

**TWO METAL DEPOSITION ON A MICRODISK ELECTRODE**

By

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# TWO METAL DEPOSITION ON A MICRODISK ELECTRODE

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**Abstract.** Some of the electrochemical problems one is interested in in the automobile industry nowadays involve microdisk electrodes. In modeling these problems one encounters a system of nonlinear PDE's which, at first sight, are very similar to the *semiconductor equations*.

It turns out, however, that the problems at hand are much harder to tackle, since, in general, more than just two species are involved (in the problem considered in this report there are four, the two metals and two ions in the supporting electrolyte).

Apart from that the equations are not merely coupled via a potential function but also via a type of conservation law called *electroneutrality*. Also, one has to deal with very nasty boundary conditions called BUTLER-VOLMER *equations*, governing the reaction on the electrode.

Since for two spatial dimensions there are no analytical results and these seem very hard to come by (if at all), this report concentrates on the description of the problem and what has been done to facilitate getting the numerical results arrived at employing techniques suggested by GM Research. From the work done there one also has some theoretical results on very closely related problems that serve to support the data provided by the numerical calculations.

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## 1. Electro-Diffusion Models

Two metal deposition on a microdisk electrode is a special topic arising in a more general context: *electro-diffusion*. Despite the fact that this is a nonlinear transport process (a combination of both *diffusion* and *migration*) it was for a long period of time viewed as being essentially a linear process. Therefore one tended to take into consideration only the linear part, diffusion, and neglect migration, the nonlinear part. In recent years, however, it turned out to be impossible to further disregard nonlinear effects, especially since many areas of application of the electro-diffusion model nowadays have to deal with microscopic scales, thus invalidating the linear approximation. Examples of those areas are *semiconductor device modeling* and electrochemical reactions on *permselective membrane* as well as on microdisk electrodes. In all these cases one has to account for migration terms as well as diffusion.

Let us take a look at the classical PDE-model of electro-diffusion. First, we shall deal with a general setting. In doing this we will encompass a variety of different applications, some of which were mentioned above. However, it is interesting to note that in spite of the fact that semiconductor device modeling and the modeling of mass transport in dilute electrochemical solutions have a lot in common with respect to the mathematics involved, the terminology in the two fields is completely different. For example, the *n*-semiconductor of electrical engineering is the analogon of an anion-exchanger in electro-chemistry. A brief comparison of terminology (at least the basic notions) is given in [RU].

In the model employed for electro-diffusion phenomena transport is governed by the so-called NERNST-PLANCK *equation*. This name honors the two pioneers in this field, W. NERNST and M. PLANCK, who first formulated the equations towards the end of the 19<sup>th</sup> century. To write them down we assume that we are dealing with *n* species (whatever they might be: electrons and holes or ions in an electrolyte solution, for example). With each of these species there is associated a *total flux*

$$\mathbf{n}_i = v c_i - D_i \left( \nabla c_i + z_i c_i \frac{F}{RT} \nabla \phi \right) .$$

The symbols in the above expression represent the following (where *p* denotes position,  $\tau$  denotes time):

- $c_i = c_i(\tau, p)$  : concentration of species *i*
- $v = v(\tau, p)$  : flow velocity (e.g. of a solution)
- $\phi = \phi(\tau, p)$  : electric potential

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- $D_i$  : diffusion coefficient of species  $i$
- $z_i$  : integer ionic charge of species  $i$
- $F$  : FARADAY's constant
- $R$  : universal gas constant
- $T$  : absolute temperature

We will restrict ourselves to cases where we have

$$v \equiv 0$$

which only goes to say, that, for example in the case we are most interested in, namely in two metal deposition on the microdisk electrode, the supporting electrolytic solution is *not in motion*. Under this assumption the so-called *convection term*,  $vc_i$ , drops out of the flux equations under consideration. We are therefore left with an expression for the fluxes which is additively composed of the (linear) *diffusion term*

$$-D_i \nabla c_i$$

and the (nonlinear) *migration term*

$$-z_i D_i c_i f \nabla \phi .$$

Here we and in the sequel use

$$f := \frac{F}{RT} .$$

Then what one has to consider is *ion conservation* (or *mass balance*), namely

$$\frac{\partial c_i}{\partial \tau} = -\nabla \cdot \mathbf{n}_i = D_i \nabla \cdot (\nabla c_i + z_i c_i f \nabla \phi) .$$

The unknowns are therefore the concentrations  $c_i$  of the different species and the electric potential  $\phi$ . These are coupled as expressed in the equations above. The latter, however, will not suffice to determine the actual values of these unknowns, since there is one equation missing (apart from the more serious lack of a geometry and the associated boundary conditions, of course). The additional equation is where there is the first major difference between semiconductor and electrolyte solution contexts. In the former case the supplement is the *electrostatic POISSON-equation*

$$k \cdot \nabla^2 \phi = \rho ,$$

where  $\rho$  denotes the *total charge density* and  $k$  denotes a constant (not specified here). In the latter case another conservation law, called *electroneutrality*, comes into play, i.e.

$$\sum_{i=1}^n z_i c_i = M,$$

where  $M$  is some bound charge. What this is saying is that at each point in the solution the total charge is zero. Both of these ways of supplementing mass balance by one more equation fit into the general setting of electro-diffusion phenomena as outlined in [RU].

If we assume further that the bound charge mentioned above is zero our system consists of the *field equations*

$$\frac{\partial c_i}{\partial \tau} = D_i [\nabla^2 c_i + z_i f (\nabla c_i \nabla \phi + c_i \nabla^2 \phi)]$$

and electroneutrality

$$\sum_{i=1}^n z_i c_i = 0.$$

This, however, is generally not the form in which one looks at the equations. Instead they are usually tailored such that they are better to deal with, i.e. they are scaled such that they end up being in *dimensionless form*. Scaling for this purpose always makes use of a characteristic length of the problem at hand. This could be either the DEBYE-length or some other suitable length; in our case it will be the radius of the microdisk. With this length, let us call it  $a$ , the independent variables of time and position are scaled as follows:

$$p \rightarrow \frac{p}{a} \quad \text{and} \quad \tau \rightarrow t := \frac{\tau}{a^2}.$$

One way of scaling the unknowns (the one we will employ) is

$$C_i := \frac{c_i}{c_i^\infty} \quad \text{and} \quad \varphi := f\phi,$$

where  $c_i^\infty$  denotes the bulk concentrations of species  $i$ . Furthermore, if we set

$$\mathbf{N}_i := \frac{a}{D_i c_i^\infty} \mathbf{n}_i,$$

we find for the dimensionless fluxes

$$\mathbf{N}_i = -(\nabla C_i + z_i C_i \nabla \varphi)$$

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and for the time derivative of  $C_i$  we have

$$C_{it} := \frac{\partial C_i}{\partial t} = \frac{a^2}{c_i^\infty} \frac{\partial c_i}{\partial \tau}.$$

Therefore our system of equations becomes

$$C_{it} = -D_i \nabla \cdot \mathbf{N}_i = D_i [\nabla^2 C_i + z_i (\nabla C_i \nabla \varphi + C_i \nabla^2 \varphi)]$$

together with

$$\sum_{i=1}^n \varepsilon_i c_i = 0,$$

where

$$\varepsilon_i := \frac{z_i c_i^\infty}{z_n c_n^\infty}.$$

Before we finally turn our attention to the special case of metal deposition we try to enhance our understanding of what we are looking at by hinting at the role of the electric potential function. To do this, we investigate *ambipolar diffusion*. That is to say that we have only two species and also we assume  $z_1 = -z_2 = 1$ . Then electroneutrality tells us

$$C_2 = k C_1$$

for some constant  $k$ . Furthermore, ion conservation says

$$\begin{aligned} C_{1t} &= D_1 \nabla^2 C_1 + D_1 \nabla \cdot (C_1 \nabla \varphi) \\ C_{2t} &= D_2 \nabla^2 C_2 - D_2 \nabla \cdot (C_2 \nabla \varphi) \end{aligned}$$

Substituting the relation between  $C_1$  and  $C_2$  established by exploiting electroneutrality into the second equation and consequently cancelling the common factor  $k$  on both sides one has

$$\begin{aligned} C_{1t} &= D_1 \nabla^2 C_1 + D_1 \nabla \cdot (C_1 \nabla \varphi) \\ C_{1t} &= D_2 \nabla^2 C_1 - D_2 \nabla \cdot (C_1 \nabla \varphi) \end{aligned}$$

Dividing both equations by  $D_1$  and  $D_2$  respectively and adding or subtracting yields after some rearrangements

$$C_{1t} = \frac{2D_1 D_2}{D_1 + D_2} \nabla^2 C_1$$

and

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$$\nabla \cdot (C_1 \nabla \varphi) = -\frac{D_1 - D_2}{D_1 + D_2} \nabla^2 C_1 .$$

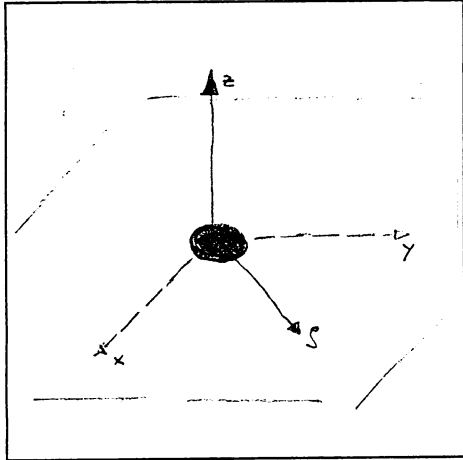
From this we can explain why the process under investigation would be called ambipolar diffusion. In fact, transport of species 1 (and then, via electroneutrality, also of species 2) is determined through a single LAPLACE-equation. The electric potential has no part in determining what happens to the concentrations of the two species; it is there only to ensure electroneutrality.

While this is not always the case it does give us a little more understanding of the physics involved. Furthermore, it is the purpose of the mathematical model to give such pieces of information which might later pertain to the design of experiments in a laboratory. While there are some cases in which analytical results have been known for some time, meaning that in those cases one could show, for example, well-posedness of the problem or even existence and uniqueness of a solution, hardly ever was it possible to give an analytical representation of the solution. Recently, however, there have been important advances in this respect (see [BAVE], [BA]). In these papers the authors were able to give an analytical representation for a large class of problems via an integral transform technique. Nonetheless, for the problem we are about to look at, the two metal deposition on a microdisk electrode, practically no analytical results are known so that we will try to gain a better understanding of the process by conducting numerical simulations.

## 2. Microdisk Electrodes in Electrolyte Solutions

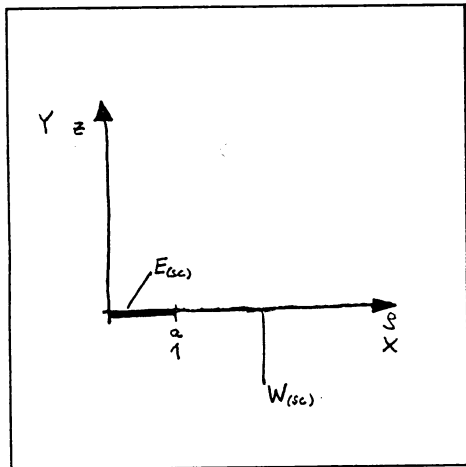
### 2.1 The microdisk environment

When we investigate two metal deposition on a microdisk electrode we are looking at a special case of mass transport in a dilute electrolyte solution. The geometry we start out with is as follows:



$$S' = \{(x, y, z) \in \mathbb{R}^3 \mid z \geq 0\}$$

Rotational symmetry of the disk electrode makes this a problem in two spatial dimensions. Employing cylindrical coordinates the geometry we deal with becomes:



$$S = \{(\rho, z) \in \mathbb{R}^2 \mid \rho, z \geq 0\}$$

$$S_{sc} = \{(X, Y) \in \mathbb{R}^2 \mid X, Y \geq 0\}$$

So originally the solution is viewed as being in an infinite container with just a bottom in which a microdisk electrode is embedded with center at the origin. In this setting we have (with  $a$  denoting the disk radius):

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$$\text{electrode : } E' = \{(x, y, z) \in \mathbb{R}^3 \mid x^2 + y^2 \leq a^2, z = 0\}$$

$$\text{container wall : } W' = \{(x, y, z) \in \mathbb{R}^3 \mid x^2 + y^2 > a^2, z = 0\}$$

$$\text{bulk of solution : } B' = \{(x, y, z) \in \mathbb{R}^3 \mid z > 0\} = S \setminus (E \cup W)$$

Making use of rotational symmetry and scaling (where the characteristic length is conveniently taken to be the disk radius  $a$ ) we have

$$\text{electrode : } E_{\text{sc}} = \{(X, Y) \in \mathbb{R}^2 \mid X \leq 1, Y = 0\}$$

$$\text{container wall : } W_{\text{sc}} = \{(X, Y) \in \mathbb{R}^2 \mid X > 1, Y = 0\}$$

$$\text{bulk of solution : } B_{\text{sc}} = \{(X, Y) \in \mathbb{R}^2 \mid Y > 0\} = S_{\text{sc}} \setminus (E_{\text{sc}} \cup W_{\text{sc}})$$

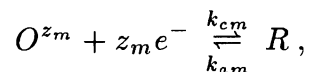
Microdisk electrode environments therefore involve two spatial dimensions so that, even when we look only at steady state and forget about the transient case, we are left with a coupled system of partial differential equations. Now it seems easy to reduce the dimensionality of the space variables to one. We might say:

*Let us make the electrode hemispherical so that, due to spherical symmetry, we would have to look at just one spatial dimension!*

This is actually a very nice theoretical case which has been dealt with in [BAVE] and [BA]. It is, however, merely theoretical. Practically there is no (economically feasible) way to produce hemispherical electrodes at the microscopic scale needed. It would be technically very difficult and much too expensive to manufacture such electrodes. Therefore one has to address the problem the way it presents itself in actual fact, i.e. we have to cope with the disk electrode geometry.

## 2.2 The model for the two metal problem

The particular problem we are interested in here is that in the dilute electrolyte solution there are two ionized metals as well as two supporting electrolyte ions. The latter do not take part in any reactions at the electrode while the former become deionized there, whereby the electrode is coated with the two metals. Both the metal species therefore undergo a reaction of the type



where species  $O^{z_m}$  goes to its reduced form  $R$  by taking on  $z_m$  (= ionic charge number) electrons leading to the metal being deposited on the electrode.  $k_{am}$  and  $k_{cm}$  are the *anodic* and *cathodic reaction rates*.

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The mathematical model for this process is as follows:

1. Electroneutrality:

$$\sum_{i=1}^n z_i c_i = 0 .$$

2. Field Equations:

$$\frac{\partial c_i}{\partial \tau} = -\nabla \cdot \mathbf{n}_i = D_i [\nabla^2 c_i + z_i f (\nabla c_i \nabla \phi + c_i \nabla^2 \phi)]$$

where

$$\mathbf{n}_i = -D_i (\nabla c_i + z_i c_i f \nabla \phi) \quad i = 1, 2, 3, 4 .$$

3. Initial Values:

$$c_i(0, x, y, z) = c_i^\infty \quad \text{bulk concentrations}$$

4. Boundary Conditions:

- a. far away:

$$\lim_{x+y+z \rightarrow \infty} c_i(\tau, x, y, z) = c_i^\infty ; \quad \lim_{x+y+z \rightarrow \infty} \phi(\tau, x, y, z) = 0 .$$

- b. insulating container wall:

$$\mathbf{n}_i \cdot \vec{\mathbf{n}} = 0 \quad (x, y, z) \in W' , \quad i = 1, 2, 3, 4 .$$

- c. disk electrode:

$$\mathbf{n}_i \cdot \vec{\mathbf{n}} = 0 \quad (x, y, z) \in E' , \quad i = 3, 4 .$$

and

$$\mathbf{n}_j \cdot \vec{\mathbf{n}} = k_{aj} \exp [(1 - \beta_j) z_j f (\tilde{v} - \phi)] - k_{cj} c_j \exp [-\beta_j z_j f (\tilde{v} - \phi)] , \\ (x, y, z) \in E' , \quad j = 1, 2 .$$

Here, as expressed verbally as well as in mathematical terms in 4.b. above, the container wall is taken to be *insulating*. Also we number the species such that the first two represent the ionized metals, which do react on the electrode, and the third and fourth are the ones that do not react but are just present in the supporting electrolyte solution. Transport along the electrode of the reactant species is then governed by a BUTLER-VOLMER-equation, given in 4.c. above. The symbols  $\beta_j$  and  $\tilde{v}$  therein represent the so called *symmetry factors* and the *applied voltage* at the electrode respectively. This equation

can be derived by analyzing the relation between *anodic current density* and the so called *exchange current density* (see [KO]). At this point it is worth pointing out that  $\phi$  is not required to satisfy POISSON's equation in the microdisk environment. Therefore the applied voltage at the electrode (from some external source) will in general be different from the electric potential function, which is also influenced by internal effects in the solution. Also, we assume the normal vector  $\vec{n}$  to the wall and the electrode to point into the solution, so that if the normal component to the flux is negative for one of the metals, this species is being deposited on the electrode, if it is positive, the species is dissolving from the electrode.

The dimensionless form of these equations is arrived at scaling the way it was done in the first section. But we need to scale the symbols appearing in the BUTLER-VOLMER-equations as well. We set

$$V := f\tilde{v}$$

and introduce parameters  $\alpha_j$  that incorporate the disk radius as well as both of the reaction rates and the bulk concentration of the species in question. We set

$$\alpha_j := \frac{ak_{cj}}{D_j} \exp(-\beta_j z_j V_{ej})$$

where

$$V_{ej} := \frac{1}{z_j} \ln \left( \frac{k_{cj} c_j^\infty}{k_{aj}} \right).$$

The latter is the *equilibrium voltage* for species  $j$ . This means, that when this particular (scaled) voltage is applied at the electrode, there will be no contribution to the total current from species  $j$ : its normal component to the flux is zero. One notices immediately that there are essentially two ways of varying these parameters: changing the bulk concentrations of either species will affect only the associated parameters of this very species itself, thereby altering the ratio of the  $\alpha$ -parameters (and changing the equilibrium voltage of the species). On the other hand, one can change the disk radius, which would result in different absolute values of the alphas but no change in their ratio or in the respective equilibrium voltages. In any case, the parameters  $V$  and  $\alpha_j$  are the only ones at our disposal if we want to influence the process at all, for example, if we would like to ensure a more uniform coating of the electrode.

With the above parameters, the dimensionless form of the boundary conditions for the reactant species along the electrode now becomes:

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$$\begin{aligned} \mathbf{N}_j \cdot \vec{n} &= \frac{a}{D_j c_j^\infty} \mathbf{n}_j \cdot \vec{n} \\ &= \alpha_j \{ \exp [(1 - \beta_j) z_j (V - V_{ej} - \varphi)] - C_j \exp [-\beta_j z_j (V - V_{ej} - \varphi)] \} . \end{aligned}$$

In terms of the scaled variables in cylindrical coordinates it is easy to see, that along the electrode as well as along the insulating container wall the *normal derivative* is  $\frac{\partial}{\partial Y}$ . Taking this into consideration we are now left with the following system of equations:

1. Electroneutrality:

$$\sum_{i=1}^n \varepsilon_i C_i = 0 .$$

2. Field Equations:

$$C_{it} = -\nabla \cdot \mathbf{N}_i = D_i [\nabla^2 C_i + z_i (\nabla C_i \nabla \varphi + c_i \nabla^2 \varphi)]$$

where

$$\mathbf{N}_i = -D_i (\nabla C_i + z_i C_i \nabla \varphi) \quad i = 1, 2, 3, 4 .$$

3. Initial Values:

$$C_i(0, X, Y) = 1$$

4. Boundary Conditions:

- a. far away:

$$\lim_{X+Y \rightarrow \infty} C_i(t, X, Y) = 1 ; \quad \lim_{X+Y \rightarrow \infty} \varphi(t, X, Y) = 0 .$$

- b. insulating container wall:

$$\frac{\partial C_i}{\partial Y} + z_i C_i \frac{\partial \varphi}{\partial Y} = 0 \quad (X, Y) \in W_{sc} , i = 1, 2, 3, 4 .$$

- c. disk electrode:

$$\frac{\partial C_i}{\partial Y} + z_i C_i \frac{\partial \varphi}{\partial Y} = 0 \quad (X, Y) \in E_{sc} , i = 3, 4 .$$

and

$$\frac{\partial C_j}{\partial Y} + z_j C_j \frac{\partial \varphi}{\partial Y} =$$

$$\begin{aligned} &\alpha_j \{ \exp [(1 - \beta_j) z_j (V - V_{ej} - \varphi)] - C_j \exp [-\beta_j z_j (V - V_{ej} - \varphi)] \} , \\ &(X, Y) \in E_{sc} , j = 1, 2 . \end{aligned}$$

As indicated in the first section, virtually nothing is known in analytical terms about this problem, not even about the steady-state one to which we will restrict ourselves. But due to the discontinuity of the boundary conditions at the disk edge and the unboundedness of the given geometry even a numerical treatment looks like a very trying task. Therefore, before we begin to compute, we submit the geometry to further scrutiny. This will be worthwhile; in fact, one does get a hint as to what one can do here by looking at a much simpler problem. It turns out that by finding the concentrations for transport without migration (a linear problem) and constant concentration along the electrode one gets equi-concentration lines and equi-flux lines that are just coordinate lines of a special coordinate system (see [MiWiAm]). Since the solution of the problem at hand is not expected to be ‘too far off’ (in whatever sense) the solution to this simpler problem, we try to deal with it in the aforementioned coordinate system. This system of *compressed oblate spheroidal coordinates* will (or so we hope) be better suited to the problem of electro-diffusion on a microdisk electrode than the cylindrical coordinates, which seem to be natural at first sight.

### 2.3 Compressed oblate spheroidal coordinates

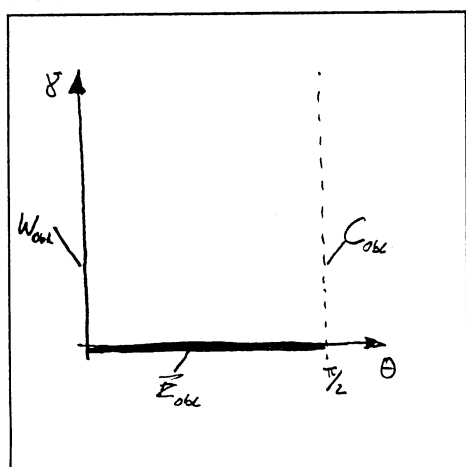
Starting with the scaled variables  $X$  and  $Y$  we first introduce oblate spheroidal coordinates (see [AbSt], [MoSp]) without compression. That is, we set

$$X = \cos \theta \cosh \gamma \quad \text{and} \quad Y = \sin \theta \sinh \gamma .$$

Since

$$S_{sc} = \{(X, Y) \in \mathbb{R}^2 \mid X, Y \geq 0\}$$

we see

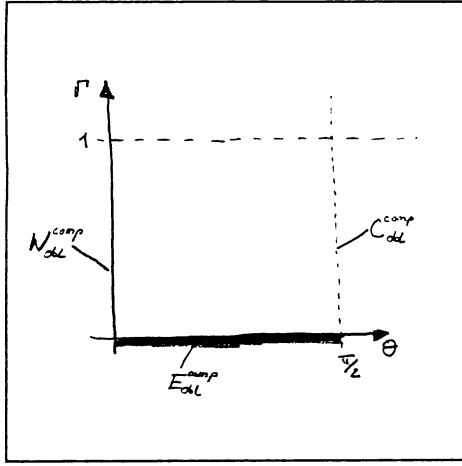


$$\begin{aligned} X \geq 0 &\stackrel{\cosh \gamma \geq 0}{\implies} \cos \theta \geq 0 \\ &\implies \theta \in I := [0, \frac{\pi}{2}] \\ Y \geq 0 &\stackrel{\theta \in I}{\implies} \sinh \gamma \geq 0 \\ &\implies \gamma \geq 0. \end{aligned}$$

Therefore the geometry is now as depicted above. However, this is still an unbounded domain. In order to get rid of the unboundedness we transform further, *compressing* the  $\gamma$ -direction by defining (see [VEBA])

$$\Gamma := \frac{\gamma}{1 + \gamma}.$$

The condition  $\gamma \geq 0$  now implies  $\Gamma \in [0, 1[$ . Since we consider boundary conditions far away from the electrode, i.e. for  $\gamma \rightarrow \infty$ , we will formally allow  $\Gamma$  to take the value 1 as well. This case then simply means that one looks at points far away from the electrode. So, ultimately, we will be using the following variables and (rectangular, compact) geometry:



$$S_{\text{obl}}^{\text{comp}} = \left\{ (\theta, \Gamma) \mid \theta \in [0, \frac{\pi}{2}], \Gamma \in [0, 1] \right\}$$

$$E_{\text{obl}}^{\text{comp}} = \left\{ (\theta, \Gamma) \mid \theta \in [0, \frac{\pi}{2}], \Gamma = 0 \right\}$$

$$W_{\text{obl}}^{\text{comp}} = \left\{ (\theta, \Gamma) \mid \theta = 0, \Gamma \in [0, 1[ \right\}$$

$$C_{\text{obl}}^{\text{comp}} = \left\{ (\theta, \Gamma) \mid \theta = \frac{\pi}{2}, \Gamma \in [0, 1[ \right\}$$

$$B_{\text{obl}}^{\text{comp}} = \left\{ (\theta, \Gamma) \mid \theta \in ]0, \frac{\pi}{2}[, \Gamma \in ]0, 1[ \right\}$$

The validity of the descriptions of the sets given above is easily checked. For example, for  $\Gamma = 0$  it follows that  $Y = 0$  and  $X = \cos \theta \leq 1$ , so that the condition  $\Gamma = 0$  only goes to say that we are looking at the electrode itself. We also notice that we had to define one more set, namely  $C_{\text{obl}}^{\text{comp}}$ , which stands for the line of symmetry through the disk center. This is a new boundary where physical (symmetry) considerations mandate to prescribe the normal component to the flux to be zero. All the other sets correspond to the ones considered in section 2.1.

In order to be able to write down the field equations and boundary conditions in these new coordinates one must perform numerous tedious calculations involving, for example, the matrix

$$A = \begin{pmatrix} \frac{\partial X}{\partial \theta} & \frac{\partial X}{\partial \gamma} \\ \frac{\partial Y}{\partial \theta} & \frac{\partial Y}{\partial \gamma} \end{pmatrix} = \begin{pmatrix} -\sin \theta \cosh \gamma & \cos \theta \sinh \gamma \\ \cos \theta \sinh \gamma & \sin \theta \cosh \gamma \end{pmatrix}$$

Seeing that (by the chain rule)

$$\begin{pmatrix} \frac{\partial}{\partial X} \\ \frac{\partial}{\partial Y} \end{pmatrix} = A^{-1} \begin{pmatrix} \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \gamma} \end{pmatrix}$$

and setting

$$\det := -\det A = \sin^2 \theta + \sinh^2 \gamma = -\cos^2 \theta + \cosh^2 \gamma,$$

we find

$$A^{-1} = \frac{1}{\det} A,$$

so that

$$\begin{aligned} \frac{\partial}{\partial X} &= \frac{1}{\det} \left[ -\sin \theta \cosh \gamma \frac{\partial}{\partial \theta} + \cos \theta \sinh \gamma \frac{\partial}{\partial \gamma} \right] \\ \frac{\partial}{\partial Y} &= \frac{1}{\det} \left[ \cos \theta \sinh \gamma \frac{\partial}{\partial \theta} + \sin \theta \cosh \gamma \frac{\partial}{\partial \gamma} \right] \end{aligned}$$

Using these expressions we can calculate the Laplacian and the dot product of two gradients in oblate spheroidal coordinates. Since in scaled cylindrical coordinates we have for a function  $f$

$$\nabla^2 f = \frac{1}{X} \frac{\partial}{\partial X} \left( X \frac{\partial f}{\partial X} \right) + \frac{\partial^2 f}{\partial Y^2} = \frac{1}{X} \frac{\partial f}{\partial X} + \frac{\partial^2 f}{\partial X^2} + \frac{\partial^2 f}{\partial Y^2}$$

the Laplacian in oblate spheroidal coordinates consists of

$$\frac{1}{X} \frac{\partial f}{\partial X} = \frac{1}{\det} \left[ -\tan \theta \frac{\partial f}{\partial \theta} + \tanh \gamma \frac{\partial f}{\partial \gamma} \right]$$

and

$$\frac{\partial^2 f}{\partial X^2} + \frac{\partial^2 f}{\partial Y^2} = \frac{1}{\det} \left( \frac{\partial^2 f}{\partial \theta^2} + \frac{\partial^2 f}{\partial \gamma^2} \right)$$

Finally we must take the compression we performed into consideration, namely

$$\Gamma := \frac{\gamma}{1 + \gamma} \iff \gamma := \frac{\Gamma}{1 - \Gamma}.$$

From this we find

$$\begin{aligned} \frac{\partial}{\partial \gamma} &= \frac{\partial \Gamma}{\partial \gamma} \cdot \frac{\partial}{\partial \Gamma} = \frac{1}{(1 + \gamma)^2} \frac{\partial}{\partial \Gamma} = (1 - \Gamma)^2 \frac{\partial}{\partial \Gamma} \\ \frac{\partial^2}{\partial \gamma^2} &= (1 - \Gamma)^2 \frac{\partial}{\partial \Gamma} \left[ (1 - \Gamma)^2 \frac{\partial}{\partial \Gamma} \right] = (1 - \Gamma)^4 \frac{\partial^2}{\partial \Gamma^2} - 2(1 - \Gamma)^3 \frac{\partial}{\partial \Gamma} \end{aligned}$$

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To facilitate writing down the Laplacian in compressed oblate spheroidal coordinates we set

$$\begin{aligned} a_\theta &:= \tan \theta \\ a_{\Gamma_1} &:= (1 - \Gamma)^4 \\ a_{\Gamma_2} &:= (1 - \Gamma)^2 \tanh\left(\frac{\Gamma}{1 - \Gamma}\right) - 2(1 - \Gamma)^3 \end{aligned}$$

We then have

$$\begin{aligned} \det &= \sin^2 \theta + \sinh^2 \gamma = \sin^2 \theta + \sinh^2\left(\frac{\Gamma}{1 - \Gamma}\right) \\ \nabla^2 f &= \frac{1}{\det} \left( \frac{\partial^2 f}{\partial \theta^2} - a_\theta \frac{\partial f}{\partial \theta} + a_{\Gamma_1} \frac{\partial^2 f}{\partial \Gamma^2} + a_{\Gamma_2} \frac{\partial f}{\partial \Gamma} \right) \\ \nabla f \cdot \nabla g &= \frac{1}{\det} \left( \frac{\partial f}{\partial \theta} \frac{\partial g}{\partial \theta} + a_{\Gamma_1} \frac{\partial f}{\partial \Gamma} \frac{\partial g}{\partial \Gamma} \right) \end{aligned}$$

It remains to find out what the normal derivatives are in order to write down the boundary conditions. We see

1. along the electrode :

$$\begin{aligned} (\theta, \Gamma) \in E_{\text{obl}}^{\text{comp}} &\implies \Gamma = 0 \implies \\ \text{normal derivative:} &\quad \frac{\partial}{\partial Y} = \frac{1}{\sin \theta} \frac{\partial}{\partial \Gamma} \end{aligned}$$

2. on the insulating container wall :

$$\begin{aligned} (\theta, \Gamma) \in W_{\text{obl}}^{\text{comp}} &\implies \theta = 0 \implies \\ \text{normal derivative:} &\quad \frac{\partial}{\partial Y} = \frac{1}{\sinh\left(\frac{\Gamma}{1 - \Gamma}\right)} \frac{\partial}{\partial \theta} \end{aligned}$$

3. along the line of symmetry through the disk center :

$$\begin{aligned} (\theta, \Gamma) \in C_{\text{obl}}^{\text{comp}} &\implies \theta = \frac{\pi}{2} \implies \\ \text{normal derivative:} &\quad \frac{\partial}{\partial X} = -\frac{1}{\cosh\left(\frac{\Gamma}{1 - \Gamma}\right)} \frac{\partial}{\partial \theta} \end{aligned}$$

Using all the above formulas we can finally write down the model for two metal deposition on a microdisk electrode in the form we will be using to get some numerical results for this problem. The model is now:

1. Electroneutrality:

$$\sum_{i=1}^n \varepsilon_i C_i = 0.$$

2. Field Equations:

$$C_{it} = D_i \left\{ \begin{aligned} & \left( \frac{\partial^2 C_i}{\partial \theta^2} - a_\theta \frac{\partial C_i}{\partial \theta} + a_{r1} \frac{\partial^2 C_i}{\partial \Gamma^2} + a_{r2} \frac{\partial C_i}{\partial \Gamma} \right) \\ & z_i \left[ C_i \left( \frac{\partial^2 \varphi}{\partial \theta^2} - a_\theta \frac{\partial \varphi}{\partial \theta} + a_{r1} \frac{\partial^2 \varphi}{\partial \Gamma^2} + a_{r2} \frac{\partial \varphi}{\partial \Gamma} \right) \right. \\ & \left. \left( \frac{\partial C_i}{\partial \theta} \frac{\partial \varphi}{\partial \theta} + a_{r1} \frac{\partial C_i}{\partial \Gamma} \frac{\partial \varphi}{\partial \Gamma} \right) \right] \right\} \quad i = 1, 2, 3, 4.$$

3. Initial Values:

$$C_i(0, \theta, \Gamma) = 1$$

4. Boundary Conditions:

a. far away:

$$C_i(t, \theta, 1) = 1; \quad \varphi(t, \theta, 1) = 0.$$

b. insulating container wall:

$$\frac{\partial C_i}{\partial \theta} + z_i C_i \frac{\partial \varphi}{\partial \theta} = 0 \quad (\theta, \Gamma) \in W_{\text{obl}}^{\text{comp}}, \quad i = 1, 2, 3, 4.$$

c. line of symmetry through the disk center:

$$\frac{\partial C_i}{\partial \theta} + z_i C_i \frac{\partial \varphi}{\partial \theta} = 0 \quad (\theta, \Gamma) \in C_{\text{obl}}^{\text{comp}}, \quad i = 1, 2, 3, 4.$$

d. disk electrode:

$$\frac{\partial C_i}{\partial \Gamma} + z_i C_i \frac{\partial \varphi}{\partial \Gamma} = 0 \quad (\theta, \Gamma) \in E_{\text{obl}}^{\text{comp}}, \quad i = 3, 4.$$

$$\text{and} \quad \frac{\partial C_j}{\partial \Gamma} + z_j C_j \frac{\partial \varphi}{\partial \Gamma} =$$

$$\alpha_j \sin \theta \{ \exp [(1 - \beta_j) z_j (V - V_{e_j} - \varphi)] - C_j \exp [-\beta_j z_j (V - V_{e_j} - \varphi)] \},$$

$$(\theta, \Gamma) \in E_{\text{obl}}^{\text{comp}}, \quad j = 1, 2.$$

### 3. Numerical Simulations

Before we can present the results of our simulation, we need to say a few words about the kind of problem we are looking at and what that implies as to the nature of results. In other words, we need to find out what it is that can be considered a result in our context.

#### 3.1 Industrial mathematics.

First of all we need to keep in mind that we are dealing with an *industrial* problem, but one that is very poorly understood, so that what we are doing is really *basic research*. This is true for both the physics and the mathematics involved. Therefore, while people have claimed the overall goal of industrial mathematics to be 'to bring harvestable technology to the manufacturing line' (JURIS PURVICS, XEROX), this long-term goal cannot be our guideline for the short range. Our guideline should instead be what has also been said about industrial mathematics, namely that there are 'four thresholds for success [in industrial mathematics]: physical/chemical understanding, mathematical understanding, computational power, and visualization of results' (MALVIN KADOS, Cornell University). But this can by no means be a top-down process; instead it will have to be a process with feedforward and feedback.

The problem of two metal deposition might serve as a very good example of this. A great deal of insight in the field of electro-chemistry has been used for the formulation of the model equations, an analysis of which has brought about new mathematical techniques to solve related problems and the problem at hand in a special case. Using these techniques in programs has provided data which have been turned into graphs to shed a light on certain effects of electro-diffusion. So, as a result of the joint work of electro-chemists and mathematicians there are observations that need to be explained to gain a better understanding of the physical as well as the mathematical aspects of the problem. This is therefore the goal we set ourselves, when we do the simulations: we want to find questions, the answer to which will ultimately enhance understanding of the process of two metal deposition.

#### 3.2 How the simulations were done.

The program that was used for the numerical simulations is a straightforward implementation of NEWTON's method to the system of nonlinear PDE in oblate spheroidal coordinates. Finite differences were used for the partial derivatives and LINPACK-routines to handle the linear algebra involved. Theoretically, the program allows any number of coupled partial (or ordinary) differential equations to be treated and has, in fact, been used for different

|                        |            |                   |                  |
|------------------------|------------|-------------------|------------------|
| $\varepsilon_1 = -0.4$ | $z_1 = 2$  | $\alpha_1 = 0.01$ | $\alpha_2 = 0.1$ |
| $\varepsilon_2 = -0.3$ | $z_2 = 2$  | $\beta_1 = 0.5$   | $\beta_2 = 0.5$  |
| $\varepsilon_3 = -0.3$ | $z_3 = 1$  | $V_{e1} = -0.5$   | $V_{e2} = -2.5$  |
| $\varepsilon_4 = 1$    | $z_4 = -1$ |                   |                  |

Table 1: Parameter values for the two metal deposition

problems also in GM-Research Labs, where it originated. The core of the program consists of NEWTON's method together with the part for the calculation of derivatives; then there is a subroutine, in which the user can specify the particular problem he is interested in. This specification incorporates the problem's parameters and the formulas for the residuals of the iterations as well as the form of the data output.

Obviously, in doing the simulations we have a significant problem. Since there is no analysis that could help us with the specific process of two metal deposition on a microdisk electrode, how can we expect to know whether we have or have not made a major blunder in the program? In other words, how can we be confident about the data we get? This is where the earlier mathematical work comes into play. As indicated in section 2.1, the theoretical case of a hemisphere electrode, which, due to spherical symmetry involves only one spatial dimension, has already been dealt with. Using the same parameters that were used there, namely the ones in table 1, we solve the problem numerically for the disk-electrode.

Since, for empirical reasons, we do not expect the overall behavior of the system to undergo great changes when we look at the disk-geometry instead of the hemisphere-geometry, we compute the average over the electrode of the concentrations of the metals, of their normal components to the flux and of the potential function and plot the results versus the applied voltage at the electrode. Comparison with the graphs for the hemisphere electrode (see [BA]) show that indeed the two cases agree very well (see Fig. 1). This observation serves two purposes: first, as indicated, we can be quite certain that our program provides the correct data and second it supports our guess based on the investigation of related problems that the process of two metal deposition does not depend greatly (at least not in its overall behavior) on the electrode geometry. So we are confident to have correct data and we can start looking for questions.

### 3.3 Sample questions from the data

The first question we get from the following observations: The average flux graph shows two *inflection points* on each of the two curves. One of them is at the respective equilibrium voltage, the other, let us tentatively call it *inflection voltage*, is somewhere else. By plotting the actual flux-distributions along the electrode for voltages in the vicinity of the inflection voltage (see Fig. 2), we notice that there are crossovers between the curves for voltages higher than the inflection voltage and no crossovers for voltages below it. What does this tell us about two metal deposition? This is certainly a question where it is not clear what the implications of an answer could be. It is therefore one which needs an estimate as to its importance and should only be pursued accordingly. We can, however, get a little more information pertaining to this question by studying the effects of lowering the bulk concentration of metal 1. Indeed, when we do so, we also lower the equilibrium voltage  $V_{e1}$  and we raise the parameter  $\alpha_1$ . When this change is drastic enough, there is no inflection point in the average flux curve anymore (see Fig. 3)! This should also be taken into consideration when the significance of this phenomenon is assessed.

Another thing we see when we conduct the simulations with the bulk concentrations lowered, is that we run into *numerical difficulties*. This, of course, is to be expected because of the exponential factors in the boundary conditions along the electrode for the metal species. So, apart from the physical questions, there are also questions concerning the convergence of the numerical scheme we use. In fact, having done the simulations on various square grids ranging from  $11 \times 11$  to  $61 \times 61$ , we find quadratic convergence in the step size of the average flux of species one, for example, at low voltages and linear convergence in the step size at high voltages. From the point of view of an numerical analyst this is certainly something to look into.

One question to be addressed, however, is clear from the outset. That is, one would like to know whether there are voltages where there is *simultaneous dissolution and deposition* along the electrode. That means, that conceivably there might be some voltage(s), where on one part of the electrode one of the species is being deposited while on another part this same species might be dissolving. So, what we want to know is whether there are voltages where sign changes in the normal component to the flux occur along the electrode. This is not a question on a hemisphere electrode, since, because of spherical symmetry, there can be no such thing as a sign change along the electrode, since in the geometry employed the electrode reduces to a point. But, even in the case of just one metal being deposited at the electrode, for a disk electrode one can

not be certain about that. From computer simulations, however, it seems that there are no sign changes in the flux of the metal species along the electrode. This is also what the numerical data indicate for the two metal problem. It is consistent with what was mentioned earlier on: at the equilibrium voltage of either species the normal component to the flux of the species in question is identically zero. Clearly, if we have no sign changes in the normal component to the flux along the electrode at any voltage and if there are positive and negative average fluxes, there must necessarily be some voltage at which the normal flux vanishes everywhere along the electrode. Since, for each species, there is only one voltage at which we have zero average flux, namely its respective equilibrium voltage, one is lead to the following conjecture, which admittedly is not corroborated by anything but numerical results:

*Conjecture.*

*Both of the metal species are being deposited everywhere along the electrode for voltages below their respective equilibrium voltage; they are dissolving at voltages higher than their equilibrium voltage.*

Here we have something that is clearly meaningful. If the conjecture were true it would be a new physical interpretation for the equilibrium voltage (apart from it being the voltage where the normal component to the flux of the respective species vanishes). Therefore mathematics is called upon to try to prove this statement analytically. A first step towards that would be a proof for the one metal problem. On the other hand, if some experiment in the laboratory should show that simultaneous dissolution and deposition can actually be observed, it might mean that the whole model needs revision! Given, however, that the model is adequate, we would be able to determine by measuring at any point on the electrode whether we have dissolution or deposition of a certain species at some fixed voltage.

### 3.4 Summary and outlook.

Our simulations have provided us with a vast amount of data. It will have to be determined which angle would be the most profitable one to look at the data in order to find significant questions that will let us gain more insight to the process of two metal deposition on a microdisk electrode. Some possible questions have been stated in this section, which also showed, that there are numerical questions to be addressed in this context. Usually it will not be easy to tell whether or not a question is important or not and the assessment of its relevance might be a slow and time consuming process. Undoubtedly, however, proof of the conjecture concerning simultaneous dissolution and deposition and the meaning of the equilibrium voltage would be very useful, although, for

the time being one cannot even prove well-posedness of the problem let alone existence and uniqueness of a solution.

In the future one will also have to look at the transient case, not merely, as was done here, at steady state. Also, there is a great number of related problems that are at least as poorly understood, such as the reactions taking place in a fuel cell, where the insights in the process of two metal deposition on a microdisk electrode might help to understand them better.

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## REFERENCES

- [AbSt] M. ABRAMOWITZ, I. STEGUN (ED.), *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, National Bureau of Standards, Applied Maths Series #55, 1964
- [Ba] D. BAKER, *Some Nonlinear Systems of Transport Equations that can be solved as Single Laplace Equations*, General Motors Research Report 7367, Warren, MI, May, 1991.
- [BaVe] D. BAKER, M. VERBRUGGE, *An Integral-Transform Formulation for the Reaction Distribution on a Stationary-Disk Electrode Below the Limiting Current*, J. Electrochem. Soc #137, 1990
- [Ko] J. KORYTA, *Ions, Electrodes, and Membranes*, Wiley-Interscience Publication, New York, 1982
- [MiWiAm] A. MICHAEL, R. WIGHTMAN, C. AMATORE, *Microdisk Electrodes*, J. Electroanal. Chem., #267, 1989
- [MoSp] P. MOON, D. SPENCER, *Field Theory Handbook (2. ed)*, Springer Verlag, Berlin, 1971
- [Ru] I. RUBINSTEIN, *Electro-Diffusion of Ions*, SIAM Studies in Applied Mathematics, Philadelphia, 1990
- [VeBa] M. VERBRUGGE, D. BAKER, *Transient Diffusion and Migration to a Disk Electrode*, General Motors Research Report, Warren, MI, 1991

FIGURES

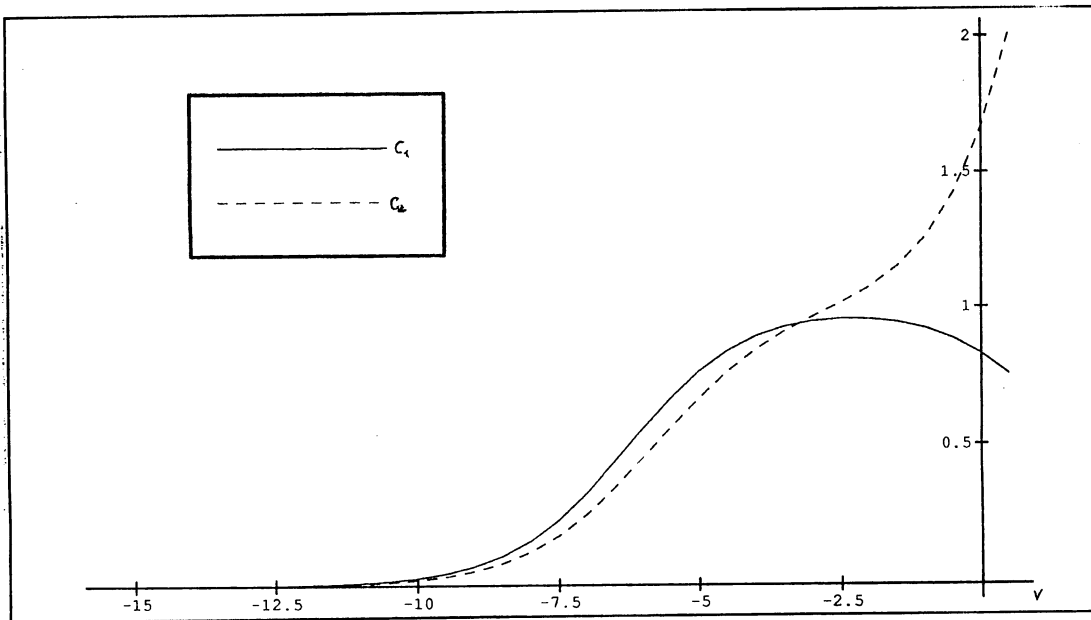


Figure 1(a): Average concentration curves (parameters as in table 1)

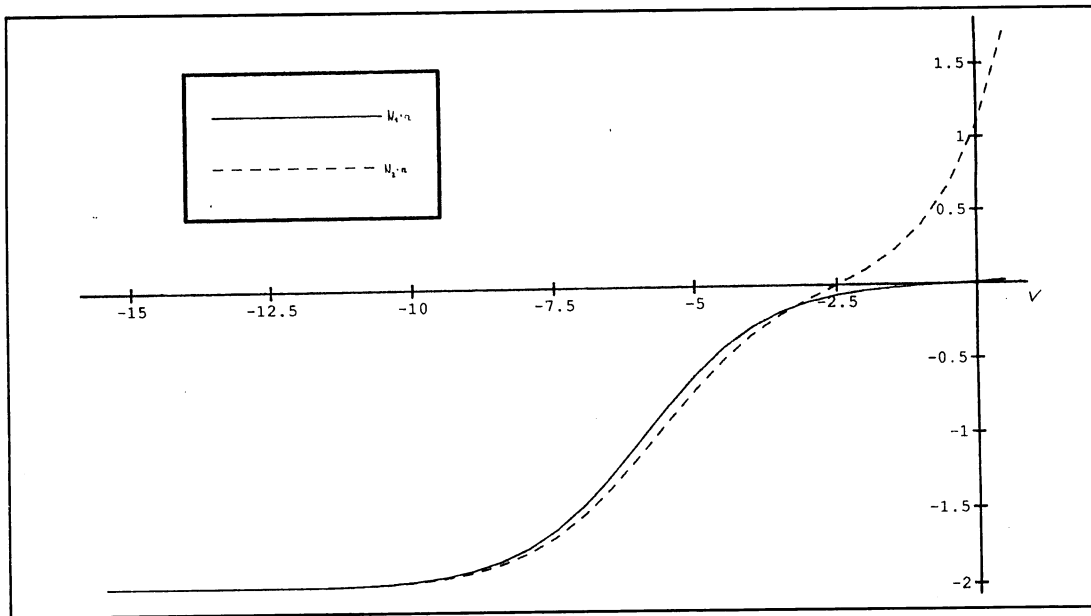


Figure 1(b): Average flux curves (parameters as in table 1)

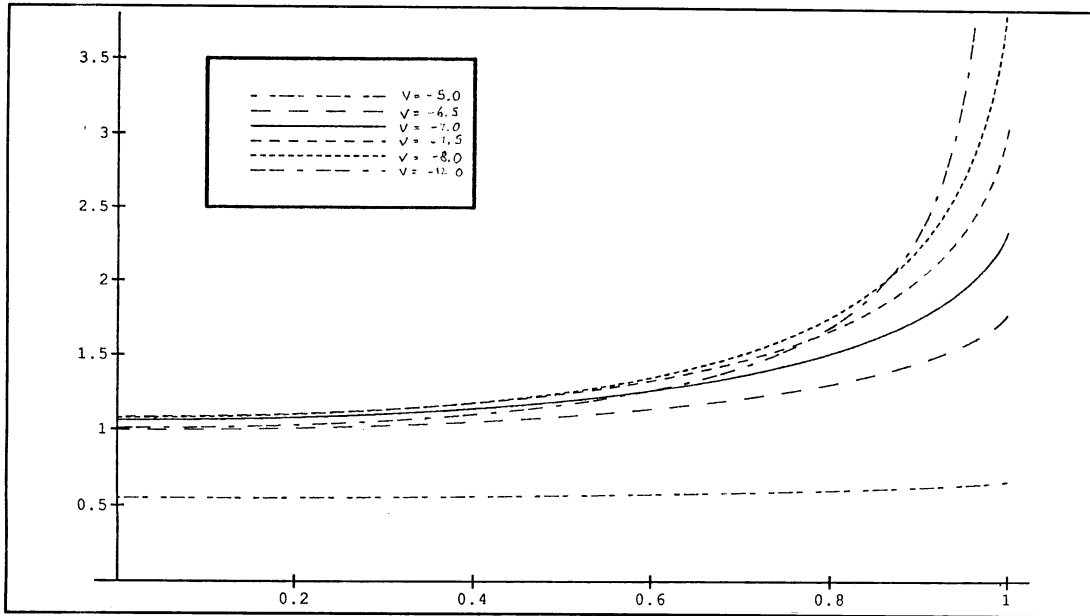


Figure 2(a): Flux distribution of species 1  
(parameters as in table 1)

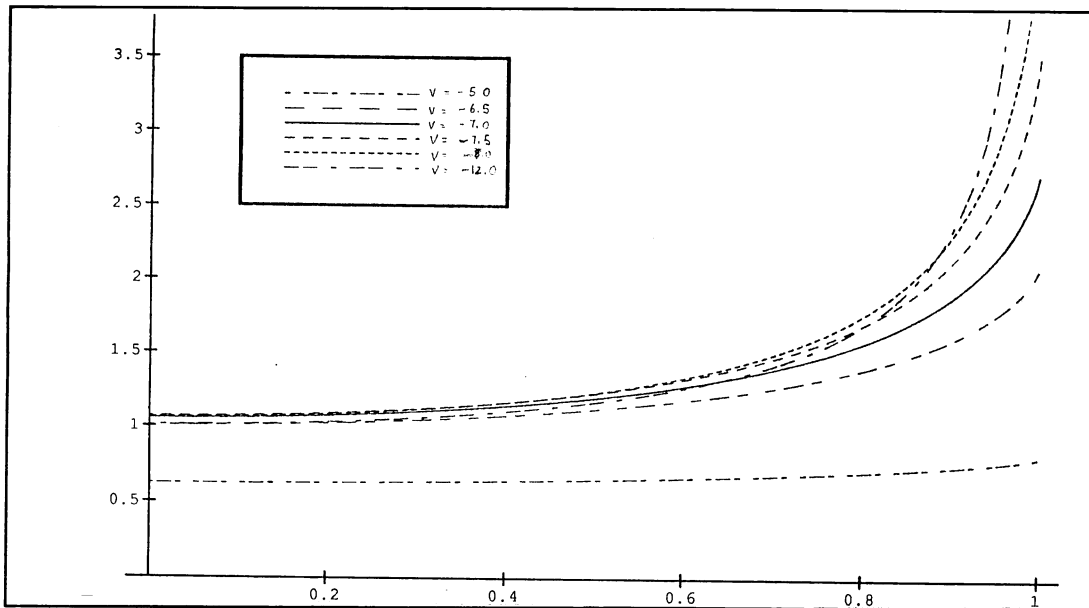


Figure 2(b): Flux distribution of species 2  
(parameters as in table 1)

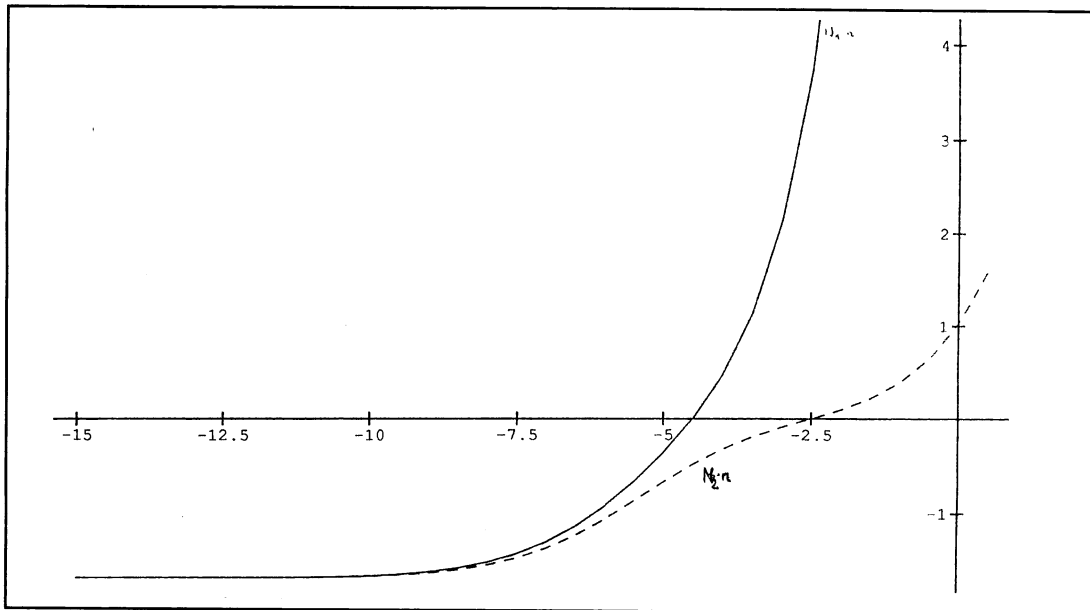


Figure 3: Average flux curves  
(with the bulk concentration of species 1 changed)

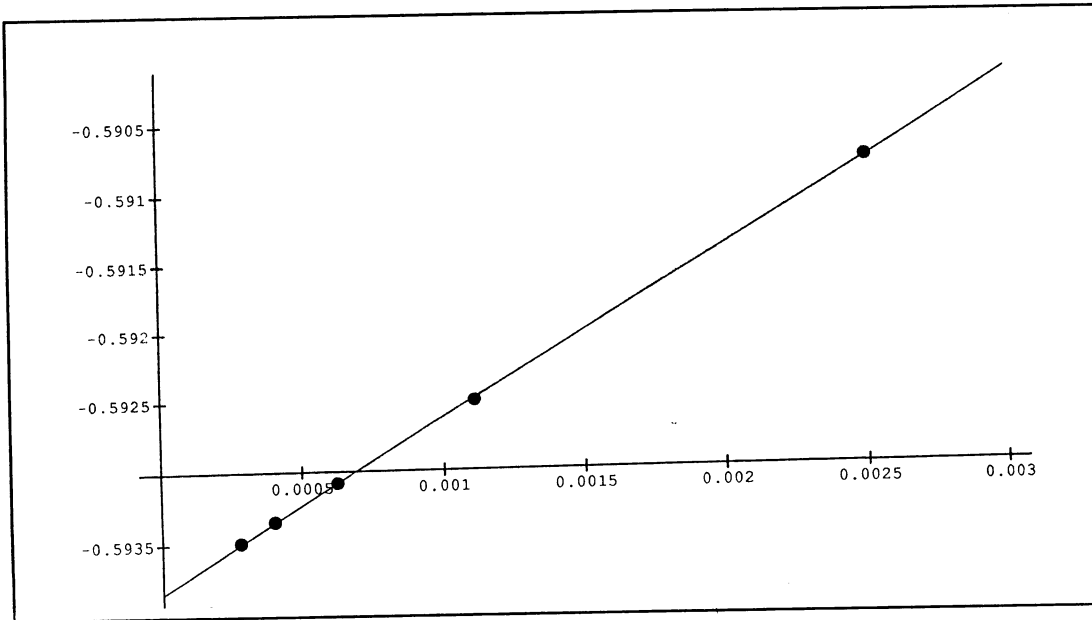


Figure 4(a): Average flux values of species 1 versus the square of the step size at  $V = -5.0$

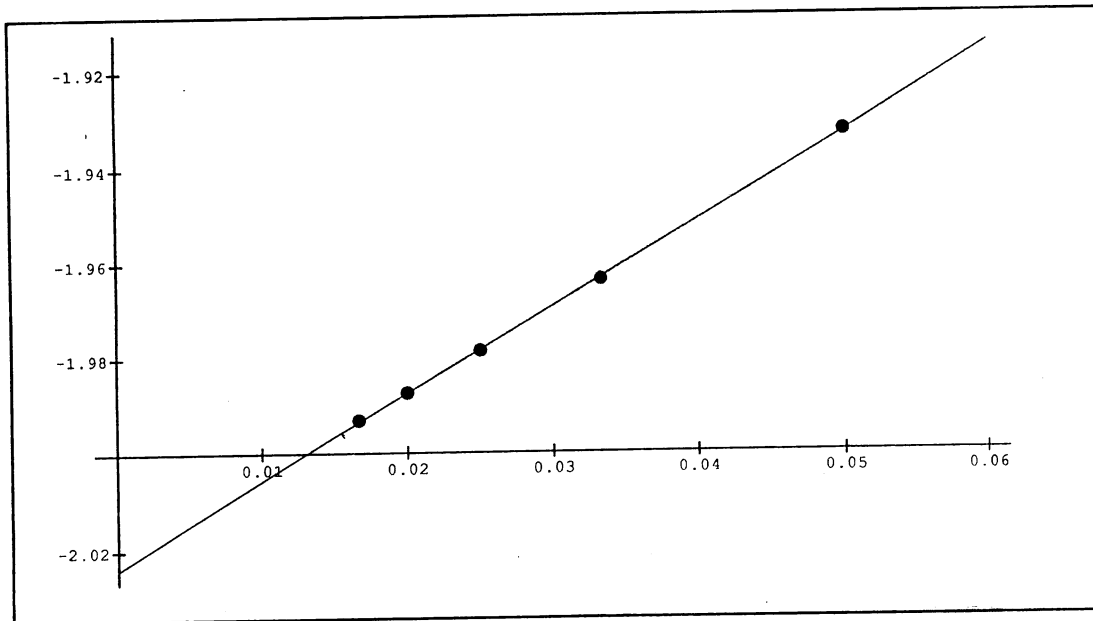


Figure 4(b): Average flux values of species 1 versus the step size at  $V = -12.5$

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