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# Free convection in an electrochemical system with nonlinear reaction kinetics

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Unsteady electrolysis of a dilute solution of a metal salt made up of two ions in a system with vertical electrodes is considered for large values of the Rayleigh and Schmidt numbers. The mass transfer at the electrodes is assumed to be related to the local charge transfer potential and concentration by a nonlinear Butler–Volmer law. Free convection of the electrolyte appears owing to the variation of the concentration field. After a short initial period, the electrolyte becomes strongly stratified and the motion takes place in boundary layers at the solid boundaries. An approximate model equation for the evolution of the stratification is derived by using perturbation theory. Predictions from the simplified model are found to be in good agreement with numerical solutions of the complete problem. Significant differences compared with earlier studies for linear kinetics, i.e. cases in which the electric current density at the electrodes is constant, are found. Among other things, for large values of the difference $\Delta V$ in electric potential between the electrodes, most of the dissolved salt eventually collects near the bottom of the cell. The concentration in the bulk of the electrolyte is, for large values of $\Delta V$, approximately given by a ninth-order polynomial to be compared with a linear behaviour for linear kinetics.

## 1. Introduction

Stratification is of primary importance in almost all large-scale fluid motions that are encountered in meteorology and oceanography. Also in many astrophysical applications of fluid mechanics, such as the dynamics of stars, stratification exerts a major control on the motion of the fluid. In industrial fluid mechanics, stratification is of importance in, e.g. the manufacture of camera films, temperature control of rooms and solidification of metals. In the majority of the cases mentioned, diffusive effects are generally weak almost everywhere in the fluid and the most striking consequence of stratification is the so-called blocking effect, which causes the fluid to move preferentially on isopycnic surfaces in order to, loosely speaking, minimize potential energy. This tendency for the fluid to move along isopycnic surfaces usually leads to the formation of boundary layers in the vicinity of solid walls where viscous and thermal diffusion is strong enough to upset the control of stratification on the motion.

A less well-known field of application of fluid mechanics, where stratification affects the motion to lowest order, is free convection in electrochemical systems that contain a liquid electrolyte. Some technically important examples of such applications are refining and electroplating of metals. Another very important application is the lead acid battery used in vehicles and for load levelling in industry.

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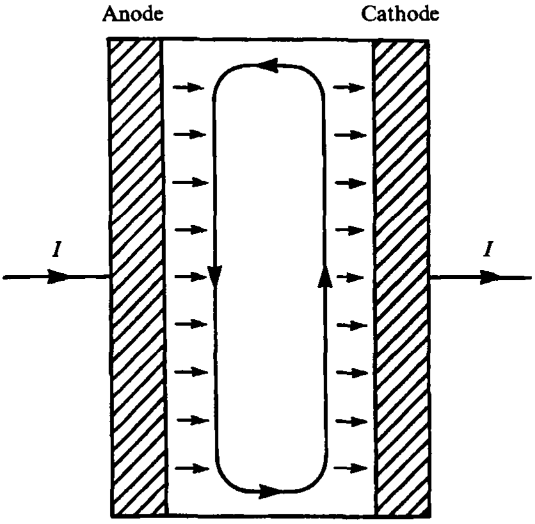

FIGURE 1. Sketch of an electrochemical cell for refining of raw copper. The arrows signify the transport of ions owing to diffusion and migration from anode into the electrolyte and from the electrolyte into the cathode. Ions are transported from anode to cathode mainly by convection as indicated by the closed curve.

The procedure for purification of raw copper is shown schematically in figure 1. The vertical anode is made of raw copper (99.7%), which contains small amounts of impurities such as Pb, Ni, Fe, Si, P, As, etc. but also the noble metals, Ag and Au. The vertical cathode is made of highly purified copper (99.99%). The electrodes are separated by a liquid electrolyte that is an aqueous solution of copper sulphate with some sulphuric acid added. The role of the sulphuric acid, which does not participate in the electrode reactions, is to reduce the resistivity of the electrolyte and hence reduce ohmic losses of the purification process. During electrolysis, the passage of an electric current through the cell, which is carried by moving ions, causes copper ions to be dissolved into the electrolyte at the anode and deposited onto the cathode. Ions are transported from anode to cathode by diffusion that is driven by concentration gradients, migration in the electric field and advection due to motion of the electrolyte. Small amounts of certain additives in the electrolyte cause precipitation of almost all impurities, which then settle at the bottom of the electrochemical cell. In continuously operating plants for metal refining, a large number of cells of the kind shown in figure 1 are coupled in parallel and a very small throughflow is imposed through the cells. A general review of the technology of copper refining can be found in the book by Hine (1985).

As copper ions are dissolved into the electrolyte at the anode, the specific weight of the electrolyte will be increased locally. The reverse process at the cathode causes a local decrease of the specific weight of the electrolyte. Thus, free convection of the electrolyte will take place as indicated in figure 1. The operating conditions of cells for commercial purification of copper are such that the Rayleigh number is very large, i.e. advective transport dominates strongly over diffusion and migration. This means that a stratification will be set up in the cell, see e.g. Walin (1971). In industrial refining of copper, the convective motion in the cell is turbulent. A numerical computation of turbulent free convection in a closed electrochemical system, under some crude but reasonable simplifying assumptions, has been carried out by Ziegler & Evans (1986). Simple order-of-magnitude estimates show that the aforementioned weak throughflow will not significantly change the stratification. To the present authors' knowledge, there are no published experimental investigations of the concentration and velocity fields in copper refining cells in the range of parameter space encountered in applications. Certain engineering aspects of electrolyte circulation in metal refining processes have been reviewed by Fukunaka & Kondo (1988).

Stratification in an electrochemical system such as a cell for metal refining or a lead acid battery has two essential effects on the performance of the cell. First, the convective motion of the electrolyte, and hence the ionic transport, is in many cases controlled by the stratification. Secondly, the transfer of charge from/to the electrodes, i.e. the electrode kinetics, depends on the local values of the concentration and the electric potential at the interface between electrode and electrolyte. In general, this dependence of reaction rate on concentration and potential is nonlinear. For the case of laminar motion of the electrolyte in a closed vertical slot, the first of these effects was investigated theoretically by Bark, Alavyoon & Dahlkild (1992) and experimentally by Karlsson, Alavyoon & Eklund (1990) and Eklund *et al.* (1991). The purpose of the present work is to extend the work by Bark *et al.* (1992) and investigate, by theoretical methods, effects of stratification on both convection and electrode kinetics in a closed vertical slot. The main reason for undertaking this study is that a fair understanding of the case of laminar flow is a necessity for a successful numerical investigation of the turbulent case, even though such a study is somewhat remote owing to present limitations in computer capacity. Another, definitely more accessible but still very relevant, extension of the present work is the generalization to systems with porous electrodes that are separated by a liquid electrolyte. One would then have to consider transport not only in the electrolyte between the electrodes but also within the electrodes. This is the configuration found in lead acid batteries. In order to compute discharge of such batteries, concentration effects on the electrode kinetics has to be accounted for. For the case of recharging of a lead acid battery, however, it turns out that effects of concentration on the kinetics can be ignored and the problem reduces to computation of transport within and between the electrodes. A theoretical and experimental study of recharging of lead acid batteries has been published by Alavyoon *et al.* (1991).

In the present work, all thermal effects are neglected. It can be shown that this is usually a very good approximation for small electrochemical cells. However, in large lead acid batteries, for example, production of heat is often a serious problem. The work by Bark *et al.* (1992) has recently been extended by Alavyoon (1994) to account for sources of both mass and heat at the vertical walls.

It should be pointed out that several of the phenomena considered in the present work have been extensively dealt with in the literature on geophysical fluid dynamics and heat transfer. For brevity's sake, however, such analogies are not stressed in detail in this work. A reasonably complete discussion of such matters is given in the paper by Bark *et al.* (1992).

The present paper is organized as follows: §2 gives the mathematical formulation of the problem to be considered. By using boundary-layer analysis, a simplified mathematical model for the evolution of the concentration field outside the boundary layers is derived in §3. On the timescale considered, this part of the concentration field depends only on the vertical coordinate and time. The number of space coordinates in the mathematical problem is thus reduced from two to one and the number of partial differential equations to be considered is reduced from five to one, the simplified partial differential equation being supplemented with an algebraic equation. Some approximate steady solutions of the simplified problem are given in §4. These solutions are shown to be in good agreement with numerical solutions of the full problem formulated in §2. Some unsteady solutions of the simplified problem, in a parameter regime that is not yet accessible for numerical simulation of the full problem are given in §5. The main conclusions are summarized in §6.

## 2. Problem formulation

The geometry of the closed two-dimensional electrochemical cell to be considered is shown in figure 2, where the coordinate system that is used in this paper is defined. The height of the cell is $2H$ and its width $2h$. Both electrodes are made of the same metallic material, *Me*, say. The electrolyte is a dilute liquid solution of a salt of the metal *Me*. The metal ions are henceforth labelled as species 1 and the corresponding cations as species 2, respectively. The electric potentials of the anode and cathode, relative to an arbitrary reference level that need not be specified, are initially the same. The system is then in equilibrium and there is no transport of charge or mass. At time $t = 0$, a difference in voltage between the electrodes is applied. For $t > 0$, the voltage of the anode is $V_1$ and that of the cathode $V_2 < V_1$. At the electrodes $x = \pm h$, the following electrochemical reactions will then take place

$$Me \leftrightarrow Me^{z_1} + z_1 e^-, \tag{1}$$

where $z_1$ is the charge number of the metal ions. At the anode ($x = -h$), the reaction proceeds to the right in formula (1), i.e. metal ions leave the crystal lattice of the electrode material and are dissolved in the electrolyte. The reversed reaction takes place at the cathode ($x = h$). In the system considered, the cations do not thus participate in the electrode reactions. The transport of ions between the electrodes will set up concentration fields of both species that, in general, are inhomogeneous. As a consequence, the specific weight of the electrolyte will vary in space and free convection will ensue. However, the rates of the reactions specified by formula (1), in the cases to be considered, depend on the local values of the concentrations and the electric potential where the reactions take place. Thus, the convective transport of species will affect its own cause and the purpose of this paper is to compute this coupling, which turns out to be highly nonlinear, for large values of the Rayleigh and Schmidt numbers. Before the initial-value problem for the electrolysis is formulated, the pertinent laws for transport of charge and mass in the electrolyte have to be stated.

In electrochemistry, one distinguishes between potentiostatic and galvanostatic electrolysis. Potentiostatic electrolysis means that the difference in voltage between electrodes is kept at the same value. Galvanostatic electrolysis, on the other hand, means that the total electric current that passes the cell is kept constant. For brevity's sake, only the potentiostatic case is considered in the present work. However, the galvanostatic case can be dealt with using only minor modifications of the methodology that is given in the present paper.

Under the assumption that concentrations are small, the mass flux $N_i$ of species $i$ is given approximately by the Planck–Nernst law (in this paper, repeated indices do not imply Einstein summation)

$$N_i = -\frac{z_i F D_i}{RT} c_i \nabla\phi - D_i \nabla c_i + c_i \boldsymbol{v} \tag{2}$$

(see e.g. Newman 1991, chapter 1). Here $c_i$ is the concentration of species $i$, $\phi$ the electric potential in the electrolyte, $\boldsymbol{v} = (u, w)$ the velocity of the electrolyte (as

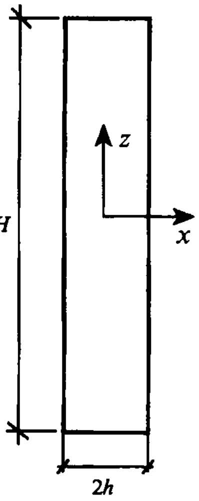

FIGURE 2. Geometry of the electrochemical cell considered in the text and definition of coordinate system.

attention is restricted to dilute solutions, the velocity of the electrolyte can be taken as that of the solvent), $F$ Faraday's constant, $D_i$ the diffusion constant for species $i$, $R$ the gas constant and $T$ the absolute temperature. The ions are thus transported by migration in the electric field, molecular diffusion and advection in the moving electrolyte. The electric current density $\boldsymbol{i}$ in the electrolyte is given by Faraday's law, which in the case under consideration reads

$$\boldsymbol{i} = F(z_1 \boldsymbol{N}_1 + z_2 \boldsymbol{N}_2). \tag{3}$$

Making use of the transport laws (2) and (3), the field equations can now be formulated.

Apart from the very thin double layers adjacent to the electrodes, effects of which are not explicitly accounted for in the present work, the electrolyte is electrically neutral, which may be expressed by the following equation

$$z_1 c_1 + z_2 c_2 = 0. \tag{4}$$

An equivalent statement of electroneutrality is that the electric current density is non-divergent, i.e.

$$\nabla \cdot \boldsymbol{i} = 0. \tag{5}$$

Equations (4) and (5) are thus equivalent. The motion of the electrolyte is to be computed from the equation for conservation of momentum, i.e.

$$\rho_0 \left( \frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{v} \right) = -\nabla p + \mu \nabla^2 \boldsymbol{v} - \rho_0 g \boldsymbol{e}_z \left[ 1 + \sum_{i=1}^{2} \alpha_i (c_i - c_{i0}) \right], \tag{6}$$

where the Boussinesq approximation has been made use of. Here $\rho_0$ is the density of the electrolyte at the (constant) reference concentrations $c_i = c_{i0}$, $p$ the pressure, $\alpha_i$ the densification coefficient for species $i$ and $g$ the acceleration due to gravity. Liquid electrolytes can usually be considered as incompressible. Thus, the velocity field fulfils the equation for conservation of volume

$$\nabla \cdot \boldsymbol{v} = 0. \tag{7}$$

Since chemical reactions take place only at the interfaces between electrodes and electrolyte, the following equations for conservation of species

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \boldsymbol{N}_i \quad (i = 1,2), \tag{8}$$

hold in the electrolyte. The five scalar equations (5)–(8) are, in principle, sufficient for the computation of the five unknowns $\boldsymbol{v} = (u, w)$, $p$, $c_i$ and $\phi$. Next, the boundary and initial conditions will be formulated.

For the velocity field $\boldsymbol{v}$, the no-slip condition is prescribed at the boundaries, i.e.

$$\boldsymbol{v} = \boldsymbol{0} \quad \text{at} \quad x = \pm h, |z| \leqslant H, \quad z = \pm H, |x| \leqslant h. \tag{9}$$

As only species 1 takes part in the electrode reactions, the normal component of the mass flux vector of species 2 is zero at the electrodes. One must thus prescribe that

$$\boldsymbol{e}_x \cdot \boldsymbol{N}_2 = 0 \quad \text{at} \quad x = \pm h, |z| \leqslant H. \tag{10}$$

Because the irreversible reactions at the surfaces† of the electrodes, as specified by formula (1), require a supply of power, the electric field is discontinuous at the interfaces between electrodes and electrolyte, i.e. $\phi(h-0, z, t) \neq V_2$ and $\phi(-h+0, z, t) \neq V_1$. Stated somewhat differently, one may say that, because $\boldsymbol{e}_x \cdot \boldsymbol{i}$ must be continuous across the interfaces between the electrolyte and the electrodes, these interfaces act like infinitesimally thin sheet resistors. The power loss in these sheet resistors makes up the power needed to sustain the reactions specified by formula (1). The magnitudes of these jumps of the electric potential, which in the electrochemical literature are called charge transfer potentials, are not known *a priori* but can be related to the local values of the concentration of species 1 and the normal component of the electric current density by semi-empirical so-called Butler–Volmer laws (see e.g. Newman 1991, chapter 1). In the present work, the following simple Butler–Volmer law‡ is chosen

$$\boldsymbol{e}_x \cdot \boldsymbol{i} = i_0 \left[ \exp\left((z_1 \gamma F/RT)(V_1 - \phi)\right) - \left(\frac{c_1}{c_{10}}\right) \exp\left((z_1(1-\gamma) F/RT)(\phi - V_1)\right) \right]$$
$$\text{at} \quad x = -h, |z| \leqslant H \quad \text{(anode)}, \tag{11}$$

$$\boldsymbol{e}_x \cdot \boldsymbol{i} = i_0 \left[ \left(\frac{c_1}{c_{10}}\right) \exp\left((z_1(1-\gamma) F/RT)(\phi - V_2)\right) - \exp\left((z_1 \gamma F/RT)(V_2 - \phi)\right) \right]$$
$$\text{at} \quad x = h, |z| \leqslant H \quad \text{(cathode)}. \tag{12}$$

In these expressions, the constants $i_0$ and $\gamma$ are the exchange current density and the transfer coefficient. For simplicity, the value of $\gamma$ will hereinafter be taken as $\frac{1}{2}$, which is quite a common value for real electrochemical systems. This form of the Butler–Volmer law has been successfully used for computation of electrolysis of aqueous solutions of $CuSO_4$ by, among others, Awakura, Ebata & Kondo (1979). It should be noted that, even though only the transport of species 1 contributes to the normal component of the electric current density $\boldsymbol{i} \cdot \boldsymbol{e}_x$ at the interfaces between electrodes and electrolyte, the transport of both species will, in general, contribute to $\boldsymbol{i}$ in the bulk of the electrolyte.

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† In electrochemistry, the notation 'surface' does in this context include the thin (~ 1 nm) double layer in the electrolyte outside the geometrical surface of the electrode.

‡ In the form of the Butler–Volmer law specified by formulae (11)–(12), the equilibrium potential at the reference concentration has been subtracted from the electric potential $\phi$. This is just a minor formality that leads to some algebraic simplifications but has no physical implications.

The top and bottom walls of the cell are assumed to be such that no mass transfer takes place there. The appropriate boundary conditions are then

$$\boldsymbol{e}_z \cdot \boldsymbol{N}_1 = \boldsymbol{e}_z \cdot \boldsymbol{N}_2 = 0 \quad \text{at} \quad z = \pm H, |x| \leqslant h. \tag{13}$$

The initial conditions for the system of equations (6)–(8) are

$$\boldsymbol{v}(\boldsymbol{x}, 0) = \boldsymbol{0}, c_i(\boldsymbol{x}, 0) = c_{i0} \quad (i = 1, 2). \tag{14}$$

For a binary electrolyte, the condition (4) of electroneutrality offers some mathematical simplifications since the concentration fields are proportional to each other. Hence, a new variable $c$, which is defined as

$$c = z_1 c_1 = -z_2 c_2, \tag{15}$$

is introduced whereby only one equation for conservation of mass has to be considered. A new reference concentration $c_0$ is defined in the same way. A convenient equation for $c$ is obtained by elimination of $\phi$ between equations (8), whereby one obtains that

$$\frac{\partial c}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} c = D \nabla^2 c. \tag{16}$$

The (positive) quantity $D$ in this equation is defined by the expression

$$D = \frac{(z_1 - z_2) D_1 D_2}{z_1 D_1 - z_2 D_2}, \tag{17}$$

the so-called 'salt diffusivity' of the electrolyte. For algebraic simplicity, attention is restricted, with one exception that will be discussed in §4, to systems with $z_1 = -z_2 = 2$, which are the values for, for example, the technically important case of an aqueous solution of $CuSO_4$. Results for other values of $z_1$ and $z_2$ can be obtained from those given below by simple but somewhat tedious transformations.

In order to define non-dimensional variables, a concentration scale $\mathscr{C}$ must be estimated, a matter that is not altogether straightforward. A physically relevant concentration scale must, of course, depend on the voltages $V_1$ and $V_2$ of anode and cathode, respectively, which are the external control parameters of the system. From the Planck–Nernst law (2), the boundary condition (10) and the Butler–Volmer law at the anode (11), one finds the following relation

$$\frac{\partial c}{\partial x} = -\frac{i_0}{2FD_1} \left[ \exp\left((F/RT)(V_1 - \phi)\right) - \left(\frac{c}{c_0}\right) \exp\left((F/RT)(\phi - V_1)\right) \right]. \tag{18}$$

It is reasonable to assume that

$$\phi \sim \tfrac{1}{2}(V_1 + V_2).$$

If the difference in electric potential across the cell is large in the sense that

$$\exp\left(F(V_1 - V_2)/RT\right) \gg 1,$$

the aforementioned estimate for $\phi$ makes the first term in the bracket in the right-hand side of (18) much larger the second one as $c/c_0$ is, at most, of order unity. Taking $h$ as the relevant lengthscale, one thus obtains the following estimate for the concentration scale

$$\mathscr{C} \sim \frac{h i_0}{2FD_1} \exp\left((F/RT)(V_1 - V_2)\right). \tag{19}$$

This estimate is, of course, not valid for arbitrarily large values of $F(V_1 - V_2)/RT$. The largest change in concentration to be expected is $\sim c_0$. In almost all electrochemical systems, the so-called limiting current phenomenon appears for a sufficiently large difference in voltage between the electrodes (see e.g. Newman 1991, chapter 1). This means that the total current becomes independent of the voltage between the electrodes and that the concentration at the cathode becomes zero. A physically reasonable upper bound on $\mathscr{C}$ is therefore $\sim c_0$. For small values of $F(V_1 - V_2)/RT$, concentration changes are expected to be small, i.e. $c \approx c_0$. One then finds from (18) that

$$\mathscr{C} = \frac{hi_0(V_1 - V_2)}{2RTD_1}. \tag{20}$$

As an interpolation formula for $\mathscr{C}$ one may, in view of (19) and (20), which are valid for large and small values of $F(V_1 - V_2)/RT$, respectively, thus take

$$\mathscr{C} = \min\left\{\frac{hi_0}{FD_1}\sinh\left[\frac{F}{RT}(V_1 - V_2)\right], c_0\right\}. \tag{21}$$

For algebraic simplicity, however, attention is restricted to cases such that $\mathscr{C} = c_0$, i.e. the magnitude of the electric current that passes the cell is assumed to be sufficiently strong that the change in concentration is of the same order of magnitude as the reference concentration. Cases with $\mathscr{C} < c_0$ can be dealt with in exactly the same way with some simple changes in notation.

Non-dimensional variables, which are denoted by $*$ superscripts, can now be defined as

$$x = hx^*, \quad t = \frac{h^2}{D}t^*, \tag{22}$$

$$(\phi + \tfrac{1}{2}(V_1 + V_2), \tfrac{1}{2}(V_1 - V_2)) = \frac{RT}{F}(\phi^*, \mathscr{V}^*), \quad i = i_0 i^*, \tag{23}$$

$$c = c_0 + \mathscr{C}c^*, \quad N_i = \frac{D\mathscr{C}}{h}\mathscr{N}_i^*, \tag{24}$$

$$v = \frac{\rho_0 \mathscr{C} g h^2(\alpha_1 + \alpha_2)}{2\mu}v^*, \quad p + \rho_0 g z = \frac{\rho_0 \mathscr{C} g h(\alpha_1 + \alpha_2)}{2}p^*. \tag{25}$$

The $*$ superscripts will be dropped in what follows. In addition to the non-dimensional difference in electric potential between the electrodes, i.e. $2\mathscr{V}$, the following non-dimensional parameters will appear

$$Ra = \frac{\rho_0 \mathscr{C} g h^3(\alpha_1 + \alpha_2)}{2\mu D}, \quad Sc = \frac{\mu}{\rho_0 D}, \tag{26}$$

$$\Gamma = \frac{2(D_1 + D_2)}{D_1 - D_2}, \quad \kappa = \frac{hi_0}{2D_1 F\mathscr{C}}, \quad \mathscr{H} = \frac{H}{h}. \tag{27}$$

The Rayleigh number $Ra$, the Schmidt number $Sc$ and the aspect ratio $\mathscr{H}$ are assumed to be large. The choice of lengthscale in the definition of the Rayleigh number is discussed in some detail in Bark *et al.* (1992, p. 669). The range of the parameter $\Gamma$ is given by the inequalities $-\frac{1}{2} \leqslant \Gamma^{-1} \leqslant \frac{1}{2}$. $\Gamma$ and the parameter $\kappa$ are assumed to be quantities of order unity. Both small and large values of the non-dimensional potential difference $2\mathscr{V}$ will be considered.

The non-dimensional versions of equations (6), (7) and (16) are

$$\frac{\partial \boldsymbol{v}}{\partial t} + Ra\boldsymbol{v}\cdot\nabla\boldsymbol{v} = Sc(-\nabla p + \nabla^2\boldsymbol{v} - c\boldsymbol{e}_z), \tag{28}$$

$$\nabla\cdot\boldsymbol{v} = 0, \tag{29}$$

$$\frac{\partial c}{\partial t} + Ra\boldsymbol{v}\cdot\nabla c = \nabla^2 c. \tag{30}$$

These equations appear to be sufficient for the computation of $\boldsymbol{v}$, $p$ and $c$. However, in order to determine these quantities, one must, in view of the boundary conditions (11) and (12), also compute the electric potential $\phi$. An equation for $\phi$ can be derived from formulae (2) and (3) and equation (5) whereby one finds that

$$\Gamma\nabla\cdot(1+c)\,\nabla\phi + \nabla^2 c = 0. \tag{31}$$

If the second term in this equation is removed, one recovers the well-known electrostatic problem for the electric potential in a medium of non-uniform conductivity in which charge is transported by electrons. However, in an electrolyte, charge is transported by ions that are moving owing to migration and diffusion. (It follows directly from (2)–(4) that advection of the bulk of the electrolyte does not contribute to the electric current density.) The physical role of migration, which is signified by the first term in equation (31), is to adjust the concentration fields so that electroneutrality is ensured.

The non-dimensional no-slip condition for the velocity field reads

$$\boldsymbol{v} = \boldsymbol{0} \quad \text{at} \quad x = \pm 1, |z| \leqslant \mathscr{H}, \quad z = \pm\mathscr{H}, |x| \leqslant 1. \tag{32}$$

The boundary conditions (10)–(12), can, after some minor manipulations, be written in the following form

$$\frac{\partial c}{\partial x} = -\kappa[\mathrm{e}^{(\mathscr{V}-\phi)} - (1+c)\,\mathrm{e}^{(\phi-\mathscr{V})}] \quad \text{at} \quad x = -1, |z| \leqslant \mathscr{H} \quad \text{(anode)}, \tag{33}$$

$$\frac{\partial c}{\partial x} = -\kappa[(1+c)\,\mathrm{e}^{(\phi+\mathscr{V})} - \mathrm{e}^{-(\mathscr{V}+\phi)}] \quad \text{at} \quad x = 1, |z| \leqslant \mathscr{H} \quad \text{(cathode)}, \tag{34}$$

$$(1+c)\frac{\partial\phi}{\partial x} = \frac{1}{2}\frac{\partial c}{\partial x} \quad \text{at} \quad x = \pm 1, |z| \leqslant \mathscr{H} \quad \text{(anode, cathode)}. \tag{35}$$

The boundary conditions (13) at the insulated horizontal boundaries can be written as

$$\frac{\partial c}{\partial z} = \frac{\partial \phi}{\partial z} = 0 \quad \text{at} \quad z = \pm\mathscr{H}, |x| \leqslant 1. \tag{36}$$

The non-dimensional initial conditions, see (14), are

$$\boldsymbol{v}(\boldsymbol{x},0) = \boldsymbol{0}, \quad c(\boldsymbol{x},0) = 0. \tag{37}$$

The formulation of the mathematical problem for the unknowns $\boldsymbol{v}$, $p$, $c$ and $\phi$ is now complete. Before an approximate method for the solution of this problem is given, some of its implications will be discussed.

Owing to the condition of electroneutrality and the fact that only species 1 reacts at the interfaces of the electrodes and the electrolyte, the net mass flux of species 1 into the cell must be zero, which means that the solution must fulfil the constraint

$$\int_{-\mathscr{H}}^{\mathscr{H}} \left.\frac{\partial c}{\partial x}\right|_{x=-1} \mathrm{d}z = \int_{-\mathscr{H}}^{\mathscr{H}} \left.\frac{\partial c}{\partial x}\right|_{x=1} \mathrm{d}z \tag{38}$$

for all values of $t$. This constraint means that the net influx of mass (and charge) at the anode must always be the same as the net outflux at the cathode. Therefore, it is not *a priori* obvious that a solution to the problem exists. However, at least heuristically, one may argue as follows in favour of the existence of a solution: for any reasonably well-behaved velocity field $\boldsymbol{v}(\boldsymbol{x}, t)$, there is certainly a solution $c(\boldsymbol{x}, t)$ of the convective–diffusive equation (30) that fulfils the boundary conditions (33), (34) and (36) and the initial condition (37) for any reasonably well-behaved function $\phi(\boldsymbol{x}, t)$. On physical grounds, there is, in a more general problem, no need to impose the constraint of mass conservation (38) on the solution $c(\boldsymbol{x}, t)$. Let us assume, for the moment, that the concentration field $c$ be known. One then observes that any solution $\phi(\boldsymbol{x}, t)$ of equation (31), which is a statement of conservation of charge, that fulfils the provisionally known boundary conditions (35) and (36) is undetermined up to an arbitrary constant. It seems very likely that this constant can be chosen so that the boundary conditions (33) and (34) indeed fulfil the constraint (38) for conservation of mass. Numerical studies of similar problems for forced convection (see e.g. Newman 1991, chapter 21, §3) support this conclusion.

Equation (30) may give the false impression that migration and diffusion in a binary electrolyte combine into a fictitious diffusive transport at the same rate of both species with the salt diffusivity $D$ that is given by formula (17). According to the Planck–Nernst law, formula (2), this is, of course, not so. In any case, one can define a non-dimensional flux vector $\mathscr{N}$ that is associated with the conservation equation (30) as follows

$$\mathscr{N} = Ra c \boldsymbol{v} - \nabla c, \tag{39}$$

even though, for the present electrochemical problem, this vector has no physical meaning. (If migration is absent or if concentration is replaced by temperature, the physical meaning of $\mathscr{N}$ is obvious.) The physical mass fluxes $\mathscr{N}_1$ and $\mathscr{N}_2$ can be expressed in terms of $\mathscr{N}$ and the non-dimensional electric current density, which, according to formulae (2), (3) and (23), (24), is given by the following expression

$$\boldsymbol{i} = -\frac{2}{\kappa(\Gamma+2)}[\Gamma(1+c)\nabla\phi + \nabla c]. \tag{40}$$

One then finds that

$$\mathscr{N}_1 = \frac{1}{2}\left[\mathscr{N} + \frac{\kappa(\Gamma+2)}{(\Gamma-2)}\boldsymbol{i}\right], \tag{41}$$

$$\mathscr{N}_2 = \tfrac{1}{2}[\mathscr{N} - \kappa \boldsymbol{i}]. \tag{42}$$

These expressions will be used in the next section.

## 3. Approximate theory for large times

The mathematical problem that was defined in the previous section can be considerably simplified by using perturbation methods. A simpler, but from a physical and mathematical point of view somewhat similar, problem has been studied in a paper by Bark *et al.* (1992, hereinafter referred to as I). Those authors considered a case where the mass fluxes from the electrodes were assumed to be known constants, which is a valid approximation in electrochemical problems if, for example, the electric current density is significantly smaller than the so-called limiting current density (see e.g. Newman 1991). However, for larger values of the electric current density, one must, in general, account for effects of nonlinear electrode kinetics as quantified by the Butler–Volmer law that was given in the previous section. The development in the present paper rests to a large extent on the results obtained in I.

It was shown in I that, after a short transient phase, a vertical stratification is set up in the cell. This stratification is caused by the simple fact that the locally heavy electrolyte outside the anode, where metal ions are dissolved into the electrolyte, sinks to the bottom of the cell. Near the cathode, the reverse process takes place, i.e. light electrolyte rises to the upper region of the cell. As stratification, once established, tends to stiffen isopycnic surfaces in the sense that vertical motion is blocked, the velocity and concentration fields will have boundary-layer character.

In the present work, the physical model that was developed in I will be used with the modification that the mass flux from the electrodes depends on the solution itself. Following the development in I, the small quantity $\epsilon = Ra^{-1/9}$ will be used as the expansion parameter. The boundary-layer structure of the concentration, electric potential and velocity fields, which are shown in figure 3, is the same as that dealt with in I. A meaningful perturbation problem results if the velocity field $\boldsymbol{v}$ and the concentration field $c$ outside the horizontal boundary layers on the top and bottom walls of the cell (see figure 3) are assumed to depend on the following stretched variables

$$\eta_+ = \frac{(1-x)}{\epsilon^2}, \quad \eta_- = \frac{(1+x)}{\epsilon^2}, \quad \zeta = \epsilon z, \quad \tau = \epsilon^2 t. \tag{43}$$

Here $\eta_+$ and $\eta_-$ are boundary-layer coordinates for the buoyancy layers at the vertical surfaces of the electrodes. The physical implications of the lengthscales and timescales that are defined by (43) will be indicated in a moment. In terms of these stretched variables, the following expansions are assumed for $c$ and $\boldsymbol{v}$

$$c = -\mathscr{S}(\zeta,\tau) + \epsilon^2[\vartheta_+(\mathscr{S},\eta_+) + \vartheta_-(\mathscr{S},\eta_-)] + \dots, \tag{44}$$

$$\boldsymbol{v} = (\epsilon^9[u_+(\mathscr{S},\eta_+) + u_-(\mathscr{S},\eta_-)], \epsilon^6[w_+(\mathscr{S},\eta_+) + w_-(\mathscr{S},\eta_-)]) + \dots. \tag{45}$$

For the quantities in these expressions,† it is assumed that $\mathscr{S} \sim 1$ for all $\zeta$ and $\tau$ and that $\{\vartheta_\pm, u_\pm, w_\pm\} \sim 1$ for $\eta_\pm \sim 1$. For large values of $\eta_\pm$, i.e. in the bulk of the electrolyte, $\{\vartheta_\pm, u_\pm, w_\pm\}$ are transcendentally small. The assumed form of the dependence on $\epsilon$ of the solution means that convective transport of mass in the buoyancy layers is of the same order of magnitude as the vertical diffusive transport and temporal variation of mass in the interior. It should be noted that $\{\vartheta_\pm, u_\pm, w_\pm\}$ depend on $\tau$ only via $\mathscr{S}$, which means that the vertical buoyancy layers, on the slow timescale considered, adjust immediately to variations in the concentration field $\mathscr{S}$ outside the boundary layers. This follows from the fact that, according to the definition (43), during a time interval $\Delta\tau \sim 1$ diffusive effects are felt over a vertical distance $\epsilon^{-1}$, which should be compared with the thickness $\epsilon^2$ of the buoyancy layers. The purpose of the analysis in this section is to derive an evolution equation for $\mathscr{S}$.

† It may be argued that $\mathscr{S}$ should also be expanded in powers of $\epsilon^2$. However, it can be shown that $\mathscr{S}$ will enter the final result only to lowest order, a state of affairs that is not obvious from the outset.

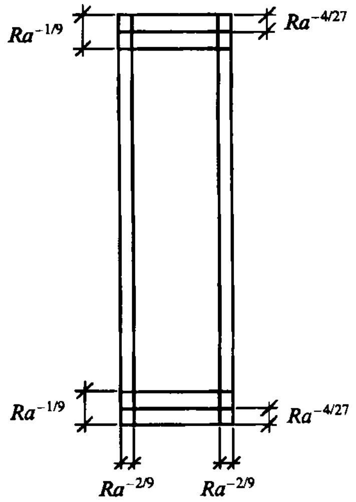

FIGURE 3. Boundary-layer structure of the non-dimensional problem for concentration, electric potential and velocity fields.

In what follows, the large aspect ratio $\mathscr{H}$ of the cell is taken to be $\sim \epsilon^{-1}$. The range of $\zeta$ is thus $|\zeta| \leqslant \epsilon\mathscr{H} = \mathscr{L}$, say, where $\mathscr{L} \sim 1$. The assumption $\mathscr{H} \sim \epsilon^{-1}$ is motivated by the result found in I that, in the steady state, the stratification in the bulk $|c_z|/c \sim \epsilon$. A stratification of the same strength is expected in the present problem as well. Thus, in order to deal with cases such that $\mathscr{C} \sim c_0$, one should take $\mathscr{H} \sim \epsilon^{-1}$. Cases where $\mathscr{H} \sim \epsilon^{\omega}$, $-1 < \omega < 1$, for which one would expect $\mathscr{C} < c_0$ can be dealt with in a similar way.†

It turns out to be convenient to introduce the following shorthand notation for the boundary conditions (33) and (34) for the concentration fields at the electrodes

$$\frac{\partial c}{\partial x} = -\lambda_-(c,\phi) \quad \text{at} \quad x = -1, |\zeta| \leqslant \mathscr{L}, \tag{46}$$

$$\frac{\partial c}{\partial x} = \lambda_+(c,\phi) \quad \text{at} \quad x = 1, |\zeta| \leqslant \mathscr{L}. \tag{47}$$

The sign convention chosen here is such that $\lambda_\pm$ are positive if there is a positive mass flux into the electrolyte from the anode or the cathode. If the quantities $\mathscr{S}$ and $\lambda_\pm$ are assumed to be known, one can readily compute approximate expressions $\vartheta_\pm$ and $w_\pm$ in terms of $\lambda_\pm$. This computation, which is carried out in I for large values of the Rayleigh and Schmidt numbers, gives

$$\vartheta_+ + \vartheta_- - 2\mathrm{i}b^2(w_+ + w_-) = \frac{1}{\beta}[\lambda_+ \exp(-\beta(1-\mathrm{i})h_+) + \lambda_- \exp(-\beta(1-\mathrm{i})h_-)] + O(\lambda_+ + \lambda_-), \tag{48}$$

where
$$\mathrm{i} = (-1)^{1/2}, \quad \beta = \left(\frac{1}{4}\frac{\partial \mathscr{S}}{\partial \zeta}\right)^{1/4}.$$

It will be shown later that the last term in (48) can be neglected.

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† The theory that is given in the present paper is valid for cells with height larger than the thickest horizontal boundary layer (see figure 3) i.e. for $\mathscr{H} \gg \epsilon$.

As in I, an equation for $\mathscr{S}$ will be derived by considering the mass balance in a section of the cell that is bounded by the electrodes at $x = \pm 1$ and the horizontal lines $\zeta = \zeta'$ and $\zeta = \zeta' + \mathrm{d}\zeta'$. The following notation will be used for horizontal averages

$$\langle \dots \rangle = \int_{-1}^{1} \dots \mathrm{d}x.$$

Conservation of species 1 in the aforementioned horizontal strip implies the following equation

$$\epsilon^2 \frac{\partial \langle c_1 \rangle}{\partial \tau} = -\epsilon \frac{\partial \langle \mathscr{N}_1 \cdot \boldsymbol{e}_z \rangle}{\partial \zeta} + (\mathscr{N}_1|_{x=-1} - \mathscr{N}_1|_{x=1}) \cdot \boldsymbol{e}_x, \tag{49}$$

where the last term on the right-hand side accounts for the mass flux from the electrodes into the electrolyte owing to the electrochemical reactions. All terms in this equation are to be expressed in terms of $\mathscr{S}$. For this purpose, it turns out to be convenient to work with the hypothetical mass flux vector $\mathscr{N}$, which is defined by formula (39), and the electric current density $\boldsymbol{i}$. From (10) and (42) one finds the following relation

$$\mathscr{N} \cdot \boldsymbol{e}_x = \kappa \boldsymbol{i} \cdot \boldsymbol{e}_x \quad \text{at} \quad x = \pm 1, \tag{50}$$

which, when combined with (41) and the fact that the electric current density $\boldsymbol{i}$ is solenoidal, see equation (5), gives

$$(\mathscr{N}_1|_{x=-1} - \mathscr{N}_1|_{x=1}) \cdot \boldsymbol{e}_x = \frac{\epsilon \kappa \Gamma}{(\Gamma - 2)} \frac{\partial \langle \boldsymbol{i} \cdot \boldsymbol{e}_z \rangle}{\partial \zeta}. \tag{51}$$

Substitution of the relation $\langle c_1 \rangle = -\mathscr{S} + O(\epsilon^2)$, which follows from (15) and (44), the expression (41) for $\mathscr{N}_1$ and expression (51) into equation (49) gives the following equation

$$\epsilon \frac{\partial \mathscr{S}}{\partial \tau} = \frac{1}{2} \frac{\partial}{\partial \zeta} (\langle \mathscr{N} \cdot \boldsymbol{e}_z \rangle - \kappa \langle \boldsymbol{i} \cdot \boldsymbol{e}_z \rangle). \tag{52}$$

The first term on the right-hand side of this equation can be computed from expressions (39) and (44)–(45) whereby one finds that

$$\langle \mathscr{N} \cdot \boldsymbol{e}_z \rangle = 2\epsilon \frac{\partial \mathscr{S}}{\partial \zeta} + \epsilon^{-1} \langle w\vartheta \rangle. \tag{53}$$

The last term in this expression can be expressed in terms of $\lambda_\pm$ and $\mathscr{S}$ by using formula (48). After a little calculation, one obtains that

$$\langle w\vartheta \rangle = -\frac{\surd 2}{4} \epsilon^2 (\lambda_+^2 + \lambda_-^2) \left( \frac{\partial \mathscr{S}}{\partial \zeta} \right)^{-5/4}. \tag{54}$$

Substitution of expressions (53) and (54) into (52) gives

$$\frac{\partial \mathscr{S}}{\partial \tau} = -\frac{\surd 2}{8} \frac{\partial}{\partial \zeta} \left[ (\lambda_+^2 + \lambda_-^2) \left( \frac{\partial \mathscr{S}}{\partial \zeta} \right)^{-5/4} \right] + \frac{\partial^2 \mathscr{S}}{\partial \zeta^2} - \frac{\kappa}{2\epsilon} \frac{\partial}{\partial \zeta} \langle \boldsymbol{i} \cdot \boldsymbol{e}_z \rangle. \tag{55}$$

This equation is a generalized version of the equation derived in I. In the problem studied in that work, the $x$-component of the mass flux and hence the electric current density was prescribed as (the same) constant value on anode and cathode. This means that the last term in (55) is exactly zero. Also, it follows from (46) and (47) that $\lambda_\pm$ are then constants and, of course, that $\lambda_+ = -\lambda_-$. In the present case, however, $\boldsymbol{i}\cdot\boldsymbol{e}_x$ varies with position on the electrodes and time. At a given height, though, $\boldsymbol{i}\cdot\boldsymbol{e}_x$ is, under the assumptions made, almost equal on anode and cathode, the difference being $\sim\epsilon$ according to (51). This difference, effects of which are quantified by the last term in (55), will, as is shown below, be significant for the evolution of $\mathscr{S}$. As both $\langle\boldsymbol{i}\cdot\boldsymbol{e}_z\rangle$ and $\lambda_\pm$ depend on $\mathscr{S}$ and $\phi$, one must compute $\phi$ in terms of $\mathscr{S}$ by solving (31) with the boundary conditions (35) and (36). Once $\phi$ is known in terms of $\mathscr{S}$, $\lambda_\pm$ can be computed in terms of $\mathscr{S}$ from expressions (33) and (34) and $\langle\boldsymbol{i}\cdot\boldsymbol{e}_z\rangle$ from (40), (44) and (48).

Equation (31) can be solved by using standard perturbation theory for boundary-layer problems. On the long timescale $\tau$, it is assumed that $\phi$ can be represented as an outer expansion that is valid in the bulk of the electrolyte and as inner expansions in the buoyancy layers of the following form

$$\phi = \phi_0(x,\zeta,\tau)+\epsilon^2\phi_1(x,\zeta,\tau)+\ldots, |x| < 1-O(\epsilon^2), |\zeta| < \mathscr{L}-O(\epsilon), \tag{56}$$

$$\left.\begin{gathered}\phi = \psi_{0+}(\eta_+,\zeta,\tau)+\psi_{0-}(\eta_-,\zeta,\tau)+\epsilon^2[\psi_{1+}(\eta_+,\zeta,\tau)+\psi_{1-}(\eta_-,\zeta,\tau)],\\ \eta_\pm \sim 1, |\zeta| < \mathscr{L}-O(\epsilon).\end{gathered}\right\} \tag{57}$$

It is thus assumed that the electric potential outside the buoyancy layers varies not only with the 'slow' variable $\zeta$ but also with $x$. The dependence on $x$ has to be included in order to compute the ohmic variation of the electric potential in the essentially stagnant electrolyte outside the boundary layers. Obviously, the problem for $\phi$ in this region will be the same as that for the electric potential in a slender solid resistor, whose conductivity varies slowly in the vertical direction. It should be noted that in the end regions $\zeta = \pm[\mathscr{L}-O(\epsilon)]$, the solution will vary with $z$ rather than $\zeta$. This matter will be taken up later in this section. A detailed discussion of this issue for a very similar problem can be found in Kevorkian & Cole (1981, p. 408).

Substitution of expressions (56) and (57) into (31) for the electric potential gives the following equations for $\phi_{0,1}$ and $\psi_{0\pm,1\pm}$

$$\frac{\partial^2\phi_0}{\partial x^2} = 0, \tag{58}$$

$$\Gamma(1-\mathscr{S})\frac{\partial^2\phi_1}{\partial x^2}+\Gamma\frac{\partial}{\partial\zeta}\left[(1-\mathscr{S})\frac{\partial\phi_0}{\partial\zeta}\right]-\frac{\partial^2\mathscr{S}}{\partial\zeta^2} = 0, \tag{59}$$

$$\Gamma(1-\mathscr{S})\frac{\partial^2\psi_{0\pm}}{\partial\eta_\pm^2} = 0, \tag{60}$$

$$\frac{\partial^2\psi_{1\pm}}{\partial\eta_\pm^2}+\frac{\partial^2\vartheta_\pm}{\partial\eta_\pm^2} = 0. \tag{61}$$

The solution of these equations is straightforward as is the matching of the outer expansion to the inner expansions. After some algebra, one obtains the following uniformly valid expansion

$$\begin{aligned}\phi = \Phi_0(\zeta,\tau)+\Phi_1(\zeta,\tau)\,x+\epsilon^2\bigg\{&\Phi_2(\zeta,\tau)+\Phi_3(\zeta,\tau)\,x\\ &-\frac{1}{\Gamma(1-\mathscr{S})}\frac{\partial}{\partial\zeta}\left[\Gamma(1-\mathscr{S})\left(\frac{x^2}{2}\frac{\partial\Phi_0}{\partial\zeta}+\frac{x^3}{6}\frac{\partial\Phi_1}{\partial\zeta}\right)-\frac{x^2}{2}\frac{\partial\mathscr{S}}{\partial\zeta}\right]-\frac{(\vartheta_++\vartheta_-)}{\Gamma(1-\mathscr{S})}\bigg\}.\end{aligned} \tag{62}$$

In this expansion, $\Phi_{0,1}$ are functions that have to be determined from the boundary conditions whereas $\Phi_{2,3}$ need not be determined to the order considered. However, because $\boldsymbol{e}_x \cdot \nabla\vartheta \sim \epsilon^{-2}$, the last term in expression (62), which accounts for effects on the electric potential of the concentration fields in the buoyancy layers, will turn out to give a contribution to lowest order.

The following useful relation is obtained from substitution of expressions (62) and (44) into boundary conditions (35)

$$\Phi_1 \pm \frac{(\Gamma+2)}{2\Gamma(1-\mathscr{S})} \frac{\partial\vartheta_\pm}{\partial\eta_\pm} = 0, \quad \eta_\pm = 0. \tag{63}$$

Combination of (33, 34), (44) and (62, 63) leads to the following system of transcendental equations for $\Phi_{0,1}$

$$\frac{2\Gamma(1-\mathscr{S})}{(\Gamma+2)} \Phi_1 = -\kappa[\exp(\mathscr{V}-\Phi_0+\Phi_1)-(1-\mathscr{S})\exp(\Phi_0-\Phi_1-\mathscr{V})], \tag{64}$$

$$\frac{2\Gamma(1-\mathscr{S})}{(\Gamma+2)} \Phi_1 = -\kappa[(1-\mathscr{S})\exp(\Phi_0+\Phi_1+\mathscr{V})-\exp(-(\mathscr{V}+\Phi_0+\Phi_1))]. \tag{65}$$

This system has the following solution for $\Phi_0$

$$\Phi_0 = -\tfrac{1}{2}\ln(1-\mathscr{S}), \tag{66}$$

whereas $\Phi_1$ has to be computed in terms of $\mathscr{S}$ as the solution of the following transcendental equation

$$\Phi_1 = -\frac{\kappa(\Gamma+2)}{\Gamma(1-\mathscr{S})^{1/2}} \sinh(\Phi_1+\mathscr{V}). \tag{67}$$

The last term in equation (55) can now be computed in terms of $\mathscr{S}$ from formulae (40), (44), (62) and (66) with the following result

$$\langle \boldsymbol{i}\cdot\boldsymbol{e}_z \rangle = -\frac{2\epsilon(\Gamma-2)}{\kappa(\Gamma+2)} \frac{\partial\mathscr{S}}{\partial\zeta}. \tag{68}$$

It remains for us to determine the quantities $\lambda_\pm$ in (55). From (33)–(34), (46)–(47) and (62)–(65) the following approximate expressions are obtained

$$\lambda_+ = -\lambda_- + O(\epsilon) = \frac{2\Gamma(1-\mathscr{S})}{(\Gamma+2)} \Phi_1 + O(\epsilon). \tag{69}$$

The correction terms, which were discussed in the paragraph following (55), are not needed to the order considered.

Substitution of (68) and (69) into (55) gives the following equation that contains $\mathscr{S}$ only

$$\frac{\partial\mathscr{S}}{\partial\tau} = \frac{\partial}{\partial\zeta}\left[\frac{2\Gamma}{\Gamma+2}\frac{\partial\mathscr{S}}{\partial\zeta} - \frac{2^{1/2}\Gamma^2(1-\mathscr{S})^2}{(\Gamma+2)^2}\Phi_1^2(\mathscr{S})\left(\frac{\partial\mathscr{S}}{\partial\zeta}\right)^{-5/4}\right], \tag{70}$$

where $\Phi_1(\mathscr{S})$ is to be computed in terms of $\mathscr{S}$ from (67). In general, the latter computation has to be carried out by using numerical methods. For steady electrolysis, however, it turns out to be possible to obtain approximate analytic solutions for large and small values of $\mathscr{V}$. Such solutions are given in the next section.

It should be pointed out that (70) can, of course, also be obtained by consideration of the mass balance for species 2. In fact, that derivation is, although not simple, somewhat simpler than the derivation that is given above. The present derivation, though, is a bit more instructive since one has to consider the flux of mass from the electrodes into the control volume. There is one important observation about (70) that should be pointed out. The physical significance of the right-hand side of the equation is evident from its primitive form (49). However, it follows directly from the electroneutrality condition that one can also write (70) as follows

$$\frac{\partial \mathscr{S}}{\partial \tau} = \frac{\partial}{\partial \zeta} \langle \mathscr{N}_2 \cdot \boldsymbol{e}_z \rangle .$$

This observation will be made use of in what follows.

Next, boundary and initial conditions have to be formulated for the parabolic equation that is defined by (67) and (70). For a satisfactory derivation of boundary conditions, one would have to consider the end regions $\zeta = \pm |\mathscr{L} - O(\epsilon)|$, where the assumption of a slow variation of the solution with the vertical coordinate $z$ breaks down. The situation is further complicated by the circumstance that one would also have to consider the nested horizontal boundary layers of thicknesses $\epsilon$ and $\epsilon^{4/3}$, respectively. (The complicated structure of these boundary layers was briefly discussed in Appendix A in I.) It is therefore evident that the two boundary conditions needed have to be formulated on an *ad hoc* basis. For this purpose, one may use the following argument: since species 2 does not take part in the electrode reactions and there is no mass transfer of any species at the top and bottom walls, it appears reasonable, from a physical point of view, to assume that there is no net flux of species 2 into the end regions at any time $\tau$. This hypothesis will be used as the boundary condition in the present work. (In Appendix A of I, it was demonstrated, using a plausible but not altogether satisfactory mathematical analogy between the Stewartson $E^{1/4}$-layer in the theory of rotating fluids (see e.g. Greenspan 1991, chapter 2, § 18) and the horizontal $\epsilon$-layer in the present work, that this boundary condition is a reasonable one for the simpler problem dealt with in that work.) Also, this boundary condition will be prescribed at $\zeta = \pm \mathscr{L}$, which may possibly introduce a small error, presumably of order $\epsilon$, in the final result. Rearranging the terms in the bracket [...] in (70), one arrives at the following boundary condition

$$\frac{\partial \mathscr{S}}{\partial \zeta} = 2^{-2/9} \left[ \frac{\Gamma}{\Gamma + 2} \right]^{4/9} [(1 - \mathscr{S}) |\Phi_1(\mathscr{S})|]^{8/9} \quad (\zeta = \pm \mathscr{L}), \tag{71}$$

which will be used for the solution $\mathscr{S}$ of (70) and (67).

Because there is no solution available on the short timescale $h^2/D$ to be used as a matching condition for the solution on the long timescale $\epsilon^2 h^2/D$, see (22) and (43), the initial condition for the solution of (70) and (67) also has to be formulated on an *ad hoc* basis. The same problem was encountered in I and the same remedy, which was discussed at length in I, will be used in the present work. It turns out that the solution is very insensitive to the details of the initial condition. The reason is that the 'diffusivity' in (70) is very large for the small values of $\partial \mathscr{S} / \partial \zeta$ that appear for small values of $\tau$. A simple order of magnitude estimate shows that the 'diffusivity' in (70) is $\sim \mathscr{S}^{-9/4}$. Thus, one may start the integration at $\tau = 0$ and as initial condition use almost any function that is of small magnitude and that fulfils (71). The following function was successfully used in I (see figure 3 of I)

$$\mathscr{S}(\zeta, 0) = \delta_1 \zeta, \quad \zeta \leqslant \mathscr{L} - \delta_2, \tag{72}$$

$$\mathscr{S} = \mathscr{S}_{0\zeta} \zeta \pm (\mathscr{L} - \delta_2)(\delta_1 - \mathscr{S}_{0\zeta}), \quad 0 \leqslant |\mathscr{L} \pm \zeta| \leqslant \delta_2, \tag{73}$$

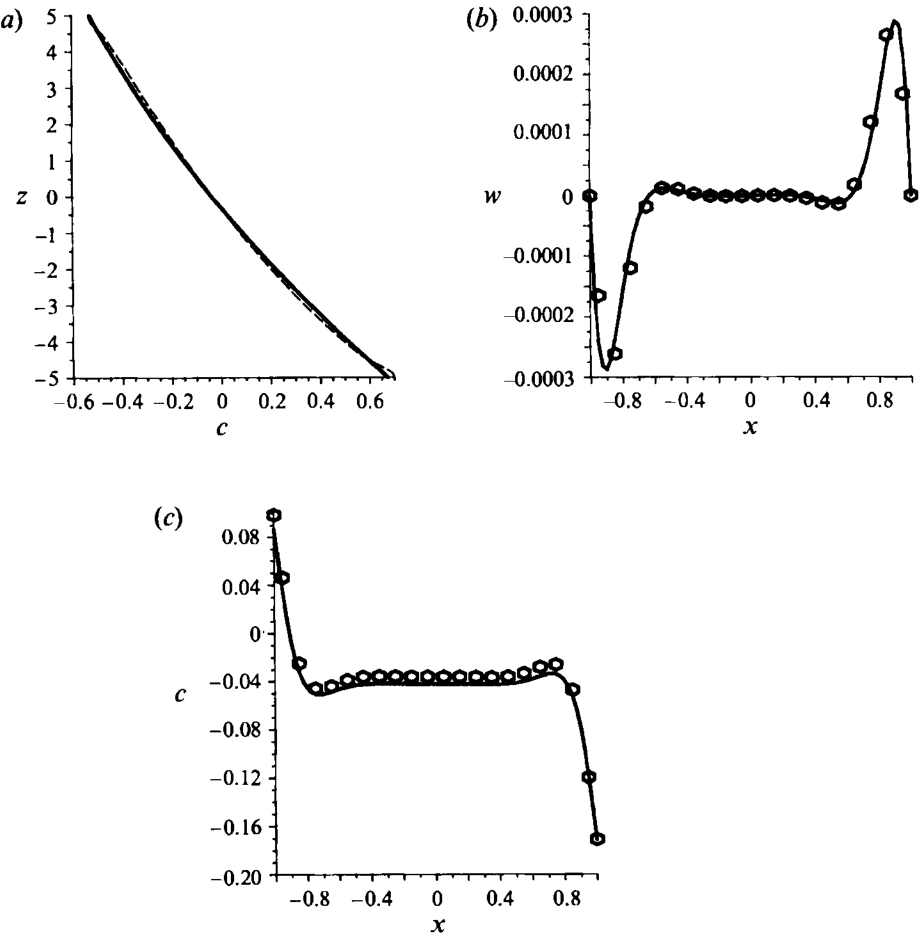

FIGURE 4. (*a*) The vertical variation of the concentration field in the midsection of the cell. ——, approximate theory; – – –, numerical solution of the full problem. (*b*) The horizontal variation of the vertical velocity component at midheight of the cell: ——, present approximate theory; ○, numerical solution of the full problem. (*c*) The horizontal variation of the concentration field at midheight of the cell: ——, present approximate theory; ○, numerical solution of the full problem. $\mathscr{H} = 5$, $Ra = 174000$, $\Gamma = -10.3$, $\kappa = 0.0701$, $\mathscr{V} = 2.75$.

where $\delta_1$ and $\delta_2$ are two small numbers that can be chosen quite arbitrarily and $\mathscr{S}_{0\zeta}$ is a number that is determined so that (71) and (67) are fulfilled. This kind of initial condition is also used in the present work.

So far, no comparison between predictions of the simplified model derived in this section and experimental data has been made. However, numerical solutions of the complete mathematical problem that was formulated in §2 have been computed by Alavyoon & Bark (1993). Values of physical constants used in the numerical examples discussed in this work are given in Appendix A. Figure 4 shows comparisons between a numerical solution of the complete problem, which has been integrated in time up to a state that is, within a very small error, steady, and the corresponding steady approximative solution computed according to the theory developed in this section. The value of $\mathscr{V}$ is here 2.75, which is too small for effects of nonlinear reaction kinetics to be strong. However, in the numerical computations of solutions of the complete problem, serious numerical difficulties were encountered for larger values of $\mathscr{V}$. Figure

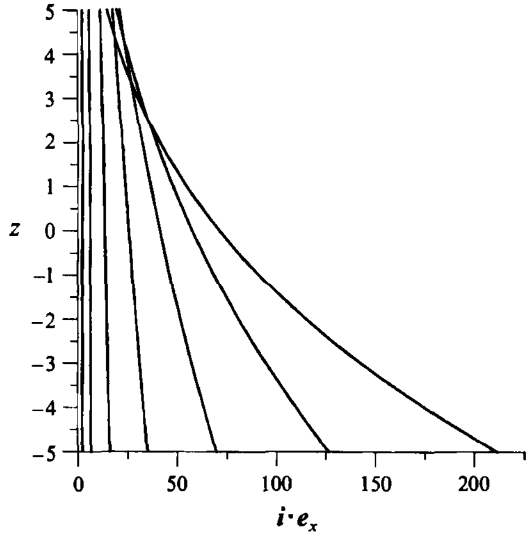

FIGURE 5. Variation of the electric current density on the electrodes at steady state as predicted by the approximate theory for values of $\mathscr{V} = 1, 2, 3, 4, 5, 6, 7$. The parameter values are the same as in figure 4.

4(*a*) shows the vertical variation of the concentration in the midsection of the cell. The agreement between the two solutions is surprisingly good in view of the fact that the perturbation parameter $\epsilon$ is not very small ($\approx 0.3$). As expected, the deviation is largest near the top and bottom of the cell, where the approximate solution for the electric potential is invalid. Some differences compared with the case with constant current densities on the electrodes that was considered in I can be inferred from figure 4(*a*). The vertical concentration profile is slightly bent rather than being a straight line as was found in I. The stratification is also somewhat asymmetric with respect to the origin which was not the case for the solution that was given in I. Figures 4(*b*) and 4(*c*) show comparisons for the horizontal variation of the vertical velocity component and the concentration at midheight of the cell. Also in these figures the agreement between the two solutions is satisfactory.

A quantity of significant interest from the engineering point of view is the distribution of the normal component of the electric current density on the electrodes. From the approximate theory that is given in this section, according to which the current densities on anode and cathode are equal to lowest order, the distribution in the steady state is shown in figure 5. This graph shows clearly how the increased conductivity at the bottom of the cell, which is caused by the stratification, for increasing values of $\mathscr{V}$ leads to a successively more non-uniform distribution of the current density.

Before some unsteady numerical solutions of the simplified approximate problem are discussed, some simple analytic steady solutions for large and small differences in voltage between the electrodes will be given in the next section.

## 4. Approximate steady solutions for large and small values of $\mathscr{V}$

For the steady case, an equation for $\mathscr{S}$ can be obtained from (70), which can be integrated directly once with respect to $\zeta$. However, one may save some algebra by making use of the observation that, in the steady state, there is no net mass flux of species 2 across any horizontal cross-section of the cell. Thus, the boundary condition (71), which in the unsteady case implies that there is no net mass flux of species 2 into the end regions at $\zeta \pm \mathscr{L}$, will, in the steady case, hold for all values of $\zeta$. One thus obtains the following first-order ordinary differential equation for $\mathscr{S}$

$$\frac{\mathrm{d}\mathscr{S}}{\mathrm{d}\zeta} = 2^{-2/9}\left[\frac{\Gamma}{\Gamma+2}\right]^{4/9} [(1-\mathscr{S})|\Phi_1(\mathscr{S})|]^{8/9} \quad (\zeta \leqslant |\mathscr{L}|). \tag{74}$$

The solution of this equation has to fulfil the requirement of global conservation of mass, which in terms of $\mathscr{S}$ is expressed as follows

$$\int_{-\mathscr{L}}^{\mathscr{L}} \mathscr{S}\,\mathrm{d}\zeta = 0. \tag{75}$$

In the first part of this section, an approximate solution for large values of $\mathscr{V}$ will be computed. For notational convenience, two additional parameters $\sigma$ and $\chi$, which are defined as

$$\sigma = \frac{\Gamma}{\kappa(\Gamma+2)}, \quad \chi = 2^{-2/9}\left[\frac{\Gamma}{\Gamma+2}\right]^{4/9} \mathscr{V}^{4/9}, \tag{76}$$

will be used in the following analysis. $\sigma$ is assumed to be of order unity whereas $\chi$, in the first part of this section, is taken to be large.

For large values of $\mathscr{V}$, one obtains, by iteration, the following approximate solution of equation (67) for $\Phi_1$ in terms of $\mathscr{S}$

$$\Phi_1 = -\mathscr{V} + \operatorname{arcsinh}[\sigma(1-\mathscr{S})^{1/2}\mathscr{V}] + \dots. \tag{77}$$

This result shows that, to lowest order, the difference in electric potential in the electrolyte between points just outside the electrodes is approximately equal to the difference in electric potential between the electrodes. The second term in expression (77) signifies a relatively small modification owing to the presence of the charge transfer potentials.

In order to proceed, it turns out to be suitable to define a new spatial coordinate $\xi$, which is defined as

$$\xi = \chi\zeta, \quad |\xi| \leqslant \mathscr{A} = \chi\mathscr{L}. \tag{78}$$

Substitution of (77) into (74) gives an approximate differential equation for $\mathscr{S}$

$$\frac{\mathrm{d}\mathscr{S}}{\mathrm{d}\xi} = (1-\mathscr{S})^{8/9}\left(1 - \frac{8}{9^9\mathscr{V}}\operatorname{arcsinh}[\sigma(1-\mathscr{S})^{1/2}\mathscr{V}] + \dots\right). \tag{79}$$

An approximate solution of this equation is obtained by iteration. One finds that

$$\mathscr{S} = 1 - \frac{1}{9^9}(\xi_0-\xi)^9 - \frac{8(\xi_0-\xi)^8}{9^9\mathscr{V}}\int_{-\mathscr{A}}^{\xi} \operatorname{arcsinh}\left\{\sigma\left[\frac{\xi_0-\xi}{9}\right]^{9/2}\mathscr{V}\right\}\mathrm{d}\xi + \dots, \tag{80}$$

where $\xi_0$ is a constant of integration that is to be determined from the constraint (75). This may be done by regular perturbation. For this purpose, $\xi_0$ is written as

$$\xi_0 = \Xi_0 + \delta\Xi_0 + \dots,$$

where $\Xi_0$ is determined so that the lowest-order part of the solution (80) fulfils the constraint (75) and $\delta\Xi_0$ so that the constraint is fulfilled for both terms in (80). Before an equation for $\Xi_0$ is derived, a comment on the solution (80) should be made. It is obvious from the lowest-order part of this expression that both the condition of positive concentration, i.e. $\mathscr{S} \leqslant 1$, cf. (44), and the condition of hydrostatic stability, i.e. $\mathscr{S}_\xi \geqslant 0$, require that $\Xi_0 \geqslant \mathscr{A}$.

Combination of (75) and (80) gives, to lowest order, the following equation for $\Xi_0$

$$(\mathscr{A}+\Xi_0)^{10}-(\mathscr{A}-\Xi_0)^{10} = 20\times 9^9 \mathscr{A}. \tag{81}$$

It can be shown that, in order for a real solution $\Xi_0 \geqslant \mathscr{A}$ of this equation to exist, there is an upper bound on $\mathscr{A}$

$$\mathscr{A} \leqslant \mathscr{A}_{max} = \tfrac{9}{2}\times 10^{1/9}. \tag{82}$$

The proof of this inequality is quite simple but a little tedious and is therefore not given here. For a given value of $\mathscr{L}$ this means that, according to the definitions (76) and (78), $\mathscr{V}$ is bounded from above by the constraint

$$\mathscr{V} \leqslant 2^{-7/4}\, 10^{1/4} \frac{\Gamma}{\Gamma+2}\left[\frac{9}{\mathscr{L}}\right]^{9/4}. \tag{83}$$

If this inequality is violated, the physical basis for the approximate theory developed in the first part of this section breaks down. More will be said about this in a moment.

In general, the algebraic equation (81) has to be solved by numerical methods. However, for the special case in which the value for $\mathscr{A}$ is chosen as the upper bound $\mathscr{A}_{max}$ in inequality (82), one can proceed a bit further by using analytic methods. The price to be paid for this choice of $\mathscr{A}$ is that one is then considering an electrochemical cell, whose aspect ratio depends on the difference in voltage between the electrodes. However, in spite of this limitation, some interesting properties of the solution can be inferred from this special case.

For $\mathscr{A} = \mathscr{A}_{max}$ one finds that

$$\Xi_0 = \mathscr{A}_{max}. \tag{84}$$

The lowest-order solution for $\mathscr{S}$ can then be written in the following form

$$\mathscr{S} = 1-\frac{1}{9^9}(\mathscr{A}_{max}-\xi)^9; \quad |\xi| \leqslant \mathscr{A}_{max}. \tag{85}$$

This solution is invalid at $\xi = \mathscr{A}_{max}$. The reason is that $\mathscr{S}_\xi = 0$ at this point. This implies that (48), which is the basis for the derivation of (70), breaks down locally. In physical terms, this failure comes from the fact that the buoyancy layers become infinitely thick at $\xi = \mathscr{A}_{max}$. However, this is not a very serious shortcoming as it can be shown that the validity of (48) requires that $\mathscr{S}_\xi \gg \epsilon^8$, which is not a very severe restriction. In fact, it can be shown that the region where (48) is invalid is of order $4^{1/8}\chi^{-1/8}\epsilon$. Furthermore, for the mass transfer in the electrochemical cell, the upper part of the cell is almost passive as concentration and conductivity are there very small. This means that the poor representation of the solution in a limited region near the top of the cell is of no practical importance.

For values of $\mathscr{V}$ that are larger than the upper bound that is given by expression (83), there is certainly a steady solution of the problem that is formulated in §2. However, its structure will most likely be significantly different from that discussed above. The results discussed above indicate that the dissolved salt will collect in a narrow, strongly stratified region near the bottom of the cell. Above this region, the concentration is probably very small and the motion of the fluid can be expected to be similar to that of a homogeneous fluid at low Reynolds number. However, this matter will not be pursued further in this work.

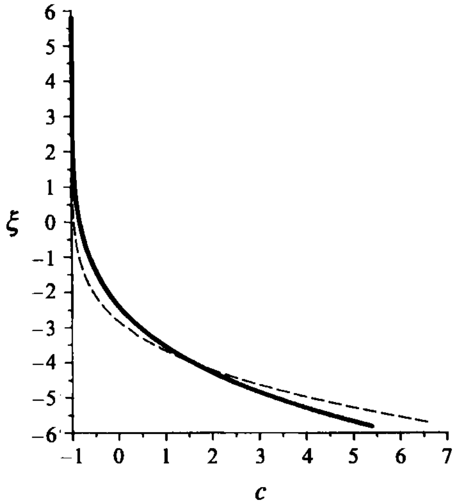

FIGURE 6. Comparison between the approximate steady solution for the bulk concentration $c(\zeta, \tau) = -\mathscr{S}$ and its asymptotic approximation for large values of $\mathscr{V}$ for $\mathscr{V} = 10$, $Ra = 40000$, $\kappa = 0.281$, $\Gamma = -34.2$. ——, numerical solution of equation (74). ---, formula (80).

The computation of $\delta\Xi_0$ from expression (80) and the constraint (75) just requires standard manipulations and details are therefore omitted. After a little algebra, one arrives at the following expression

$$\delta\Xi_0 = -\frac{8}{45\mathscr{V}(\sigma\mathscr{V})^{20/9}} \int_0^{10^{1/2}\alpha\mathscr{V}} x^{11/9} \operatorname{arcsinh} x \, \mathrm{d}x. \tag{86}$$

An asymptotic expansion of the integral that appears in this expression is computed in Appendix B, where it is shown that, for large values of the number $\mathscr{K}$,

$$\int_0^{\mathscr{K}} x^{11/9} \operatorname{arcsinh} x \, \mathrm{d}x = \tfrac{9}{20}[\mathscr{K}^{20/9} \ln \mathscr{K} - \tfrac{9}{20}\mathscr{K}^{20/9} + \tfrac{5}{2}\mathscr{K}^{2/9} + O(1)].$$

Collecting results from (80), (84)–(86) then gives the following approximate expression for $\mathscr{S}$

$$\mathscr{S} = 1 - \frac{1}{9^9}(\mathscr{A}_{max} - \xi)^9 + \frac{2}{9^8\mathscr{V}}(\mathscr{A}_{max} - \xi)^8$$
$$\times \Biggl[\Biggl\{\frac{10^{10/9}}{25}[\ln \sigma\mathscr{V} + \tfrac{1}{2}\ln 40 - \tfrac{9}{20}] - \frac{4}{9}\int_{-\mathscr{A}_{max}}^{\xi} \operatorname{arcsinh}\left(\sigma\mathscr{V}\left[\frac{\mathscr{A}_{max} - \xi}{9}\right]^{9/2}\right)\mathrm{d}\xi\Biggr\} + \dots \tag{87}$$

It is obvious that the accuracy of this approximate formula deteriorates for large values of the parameter $\sigma$. For the geometries that are considered in this work, this turns out to be the case for the system under consideration, i.e. $|\mathrm{Cu(s)}|\,\mathrm{CuSO_4(aq)}\,|\mathrm{Cu(s)}|$, because the exchange current density $i_0$ for this system is very small, see formulae (27) and (76) and the numerical values of physical constants given in Appendix. Therefore, in order to compare formula (87) and a numerical solution of the problem defined by (74) and the constraint (75), the system $|\mathrm{Ag(s)}|\,\mathrm{AgNO_3(sq)}\,|\mathrm{Ag(s)}|$ was chosen. The comparison is shown in figure 6. As can be seen from this graph, the approximate formula is quite accurate.

A relation of fundamental interest in electrochemistry is the so-called polarization curve, which is the relation between the total current $\mathscr{I}$, say, that is passing through the electrochemical cell and the difference in voltage between the electrodes, which is here measured by half its value, i.e. $\mathscr{V}$. For algebraic simplicity, only the lowest-order expression for the polarization curve is given in this work. It is a very fortunate circumstance that this relation turns out to be independent of $\xi_0$ and can thus be computed for any value of $\mathscr{V}$ being subject to the upper bound (83) without having to solve equation (81). The normal component of the local electric current density on the anode, which is approximately the same as that on the cathode, can be computed in terms of $\mathscr{S}$ from formulae (40), (44), (48) and (62)–(63) whereby one finds that

$$i\cdot e_x = \frac{2^{3/2}\chi^{9/8}}{\kappa}\left(\frac{\Gamma}{\Gamma+2}\right)^{1/2}(1-\mathscr{S})+\dots \tag{88}$$

Thus, to lowest order, the distribution of the normal component of the electric current density on the electrodes is proportional to the concentration outside the buoyancy layers. In view of (77), which says that the charge transfer potentials are of minor importance for large values of $\mathscr{V}$, this result has a simple explanation. As the difference in electric potential per unit length in the horizontal direction is $\sim -\mathscr{V}$ everywhere in the electrolyte, the strength of the electric density will be determined by the local value of the conductivity, which is proportional to the concentration. It is a bit surprising, though, that (88) holds for any value of $\mathscr{V}$.

Integration of expression (88) and making use of the constraint (75) gives the expression for the polarization curve

$$\mathscr{I} = \frac{2^{5/4}\Gamma\mathscr{L}}{5\kappa(\Gamma+2)}\mathscr{V}^{1/2}+\dots \tag{89}$$

This formula is of limited practical value since the aspect ratio of the electrochemical cell depends on the applied voltage. However, it can be shown that the relation $\mathrm{d}\mathscr{I}/\mathrm{d}\mathscr{V} \sim \mathscr{V}^{-1/2}$ holds also for a fixed value of $\mathscr{L}$. Thus, the electrochemical system that is considered in this work is somewhat unusual in the sense that the electric current density does not seem to approach a limiting value as the voltage between the electrodes becomes large, at least not for the range of applied voltage for which the theory is valid. The reason for this is quite simple. Because the system is closed and mass is conserved, the hydrostatic pressure outside the buoyancy layers prevents complete depletion of dissolved salt at all parts of the vertical cathode.

Another important integral measure of the operation of electrochemical systems is the Sherwood number, i.e. the ratio between the total mass transfer with and without convection but accounting for diffusion, migration and nonlinear electrode kinetics in both cases. (The case without convection can be realized experimentally with horizontal electrodes with the cathode above the anode.) As there is only mass transfer of species 1 and this is the only species carrying electric charge, the Sherwood number is, for the system considered, equal to the ratio between the total currents in the two cases. The exact solution for the polarization curve in the case of a stagnant electrolyte has recently been given by Sokirko & Bark (1993). Taking the two first terms of the asymptotic expansion for $\mathscr{V} \gg 1$ of the expression for the polarization curve given by those authors, one finds that

$$Sh = \frac{2^{5/4}\Gamma\mathscr{V}^{1/2}}{15(\Gamma+2)}\left(1+\frac{2\mathrm{e}^{-2\mathscr{V}}}{((9+8\kappa^2)^{1/2}-3)^{1/2}}\right)+\dots \tag{90}$$

The second limiting case to be considered is $\mathscr{V} \ll 1$, which offers considerably simpler mathematics compared to the previous case. To lowest order, this limit is similar to the case considered in I. In the present work, the results given in I are extended into the regime of slightly nonlinear electrode kinetics. The computation of $\mathscr{S}(\zeta)$ and $\mathscr{I}$ can be carried out by regular perturbation and the results are

$$\mathscr{S} = 2^{-2/9}\left[\frac{\Gamma+2}{\Gamma}\right]^{4/9}\left[\frac{\kappa\Gamma}{\Gamma+\kappa(\Gamma+2)}\right]^{8/9}$$

$$\times\left\{\mathscr{V}^{8/9}\zeta-\frac{8\times 2^{-2/9}}{9}\left[\frac{\Gamma+2}{\Gamma}\right]^{13/9}\left[\frac{\kappa\Gamma}{\Gamma+\kappa(\Gamma+2)}\right]^{17/9}\mathscr{V}^{16/9}(\zeta^2-\tfrac{1}{3}\mathscr{L}^2)\right\}+\dots \qquad (91)$$

$$\mathscr{I} = \frac{2^{9/4}\Gamma\mathscr{L}}{\Gamma+\kappa(\Gamma+2)}\left\{\mathscr{V}+\frac{2^{5/9}}{27}\left[\frac{\Gamma+2}{\Gamma}\right]^{26/9}\left[\frac{\kappa\Gamma}{\Gamma+\kappa(\Gamma+2)}\right]^{34/9}\mathscr{L}^2\mathscr{V}^{25/9}\right\}+\dots \qquad (92)$$

The Sherwood number in this limit is simply computed by dividing this expression for $\mathscr{I}$ by the following approximate expression for the total current $\mathscr{I}'$ in the case without convection

$$\mathscr{I}' = \frac{\mathscr{L}}{(1+2\kappa)}\mathscr{V}+O(\mathscr{V}^3), \qquad (93)$$

which is obtained from the lowest-order approximation of the solution given by Sokirko & Bark (1993).

The measurements of velocity by Karlsson *et al.* (1990) and of concentration by Eklund *et al.* (1991) in a small copper sulphate cell could be predicted quite well in I under the assumption that the electric current density on the surfaces of the electrodes is constant. However, it should be pointed out that the value of $\mathscr{V}$ in those experiments was not small. Typical values for the dimensional mean current density were 50 and 100 A m$^{-2}$. As the current density is non-dimensionalized with the exchange current density $i_0$, see (23), whose value is of order 1 A m$^{-2}$ for the copper sulphate cell (see Appendix A), figure 5 shows that, in the aforementioned experiments, there was a significant variation of the current density on the electrodes. Thus, the theoretical predictions in I were to some extent fortuitous. For example, the dimensional stratification, i.e. $\mathscr{C}\mathscr{S}_z/h$, which was measured by Eklund *et al.* (1991), it can be shown that its dependence on the local (dimensional) current density $\boldsymbol{i}\cdot\boldsymbol{e}_x$ at the electrodes is of the form $\mathscr{C}\mathscr{S}_z/h \sim (i_0\,\boldsymbol{i}\cdot\boldsymbol{e}_x)^{-1/9}$. Thus, the deviation from linearity of the stratification depends very weakly on the current density on the electrodes and the measured almost linear stratification appeared to be due a constant current density on the electrodes. As for the dimensional vertical component of the velocity field in the buoyancy layers, which was measured by Karlsson *et al.* (1990), the corresponding dependence is found to be $\sim (i_0\,\boldsymbol{i}\cdot\boldsymbol{e}_x)^{-1/3}$, which is also quite weak and explains the good agreement between theory and experiments.

## 5. Unsteady electrolysis

The simplified unsteady problem, which was defined in the previous section by (67) and (70) with the initial condition (72), (73) and the boundary conditions (71), has been solved numerically for values of $\mathscr{V}$ that are too large for successful numerical integration of the complete problem. The evolution of $\mathscr{S}$ for $\mathscr{V} = 4$ is shown in figure 7. As pointed out in §3, the unsteady solution is, strictly speaking, valid only for $\tau \sim$

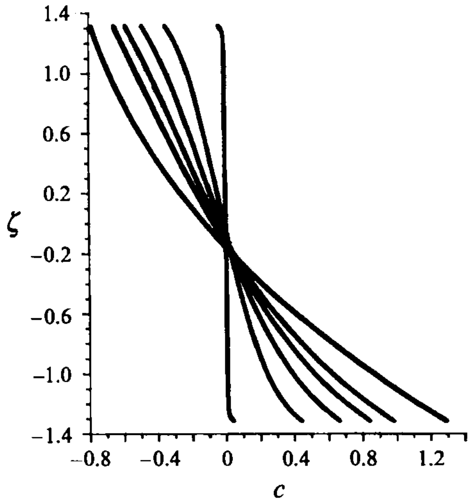

FIGURE 7. Evolution of the bulk concentration $c(\zeta, \tau)$ according to the approximate theory for $\mathscr{V} = 5$, $Ra = 174000$, $\kappa = 0.0701$, $\Gamma = -10.3$. The values of $\tau$ for the curves in the graph are 0, 0.1, 0.3, 0.6, 1, 5.

1, which, for the case shown in the graph, would correspond to $t > 3$. However, as in the case dealt with in I, numerical experiments indicate that the solution is valid for $t \sim 1$ or even smaller. Two observations can be made from this figure. First, the response of the system for small values of $t < 1$, for which the solution may not be a very good approximation, is quite rapid. As was discussed in some detail in I, this is due to the fact that the strength of the stratification increases with time. Thus, the suction into the divergent buoyancy layers, which control the evolution of the stratification in very much the same way as the Ekman-layer suction controls the spin-up of a rotating fluid (see e.g. Veronis 1970) decreases with time. Secondly, the variation with time of the stratification is larger in the lower part of the cell than in the upper part. This effect is due to the larger electric current density near the bottom, which is a consequence of the vertical variation of conductivity (cf. expression (88)).

## 6. Conclusions

Potentiostatic unsteady electrolysis of a dilute liquid solution of a metal salt in a cell with vertical electrodes has been considered for large Rayleigh and Schmidt numbers with particular emphasis on effects of reaction kinetics on mass transport and convective motion of the electrolyte. A simplified but accurate theory has been derived by using perturbation methods. Results from the simplified theory are in good agreement with numerical solutions of the complete problem.

It was shown that a strong stratification of the electrolyte and buoyancy layers on the electrodes appear after a short initial period. The stratification evolves on a long timescale $\sim Ra^{-2/9}h^2/D$, where $Ra$ is the Rayleigh number, $h$ half the distance between the electrodes and $D$ the salt diffusivity. During this process, the net advective transport in the vertical buoyancy layers is of the same order of magnitude as that of the vertical diffusion in the practically stagnant interior. The system approaches a steady state, in which the stratification, in the general case, is nonlinear. This is in contrast to cases where the electric current density on the electrodes is approximately constant for which it was shown by Bark *et al.* (1992) that the steady stratification is linear. The deviation from linearity of the steady stratification increases with increasing values of the different $\Delta V$ in voltage between the electrodes.

The horizontal component of the electric current density on the electrodes is, except for small values of $\Delta V$, non-uniform. Its value decreases monotonically with the vertical distance from the bottom of the cell. This is a consequence of the stratification of the electrolyte. The electric current prefers to flow in regions of large conductivity, i.e. where the concentration is large.

Finally, it has been demonstrated that the major part of the ionic transport outside the boundary layers is made up by horizontal migration. In the buoyancy layers, however, horizontal transport due to diffusion and migration are of the same order of magnitude.

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## Appendix A. Values of physical constants

In this Appendix, the values of electrochemical constants that are used in the numerical examples are given. All data are for 25 °C.

For the copper sulphate solution, the concentration chosen was $c_0 = 0.1 \text{ mol l}^{-1}$ and the dimensions of the cell were $h = 1$ mm and $H = 5$ mm. The value of the exchange current density $i_0$ varies significantly in the literature. Experiments that were carried out by Alavyoon showed that the value $i_0 = 1 \text{ A m}^{-2}$, which is of the same order of magnitude as reported elsewhere (see e.g. Tanaka & Tamamushi 1964), is a reasonable estimate. For the remaining constants, the following values were used

$$\alpha = 0.1678 \text{ l mol}^{-1} \quad \text{(Landolt–Börnstein 1967)},$$
$$\nu = 1.1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \quad \text{(Lobo 1989)},$$
$$D_1 = 0.72 \times 10^{-9}, \quad D_2 = 1.065 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \quad \text{(Newman 1991)}.$$

These constants lead to the following values of the non-dimensional parameters

$$Ra = 1.74 \times 10^5, \quad Sc = 1.28 \times 10^3, \quad \kappa = 7 \times 10^{-2}, \quad \Gamma = -10.3, \quad \mathscr{H} = 5.$$

The concentration of the silver nitrate solution was taken as $c_0 = 0.6 \text{ mol l}^{-1}$. The width of the cell was chosen as 2 mm and the aspect ratio is specified by formulae (76) and (78) and the quantity $\mathscr{A}_{max}$ as given by (82). The values of the electrochemical constants for the system were

$$i_0 = 100 \text{ A m}^{-2} \quad \text{(Bard 1978)},$$
$$\alpha = 0.1336 \text{ l mol}^{-1}, \quad \text{(Landolt–Börnstein 1967)},$$
$$\nu = 0.9005 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \quad \text{(Lobo 1989)},$$
$$D_1 = 1.648 \times 10^{-9}, \quad D_2 = 1.902 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \quad \text{(Newman 1991)}.$$

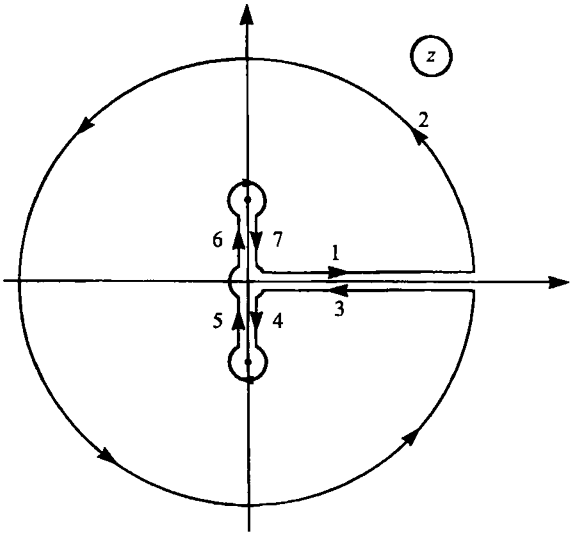

FIGURE 8. Path of integration.

From these constants, one finds values of the non-dimensional parameters as follows

$$Ra = 0.989\times 10^6,\quad Sc = 1.02\times 10^3,\quad \kappa = 0.26,\quad \Gamma = -28.0.$$

## Appendix B. Evaluation of the integral in formula (86)

In order to evaluate the integral (86) for large values of $\mathscr{K}$, one may make use of the following identity

$$\int_0^{\mathscr{K}} x^{11/9}\operatorname{arcsinh} x\,\mathrm{d}x = \tfrac{9}{20}\left\{\mathscr{K}^{11/9}[\operatorname{arcsinh}\mathscr{K}-(1+\mathscr{K}^2)^{1/2}]+\frac{11}{9}\int_0^{\mathscr{K}} x^{2/9}(1+x^2)^{1/2}\,\mathrm{d}x\right\}. \tag{94}$$

The integral on the right-hand side may be evaluated by integration along the path shown in figure 8 and using Cauchy's theorem. The contributions from the small circular paths around the branch points at $z = 0$, $z = \pm\iota$ vanish. If the contribution from a path labelled $k$ in figure 8 is denoted by $I_k$, one finds, after some simple computations, that

$$I_1+I_3 = (1-\exp(4\mathrm{i}\pi/9))\int_0^{\mathscr{K}} x^{2/9}(1+x^2)^{1/2}\,\mathrm{d}x,$$

$$\sum_{k=4}^{k=7} I_k = -2\mathrm{i}\,(\exp(\mathrm{i}\pi/9)+\exp(\mathrm{i}\pi/3))\int_0^1 y^{2/9}(1-y^2)\,\mathrm{d}y,$$

$$I_2 = \frac{9\mathscr{K}^{20/9}}{20}(\exp(4\mathrm{i}\pi/9)-1)\left[1+\frac{5}{\mathscr{K}^2}-\frac{5}{32\mathscr{K}^4}+O(\mathscr{K}^{-6})\right].$$

Summation of these expressions leads to the following result

$$\int_0^{\mathscr{K}} x^{2/9}(1+x^2)^{1/2}\,\mathrm{d}x = \frac{9\mathscr{K}^{20/9}}{20}\left[1+\frac{5}{\mathscr{K}^2}-\frac{5}{32\mathscr{K}^4}+O(\mathscr{K}^{-6})\right]-\frac{\int_0^1 y^{2/9}(1-y^2)^{1/2}\,\mathrm{d}y}{\sin(\pi/9)}. \tag{95}$$

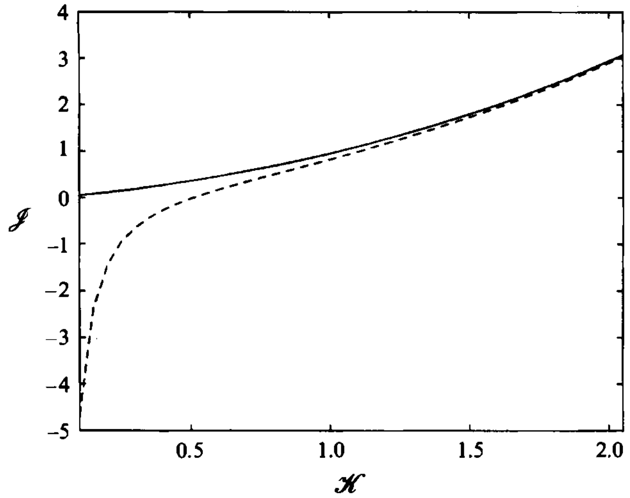

FIGURE 9. Comparison between numerical evaluation of the integral $\mathscr{I} = \int_0^{\mathscr{X}} x^{2/9}(1+x^2)^{1/2}\,\mathrm{d}x$ and its asymptotic approximation given by formula (95) as function of $\mathscr{X}$.

The last term on the right-hand side of this expression has to be evaluated numerically. Its value is 1.802951068.... Substitution of (95) into (94) leads to (86). The accuracy of formula (95) is, as can be seen from figure 9, very good.

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