The Application of Runge-Kutta Integration in Digital Simulation of Electroanalytical Experiments. An Accurate Treatment of the Homogeneous Kinetics

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In order to find a generally applicable method for calculation of the theoretical electrode response for reactions coupled to heterogeneous charge transfer, a detailed comparison has been made of various numerical methods for treatment of the homogeneous kinetic terms in explicit finite difference methods in which the diffusion and the homogeneous kinetics are treated sequentially.

The methods for treatment of the homogeneous kinetic terms include (i) analytical integration of the rate laws, (ii) linearization of the rate laws followed by analytical integration, (iii) finite difference integration, and (iv) higher order Runge-Kutta integrations.

The error introduced by the approximate methods during treatment of the homogeneous kinetics as well as that introduced by the sequential treatment of diffusion and homogeneous kinetics was evaluated for a number of reaction mechanisms.

Of the approximate methods, 4th order Runge-Kutta integration was found to be superior and to give data indistinguishable from those obtained by analytical integration within the time step limits imposed by the sequential treatment of diffusion and homogeneous kinetics.

Fourth order Runge-Kutta integration is a general, easily applicable method even for complicated reaction mechanisms and is recommended in cases where analytical integration of the rate law is impossible, or where analytical integration results in expressions from which the concentration of interest cannot be explicitly calculated.

Over the past twenty years digital simulation has been used extensively to obtain theoretical data for the electrode response for a number of different experimental situations. Several numerical methods have been applied to the general problem which consists of solving a number of coupled partial differential equations for which the initial and boundary conditions are dependent upon the particular experimental requirements.[1-3] In order to secure a uniform and unambiguous terminology the presentation which follows is confined to only one electroanalytical technique, linear sweep voltammetry (LSV).

In the case of a reversible electron transfer followed by a homogeneous chemical reaction which is so fast that the steady state assumption is valid for the primary electrode product, the mathematical problem reduces, by application of Laplace transformations, to numerical solution of integral equations. In the transition zone between pure diffusion control (a totally reversible voltammogram) and pure kinetic control (a totally irreversible voltammogram) reduction of the problem to equations in one variable is generally not possible, and numerical methods are required to solve the associated set of partial differential

equations. The methods employed for this purpose have been (a) explicit finite difference methods, (b) (semi-)implicit finite difference methods, and (c) orthogonal collocation.

In general, all three methods are readily applicable to the most simple mechanisms. This is, however, not the case when more complicated kinetic terms are involved in the mathematical description of the electrochemical system. The aim of this study has therefore been to find a general numerical method satisfying the following requirements:

(i) The method must be applicable even for complex reaction schemes with large rate constants.
(ii) The method must be easily implemented even on small laboratory computers and therefore be independent of access to sophisticated computer library routines.
(iii) The application of the method should not require detailed mathematical knowledge.
(iv) The simplicity of the method must not be achieved at the expense of accuracy in the theoretical data obtained.

Of the methods mentioned above, orthogonal collocation [method (c)] requires access to computer library routines for solving sets of ordinary differential equations in order to be efficiently implemented.[3] Furthermore, the use of large, dimensionless rate constants requires combination with the heterogeneous equivalent method in order to give data of satisfactory accuracy.[4] We therefore eliminated orthogonal collocation from consideration at an early stage.

Of the finite difference methods, the semi-implicit method is mathematically the most satisfactory.[5] However, when the reaction mechanism becomes complex, the application of the semi-implicit method is not straightforward and iterative procedures have to be included if the semi-implicitness is to be retained (see Appendix 1 for further discussion of this point). Consequently, the derivation of the necessary equations and the programming involved become much more elaborate.

We therefore concluded that optimization of an explicit finite difference method was the most promising approach in the search for a general numerical method fulfilling requirements (i)–(iv).

For a given reaction mechanism, the mathematical description of a voltammetric experiment consists of a number of normalized differential equations of the general form

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial x^2} + \text{kin}_a(a, b, \dots)$$

$$\frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial x^2} + \text{kin}_b(a, b, \dots)$$

$$\cdot$$
$$\cdot$$
$$\cdot \tag{1}$$

with known initial and boundary conditions. The terms $\partial^2 a/\partial x^2$, $\partial^2 b/\partial x^2$, ... represent the diffusion (Fick's 2nd law for semi-infinite linear diffusion to a planar electrode), and the terms $\text{kin}_a(a, b, ..)$, $\text{kin}_b(a, b, ..)$, ... represent the homogeneous kinetics for the species A, B etc. The variables are in dimensionless notation: $a = C_A/C_A^0$, $b = C_B/C_A^0$... (C_A^0 is the initial molar concentration of substrate, C_A, C_B, ... are the solution molar concentrations of species A, B etc.), $t = t' \cdot \theta$ (t' is the time in seconds and θ is equal to $nFv/(RT)$ where v is the voltammetric sweep rate in Vs^{-1}) and $x = X/\sqrt{(D/\theta)}$ (X is the distance from the electrode in cm and D is the diffusion coefficient in cm^2s^{-1}, which in general is assumed to be identical for all species). In the kinetic terms, the normalized first order rate constants are of the form $\lambda = k/\theta$ (k in s^{-1}), and correspondingly for the normalized second-order rate constants $\lambda = kC_A^0/\theta$ (k in $M^{-1}s^{-1}$).

The discretization of time and space variables, t and x, in Δt and Δx units is common for all finite difference methods. The explicit methods require that the stability criterion $\Delta t/(\Delta x)^2 < 0.5$ is fulfilled, and the value of 0.45 has commonly been chosen for this quantity.[1,2] Having selected the size of $\Delta t/(\Delta x)^2$, only the size of Δt or Δx can be determined independently. Since the homogeneous kinetic terms are dependent only on Δt, the free choice of Δt is preferred.

The number of Δx units required in the simulation, corresponding to the thickness of the diffusion layer, remains to be determined. Normally, the approximation for the diffusion layer thickness in dimensionless formulation is given by eqn. (2), from which the number of volume elements (NVE) can be estimated as shown in

$$x = 6\sqrt{t} \qquad (2)$$

eqn. (3), where NTS is the number of time steps.

$$NVE = 6\sqrt{\Delta t/(\Delta x)^2 \cdot NTS} \qquad (3)$$

The number of volume elements, and thereby the computation time may be reduced by introduction of expanding volume elements.[6-8] This approach is not included in the following discussion, but may be applied independent of the method chosen for treatment of the homogeneous kinetics.

The most frequently used version of the explicit finite difference method is due to Feldberg[1] and is based on sequential treatment of diffusion and homogeneous kinetics, which is convenient from a programming point of view. For each time step the procedure consists of the following three steps:

(1) Establishment of the boundary conditions at the electrode surface and calculation of the fluxes of the electroactive species to determine the current.
(2) For each species: adjustment of the "old" concentrations in each volume element to account for diffusion, as described by the finite difference formulation.
(3) For each species: adjustment of the concentrations calculated in step 2 to account for the homogeneous kinetic terms in the differential equations.

The discussion below deals with various options for modification of step 3 in the above sequence.

However, the sequential treatment of diffusion and homogeneous kinetics (steps 2 and 3) is not the only possible explicit approach. Another possibility is to calculate the changes due to homogeneous kinetics using the "old" concentrations as input values instead of the diffusion-changed concentrations,[2,9] but it is easy to demonstrate that this approach does not constitute an improvement of the explicit method (see Appendix 2).

Results and discussion

The integration methods. Having accepted the sequential treatment of diffusion and homogeneous kinetics in the simulation, the problem is now the following: how are the concentration changes due to the homogeneous kinetic terms calculated most satisfactorily, or in other words: which is the best way to solve a set of ordinary differential equations of the form

$$\frac{da}{dt} = \mathrm{kin}_a(a,b,...)$$

$$\frac{db}{dt} = \mathrm{kin}_b(a,b,...)$$

.

.

. $\qquad (4)$

in each time step?

The most satisfactory method would obviously be application of the *analytically integrated* form of the kinetic terms, which involves no approximation. Application of this method was actually proposed by Feldberg and Auerbach,[10] but was not included in Ref. 1 and for that reason has apparently received only little attention.[11-13] Unfortunately, analytical solutions to the differential equations describing the homogeneous kinetics are normally not available for complex reaction schemes, and in some of the cases where a solution is available an explicit expression for the new concentration cannot be derived.

A semi-analytical method has been suggested for kinetic terms for which direct analytical integration is impossible.[11] This method consists in *linearization of the kinetic term* into a form to which analytical integration can be applied (see Appendix 3 for discussion of an example of this approach). Although the linearization followed by analytical integration expands the number of reaction mechanisms for which analytical or semianalytical integration is possible, there still remain a number of complex mechanisms for which other integration methods must be found.

In spite of the fact that an analytical solution exists for many reaction schemes, the most frequently used method for the treatment of the homogeneous kinetic terms is simply the application of the *finite difference version* of the differential equation.[1] The advantage of the finite difference method is the straightforward programming of even the most complex reaction mechanisms. The disadvantage is that it is a rather crude approximation of the differential equations unless very small time steps are used,

which may result in unacceptably long computation times.

Another completely general and much more powerful method for the treatment of the kinetic terms is *Runge-Kutta integration* (RKI).[14-16] This method has previously been proposed[12] for integration of rate laws for which analytical integration is impossible, but to the best of our knowledge the method has never actually been used as a sub-method in digital simulation. Since the application of RKI appears to be new in this context, a brief description seems relevant.

Explicit RKI belongs, like the simple finite difference version, to a larger class of single step methods for numerical solution of ordinary differential equations.[14] For the ordinary differential equation describing the kinetics of e.g. species A [the first part of eqn. (4)], the general expression for RKI is given by eqn. (5), in which a' is the starting concentration and h_i is defined as in eqns. (6) and (7):

$$a = a' + \sum_{i=1}^{v} w_i h_i \qquad (5)$$

$$h_i = \Delta t \cdot \text{kin}_a(a' + \sum_{j=1}^{i-1} q_{ij} h_j) \quad i = 1,2,...,v \qquad (6)$$

i.e.

$$h_1 = \Delta t \cdot \text{kin}_a(a')$$
$$h_2 = \Delta t \cdot \text{kin}_a(a' + q_{21} h_1)$$
$$h_3 = \Delta t \cdot \text{kin}_a(a' + q_{31} h_1 + q_{32} h_2)$$
$$h_4 = \Delta t \cdot \text{kin}_a(a' + q_{41} h_1 + q_{42} h_2 + q_{43} h_3)$$
$$\cdot$$
$$\cdot$$
$$\cdot \qquad (7)$$

The parameter v indicates the number of intermediate evaluations of a made between t and $t+\Delta t$. If $v = 1$, the method reduces to the simple finite difference version, which means that the evaluation of a is made only at the end of the interval. For simplicity, the simple finite difference approximation (the Feldberg approach) is referred to in the following as RKI-1. The larger the number v, the more accurate the RKI is supposed to be.[14]

A number of undetermined parameters appear in eqns. (5) and (6): the weights $w_1, w_2,..., w_v$ and the coefficients $q_{21},..., q_{v,v-1}$. The key point in

RKI is to choose these parameters so that the determination of $a(t+\Delta t)$ fits the Taylor series expansion in a' to as high an order as possible.[14]

A number of combinations of the undetermined parameters satisfy the requirements for fitting the Taylor series for higher order RKI.[14]

The limitations normally encountered in the application of Runge-Kutta methods are not related to the complexity of the reaction mechanism but to the stiffness of the set of ordinary differential equations.[14-17] However, during the application of Runge-Kutta integration as a sub-method in digital simulation, problems due to stiffness are not likely to be encountered. First, the nature of the chemical processes associated with heterogeneous charge transfer is in general such that the steady state approximation is valid for the intermediates formed during the reaction of the primary electrode product; second, the time step length in digital simulation is generally small. Introduction of more sophisticated and efficient numerical treatments such as predictor-corrector methods[14-20] is therefore normally not necessary.

The reaction mechanisms. In order to compare the accuracy of the different approximate numerical methods, five reaction mechanisms have been chosen for which direct analytical integration of the homogeneous kinetics is possible. A summary of the five mechanisms, together with the differential equations describing the homogeneous kinetics after application of the relevant steady-state approximations, is given in Table 1. The variables (time, distance, rate constants and concentrations) are in the usual dimensionless form. For mechanism IV a simplification was obtained by addition of the equations describing a and b, which reduced the number of equations for which changes due to homogeneous kinetics had to be calculated from three to two, thereby reducing the computation time.

The equations resulting from analytical integration of the rate laws are summarized in Table 2. For mechanisms IV and V in particular, the integration was performed by taking advantage of the stoichiometric conditions: $b-b' = c-c' \Leftrightarrow c = c'+b-b'$ (mechanism IV) and $b-b' = 2(a-a') \Leftrightarrow b = b'+2(a-a')$ (mechanism V). However, the differential equations associated with mechanisms IV and V can also be solved by the linearization procedure already described,

Table 1. Mechanisms and rate laws.

Mechanism		Rate law	Linearized rate law
I	A + e $\rightleftharpoons$ B B $\rightarrow$ C (k_1)	$\frac{\partial b}{\partial t} = -\lambda_1 b$	
II	A + e $\rightleftharpoons$ B 2B $\rightarrow$ C (k_1)	$\frac{\partial b}{\partial t} = -2\lambda_1 b^2$	
III	A + e $\rightleftharpoons$ B A + B $\rightarrow$ C (k_1) B + C $\rightarrow$ D + A (fast)	$\frac{\partial b}{\partial t} = -2\lambda_1 ab^a$	
IV	A + e $\rightleftharpoons$ B B + C $\rightarrow$ D + E (k_1) B + D $\rightarrow$ A + F (fast) F + C $\rightarrow$ G + E (fast)	$\frac{\partial(2a+b)}{\partial t} = 0^{b,c}$ $\frac{\partial b}{\partial t} = -2\lambda_1 bc$ $\frac{\partial c}{\partial t} = -2\lambda_1 bc$	$\frac{\partial b}{\partial t} = -\lambda_1 c'b - \lambda_1 b'c$ $\frac{\partial c}{\partial t} = -\lambda_1 c'b - \lambda_1 b'c$
V	A + e $\rightleftharpoons$ B A + B $\rightarrow$ C + D (k_1) B + C $\rightarrow$ A + E (fast) E + A $\rightarrow$ F + D (fast)	$\frac{\partial a}{\partial t} = -\lambda_1 ab^d$ $\frac{\partial b}{\partial t} = -2\lambda_1 ab$	$\frac{\partial a}{\partial t} = -\tfrac{1}{2}\lambda_1 b'a - \tfrac{1}{2}\lambda_1 a'b$ $\frac{\partial b}{\partial t} = -\lambda_1 b'a - \lambda_1 a'b$

[a]Assumption: $\partial c/\partial t = 0$. [b]Assumption: $\partial d/\partial t = \partial f/\partial t = 0$. [c]The ordinary flux expression, flux$_A$ =

$$\frac{\exp[-\xi(t+\Delta t)]\cdot a_1 - b_1}{\{\exp[-\xi(t+\Delta t)]+1\}/[2\cdot\Delta t/(\Delta x)^2]} \text{ should be substituted by: flux}_A = \frac{\exp[-\xi(t+\Delta t)][(2a+b)_1-b_1]/2 - b_1}{\{\exp[-\xi(t+\Delta t)]+1\}/[2\cdot\Delta t/(\Delta x)^2]}.$$

[d]Assumption: $\partial c/\partial t = \partial e/\partial t = 0$.

which made it possible to evaluate this method as well. The resulting set of linear ordinary differential equations is also given in Table 1, and the explicit expressions for the new concentrations are found in Table 2. The details of the analytical integration using this approach are described in Appendix 3.

Table 2 also gives the simple finite difference approximations, RKI-1, of the rate laws for all five mechanisms. As examples of higher order RKI's, the 3rd order Nyström version (RKI-3) and the 4th order classic version (RKI-4) have been chosen.[14] The expressions resulting from the straightforward applications of RKI-3 and RKI-4 to the five mechanisms are given in the last two columns in Table 2.

The numerical results presented in the follow-

ing serve several purposes according to the following outline.

(1) Evaluation of the accuracy of the different numerical methods for integration of the rate laws in one volume element.
(2) Determination of the error introduced in the values of E_p, $E_{p/2}$ and I_p by the sequential treatment of diffusion and kinetics as a function of (i) the mechanism and (ii) the material conversion, which reflects simultaneously the values of the dimensionless rate constant and the time step length.
(3) Determination of the additional error introduced in E_p, $E_{p/2}$ and I_p by the various approximate methods of integration of the rate laws.

Table 2. Expressions for the concentration calculation in each time step.

| Mech.	Analytical integration	Linearization and analytical integration	RKI-1	RKI-3	RKI-4
I	$b = b'\exp(-\lambda_1\Delta t)$	—	$b = b' - \lambda_1\Delta t b'$	$b = b' + 1/8(2h_1 + 3h_2 + 3h_3)$ $h_1 = -\lambda_1\Delta t b'$ $h_2 = -\lambda_1\Delta t(b' + 2/3h_1)$ $h_3 = -\lambda_1\Delta t(b' + 2/3h_2)$	$b = b' + 1/6(h_1 + 2h_2 + 2h_3 + h_4)$ $h_1 = -\lambda_1\Delta t b'$ $h_2 = -\lambda_1\Delta t(b' + h_1/2)$ $h_3 = -\lambda_1\Delta t(b' + h_2/2)$ $h_4 = -\lambda_1\Delta t(b' + h_3)$
II	$b = b'/(2\lambda_1\Delta t b' + 1)$	—	$b = b' - 2\lambda_1\Delta t b'^2$	$b = b' + 1/8(2h_1 + 3h_2 + 3h_3)$ $h_1 = -2\lambda_1\Delta t b'^2$ $h_2 = -2\lambda_1\Delta t(b' + 2/3h_1)^2$ $h_3 = -2\lambda_1\Delta t(b' + 2/3h_2)^2$	$b = b' + 1/6(h_1 + 2h_2 + 2h_3 + h_4)$ $h_1 = -2\lambda_1\Delta t b'^2$ $h_2 = -2\lambda_1\Delta t(b' + h_1/2)^2$ $h_3 = -2\lambda_1\Delta t(b' + h_2/2)^2$ $h_4 = -2\lambda_1\Delta t(b' + h_3)^2$
III	$b = b'\exp(-2\lambda_1\Delta t a')$	—	$b = b' - 2\lambda_1\Delta t a'b'$	$b = b' + 1/8(2h_1 + 3h_2 + 3h_3)$ $h_1 = -2\lambda_1\Delta t a'b'$ $h_2 = -2\lambda_1\Delta t a'(b' + 2/3h_1)$ $h_3 = -2\lambda_1\Delta t a'(b' + 2/3h_2)$	$b = b' + 1/6(h_1 + 2h_2 + 2h_3 + h_4)$ $h_1 = -2\lambda_1\Delta t a'b'$ $h_2 = -2\lambda_1\Delta t a'(b' + h_1/2)$ $h_3 = -2\lambda_1\Delta t a'(b' + h_2/2)$ $h_4 = -2\lambda_1\Delta t a'(b' + h_3)$
IV	$b = \dfrac{b'(c' - b')}{c'\exp[2\lambda_1\Delta t(c' - b')] - b'}$ $c = c' + (b - b')$	$b = \dfrac{2K - b'c' + b'^2}{b' + c'}$ $c = \dfrac{2K - b'c' + c'^2}{b' + c'}$ $K = b'c'\exp[-\lambda_1\Delta t(b' + c')]$	$b = b' - 2\lambda_1\Delta t b'c'$ $c = c' - 2\lambda_1\Delta t b'c'$	$b = b' + 1/8(2h_1 + 3h_2 + 3h_3)$ $c = c' + 1/8(2h_1 + 3h_2 + 3h_3)$ $h_1 = -2\lambda_1\Delta t b'c'$ $h_2 = -2\lambda_1\Delta t(b' + 2/3h_1)(c' + 2/3h_1)$ $h_3 = -2\lambda_1\Delta t(b' + 2/3h_2)(c' + 2/3h_2)$	$b = b' + 1/6(h_1 + 2h_2 + 2h_3 + h_4)$ $c = c' + 1/6(h_1 + 2h_2 + 2h_3 + h_4)$ $h_1 = -2\lambda_1\Delta t b'c'$ $h_2 = -2\lambda_1\Delta t(b' + h_1/2)(c' + h_1/2)$ $h_3 = -2\lambda_1\Delta t(b' + h_2/2)(c' + h_2/2)$ $h_4 = -2\lambda_1\Delta t(b' + h_3)(c' + h_3)$
V	$a = \dfrac{a'(b' - 2a')}{b'\exp[\lambda_1\Delta t(b' - 2a')] - 2a'}$ $b = b' + 2(a - a')$	$a = \dfrac{2K - a'b' + 2a'^2}{2a' + b'}$ $b = \dfrac{4K - 2a'b' + b'^2}{2a' + b'}$ $K = a'b'\exp[-\tfrac{1}{2}\lambda_1\Delta t(2a' + b')]$	$a = a' - \lambda_1\Delta t a'b'$ $b = b' - 2\lambda_1\Delta t a'b'$	$a = a' + 1/8(2h_1 + 3h_2 + 3h_3)$ $b = b' + 1/4(2h_1 + 3h_2 + 3h_3)$ $h_1 = -\lambda_1\Delta t a'b'$ $h_2 = -\lambda_1\Delta t(a' + 2/3h_1)(b' + 4/3h_1)$ $h_3 = -\lambda_1\Delta t(a' + 2/3h_2)(b' + 4/3h_2)$	$a = a' + 1/6(h_1 + 2h_2 + 2h_3 + h_4)$ $b = b' + 1/3(h_1 + 2h_2 + 2h_3 + h_4)$ $h_1 = -\lambda_1\Delta t a'b'$ $h_2 = -\lambda_1\Delta t(a' + h_1/2)(b' + h_1)$ $h_3 = -\lambda_1\Delta t(a' + h_2/2)(b' + h_2)$ $h_4 = -\lambda_1\Delta t(a' + h_3)(b' + 2h_3)$
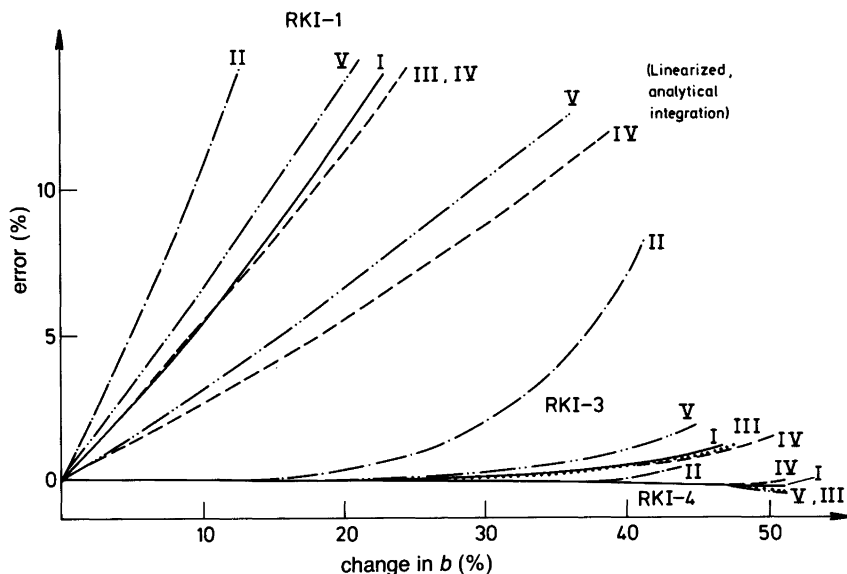
Fig. 1. One volume element comparisons of the errors introduced by various approximate methods of integration of the kinetic terms.

The accuracy of the different methods of integration – one volume element comparisons. The difference between the concentration changes in single volume elements calculated by each method of integration and the concentration changes calculated by analytical integration have been determined in order to specifically evaluate the approximate methods for integration of the rate laws. In the following this difference is referred to as the error.

For mechanisms I and IV, a given value of $\lambda_1 \cdot \Delta t$ and $\lambda_1 \cdot c^0 \cdot \Delta t$ ($c \gg b$), respectively, corresponds to a certain percentage change in the concentration (b) of the primary electrode product independent of the initial value of b. Consequently, the deviation from the analytical integration result which is observed for the other integration methods can be recorded as a function of the percentage change in b, when the calculations are made for a single volume element.

For mechanisms II, III and V, the percentage change in b depends on the initial value of b. For mechanism II, the *maximum* change occurs when the initial value of b is 1. This maximum initial value of b has been used for the comparison for mechanism II.

For mechanisms III and V, the percentage change in b is influenced by the fact that a and b are interdependent. However, the *maximum* change in b is obtained when a equals 1. This maximum value of a has been used for the comparisons for mechanisms III and V. The results for all the one volume element comparisons are illustrated in Fig. 1. The most remarkable result is the considerable improvement in accuracy resulting from the application of RKI-4 compared to RKI-1. For all five mechanisms, the error introduced by RKI-4 was less than 0.2 % for a 40 % change in b.

The results obtained by linearization followed by analytical integration for mechanisms IV and V show that this method offers an improvement compared to RKI-1, but in both cases the error was considerably greater than that observed for RKI-4.

A third point of interest is that larger errors appear in general to be associated with mechanism II, the only mechanism for which the rate-law is second-order in b. However, it should be kept in mind that the definition of the material conversion for mechanism II differs somewhat from that for mechanisms I and IV, and that for mechanisms III and V.
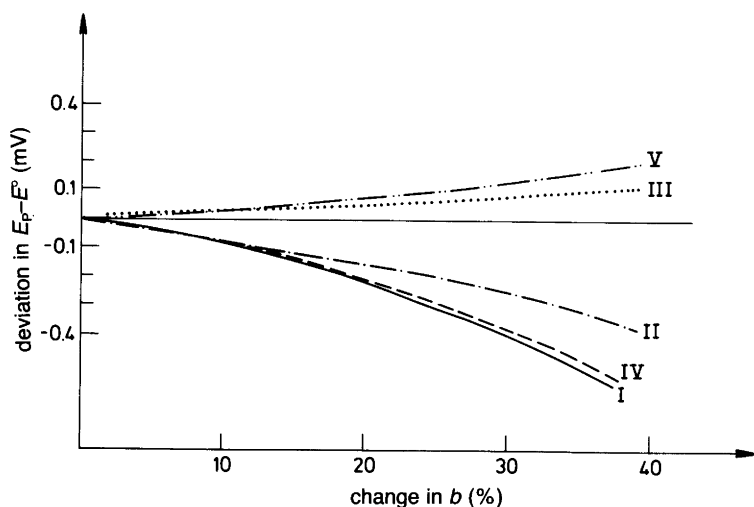
Fig. 2. Deviations of $E_p - E^0$ from the true value, caused by the separate treatment of diffusion and kinetics, as a function of the percentage change in b per time step.

Another notable result is the sign of the error. In all cases, except for RKI-4 applied to mechanisms I, III and V, the numerical integration results in overestimation of the concentration changes; in other words, the response is as if the rate constants are larger than is actually the case.

Comparison of the results for RKI-3 and RKI-4 indicates that RKI-4 should be recommended for treatment of new mechanisms, especially those for which the rate-law contains second-order terms in b.

The error introduced by the sequential treatment of diffusion and homogeneous kinetics. For a reversible system without chemical follow-up reactions, the deviation in $E_p - E^0$ on going from 1 mV per time step to 0.1 mV per time step is only ≈ 0.02 mV, which illustrates that simulation errors due to the numerical treatment of the diffusion alone are small and may safely be neglected for Δt values in this range or smaller. To evaluate the error introduced by the separate treatment of diffusion and homogeneous kinetics in the Feldberg approach, LSV simulations were carried out using analytical integration of the kinetic terms for all five mechanisms. The parameters evaluated were the values of $E_p - E^0$ and $E_{p/2} - E^0$ which are of most interest in LSV, but for the sake of completeness the values of I_p were evaluated as well, although the mechanistic and kinetic information obtainable from the peak current is, in general, rather limited.

The results of simulations carried out with values of Δt so small that the effect on the potential values of bisecting Δt was less than 0.02 mV were chosen as the "true" values for $E_p - E^0$, $E_{p/2} - E^0$ and I_p. This choice was justified by the agreement between the limiting potential values for $\Delta t \rightarrow 0$ and previously published values calculated by other methods which are not based on the separate treatment of diffusion and kinetics.[21-23]

The errors in the simulated values of $E_p - E^0$ and $E_{p/2} - E^0$ as a function of the percentage change in b as defined previously are illustrated in Figs. 2 and 3. By comparison of the results in these two figures it is seen that the five mechanisms fall into two groups. In the first of these, which consists of mechanism I, II and IV, the deviations of $E_p - E^0$ and $E_{p/2} - E^0$ from the "true" values are in all three cases negative and of similar magnitude. As a consequence of this, the errors in the differences between $E_p - E^0$ and $E_{p/2} - E^0$ almost cancel, resulting in values of the half peak width, $E_{p/2} - E_p$, which are very close to the "true" values (Fig. 4). In the other group, i.e. mechanisms III and V, the deviations in $E_p - E^0$ and $E_{p/2} - E^0$ are all positive, but in this group the deviations are much more pronounced for $E_{p/2} - E^0$ than for $E_p - E^0$. It appears that the positive deviation in $E_{p/2} - E^0$ is compensated for to some extent during the simulation between the half peak and the peak, and consequently, the errors in $E_{p/2} - E_p$ (Fig. 4) are of similar magni-
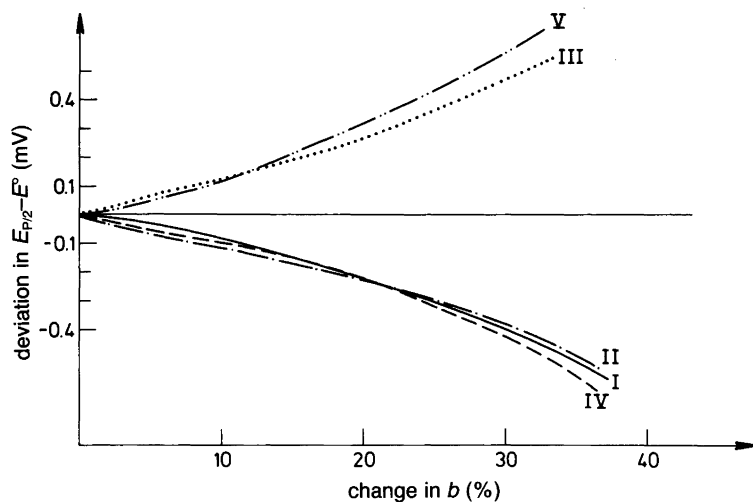
Fig. 3. Deviations of $E_{p/2}-E^0$ from the true value, caused by the separate treatment of diffusion and kinetics, as a function of the percentage change in b per time step.

tude to those in E_p-E^0, although the signs are reversed.

The difference in response for the mechanisms in the two groups is clearly significant, and is most likely related to the fact that only b appears in the rate law for mechanisms I, II, and IV, whereas for mechanisms III and V both the substrate concentration, a, as well as b contribute to the kinetic term.

Since E_p-E^0 and $E_{p/2}-E_p$ are the calculated results of most importance in LSV-simulations, it

is of interest to determine the maximum change in b which may be allowed in a simulation in order to attain a certain accuracy in these two quantities. Tables 3 and 4 summarize the maximum percentage change in b for the five mechanisms if the errors in E_p-E^0 or $E_{p/2}-E_p$ are to be kept below the two arbitrarily chosen limits, viz. ± 0.1 mV and ± 0.4 mV. The trends in the data are as expected from the discussion in the previous paragraphs and in addition, it is of interest to note that if the errors in E_p-E^0 and $E_{p/2}-E_p$
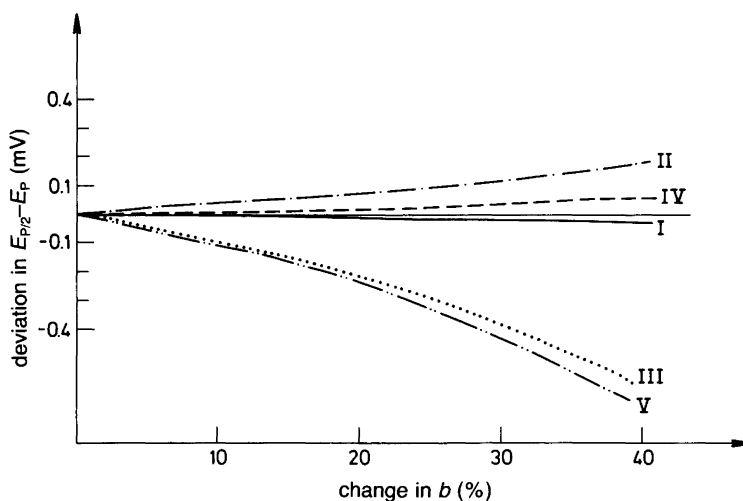

Fig. 4. Deviations of $E_{p/2}-E_p$ from the true value, caused by the separate treatment of diffusion and kinetics, as a function of the percentage change in b per time step.
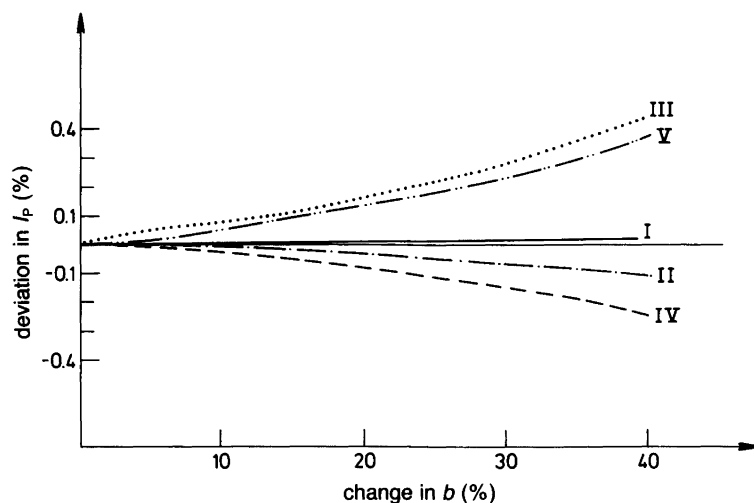
Fig. 5. Deviations of I_p from the true value, caused by the separate treatment of diffusion and kinetics, as a function of the percentage change in *b* per time step.

should simultaneously be less than ± 0.1 mV, the change in *b* should be kept at a maximum of approximately 10 % almost independent of the mechanism.

The ± 0.1 mV and ± 0.4 mV levels of error toleration result in deviations in the peak current, I_p, of less than 0.1 % and 0.3 %, respectively, for all five mechanisms. This illustrates that the magnitude of the peak current in an LSV-simulation is not very sensitive to errors introduced by the approximations used. It is seen from Fig. 5 that the signs of the peak current deviations correspond to the deviations in $E_{p/2} - E_p$ as expected: peaks which are too narrow are associated with peak currents which are too high (mechanisms III and V), and peaks which are too broad are associated with peak currents lower than the "true" values (mechanisms II and IV).

Since, as it was pointed out in the beginning of this part of the discussion, the errors introduced in the simulation by the explicit treatment of the diffusion alone are small, and since the treatment of the homogeneous kinetic part in the calculations reported above has been exact, the obvious conclusion is that the deviations from the "true" values shown in Figs. 2–4 are caused mainly by the separation of diffusion and kinetics in the calculations.

The additional influence of the inaccuracy in the treatment of the homogeneous kinetics on the simulated potentials. The influence of the errors in-

troduced by the non-analytical integration methods on the simulated $E_p - E^0$ and $E_{p/2} - E_p$ values can be determined in several ways. We have found it most relevant to compare simulated values of $E_p - E^0$ and $E_{p/2} - E_p$ with the limiting values obtained at small values of Δt. Thus, the resulting errors include contributions from both the inaccuracy in the numerical integration of the kinetic terms and the separation of diffusion and kinetics.

As discussed previously, the simple finite difference integration, RKI-1, as well as linearization followed by analytical integration, results in overestimation of changes in the concentration of B due to homogeneous kinetics (Fig. 1). Consequently, the simulated peak potentials are expected to be more positive than the "true" values, and this is in fact the case (Fig. 6). The peak potentials calculated for mechanisms I and IV are affected most strongly, especially when it is recalled that sequential diffusion and homogeneous kinetics caused $E_p - E^0$ to adopt too *negative* values when analytical integration was used (Fig. 2), i.e. the error in the treatment of the homogeneous kinetics not only compensates for the built-in error caused by the sequential treatment of diffusion and kinetics, but owing to its magnitude results in an over-all error in the opposite direction.

The largest error in the one volume element comparisons was associated with the second-order reaction (mechanism II), and although the
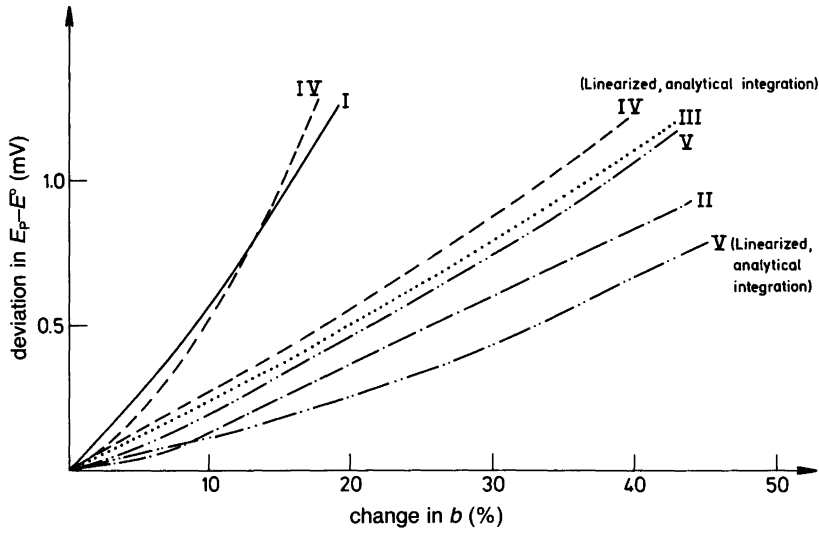
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Fig. 6. Deviations of $E_p - E^0$ from the true value, caused by the separate treatment of diffusion and kinetics *and* the application of simple finite difference integration (RKI-1) or linearization followed by analytical integration of the kinetic terms.

absolute value of the error introduced by the sequential treatment for this mechanism is smaller than that for mechanisms I and IV, the error using RKI-1 in the simulation is much smaller for mechanism II than for mechanisms I and IV.

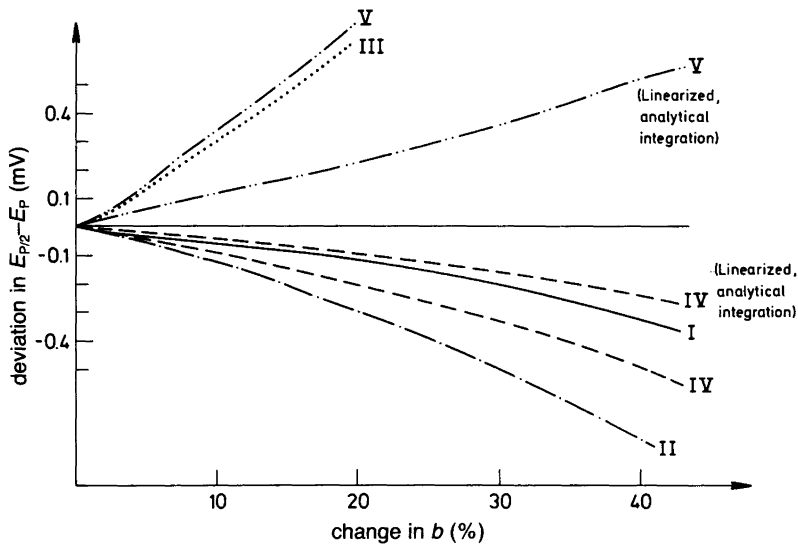The simulations for mechanisms III and V behave almost identically when RKI-1 is applied.

Fig. 7. Deviations of $E_{p/2} - E_p$ from the true value, caused by the separate treatment of diffusion and kinetics *and* the application of simple finite difference integration (RKI-1) or linearization followed by analytical integration of the kinetic terms.

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Also, for these mechanisms the simulated E_p-E^{0} values are too positive; this was, however, also the case when analytical integration was used, so that the error caused by use of the approximate method is apparently just amplified.

For the two mechanisms IV and V, for which linearization of the kinetic terms is possible, it is clear from Fig. 6 that this method represents an improvement compared to RKI-1, especially for mechanism IV. This improvement corresponds rather closely to the improvement in the calculation of the concentration changes due to homogeneous kinetics as shown in Fig. 1.

A comparison of the values of $E_{p/2}-E_p$ calculated by application of RKI-1 with the "true" values (Fig. 7) reveals that the simulations for mechanisms III and V are the most sensitive towards errors in the concentration change. The peaks are too broad, which for these mechanisms would correspond to an apparent rate constant larger than was actually used, and this is the opposite of the results found for the same two mechanisms using the analytical integration. This effect is similar to that seen for mechanisms I, II and IV with respect to the peak potential. Sim-

ulations using RKI-1 for mechanisms I, II and IV result in peaks that are too narrow, which for these three mechanisms also corresponds to rate constants larger than those actually used.

Again, linearization followed by analytical integration is an improvement compared to RKI-1, but for the $E_{p/2}-E_p$ values the improvement is now most significant for mechanism V and not mechanism IV.

Choosing, as previously, ±0.1 mV and ±0.4 mV as the tolerable error limits for E_p-E^0 and $E_{p/2}-E_p$, the maximum acceptable concentration changes are summarized in Tables 3 and 4.

In general, it may be concluded that both RKI-1 and linearization followed by analytical integration lead to excessive changes in b; consequently, the simulations respond by predicting peak potentials and peak widths corresponding to apparent rate constants larger than those actually used. From inspection of Figs. 6 and 7, and Tables 3 and 4, it appears that there is no simple relationship between the magnitude of the errors introduced in the simulation and the magnitude of the errors introduced in the kinetic terms alone on going from analytical integration to RKI-1 or

Table 3. The maximum percentage change in b due to homogeneous kinetics corresponding to an error in the peak and half-peak potentials of less than ±0.1 mV.

Mechanism	$E_p-E^{0\ a}$			$E_{p/2}-E_p{}^a$			E_p-E^0 and $E_{p/2}-E_p{}^a$		
I	12	2	–	>50	18	–	12	2	–
II	12	9	–	25	8	–	12	8	–
III	40	4	–	10	4	–	10	4	–
IV	12	3	4	>50	12	23	12	3	4
V	25	6	8	10	4	11	10	4	8

[a]First column: analytical integration or 4th order Runge-Kutta integration; second column: ordinary Feldberg approach (1st order Runge-Kutta integration); third column: analytical integration of linearized expressions.

Table 4. The maximum percentage change in b due to homogeneous kinetics corresponding to an error in the peak and half-peak potentials of less than ±0.4 mV.

Mechanism	$E_p-E^{0\ a}$			$E_{p/2}-E_p{}^a$			E_p-E^0 and $E_{p/2}-E_p{}^a$		
I	30	7	–	>50	>50	–	30	7	–
II	40	21	–	>50	26	–	40	21	–
III	>50	16	–	30	13	–	30	13	–
IV	30	8	14	>50	26	>50	30	8	14
V	>50	17	28	28	12	32	28	8	28

[a]See footnote to Table 3.

Table 5. Maximum values of the kinetic simulation parameters during analytical integration or 4th order Runge-Kutta integration corresponding to errors in the peak *and* half-peak potentials of less than ±0.1 mV and ±0.4 mV.

Mechanism	Simulation parameter[a]	±0.1 mV	±0.4 mV
I	$k/\theta \cdot \Delta t$	3.28	9.15
II	$C_A^0 k/\theta \cdot \Delta t$	1.75	8.55
III	$C_A^0 k/\theta \cdot \Delta t$	1.35	4.60
IV	$C_C^0 k/\theta \cdot \Delta t^b$	1.64	4.59
V	$C_A^0 k/\theta \cdot \Delta t$	1.37	4.39

[a] Δt in mV/time step. [b] $C_C^0 \gg C_A^0$ is assumed.

linearization followed by analytical integration. It is therefore recommended that the changes in b due to homogeneous kinetics should not exceed a few per cent when the electrode response of a new mechanism is calculated by application of RKI-1 or the linearization procedure if the errors in the simulated values of $E_p - E^0$ and $E_{p/2} - E_p$ should not exceed ±0.1 mV.

In contrast to this, the results presented for RKI-4 in Fig. 1 demonstrate that the concentration changes calculated by this method are almost identical to those originating from analytical integration when the conversion of B ranges from 0 to 30-40 %; consequently, simulated data based on the RKI-4 treatment of the kinetic terms will be practically indistinguishable from those based on the integrated rate laws. The data in Table 4 show that a conversion of 30-40 % corresponds to an error limit of ±0.4 mV, but even at ±0.1 mV RKI-4 permits concentration changes as high as 10 % (Table 3).

The maximum percentage change in b can be converted to the approximate values of the dimensionless kinetic simulation parameter found in Table 5. As an example of how to use Table 5, let us consider mechanism I and a dimensionless rate constant, k/θ, equal to 10. A simulation in which the peak potential and the half-peak width are both determined with an error of less than ±0.1 mV requires $\Delta t \le 3.28/(k/\theta)$ mV per time step = 0.328 mV per time step. For a potential range of 200 mV this corresponds to a minimum of 610 time steps. In order to carry out the same simulation using RKI-1 with the same accuracy, a

maximum concentration change of only 2 % is allowed (Table 3), which translates to $k/\theta \cdot \Delta t = 0.5088$ and $\Delta t \le 0.5088/(k/\theta)$ mV per time step = 0.05088 mV per time step; in other words, 3931 time steps as a minimum or about 6.5 times as many time steps as for analytical integration or RKI-4.

For a fixed number of time steps a simulation based on RKI-4 is approximately twice as time-consuming as a simulation based on the simple finite difference approximation, while the computation time for simulations including analytical integration is similar to that based on RKI-4 if exponentials have to be evaluated in each volume element and similar to that based on RKI-1 if this is not the case.

In the example above, the RKI-1 simulation required about 8 times as much computer time as the RKI-4 simulation, and about 16 times as much computer time as the simulation involving analytical integration to achieve the same degree of accuracy.

Conclusions

The application of analytically integrated rate-laws for evaluation of the homogeneous kinetic terms in digital simulation based on an explicit formulation of the diffusion kinetic problem represents a considerable improvement over the ordinary finite difference approach for the same number of time steps. For the same accuracy the computation time may be reduced by a factor of 6 to 10.

In cases where analytical integration is not possible or where an explicit expression for the new concentrations cannot be derived, the application of 4th order Runge-Kutta integration is recommended. For the five mechanisms investigated, 4th order Runge-Kutta integration gave results indistinguishable from those obtained by analytical integration within the error limits imposed by the separation of diffusion and kinetics in the calculations at material conversions of up to 30-40 % in each volume element in each time step. Fourth order Runge-Kutta integration is easily applied even to very complicated reaction schemes.[14-16,24-25]

In practical work, the separation of diffusion and kinetics does not constitute a problem. Peak potentials and half-peak potentials may be simulated to an accuracy of ±0.4 mV at material

conversions of up to 30–40 %, and ±0.1 mV at material conversions close to 10 % in a single time step.

Computational details

All calculations were carried out in PASCAL on an HP9826A desk-top computer working using 8 bytes in the internal representation of real numbers.

Simulations of LSV were carried out using a 200 mV interval positioned on the potential scale relative to $E°$ so that the peak appeared approximately 5 mV before the end of the interval.

In order to obtain the peak potential, E_p, with the same precision independent of the step size, the normalized current values in a potential range of ±1 mV around the apparent peak point were fitted to a second-order polynomial from which the peak potential was determined by differentiation. The second-order polynomial was subsequently used to determine the dimensionless peak current, I_p.

To calculate the half-peak width, $E_{p/2}-E_p$, where $E_{p/2}$ is the value of E at $I = I_p/2$, the normalized current values in a range of ±1 mV or less around the apparent half-peak point were fitted to a first-order polynomial from which the half peak potential was calculated.

All simulations were carried out using $\Delta t/(\Delta x)^2$ = 0.45, and the necessary number of volume elements in each time step was estimated from eqn. (3). The current function was calculated in the manner described by Feldberg,[1] since higher order approximations[26–27] were deemed unnecessary.

For the sake of convenience the time step size in Table 5 is given in mV per time step. In the simulations, this value was converted to dimensionless form according to the expression:

Δt (dimensionless) =

Δt (mV per time step) $F/(1000RT)$

with $T = 298.13$ K. All other variables (concentrations, distance from electrode, rate constants etc.) were normalized in the usual way, as described in the introduction.

Appendix 1

The semi-implicit finite difference method, or the Crank-Nicholson method, was primarily developed in the context of partial differential equations of parabolic form, i.e for application to "pure" diffusion problems, for which it has been shown to be superior to the explicit finite difference methods with respect to computer time requirements vs. accuracy.[5] This improvement is achieved by greater stability, which allows $\Delta t/(\Delta x)^2$ values larger than 0.5 to be used in the calculations.[2,5] However, if diffusion takes place in more than one direction, or if the homogeneous chemical reactions are not simple first-order or pseudo first-order processes, no straightforward application of the semi-implicit method is available.

In general, the finite difference approximation of the pure diffusion equation for a species C in one dimension for a single volume element, i, can be written as eqn. (A1):

$$\frac{c_i'-c_i}{\Delta t} = \frac{1}{(\Delta x^2)} \cdot$$

$$[\gamma(c_{i+1}'-2c_i'+c_{i-1}')+(1-\gamma)(c_{i+1}-2c_i+c_{i-1})] \quad \text{(A1)}$$

If $\gamma = 0$, only "old" concentration values, c, appear on the right hand side of (A1), and the eqn. is then identical with the usual explicit finite difference form. If $\gamma = 1$, only "new" concentration values, c', appear on the right-hand side of (A1) and the formulation is fully implicit. This form is normally not used, although it has been suggested.[28]

The Crank-Nicholson semi-implicit method entails $\gamma = \frac{1}{2}$, corresponding to an average of "old" and "new" concentration values on the right-hand side of (A1).

The consequence of the semi-implicit formulation is that the calculation of the diffusion cannot be carried out volume element by volume element; instead, the entire concentration array must be changed simultaneously, normally by a Gauss-elimination procedure.[2,5]

The major problem associated with the semi-

implicit method is, however, the treatment of the homogeneous kinetic terms. To maintain the improvement in stability, the *entire* set of differential equations must be treated semi-implicitly. For a simple EC-mechanism this approach is possible. The semi-implicit formulation of eqn. (A2)

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} - \lambda c \tag{A2}$$

takes the form (A3)

$$\frac{c_i'-c_i}{\Delta t} = \frac{1}{2(\Delta x)^2}(c_{i+1}'-2c_i'+c_{i-1}'+c_{i+1}-2c_i+c_{i-1})$$
$$-\tfrac{1}{2}\lambda(c_i'+c_i) \tag{A3}$$

which, like (A1), can be rearranged to an equation containing only "old" concentrations on one side and only "new" concentrations on the other side, so that the Gauss-elimination procedure can now be applied with different coefficients for the c_i and c_i' terms. However, Heinze et al.[29] have suggested another treatment of the simple EC-case, using the approximation $-\lambda c_i'$ for the kinetic term instead of $-\lambda(c_i' + c_i)/2$, i.e. an implicit instead of a semi-implicit treatment of the homogeneous kinetics. This method was claimed to be consistent with previous results and to be capable of handling dimensionless rate constants up to 10^4.

If the mechanism is more complicated and includes a second-order reaction [eqn. (A4)], the semi-implicit formulation takes the form (A5):

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} - 2\lambda c^2 \tag{A4}$$

$$\frac{c_i'-c_i}{\Delta t} = \frac{1}{2(\Delta x)^2}(c_{i+1}'-2c_i'+c_{i-1}'+c_{i+1}-2c_i+c_{i-1}) -$$
$$2\lambda[(c_i'+c_i)/2]^2 \tag{A5}$$

Eqn. (A5) *cannot* be rearranged to a form suitable for application of the Gauss-elimination procedure because of the second order term in $c_i{}'$.

Two approximate methods have been suggested to overcome this problem.[23,30–32] The first method[23,31] consists of an iterative procedure in which c_i' in the first iteration is substituted by c_i in the term $-2\lambda[(c_i'+c_i)/2]^2$ and a value for c_i' is calculated. In the next iteration the first calculated value for c_i' is inserted in the kinetic term, still with the original value for c_i. The process is repeated until the calculated values of c_i' differ insignificantly in two consecutive iterations. The other method[30] entails a linearization of the term $-2\lambda c^2$ to $-2\lambda c_i' c_i$. Substitution of $-2\lambda[(c_i'+c_i)/2]^2$ with $-2\lambda c_i' c_i$ in (A5) allows rearrangement of (A5) to a form to which the Gauss-elimination procedure can be applied.

An explicit treatment of second-order kinetic terms has also been suggested, but in this way the stability improvement is clearly lost.

Second-order reactions in two different species, A and B, cause difficulties also. The strictly semi-implicit formulation of the kinetic term in (A6):

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial x^2} - \lambda ab \tag{A6}$$

is

$$-\lambda\left(\frac{a'+a}{2}\cdot\frac{b'+b}{2}\right) \tag{A7}$$

which gives rise to a term containing the product of the "new" concentrations, $a'b'$, making the appropriate rearrangement impossible. Linearizations and iterative procedures have also been suggested in this case.[32,33] The most simple form replaces (A7) with (A8). Eqn. (A8a) is then used in the eqn. related to species A, and eqn. (A8b) in the equations related to species B:[33]

$$-\lambda a'b \tag{A8a}$$

$$-\lambda ab' \tag{A8b}$$

The other linearization method replaces (A7) with (A9) where (A9a) and (A9b) are used in the equations for species A and B, respectively.[32]

$$-\lambda \left(\frac{a'b}{2} + \frac{ab}{2} \right) \tag{A9a}$$

$$-\lambda \left(\frac{ab'}{2} + \frac{ab}{2} \right) \tag{A9b}$$

Alternatively, the same kind of iteration as for the reaction second-order in a single species can be applied to (A7). First, Gauss-elimination is applied to the equations related to species A with b' in (A7) substituted with b. Second, Gauss-elimination is applied to the equations related to species A using the values just calculated for species A as a'-values. Third, recalculation of the new values for species A using the newly calculated values for species B as b'-values, and so on, until the concentration values for A (and B) calculated in two consecutive iterations differ insignificantly. Obviously these iterative procedures require additional computer time, and the work involved in the programming for both the linearization methods and the iterative method is much more complicated than for any of the explicit methods.

For mixed first order kinetic terms as in (A10) the semiimplicit formulation of the kinetics is given by (A11). In this case it is possible to handle the equations related to species A and B simultaneously and keep the strict formulation of (A11).

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial x^2} - \lambda_1 a + \lambda_2 b \tag{A10}$$

$$-\lambda_1 \left(\frac{a'+a}{2} \right) + \lambda_2 \left(\frac{b'+b}{2} \right) \tag{A11}$$

Appendix 2

As pointed out in the introduction, the application of the diffusion-changed concentrations as input values for the kinetic calculations is not the only explicit approach. Alternatively, the "old" concentration values might have been used.

Let us as a beginning emphasize that when a new volume element is included in the calculation, b ("old" value) in that volume element is zero. If we now for simplicity consider only the first two time steps in a simulation of a reversible electron transfer process followed by a simple irreversible first-order reaction of the primary electrode product, B, we have the following events: After the calculations associated with the first time step, only the first volume element contains a non-zero concentration of B (b_1). During the second time step the concentration of B in the first volume element is reduced due to diffusion by $0.45b_1$, which is transferred to the second volume element assuming the value of $\Delta t/(\Delta x)^2$ to be 0.45. If now 20 % of the "old" value of b_1 disappears due to the follow-up reaction, the total amount of B remaining in the first volume element after diffusion and kinetics corresponds to $b_1 - 0.45b_1 - 0.2b_1 = 0.35b_1$. Since the "old" concentration of B in the second volume element, (b_2) is zero the value of the kinetic term is also zero; accordingly, the amount of B in the second volume element after diffusion and kinetics corresponds to $0 + 0.45b_1 - 0 = 0.45b_1$. In other words, the "new" concentration of B in the second volume element is *larger* than that in the first volume element, which is an impossible physical situation. The problem is obviously caused by the rather high conversion of B in the kinetic step, and it is easy to see that the conversion should never exceed 10 % if this unpleasant situation is to be avoided.

Using instead the diffusion changed values as input in the kinetic calculations we arrive at the following "new" values of b in the second time step. In the first volume element we have $b_1 - 0.45b_1 - 0.2(1-0.45)b_1 = 0.44b_1$, and in the second volume element $0 + 0.45b_1 - 0.2 \cdot 0.45b_1 = 0.36b_1$. It is seen that the value in the second volume element is now smaller than that in the first volume element and this will always be the case independent of the degree of conversion.

When the two methods are compared in test simulations using conversions lower than 10 % in the kinetic step, the results demonstrate that the method based on diffusion changed concentrations as input values in the kinetic step is still superior and converges much faster to the "true" potential and current values.

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Appendix 3

The linearized form of the differential equations describing the homogeneous kinetics for mechanism IV (cf. Table 1) is of the general form (A12) for which an analytical solution exists, (A13):

$$\left.\begin{aligned} \frac{\partial b}{\partial t} &= -\alpha b - \beta c \\ \frac{\partial c}{\partial t} &= -\gamma b - \delta c \end{aligned}\right\} \equiv$$

$$\frac{-\partial}{\partial t}\begin{pmatrix} b \\ c \end{pmatrix} = \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix}\begin{pmatrix} b \\ c \end{pmatrix} \equiv$$

$$\frac{-\partial}{\partial t}\begin{pmatrix} b \\ c \end{pmatrix} = \mathbf{K}\begin{pmatrix} b \\ c \end{pmatrix} \tag{A12}$$

$$\begin{pmatrix} b \\ c \end{pmatrix} = \mathbf{L}\, e^{-\mathbf{M}\Delta t}\, \mathbf{L}^{-1} \begin{pmatrix} b' \\ c' \end{pmatrix} \tag{A13}$$

Here, $\mathbf{M}$ is the diagonal matrix of eigenvalues (equal to the roots in the characteristic polynomial of $\mathbf{K}$), $\mathbf{L}$ is the corresponding matrix of eigenvectors, and $\begin{pmatrix} b' \\ c' \end{pmatrix}$ is the column vector of the diffusion-corrected concentrations.

The characteristic polynomial for $\mathbf{K}$ is given by (A14) and the eigenvalues for $\mathbf{K}$ are given as the roots of this polynomial, (A15):

$$\det(\mathbf{K} - m\mathbf{E}) = \begin{vmatrix} \alpha-m & \beta \\ \gamma & \delta-m \end{vmatrix} =$$

$$m^2 - (\alpha + \delta)m + (\alpha\delta - \beta\gamma) \tag{A14}$$

$$m_1 = \frac{(\alpha + \delta) + \sqrt{(\alpha + \delta)^2 - 4(\alpha\delta - \beta\gamma)}}{2} \tag{A15}$$

$$m_2 = \frac{(\alpha + \delta) - \sqrt{(\alpha + \delta)^2 - 4(\alpha\delta - \beta\gamma)}}{2}$$

$\mathbf{M}$ is then of the form (A16). A matrix of eigenvectors, $\mathbf{L}$, is found from the identity (A17). Still using m_1 and m_2 as the eigenvalues, $\mathbf{L}$ can take the form (A18) and from this expression for $\mathbf{L}$ follows (A19):

$$\mathbf{M} = \begin{pmatrix} m_1 & 0 \\ 0 & m_2 \end{pmatrix} \tag{A16}$$

$$\mathbf{K} \times \mathbf{L} = \mathbf{L} \times \mathbf{M} \tag{A17}$$

$$\mathbf{L} = \begin{pmatrix} \beta & \beta \\ m_1-\alpha & m_2-\alpha \end{pmatrix} \tag{A18}$$

$$\mathbf{L}^{-1} = \frac{1}{\beta(m_2-m_1)}\begin{pmatrix} m_2-\alpha & -\beta \\ -(m_1-\alpha) & \beta \end{pmatrix} \tag{A19}$$

Using (A16), (A18), and (A19) the expression for (A13) becomes (A20), which can be reduced to (A21) in which φ_1 and φ_2 are given by (A22):

$$\begin{pmatrix} b \\ c \end{pmatrix} = \frac{1}{\beta(m_2-m_1)}\begin{pmatrix} \beta & \beta \\ m_1-\alpha & m_2-\alpha \end{pmatrix} \cdot$$
$$\begin{pmatrix} e^{-m_1\Delta t} & 0 \\ 0 & e^{-m_2\Delta t} \end{pmatrix}\begin{pmatrix} m_2-\alpha & -\beta \\ -(m_1-\alpha) & \beta \end{pmatrix}\begin{pmatrix} b' \\ c' \end{pmatrix} \tag{A20}$$

$$\begin{pmatrix} b \\ c \end{pmatrix} = \frac{1}{m_2-m_1}\begin{pmatrix} \varphi_1 - \varphi_2 \\ \frac{m_1-\alpha}{\beta}\varphi_1 - \frac{m_2-\alpha}{\beta}\varphi_2 \end{pmatrix} \tag{A21}$$

$$\begin{aligned} \varphi_1 &= ((m_2-\alpha)b' - \beta c)e^{-m_1\Delta t} \\ \varphi_2 &= ((m_1-\alpha)b' - \beta c)e^{-m_2\Delta t} \end{aligned} \tag{A22}$$

Having now calculated the values of m_1 and m_2 (A15) in a given time step it is possible to calculate b and c, the new concentrations of species B and C, by application of (A21) and (A22).

The same method can be applied to sets of 3,4,5... linear differential equations.

References

1. Feldberg, S. W. Electroanal. Chem. 3 (1969) 199.
2. Britz, D. Digital Simulation in Electrochemistry, Springer Verlag, Berlin-Heidelberg 1981.
3. Whiting, L. F. and Carr, P. W. J. Electroanal. Chem. 81 (1977) 1.

4. Speiser, B. *J. Electroanal. Chem. 171* (1984) 95.

5. Smith, G. D. *Numerical Solution of Partial Differential Equations: Finite Difference Methods,* Oxford Press, New York 1978.

6. Joslin, T. and Pletcher, D. *J. Electroanal. Chem. 49* (1974) 171.

7. Feldberg, S. W. *J. Electroanal. Chem. 127* (1981) 1.

8. Magno, F., Bontempelli, G. and Perosa, D. *Anal. Chim. Acta 147* (1983) 65.

9. Bellamy, A. J., Howat, G. and MacKirdy, I. S. *J. Chem. Soc., Perkin Trans. 2* (1978) 786.

10. Feldberg, S. W. and Auerbach, C. *Anal. Chem. 36* (1964) 505.

11. Amatore, C. and Savéant, J. M. *J. Electroanal. Chem. 102* (1979) 21.

12. Flanagan, J. B. and Marcoux, L. *J. Phys. Chem. 77* (1973) 1051.

13. Nielsen, M. F., Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. B 40* (1986) 101.

14. Lapidus, L. and Seinfeld, J. H. *Numerical Solution of Ordinary Differential Equations,* Academic Press, New York 1971.

15. Margenau, H. and Murphy, G. M. *The Mathematics of Physics and Chemistry,* Van Nostrand, London 1956.

16. Côme, G.-M. *The Use of Computers in the Analysis and Simulation of Complex Reactions.* In: Bamford, C. H. and Tipper, C. F. H., Eds. , *Comprehensive Chemical Kinetics,* Elsevier, Amsterdam 1983, Vol. 24 and references therein.

17. Warner, D. D. *J. Phys. Chem. 81* (1977) 2329.

18. Winslow, A. M. *J. Phys. Chem. 81* (1977) 2409.

19. Young T. R. and Boris, J. P. *J. Phys. Chem. 81* (1977) 2424.

20. Côme, G.-M. *J. Phys. Chem. 81* (1977) 2560.

21. Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem. 48* (1973) 113.

22. Nicholson, R. S. and Shain, l. *Anal. Chem. 36* (1964) 706.

23. Olmstead, M. L., Hamilton, R. G. and Nicholson, R. S. *Anal. Chem. 41* (1969) 260.

24. Ambrosetti, R., Bellucci, G. and Bianchini, R. *J. Phys. Chem. 90* (1986) 6261.

25. Wiberg, K. B. *Use of Computers,* In: Bernasconi, C. F., Ed., *Techniques of Chemistry,* 4th ed., Wiley, New York 1986, Vol. 5.

26. Britz, D. *Anal. Chim. Acta. 193* (1987) 277.

27. Lasia, A. *J. Electroanal. Chem. 146* (1983) 397.

28. Winograd, N. *J. Electroanal. Chem. 43* (1973) 1.

29. Heinze, J., Störzbach, M. and Mortensen, J. *J. Electroanal. Chem. 165* (1984) 61.

30. Mastragostino, M., Nadjo, L. and Savéant, J. M. *Electrochim. Acta 13* (1968) 721.

31. Booman, G. L. and Pence, D. T. *Anal. Chem. 37* (1965) 1366.

32. Joslin, T. and McKee, S. *J. Inst. Math. Appl. 15* (1975) 373.

33. Andrieux, C. P., Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem. 26* (1970) 147.