is lowered by the streaming from the surface.

The values of grad C obtained by numerical solution of equations (*12*) and (*13*) (denoted as $(\mathrm{grad}\ C)_n$ in the text below) were used for the determination of the coefficients $k_0(\vartheta)$, $k_1(\vartheta)$ and $k_2(\vartheta)$ in Eq. (*16*). This empirical formula can be rewritten as

$$W(\vartheta) = (Pe/Ra)\,\mathrm{grad}\ C(0, \vartheta) = k_0(\vartheta) + k_1(\vartheta)\,Pe^{-1/3} + k_2(\vartheta)\,Ra\,Pe^{-4/3}\,. \qquad (20)$$

If $W(\vartheta)$ is calculated from $(\mathrm{grad}\ C)_n$, it turns out that the influence of the last term in Eq. (*20*) is small and for $Ra = 16$ it is quite negligible. This was made use of in the calculation of $k_0(\vartheta)$ and $k_1(\vartheta)$ from the approximate formula for $Ra = 16$

$$W(\vartheta) \approx k_0(\vartheta) + k_1(\vartheta)\,Pe^{-1/3}$$

by the least squares method. Further, Eq. (20) implies that

$$k_2(\vartheta) = Ra^{-1}[Pe^{4/3}(W(\vartheta) - k_0(\vartheta)) - Pe\, k_1(\vartheta)]\,. \tag{21}$$

TABLE I

Values of $(\text{grad } C)_n$ calculated from the numerical solution

ϑ^0	Ra	grad C		
		$Pe = 512$	$Pe = 1\,000$	$Pe = 1\,728$
0	16	−0·01609	−0·01079	−0·00688
	81	−0·08308	−0·05741	−0·03706
	256	−0·25895	−0·18436	−0·12025
	625	−0·59215	−0·43406	−0·28724
30	16	−0·00477	−0·00311	−0·00153
	81	−0·02479	−0·01746	−0·00905
	256	−0·07092	−0·05583	−0·03020
	625	−0·11605	−0·11912	−0·06856
60	16	0·00712	0·00416	0·00308
	81	0·03605	0·02048	0·01527
	256	0·11948	0·06488	0·04770
	625	0·32881	0·16633	0·11716
90	16	0·01031	0·00579	0·00389
	81	0·05230	0·02925	0·01980
	256	0·16755	0·09252	0·06247
	625	0·42417	0·22683	0·15100
120	16	0·00944	0·00518	0·00336
	81	0·04787	0·02630	0·01722
	256	0·15198	0·08309	0·05444
	625	0·37659	0·20155	0·13105
150	16	0·00719	0·00385	0·00236
	81	0·03635	0·01950	0·01205
	256	0·11486	0·06139	0·03803
	625	0·28241	0·14848	0·09151
180	16	0·00480	0·00246	0·00138
	81	0·02412	0·01233	0·00693
	256	0·07579	0·03857	0·02172
	625	0·18540	0·09324	0·05238

Using the calculated values of k_0 and k_1, we found k_2 from this equation for $Ra = 256$ and 625 (denoted as $k_2(\vartheta)_{256}$ and $k_2(\vartheta)_{625}$), since at these Ra values the last term in Eq. (*16*) is especially significant. This was done for all Pe values used, since the last term in Eq. (*16*) is actually the residual of an asymptotic expansion analogous to the expansion (*14*) and may therefore depend on Pe. The coefficient $k_2(\vartheta)$ in the formula (*16*) was then calculated as the weighted average

$$k_2(\vartheta) = [256k_2(\vartheta)_{256} + 625k_2(\vartheta)_{625}]/(256 + 625)\,.$$

The coefficients $k_0(\vartheta)$, $k_1(\vartheta)$ and $k_2(\vartheta)$ thus obtained were used to calculate grad $C(0, \vartheta)$ from Eq. (*16*), which is denoted as (grad $C)_e$. The results are given in Table II; the per cent deviation is given as

$$p = 100\,\frac{(\text{grad } C)_e - (\text{grad } C)_n}{(\text{grad } C)_n}\,.$$

It is seen that the empirical formula (*16*) is a good approximation except for small angles ϑ.

The coefficients K_0, K_1 and K_2 in Eq. (*18*) were calculated as the above coefficients by using numerically calculated values of I, denoted as I_n. We obtained

$$K_0 = 0{\cdot}3907\,, \quad K_1 = -1{\cdot}506\,.$$

In Table III are given the values of K_2, I_n, I calculated from Eq. (*18*) and denoted as I_e, and the per cent deviation

$$q = 100\,\frac{I_e - I_n}{I_n}\,.$$

A comparison of these results with our preceding work[5] reveals that the contribution of free convection to the total diffusion current for $Pe = Ra$ amounts to 3–4% in the region of Pe values considered.

In conclusion, we present a discussion of possible errors in the calculation of grad C from Eq. (*19*). These are as follows: *a*) Transfer of the discretization error of C_{ij} due to replacement of the differential equations by difference equations. *b*) Transfer of errors of C_{ij} values arising in the internal iteration by Newton's method. *c*) Transfer of errors of C_{ij} due to the external iteration. *d*) Transfer of errors of C_{ij} due to the use of approximate values of C and Φ for $z = 1/4$ in the third stage. *e*) Discretization error $O(h)^3$ in Eq. (*19*). A detailed analysis revealed that the values of grad C are subject practically only to the discretization error (*a*) and to the boundary error (*d*), the other errors being negligible. The upper estimates of the above errors for $Ra = 81$ and given Pe values are summarized in Table IV.

APPENDIX

Approximation of the Diffusion Equation

The functions C_2 and Ψ_2 (Eq. (*8a*)) can in the proximity of the sphere surface be expressed in the form of power series

$$C_2(y, \vartheta) = a_0(\vartheta) + a_1(\vartheta)\, y + a_2(\vartheta)\, y^2 + \ldots \tag{A1}$$

$$\Psi_2(y, \vartheta) = A_0(\vartheta) + A_1(\vartheta)\, y + A_2(\vartheta)\, y^2 + \ldots \tag{A2}$$

From the boundary conditions (*9a–c*) follows

$$a_0(\vartheta) = A_0(\vartheta) = A_1(\vartheta) = 0\,, \quad \vartheta \in \langle 0, \pi \rangle\,.$$

Coefficient a_1 in Eq. (*A1*) is obviously equal to the concentration gradient at the surface of the sphere. We introduce

$$u = a_1(\vartheta)\, y \tag{A3}$$

and set for convenience

$$C(u, \vartheta) = C_2(u/a_1(\vartheta), \vartheta)\,, \quad \Psi(u, \vartheta) = \Psi_2(u/a_1(\vartheta), \vartheta)\,.$$

Equation (*8a*) then takes the form

$$\begin{aligned}
&(1 + u/a_1(\vartheta))^{-2}\,(1/\sin\vartheta)\, Sc[(\partial C_1/\partial y)\,(a'_1(\vartheta)\, u/a_1(\vartheta))\, \partial\Psi/\partial u + \\
&+ \partial\Psi/\partial\vartheta + a_1(\vartheta)\,(\partial\Psi_1/\partial\vartheta)\, \partial C/\partial u + a_1(\vartheta)\,(\partial C/\partial u)\, \partial\Psi/\partial\vartheta - \\
&- a_1(\vartheta)\,(\partial C_1/\partial\vartheta)\, \partial\Psi/\partial u - (\partial\Psi_1/\partial y)\,(a'_1(\vartheta)\, u/a_1(\vartheta))\, \partial C/\partial u + \\
&+ \partial C/\partial\vartheta - a_1(\vartheta)\,(\partial C/\partial\vartheta)\, \partial\Psi/\partial u] = a_1^2(\vartheta)\, \partial^2 C/\partial u^2 + \\
&+ (1 + u/a_1(\vartheta))^{-2}\, [(a'_1(\vartheta)\, u/a_1(\vartheta))^2\, \partial^2 C/\partial u^2 + \partial^2 C/\partial\vartheta^2 + \\
&+ (2a'_1(\vartheta)\, u/a_1(\vartheta))\, \partial^2 C/\partial u\, \partial\vartheta + (a''_1(\vartheta)\, u/a_1(\vartheta))\, \partial C/\partial u] + \\
&+ 2(1 + u/a_1(\vartheta))^{-1}\, a_1(\vartheta)\, \partial C/\partial u + (1 + u/a_1(\vartheta))^{-2} \times \\
&\times \operatorname{cotg}\vartheta(a'_1(\vartheta)\, u/a_1(\vartheta))\, \partial C/\partial u + \partial C/\partial\vartheta)\,.
\end{aligned} \tag{A4}$$

Equations (*A1–3*) give

$$C(u, \vartheta) = u + (a_2(\vartheta)/a_1^2(\vartheta))\, u^2 + \ldots \tag{A5}$$

$$\Psi(u, \vartheta) = (A_2(\vartheta)/a_1^2(\vartheta))\, u^2 + \ldots \tag{A6}$$

The function C_1 and its derivatives can be expressed analogously as

$$C_1(y, \vartheta) = b_1(\vartheta)\, y + b_2(\vartheta)\, y^2 + \ldots$$

$$\frac{\partial C_1}{\partial y} = b_1(\vartheta) + 2b_2(\vartheta)\, y + \ldots = b_1(\vartheta) + (2b_2(\vartheta)/a_1(\vartheta))\, u + \ldots \tag{A7}$$

$$\frac{\partial C_1}{\partial\vartheta} = b'_1(\vartheta)\, y + \ldots = (b'_1(\vartheta)/a_1(\vartheta))\, u + \ldots \tag{A8}$$

TABLE II

Coefficients in Eq. (*16*), (grad $C)_e$, and percent deviation p

ϑ^0	Ra	k_0	k_1	$Pe = 512$			$Pe = 1\,000$			$Pe = 1\,728$		
				k_2	(grad $C)_e$	p	k_2	(grad $C)_e$	p	k_2	(grad $C)_e$	p
0	16	−1·1981	5·391	0·211	−0·0164	1·7	−1·098	−0·0106	−2·0	−2·546	−0·0070	1·1
	81				−0·0823	−1·0		−0·0541	−5·8		−0·0356	−4·0
	256				−0·2555	−1·3		−0·1759	−4·6		−0·1156	−3·9
	625				−0·6006	1·4		−0·4335	−0·1		−0·2986	4·0
30	16	−0·1904	0·188	0·450	−0·0052	8·3	−0·743	−0·0028	−11·2	−1·034	−0·0016	6·3
	81				−0·0250	0·8		−0·0144	−17·6		−0·0084	−7·4
	256				−0·0694	−2·2		−0·0488	−12·6		−0·0278	−7·9
	625				−0·1199	3·3		−0·1363	14·4		−0·0745	8·6
60	16	0·5434	−2·628	0·365	0·0068	−5·1	−0·473	0·0045	7·7	−0·070	0·0030	−2·6
	81				0·0351	−2·5		0·0224	9·5		0·0152	−0·5
	256				0·1189	−0·5		0·0687	5·9		0·0479	0·5
	625				0·3303	0·5		0·1569	− 5·7		0·1166	−0·5

90	16	0·6009	−2·243	0·193	0·0100	−2·6	−0·328	0·0060	4·0	0·262	0·0038	−1·4
	81				0·0513	−1·9		0·0303	3·5		0·0195	−1·7
	256				0·1663	−0·8		0·0943	1·9		0·0618	−1·1
	625				0·4272	0·7		0·2226	−1·9		0·1526	1·1
120	16	0·4855	−1·517	0·096	0·0093	−1·9	−0·233	0·0053	3·0	0·275	0·0033	−1·1
	81				0·0471	−1·6		0·0269	2·2		0·0169	−1·9
	256				0·1510	−0·7		0·0839	1·0		0·0537	−1·3
	625				0·3791	0·7		0·1995	−1·0		0·1329	1·4
150	16	0·3049	−0·613	0·021	0·0071	−0·7	−0·111	0·0039	1·1	0·049	0·0024	−0·5
	81				0·0362	−0·5		0·0197	0·8		0·0119	−1·2
	256				0·1148	−0·1		0·0616	0·4		0·0377	−0·9
	625				0·2826	0·1		0·1479	−0·4		0·0923	0·9
180	16	0·1388	0·129	−0·030	0·0048	0·7	−0·041	0·0024	−1·4	−0·182	0·0014	0·5
	81				0·0244	1·2		0·0123	−0·5		0·0070	0·7
	256				0·0765	1·0		0·0386	0·0		0·0218	0·5
	625				0·1835	−1·0		0·0932	0·0		0·0521	−0·5

By using equations (3), (4), and the so-called Stokes velocity components[6]

$$v_r = v\cos\vartheta[1 - \tfrac{3}{2}(1+y)^{-1} + \tfrac{1}{2}(1+y)^{-3}],$$
$$v_\vartheta = -v\sin\vartheta[1 - \tfrac{3}{4}(1+y)^{-1} - \tfrac{1}{4}(1+y)^{-3}]$$

we express the derivatives of the function Ψ_1 as

$$\frac{\partial\Psi_1}{\partial y} = Re(1+y)\sin^2\vartheta(\tfrac{3}{2}y + \ldots) = \tfrac{3}{2}Re\sin^2\vartheta u/a_1(\vartheta) + \ldots \qquad (A9)$$

TABLE III
Values of I given by Eq. (18)

Pe	Ra	K_2	I_n	I_e	q
512	16	0·217	0·00661	0·00635	−3·84
	81		0·03338	0·03271	−2·02
	256		0·10848	0·10800	−0·44
	625		0·28656	0·28755	0·35
1 000	16	−0·371	0·00361	0·00383	6·06
	81		0·01790	0·01920	7·29
	256		0·05647	0·05903	4·54
	625		0·14185	0·13557	−4·43
1 728	16	−0·052	0·00251	0·00246	−2·18
	81		0·01251	0·01242	−0·71
	256		0·03915	0·03919	0·11
	625		0·09549	0·09535	−0·14

TABLE IV
Upper estimates of the errors

Pe	Upper estimate of error, %				
	(a)	(b)	(c)	(d)	(e)
512	0·9	0·002	0·18	0·75	0·20
1 000	1·9	0·002	0·18	0·75	0·25
1 728	3·0	0·002	0·28	1·25	0·30

$$\frac{\partial \Psi_1}{\partial \vartheta} = Re(1 + y)^2 \sin \vartheta \cos \vartheta(\tfrac{3}{2}y^2 + \ldots) = \tfrac{3}{2}Re \sin \vartheta \cos \vartheta u^2/a_1^2(\vartheta) + \ldots, \quad (A10)$$

where $Re = av/\nu$. If the expansions (*A7*–*10*) and the derivatives of the power series (*A5*) and (*A6*) are substituted into Eq. (*A4*) and only the terms with the lowest powers of u are left on each side, we obtain the differential equation

$$a_1^2(\vartheta)\,\partial^2 C/\partial u^2 + M(u, \vartheta)\,\partial C/\partial u = N(u, \vartheta)\,, \quad (A11)$$

where

$$M(u, \vartheta) = 2a_1(\vartheta)\,(1 + u/a_1(\vartheta))^{-1} + (a_1'(\vartheta)\,u/a_1(\vartheta)) \times$$
$$\times\,(1 + u/a_1(\vartheta))^{-2}\,(1/\sin \vartheta)\,Sc\,\partial \Psi_1/\partial y - a_1(\vartheta)\,(1 + u/a_1(\vartheta))^{-2} \times$$
$$\times\,(Sc/\sin \vartheta)\,(\partial \Psi_1/\partial \vartheta + \partial \Psi/\partial \vartheta)\,,$$
$$N(u, \vartheta) = (1 + u/a_1(\vartheta))^{-2}\,(Sc/\sin \vartheta)\,[-a_1(\vartheta)\,(\partial C_1/\partial \vartheta)\,\partial \Psi/\partial u +$$
$$+\,(\partial C_1/\partial y)\,(a_1'(\vartheta)\,u/a_1(\vartheta))\,\partial \Psi/\partial u + \partial \Psi/\partial \vartheta]\,.$$

Equation (*A11*) can be treated as an ordinary differential equation of the second order for the function $C = C(u, \vartheta)$ with ϑ as parameter. It is satisfied in the proximity of the sphere surface as a good approximation. Since the changes of the functions C and Ψ are most profound in the mentioned region, it can be expected that Eq. (*A11*) is a satisfactory approximation in the entire region under consideration and that the concentration gradient at the surface of the sphere can be calculated from its solution with a good accuracy.

Calculation of $a_1(\pi)$

Equations (*A11*) and (*A5*) yield simply

$$C(u, \vartheta) = I_1(u) + I_2(u) \quad (A12)$$

with

$$I_1(u) = \int_0^u \exp\left\{-\int_0^w [M(t, \vartheta)/a_1^2(\vartheta)]\,dt\right\} dw\,,$$

$$I_2(u) = \int_0^u \left\{\exp\left[-\int_0^w (M(t, \vartheta)/a_1^2(\vartheta))\,dt\right] \int_0^w [N(t, \vartheta)/a_1^2(\vartheta)] \times \right.$$
$$\left. \times \exp\left[\int_0^t (M(\tau, \vartheta)/a_1^2(\vartheta))\,d\tau\right] dt\right\} dw\,.$$

Further we denote

$$I_k = \lim_{u \to \infty} I_k(u)\,, \quad k = 1, 2\,.$$

From the second one of the conditions (*9a*) we obtain

$$\lim_{u \to \infty} C(u, \vartheta) = 0\,,$$

hence Eq. (*A12*) for $u \to \infty$ takes the form

$$I_1 = -I_2 \,. \tag{A13}$$

This is a differential equation for the function a_1 occurring in the expansion (*A1*) and giving the gradient of the concentration C_2 at the surface of the sphere. Equation (*A13*), however, involves also unknown functions $\partial\Psi/\partial u$ and $\partial\Psi/\partial\vartheta$ in addition to a_1 and a'_1. For this reason, it is not suitable for even an approximate calculation of a_1. Nevertheless, we shall show that an asymptotical expansion of $a_1(\pi)$ for $Pe \to \infty$ can be obtained on the basis of some data about the course of $\partial\Psi/\partial u$ and $\partial\Psi/\partial\vartheta$.

To obtain the necessary data about Ψ, we introduce the expansions (*A1*), (*A2*), (*A7*), and (*A8*) into Eq. (*8b*) and compare the multipliers standing before the powers of y. Thus,

$$4!\, A_4(\vartheta) + 4A''_2(\vartheta) - 4A'_2(\vartheta)\operatorname{cotg}\vartheta = Gr\sin^2\vartheta(a_1(\vartheta) + b_1(\vartheta)) \,. \tag{A14}$$

In calculating the integrals I_1 and I_2, it is convenient to use the substitution (*11*)

$$z = y/(1 + y)\,, \quad y = z/(1 - z)\,, \quad z \in \langle 0, 1) \,. \tag{A15}$$

The expansion (*A2*) then takes the form

$$\Psi_2\left(\frac{z}{1 - z}, \vartheta\right) = A_0(\vartheta) + A_1(\vartheta)\frac{z}{1 - z} + A_2(\vartheta)\frac{z^2}{(1 - z)^2} + \ldots =$$
$$= B_0(\vartheta) + B_1(\vartheta)\, z + B_2(\vartheta)\, z^2 + B_3(\vartheta)\, z^3 + B_4(\vartheta)\, z^4 + \ldots,$$

where $B_0 = B_1 = 0$ owing to the boundary conditions. By comparing both infinite series after expanding the terms $(1 - z)^{-k}$, we obtain

$$A_2 = B_2\,, \quad A_3 = B_3 - 2B_2\,, \quad A_4 = B_4 - 3B_3 + 3B_2 \,.$$

By substituting into Eq. (*A14*) and rearranging we obtain

$$4!\left(\frac{B_4(\vartheta)}{Gr\sin\vartheta} - 3\,\frac{B_3(\vartheta)}{Gr\sin\vartheta} + 3\,\frac{B_2(\vartheta)}{Gr\sin\vartheta}\right) + 4\,\frac{B''_2(\vartheta)}{Gr\sin\vartheta} - 4\,\frac{B'_2(\vartheta)}{Gr\sin\vartheta}\operatorname{cotg}\vartheta =$$
$$= (a_1(\vartheta) + b_1(\vartheta))\sin\vartheta \,. \tag{A16}$$

Analysis of numerical results revealed that the equations

$$\lim_{\vartheta\to\pi-}\frac{B_2(\vartheta)}{Gr\sin\vartheta} = \lim_{\vartheta\to\pi-}\frac{B_3(\vartheta)}{Gr\sin\vartheta} = 0\,, \tag{A17}$$

$$B'_2(\vartheta)/Gr\sin\vartheta \approx \alpha\, Pe^{-1/3}\,, \tag{A18}$$

$$B'_3(\vartheta)/Gr\sin\vartheta \approx \beta\,, \tag{A19}$$

where $\vartheta \approx \pi$ and α, β are constants, can be considered as very good approximations. Thus,

$$B_4(\vartheta) \approx \frac{Gr}{24}\left(a_1(\vartheta) + b_1(\vartheta)\right)\sin^2\vartheta\,, \tag{A20}$$

$$B_4'(\vartheta)/Gr\sin\vartheta \approx 24^{-1}\left(a_1'(\vartheta) + b_1'(\vartheta)\right)\sin\vartheta + \\ + 12^{-1}\left(a_1(\vartheta) + b_1(\vartheta)\right)\cos\vartheta\,,\quad \vartheta \approx \pi\,. \tag{A21}$$

The following substitutions are used in calculating the integral I_1:

$$z = \left(u/a_1(\vartheta)\right)/\left(1 + u/a_1(\vartheta)\right),$$
$$x = \left(w/a_1(\vartheta)\right)/\left(1 + w/a_1(\vartheta)\right),$$
$$x\gamma = s\,,\quad \gamma^3 = \tfrac{1}{2}Pe\left(a_1'(\vartheta)\sin\vartheta/a_1(\vartheta) - \cos\vartheta\right).$$

With the aid of the Taylor series, we thus arrive at the result

$$I_1 \approx \gamma^{-1}a_1(\vartheta)\int_0^\gamma \exp\left(-s^3\right)\{1 + (Ra/Gr)\,(1/\sin\vartheta)\left[B_2'(\vartheta)\,s^3/3\gamma^3 + \right. \\ \left. + B_3'(\vartheta)\,s^4/4\gamma^4 + B_4'(\vartheta)\,s^5/5\gamma^5\right] - \left(a_1'(\vartheta)/a_1(\vartheta)\right)\left[\tfrac{2}{3}B_2(\vartheta)\,s^3/\gamma^3 + \right. \\ \left. + \tfrac{3}{4}B_3(\vartheta)\,s^4/\gamma^4 + \tfrac{4}{5}B_4(\vartheta)\,s^5/\gamma^5\right] - \tfrac{1}{2}Pe\left[9a_1'(\vartheta)\sin\vartheta s^4/8a_1(\vartheta)\,\gamma^4 - \right. \\ \left. - \tfrac{5}{4}\cos\vartheta s^4/\gamma^4\right]\}\,\mathrm{d}s\,.$$

For sufficiently high values of Pe and γ, considering equations (*A17–21*), we obtain the following approximate formula for I_1 valid for ϑ equal to or slightly less than π:

$$I_1 \approx \left(a_1(\vartheta)\,E_0/\gamma\right)\left[1 + \left(Ra/E_0Gr\sin\vartheta\right)\left(B_2'(\vartheta)\,E_3/3\gamma^3 + \right.\right. \\ \left.\left. + B_3'(\vartheta)\,E_4/4\gamma^4 + B_4'(\vartheta)\,E_5/5\gamma^5\right) + 5Pe\,E_4\cos\vartheta/8\gamma^4\right].$$

Here, E_n is defined for nonnegative integer n as

$$E_n = \int_0^\infty s^n \exp\left(-s^3\right)\mathrm{d}s\,.$$

Similarly, the integral I_2 can be approximated as

$$I_2 \approx \left(Ra/E_0\right)\left[B_2'(\vartheta)\,E_3/(3Gr\sin\vartheta\delta^3) + B_3'(\vartheta)\,E_4/(4Gr\sin\vartheta\delta^4) + \right. \\ \left. + B_4'(\vartheta)\,E_5\cos\vartheta/5\delta^5\right],$$

where

$$\delta^3 = \tfrac{1}{2}Pe\left(b_1'(\vartheta)\sin\vartheta/b_1(\vartheta) - \cos\vartheta\right).$$

A formula for $a_1(\pi)$ in the form of Eq. (*14*) can then be derived from Eq. (*A13*) by using the above approximate expressions for I_1 and I_2.

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