CONVECTIVE DIFFUSION TO A SLOWLY ROTATING SPHERICAL ELECTRODE; THE EFFECT OF AXIAL DIFFUSION IN THE BULK LIQUID FOR Re < 10, Pe > 10

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A complete mathematical model has been solved of the steady axially symmetric convective diffusion toward the surface of a spherical electrode of radius R rotating at an angular velocity Ω under the creeping flow conditions $Re \equiv \Omega R^2 \varrho/\eta < 10$ and $Pe \equiv \Omega^2 R^4 \varrho/(12 D\eta) > 10$ by the the method of singular perturbations. For $Pe > 300$ the effect of axial diffusion has been found entirely negligible; for $10 < Pe < 300$ it causes an increase of local transfer coefficients by 1—10%. For $Pe < 10$ the applied asymptotic method of solution, assuming $Pe \gg 1$ is no longer applicable.

Rotating spherical electrode, working under the creeping flow regime, *i.e.* at very low values of the Reynolds numbers, has been utilized recently for accurate measurements of diffusivity in high viscosity solutions[1-3]. Corresponding theory[2,4] of convective diffusion, for the case when the working electrode is an arbitrary axially symmetric segment of the surface of a rotating sphere, has been elaborated so far only under various simplifications typical for the theory of the concentration boundary layer. In the work[2] this problem was attacked by neglecting longitudinal diffusion and by linear approximation of the velocity field in the proximity of the electrode surface. This solution shall be referred to in the following as the CBL approximation. The work[4] also neglects longitudinal diffusion but the analysis takes into account complete description of the meridional components of the velocity field pertaining to the rotating sphere in an unconfined liquid and under the creeping flow regime. Solution[4] shall be referred as IS (improved similarity) approximation. For the case that the whole surface is the working electrode, the IS approximation leads to an exact description of the convective diffusion, not only for the asymptotic case of the concentration boundary layer, *i.e.* for $Pe \to \infty$, but also for the asymptotic case of pure diffusion free of the convective effects, $Pe \to 0$. Nevertheless, a mere qualitative analysis of the complete mathematical model of the convective diffusion under the given conditions clearly shows that in the region of intermediate Pe numbers the effects of the longitudinal diffusion, which had been neglected in the IS approximation, may be fairly large. The aim of the presented paper is to analyse the effect of the longitudinal diffusion under the conditions $Pe \gg 1$ when the character of the existing convective-diffusional processes does not differ from the conditions given by the CBL conditions. The analysis is limited to the case when the whole surface of the rotating sphere is maintained at constant concentration of the depolarizer and when the effect of the longitudinal diffusion thus manifests only at a greater distance from the surface of the sphere.

The employed method of singular perturbations leads to a simultaneous set of onedimensional boundary value problems of the boundary layer type. In the solution of this set it turned out useful to combine the analytical and numerical approach.

FORMULATION OF THE PROBLEM

The velocity field for the axially symmetric flow of a Newtonian fluid of density ϱ and viscosity η, around a sphere of radius R rotating at a constant angular velocity Ω under the creeping flow regime, $Re \to 0$, may be expressed in spherical coordinates (r, θ, φ), where $\theta = 0$ represents the axis of symmetry, as follows[5–7]:

$$v_r = -U_M[3\xi^2(1 - \xi)^2 (1 - x^2/2) + O(Re^2)] , \tag{1a}$$

$$v_\theta = U_M[3\xi^3(1 - \xi) x \sqrt{(1 - x^2)} + O(Re^2)] , \tag{1b}$$

$$v_\varphi = \Omega R[3\xi^2 x + O(Re^2)] , \tag{1c}$$

where $\xi = R/r$, $x = \sin \theta$. A more detailed hydrodynamic analysis[8] shows that an asymptotic description of the velocity field by the above equations is sufficiently accurate for practical purposes for $Re < 5 \div 10$.

Under axially symmetric concentration conditions at the boundaries of the examined system, the azimutal velocity component v_φ has no effect on the course of the convective diffusion. Its description thus reduces to a twodimensional elliptic partial differential equation. Let us write it down in the form

$$\mathscr{L}[C] = (B - y)^{-2} \mathscr{M}_D[C] , \tag{2}$$

where the operator

$$\mathscr{L}[C] = \partial^2_{yy}C - 3[(1 - x^2)\, yx\, \partial_x C - (1 - \tfrac{1}{2}x^2)\, y^2\, \partial_y C] \tag{3a}$$

characterizes the convection and radial diffusion while the operator

$$\mathscr{M}_D[C] = (1 - x^2)\, \partial^2_{xx}C + (x^{-1} - 2x)\, \partial_x C \tag{3b}$$

represents the effect of longitudinal diffusion, neglected in the previous analyses[2,4].

The meridional variable $x = \sin \theta$, instead of the angular variable, θ, has been selected because the polynomial expansions of the meridional dependences, in the following taken in the form $\sum a_i x^i$, converge faster than those in the form $\sum a_i^* \theta^i$. The radial variable in the form $y = B(1 - \xi)$, with $B = Pe^{1/3}$, has been taken because for $B \gg 1$ the concentration field in the form $C(y, x)$ near the surface of the sphere, $y \ll B$, is practically independent of B. In the chosen normalization of the concentration field (see the list of symbols) the boundary conditions on the surface of the sphere, $y = 0$, and at infinity, $y = B$, take the following form

$$C = F(B) \quad \text{for} \quad y = 0 \tag{4a}$$

$$C = 0 \quad \text{for} \quad y = B\,. \tag{4b}$$

The function $F(p)$, for an arbitrary $p \geqq 0$, is defined by the integral[2,4,9]

$$F(p) = \int_0^p \exp\left(-s^3\right) \mathrm{d}s\,. \tag{5}$$

The boundary conditions considered for the elliptic problem must be supplemented by the conditions of symmetry with respect to the axis $x = 0$ and with respect to the equator plane $x = 1$, *e.g.* in the form

$$\partial_x C = 0 \quad \text{for} \quad x = 0\,, \quad \text{resp.} \quad x = 1\,. \tag{4c,d}$$

Local diffusional fluxes on the surface of the sphere, $y = 0$, are expressed, for the given normalization, as

$$Sh = Sh(x) = \frac{R}{c_\infty - c_0}\, \partial_r c \bigg|_{r=R} = \frac{B}{F(B)} \left(-\partial_y C|_{y=0}\right). \tag{6}$$

Solution of the above formulated boundary value problem shall be sought in the form of an functional expansion of the type

$$C = \exp\left(-y^3\right) \sum_{k=0,2,4,\dots} x^k H_k(y)\,, \tag{7}$$

where due to the symmetry of the problem with respect to the axis, $C(-x, y) = C(x, y)$, we summ up only over even values of the summation index ($k = 0, 2, 4, 6, \dots$). Substitution of this expansion into the differential equation (2) leads to an infinite linear system of differential equations for the functions $\{H_k\}$:

$$\mathscr{K}_k[H_k] - \mathscr{R}_{k-2}[H_{k-2}] = (B - y)^{-2}\, q_k[H_k, H_{k+2}]\,. \qquad (8)$$

For arbitrary functions G, H and for $k = 0, 2, 4, 6, \ldots$ we have here

$$q_k[G, H] = k(k + 1)\, G + (k + 2)^2\, H\,, \qquad (9a)$$

$$\mathscr{K}_k[H] = \frac{d^2H}{dy^2} - 3y^2\frac{dH}{dy} - 3(k + 2)\, yH\,, \qquad (9b)$$

$$\mathscr{R}_k[H] = 9/2y^2\left(\frac{dH}{dy} - 3y^2H\right) - 3kyH\,. \qquad (9c)$$

For $k = 0$ we have in Eq. (8) $\mathscr{R}_{-2} = 0$.

The boundary conditions, according to (4a,b) change to

$$H_0(0) = F(B)\,, \quad H_0(B) = 0 \qquad (10a)$$

$$H_k(0) = 0\,, \qquad H_k(B) = 0\,, \quad k = 2, 4, 6, \ldots \qquad (10b)$$

The condition (4c) is satisfied indentically by the choice of the expansion (7) into the even powers x^k. The condition (4d) requires satisfaction of the non-trivial functional identity

$$\sum k\, H_k(y) = 0 \quad \text{for} \quad y \in (0; B)\,. \qquad (11)$$

The profile of local diffusional fluxes in the normalization (6) is given by

$$Sh(x) = \frac{B}{F(B)} \sum_{k=0,2,4,\ldots} x^k(-H'_k(0))\,. \qquad (12)$$

It is obvious that the set (8) cannot be solved successively, term by term, as in the equation for K_k appears, apart from the known H_{k-2}, also the unknown H_{k+2} function. The infinite set of differential equations (8) is completed by the supplementary condition (11). Nevertheless, in the following we shall prove that for $B = \infty$ there exist simple asymptotic solutions of this set, represented by a series of the functions $\{A_k\}$. About this set one can find then a perturbation expansion of the type

$$H_k(y) = A_k(y) + \sum_{j=2,3,4,\ldots} B^{-j}\, \psi^j_k(y)\,, \quad B \gg 1\,, \qquad (13)$$

where $\psi_k^j(y)$ are functions independent of the parameter B. These functions can be determined already by the term-by-term integration of the corresponding infinite set of differential equations. This circumstance shall be made use of, on the one hand, for an explicit asymptotic analytical expression of the local diffusional fluxes, and, on the other hand, for the analysis of accuracy of the direct numerical solutions of the set (8).

BASIS FOR PERTURBATION

Already the earlier mentioned CBL and IS approximations[2,4] represent certain asymptotic solutions of the problem under consideration for $B \gg 1$. The CBL approximation is a result of the common application of the Lighthill–Acrivos transformation for the axially symmetric case[10,11]:

$$C_A(x, y) = F(\infty) - F(y\,G(x))\,. \tag{14}$$

The IS approximation is then an improvement of the former[4] for finite values of B:

$$C_A^*(x, y) = F(B) - \frac{F(B)\,F(y\,G(x))}{F(B\,G(x))}\,. \tag{15}$$

The function $G(x)$ is the principal parameter of the Lighthill–Acrivos transformation[10,11]. It may be found as an integral of the differential equation

$$(1 - x^2)\,x\,G' = (1 - 3/2x^2 - G^3)\,G \tag{16}$$

in the form of the following quadrature

$$G(x) = x(1 - x^2)^{1/4}\left[3\int_0^x (1 - t^2)^{-1/4}\,t^2\,\mathrm{d}t\right]^{-1/3} \tag{17}$$

or, for $x < 1$, in the form of the series

$$G(x) = -\sum_{k=0,2,4,\ldots} a_k x^k\,, \tag{18}$$

where

$$\begin{aligned} a_0 &= -1 \\ a_2 &= 3/10 \qquad a_4 = 69/700 \\ a_6 &= 1\,151/21\,000 \qquad a_8 = 210\,951/5\,390\,000 \\ a_{10} &= 22\,405\,974/700\,700\,00\ \ldots \end{aligned} \tag{19}$$

In the region $B > 2$, $x < 0{\cdot}9$ there is no apparent difference between both approximations. The IS approximation $C \approx C_A^*$, satisfies identically the two boundary conditions (*4a,b*) and the parabolic differential equation $\mathscr{L}[C] = 0$ with a small error of the order ε_B, $\mathscr{L}[C_A^*] = 0(\varepsilon_B)$. The CBL approximation, $C \approx C_A$ in contrast, satisfies the differential equation $\mathscr{L}[C] = 0$ identically, the boundary condition at infinity, $y = B$, however, merely with an error of the already mentioned order ε_B.

The CBL and IS approximations of the concentration field may be expressed as power expansions analogous to (7).
These expansions

$$\exp(y^3)\, C_A(x, y) = \sum_{k=0,2,4,\ldots} x^k A_k(y) \tag{20a}$$

$$\exp(y^3)\, C_A^*(x, y) = \sum_{k=0,2,4,\ldots} x^k A_k^*(y) \tag{20b}$$

define the series of functions $\{A_k\}$, $\{A_k^*\}$. In the following we shall study the relationship of these two series of the functions to a series $\{H_k\}$, representing the exact solution for $B \gg 1$ by an asymptotic expansion (7) of the problem studied.

An explicit expression of the functions A_k^*, A_k can be found by an expansion of the functions $C_A^*(x, y)$ or $C_A(x, y)$ into the Taylor series for a fixed y:

$$\begin{aligned}
A_0^*(y) &= \exp(y^3)\,[F(B) - F(y)] \\
A_2^*(y) &= a_2 E_1 \\
A_4^*(y) &= a_4 E_1 - a_2^2 E_2 \\
A_6^*(y) &= a_6 E_1 - 2a_2 a_4 E_2 + a_2^3 E_3 \\
A_8^*(y) &= a_8 E_1 - (2a_2 a_6 + a_4^2)\, E_2 + 3a_2^2 a_4 E_3 - a_2^4 E_4\,. \\
&\vdots
\end{aligned} \tag{21}$$

The functions $E_m = E_m(y)$ are defined recurrently by the set

$$\begin{aligned}
E_1 &= \alpha_1 - \beta_1 \alpha_0 \\
E_2 &= \alpha_2 - \beta_1 E_1 - \beta_2 \alpha_0 \\
E_3 &= \alpha_3 - \beta_1 E_2 - \beta_2 E_1 - \beta_3 \alpha_0 \\
E_4 &= \alpha_4 - \beta_1 E_3 - \beta_2 E_2 - \beta_3 E_1 - \beta_4 \alpha_0\,. \\
&\vdots
\end{aligned} \tag{22}$$

Here, the functions α_0, $\alpha_m = \alpha_m(y)$, $\beta_m = \beta_m(B)$, $(m = 1, 2, 3, \ldots)$ are the coefficients of the Taylor expansions of the functions $\exp(y^3)\, F(y(1 + \zeta))$ and $F(B(1 + \zeta))/F(B)$

with respect to the variable ζ:

$$\alpha_m(y) = \frac{\exp(y^3)\,y^m}{m!}\frac{d^m F(y)}{dy^m}, \tag{23}$$

$$\beta_m(B) = \alpha_m(B)/\alpha_0(B). \tag{24}$$

Particularly

$$\begin{aligned} \alpha_0(y) &= \exp(y^3)\,F(y) \\ \alpha_1(y) &= y \\ \alpha_2(y) &= -3/2y^4 \\ \alpha_3(y) &= -y^4 + 3/2y^7 \\ \alpha_4(y) &= -1/4y^4 + 9/4y^7 - 9/8y^{10}. \\ &\vdots \end{aligned} \tag{25}$$

From (24) and (25) it is apparent that for $B \to \infty$ we have $\beta_m(B) \to 0$:

$$\beta_m(B) = 0(B^{3m-2}\exp(-B^3)). \tag{26}$$

The derivatives of the functions A_0^*, A_k^* in the origin, $y = 0$, are given, according to (21)–(25), by the relations

$$\begin{aligned} A_0^{*\prime}(0) &= -1 \\ A_2^{*\prime}(0) &= a_2\gamma_1 \\ A_4^{*\prime}(0) &= a_4\gamma_1 - a_2^2\gamma_2 \\ A_6^{*\prime}(0) &= a_6\gamma_1 - 2a_2a_4\gamma_2 + a_2^3\gamma_3 \\ A_8^{*\prime}(0) &= a_8\gamma_1 - (2a_2a_6 + a_4^2)\gamma_2 + 3a_2^2a_4\gamma_3 - a_2^4\gamma_4, \\ &\vdots \end{aligned} \tag{27}$$

where $\gamma_m = E_m'(0)$ are the derivatives of the functions $E_m(y)$ in the point $y = 0$. As a special case

$$\begin{aligned} \gamma_1 &= 1 - \beta_1 \\ \gamma_2 &= -\beta_1\gamma_1 - \beta_2 \\ \gamma_3 &= -\beta_1\gamma_2 - \beta_2\gamma_1 - \beta_3 \\ \gamma_4 &= -\beta_1\gamma_3 - \beta_2\gamma_2 - \beta_3\gamma_1 - \beta_4. \\ &\vdots \end{aligned} \tag{28}$$

The functions $A_k(y)$ are special cases of the functions $A_k^*(y)$ for $B = \infty$, where we have the identity $E_m = \alpha_m(y)$, as, according to (*24*) one can write $\beta_m = 0$ for $B = \infty$. As a special case

$$A_0'(0) = -1, \quad A_k'(0) = a_k, \quad k = 2, 4, 6, \ldots \tag{29}$$

The course of the functions A_0^*, A_2^*, A_4^* for several selected values of the parameter B is shown graphically in Figs 1*a*,*b*,*c* together with the corresponding asymptotic courses of the functions A_k for $B = \infty$. From these figures it is apparent that for $B > 2$ the difference between A_k^* and corresponding A_k is very small. Only in the close proximity of the boundary point, $y \to B$, the individual functions A_k^* for finite B separate from the course for $B = \infty$ and drop sharply to zero at the point $y = B$.

This qualitative finding may be expressed quantitatively by the following asymptotic estimates for $y \ll B$, $B \to \infty$:

$$(A_k - A_k^*) = O(\omega_k), \quad (A_k' - A_k^{*\prime}) = O(\omega_k), \tag{30a,b}$$

where

$$\omega_k = B^{1.5k-2} \exp\left(-B^3\right). \tag{31}$$

Putting the right hand sides in equation (*8*) equal zero means, in the physical interpretation, neglecting the effect of longitudinal diffusion. Corresponding system of the differential equations (*8*) with zero right hand sides and with the boundary conditions (*10a*,*b*) is satisfied for finite values of B by neither A_k nor A_k^*. Although the functions A_k identically satisfy the set of differential equations

$$\mathscr{K}_k[A_k] - \mathscr{R}_{k-2}[A_{k-2}] = 0 \tag{32}$$

they do not satisfy the boundary conditions (*10b*). On the contrary, the functions A_k^* satisfy the boundary conditions $A_k^*(B) = 0$, but do not satisfy the differential equations (*32*). It can be shown that both mentioned deviations are of the same order

$$\mathscr{K}_k[A_k^*] - \mathscr{R}_{k-2}[A_{k-2}^*] = O(\omega_k), \quad A_k(B) = O(\omega_k), \tag{33a,b}$$

see also the estimates (*35a*,*b*).

Nevertheless, both A_k^* and A_k represent the asymptotes of the sought solution H_k, since in the asymptotic sense they satisfy for $B \to \infty$ both the differential equations (*8*) and the boundary conditions (*10a*,*b*). The problem of the asymptotic fulfilment of the boundary conditions for $B \gg 1$ and their effect on the course of the global solution is examined in more detail in the Appendix. Since for $y \ll B$, $B \gg 1$ the following estimates clearly hold

$$(B - y)^{-2} q_k[A_k, A_{k+2}] = 0(B^{-2}) \tag{34a}$$

$$(B - y)^{-2} q_k[A_k^*, A_{k+2}^*] = 0(B^{-2}) \tag{34b}$$

the character of the asymptotic approximations $A_k \to H_k$, or $A_k^* \to H_k$ for $y \ll B$, $B \to \infty$, may be expressed in a greater detail by the estimates

$$(H_k - A_k) = 0(B^{-2}) + 0(\omega_k) \tag{35a}$$

$$(H_k - A_k^*) = 0(B^{-2}) + 0^*(\omega_k)\,, \tag{35b}$$

where the terms $0(B^{-2})$ are in both cases identical and the terms $0(\omega_k)$, $0^*(\omega_k)$ mutually differ. Because for an arbitrary finite i the terms of the order $0(\omega_k)$ are subdominant with respect to the terms of the order $0(B^{-i})$, it is possible (and there is no other way) to neglect them in the construction of the asymptotic power expansion represented by Eq. (*13*).

Perturbation Expansion for $B \gg 1$

In the Appendix it is shown that for the set of differential equations of the type (*8*) it is not important, in case that $B \gg 1$, if the exact boundary condition at infinity, $y = B$, is replaced by the condition $H_k(\infty) = 0$, or, on the contrary, by the condition $H_k((1 - \lambda) B) = 0$, where $\lambda \ll 1$.

The perturbation solution of the set (*8*) for $B \gg 1$ shall therefore be sought in the form (*13*) with the modified boundary conditions $H_0(0) = F(\infty) = \Gamma(4/3)$, $H_0(\infty) = 0$ and $H_k(0) = H_k(\infty) = 0$ for $k = 2, 4, \ldots$ For an arbitrary finite $y \ll B$ the sum on the right hand side of equation

$$(B - y)^{-2} = \sum_{j=0}^{\infty} (j + 1) B^{-2-j} y^j \tag{36}$$

converges. Substitution of the expansions, according to (*13*) and (*36*), into leads to the following recurrent set of equations for the functions ψ_k^j

$$\mathcal{K}_k[\psi_k^j] = Q_k^j\,, \tag{37}$$

where for $k = 0, 2, 4, \ldots, j = 2, 3, 4 \ldots$ we have

$$Q_k^2 = \mathscr{R}_{k-2}[\psi_{k+2}^2] + \quad q_k[A_k, A_{k+2}]$$
$$Q_k^3 = \mathscr{R}_{k-2}[\psi_{k-2}^3] + 2yq_k[A_k, A_{k+2}]$$
$$Q_k^4 = \mathscr{R}_{k-2}[\psi_{k-2}^4] + 3y^2q_k[A_k, A_{k+2}] + q_k[\psi_k^2, \psi_{k+2}^2]$$
$$Q_k^5 = \mathscr{R}_{k-2}[\psi_{k-2}^5] + 4y^3q_k[A_k, A_{k+2}] + 2yq_k[\psi_k^2, \psi_{k+2}^2] + q_k[\psi_k^3, \psi_{k+2}^3] \, . \quad (38)$$
$$\vdots$$

The homogeneous boundary conditions (*10b*) shall be modified in the sense of preceding considerations to the form

$$\psi_k^j(y) = 0 \quad \text{for} \quad y = 0 \quad (39a)$$

$$\exp(y^3)\,\psi_k^j(y) \to 0 \quad \text{for} \quad y \to \infty \, . \quad (39b)$$

The set (*38*) with the boundary conditions (*39a,b*) may be solved term-by-term as individual boundary value problems, as shown in more detail in the Appendix. The algorithm of the recurrent solution of the set (*37*) may be clarified by the following scheme

$$\begin{array}{llll}
(A_0, A_2) \rightarrow (\psi_0^2, \psi_0^3) & & & \\
\qquad\qquad\quad \downarrow \quad \searrow & & & \\
(A_2, A_4) \rightarrow (\psi_2^2, \psi_2^3) \rightarrow (\psi_0^4, \psi_0^5) & & & \\
\qquad\qquad\quad \downarrow \qquad\qquad\quad \searrow & & & \\
(A_4, A_6) \rightarrow (\psi_4^2, \psi_4^3) \rightarrow (\psi_2^4, \psi_2^5) \rightarrow (\psi_0^6, \psi_0^7) \, , & & & \\
\vdots & & &
\end{array} \quad (40)$$

where the arrows show the direction of proceeding from the already known functions to the functions being determined by solving Eq. (*37*).

For the physical interpretation of the solution, *i.e.* determination of the local diffusional fluxes, it is important to know primarily the values of the derivatives of the functions ψ_k^j at the point $y = 0$. According to (*6*), (*12*) and (*13*) we have

$$Sh(x) = \frac{B}{F(B)} \sum_{k=0,2,4,\ldots} x^k[-A_k'(0) + \sum_{j=2,3,4,\ldots} B^{-j}\lambda_k^j] \, , \quad (41a)$$

where

$$\lambda_k^j = - \left. \frac{d\psi_k^j(y)}{dy} \right|_{y=0} . \quad (41b)$$

The parameters λ_k^j can be expressed, according to Eqs (*A6*), (*A8*), directly as linear functionals of the corresponding right hand sides Q_k^j in the differential equations (*37*)

$$\lambda_k^j = \mathscr{L}_k^\infty[Q_k^j], \tag{42}$$

where $\mathscr{L}_k^\infty$ designates the operator $\mathscr{L}_k^B$ for $B = \infty$, see Eq. (*A6*) in the **Appendix.**

In the special case of $k = 0$, $j = 2, 3$ we have $Q_0^2(y) = 4A_2(y) = 4a_2 y$, $Q_0^3(y) = 8y\, A_2(y) = 8a_2 y^2$ and from (*A8*) thus

$$\lambda_0^2 = (\Gamma(4/3))^{-1} \int_\infty^0 \exp(-s^3) \int_0^s (4a_2 t)\, dt\, ds = (5\Gamma(4/3))^{-1} \tag{43a}$$

$$\lambda_0^3 = (\Gamma(4/3))^{-1} \int_\infty^0 \exp(-s^3) \int_0^s (8a_2 t^2)\, dt\, ds = 4/15\,. \tag{43b}$$

Also in the case $k = 2$, $j = 2, 3$ the calculation of λ_k^j can be performed relatively easily since we have

$$\mathscr{R}_0[\psi_0^j] = 9/2y^2(d\psi_0^j/dy - 3y^2\psi_0^j) = 9/2y^2 \left[-\lambda_0^j + \int_0^y Q_0^j(t)\, dt \right]. \tag{44}$$

Thus

$$Q_2^2(y) = 9/2y^2(-\lambda_0^2 + 2a_2 y^2) + 6a_2 y + 16(a_4 y + 3/2a_2^2 y^4) \tag{45a}$$

$$Q_2^3(y) = 9/2y^2(-\lambda_0^3 + 8/3a_2 y^3) + 12a_2 y^2 + 32(a_4 y^2 + 3/2a_2^2 y^5)\,. \tag{45b}$$

Resulting values given by equations

$$\lambda_2^2 = \int_\infty^0 \exp(-s^3)\, f_2^{-2}(s) \int_0^s f_2(t)\, Q_2^2(t)\, dt\, ds \tag{46a}$$

$$\lambda_2^3 = \int_\infty^0 \exp(-s^3)\, f_2^{-2}(s) \int_0^s f_2(t)\, Q_2^3(t)\, dt\, ds\,, \tag{46b}$$

were determined by numerical quadrature while the function $f_2(y)$ was evaluated from the series (*A4*) and, for $y > 1{\cdot}2$, from the asymptotic expansion (*A5*).

A numerical experiment, in accord with the asymptotic estimates according to (*A12*), has proven that for the determination of the parameters λ_k^j ($k = 0, 2$ and $j = 2, 3$) with the accuracy to four decimal places it suffices to integrate over the interval of $s \in (0; 2{\cdot}2)$. Numerical values of these parameters are summarized in Table I.

For the remaining combinations k, j the evaluation of ψ_k^j mandates substitution of the functions ψ_{k-2}^j, ψ_k^{j-2}, ψ_{k+2}^{j-2}, *etc.* into the integrals $\mathscr{L}_k^\infty[Q_k^j]$, according to the recurrent formula (*40*). These functions, as show the order of magnitude estimates from (*A12*), suffice roughly over the interval $y \in (0; 3)$, while for $y > 1$ their representations need not be very accurate. A suitable method of finding the necessary representation of the functions ψ_k^j is their superposition in the form of a power expansion with the known first derivative $(-\lambda_k^j)$ and determination of additional coefficients from the already once differentiated equation (*A1*) respectively (*A7*). This method served to find numerical estimates λ_4^2, λ_4^3 also shown in Table I.

NUMERICAL SOLUTION

Initially we had expected that the set of linear differential equations with the boundary conditions on a finite interval of the type (*8*), (*10a,b*) should pose no problem, when using the routines in the Fortran SSP of the IBM/360 system. This expectation, however, failed to materialize. Any progress in tackling the three major obstacles that gradually emerged and on which we shall now report would be unthinkable without a parallel study of the problem by the methods of asymptotic analysis, described in the preceding paragraphs and in the Appendix.

The first problem was the fact that in the search for a solution in the "natural" form $C = \sum x^k W_k(y)$ for $B > 2{\cdot}5$ the behaviour of the set of the functions $W_k(y)$ was little sensitive to the change in the initial conditions. The theoretical explanation for this observation rests in the fact that the course of the functions $W_k(y)$ may be qualitatively modelled in the form $y^k \exp(-y^3)$ and thus we are dealing with extremely fast decaying functions. This problem was overcome by substitution according to (*17*) with the weighting function $\exp(-y^3)$. This ensures polynomial behaviour of the functions $H_k(y)$ as indicated by the found asymptotic representations of the functions H_k by the functions A_k, respectively A_k^*. Introduction of the above weighting function, of course, extremely increased the sensitivity of the numerically generated course of the functions H_k in region $y \gg 1$ on the initial values $H_k(0)$,

TABLE I

Parameters of perturbation expansion according to Eq. (*41a*)

k	0	2	4
$-A_k'(0)$	1·0000	−0·3000	−0·0986
λ_k^2	0·2240	0·4758	0·55
λ_k^3	0·2666	0·5792	0·60
λ_k^4	(−0·35)[a]	—	—

[a] Obtained by empirical correlation of results of numerical integration.

$H_k'(0)$ and on the round-off errors of the numerical integration over the intervals $y \in \in (0; 1)$. All integrations were carried out in the forward manner using the Runge--Kutta method and the standard procedures of the IBM-360 system Fortran library. For the removal of instabilities of the type characterized by the estimate (*A16*) it was necessaey (and it proved sufficient) to work in region $B \in (2; 6)$ using double precision arithmetic while ajusting the parameter EPS, characterizing in the library procedure DRKGS the relative accuracy to 10^{-10}. For the given boundary conditions $H_k(B_1) = 0$ with fixed $B_1 < B$ the above procedure yielded value of the initial derivative $H_k(0)$ with relative accuracy better than 10^{-8}.

The second problem in the numerical integration of the set (*8*) with the boundary conditions (*10a,b*) was associated with the fact that in the boundary point $y = B$ the functions on the right hand side of the differential equation (*8*) have singularities, unless we have exactly that $q_k = 0((B - y^2))$ for $y \to B$. The exact solution though ensures finite values of the expression $((B - y)^{-2} q_k)$ for $y \to B$, but for the above iterative procedure with initially guessed values it is not certain that $q_k(B) \to 0$ for $y \to B$. The mentioned singularity then makes impossible to complete the integration up to the boundary point. For the numerically investigated region of $B \in (2; 6)$ this difficulty was circumvented by using an alternative boundary condition in the form $H_k(B_1) = 0$ with a suitably selected $B_1 < B$. For $B > 2{\cdot}2$ it was proven by numerical experiments, that in order to find $H_k'(0)$ with an accuracy of the order 10^{-8} it is sufficient to fix B_1 at a value $B_1 = 2{\cdot}1$. This empirical findings is in accord with the theoretical estimate of the error $H_k'(0)$ from (*A12*). In the numerical solution of the problem in region $B \in (1{\cdot}5; 2)$ it posed no problems to solve the task iteratively with successive halving of the interval $(B_1 - B)$. The accuracy of $H_k'(0)$ to six digits was achieved already for $B_1/B = 0{\cdot}98$.

The third, most serious problem was the fact that the set (*8*) consists for a finite value of the parameter B of an infinite number of equations for an infinite number of unknown function H_k and this set cannot be solved term-by-term. A possibility how to reduced this infinite set to a manageable number of finite subsystems of N equations, $k = 0, 2, \ldots, 2N - 2$, is to replace in the last equation of the set the unknown function H_{2N} by some suitable approximation, H_{2N}^*. One solves a set whose terms for $k = 0, \ldots, 2N - 4$ have an exact form (*8*) and the equation for $k = 2N - 2$ is is approximated in the following manner

$$\mathscr{K}_k[H_k] - \mathscr{R}_{k-2}[H_{k-2}] = (B - y)^{-2}\, q_k[H_k, H_{2N}^*]\,. \qquad (47)$$

From the perturbation scheme (*13*) it is apparent that for a change of the initial guess $H_{2N}^* \to H_{2N}^* + \delta_{2N}$, in linear dependence on δ_{2N} will correspondingly change just the coefficients $(\psi_{2N-k}^n, \psi_{2N-k}^{n+1})$, $(n = 2, 4, \ldots, 2N)$ of the perturbation expansion of the functions $(H_{2N-2}, \ldots, H_0)$ from (*13*). For $j + k < 2N$ the coefficients ψ_k^j remain unaffected by the change of δ_{2N}. The function H_{2N-n} will thus be affected only by the increments of the order $0(B^{-n})$, $n = 2, 4, \ldots$, which in case of $B \to \infty$ is certainly a positive finding representing a starting point for the numerical realization of the perturbation analysis.

For the set of two and three equations, $N = 2$, respectively $N = 3$, we took as an approximation of H_{2N}^* corresponding asymptote A_{2N}. This approach seemed logical, since for $B \gg 1$ A_{2N} is also a legitimate approximation of the function H_{2N}. Nevertheless, in region $B \in (2; 4)$ this guess lead unexpectedly to clearly incorrect courses of the functions H_{2N-2}, H_{2N-4}.

In the following stage of the calculation we thus took for the set of two and three equations, $N = 2$, respectively $N = 3$, the trivial approximation $H_{2N}^* = 0$. The numerical experiment resting in comparison of results for $N = 2$ and $N = 3$ showed that by the given procedure H_{2N-2} is approximated already in the whole studied region $B \in (2; 6)$ with very good accuracy. The characteristic course of the functions H_0, H_2, H_4, determined by the given procedure in region of intermediate values of B, is shown graphically in Fig. 2 in comparison with corresponding asymptotes A_0, A_2, A_4.

RESULTS AND DISCUSSION

The result of the numerical solution of the set (*8*) with the boundary conditions (*10a,b*) are primarily the data on the derivatives $H_k'(0)$, $k = 0, 2, 4, \ldots$ Corresponding results of the analytical solution are data on the parameters $A_k'(0)$, λ_k^2, λ_k^3, $k = 0, 2, 4$, summarized in Table I. For comparison of the two alternative solutions of the same problem, we shall introduce an auxiliary function

$$\varepsilon_k(B) = B^2(1 - H_k'(0)/A_k'(0)) \qquad (48)$$

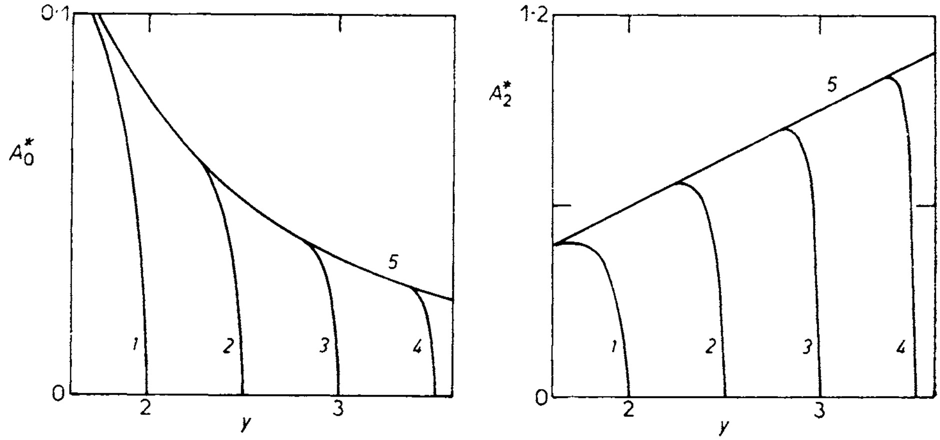
which sufficiently sensitively reflects even small differences of various approximations for large values of B, see Fig. 3.

Asymptotic courses $\varepsilon_k(B)$, according to the analytical approximation (*13*), are given by the following dependences

$$\varepsilon_k(B) = (\lambda_k^2 + \lambda_k^3 B^{-1})/A_k'(0) + 0(B^{-2}) \qquad (49)$$

shown for $k = 0, 2, 4$ in Fig. 3 by straight lines. Empty points in the same figure represent the result of numerical integration of two equations ($N = 2$; $k = 0, 2$), full points show the result of integration of three equations ($N = 3$; $k = 0, 2, 4$) of the set (*8*).

For $k = 0$ there is no significant difference between both numerical solutions, nor is there such a difference for the lowest value of B considered, $B = 2$, where



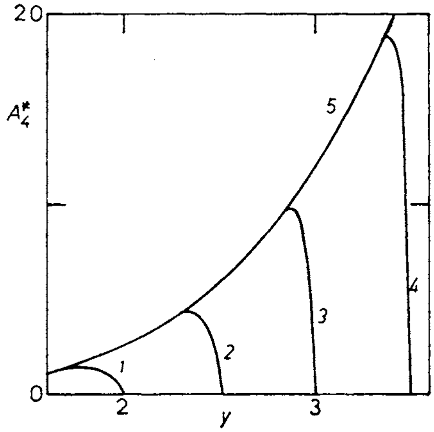


FIG. 1

Courses of functions $A_k^*(y)$, $k = 0, 2, 4$ in the neighbourhood of the boundary $y = B$. Numbers *1*, *2*, *3*, *4* designate the courses for $B = 2$, 2·5, 3, 3·5, label *5* designates the case $B = \infty$ when $A_k^* = A_k$

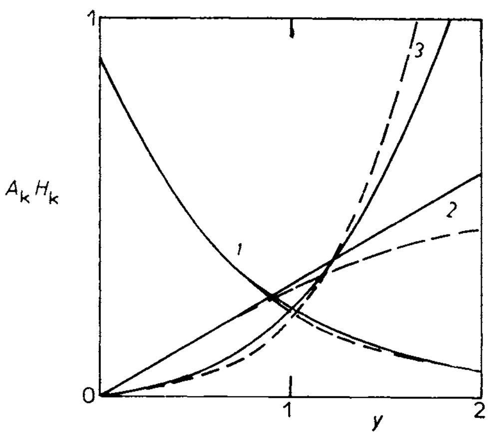


FIG. 2

Courses of functions $A_k(y)$ and $H_k(y)$, $k = 0, 2, 4$ near the origin, $y = 0$. Solid lines indicate courses of the asymptotes $A_k(y)$, broken lines courses of the functions $H_k(y)$ for $B = 4$, determined by numerical integration with the approximation $H_6^*(y) = 0$. Numbers *1*, *2*, *3* designate the functions for $k = 0, 2$ and 4 the shown differences correspond to about 1·5% difference in the value of $H'_0(0)$. Numerical results of $\varepsilon_2(B)$, for $N = 2$, respectively $N = 3$, however, indicate considerable discrepancies suggesting that the data on ε_k for $k = 2N - 2$ should be taken with caution. Nevertheless, the differences between the analytical approximation (*49*) and the results of the numerical integration for $N = 3$ represent for $B = 3$ less than 5% change in values of $H'_2(k)$. The data on $\varepsilon_4(B)$, obtained by numerical integration for $N = 3$, cannot be regarded as quantitative. It seems adequate in this case to confine the approximation to an increment of the order $0(B^{-2})$

$$H'_4(0) = A'_4(0) + \lambda_4^2 B^{-2} + 0(B^{-3}) \qquad (50)$$

since the differences between the analytical approximation and the result of the numerical integration suggest that for $B < 3$ the increments of the order $0(B^{-3})$ and $0(B^{-4})$ are already comparable. On the contrary, for $k = 0$ are numerical results, for $N = 3$, reliable enough that their processing by linear regression following the empirical equation

$$H'_0(0) = c_0 + c_2 B^{-2} + c_3 B^{-3} + c_4 B^{-4} \qquad (51)$$

leads to values for c_0, c_2, c_3 identical to three decimal places with the analytical data on $A'_0(0)$, λ_0^2, λ_0^3. Accordingly, one may take as adequate also the approximation $c_4 \doteq \lambda_0^4$, shown also in Table I.

For $k = 6, 8, 10$,,, we have no data on the perturbation parameters $H'_k(0)$ but we know that for $B \to \infty$ we may write $H'_k(0) \to A'_k(0)$. It is proper to include also this information into the resulting expression of $Sh(x)$ following the asymptotic scheme (*41a*):

$$Sh(x) = \frac{B}{F(B)} \left[(1 + 0{\cdot}224B^{-2} + 0{\cdot}267B^{-3} - 0{\cdot}35B^{-4}) - 0{\cdot}300x^2 \,.\right.$$
$$\left. .(1 - 1{\cdot}58B^{-2} - 1.93B^{-3}) - 0{\cdot}099x^4(1 - 5{\cdot}6B^{-2}) - 0{\cdot}055x^6 - 0{\cdot}039x^8 - 0{\cdot}032x^{10}\right] . \qquad (52)$$

We estimate that the relative accuracy of this resulting expression in region $B \geqq 3$, $x < 0{\cdot}9$ is better than $\pm 0{\cdot}5\%$ and in region $B \geqq 2$, $x < 0{\cdot}8$ better than $\pm 2\%$.

The region $B \geqq 2$, $x < 0{\cdot}9$ represents a limit where the considered type of approximate solution still ensures the acceptable accuracy of the $Sh(x)$ data.

The effect of longitudinal diffusion on local transfer coefficients, represented by the dependence $Sh = Sh(x)$, is not very large in region of validity of the expression (*52*), $B > 2$. This is apparent from Fig. 4 showing the profiles of $Sh(x)$ computed from (*52*) in comparison with the courses, according to the CBL approximation:

$$Sh_A(x) = B\,G(x)/F(\infty) \tag{53}$$

and the IS approximation

$$Sh_A^*(x) = B\,G(x)/F(B\,G(x))\,. \tag{54}$$

The results of this work on the effect of longitudinal diffusion in the bulk liquid on the local transfer coefficients may be summarized as follows:

1) Relation (*52*) is correctly applicable under the conditions when $B\,G(x) > 2$.

2) The effect of the longitudinal diffusion in the bulk liquid is entirely negligible (below 0·5%) for $B > 6{\cdot}6$, *i.e.* for $Pe > 300$. For $B = 3$ it leads to increased transfer coefficients by 3%, for $B = 2$ by 10%. At lower values of B the presented analysis is no longer correct.

3) The effect of longitudinal diffusion somewhat expands the region near the pole of the rotating sphere where the surface is uniformly accessible in the transport sense.

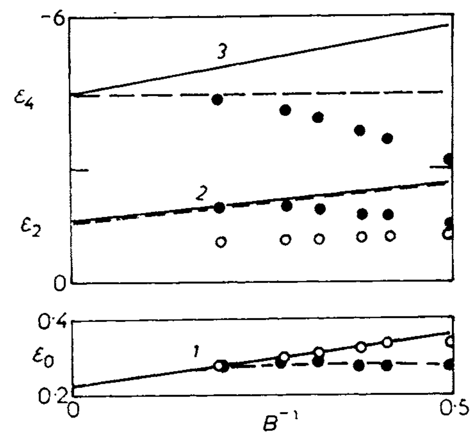


FIG. 3

A comparison of the analytical and numerical solution of the set (*8*). Solid lines — linearized analytical estimate ε_k from (*49*), (*50*), empty points — numerical integration for $N = 2$, full points — numerical integration for $N = 3$. Broken lines — courses of the functions $\varepsilon_k(B)$ implemented into (*52*). Numbers *1*, *2*, *3* designate data on ε_k for $k = 0$, 2, and 4

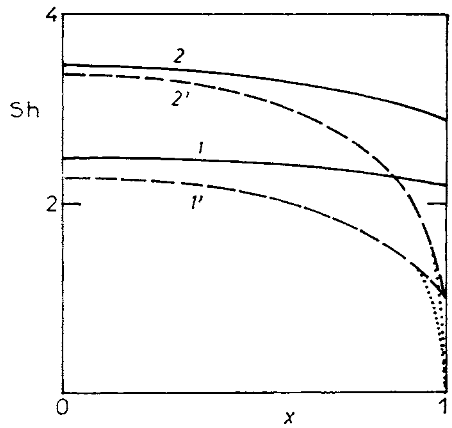


FIG. 4

Longitudinal profiles of local transfer coefficients. Solid lines — results of perturbation analysis according to Eq. (*52*) incorporating the effect of longitudinal diffusion. Broken lines — IS approximation, dotted lines — CBL approximation. Numbers *1*, *1'* designate the courses for $B = 2$, numbers 2, 2' the courses for $B = 3$

It should be noted that the presented analysis is limited to the case when the whole surface of the sphere represents the working surface of the electrode. In electrochemical practice, however, a more common case is such that the electrode is situated only in the polar region of the rotating sphere and its terminating edge falls into the latitude $x = x_0$. In such case the effect of longitudinal diffusion in the proximity of the edge of the electrode is substantially stronger than the effect of longitudinal diffusion in the bulk liquid considered in this work.

The overall transfer coefficient averaged over the surface of the rotational polar electrode is then claerly given by

$$\overline{Sh} = \int_0^{x_0} \frac{Sh(x)\, x\, \mathrm{d}x}{\sqrt{(1 - x^2)}} \Big/ \int_0^{x_0} \frac{x\, \mathrm{d}x}{\sqrt{(1 - x^2)}} \,. \tag{55}$$

Substitution of the resulting expression (52) into the definition (55) and confining the result to the terms $0(x_0^2)$, $0(B^{-2})$ leads to the following expression of the mean diffusional fluxes

$$\overline{Sh}_0(x_0, B) = \frac{B}{F(\infty)} [1 + 0{\cdot}224B^{-2} - 0{\cdot}15x_0^2(1 - 2{\cdot}0B^{-2})] =$$

$$= 0{\cdot}489Sc^{1/3}Re^{2/3}[1 - 0{\cdot}15x_0^2 + 0{\cdot}51B^{-2}(1 + 1{\cdot}3x_0^2)] \,. \tag{56}$$

The effect of longitudinal diffusion in the immediate proximity of the edge of the electrode was studied by the method of singular perturbation by Smyrl and Newman[12]. Their results may be recalculated to the form

$$\overline{Sh}_{SN}/\overline{Sh}_\infty = 1 + 0{\cdot}8(x_0B)^{-3/2}(1 + x_0^2/12) \,, \tag{57}$$

where $\overline{Sh}_{SN}$ represents the mean diffusional fluxes, including the edge effects and Sh_∞ represents $\overline{Sh}_0$ for $B = \infty$. It is seen that the edge effect of the longitudinal diffusion which is of the order of $0(B^{-3/2})$, is dominant for $B \to \infty$ in comparison with the effect of longitudinal diffusion in the bulk liquid, the latter being of the order of $0(B^{-2})$. It is obvious that for $B \in (2; 6)$ the effect of longitudinal diffusion in the bulk liquid is entirely negligible in comparison with the edge effect.

LIST OF SYMBOLS

a_k — coefficients of expansion for $G(x)$, Eq. (*19*)
A_k, A_k^* — characteristic functions of CBL and IS approximation, Eq. (*20a,b*)
$B = Pe^{1/3}$
$c(x, y)$ — concentration field of depolarizer
$c_0(x)$ — concentration on the surface of sphere ($y = 0$)

c_∞	concentration at infinity
$C = [(c - c_\infty)/(c_0 - c_\infty)]\, F(B)$	
C_A	similarity (CBL) asymptote of concentration field for $B \to \infty$, Eq. (*14*)
C_k^*	improved similarity (IS) approximation of concentration field, Eq. (*15*)
D	diffusivity of depolarizer
f_m	eigenfunction of the operator $\mathscr{K}$, Eq. (*A2*), (*A3*)
$F(\xi)$	similarity concentration profile, Eq. (*5*)
$G(x)$	parameter of similarity transform, Eq. (*17*)
H_k	characteristic function of perturbation solution, Eq. (*17*)
$J = D\, \partial_r c\|_{r=R}$	diffusional flux on the surface of the sphere
$\mathscr{K}_k$	differential operator of perturbation solution, Eq. (*9b*)
$Pe = Sc\, Re^2/12 = U_M R/D$	Peclet number
q_k	operator, Eq. (*9a*)
$\mathscr{R}_k$	operator, Eq. (*9c*)
R	radius of sphere
$Re = \Omega R^2 \varrho/\eta$	Reynolds number
$Sc = \eta/\varrho D$	Schmidt number
$Sh = JRD^{-1}(c_\infty - c_0)^{-1}$	local Sherwood number
$U_M = \Omega R\, Re/12$	characteristic meridional velocity of creeping flow
$(v_r, v_\theta, v_\varphi)$	physical components of velocity in spherical coordinates
$x = \sin \Theta$	meridional variable
$y = B(1 - R/r)$	radial variable
ε_k	parameter defined by Eq. (*48*)
η	viscosity
λ_k^j	terms of perturbation expansion for diffusional fluxes, Eq. (*41a,b*)
ψ_k^j	terms of perturbation expansion for concentration field, Eq. (*13*)
ϱ	density
Ω	angular velocity of rotation of sphere

APPENDIX

Let $\psi^* = \psi^*(y)$ be a solution of a differential equation $\mathscr{K}_m[\psi^*] = q$ on an interval $y \in \langle 0; B \rangle$ with the homogeneous boundary conditions $\psi^* = 0$ for $y = 0$ and $\exp(-y^3)\, \psi^*(y) \to 0$ for $y \to B$. Here $\mathscr{K}_m$, $m = 0, 1, 2, \ldots$ is a differential operator defined by Eq. (*9b*) in the main text. Let the right hand side $q = q(y)$ be integrable on every finite interval $y \in (0; s)$. Formal solution of this boundary value problem may be written in the form

$$\psi^*(y) = -\exp(y^3)\, f_m(y) \int_y^B \exp(-s^3)\, f_m^{-2}(s) \int_0^s f_m(t)\, q(t)\, \mathrm{d}t\, \mathrm{d}s \qquad (A1)$$

for finite B as well as for $B = \infty$.

The core of the solution is a function f_m, defined as an integral of the Cauchy problem

$$f_m'' + 3y^2 f_m' - 3my f_m = 0 \qquad (A2)$$

with the initial conditions

$$f_m(0) = 0\,, \quad f'_m(0) = 1\,. \tag{A3}$$

For $m = 0$ we have $f_0(y) = F(y)$, see Eq. (5) in the main text. For an arbitrary $m \geqq 0$ one can find f_m in the form of a series with infinite radius of convergence

$$f_m(y) = y\left(1 + \frac{m-1}{4}\,y^3\left(1 + \ldots + \frac{m-1-3i}{(i+1)(4+3i)}\,y^3\right)\right) + O(y^{3i+7})\,, \tag{A4}$$

where $i = 0, 1, 2, \ldots$ From (A4) it is apparent that for $m = 1, 4, (3j + 1), \ldots f_m(y)$ is an finite polynomial $0(y^m)$. For $m > 1$, $y > (m/3)^{3/2}$ an effective approximation of the function f_m is gived by the asymptotic expansion in the form

$$f_m(y) \approx \varkappa_m y^m \left(1 + \frac{m(m-1)}{9}\,y^{-3}\left(1 + \ldots + \frac{(m-1-3i)(m-3i)}{9(1+i)}\,y^{-3}\right)\right). \tag{A5}$$

The constant $\varkappa_m$ should be found by an independent method, *i.e.* matching the courses (A4) and (A5) in the neighbourhood of $y \approx (m/3)^{3/2}$. In the special case $\varkappa_2 = 0{\cdot}990$, $\varkappa_4 = 0{\cdot}447$.

The derivative $\psi^{*\prime}(0)$ of the solution ψ^* at the point $y = 0$, can be expressed, according to (A1), by the following linear functional

$$-\psi^{*\prime}(0) = \mathscr{L}_m^B[q] = \int_0^B \exp(-s^3)\, f_2^{-m}(s) \int_0^s f_m(t)\, q(t)\, dt\, ds \tag{A6}$$

whose argument $q = q(y)$ is the right hand side of the solved differential equation $\mathscr{K}_m[\psi^*] = q$.

In the special case $m = 0$ the solution of the problem under investigation may be expressed according to (A1), in a somewhat simpler form

$$\psi^*(y) = \exp(y^3) \int_y^B \exp(-s^3)\left[-\psi^{*\prime}(0) - \int_0^s q(t)\right] ds\,, \tag{A7}$$

where

$$-\psi^{*\prime}(0) = \mathscr{L}_0^B[q] = \frac{\int_0^B \exp(-s^3) \int_0^s q(t)\, dt\, ds}{\int_0^B \exp(-s^3)\, ds}\,. \tag{A8}$$

Our main aim is to find the effect of the parameter B, delimiting the upper limit of the definition interval of the function ψ^*, on the behaviour of this function in case that $B \to \infty$. Let us keep the same meaning of the symbols ψ^*, $\psi^*(0)$ for finite B while using the symbols $\psi = \psi(y)$ and $\psi'(0)$ for the solution and its derivative at the point $y = 0$ and for $B = \infty$.

It can be seen easily that following identities hold in view of (A1) and (A6)

$$\psi(y) - \psi^*(y) = -\exp(y^3)\, f_m(y)\, S_B[q] \tag{A9}$$

$$\psi'(0) - \psi^{*\prime}(0) = S_B[q]\,, \tag{A10}$$

where

$$S_B[q] = \int_{\infty}^{B} \exp(-s^3) f_m^{-2}(s) \int_0^s f_m(t)\, q(t)\, dt\, ds\,. \qquad (A11)$$

Assuming a power law course of the right hand side $q(y) \sim y^p$ we have for $B \gg 1$ clearly the following asymptotic estimate

$$S_B[q] \sim \frac{\exp(-B^3)\, q(B)}{3(m + p + 1)\, f_m(B)\, B}\,. \qquad (A12)$$

Substitution of the estimate (*A12*) into the right hand sides of Eqs (*A9*), (*A10*) we arrive at the asymptotic estimates from which it is apparent that for sufficiently large value of the parameter B the course of the function is neither globally, for $y \ll B$, nor locally, for $y \to 0$, significantly dependent on the actual value of B, where we had stipulated the boundary condition

$$\psi^*(y) \to 0 \quad \text{for} \quad y \to B\,. \qquad (A13)$$

In cases considered in the main text it is important to know the deviation of two solutions ψ_1 and ψ_2 with the boundary condition (*A13*), formulated in the point $y = B_1$, respectively $y = B_2$. Since $S_B[q]$ is for fixed q a decreasing function of the argument B and according to (*A9*), (*A10*) we have

$$\psi_1(y) - \psi_2(y) = -\exp(y^3)\, f_m(y)\, (S_{B_1}[q] - S_{B_2}[q]) \qquad (A14)$$

$$\psi_1'(0) - \psi_2'(0) = S_{B_1}[q] - S_{B_2}[q] \qquad (A15)$$

the shift of the boundary condition (*A13*) from the point B_1 into $B_2 < B_1$ leads to relative errors in $\psi_1(y)$ for $y \ll B_2$ and and in $\psi_1'(0)$ which are smaller than $S_{B_1}[q]$. We note that with the power expansion of the right hand side $q(y) \sim y^p$ the mentioned relative deviations amount, for $m \leqq 6, p \leqq 10$, according to the numerical calculations, to less than 10^{-10} already for $B = 3$. It may be said that for the studied class of problems $B \geqq 3$ represents actually infinity.

From Eqs (*A9*), (*A10*), however, it is apparent also the following property of the solution of the given class of problems

$$\psi_1(y) - \psi_2(y) = \exp(y^3)\, f_m(y)\, [\psi_2'(0) - \psi_1'(0)]\,, \qquad (A16)$$

where ψ_1, ψ_2 now represent two solutions with different initial conditions. For the numerical solution of the boundary value problem one usually uses iteration with a guessed initial value of the derivative. Eq. (*A16*) indicates how sensitive the result is to already minute deviations in the estimates of the first derivative in the origin. It is thus clear that in an analogous manner does the solution react in region $y \gg 1$ to any numerical error, *e.g.* the round-off error in region $y < 1$. For instance an error $\pm 10^{-5}$ in the value of $\psi(y)$ in the point $y = 1$ leads to deviations of the order of magnitude $\pm 10^5$ in the point $y = 3$.

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