NON-STEADY-STATE CONVECTIVE DIFFUSION IN A THIN SPHERICAL LAYER

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Non-steady-state convective diffusion in a thin spherical layer is considered.

This study will consider nonsteady convective diffusion in a thin spherical layer, produced by a time-varying gravitational field or variable linear acceleration. The spherical layer is formed by a sphere of radius R_1, located within a sphere of radius $R_2 \gtrsim R_1$. The space between the spheres is filled with an electrolyte. The outer surface of the inner sphere and inner surface of the outer sphere act as anode and cathode in an oxidation–reduction reaction. We will assume that the chemical reaction rate at the electrodes is significantly higher than the rate at which material arrives at the electrodes. In this case, as the chemical reaction occurs a concentration gradient appears in the system, which leads to a solution density gradient [1]. As a result, in an external gravitational field or acceleration field the liquid equilibrium state becomes unstable and convective motion of the solution develops, which in turn leads to a change in the rate at which reagents reach the electrodes. In the liquid at rest the reactions are limited by diffusion of the reagent from anode to cathode, but if the liquid is set in motion, then convective transfer occurs together with ionic diffusion, sharply increasing the reaction rate and limiting current in the circuit.

This process can be described by a system of nonstationary convective diffusion equations, which in the Boussinesq approximation have the following form [2]:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\,\mathbf{v} = -\rho^{-1}\nabla p + \nu\Delta\mathbf{v} + \beta c\mathbf{g}, \tag{1}$$

$$\operatorname{div}\mathbf{v} = 0, \tag{2}$$

$$\frac{\partial c}{\partial t} + \mathbf{v}\cdot\nabla c = D\Delta c. \tag{3}$$

The system (1)-(3) must be supplemented by boundary conditions:

$$\mathbf{v}|_{R_1} = 0,\ \mathbf{v}|_{R_2} = 0, \tag{4}$$

$$c|_{R_1} = 0,\ c|_{R_2} = c_0. \tag{5}$$

The concentration c_0 in Eq. (5) is specified in preparation of the "working" electrolyte and can vary over wide limits.

As is well known [2], when $\operatorname{rot}(c\mathbf{g}) \neq 0$, convection occurs at any Grashof number λ, no matter how small. In this case, a solution of Eqs. (1)-(5) can be sought in the form of a series in the small parameter λ:

$$\mathbf{v} = \lambda\mathbf{v}_1 + \lambda^2\mathbf{v}_2 + \lambda^3\mathbf{v}_3 + \cdots, \tag{6}$$

$$c = c^0 + \lambda c_1 + \lambda^2 c_2 + \cdots \tag{7}$$

It should be noted that the method of expansion in a small parameter is obviously inapplicable if $\operatorname{rot}(c\mathbf{g}) = 0$, since in this case the system has a threshold stability λ_{cr}, with convection beginning only at $\lambda > \lambda_{cr}$ [2].

The equation for the zeroth approximation to the concentration c^0 corresponds to diffusion in the liquid at rest. Since in view of the spherical symmetry c^0 depends solely on the modulus of r, the solution of Eqs. (3), (5) has the form

$$c^0(r) = c_0\frac{R_2}{R_2 - R_1}\left(1 - \frac{R_1}{r}\right). \tag{8}$$

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In the present study we will limit ourselves to determining the linear response of the system to an external perturbation, which we will specify in the form $g(t) = g\exp(i\omega t)$. Initially, we will find the hydrodynamic liquid velocity field produced by this perturbation.

Hydrodynamic Problem. At low frequencies, where $\omega(R_2 - R_1)^2 \ll \nu$, the frequency dependence of the current is determined by the parameter $\omega(R_2 - R_1)^2 D^{-1}$, so that in the Navier–Stokes equation we may confine ourselves to the linear approximation. Applying the operation rot to Eq. (1) and collecting terms linear in λ, we obtain the equation of the linear approximation for solution velocity

$$\nu \,\mathrm{rot}\, \Delta \mathbf{v} = -\,\mathrm{rot}\,(\beta c \mathbf{g}). \tag{9}$$

We will seek a solution of Eq. (9) in the form

$$\mathbf{v} = \mathrm{rot}\,\mathrm{rot}\,(f\mathbf{g}), \tag{10}$$

where f is a scalar function of the modulus r.

Substituting Eq. (10) in (9) and integrating, we obtain

$$\frac{df}{dt} = \gamma \frac{r^2 \ln r}{6} - \frac{5}{36}\gamma r^2 - \frac{c_1 r}{6} + \frac{c_2 r^2}{6} - \frac{c_3}{r} + c_4, \tag{11}$$

where the following notation is introduced:

$$\gamma = \nu^{-1} c_0 \rho^{-1} \frac{\partial \rho}{\partial c} \frac{R_2 R_1}{R_2 - R_1}.$$

Substituting Eq. (11) in Eq. (10) and defining the integration constants from boundary conditions (4), we obtain for the solution velocity v the expression

$$\begin{aligned}\mathbf{v} = {} & \mathbf{g}\gamma \frac{R_1}{(x-1)^3}\left[-\frac{(x-1)^3 r \ln r}{2} + \left(\frac{x^2(x-3)\ln x}{2} + \frac{x^3-1}{3}\right) r + \right. \\ & \left. + 2x^2 \ln x - \frac{(x+1)(x^3-1)}{3} + \left(\frac{x(x^3-1)}{3} - \frac{x^2(x+1)\ln x}{2}\right)\frac{1}{r}\right] + \\ & + \mathbf{n}(\mathbf{g}\cdot\mathbf{n})\frac{\gamma R_1}{(x-1)^3}\left[\frac{(x-1)^3}{6} r \ln r - \left(\frac{x^2(x-3)\ln x}{6} - \frac{x^2(x+1)\ln x}{2}\right) r + \right. \\ & \left. + \left(\frac{2}{3}x^3 \ln x - \frac{x^2(x^2-1)}{3}\right)\frac{1}{r^2} + \left(\frac{x(x^3-1)}{3} - \frac{x^2(x+1)\ln x}{2}\right)\frac{1}{r}\right].\end{aligned} \tag{12}$$

Here we introduce the dimensionless parameter $x = R_2/R_1$ and make the replacement $r \to r/R_1$. In the linear approximation in g, Eq. (12) describes natural convection of the liquid in the spherical layer.

Convective Diffusion Current. The equation of the linear approximation for concentration of the reagent has the form

$$\Delta c_1 - \frac{i\omega}{D} c_1 = D^{-1}(\mathbf{v}\cdot\nabla c^0). \tag{13}$$

The scalar product $\mathbf{v}\cdot\nabla c^0$ will be written in the form $\varphi(r)\cos\theta$, where $\cos\theta = g^{-1}(\mathbf{n}\cdot\mathbf{g})$, and in accordance with Eqs. (12), (8) $\varphi(r)$ is defined by

$$\varphi(r) = -\frac{(x-1)^3}{3}\frac{\ln r}{r} + \frac{a}{r} + \frac{b}{r^2} + \frac{c}{r^3} + \frac{d}{r^4}, \tag{14}$$

where

$$a = \frac{x^2(x-3)\ln x}{3} + \frac{(x-1)(x^2+1)}{3};$$

$$b = 2x^2 \ln x - \frac{(x+1)(x^3-1)}{3};$$

$$c = \frac{2x(x^3-1)}{3} - x^2(x+1)\ln x;$$

$$d=\frac{2}{3}x^3\ln x-\frac{x^2(x^2-1)}{3}.$$

We seek a solution of Eq. (13) in the form

$$c_1(r)=p(r)\cos\theta.$$

For p(r) we obtain the following equation:

$$\frac{d^2p}{dr^2}+\frac{2}{r}\frac{dp}{dr}-\frac{2p}{r^2}-\frac{i\omega}{D}p=D^{-1}\varphi(r). \tag{15}$$

Below we will consider a thin spherical layer in which $R_2 - R_1 \ll R_1$. In this case the first term on the left side of Eq. (15) is significantly larger than the two following ones. Neglecting the latter terms, we rewrite Eq. (15),

$$\frac{d^2p}{dr^2}-\frac{i\omega}{D}p=D^{-1}\varphi(r). \tag{15}$$

The general solution of Eq. (16) has the form

$$p(r)=c_1\exp(\varkappa r)+c_2\exp(-\varkappa r)+\exp(\varkappa r)\int\limits_{R_1}^{r}\frac{dr_1}{D}\exp(-2\varkappa r_1)\int\limits_{R_1}^{r_1}\varphi(r_2)\exp(\varkappa r_2)\,dr_2, \tag{17}$$

where

$$\varkappa=\left(\frac{\omega}{2D}\right)^{1/2}(1+i). \tag{18}$$

The integration constants c_1 and c_2 in Eq. (17) are defined from the boundary conditions of Eq. (5).

The change in electrical current ΔI produced by action of the external acceleration g is determined by the following expression:

$$\Delta I=-D\int(\nabla c_1\mathbf{n})\,dS. \tag{19}$$

Since $c_1 \sim \cos\theta$, the result of integrating over the entire sphere surface is equal to zero. This means that the diffusion flow flowing from one of the hemispheres of an electrode, divided by a plane the normal to which coincides with the vector g, is exactly equal to the diffusion flow incident on the second hemisphere of the electrode. To obtain a nonzero result these hemispheres must be separated by an insulating interlayer [3]. Integrating over one hemisphere, we obtain for ΔI the equation

$$\Delta I=\frac{2\pi}{3}\frac{g\gamma c_0R_1^3}{(x-1)^4}\frac{Y}{\exp[\varkappa(R_2-R_1)]-\exp[-\varkappa(R_2-R_1)]}, \tag{20}$$

where

$$Y=\int\limits_1^x\varphi(y)\{\exp[\varkappa R_1(x-y)]-\exp[\varkappa R_1(y-x)]\}\,dy.$$

We will now consider some limiting cases. First we let $\omega \to 0$, and from Eq. (20) we obtain an expression for the linear response to a static perturbation

$$\Delta I=\frac{4\pi}{5}g\gamma c_0R_1^3. \tag{21}$$

At high frequencies, where $\varkappa R_1 \gg 1$, the expression for ΔI has the following form

$$\Delta I=\frac{2\pi}{3}g\gamma c_0R_1^2D^{3/2}(R_2-R_1)^{-2}\omega^{-3/2}. \tag{22}$$

NOTATION

R_2, radius of outer sphere; R_1, radius of inner sphere; v, velocity of solution; ν, kinematic viscosity; g, acceleration; c_0, ion concentration; D, diffusion coefficient; ρ, solution density; n, unit normal vector; $\beta = \rho^{-1}\partial\rho/\partial c$.

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TEMPERATURE FIELD OF A PLATE WITH INTERNAL TEMPERATURE-DEPENDENT HEAT SOURCE

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The problem of asymmetric heating of a plate is considered in a medium with variable temperature in the presence of an internal heat source, the power of which is dependent on temperature and time.

In many engineering problems related to calculation of heat-transfer processes, it becomes necessary to analyze the effect on the temperature field of the body under study of internal heat sources, usually those produced by exothermal chemical reactions. In calculations the power of such heat sources is usually taken as constant, or its dependence on time and coordinate is specified in the form of certain known functions which make possible use of existing solutions of the thermal conductivity equation for calculation of the temperature field [1]. However, in the majority of real processes, the internal heat source power is significantly dependent on temperature. Thus, in hardening of a number of structural materials, hydration of various cement substances takes place, accompanied by heat liberation. With increase in temperature the intensity of the hydration reaction increases, so that heat liberation also increases. With the passage of time the initial reagent concentrations decrease, leading to a slowage of the reaction and heat liberation. A detailed analysis of heat liberation in hardening concrete was performed in [2]. The analysis reveals that the temperature–time dependence of the quantity of heat Q_e, liberated upon hardening 1 kg of cement, can be written in the form $Q_e = f^*(\tau)t$. The power of the internal heat source is proportional to the derivative

$$\frac{\partial Q_e}{\partial \tau} = \frac{\partial f^*(\tau)}{\partial \tau} t + f^*(\tau)\frac{\partial t}{\partial \tau}.$$

With consideration of this fact, the differential equation for heat transfer for the plate has the form

$$[1 - f(\tau)]\frac{\partial t}{\partial \tau} = a\frac{\partial^2 t}{\partial x^2} + \frac{\partial f(\tau)}{\partial \tau} t, \tag{1}$$

where $f(\tau) = \frac{M}{c\gamma} f^*(\tau)$; M is the quantity of cement in 1 m^3 of the concrete mixture. In [2] solutions of Eq. (1) were obtained for a number of special cases. Below a more general solution will be attempted.

Locating the origin of the coordinate system at the center of the plate, we write the initial boundary conditions of the problem in the form

$$t(x, 0) = t_0, \tag{2}$$

$$\left[(-1)^i \lambda \frac{\partial t}{\partial x} + \alpha_i t\right]\Big|_{x=X_i} = \alpha_i t_m(\tau), \tag{3}$$

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