Modelling Cyclic Voltammetry without Digital Simulation

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Abstract  A means of modelling cyclic voltammetry by numerical algorithm is described, derived, exemplified, verified, and advocated. A listing of the mechanistic schemes that can be addressed by the procedure includes E, EE, CE, EC and ECE, all with various degrees of reversibility. The approach has advantages and disadvantages when compared with digital simulation.

Keywords  cyclic voltammetry, digital simulation, electrochemical algorithms, modelling

1 Introduction

Cyclic voltammetry has become the default investigatory tool for electroanalytical chemists. This technique is customarily performed under the following conditions:

(a) A three-electrode cell is served by a potentiostat. The uncompensated resistance is small and ignored.

(b) Supporting electrolyte is present at a concentration large enough that the migration of the species of interest can be ignored. The solution is quiescent. These two features ensure that transport, to and from the working electrode, is purely diffusive.

(c) The working electrode is a planar conductor of an area large enough that the edge effect may be ignored. This, together with the provision of an unobstructed zone in front of the electrode, allows diffusion to be treated as planar and semiinfinite.

(d) Generally, only one pertinent species is present initially. If this species is not itself electroactive, it converts to an electroreactant by a “preceding” homogenous chemical reaction. The electroproduct may, or may not, undergo a “following” chemical reaction and/or a second electrode reaction.
(e) At the commencement of the experiment, the potential of the working electrode is chosen, whenever feasible, to have a value at which the faradaic current is either negligible or small.

(f) The potential of the working electrode is linearly scanned at a constant rate from a starting potential, to a reversal potential, and back to its starting value.

(g) The formal potential(s) of the electrode reaction(s) under study generally lie(s) well within the doubly scanned potential range.

(h) The current is measured as a function of time. However, cyclic voltammograms are mostly reported as dual curves of the forward and backward current branches versus potential.

(i) The nonfaradaic current arising from the charging of the double layer at the working electrode is either ignored or crudely compensated by adding or subtracting the product of the scan rate and the capacitance, assumed constant.

Throughout what follows, it is assumed that all the above standard conditions hold.

Cyclic voltammetry is executed in two varieties according as the initial direction of the potential scan is positive-going or negative-going. This polarity choice usually corresponds to whether an oxidation or a reduction is the prime subject of the investigation. To avoid the need to duplicate all our equations to cater to the two varieties, we adopt a notation in this article that provides polarity inclusivity. Thus, in depicting the electron-transfer reaction that the first scan elicits by the equation

\[ R \rightleftharpoons e^- \longrightarrow P \]

we use \( R \) to denote the electroreactant (not “reduced form”!) and \( P \) to denote the electroproduct irrespective of whether the process is an oxidation (upper sign) or a reduction (lower sign). The alternative upper lower signs in process 1:1 also occur in many of the mathematical equations that follow, for example in equations 2:2 and 2:4. These alternative signs invariably have the same
significance: the upper signs apply when, consequent on interest in an early oxidation process, the potential is initially scanned positively; conversely the lower signs relate to an experiment in which the first potential scan proceeds negatively, fostering a reduction. Do not make the easy mistake of imagining that the signs change on reversal; they don’t!

2 Methods of modelling cyclic voltammetry

Thankfully, the days when cyclic voltammograms were analyzed solely on the basis of the location of their peaks are almost past. Mostly, nowadays, the entire cyclic voltammogram is modelled and concordance between the experimental curve and the synthetic curve provides the basis on which conclusions are drawn.

There are three broad routes by which cyclic (and other) voltammograms may be modelled:

\[
\text{voltammetric modelling} \begin{cases} 
\text{mathematical analysis} \\
\text{numerical algorithms} \\
\text{digital simulation}
\end{cases} 2:1
\]

although the distinctions between the alternatives is not always clear-cut. One basis for the threefold classification is provided by the “progressivity” of the approach. In the present context, a progressive model is one that calculates a sought answer (a current or a concentration in the case of cyclic voltammetry) iteratively from previous answers. Digital simulation is doubly progressive: it progresses in both space and time. Numerical algorithms are mostly progressive in time alone. Mathematical analysis yields solutions that are not progressive: the overall answer is immediately calculable without reference to any previous result.

Digital simulation [1] is the method used, nowadays almost invariably, to model cyclic voltammetry. It is an extremely versatile and powerful technique. However, to construct a
digital simulation from scratch is such a lengthy and exacting task that hardly any of us perform it. We rely, instead, on programs such as *DigiSim* [2] and *DigiElch* [3], designed by experts. Such reliance on a perhaps-poorly-understood, “black box” is potentially risky [4]. Moreover, it is often unnecessary. The purpose of this article is to demonstrate that cyclic voltammograms may be modelled “by hand” with nothing more complex than a spreadsheet or a small self-constructed computer program. Such in-house procedures may have less versatility and may be more demanding than reliance on software offered commercially, but they have the great advantages of transparency and financial prudence.

Mathematical analysis may be considered the acme of modelling, because it is unquestionably exact. Sadly, exact mathematical solutions rarely exist. We are unaware of the existence of mathematical solutions in cyclic voltammetry other than for straightforward reversible processes. Those solutions [5] are seldom used.

In the remainder of this article, we shall concentrate on modelling cyclic voltammetry through numerical algorithms. The approach is not new. There are close parallels between the methods advanced here and those adopted by Nicholson and Shain [6] at the dawn of cyclic voltammetry, and by many others [7] more recently.

Whichever of the three modelling routes is followed, a large number of input data goes into the construction of a synthetic cyclic voltammogram. An inventory of these data, which will also serve as a glossary of the symbols used in this article, follows:

(i) Fundamental constants: the gas constant $R$; Faraday’s constant $F$.
(ii) Experimental constants: the Kelvin temperature $T$; the electrode area $A$.
(iii) Electrical constants: the scan rate $\nu$; the starting and reversal potentials, $E(0)$ and $E_{rev}$. These three parameters appear in the formula,
that delineates the triangular dependence of the electrode potential on time [8]. Here \( t \) is time measured from the commencement of the first scan, while the \( \pm \) symbol signifies the absolute value of the symbol’s content. With the appropriate sign choice, equation 2.2 is valid for either variety of cyclic voltammetry and it applies, without change, during both scans.

(iv) Concentrative constants: the bulk concentration \( c^b \) of the, usually only one, solute species that is present initially. This may be the bulk concentration \( c_{bR}^b \) of the reactant \( R \) itself. Alternatively, if \( R \) is created by a preceding homogeneous reaction from a substrate species \( S \), as in process 2.5 below, it is the sum of their bulk concentrations:

\[
c^b = c_s^b + c_r^b
\]

because these two species will have attained equilibrium prior to the voltammetry.

(v) Transport constants: the diffusivity \( D_i \) of each pertinent solute species \( i \). The diffusion occurs along a linear dimension \( x \), perpendicular to the electrode, equiconcentration surfaces being planes. Diffusivity values are needed not only for species present in the bulk, but also for products and intermediates. In the frequent absence of such data, or for algebraic convenience, it is common to assume that several species share the same diffusivity.

(vi) Electrode kinetic constants: the formal potential \( E^{\nu} \) of each electrode reaction involved. Also, for each such reaction that does not behave reversibly: the formal heterogeneous rate constant \( k^{\nu} \) and the transfer coefficient \( \alpha \). These latter constants are employed in the context of the Butler-Volmer equation
which is assumed to be obeyed by reaction 1:1. We associate the symbol $\alpha$ with the $R \rightarrow P$ electron-transfer reaction that is initiated by the first scan of the cyclic voltammogram, irrespective of whether this is an oxidation or a reduction. In equation 2:4, each $c_i^e(t)$ denotes the concentration of the subscript species at the electrode surface at time $t$, and $I(t)$ is the contemporary faradaic current, positive when the electrode is anodic.

(vii) Homogenous kinetic constants: the first (or pseudo-first) order rate constants $\tilde{k}$ and $\bar{k}$ for each solution-phase reaction involved. It will frequently prove convenient to replace the sum $\tilde{k} + \bar{k}$ of the rate constants by $k$ and their ratio $\tilde{k} / \bar{k}$ by $K$, the equilibrium constant. There are three scenarios in which such a reaction may occur. In a “preceding” reaction, the rate and equilibrium constants are assigned as follows

\[ \text{S} \xrightleftharpoons[k]{\bar{k}} \text{R} \quad k = \tilde{k} + \bar{k} \quad K = \frac{\tilde{k}}{\bar{k}} \]  \hspace{1cm} 2:5

where S denotes an electropassive substrate. Similarly, in a “following” reaction:

\[ \text{P} \xrightleftharpoons[k]{\bar{k}} \text{U} \quad k = \tilde{k} + \bar{k} \quad K = \frac{\tilde{k}}{\bar{k}} \]  \hspace{1cm} 2:6

the electroproduct converts to some ultimate product U. In the third scenario, an intermediate I is subject to a further homogeneous reaction, such as

\[ \text{I} \xrightleftharpoons[k]{\bar{k}} \text{J} \quad k = \tilde{k} + \bar{k} \quad K = \frac{\tilde{k}}{\bar{k}} \]  \hspace{1cm} 2:7

(viii) Algorithmic constants. To implement the algorithms that will be expounded in this article, one needs to choose and input the value of a small time interval $\delta$. This could conveniently be an even submultiple, say one-thousandth, of the total duration of the experiment, which is
As well, the program needs to know the number $N_{\text{max}}$ of outputs sought, which would usually be $2|E_{\text{rev}} - E(0)|/[\nu \delta]$.

The objective of the modelling exercise is to predict the evolution in time of the faradaic current $I(t)$. The $c^d_i(t)$ parameters that appear in equation 2:4 play a crucial role in the modelling, but they are not usually included in the output, though some commercial simulation packages provide this information.

### 3 Relations obeyed by diffusing solutes

Intrinsic to the models that will be developed later in this article are relationships that link the diffusive flux of a solute species at the electrode surface to its concentration there, and to its bulk concentration, if any. We shall investigate two scenarios: in the first, there is a single diffusant; in the second there are two interconverting diffusants.

The goal of this section is to derive equations 3:8, 3:28, and 3:29, none of which incorporates the $x$ spatial coordinate. It is by the use of these equations that the spatial progressivity characteristic of digital simulation is obviated.

#### 3-1 Single diffusant

Consider a species $A$, present initially in the electrolyte solution at a uniform concentration $c^b_A$ (which may be zero) and which is thereafter subject to planar semiinfinite diffusion in the $0 \leq x \leq \infty$ space, as depicted in the simple scheme illustrated in Figure 1. The equation

$$\frac{\partial c_A}{\partial t}(x,t) = D_A \frac{\partial^2 c_A}{\partial x^2}(x,t)$$

expressing Fick’s second law, is obeyed. Its Laplace transform is
Subject to the requirement that the concentration of $A$ far from the electrode retains its original value, a solution to differential equation 3:2 is

$$\overline{c}_A(x,s) = \frac{c_A^b}{s} + \Lambda(s) \exp\left\{-x\sqrt{\frac{s}{D_A}}\right\}$$  

Here $\Lambda(s)$ is an arbitrary function of the Laplace variable $s$. Fick’s first law expresses the flux density $j_A(x,t)$ at any point in the $x$ column as $-D_A \frac{\partial c_A}{\partial x}$ or, in the Laplace domain, as

$$\overline{j}_A(x,s) = -D_A \frac{d\overline{c}_A}{dx}(x,s) = \Lambda(s)\sqrt{D_A s} \exp\left\{-x\sqrt{\frac{s}{D_A}}\right\}$$  

The elimination of the $\Lambda(s)$ function between equations 3:3 and 3:4 now leads to

$$\overline{c}_A(x,s) = \frac{c_A^b}{s} + \frac{\overline{j}_A(x,s)}{\sqrt{D_A s}}$$  

Making use of the convolution theorem [9], Laplace inversion of equation 3:5 generates

$$c_A(x,t) = c_A^b + \frac{1}{\sqrt{D_A}} \int_0^t \frac{j_A(x,\tau)}{\sqrt{\pi t - \tau}} d\tau$$  

The integral transform in equation 3:6 is, in fact, the Riemann-Liouville [10,11] definition of the semiintegral of $j_A(x,t)$; so that

$$c_A(x,t) = c_A^b + \frac{1}{\sqrt{D_A}} \frac{d^{-1/2}}{dt^{-1/2}} j_A(x,t)$$  

This is a well-known result [12]; it has been derived here as a prelude to the similar, but more elaborate, derivation in the upcoming subsection.
Equation 3:7 applies at all values of the \( x \) coordinate, but our interest is restricted to the electrode surface, \( x = 0 \). Using a superscript \(^s\) notation to denote the electrode surface, the superficial concentration of species \( A \) is seen to be

\[
c^s_A(t) = c^s_A(0,t) = c^b_A + \frac{1}{\sqrt{D}} \frac{d^{1/2}}{dt^{1/2}} J^s_A(t)
\]

This result gives an expression for the time-evolution of the surface concentration of the species in question. It is valid whether or not the bulk concentration of species \( A \) is zero and irrespective of the direction in which the diffusion occurs. It will be invalid if the diffusing species indulges in any chemical reaction during its journey.

**3-2 Two interconverting diffusants**

Next, consider the electrolyte solution to contain two solutes, \( A \) and \( B \), at initial concentrations of \( c^b_A \) and \( c^b_B \) (either, or both, of which may be zero). The two species interconvert chemically

\[
A \xrightarrow{k} B
\]

with first (or pseudo-first) order homogeneous rate constants \( \tilde{k} \) and \( \bar{k} \) (either, but not both, of which may be zero). If both species are present in the bulk, they will have attained equilibrium

\[
\tilde{k}c^b_A = \bar{k}c^b_B
\]

prior to the voltammetry, so that

\[
(1 + K)c^b_A = \left(1 + \frac{\tilde{k}}{k}\right)c^b_A = c^b_A + c^b_B = c^b
\]

Here, as in equation 2:3, the unsubscripted \( c^b \) represents the total bulk concentration. The scheme shown in Figure 2 illustrates the processes taking place.
Because the homogeneous kinetics provides two additional routes by which local concentrations may change, Fick’s second law needs augmentations, namely:

\[
\frac{\partial c_A}{\partial t}(x,t) = D \frac{\partial^2 c_A}{\partial x^2}(x,t) - \bar{k}c_A(x,t) + \bar{k}c_B(x,t) \tag{3:12}
\]

and

\[
\frac{\partial c_B}{\partial t}(x,t) = D \frac{\partial^2 c_B}{\partial x^2}(x,t) + \bar{k}c_A(x,t) - \bar{k}c_B(x,t) \tag{3:13}
\]

Notice that we have assumed equal diffusivities \(D\) for the two species. To proceed further, two composite concentrations are defined: one, \(c_\Sigma\), is the sum of the two individual concentrations,

\[
c_\Sigma(x,t) = c_A(x,t) + c_B(x,t) \tag{3:14}
\]

while the second, \(c_\Delta\), is the difference between the prevailing concentration of species A and the concentration that it would have had if equilibrium with \(B\) had been established:

\[
c_\Delta(x,t) = c_A(x,t) - \frac{\bar{k}}{k}c_B(x,t) = c_A(x,t) - \frac{c_B(x,t)}{K} \tag{3:15}
\]

Combination of these definitions with Fick’s equations 3:12 and 3:13 leads to

\[
\frac{\partial c_\Sigma}{\partial t}(x,t) = D \frac{\partial^2 c_\Sigma}{\partial x^2}(x,t) \tag{3:16}
\]

and

\[
\frac{\partial c_\Delta}{\partial t}(x,t) = D \frac{\partial^2 c_\Delta}{\partial x^2}(x,t) - [\bar{k} + \bar{k}]c_A(x,t) = D \frac{\partial^2 c_\Delta}{\partial x^2}(x,t) - kc_A(x,t) \tag{3:17}
\]

Equation 3:16 resembles equation 3:1, the standard version of Fick’s second law. Hence, by analogy with the derivation reported in Subsection 3-1, a result analogous to equation 3:8, namely

\[
c^*_\Sigma(t) = c^b + \frac{1}{\sqrt{D}} \frac{\text{d}^{-1/2}}{\text{d}t^{-1/2}} J^*_\Sigma(t) \tag{3:18}
\]
holds. This becomes

\[ c_A^b(t) + c_B^b(t) = c^b + \frac{1}{\sqrt{D}} \left[ \frac{d^{-1/2}}{dt^{-1/2}} J_A^b(t) + \frac{d^{-1/2}}{dt^{-1/2}} J_B^b(t) \right] \]

when expressed in terms of the individual components, A and B.

The partial differential equation 3:17 must be treated somewhat differently. It becomes

\[ s\bar{c}_A(x,s) - c_b^b = D\frac{d^2 \bar{c}_A}{dx^2}(x,s) - k\bar{c}_A(x,s) \]

on Laplace transformation, and a pertinent solution of this ordinary differential solution is

\[ \bar{c}_A(x,s) = \Lambda(s) \exp \left\{ -\sqrt{\frac{s+k}{D}}x \right\} + \frac{c_b^b}{s+k} \]

However, because equilibrium prevails in the bulk, \( c_b^b \) will be zero, nullifying the final term in 3:21. Then on differentiation of this result, Fick's first law leads to

\[ \bar{j}_A(x,s) = -D\frac{d}{dx}\bar{c}_A(x,s) = \Lambda(s) \sqrt{(s+k)D} \exp \left\{ -\sqrt{\frac{s+k}{D}}x \right\} \]

and subsequent elimination of the \( \Lambda(s) \) term through the use of equation 3:21 then produces

\[ \bar{c}_A(x,s) = \frac{\bar{j}_A(x,s)}{\sqrt{D} \sqrt{s+k}} \]

With help for the right-hand side from the convolution theorem, Laplace inversion now yields

\[ c_A(x,t) = \frac{1}{\sqrt{D}} \int_0^t \frac{\bar{j}_A(x,\tau) \exp\{-k(t-\tau)\}}{\sqrt{\pi \sqrt{t-\tau}}} \, d\tau \]

After extraction of \( \exp\{-kt\} \), the integral in 3:24 may be identified as another semiintegral, namely:

\[ c_A(x,t) = \frac{\exp\{-kt\}}{\sqrt{D}} \frac{d^{-1/2}}{dt^{-1/2}} \left[ \bar{j}_A(x,t) \exp\{kt\} \right] \]
It remains to dispense with the \( \Delta \) notation, by writing

\[
c_A(x,t) - \frac{c_B(x,t)}{K} = \frac{\exp\{-kt\}}{\sqrt{D}} \frac{d}{dt} \left[ \left( j_A(x,t) - \frac{j_B(x,t)}{K} \right) \exp\{kt\} \right] \tag{3:26}
\]

On specialization to the electrode surface by setting \( x = 0 \), the result

\[
c^*_A(t) - \frac{c^*_B(t)}{K} = \frac{\exp\{-kt\}}{\sqrt{D}} \frac{d}{dt} \left[ \left( j^*_A(t) \exp\{kt\} - \frac{j^*_B(t)}{K} \exp\{kt\} \right) \right] \tag{3:27}
\]

is attained.

The surface concentrations of both A and B are contained in equations 3:19 and 3:27. On disentangling the individual concentrations by solving these equations simultaneously, one finds

\[
c^*_A(t) = \frac{c^b}{1+K} + \frac{1}{(1+K)\sqrt{D}} \frac{d}{dt} \left\{ j^*_A(t) + j^*_B(t) \right\} + \frac{\exp\{-kt\}}{(1+K)\sqrt{D}} \frac{d}{dt} \left\{ \left[ Kj^*_A(t) - j^*_B(t) \right] \exp\{kt\} \right\} \tag{3:28}
\]

and

\[
c^*_B(t) = \frac{Kc^b}{1+K} + \frac{K}{(1+K)\sqrt{D}} \frac{d}{dt} \left\{ j^*_A(t) + j^*_B(t) \right\} - \frac{\exp\{-kt\}}{(1+K)\sqrt{D}} \frac{d}{dt} \left\{ \left[ Kj^*_A(t) - j^*_B(t) \right] \exp\{kt\} \right\} \tag{3:29}
\]

If either A or B is electropassive, then the corresponding \( j^*_i(t) \) is zero and disappears from the last two equations, because there can be no flux density of an electropassive species across an electrode interface. On the other hand, when A or B is electroactive, the corresponding surface flux density is proportional to an electric current. These properties prove to be invaluable.

4 Linking to the electrical variables

The derivations of the previous section have effectively removed the distance coordinate from the problem. We now address the need to relate the surface concentrations and surface flux...
densities of species involved in the electrode reaction to the electrical variables – the electrode potential $E(t)$ and the faradaic current $I(t)$. Ultimately it is the time-dependent relation between $I$ and $E$ that is sought in modelling cyclic voltammetry.

When the electron transfer reaction is no more complicated than a single instance of an event that conforms to process 1:1, then the simple expressions

$$j^0_R(t) = \frac{\pm I(t)}{F_A} \quad \text{and} \quad j^0_P(t) = \frac{\pm I(t)}{F_A}$$

are direct consequences of Faraday’s law. Recall that the alternative signs refer to the polarity of the cyclic voltammetry; that is, whether the initial $dE/dt$ is positive (upper signs) or negative (lower signs). Relations 4:1 and 4:2 need modifications if the stoichiometry of the electrode reaction is more elaborate than in 1:1; as with the electrode process

$$3I^- - 2 e^- \longrightarrow I_3^-$$

for example. However, because the modifications needed are simple and obvious, and because an electrode reaction as complex as 4:3 is unlikely to occur as a single step, treatment here will be confined to the simplest stoichiometry: when the transfer of a single electron converts a single molecule or ion to another, single but different, molecule or ion.

It is convenient to express the voltage aspects of the experiment through a function defined by

$$\xi(t) = \exp \left\{ \frac{\pm F}{RT} \left[ E(t) - E^{\circ'} \right] \right\}$$

rather than by the electrode potential $E(t)$ itself. In this terminology, the Butler-Volmer equation 2:4 adopts the form

$$\frac{\pm I(t)}{F A k^{\circ'} \left[ \xi(t) \right]^\alpha} = c^0_R(t) - \frac{c^0_P(t)}{\xi(t)}$$
Equation 4.5 is the most general, or quasireversible, form of the relationship. Simpler forms emerge under irreversible

\[
\frac{I(t)}{FAk^\circ} = \pm c_\text{R}^\circ(t)[\xi(t)]^n
\]

or reversible

\[
c_\text{R}^\circ(t)\xi(t) = c_\text{P}^\circ(t)
\]

conditions. Equation 4.7 is an expression of Nernst’s law.

All the elements of a numerical solution are now in place. The equations of this section link the electrical variables to the surface concentrations and flux densities, while the latter are themselves interrelated in Section 3. However, the surface flux densities appear as their semiintegrals in Section 3, and therefore, before proceeding further, an algorithm for semiintegration is needed.

5 Semiintegration algorithm

The operation of semiintegration with respect to time, signified here by the operator

\[
d^{-1/2} \int dt^{-1/2}
\]

is the \( n = -\frac{1}{2} \) instance of a generalized “differintegration” operator [13] applied to some function \( f \) of the variable \( t \), can be defined [14] by the limiting operation

\[
\frac{d^n}{dt^n} f(t) = \lim_{\delta \to 0} \left\{ \frac{\delta^{-n}}{\Gamma\{-n\}} \sum_{n=0,1} \frac{\Gamma\{n-v\}}{\Gamma\{n+1\}} f(t-n\delta) \right\}
\]

in which \( \Gamma\{ \} \) denotes the gamma function [15] and \( n \) is a summation index. In electrochemical applications, \( t \) is invariably time, while \( f \) may be a current, a flux density, or a concentration.

This definition may be converted into a numerical algorithm simply by allowing \( \delta \) to be a small,
but not infinitesimal, time interval. After choosing \( v = \frac{1}{2} \), the algorithm may be recast as a weighted sum

\[
\frac{d^{-1/2}}{dt} f(t) = \sqrt{\frac{t}{N}} \sum_{n=0}^{N-1} w_n f\left(\frac{N-n}{N} t\right) \quad \text{with} \quad N = \frac{t}{\delta}
\]

where the appropriate weights are given by [16]

\[
w_n = \frac{\Gamma\{n + \frac{1}{2}\}}{\sqrt{\pi} \Gamma\{n + 1\}} = \frac{(2n)!}{(2^n n!)^2} = \frac{(2n-1)!!}{(2n)!!}
\]

The simplicity of the algorithm is evident on writing out a few terms

\[
\frac{d^{-1/2}}{dt} f(t) = \sqrt{\delta} \left[ f(t) + \frac{1}{2} f(t - \delta) + \frac{3}{8} f(t - 2\delta) + \frac{5}{16} f(t - 3\delta) + \cdots + \frac{(2N-3)!!}{(2N-2)!!} f(\delta) \right]
\]

The weighting factors may be calculated from formula 5:3 or, more conveniently and safely [17], from the iteration

\[
w_0 = 1, \ w_1 = \frac{1}{2}, \ldots, \ w_n = \frac{2n-1}{2n} w_{n-1}
\]

The algorithm finds use with the first summand withdrawn from the summation, so that

\[
\frac{d^{-1/2}}{dt} f(t) = \sqrt{\delta} f(t) + \sqrt{\delta} \sum_{n=1}^{N-1} w_n f\left(\frac{N-n}{N} t\right)
\]

In operation, the algorithm calculates the semiintegral, with respect to time, at the instant \( t \) (equal to \( N\delta \)) from a number of values of the function evenly spaced in the range between 0 and \( t \), including the function’s value at \( t \) itself, but excluding the \( t = 0 \) value. The algorithm is crude when the number of contributing data is small, but it rapidly approaches exactitude as the number of data points increases. Other semiintegration algorithms exist, some of which [18] are preferable when early points are important, as for potential-step experiments.
In this article, there are two types of function on which the semiintegration algorithm is called to operate: either a time-dependent current \( I(t) \), or the product of such a current and the exponential function \( \exp\{kt\} \). In the first of these two cases, the operation is

\[
\frac{d^{-1/2}}{dt^{-1/2}} I(t) = \sqrt{\delta} \left[ I(t) + \sum_{n=1}^{N-1} w_n I\left(\frac{N-n}{N} t\right) \right]
\]

The second way in which semiintegration enters the voltammetric theory is as the term

\[
\exp\{-kt\} \frac{d^{-1/2}}{dt^{-1/2}} \left[ I(t) \exp\{kt\} \right]
\]

for which the same algorithm leads to

\[
\exp\{-kt\} \frac{d^{-1/2}}{dt^{-1/2}} \left[ I(t) \exp\{kt\} \right] = \sqrt{\delta} \exp\{-kt\} \left[ I(t) \exp\{kt\} + \sum_{n=1}^{N-1} w_n I\left(\frac{N-n}{N} t\right) \exp\{\frac{n}{N} kt\} \right]
\]

\[
= \sqrt{\delta} \left[ I(t) + \sum_{n=1}^{N-1} w_n I\left(\frac{N-n}{N} t\right) \exp\{\frac{n}{N} kt\} \right]
\]

Notice that, in both equations 5:7 and 5:9, there are two contributions to the semiintegral: the current at time \( t \), and a term arising from the currents flowing at times prior to that instant.

In the interest of brevity in equations later in this article, it is useful to adopt abbreviations for the summation terms in these equations and we choose these to be

\[
\sum_{n=1}^{N-1} w_n I\left(\frac{N-n}{N} t\right) = I(<t) \quad \text{and} \quad \sum_{n=1}^{N-1} w_n I\left(\frac{N-n}{N} t\right) \exp\{\frac{n}{N} kt\} = I(<t,k)
\]

The symbol \( I(<t) \) is appropriate because it represents the contribution to the semiintegral from currents flowing at times less than \( t \).

### 6 Numerical modelling of cyclic voltammograms

The principles embodied in this article apply to any form of voltammetry in which the potential is caused to change with time. Our treatment is well adapted to experiments in which
the potential is changed gradually (though not necessarily linearly), rather than in steps; it is not restricted to cyclic voltammetry. Nevertheless, in view of the ubiquity of cyclic voltammetry, we shall give examples only of that popular form of potentiodynamic voltammetry.

The only aspect that makes cyclic voltammetry unique is the form of the potential excursion, described by equation 2:2. Combination of that equation with definition 4:4 gives

\[
\xi(t) = \exp\left(\pm \frac{F}{RT} \left[ E_{\text{rev}} \mp \Delta t \mp E_{\text{rev}} \pm E(0) - E^{\text{ox}} \right]\right)
\]

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\]

[8]. Throughout, the upper sign options reflect the variety of cyclic voltammetry; that is, whether the initial scan proceeds towards more positive potentials. In the next several sections, we address examples, by way of illustrating and validating the numerical algorithmic procedure. We follow the popular acronymic style of using C to denote a chemical step and E to denote an electron transfer, with subscripts \( r \), \( q \), and \( i \) signifying “reversible”, “quasireversible” and “irreversible”. In all cases, equation 6:1 – defining \( \xi(t) \) for cyclic voltammetry – and formula 5:5 – providing access to the algorithmic weights – are considered to be implicit components of the algorithms.

At the outset, we apologize to the reader for the tedious algebra in many of the following sections. Algebraic elaboration is an unavoidable adjunct to the numerical algorithm approach, – as it more emphatically is in digital simulation. Notwithstanding the tedium, we believe it is important to demonstrate explicitly how the final algorithms are derived.

The validation of our numerical algorithms is, for the most part, made by comparing their output with that of Version 3.03 of DigiSim [2]. This is the original, and still widely used, software package designed specifically to simulate cyclic voltammetry digitally. It is a justifiably trusted product. For the most part, we used the default settings of DigiSim as the basis of our own algorithms [19]. Throughout we used a value of \( \delta \) (one millisecond) that accords
with the point-density setting (one millivolt) of DigiSim. The implementation of our numerical algorithms was made on an Excel spreadsheet.

In the case of the \(E_r\) scheme described in Section 7, we were able to verify our algorithm, not only by comparison with DigiSim, but also against a result of unquestionable accuracy – one derived by mathematical analysis.

### 7 Scheme \(E_r\): reversible electron transfer without homogeneous chemistry

This is the classic case that yields a cyclic voltammogram of the familiar “hybrid” shape. The diagram in Figure 3 illustrates the simple mechanism.

In this simplest of cases, the algorithm is derived by applying equation 3:8 to each species, the electroreactant and the electroproduct, yielding

\[
c^a_R(t) = c^b_R + \frac{1}{\sqrt{D_R}} \frac{d^{-1/2}}{d t^{-1/2}} j^a_R(t) \quad \text{and} \quad c^a_P(t) = \frac{1}{\sqrt{D_P}} \frac{d^{-1/2}}{d t^{-1/2}} j^a_P(t)
\]

and then replacing the surface flux densities by the current through use of equations 4:1 and 4:2

\[
c^a_R(t) = c^b_R \pm \frac{1}{FA\sqrt{D_R}} \frac{d^{-1/2}}{d t^{-1/2}} I(t) \quad \text{and} \quad c^a_P(t) = \pm \frac{1}{FA\sqrt{D_P}} \frac{d^{-1/2}}{d t^{-1/2}} (t)
\]

The next step is to combine these last two equations by invoking the Nernst equation 4:7, which gives

\[
\left[1 + \frac{\sqrt{D_R}}{\bar{\xi}(t)\sqrt{D_P}} \right] \frac{d^{-1/2}}{d t^{-1/2}} I(t) = \pm FAc^b_R\sqrt{D_R}
\]

after rearrangement.

Equation 7:5 is an exact result. It becomes an approximation – though, as will emerge, a very good approximation – when the semiintegral is replaced by algorithm 5:6, which leads to
\[
\left(1 + \frac{\sqrt{D_R}}{\xi(t)\sqrt{D_p}} \right) \left(\sqrt{\delta} I(t) + \sqrt{\delta} \sum_{n=1}^{N-1} w_n I\left(\frac{n \pi}{N} t\right)\right) = \pm FAc^b R \sqrt{D_R} \quad 7:6
\]

It is now merely a matter of reorganizing this result to arrive at the final numerical algorithm

\[
I(t) = \frac{\pm FAc^b \sqrt{D_R} / \delta}{1 + \sqrt{D_R} / D_p / \xi(t)} - \sum_{n=1}^{N-1} w_n I\left(\frac{n \pi}{N} t\right) \quad 7:7
\]

To implement this algorithm – and all of those that follow in upcoming sections – one first sets \(N=1\), and calculates \(I(\delta)\); during this calculation the sum in formula 7:7 is empty.

Then one calculates \(I(2\delta)\) by setting \(N=2\). This calculation uses the previously computed value of \(I(\delta)\). Similarly, when \(N=3\), two previously calculated current values are used recursively to find \(I(3\delta)\). And so on. Notice that no action needs to be taken when the reversal potential is reached; the absolute-value function in equation 6:1 smoothly makes the transition from the first branch of the cyclic voltammogram to the second branch. Computation ceases when the predetermined maximum value, \(N_{\text{max}}\), of \(N\) is reached.

We chose to implement the algorithm by modelling the cyclic voltammogram of a reversible oxidation, thereby selecting the upper sign option in equation 7:7. The following parameters were used: \(A = 1 \times 10^{-4} \text{ m}^2\), \(E(0) = -0.3 \text{ V}\), \(E_{\text{rev}} = +0.3 \text{ V}\), \(v = 1 \text{ V s}^{-1}\), \(c_R^b = 1 \text{ mol m}^{-3}\), \(D_R = D_p = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}\), \(E'_\ominus = 0 \text{ V}\), \(\delta = 1 \times 10^{-3} \text{ s}\) and \(N_{\text{max}} = 1200\). The resulting voltammogram was drawn in large scale and superimposed on two other voltammograms – that generated by DigiSim and that produced by the exact formulation [5] – using identical data. No differences whatsoever could be discerned! For a more exacting comparison, we carefully measured the coordinates of the peaks from the three sources. They are compared in Table 1.

The small discrepancies between the output values from the three methods are trifling and
certainly not experimentally significant. We conclude that, in this example, the numerical algorithm method of predicting cyclic voltammograms is valid and accurate.

Recognize that the three methods that are intercompared in Table 1 are examples of the three delineated in 2:1. It is encouraging to find that three quite disparate methods of modelling cyclic voltammetry lead to virtually identical results – at least in the one instance in which a threefold comparison is feasible.

8 Scheme $E_q$: quasireversible electron transfer without homogeneous chemistry

The mechanism addressed in this section, illustrated schematically in Figure 4, differs from that in Section 7 only in as much as the electron transfer is not now necessarily reversible. As before, solutes R and P are transported to and from the electrode by diffusion processes uncomplicated by any concurrent homogeneous kinetics, but only species R is present in the bulk.

Equations 7:1, 7:2, 7:3, and 7:4 apply unchanged, but instead of combining 7:3 and 7:4 through the Nernst equation, the full Butler-Volmer formula, 4:5 is needed. This leads to

$$\frac{I(t)}{F A k^b \left[\xi(t)\right]^a} = \pm c_R^b - \left[\frac{1}{\sqrt{D_R}} + \frac{1}{\xi(t) \sqrt{D_p}}\right] \frac{d^{1/2}}{dt^{1/2}} \frac{I(t)}{F A} \tag{8:1}$$

instead of 7:5. As before, algorithm 5:6 is used at this stage to replace the semiintegral by a sum of currents:

$$\frac{I(t)}{F A k^b \left[\xi(t)\right]^a} = \pm c_R^b - \left[\frac{1}{\sqrt{D_R}} + \frac{1}{\xi(t) \sqrt{D_p}}\right] \sqrt{\frac{\delta I(t)}{F A}} + \frac{\sqrt{\delta}}{F A} \sum_{n=1}^{N-1} w_n I\left(\frac{2n-N}{N} t\right) \tag{8:2}$$

Collection of the terms involving $I(t)$ into the left-hand side, followed by rearrangement, then leads to the final result,
\[
I(t) = \pm F A c_{R}^b \sqrt{D_R} \sqrt{\delta} - \left[ 1 + \sqrt{\frac{D_R}{D_p}} \right] \sum_{n=1}^{N-1} w_n I \left( \frac{N-n}{N} t \right)
\]

which is to be used in conjunction with equation 6:1 and definition 5:5.

For variety’s sake, we chose to model a reduction in this case and therefore chose the lower signs in equations 8:3 and 6:1. **Figure 5** compares the quasireversible cyclic voltammogram predicted by our numerical algorithm compared with that of *DigiSim* for the parameters given in the figure legend.

Note that as \( k^{o'} \) approaches infinity, corresponding to reversible conditions, the third denominatorial term in 8:3 disappears, leaving a result identical to 7:7. For the \( E_i \) scheme, it is the \( \sqrt{D_R/D_p}/\xi(t) \) terms that become inconsequential, so that the equation governing a straightforward irreversible cyclic voltammogram is

\[
I(t) = \pm F A c_{R}^b \sqrt{D_R} \sqrt{\delta} - \left[ 1 + \sqrt{\frac{D_R}{D_p}} \frac{k^{o'}}{[\xi(t)]^a} \right] \sum_{n=1}^{N-1} w_n I \left( \frac{N-n}{N} t \right)
\]

9 **Scheme CE\(_r\) : reversible electron transfer preceded by homogeneous kinetics**

Here we consider a scheme in which the original electropassive substrate \( S \) isomerizes to produce the electroactive species \( R \), which undergoes an electron transfer to give a product \( P \), as depicted in **Figure 6**. The nominal bulk concentration of the substrate is \( c^b \), but the establishment of the equilibrium detailed in 2:5 ensures that the actual bulk concentrations are

\[
c_{S}^b = \frac{c^b}{1 + K} \quad \text{and} \quad c_{R}^b = \frac{Kc^b}{1 + K}
\]
Because the electroproduct P diffuses straightforwardly away from, and later towards, the electrode and the bulk solution is devoid of P, the surface concentration of this species is related by equation 3:8 to its surface flux density by the first equality in the expression

\[ c_p^s(t) = \frac{1}{\sqrt{D_p}} \frac{d^{-1/2}}{dt^{-1/2}} j_p^s(t) = \pm \frac{1}{FA \sqrt{D_p}} \frac{d^{-1/2}}{dt^{-1/2}} I(t) \]

9:3

The second equality in 9:3 arises from incorporation of Faraday’s law, relation 4:2.

The codiffusion of the species S and R conforms to the protocol established in Subsection 3-2, with S playing the role of A and with R replacing B. After making these notational changes, and setting \( j_s^b(t) \) to zero because of the electropassivity of S, equation 3:28 becomes

\[ c_R^s(t) = \frac{K c_b^s}{1 + K} + \frac{K}{(1 + K) \sqrt{D}} \frac{d^{-1/2}}{dt^{-1/2}} j_R^s(t) + \frac{\exp(-kt)}{(1 + K) \sqrt{D}} \frac{d^{-1/2}}{dt^{-1/2}} \left[ j_R^s(t) \exp\{kt\} \right] \]

9:4

Relation 4:1 can now be used to replace the surface flux density by the current. One discovers that

\[ c_R^s(t) = \frac{K c_b^s}{1 + K} + \frac{K}{(1 + K) \sqrt{D}} \frac{d^{-1/2}}{dt^{-1/2}} I(t) + \frac{\exp(-kt)}{FA(1 + K) \sqrt{D}} \frac{d^{-1/2}}{dt^{-1/2}} \left[ I(t) \exp\{kt\} \right] \]

9:5

Because the electron transfer step is reversible, Nernst’s law, equation 4:7, gives a simple linkage between the surface concentrations of R and P and provides a means of conjoining equations 9:3 and 9:5 into

\[ \left[ 1 + \frac{(1 + K) \sqrt{D}}{K \zeta(t) \sqrt{D_p}} \right] \frac{d^{-1/2}}{dt^{-1/2}} I(t) + \frac{\exp(-kt)}{K} \frac{d^{-1/2}}{dt^{-1/2}} \left[ I(t) \exp\{kt\} \right] = \pm F A c_b^s \sqrt{D} \]

9:6

It is at this stage that we replace the two semiintegrals in equation 9:6 by the algorithms developed in Section 5. The first semiintegral – that of the current alone – is evaluated directly via equation 5:6, whereas the second semiintegral in 9:6 is replaced as follows:
\[
\frac{d^{-1/2}}{dt^{-1/2}}[I(t)\exp\{kt\}] = \exp\{kt\}\sqrt{\delta} \left[ I(t) + \sum_{n=1}^{N-1} w_n I\left(\frac{\nu_n}{N}t\right)\exp\left\{\frac{\nu_n}{N}kt\right\} \right]
\]

as established in equation 5:9. After substituting these results into expression 9:6 and then collecting together all terms involving \( I(t) \), the final algorithm emerges as

\[
I(t) = \pm \frac{FAe^b}{\sqrt{\delta}} \frac{\sqrt{D}}{K\sqrt{\delta}} \left[ 1 + \frac{(1+K)\sqrt{D}}{K\xi(t)\sqrt{D_p}} \right]^{N-1} \sum_{n=1}^{N-1} w_n I\left(\frac{\nu_n}{N}t\right) - \frac{1}{K} \sum_{n=1}^{N-1} w_n I\left(\frac{\nu_n}{N}t\right)\exp\left\{\frac{\nu_n}{N}kt\right\}
\]

Figure 7 compares the cyclic voltammogram predicted by our numerical algorithm with that of DigiSim for the parameters given in the figure legend. Because the scan is initially positive, promoting an oxidation, we used the upper signs in equations 9:8 and 6:1.

A limiting case of result 9:8 is noteworthy. If the equilibrium so favours S that \( K \) is insignificant in comparison with unity, then the term \( (1+K) \), that appears twice in 9:8, becomes unity. Moreover, the \( k \) in the exponential term may then be replaced by \( \tilde{k} \).

10 Scheme E\(_q\)C: quasireversible electron transfer followed by homogeneous kinetics

Here we consider the scheme in which the product \( P \) of an electron-transfer reaction undergoes a first (or pseudo-first) order chemical reaction, as outlined in Figure 8. For maximal generality, the chemical step is treated as bidirectional.

The diffusion of the electroreactant \( R \) is uncomplicated and it therefore obeys equation 3:8, which in this case takes the form of the first equality in the expression

\[
c^s_R(t) = c^b_R + \frac{1}{\sqrt{D_R}} \frac{d^{-1/2}}{dt^{-1/2}} f_R^s(t) = c^b_R + \frac{1}{FA\sqrt{D_R}} \frac{d^{-1/2}}{dt^{-1/2}} I(t)
\]

the second step being a consequence of relationship 4:1.
In this example, species P and U are the codiffusing pair, neither of which has a bulk concentration. In adapting equation 3:28 to the present problem, we associate P with species A from Subsection 3-2, U with B, and assume that P and U share a common diffusivity $D$. We have little interest in species U beyond setting $j_U(t)$ to zero on account of U’s electropassivity. Thereby 3:28 becomes modified to

$$c_p(t) = \frac{1}{(1 + K)\sqrt{D}} \int_{t-1/2}^t j_p(t) \, dt + \frac{K \exp\{-kt\}}{(1 + K)\sqrt{D}} \int_{t-1/2}^t j_p(t) \exp\{kt\} \, dt \quad 10:2$$

and

$$= \frac{\pm 1}{FA(1 + K)\sqrt{D}} \int_{t-1/2}^t I(t) \, dt + \frac{K \exp\{-kt\}}{FA(1 + K)\sqrt{D}} \int_{t-1/2}^t [I(t) \exp\{kt\}] \, dt$$

the second step in which follows from equation 4:2.

Equations 10:1 and 10:2 provide the surface concentration expressions needed by the Butler-Volmer equation 4:5, which thereby becomes

$$\frac{I(t)}{k'o'[\xi(t)]^{n-o}} = \pm FAC^b - \frac{1}{\sqrt{D_R}} \int_{t-1/2}^t I(t) \, dt - \frac{1}{(1 + K)\xi(t)\sqrt{D}} \int_{t-1/2}^t I(t) \, dt$$

$$- \frac{K \exp\{-kt\}}{(1 + K)\xi(t)\sqrt{D}} \int_{t-1/2}^t [I(t) \exp\{kt\}] \, dt \quad 10:3$$

after rearrangement. Introduction of the semiintegration algorithms from Section 5, and further reorganization, lead to the following result

$$I(t) = \pm \frac{FAc^b\sqrt{D_R}}{\sqrt{\xi'(t)}} \left[ 1 + \frac{\sqrt{D_R}/D}{[1 + K]\xi(t)} \right]^{N-1} w_n I \left( \frac{N-n}{N} t \right) - \frac{K \sqrt{D_R}/D}{[1 + K]\xi(t)} \sum_{n=1}^{N-1} w_n I \left( \frac{N-n}{N} t \right) \exp\left\{ \frac{-n}{N} kt \right\}$$

$$+ \frac{1}{k'o'[\xi(t)]^{n-o} \sqrt{\xi'(t)}} \frac{\sqrt{D_R}}{\sqrt{\xi'(t)}} \quad 10:4$$

Figure 9 compares the cyclic voltammogram predicted by our numerical algorithm with that of DigiSim for the parameters given in the figure legend. The scan is initially negative. Notice that equation 10:4 becomes identical with result 8:3 as $k \to 0$. Also note that the
numerical algorithm for the reversible case, $E_r C$, of cyclic voltammetry is identical to equation 10:4, except that the term involving $k^{\sigma'}$ is absent.

11 Scheme C E: homogeneous regeneration of the electroreactant

In this scheme, an electropassive species X, present in large concentration, homogeneously converts the electroproduct P of an electron transfer reaction back to the electroreactant R as outlined in Figure 10. This is referred to as a “catalytic” scheme because the electrode reaction serves to catalyze the conversion of X to some other electropassive product Y. The large excess of X serves to make the homogeneous X + P $\xrightarrow{k}$ R + Y reaction pseudo-first order in P, with a rate constant $\tilde{k}$ that incorporates the concentration of X. Species X and Y have been omitted from Figure 10 because they do not participate in the algebra. In many experimental manifestations of this mechanism, the rate of the reverse homogeneous reaction is negligible but, in the interest of generality, we first assume that the reverse reaction occurs with a rate constant $\tilde{k}$, also pseudo-first order. Thus the equilibrium constant of the regeneration reaction is

$$K = \frac{c_R^b c_X^b}{c_P^b c_Y^b} = \frac{\tilde{k} c_R^b}{\tilde{k} c_p^b}$$

11:1

Because equilibrium will prevail at $t = 0$, thermodynamics enforces a relationship between this equilibrium constant and the starting potential of the voltammetry. Nernst’s law then requires that $\xi(0) = c_p^a / c_R^a = c_p^b / c_R^b$, and hence it follows from 11:1 that $K \xi(0) = c_X^b / c_Y^b$.

R and P are assumed to have equal diffusivities as they codiffuse through the electrolyte column in obedience to the laws derived in Subsection 3-2, with P playing the role of A and R replacing B. Thus, equations 3:28 and 3:29 are obeyed in the forms
\[ c_p^s(t) = \frac{\tilde{K}c^b}{\tilde{k} + k} + \frac{\tilde{k}}{(\tilde{k} + k)\sqrt{D}} \frac{d^{-1/2}}{dt} [j_p^b(t) + j_R(t)] + \frac{\tilde{k} \exp\{-kt\}}{(\tilde{k} + k)\sqrt{D}} \frac{d^{-1/2}}{dt} [\tilde{k}j_p^b(t) - \tilde{k}j_R^s(t)] \exp\{kt\} \] 11:2

and

\[ c_p^s(t) = \frac{\tilde{K}c^b}{\tilde{k} + k} + \frac{\tilde{k}}{(\tilde{k} + k)\sqrt{D}} \frac{d^{-1/2}}{dt} [j_p^b(t) + j_R(t)] - \frac{\tilde{k} \exp\{-kt\}}{(\tilde{k} + k)\sqrt{D}} \frac{d^{-1/2}}{dt} [\tilde{k}j_p^b(t) - \tilde{k}j_R^s(t)] \exp\{kt\} \] 11:3

So as not to involve species X and Y, which appear in the expression for the equilibrium constant, we have replaced \( K \) by \( \tilde{k} / \tilde{k} \) in adapting equations from Section 3 to the present scenario.

Via expressions 4:1 and 4:2, the flux densities in the previous two equations may be replaced by the current. This replacement nullifies some of the terms and simplifies others, the results being

\[ c_p^s(t) = \frac{\tilde{K}c^b}{\tilde{k} + k} \pm \frac{\exp\{-kt\}}{FA\sqrt{D}} \frac{d^{-1/2}}{dt} [I(t) \exp\{kt\}] \] 11:4

and

\[ c_R^s(t) = \frac{\tilde{K}c^b}{\tilde{k} + k} \frac{\exp\{-kt\}}{FA\sqrt{D}} \frac{d^{-1/2}}{dt} [I(t) \exp\{kt\}] \] 11:5

Next, these surface concentration expressions are inserted into the Butler-Volmer equation 4:5, whereby the equation

\[ \frac{I(t)}{k''[\xi(t)]^{\gamma}} = \pm FAc^b \frac{k}{\tilde{k} + k} \left[ \frac{\tilde{k}}{\tilde{k} - \tilde{k} \exp\{-kt\}} \frac{1 + \xi(t)}{\xi(t)} \right] \frac{d^{-1/2}}{dt} \frac{1}{\sqrt{D}} [I(t) \exp\{kt\}] \] 11:6

emerges after some reorganization. After adoption of our semiintegration algorithm 5:9, collection of the \( I(t) \) terms, and further rearrangement, the final result is found to be
\[ I(t) = \frac{\pm F \Delta c^b \sqrt{D}}{(k + \tilde{k})\sqrt{\delta}} \left[ \tilde{k} - \tilde{k} \right] - \frac{1 + \xi(t) \sum_{n=1}^{N-1} w_n I(\frac{N-n}{N} t) \exp\{\frac{-n}{N} k t\}}{\sqrt{D} + 1 + \frac{k^o}{k^o}[\xi(t)]^n + \frac{1}{\xi(t)}} \]  

It is this equation that provides the basis of the voltammogram shown in Figure 11.

Commonly, the regeneration is virtually irreversibly, implying that \( \tilde{k} \ll \tilde{k} \) and that the bulk solution will be devoid of \( P \). In this circumstance

\[ I(t) = \frac{\pm F \Delta c^b \sqrt{D}}{\sqrt{\delta}} - \frac{1 + \xi(t) \sum_{n=1}^{N-1} w_n I(\frac{N-n}{N} t) \exp\{\frac{-n}{N} \tilde{k} t\}}{\sqrt{D} + 1 + \frac{k^o}{k^o}[\xi(t)]^n + \frac{1}{\xi(t)}} \]  

12 Scheme \( E_qE_q \): two quasireversible electron transfers without homogeneous kinetics

Here we consider the case of two successive electron transfers, linked via an intermediate species \( I \). Each electrode reaction has its own set of electrode kinetic constants, as described in item (vi) of Section 2, that we distinguish by use of 1 or 2 subscripts. The original reactant \( R \) is present at concentration \( c_R^b \) in the bulk, where neither the intermediate \( I \) nor the final product \( P \) exists. The proportionation reactions \( P + R \rightleftharpoons 2I \) do not occur. All three species freely diffuse to and from the electrode, as in Figure 12.

Though they are not separable in a voltammetric experiment, two distinct currents, \( I_1(t) \) and \( I_2(t) \), may be recognized, arising from the first and second electron transfers respectively. Via equations 4:1 and 4:2, they may be associated with the surface flux densities through the equations

\[ j_R^s(t) = \frac{\pm I_1(t)}{FA}, \quad j_R^s(t) = \frac{\pm I_2(t)}{FA}, \quad \text{and} \quad j_R^s(t) = \frac{\pm I_1(t) \mp I_2(t)}{FA} \]  

12:1, 12:2 and 12:3
As in Subsection 3-1, the diffusion of the three species is described by the equations

\[
c_R^s(t) = c_R^b + \frac{1}{\sqrt{D_R}} \frac{d^{-1/2}}{dt^{-1/2}} J_R^s(t), \quad c_I^s(t) = \frac{1}{\sqrt{D_I}} \frac{d^{-1/2}}{dt^{-1/2}} J_I^s(t), \quad \text{and} \quad c_P^s(t) = \frac{1}{\sqrt{D_P}} \frac{d^{-1/2}}{dt^{-1/2}} J_P^s(t)
\]

There are two Butler-Volmer equations to be obeyed. They are

\[
\frac{\pm I_1(t)}{FAk_1'} = [\xi_1(t)]^{\alpha_1} \left[ c_R^s(t) - c_I^s(t) \right] \quad \text{and} \quad \frac{\pm I_2(t)}{FAk_2'} = [\xi_2(t)]^{\alpha_2} \left[ c_I^s(t) - c_P^s(t) \right]
\]

in a self-evident notation.

Equations 12:1, 12:3, 12:4, 12:5 and 12:7 may be combined with our semiintegration algorithm 5:7 to produce

\[
\frac{\pm I_1(t)}{FAk_1'[\xi_1(t)]^{\alpha_1}} = c_R^b + \frac{\sqrt{\delta / D_R}}{FA} \left[ I_1(t) + I_1(<t) \right] + \frac{\sqrt{\delta / D_I}}{FA[\xi_2(t)]^{\alpha_2}} \left[ I_1(t) - I_1(<t) - I_2(t) - I_2(<t) \right]
\]

where we are using the abbreviations, namely

\[
I_1(<t) = \sum_{n=1}^{N-1} w_n I_1 \left( \frac{N-n}{\delta} t \right) \quad \text{and} \quad I_2(<t) = \sum_{n=1}^{N-1} w_n I_2 \left( \frac{N-n}{\delta} t \right)
\]

described in Section 5. Similarly, equations 12:2, 12:3, 12:5, 12:6 and 12:8 combine into

\[
\frac{\pm I_2(t)}{FAk_2'[\xi_2(t)]^{\alpha_2}} = \pm \frac{\sqrt{\delta / D_I}}{FA} \left[ I_1(t) + I_1(<t) - I_2(t) - I_2(<t) \right] + \frac{\sqrt{\delta / D_P}}{FA[\xi_2(t)]^{\alpha_2}} \left[ I_2(t) + I_2(<t) \right]
\]

Relationships 12:11 and 12:12 are simultaneous equations in \( I_1(t) \) and \( I_2(t) \); they solve to give

\[
I_1(t) = \frac{\pm [W(t) + V(t)]\xi_1(t)FAc_R^b \sqrt{D_I/\delta - \left( Y(t) \frac{W(t) + V(t)}{W(t) + V(t)} - 1 \right)} I_1(<t) + W(t)I_2(<t)}{[Z(t) + Y(t)][W(t) + V(t)] - 1}
\]

and

\[
I_2(t) = \frac{\pm \xi_1(t)FAc_R^b \sqrt{D_I/\delta + Z(t)}I_1(<t) - \left( V(t) \frac{Z(t) + Y(t)}{Z(t) + Y(t)} - 1 \right) I_2(<t)}{[Z(t) + Y(t)][W(t) + V(t)] - 1}
\]
where

\[ Z(t) = \left[ \xi_1(t) \right]^{1-\alpha_1} \frac{D_1}{k_t' \sqrt{\delta}}, \quad Y(t) = 1 + \xi_1(t) \frac{D_1}{D_R}, \quad W(t) = \frac{\sqrt{D_1}}{k_2' \sqrt{\delta} \left[ \xi_2(t) \right]^{1/2}}, \quad \text{and} \quad V(t) = 1 + \frac{1}{\xi_2(t)} \frac{D_1}{D_p}. \]

12:15, 12:16, 12:17, and 12:18

Despite the algebraic complexity, the algorithm proceeds in the standard way, with the output being the sum

\[ I(t) = I_1(t) + I_2(t) \]

12:19

Though only the sum need be output, the individual values of the two currents must be retained by the program to provide data for the right-hand sides of equations 12:13 and 12:14. The algorithm is arithmetically intensive, because the right-hand sides of many equations must be recalculated \( N_{\text{max}} \) times, in addition to the repeated summations. Figure 13 shows an example; it is seen to accurately match the DigiSim model.

**13 Scheme E,CE\(_r\) : two reversible electron transfers coupled by homogeneous kinetics**

Here the product, species I, of one electron transfer is electropassive, but it converts homogeneously to an electroactive isomer, species J, which undergoes a second electron transfer. Only the first electroreactant, species R, is present in the bulk. Figure 14 summarizes the events. As in the preceding section, species I and J are prohibited from taking part in any conproportionation or disproportionation reaction.

Species R and P undergo straightforward diffusion and each therefore obeys equation 3:8 which, in the present context, becomes

\[ c_\text{R}^* (t) = c_\text{R}^b + \frac{1}{\sqrt{D_\text{R}}} \frac{d^{-1/2}}{dt} J_\text{R}^* (t) \quad \text{and} \quad c_\text{P}^* (t) = \frac{1}{\sqrt{D_\text{P}}} \frac{d^{-1/2}}{dt} J_\text{P}^* (t) \]

13:1 and 13:2
Furthermore, Nernst’s law, equation 4.7, allows these two diffusional equations also to provide the following expressions for the concentrations of the intermediate species I and J at the electrode surface:

\[ c_I^s(t) = \xi_1(t)c_R^b + \frac{\xi_1(t)}{\sqrt{D_R}} \frac{d^{-1/2}}{dt^{-1/2}} j_R^s(t) \quad \text{and} \quad c_J^s(t) = \frac{1}{\xi_2(t)\sqrt{D_R}} \frac{d^{-1/2}}{dt^{-1/2}} j_J^s(t) \]

13:3 and 13:4

An alternative expression for the surface concentration of I is available from equation 3.28. In adapting this expression from Subsection 3-2, we change the species subscripts from A to I and from B to J and also set the bulk concentrations to zero, as befits the present circumstance. Combination of the result with equation 13:3 generates

\[ \xi_1(t)c_R^b + \frac{\xi_1(t)}{\sqrt{D_R}} \frac{d^{-1/2}}{dt^{-1/2}} j_R^s(t) = \frac{1}{(1 + K)\sqrt{D}} \frac{d^{-1/2}}{dt^{-1/2}} \left\{ j_I^s(t) + j_J^s(t) \right\} \]

13:5

The flux densities may be replaced by the appropriate currents by invoking the equations

\[ j_R^s(t) = -j_I^s(t) = \frac{\mp I_1(t)}{FA} \quad \text{and} \quad j_J^s(t) = \frac{\mp I_2(t)}{FA} \]

13:6 and 13:7

which convert equation 13:5 to

\[ \pm FA\xi_1(t)c_R^b / \sqrt{D} - \frac{\xi_1(t)\sqrt{D}}{\sqrt{D_R}} \frac{d^{-1/2}}{dt^{-1/2}} I_1(t) = \frac{1}{1 + K} \frac{d^{-1/2}}{dt^{-1/2}} \left[ I_1(t) - I_2(t) \right] \]

13:8

\[ + \frac{\exp\{-kt\}}{1 + K} \frac{d^{-1/2}}{dt^{-1/2}} \left[ (KI_1(t) + I_2(t)) \exp\{kt\} \right] \]

after minor rearrangement. Up to this point our equations are exact.

Next, we replace the semiintegrals in equation 13:8 by the algorithms from Section 5. In so doing, we utilize the abbreviations defined in equations 5:10 and 5:11.
\[
\pm FAe^b c_R \sqrt{D} - \frac{\xi_1(t)}{\sqrt{D_R}} \sqrt{\delta} \left[ I_1(t) + I_1(<t) \right] = \frac{\sqrt{\delta}}{1 + K} \left[ I_1(t) + I_1(<t) - I_2(t) - I_2(<t) \right]
\]
\[
+ \frac{\sqrt{\delta}}{1 + K} \left[ KI_1(t) + KI_1(<t, k) + I_2(t) + I_2(<t, k) \right]
\]

Cancellations occur and reorganization of the remnants results in

\[
I_1(t) = \pm FAe^b c_R \sqrt{D} - \frac{D}{\sqrt{D_R}} + \frac{1}{(1 + K) \xi_1(t)} I_1(<t) - \frac{KI_1(<t, k) - I_2(<t, k) + I_2(<t, k)}{(1 + K) \xi_1(t)}
\]

Starting with equation 3:29 and following a route analogous to that in the previous paragraph, leads to

\[
I_2(t) = - \left[ \xi_2(t) \sqrt{D} + \frac{K}{1 + K} \right] I_2(<t) - \frac{I_2(<t, k) - KI_1(<t) + KI_1(<t, k)}{1 + K}
\]

The total current is the sum of the contributions from equations 13:10 and 13:11. It is this total sum that is plotted in Figure 15 and compared there with the prediction of \textit{DigiSim} for the case of two consecutive oxidations.

**14 Square Scheme: alternative electron transfers with homogeneous interconversions**

Figure 16 depicts what is commonly called a “square scheme”. Two reactants, \( R_1 \) and \( R_2 \), interconvert homogeneously through first (or pseudo-first) order processes. Both are electroactive, yielding products \( P_1 \) and \( P_2 \) that are absent initially; subsequently these products also interconvert by first-order chemical reactions. Thermodynamics requires a relationship between the two solution-phase equilibrium constants.
\[
R_1 \xleftrightarrow[k_R^{-1}]{k_R} R_2 \quad \frac{k_R}{k_R^{-1}} = K_R \quad \text{and} \quad P_1 \xleftrightarrow[k_P^{-1}]{k_P} P_2 \quad \frac{k_P}{k_P^{-1}} = K_P
\]  
14:1 and 14:2

on the one hand, and the formal potentials of the two electron transfer reactions

\[
R_1 + e^- \xrightarrow{E_1^{o'}, k_{R_1}^{o'}, \alpha_1} P_1 \quad \text{and} \quad R_2 + e^- \xrightarrow{E_2^{o'}, k_{R_2}^{o'}, \lambda^{o'}} P_2
\]  
14:3 and 14:4

on the other. The relationship follows from two applications of Nernst’s law and is

\[
\frac{K_R}{K_P} = \exp\left\{ \frac{\pm F}{RT} [E_2^{o'} - E_1^{o'}] \right\} = \frac{\xi_1(t)}{\xi_2(t)}
\]  
14:5

Commonly the interconversion reactions are acid/base, or other very rapid exchange, reactions. In those cases, the homogeneous equilibrium between the two R forms is established rapidly throughout the solution. The same is true for the two P species. In the interest of generality, however, we do not here insist that equilibria exist other than in the bulk. P_1 and P_2 are taken to have a common diffusivity \( D_P \).

As in equations 12:7 and 12:8, there are two Butler-Volmer equations to be obeyed; they may be written

\[
\frac{\pm I_1(t)}{FAk_{1}^{o'} \left[ \xi_1(t) \right]^{o'}} = c_{R_1}^s(t) - c_{P_1}^s(t) \quad \text{and} \quad \frac{\pm I_2(t)}{FAk_{2}^{o'} \left[ \xi_2(t) \right]^{o'}} = c_{R_2}^s(t) - c_{P_2}^s(t)
\]  
14:6 and 14:7

After a single value, \( D_R \), is allotted to the diffusivities of both R_1 and R_2, equation 3:28 applies to the R_1/R_2 codiffusion in the form

\[
c_{R_1}^s(t) = \frac{c_{R_1}^b}{1 + K_R} + \frac{1}{(1 + K_R)\sqrt{D_R}} \frac{d^{-1/2}}{dt} \left\{ j_{R_1}^s(t) + j_{R_2}^s(t) \right\} \\
+ \frac{\exp\left\{ -k_R_{R_1}t \right\}}{(1 + K_R)\sqrt{D_R}} \frac{d^{-1/2}}{dt} \left[ K_R j_{R_1}^s(t) - j_{R_2}^s(t) \right] \exp\left\{ k_R t \right\}
\]  
14:8

and application of Faraday’s law, equation 4:1, then leads to
\[ c_{R_1}(t) = \frac{c_{R}^{b}}{1 + K_{R}} \pm \frac{1}{FA(1 + K_{R})\sqrt{D_{R}}} \frac{d^{-1/2}}{dt^{-1/2}} \{ I_1(t) + I_2(t) \} + \exp\{-k_{R}t\} \frac{d^{-1/2}}{FA(1 + K_{R})\sqrt{D_{R}}} dt^{-1/2} \{ [K_{R}I_1(t) - I_2(t)] \exp\{k_{R}t\} \} \]

Adoption of the semiintegration algorithms now converts 14:9 initially to

\[ c_{R_1}(t) = \frac{c_{R}^{b}}{1 + K_{R}} \pm \frac{\sqrt{\delta} [I_1(t) + I_2(t) + I_1(< t) + I_2(< t)]}{FA(1 + K_{R})\sqrt{D_{R}}} \]

\[ \pm \frac{\sqrt{\delta} [K_{R}I_1(t) - I_2(t) + K_{R}I_1(< t, k_{R}) - I_2(< t, k_{R})]}{FA(1 + K_{R})}\sqrt{D_{R}} \]

and, after some cancellations and rearrangements, into

\[ \pm FA\frac{\sqrt{D_{R}}}{\sqrt{\delta}} c_{R_1}(t) = \pm FAc_{R_1}^{b} \frac{\sqrt{D_{R}}}{(1 + K_{R})\sqrt{\delta}} - I_1(t) - I_1(< t) + I_2(< t) + K_{R}I_1(< t, k_{R}) - I_2(< t, k_{R}) \]

There are seen to be several distinct terms contributing to the surface concentration of R; these are summarized in the second line of Table 2. The third line in the table arises from applying equation 3:29 to the codiffusing reactant R. The fourth and fifth lines contain the coefficients of the various currents that originate by application of equations 3:28 and 3:29 to the codiffusing product species P and P; there is no “bulk” term here, reflecting the initial absence of product.

Now return to equation 14:6 and rewrite it as

\[ \frac{I_1(t)\sqrt{D_{R}}}{k_{1}^{o}[\xi_1(t)]^{\xi_1}} = \pm FAc_{R_1}^{b} \frac{\sqrt{D_{R}}}{\sqrt{\delta}} \frac{FAc_{R_1}(t)\sqrt{D_{R}}}{\xi_1(t)\sqrt{\delta}} \]

Expressions for the right-hand terms may be found from the table and lead to

\[ \frac{I_1(t)\sqrt{D_{R}}}{k_{1}^{o}[\xi_1(t)]^{\xi_1}} = \pm FAc_{R_1}^{b} \frac{\sqrt{D_{R}}}{(1 + K_{R})\sqrt{\delta}} - \left[ 1 + \frac{\sqrt{D_{R}}}{\xi_1(t)\sqrt{D_{P}}} \right] I_1(t) \]

\[ - \frac{I(< t) + K_{R}I_1(< t, k_{R}) - I_2(< t, k_{R})}{1 + K_{R}} - \frac{I(< t) + K_{P}I_1(< t, k_{P}) - I_2(< t, k_{P})}{(1 + K_{P})\xi_1(t)\sqrt{D_{P}}/\sqrt{D_{R}}} \]
where we have written $I(<t)$ to replace $I_1(<t) + I_2(<t)$. Collection of terms now leads to

$$I_i(t) = \frac{\pm FA_c b \sqrt{D_R}}{(1 + K_R)\sqrt{\delta}} \frac{I(<t) + K_R I_i(<t, k_R) - I_2(<t, k_R)}{1 + K_R} - \frac{I(<t) + K_P I_i(<t, k_P) - I_2(<t, k_P)}{(1 + K_P)\zeta_i(t)\sqrt{D_P / D_R}}$$

$$\frac{\sqrt{D_R}}{k_i \zeta_i(t)^{\zeta_i} \sqrt{\delta} + 1 + \frac{\sqrt{D_R}}{\zeta_i(t)\sqrt{D_P}}}$$

14:14

The corresponding expression for the current arising from the second electron transfer is

$$I_2(t) = \frac{\pm K_R F A c b \sqrt{D_R}}{(1 + K_R)\sqrt{\delta}} \frac{K_R I(<t) - K_R I_1(<t, k_R) + I_2(<t, k_R)}{1 + K_R} - \frac{K_P I(<t) - K_P I_1(<t, k_P) + I_2(<t, k_P)}{(1 + K_P)\zeta_2(t)\sqrt{D_P / D_R}}$$

$$\frac{\sqrt{D_R}}{k_2 \zeta_2(t)^{\zeta_2} \sqrt{\delta} + 1 + \frac{\sqrt{D_R}}{\zeta_2(t)\sqrt{D_P}}}$$

14:15

The total current is, of course, given by the sum of equations 14:14 and 14:15. The cyclovoltammetric current calculated as this sum in shown in Figure 17 for the parameters reported in the caption. Agreement with the corresponding DigiSim prediction, shown by the points, is almost perfect.

15 Summary

The validity and versatility of the numerical algorithmic route for modelling cyclic voltammograms has been amply demonstrated. The approach is more flexible than mathematical analysis but more limited than digital simulation. Although they may have exhausted the reader, by no means do the examples addressed in Sections 7–14 exhaust the mechanistic schemes that can be successfully modelled by the numerical algorithmic approach. Numerical algorithms of this kind cannot address homogeneous reactions of orders in excess of unity; nor, in their present form, can they model voltammetries in geometries more complex than the one considered here.
Moreover a distinction between diffusivities cannot always be maintained. Nevertheless, the approach can satisfactorily model most of the mechanisms postulated in the literature to account for experimental voltammograms.

Advantages of numerical algorithms are their transparency, simplicity, immediacy and trustworthiness; by using this tool, the electrochemist need not delegate the modelling of his/her experiment to a remote commercial venture. On the other hand, once purchased, digital simulation packages are undeniably faster and more versatile.

**Acknowledgement**

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**References**


On occasion (see page 513 of A.J. Bard, L.R. Faulkner, Electrochemical Methods: fundamental and applications, 2E, Wiley, New York, 2001 for illustrations) it is useful to add a third, or more, scans. In such cases, replace $vt$ in formula 2:2 by

$$vt - 2|E_{rev} - E(0)|\text{Int}\left\{\frac{vt}{2|E_{rev} - E(0)|}\right\},$$

where $\text{Int}\{\}$ denotes the integer value function.


[16] See Chapter 2 of ref [15] for the double factorial function, $z!!$

[17] There is danger of computational overflow in calculating the factorials of large integers.


[19] Even to the extent of adopting DigiSim’s built-in values of $R$, $T$, and $F$, despite these differing somewhat from currently accepted values.
Table 1

<table>
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<th></th>
<th>Forward peak</th>
<th></th>
<th>Backward peak</th>
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<td>Current</td>
<td>Current</td>
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<td>849.61 (\mu\text{A})</td>
<td>$E^{\circ'} - 29.143 \text{ mV}$</td>
<td>$-632.05 \mu\text{A}$</td>
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<td>Equation 7:7</td>
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<td>DigiSim</td>
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<td>$E^{\circ'} - 29.31 \text{ mV}$</td>
<td>$-631.9 \mu\text{A}$</td>
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Table 2

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<th>$\frac{\pm FA c_\delta^b}{\sqrt{\delta}}$</th>
<th>$I_1(t)$</th>
<th>$I_2(t)$</th>
<th>$I_1(&lt;t) + I_2(&lt;t)$</th>
<th>$I_1(&lt;t, k_R)$</th>
<th>$I_2(&lt;t, k_R)$</th>
<th>$I_1(&lt;t, k_p)$</th>
<th>$I_2(&lt;t, k_p)$</th>
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<td></td>
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<td></td>
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<td>$\frac{K_R}{1 + K_R}$</td>
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<td>$\frac{1}{1 + K_R}$</td>
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<tr>
<td>$\frac{\pm FA \sqrt{D_R}}{\sqrt{\delta}} c_{p_1}^s(t)$</td>
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<td>$\frac{\sqrt{D_R}}{(1 + K_p)\sqrt{D_p}}$</td>
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**Figures and Legends**

**Figure 1:** Diffusion of a single species A.

**Figure 2:** The diffusing species A and B interconvert in the solution.

**Figure 3:** In the simple E_r scheme, electroreactant R undergoes reversible electron transfer.
Figure 4: A quasireversible electron transfer, uncomplicated by solution chemistry.

Figure 5: Comparison of an algorithmically predicted $E_q$ cyclic voltammogram (full curve) with that provided by DigiSim (open circles). Parameters:

- $A = 1 \times 10^{-4} \text{ m}^2$, $E(0) = 0.3 \text{ V}$, $E_{rev} = -0.3 \text{ V}$, $\nu = 1$ V s$^{-1}$,
- $c_R^b = 1 \text{ mol m}^{-3}$, $D_R = D_p = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$,
- $E^{o^r} = 0 \text{ V}$, $k^{o^r} = 1 \times 10^{-5} \text{ m s}^{-1}$, $\alpha = 0.5$, and
- $\delta = 1 \times 10^{-3} \text{ s}$; lower signs selected.
Figure 6: A reversible electron transfer with a preceding homogeneous reaction.

Figure 7: Comparison of an algorithmically predicted CE\textsubscript{r} cyclic voltammogram (full curve) with that provided by DigiSim (open circles). Parameters used are: \(A=1\times10^{-4} \text{ m}^2\), \(E(0) = -0.3 \text{ V}\), \(E_{\text{rev}} = +0.3 \text{ V}\), \(\nu = 1 \text{ V s}^{-1}\), \(c^b = 1 \text{ mol m}^{-3}\), \(D = D_p = 1\times10^{-9} \text{ m}^2\text{s}^{-1}\), \(E^{\circ'} = 0 \text{ V}\), \(\tilde{k} = 1 \text{ s}^{-1}\), \(\tilde{k} = 10 \text{ s}^{-1}\), and \(\delta = 1\times10^{-3} \text{ s}\). Upper signs throughout.
Figure 8: A quasireversible electron transfer with a following homogeneous reaction.

Figure 9: Comparison of an algorithmically predicted $E_qC$ cyclic voltammogram (full curve) with that provided by DigiSim (open circles). Parameters used are: $A = 1 \times 10^{-4}$ m$^2$, $E(0) = -0.3$ V, $E_{rev} = 0.3$ V, $v = 1$ V s$^{-1}$, $c = 1$ mol m$^{-3}$, $D = D_R = 1 \times 10^{-9}$ m$^2$ s$^{-1}$, $E^{o'} = 0$ V, $k^{o'} = 1 \times 10^{-5}$ m s$^{-1}$, $\alpha = 0.3$, $\tilde{k} = 1$ s$^{-1}$, $\tilde{k} = 10$ s$^{-1}$, and $\delta = 1 \times 10^{-3}$ s, with lower signs throughout.
Figure 10: The catalytic scheme.

Figure 11: A voltammogram for the scheme shown in Figure 10. Full curve from algorithm 11:7, open circles provided by DigiSim. Parameters used are: $A = 1 \times 10^{-4}$ m$^2$, $E(0) = -0.3$ V, $E_{rev} = 0.3$ V, $\nu = 1$ V s$^{-1}$,

$c^b = 1$ mol m$^{-3}$, $c_X^b = 1000$ mol m$^{-3}$, $c_Y^b = 1000$ mol m$^{-3}$,

$D = 1 \times 10^{-9}$ m$^2$ s$^{-1}$, $E^{o'} = 0$ V, $k^{o'} = 1 \times 10^{-4}$ m s$^{-1}$,

$\alpha = 0.5$, $\tilde{k} = 10$ s$^{-1}$, and $\delta = 1 \times 10^{-3}$ s, with upper signs throughout.
Figure 12: Two successive quasireversible electron transfers without homogeneous kinetics.

Figure 13: Cyclic voltammogram of two quasireversible electron transfers without solution chemistry. The full curve is generated by the algorithm described here whereas the open circles are from DigiSim. Input data are: $A = 1 \times 10^{-4}$ m$^2$, $E(0) = -0.3$ V, $E_{\text{rev}} = 0.3$ V, $\nu = 1$ V s$^{-1}$, $c^b = 1$ mol m$^{-3}$, $D_R = D_I = D_P = 1 \times 10^{-9}$ m$^2$ s$^{-1}$, $E_{1}^{0'} = -0.1$ V, $k_{1}^{0'} = 1 \times 10^{-4}$ m s$^{-1}$, $\alpha_1 = 0.5$, $E_{2}^{0'} = 0.1$ V, $k_{2}^{0'} = 5 \times 10^{-5}$ m s$^{-1}$, $\alpha_2 = 0.5$, and $\delta = 1 \times 10^{-3}$ s, with upper signs throughout.
Figure 14: Two reversible electron transfers coupled by homogeneous kinetics.

Figure 15: Cyclic voltammogram of two reversible electron transfers linked by a homogeneous chemical reaction. The full curve is generated by the algorithm described here whereas the open circles are from DigiSim. Input data are: 

\[ A = 1 \times 10^{-4} \text{ m}^2, \quad E(0) = -0.3 \text{ V}, \quad E_{\text{rev}} = 0.3 \text{ V}, \quad v = 1 \text{ V s}^{-1}, \]
\[ c^b = 1 \text{ mol m}^{-3}, \quad D_R = D = D_P = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}, \]
\[ E_1^{\circ'} = -0.1 \text{ V}, \quad E_2^{\circ'} = 0.1 \text{ V}, \quad \tilde{k} = k = 10 \text{ s}^{-1}, \]
\[ \delta = 1 \times 10^{-3} \text{ s}, \quad \text{with upper signs throughout.} \]
**Figure 16:** The quasireversible square scheme.

**Figure 17:** Cyclic voltammogram for an instance of the square scheme. The full curve is generated by the algorithm described here whereas the open circles are from *DigiSim*. Input data are: \( A = 1 \times 10^{-4} \text{ m}^2 \),

\[
E(0) = -0.3 \text{ V}, E_{\text{rev}} = 0.3 \text{ V}, \ \nu = 1 \text{ V s}^{-1}
\]

\[
c^b = 1 \text{ mol m}^{-3}, D_R = D_P = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1},
\]

\[
E_1^{\text{ref}} = -0.1 \text{ V}, k_1^{\text{ref}} = 100 \text{ m s}^{-1}, \ \alpha_1 = 0.5, \ E_2^{\text{ref}} = 0.1 \text{ V},
\]

\[
k_2^{\text{ref}} = 2 \times 10^{-5} \text{ m s}^{-1}, \ \alpha_2 = 0.5, K_R = 490, K_P = 0.204,
\]

\[
\tilde{k}_R = \tilde{k}_p = 100 \text{ s}^{-1}, \text{ and } \delta = 1 \times 10^{-3} \text{ s}, \text{ with upper signs throughout.}