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Discussion of some mathematical aspects of an anodic stripping voltammetry problem

by

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Summary.

A model of the linear potential sweep voltammetry on an extremely thin mercury film electrode is considered. The flux at the boundary surface of the electrode and the adjoining watery solution is a function of the time t and a small parameter ε. An asymptotic expansion of the flux for small values of t is found. A simple relation between ε and the corresponding time t_{max}, for which the flux reaches a maximum, can be derived.

1. Introduction

Anodic stripping voltammetry is an electro-analytical method for the determination of traces of metal in electrolyte solution. Concentrations of 10^{-4} to 10^{-8} gram/litre of metal can be determined. This method has found many applications; a description of the method and a review of its theory and application is given by BARENDRECHT [1,2].

In this report we consider the current-potential curve, which in this case will correspond with the flux-time curve, obtained during the oxidation of reduced metal dissolved in an extremely thin, plane mercury film electrode. The integral equation for the current-potential curve obtained during the dissolution of reduced metal from a mercury film has been derived by DE VRIES and VAN DALEN [6,7,8] for the general case, and has been solved numerically by Huber's method [6].

When the parameter ε, describing the effect of mercury film thickness and rate of potential change, approaches zero, the integral equation for the dimensionless flux, $z(x)$, reduces to

$$e^x - e^x \int_0^x z(\xi)\, d\xi = 1 + \frac{1}{\varepsilon\sqrt{\pi}} \int_0^x \frac{z(\xi)}{\sqrt{x-\xi}} d\xi, \qquad (1.1)$$

where x is a dimensionless time-variable [8]. For realistic values of experimental parameters $\varepsilon << 1$.

The numerical results obtained by DE VRIES [6] from (1.1) are given in Table 1 and Figure 2. It appears that $z(x)$ is a peak-shaped function.

From Table 1 it can be seen that z_{max}, just as $\beta_{\frac{1}{2}}$ (the width at half height), is practically independent of the value of ε, provided ε is not too large.

For the position x_{max} of z_{max}, the following simple approximate relation

$$x_{max} + \ln \varepsilon = - 0.055 \qquad (1.2)$$

holds.

The main purpose of this report is to establish such a relation by analytical means.

Table 1.

$1/(\varepsilon\sqrt{\pi})$	$x_{max} + \ln \varepsilon$	z_{max}	$\beta_{\frac{1}{2}}$
250	-0.0537	0.29885	2.9369
500	-0.0549	0.29801	2.9383
1000	-0.0552	0.29757	2.9389
2000	-0.0552	0.29733	2.9397
3000	-0.0553	0.29726	2.9397
4000	-0.0555	0.29721	2.9396
6000	-0.0556	0.29717	2.9397
8000	-0.0555	0.29715	2.9395
10000	-0.0554	0.29714	2.9399
12000	-0.0556	0.29713	2.9396

2. Mathematical Model

The model considered is of the following form.

In an extremely thin mercury film of thickness L a metal M^{o} is dissolved. In the adjoining solution of infinite extension M^{n+}-ions are dissolved (Figure 1).

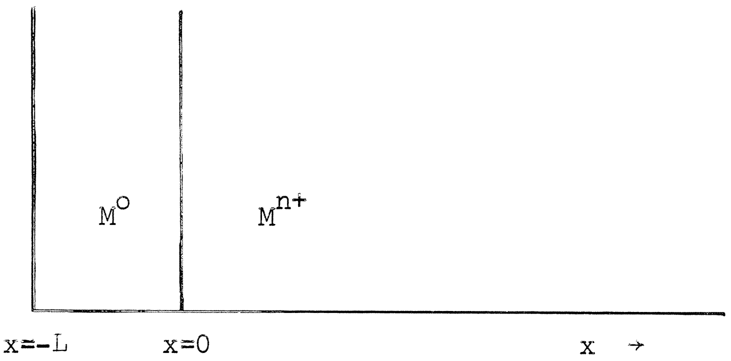

Figure 1

The potential of the mercury film will be changed linearly with the time t, starting at t = 0. During this change the metal M^o will produce M^{n+}-ions, which will diffuse into the solution.

We assume that the concentration of M^{n+}, $C_1(x,t)$, satisfies the diffusion equation:

$$D \frac{\partial^2 C_1}{\partial x^2} = \frac{\partial C_1}{\partial t}, \qquad 0 < x < \infty, \tag{2.1}$$

where D is the diffusion coefficient.

Because the mercury layer is extremely thin, we suppose that the concentration C_2 of M^o in this layer is a function of t only,

$$C_2 = C_2(t), \qquad -L < x < 0. \tag{2.2}$$

The initial conditions are

$$C_1(x,0) = \theta C_0, \qquad 0 < x < \infty \tag{2.3}$$

and

$$C_2(0) = C_0, \qquad -L < x < 0, \tag{2.4}$$

where θ and C_0 are positive constants and $\theta << 1$.

The boundary conditions are

$$D \frac{\partial C_1}{\partial x} = L \frac{\partial C_2}{\partial t} \tag{2.5}$$

and

$$C_1(0,t) = \theta C_2(t)e^{\sigma t} \tag{2.6}$$

for $x = 0$, $t \geq 0$, where σ is a positive constant.

The definition of the flux $q(t)$ at the boundary surface $x = 0$ is

$$q(t) = -D\left(\frac{\partial C_1(x,t)}{\partial x}\right)_{x=0}. \tag{2.7}$$

We now introduce the dimensionless variables

$$t' = \sigma t, \tag{2.8}$$

$$x' = \frac{x}{\varepsilon}\sqrt{\frac{\sigma}{D}}, \tag{2.9}$$

$$u = \frac{C_1}{\theta C_0} \tag{2.10}$$

where

$$\varepsilon = \frac{\theta}{L}\sqrt{\frac{D}{\sigma}} \ll 1. \tag{2.11}$$

Eliminating C_2 with the aid of (2.6), we find:

$$\frac{\partial^2 u}{\partial x'^2} = \varepsilon^2 \frac{\partial u}{\partial t'}, \quad 0 < x' < \infty, \tag{2.12}$$

$$u = 1, \qquad t' = 0, \tag{2.13}$$

$$\frac{\partial u}{\partial x'} = \frac{\partial}{\partial t'}(e^{-t'}u), \; x' = 0, \tag{2.14}$$

$$q(t'/\sigma) = -L\sigma C_0\left(\frac{\partial u}{\partial x'}\right)_{x'=0}. \tag{2.15}$$

In the following the dashes of the dimensionless variables will be omitted. Instead of q we shall consider the function $z(\varepsilon,t)$, which is defined by

$$z(\varepsilon,t) = -\left(\frac{\partial u}{\partial x}\right)_{x=0}. \tag{2.16}$$

This function can be determined either by means of an integral equation, which is suited to numerical treatment, or by means of the corresponding difference equation, which can be treated analytically.

In order to derive these equations a Laplace transformation with respect to t is applied to the function $u(x,t)$,

$$\bar{u}(x,s) = \int_0^\infty e^{-st}\, u(x,t)dt. \tag{2.17}$$

With the aid of the initial condition (2.3), formula (2.12) becomes

$$\frac{\partial^2 \bar{u}}{\partial x^2} = \varepsilon^2(s\bar{u} - 1). \tag{2.18}$$

The general solution of this equation which is bounded at infinity is of the form

$$\bar{u}(x,s) = \frac{1}{s} + \frac{\bar{\phi}(\varepsilon,s)}{\sqrt{s}}\, e^{-\varepsilon x\sqrt{s}}, \tag{2.19}$$

where $\bar{\phi}(\varepsilon,s)$ is an unknown function.

To find the integral equation we proceed in the following way.

Using the relation (2.16) we have

$$\bar{z}(\varepsilon,s) = \varepsilon\bar{\phi}(\varepsilon,s). \tag{2.20}$$

Taking the special case $x = 0$ the inverse Laplace transform of (2.19) is given by

$$u(0,t) = 1 + \frac{1}{\varepsilon\sqrt{\pi}} \int_0^t \frac{z(\varepsilon,\tau)}{\sqrt{t-\tau}}\, d\tau. \tag{2.21}$$

On the other hand, by integrating (2.14) with respect to t, we have

$$u(0,t) = e^t - e^t \int_0^t z(\varepsilon,\tau)\, d\tau. \tag{2.22}$$

Combining (2.21) and (2.22) we find the integral equation which determines $z(\varepsilon,t)$

$$e^t - e^t \int_0^t z(\varepsilon,\tau)\, d\tau = 1 + \frac{1}{\varepsilon\sqrt{\pi}} \int_0^t \frac{z(\varepsilon,\tau)}{\sqrt{t-\tau}} d\tau. \tag{2.23}$$

This equation is mentioned in the introduction (1.1), where x is used instead of t as the independent variable.

The corresponding difference equation is derived by taking the Laplace transform of formula (2.14)

$$\left(\frac{\partial \bar{u}}{\partial x}\right)_{x=0} = s\bar{u}(0,s+1) - 1, \tag{2.24}$$

and substituting (2.19) into this equation, which gives

$$\frac{\bar{\phi}(\varepsilon,s+1)}{\sqrt{s+1}} + \frac{\varepsilon\bar{\phi}(\varepsilon,s)}{s} = \frac{1}{s(s+1)}. \tag{2.25}$$

In the following section we consider a method by means of which this equation can be treated.

3. Method of solution

By replacing s by $s-\frac{1}{2}$ we bring (2.25) in the following more symmetrical form, which is appropriate to analytical treatment,

$$\frac{\bar{\phi}(\varepsilon,s+\frac{1}{2})}{\sqrt{s+\frac{1}{2}}} + \frac{\varepsilon\bar{\phi}(\varepsilon,s-\frac{1}{2})}{s-\frac{1}{2}} = \frac{1}{(s+\frac{1}{2})(s-\frac{1}{2})}. \tag{3.1}$$

This equation can be reduced to a very simple difference equation by multiplying both sides with the factor $\varepsilon^{-s-\frac{1}{2}}\Gamma^{\frac{1}{2}}(s+\frac{1}{2})$ and by substituting

$$\bar{f}(s) = \varepsilon^{-s} s^{-\frac{1}{2}} \Gamma^{\frac{1}{2}}(s)\bar{\phi}(s) \tag{3.2}$$

and

$$\bar{h}(s) = \varepsilon^{-s-\frac{1}{2}}(s^2-\tfrac{1}{4})^{-1}\Gamma^{\frac{1}{2}}(s+\tfrac{1}{2}). \tag{3.3}$$

In this way we find

$$\bar{f}(s+\tfrac{1}{2}) + \bar{f}(s-\tfrac{1}{2}) = \bar{h}(s). \tag{3.4}$$

This difference equation is solved by

$$\bar{f}(s) = \frac{1}{2i}\int_{-i\infty}^{i\infty} \frac{\bar{h}(s+z)}{\cos \pi z}\,dz, \tag{3.5}$$

for Re $s > \frac{1}{2}$, as one can easily see by substituting (3.5) in (3.4).

To find the general solution of the difference equation the general solution of the homogeneous equation,

$$\bar{f}(s+\tfrac{1}{2}) + \bar{f}(s-\tfrac{1}{2}) = 0, \tag{3.6}$$

has to be added to (3.5).

The last mentioned solution is a periodic function. Because its inverse Laplace transform has to exist, this function must vanish everywhere (VAN DER POL & BREMMER [5], p. 278).

With the aid of (2.16), (2.19) and (3.2) we find for the Laplace transform of $z(\varepsilon,t)$:

$$\bar{z}(\varepsilon,s) = \varepsilon\bar{\phi}(\varepsilon,s) = \frac{\varepsilon^{s+1}s^{\frac{1}{2}}\bar{f}(s)}{\Gamma^{\frac{1}{2}}(s)} . \tag{3.7}$$

With (3.3) and (3.5) this results into

$$\bar{z}(\varepsilon,s) = \frac{\varepsilon^{\frac{1}{2}}s^{\frac{1}{2}}}{2\Gamma^{\frac{1}{2}}(s)}\int_{-\infty}^{\infty} \frac{\varepsilon^{-ip}\Gamma^{\frac{1}{2}}(s+ip+\frac{1}{2})}{(s+ip+\frac{1}{2})(s+ip-\frac{1}{2})\,\mathrm{ch}\,\pi p}\,dp. \tag{3.8}$$

It is difficult to reduce this integral to a simpler expression in view of the presence of the root of the gamma function in the integrand. However, a discussion is possible by using asymptotic methods.

For small values of the time t an asymptotic approximation of $z(\varepsilon,t)$ is found, as is indicated in section 4.

For larger values of t the factor $\frac{1}{(s+ip+\frac{1}{2})(s+ip-\frac{1}{2})}$ prevents us from calculating the maximum of $z(\varepsilon,t)$. We can trace this factor back to the structure of the right-hand side of (3.1). Therefore we first solve the difference equation

$$\frac{\overline{\psi}(\varepsilon,s+\frac{1}{2})}{\sqrt{s+\frac{1}{2}}}+\frac{\varepsilon\overline{\psi}(\varepsilon,s-\frac{1}{2})}{s-\frac{1}{2}}=1, \tag{3.9}$$

which does not contain the disturbing factor $(s-\frac{1}{2})^{-1}(s+\frac{1}{2})^{-1}$.

With the aid of the solution of this equation we find a fairly good approximation of $z(\varepsilon,t)$, as will be shown in section 5.

This last approximation also shows the desired type of relation between ε and t_{max}.

4. The asymptotic expansion for small values of t

We want to expand the function $z(\varepsilon,t)$ for small values of t. This can be done by expansion of $\overline{z}(\varepsilon,s)$ for large values of s and by inverse Laplace transformation of the resulting series.

To find the expansion of

$$\frac{\Gamma^{\frac{1}{2}}(s+ip+\frac{1}{2})}{\Gamma^{\frac{1}{2}}(s)}, \tag{4.1}$$

we make use of the beta function (see WHITTAKER and WATSON [9], p. 253), defined by

$$B(s,ip+\tfrac{1}{2})=\frac{\Gamma(s)\Gamma(ip+\frac{1}{2})}{\Gamma(s+ip+\frac{1}{2})} \tag{4.2}$$

and by

$$B(s,ip+\tfrac{1}{2})=\int_0^1 y^{s-1}(1-y)^{ip-\frac{1}{2}}dy. \tag{4.3}$$

In (4.3) we substitute $y=e^{-u}$, by which the integral transforms into

$$B(s,ip+\tfrac{1}{2})=\int_0^\infty e^{-su}u^{ip-\frac{1}{2}}(1-\frac{u}{2!}+\frac{u^2}{3!}-\dots)^{ip-\frac{1}{2}}du$$

$$=\int_0^\infty e^{-su}u^{ip-\frac{1}{2}}\left[1-\frac{ip-\frac{1}{2}}{2!}+\left\{\frac{ip-\frac{1}{2}}{3!}+\frac{(ip-\frac{1}{2})(ip-\frac{3}{2})}{(2!)^3}\right\}u^2+\dots\right]du$$

$$=\frac{\Gamma(ip+\frac{1}{2})}{s^{ip+\frac{1}{2}}}-\frac{ip-\frac{1}{2}}{2!}\cdot\frac{\Gamma(ip+\frac{3}{2})}{s^{ip+3/2}}+\dots . \tag{4.4}$$

So, with (4.4), we find the required quotient (4.1)

$$\frac{\Gamma^{\frac{1}{2}}(s+ip+\frac{1}{2})}{\Gamma^{\frac{1}{2}}(s)} = s^{ip+\frac{1}{2}}\left\{1 + \frac{(ip-\frac{1}{2})(ip+\frac{1}{2})}{4s} + \ldots\right\}. \tag{4.5}$$

Also,

$$\frac{1}{(s+ip+\frac{1}{2})(s+ip-\frac{1}{2})} = \frac{1}{s^2}\left(1 - \frac{2ip}{s} + \ldots\right). \tag{4.6}$$

With these results, (3.8) becomes

$$\overline{z}(\varepsilon,s) \sim \frac{\varepsilon^{1/2}s^{-5/4}}{2}\int_{-\infty}^{\infty} \frac{\varepsilon^{-ip}s^{ip/2}}{\text{ch}\,\pi p}\,dp. \tag{4.7}$$

This integral may be considered as an exponential Fourier transform:

$$\overline{z}(\varepsilon,s) \sim \varepsilon^{1/2}s^{-5/4}\int_{-\infty}^{\infty} \frac{e^{-ip\,\ln(\varepsilon/s^{\frac{1}{2}})}}{e^{\pi p} + e^{-\pi p}}\,dp$$

$$= \frac{\varepsilon}{s(s^{\frac{1}{2}}+\varepsilon)}\,, \tag{4.8}$$

in virtue of ERDELYI [3], (3.2.15).

The inverse Laplace transform of (4.8) is

$$z(\varepsilon,t) \sim 1 - e^{\varepsilon^2 t}\,\text{erfc}(\varepsilon t^{\frac{1}{2}}), \tag{4.9}$$

ERDELYI [3], (5.3.5).

This approximate solution agrees with the numerical results of de Vries for small values of t (see Figure 2).

5. An approximation method for the neighbourhood of the maximum of $z(\varepsilon,t)$

In this section we reach an approximate solution of (3.1),

$$\frac{\overline{\phi}(\varepsilon,s+\frac{1}{2})}{\sqrt{s+\frac{1}{2}}} + \frac{\varepsilon\overline{\phi}(\varepsilon,s-\frac{1}{2})}{s-\frac{1}{2}} = \frac{1}{(s-\frac{1}{2})(s+\frac{1}{2})}\,,$$

by means of the solution of (3.9),

$$\frac{\overline{\psi}(\varepsilon,s+\frac{1}{2})}{\sqrt{s+\frac{1}{2}}} + \frac{\varepsilon\overline{\psi}(\varepsilon,s-\frac{1}{2})}{s-\frac{1}{2}} = 1.$$

Just as in section 3, we multiply both sides of (3.9) with $\varepsilon^{-s-\frac{1}{2}}\Gamma^{\frac{1}{2}}(s+\frac{1}{2})$. In the new equation we substitute

$$\overline{g}(s) = \varepsilon^{-s}s^{-\frac{1}{2}}\Gamma^{\frac{1}{2}}(s)\overline{\psi}(\varepsilon,s) \tag{5.1}$$

and

$$\overline{k}(s) = \varepsilon^{-s-\frac{1}{2}}\Gamma^{\frac{1}{2}}(s+\tfrac{1}{2}), \tag{5.2}$$

hence

$$\overline{g}(s+\tfrac{1}{2}) + \overline{g}(s-\tfrac{1}{2}) = \overline{k}(s). \tag{5.3}$$

In the same way as in section 3 a solution of the difference equation is found, so that

$$\overline{\psi}(\varepsilon,s) = \frac{s^{\frac{1}{2}}}{2\Gamma^{\frac{1}{2}}(s)} \int_{-\infty}^{\infty} \frac{\varepsilon^{-ip-\frac{1}{2}}\Gamma^{\frac{1}{2}}(s+ip+\frac{1}{2})}{\text{ch } \pi p}\, dp. \tag{5.4}$$

With (3.7) and (3.8),

$$\overline{\phi}(\varepsilon,s) = \frac{s^{\frac{1}{2}}}{2\Gamma^{\frac{1}{2}}(s)} \int_{-\infty}^{\infty} \frac{\varepsilon^{-ip-\frac{1}{2}}\Gamma^{\frac{1}{2}}(s+ip+\frac{1}{2})}{(s+ip+\frac{1}{2})(s+ip-\frac{1}{2})\text{ch } \pi p}\, dp. \tag{5.5}$$

The functions $\overline{\psi}(\varepsilon,s)$ and $\overline{\phi}(\varepsilon,s)$ are related by the Euler equation

$$\varepsilon^2 \frac{\partial^2\overline{\phi}}{\partial\varepsilon^2} + 2(1-s)\varepsilon \frac{\partial\overline{\phi}}{\partial\varepsilon} + s(s-1)\overline{\phi} = \overline{\psi}, \tag{5.6}$$

as can easily be verified by differentiation of (5.5).

This equation can be solved, the resulting $\overline{\phi}(\varepsilon,s)$ has the same degree of exactitude as the approximation of $\overline{\psi}(\varepsilon,s)$, which is used.

An asymptotic expression for $\overline{\psi}(\varepsilon,s)$ is

$$\overline{\psi}(\varepsilon,s) \sim \frac{s}{s^{\frac{1}{2}}+\varepsilon}, \tag{5.7}$$

brought about with the aid of (4.5).

The fact that ε is a small quantity makes it possible to expand $\overline{\phi}$ in the following manner

$$\overline{\phi}(\varepsilon,s) = \overline{\phi}_0(\varepsilon,s) + \varepsilon\overline{\phi}_1(\varepsilon,s) + \varepsilon^2\overline{\phi}_2(\varepsilon,s) + \dots . \qquad (5.8)$$

Substituting this series in the Euler equation (5.6), with

$$\overline{\psi} = \frac{s}{s^{\frac{1}{2}} + \varepsilon}$$

and comparing the coefficients of equal powers of ε, we get

$$\overline{\phi}_0 = \frac{1}{(s^{\frac{1}{2}}+\varepsilon)(s-1)} , \qquad (5.9)$$

$$\overline{\phi}_1 = \frac{-2}{(s^{\frac{1}{2}}+\varepsilon)^2(s-1)(s-2)} , \qquad (5.10)$$

....

We have chosen this incomplete way of expanding to preserve the factors $s^{\frac{1}{2}}+\varepsilon$, which generate the desired relation between t_{max} and $\ln \varepsilon$. In the case of the complete expansion, the coefficients of the ε-powers are polynomials in s. Under inverse Laplace transformation this results in a power series in t, which hides completely the relation mentioned above.

To find the general solution of (5.6) we combine this particular solution with the solution of the homogeneous Euler equation (INCE [4], p. 141).

$$\overline{\phi}(\varepsilon,s) = \overline{\phi}_h(\varepsilon,s) + \frac{1}{(s^{\frac{1}{2}}+\varepsilon)(s-1)} - \frac{2\varepsilon}{(s^{\frac{1}{2}}+\varepsilon)^2(s-1)(s-2)} + \dots, \qquad (5.11)$$

where

$$\overline{\phi}_h(\varepsilon,s) = \overline{A}(s)\varepsilon^s + \overline{B}(s)\varepsilon^{s-1}, \qquad (5.12)$$

with $\overline{A}(s)$ and $\overline{B}(s)$ arbitrary functions of s.

To calculate the inverse Laplace transforms we need the following relations

$$\frac{1}{s-1} \doteqdot e^{t}, \qquad (5.13)$$

$$\frac{1}{s-2} \doteqdot e^{2t} \qquad (5.14)$$

and

$$\frac{1}{s^{\frac{1}{2}}+\varepsilon} \doteqdot \frac{1}{\sqrt{\pi t}} - \varepsilon e^{\varepsilon^2 t}\operatorname{erfc}(\varepsilon t^{\frac{1}{2}}) \qquad (5.15)$$

see ERDELYI [3], (5.2.1) and (5.3.4).

The function $\overline{\phi}_0$ now corresponds with the subjoined convolution integral

$$\frac{1}{(s^{\frac{1}{2}}+\varepsilon)(s-1)} \doteqdot \int_0^t e^{t-\tau}\{(\pi\tau)^{-\frac{1}{2}}-\varepsilon e^{\varepsilon^2 \tau}\operatorname{erfc}(\varepsilon\tau^{\frac{1}{2}})\}d\tau$$

$$= \frac{1}{1-\varepsilon^2} e^{t}\operatorname{erf}(t^{\frac{1}{2}}) - \frac{\varepsilon}{1-\varepsilon^2} e^{t} + \frac{\varepsilon}{1-\varepsilon^2} e^{\varepsilon^2 t}\operatorname{erfc}(\varepsilon t^{\frac{1}{2}}). \qquad (5.16)$$

We calculate the inverse transform of $\overline{\phi}_1$ in the following way.

The convolution of (5.14) and (5.16) gives

$$\frac{1}{(s^{\frac{1}{2}}+\varepsilon)(s-1)(s-2)} \doteqdot \int_0^t e^{2(t-\tau)}\{\frac{1}{1-\varepsilon^2} e^{\tau}\operatorname{erf}(\tau^{\frac{1}{2}}) - \frac{\varepsilon}{1-\varepsilon^2} e^{\tau} +$$

$$+ \frac{\varepsilon}{1-\varepsilon^2} e^{\varepsilon^2\tau}\operatorname{erfc}(\varepsilon\tau^{\frac{1}{2}})\}d\tau = -\frac{1}{1-\varepsilon^2} e^{t}\operatorname{erf}(t^{\frac{1}{2}}) + \frac{\sqrt{2}}{2-\varepsilon^2} e^{2t}\operatorname{erf}(2t)^{\frac{1}{2}} +$$

$$+ \frac{\varepsilon}{1-\varepsilon^2} e^{t} - \frac{\varepsilon}{2-\varepsilon^2} e^{2t} - \frac{\varepsilon}{(1-\varepsilon^2)(2-\varepsilon^2)} e^{\varepsilon^2 t}\operatorname{erfc}(\varepsilon t^{\frac{1}{2}}). \qquad (5.17)$$

Differentiation of this result with respect to ε yields

$$\frac{1}{(s^{\frac{1}{2}}+\varepsilon)^2(s-1)(s-2)} \doteqdot \frac{2\varepsilon}{(1-\varepsilon^2)^2} e^{t}\operatorname{erf}(t^{\frac{1}{2}}) - \frac{2\sqrt{2}}{(2-\varepsilon^2)^2} e^{2t}\operatorname{erf}(2t)^{\frac{1}{2}} +$$

$$- \frac{1+\varepsilon^2}{(1-\varepsilon^2)^2} e^{t} + \frac{2+\varepsilon^2}{(2-\varepsilon^2)^2} e^{2t} + \frac{2+3\varepsilon^2-3\varepsilon^4}{(1-\varepsilon^2)^2(2-\varepsilon^2)^2} e^{\varepsilon^2 t}\operatorname{erfc}(\varepsilon t^{\frac{1}{2}}) +$$

$$+ \frac{2\varepsilon^2}{(1-\varepsilon^2)(2-\varepsilon^2)} te^{\varepsilon^2 t}\mathrm{erfc}(\varepsilon t^{\frac{1}{2}}) - \frac{2\varepsilon}{\sqrt{\pi}(1-\varepsilon^2)(2-\varepsilon^2)} t^{\frac{1}{2}}. \qquad (5.18)$$

If the inverse Laplace transform of $\overline{A}(s)$, respectively $\overline{B}(s)$, is $A(t)$, respectively $B(t)$, the inverse transform of $\overline{\phi}_h$ is

$$\phi_h(\varepsilon,t) = A(t+\ln\varepsilon)H(t+\ln\varepsilon) + \frac{1}{\varepsilon} B(t+\ln\varepsilon)H(t+\ln\varepsilon), \qquad (5.19)$$

where H denotes the Heaviside step function. See ERDELYI [3], (4.1.4). The flux function becomes

$$z(\varepsilon,t) = \varepsilon\overline{\phi}(\varepsilon,t) = B(t+\ln\varepsilon)H(t+\ln\varepsilon) + \varepsilon A(t+\ln\varepsilon)H(t+\ln\varepsilon) +$$

$$+ \frac{\varepsilon(1-5\varepsilon^2)}{(1-\varepsilon^2)^2} e^t\mathrm{erf}(t^{\frac{1}{2}}) + \frac{4\sqrt{2}\,\varepsilon^3}{(2-\varepsilon^2)^2} e^{2t}\mathrm{erf}(2t)^{\frac{1}{2}} + \frac{\varepsilon^2(1+3\varepsilon^2)}{(1-\varepsilon^2)^2} e^t +$$

$$- \frac{2\varepsilon^2(2+\varepsilon^2)}{(2-\varepsilon^2)^2} e^{2t} - \frac{(14-11\varepsilon^2+\varepsilon^4)\varepsilon^4}{(1-\varepsilon^2)^2(2-\varepsilon^2)^2} e^{\varepsilon^2 t}\mathrm{erfc}(\varepsilon t^{\frac{1}{2}}) +$$

$$- \frac{4\varepsilon^4}{(1-\varepsilon^2)(2-\varepsilon^2)} te^{\varepsilon^2 t}\mathrm{erfc}(\varepsilon t^{\frac{1}{2}}) + \frac{4\varepsilon^3}{\sqrt{\pi}(1-\varepsilon^2)(2-\varepsilon^2)} t^{\frac{1}{2}}. \qquad (5.20)$$

For small values of ε,

$$z(\varepsilon,t) \sim \{B(t+\ln\varepsilon) + \varepsilon A(t+\ln\varepsilon)\}H(t+\ln\varepsilon) + \varepsilon e^t\mathrm{erf}(t^{\frac{1}{2}}) +$$

$$+ \varepsilon^2 e^t - \varepsilon^2 e^{2t}. \qquad (5.21)$$

In the region $0 < t < -\ln\varepsilon$

$$z(\varepsilon,t) \sim \varepsilon e^t\mathrm{erf}(t^{\frac{1}{2}}) + \varepsilon^2(e^t - e^{2t}). \qquad (5.22)$$

Rough computations easily show that for the range of ε, indicated in Table 1, this function $z(\varepsilon,t)$ has a maximum in this region, for such large values of t, that we can write for $\frac{\partial z}{\partial t}$:

$$\frac{\partial z(\varepsilon,t)}{\partial t} \sim \varepsilon e^t\mathrm{erf}(t^{\frac{1}{2}}) + \frac{\varepsilon}{(\pi t)^{\frac{1}{2}}} + \varepsilon^2(e^t-2e^{2t})$$

$$\sim \varepsilon e^t(1-2\varepsilon e^t). \qquad (5.23)$$

At the maximum z_{max}

$$1 - 2\varepsilon e^{t} = 0$$

holds. By taking the logarithm, we find a simple relation between ε and the accessory values of t_{max}

$$t_{max} + \ln \varepsilon = - \ln 2, \qquad (5.24)$$

as was required in the introduction.

If we choose $\varepsilon = (2000\sqrt{\pi})^{-1}$, we find

$$t_{max} \sim 7.48$$

and

$$z_{max} \sim 0.25.$$

Compared to Table 1, the maximum is shifted to a smaller value of t. This is caused by the different constants, which appear in the relations (1.2) and (5.24).

In Figure 2 the function $z(\varepsilon,t)$ is plotted for the chosen value of ε. When we compare the results of de Vries with those obtained with the aid of formula (5.22), we find a remarkable agreement. We notice that the maximum is shifted down the curve when asymptotic methods are used.

The nature of the problem is such, that the current approximation methods fail, so that we have to resort to the complicated method of this section.

Bearing this in mind, the numerical agreement is fairly good.

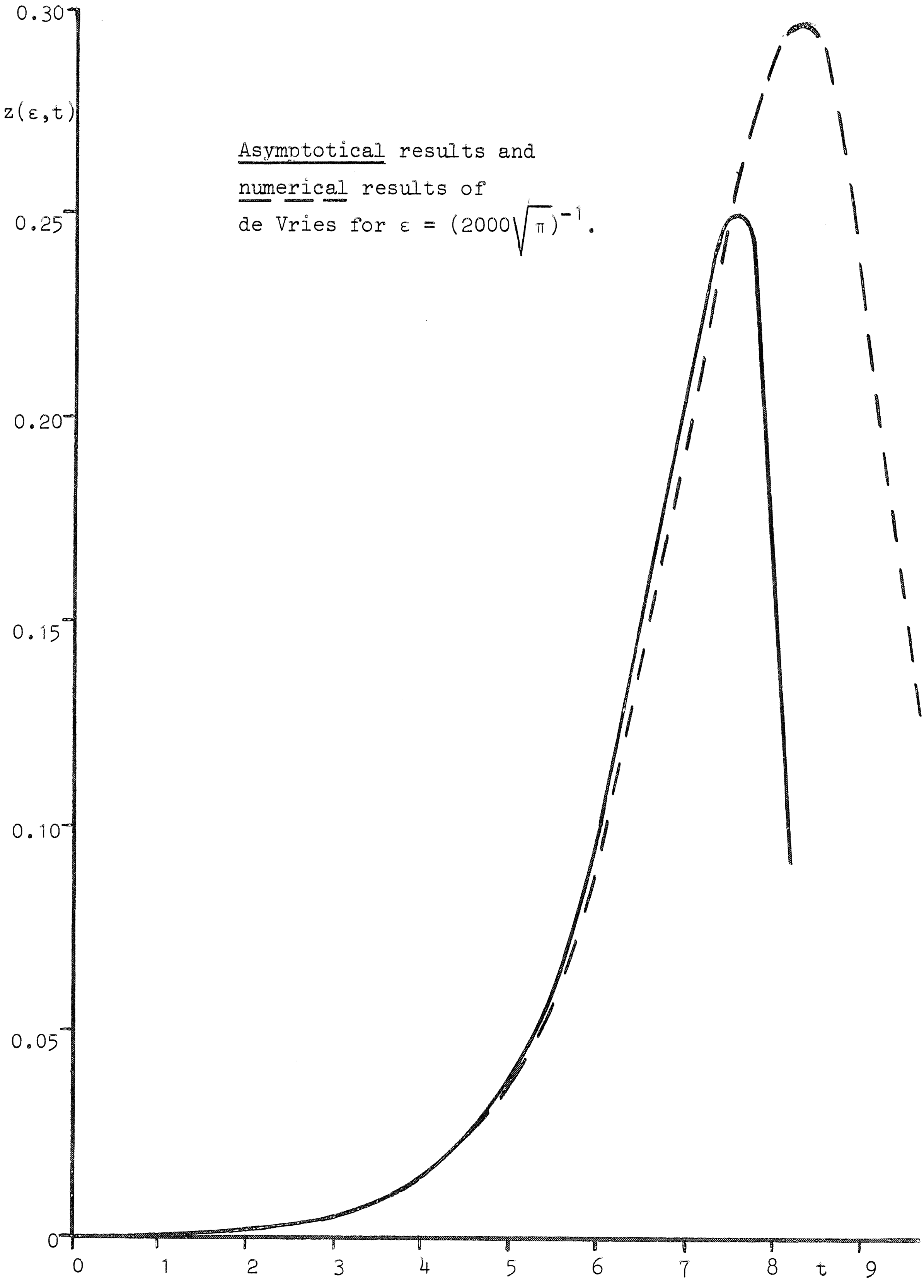
0.30
z(ε,t)
Asymptotical results and
numerical results of
de Vries for ε = (2000√π)⁻¹.
0.25
0.20
0.15
0.10
0.05
0
0
1
2
3
4
5
6
7
8
t
9

Figure 2

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