The superposition principle in the theoretical analysis of electrochemical techniques for different electrode geometries

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ABSTRACT
In this article we establish the necessary mathematical conditions for the superposition principle to be applicable in obtaining the response for different electrochemical techniques on plane, spherical and cylindrical electrodes.

In potential controlled techniques, this principle can be only applied when the electrical transference is reversible. No additional restrictions exists for planar electrodes. When the electrode is spherical or cylindrical, in addition, the reactive and product diffusion coefficients must be equal and the reaction product must be soluble in the solution. When these conditions are fulfilled, the superposition principle can be applied to any sequence of pulses. Moreover, for spherical electrodes this principle can be applied although the amalgamation took place when only the first order spherical correction is considered.

In current controlled techniques this principle can be used independently of the reversibility of the system and the solutions thus obtained are valid for any electrode geometry both in the case of the reaction product being soluble in the solution and in the electrode (amalgam formation).

INTRODUCTION
The general study of the response of a system obtained in most electrochemical techniques is based on solving a system of linear differential equations, which is a function of the variables, the distance of the solution to the surface of the electrode and the duration of the application of a determined electrical perturbation to the same. The solution of this system of differential equations is determined by a set of subsidiary conditions corresponding to particular solutions.

Today the electrochemical methods aimed at enlightening electrode processes are many and varied [1, 2]. However, they can be divided into two large groups:
- a) Controlled potential methods.
- b) Controlled current methods.

The former consist of the application to an electrode of a constant or time variable potential with the aim of measuring the response produced in the system, which in this case is an electric current. In the latter, the response measured is a time variable potential, which is a consequence of the application of a determined current (either constant or programmed).

The application to either group of several electrical perturbations in a stepped and successive way is of interest both from the kinetic and the analytical point of view, since the response obtained under these conditions is much more sensitive to the kinetic characteristics of the electrode process and much less influenced by the capacitative effects of the charge current, which distort the results obtained. Because of these advantages, in recent years the study of
electrochemical methods in which the perturbation is applied more than once, has received much attention [1-5]. Anyone of these methods is characterised by the application of successive perturbations (potential or current) without the equilibrium in the electrode-solution interface being re-established between perturbation and the next. Therefore, the initial conditions for solving the problem corresponding to a determined potential step, \( m \), are those corresponding to the system perturbed by the step \( m-1 \) when the total time, \( t \), is given by

\[
 t = t_{1,m-1} + \sum_{i=2}^{m-1} t_i
\]

with \( t_i \) (\( i \geq 1 \)) being the duration of any step.

The difficulty in finding a rigorous and manageable analytical solution for many problems is well-known. This is seen in the introductions of the references 6 and 7, which deal only with the application of two successive potential steps. It is pointed out that the analytical equations related to the study of a slow charge transfer obtained by a great number of authors cannot be considered as rigorous, but only as approximate. Moreover, in case of the application of two potential steps, there are many, more up to date references in which the same error is committed when dealing with irreversible processes [8-13] and even when reversible processes main. In planar diffusion are analyzed [14]. Faced with such a situation, these problems of multistep application of potential or current to an electrode are usually solved by using simulation methods, which, while possessing many advantages are clearly not comparable to an analytical solution.

The difficulties referred to above are due to the fact that, while the system of differential equations to be solved is linear, this linearity is lost in most cases with the establishment of the boundary value problem. Nevertheless, certain situations do exist where it is easy to obtain such an expression for the response corresponding to the \( j \)-th step of a determined sequence of potentials, \( E_1, E_2, \ldots, E_n \), due to the fact that the boundary value problem is also linear. In these conditions a problem with \( j \) potential steps can be treated as \( j \) problems of a single step, which are independent. This is the same as saying that the superposition principle is fulfilled and, in consequence, the current corresponding to any pulse \( j \) is given by \( j \) responses corresponding to \( j \) single potential steps.

In voltammetry (when several potential steps are applied) the superposition principle can be applied rigorously for a reversible charge transfer process and does not depend on the diffusion coefficient values of the electroactive couple for any plane electrode of a fixed area or of an area growing with an arbitrary power of time. For electrodes of non-planar geometry this principle can only be applied with rigour if the diffusion coefficients of the implied species are equal and if the reduced species is soluble in the electrolyte solution (in absence of adsorption or amalgamation). In these conditions we have demonstrated that the solution for the concentrations of the different species as functions of the distance to the electrode surface and the time of application of the perturbation, and also the current corresponding to the \( j \)-th step can be deduced by knowing the solution to the first pulse (\( j=1 \)) for electrodes of constant area, or of those corresponding to the first and second pulses (\( j=1 \) and \( 2 \)) for electrodes of variable area, such as the dropping mercury electrode (DME). We also show that for spherical electrodes, when only the first order spherical correction is taken into account (i.e., when we only take the first term of the series of the electrode sphericity parameter \( \xi = 2\sqrt{D t / r_e} \) the superposition principle can be applied for any value of the diffusion coefficients and when the reaction product is soluble in the electrode or in the electrolyte solution.

In cyclic chronopotentiometry with different current-time functions, the superposition principle can be used independently of the reversibility of system since, in this kind of techniques the reversibility or irreversibility of the process under study is not a boundary value problem. The solutions thus obtained are valid for any electrode geometry both in the case of the
reaction product being soluble in the solution and in the electrode (amalgam formation).

We have studied the electrochemical technique called cyclic chronopotentiometry (introduced by Herman and Bard in 1963 [15]) in which successive and alternating sign current steps are applied to a plane electrode. These are of the general form \((-1)^j I_j\) (where \(j\) is the number of the current step being considered). We have recently broadened this study by applying some current-time functions in the same way as cyclic chronopotentiometry: a) An alternating sign power current-time function of the form \((-1)^j I_j r_j^{\alpha}\) [16], and b) An alternating sign exponential current-time function of the form \((-1)^j I_j e^{r_j}\) for any value of \(\alpha\) [16]. In both cases the superposition principle is applicable since we have demonstrated that the boundary value problem to be fulfilled by the solutions is linear.

Finally, we have obtained the solutions corresponding to the application of a power-exponential current to the study of multistep electrode processes and systems with several components in electrodes of different geometries [17]. Again, the solutions obtained by following a recurrent method are based only on the linearity of the operators and the subsidiary boundary value problem. The study of multistep electrode processes is of great interest today. Thus, for example, fullerenes in general and \(C_{60}\) in particular, can present up to five reversible one electron reductions [18, 19].

Both in the above mentioned cyclic multipulse chronopotentiometric techniques and in the case of multistep electrode processes, the superposition principle is applicable to electrodes of different geometries and this applicability is independent of the method used in solving the differential equations, of the values of the diffusion coefficients of the different species and, in the case of an expanding spherical electrode (as the DME), it is also independent of the fact that the reaction products are soluble in the electrolyte solution or in the electrode.

a) **POTENTIAL CONTROLLED TECHNIQUES.**

When these techniques are used with reversible electrode processes, we have demonstrated that the superposition principle can be applied in order to deduce the analytical expression for the current corresponding to the \(j\)-th potential step, \(I_j\), of a determined sequence of pulses in the following cases:

a1) For any plane electrode whose area grows with an arbitrary power of time, independently of the diffusion coefficient values of the electroactive couple, and for spherical (with a growing area with an arbitrary power of time) and cylindrical electrodes if the diffusion coefficients of both species are equal and if the reduced species is soluble in the electrolytic solution [20]. In these cases, as we will see later, the problem is linear and, therefore, the applicability of the superposition principle is independent of the method used for solving it.

a2) For spherical electrodes whatever the values of diffusion coefficients of the electroactive couple and if reduced species is soluble in the electrolytic solution or in the electrode [21-23]. In this case, the applicability of the superposition principle is restricted to the use of the dimensionless parameters method, which enables us to find the solutions when only first order spherical correction is considered.

Below, we are going to set out the theoretical background in both cases.

a1) Different electrode geometries, with equal diffusion coefficients and product soluble in the electrolytic solution.

If we consider the reversible charge transfer reaction

\[
A + ne^- x2 B
\]

(1)

mass transport to the electrode is given by the
following system of differential equations
\[ \hat{\delta}_A C_A = \hat{\delta}_B C_B = 0 \]  
(1)

where the operator \( \hat{\delta}_i \) (i = A or B) is given by
\[ \hat{\delta}_i = \frac{\partial}{\partial r} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{z_i n_0}{2 r_i t_i} \frac{\partial}{\partial r} \]  
(2)

if we consider a spherical electrode whose area increases with \( t \), \( \geq 0 \), and
\[ \hat{\delta}_i = \frac{\partial}{\partial r} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) \]  
(3)

for a stationary cylinder.

The operators given by equations (2) and (3) are linear [28].

From the solutions previously found for \( C_i'(r,t) \) and \( C_i'(r,t) \) when a potential step \( E \) is applied, it is easily deduced that if \( D_A = D_B = D \) and both species are soluble in the electrolytic solution, the surface concentrations are a function of potential alone [4, 22, 24-26]. In these conditions
\[ \begin{align*}
C_A'(r_0,t) + C_B'(r_0,t) &= C_A' \\
C_A'(r_0,t) &= \frac{K_1}{1 + K_1} \\
C_B'(r_0,t) &= C_B'
\end{align*} \]  
(4)

is fulfilled.

\[ K_j = \exp[nF(E_j - E^0)/RT] \]  
(5)

Equations (4) are independent both of the geometry of the electrode and of whether its area is constant or variable with time. In contrast, if \( D_A = D_B \) and/or \( B \) is amalgamated into the electrode, \( C_A'(r_0,t) \) and \( C_B'(r_0,t) \) do depend on the time for non planar electrodes [21-27].

The superscript \( j \) in \( C_i' \) in equation (4) and thenceforth, refers to the number of the potential pulse considered.

If to \( t = t \), the potential is stepped up to a value \( E_2 \), over an interval \( 0 \leq t \leq t_2 \) (with \( t = t_1 + t_2 \)), the solutions to the equations system (1), \( C_A' \) and \( C_B' \), can be expressed as below due to operators (2) and (3) being linear:
\[ \begin{align*}
C_A'(r,t) &= C_A'(r,t) + C_A'(r,t) \\
C_B'(r,t) &= C_B'(r,t) + C_B'(r,t)
\end{align*} \]  
(6)

The boundary value problem for \( C_A'(r,t) \) and \( C_B'(r,t) \) in this second pulse can be expressed only in terms of the new unknowns \( C_A' \) and \( C_B' \) as below, taking into consideration equations (4) and (6)
\[ \begin{align*}
\tau_2 = 0; r \geq r_0 & \quad \overline{C}_A'(r,t) = \overline{C}_B'(r,t) = 0 \\
\tau_2 > 0; r \to \infty & \quad \overline{C}_A'(r,t) = \overline{C}_B'(r,t) = 0
\end{align*} \]  
(7)

\[ \tau_2 > 0; r = r_0: \quad \left( \frac{\overline{C}_A'(r,t)}{\overline{C}_B'(r,t)} \right)_{r = r_0} = \left( \frac{\overline{C}_A'(r,t)}{\overline{C}_B'(r,t)} \right)_{r = r_0} \]  
(8)

\[ \overline{C}_A'(r_0,t) = K_j \overline{C}_A'(r_0,t) + \frac{K_1 - K_1}{1 + K_1} C_A' \]  
(9)

\[ \frac{i(t)}{nFA(t)D} = \left( \frac{\overline{C}_A'(r,t)}{\overline{C}_B'(r,t)} \right)_{r_0} + \left( \frac{\overline{C}_A'(r,t)}{\overline{C}_B'(r,t)} \right)_{r_0} \]  
(10)

with \( A(t) = A_0 t^t \)  
(11)

and \( A_0 \) being the electrode area when \( t = 1 \) s.

Due to the reversibility of the process, the simplicity of equation (9) means that the solutions for this second pulse \( C_A'(r,t) \) and \( C_B'(r,t) \) at the surface of the electrode are, like the previous pulse, independent of time and of the geometry of the
electrode, thus fulfilling

$$
\frac{C_A^2(r_0, t)}{C_A} = 1 - \sum_{m=1}^{2} Z_m = \frac{K_2}{1 + K_2}
$$

$$
C_A^2(r_0, t) + C_B^2(r_0, t) = C_A^* \tag{12}
$$

with

$$
Z_j = \frac{1}{1 + K_j} - \frac{1}{1 + K_{j-1}}, \quad j > 1
$$

$$
Z_1 = \frac{1}{1 + K_1} \tag{13}
$$

For any pulse \( j \geq 2 \), the linearity of equations (12) implies that

$$
C_j^i(r, t) = C_j^{i-1}(r, t) + \tilde{C}_j^i(r, t)
$$

$$
C_j^{i-1}(r, t) = C_j^i(r, t) + \sum_{m=2}^{j-1} \tilde{C}_m^i(r, t) \tag{14}
$$

From equations (4) and (12)-(14) it is easily demonstrated by induction that the surface concentration corresponding to any pulse \( j \geq 1 \) fulfills

$$
\frac{C_A^j(r_0, t)}{C_A} = 1 - \sum_{m=1}^{j} Z_m = \frac{K_j}{1 + K_j}
$$

$$
C_A^j(r_0, t) + C_B^j(r_0, t) = C_A^* \tag{15}
$$

Moreover, in this situation it is demonstrated that, for any pulse

$$
C_A^j(r, t) + C_B^j(r, t) = C_A^* \quad \text{for} \quad r_0 \leq r \leq \infty \tag{16}
$$

holds.

If we take into consideration equations (14)-(15) we can express the boundary value problem for any pulse \( j \) only in terms of the unknown \( \tilde{C}_j^i(r, t) \), where \( t = t_1 + t_2 + \ldots + t_j \), \( 0 \leq t_j \leq t_j \), in the form

$$
\tau_j = 0; \quad r \geq r_0
$$

$$
\tau_j > 0; \quad r \rightarrow \infty
$$

$$
\tilde{C}_j^i(r, t) = \tilde{C}_j^i(r, t) = 0 \tag{17}
$$

$$
\tau_j > 0; \quad r = r_0
$$

$$
\left( \frac{\partial \tilde{C}_j^i(r, t)}{\partial r} \right)_{r=r_0} = \left( \frac{\partial \tilde{C}_j^i(r, t)}{\partial r} \right)_{r=r_0} \tag{18}
$$

$$
\tilde{C}_j^i(r_0, t) = K_j \tilde{C}_j^i(r, t) + \frac{K_{j-1} - K_j}{1 + K_{j-1}} C_A^* \tag{19}
$$

This generalisation of the boundary value problem for any pulse (equations (17)-(19)), together with the linearity conditions given by equations (14), give rise to the current corresponding to the \( j \)-th pulse takes the simple following form

$$
\frac{i_j(t)}{nF\tilde{A}(t)D} = \left( \frac{\partial \tilde{C}_j^i(r, t)}{\partial r} \right)_{r=r_0} + \sum_{m=2}^{j} \left( \frac{\partial \tilde{C}_m^i(r, t)}{\partial r} \right)_{r=r_0} \tag{20}
$$

As is shown in equations (7)-(10) and (17)-(20), the boundary value problem which has to satisfy the unknown \( \tilde{C}_j^i(r, t) \) can be expressed in the same general form for any pulse \( j \geq 2 \). That is to say, the problem of \( j \) pulses has been reduced to \( j \) independent problems of a single pulse and, therefore, both the concentration corresponding to pulse \( j \), \( C_j^i(r, t) \) (equation (14)), and, consequently, the current associated to the same, \( i_j \) (equation (20)), can be expressed as the sum of \( j \) terms corresponding to \( j \) single potential steps [28]. In other words, the principle of superposition for spherical and cylindrical electrodes is fulfilled when process (I) is reversible, the diffusion coefficients of both species are equal and species B is soluble in the electrolytic solution. If all three previous conditions are not given, the surface
concentrations depend on the time and equation (19) does not hold. In these conditions the linearity of the problem is lost and the solution is much more complex [21-27]. This complexity increases with the number of potential pulses applied (i).

From the above, and by applying the superposition principle, we have deduced a general expression for the current corresponding to pulse \(j\) for an increasing spherical electrode with any power of time (taking into account the second order spherical correction). For this aim, we have used the expressions obtained for the first and second pulses and equations (14) and (17)-(20). So, by using the dimensionless parameters method [21-23, 27], we deduce:

\[
i_1 = nFA(t_1) \sqrt{\frac{(2\pi + 1)D}{\pi \eta}} C_A Z \left(1 + \theta_1 \xi_1 + \lambda_1 \xi_1^2\right)
\]

\[
i_2 = i_1(t_1) + nFA(t_1) \sqrt{\frac{D}{\eta}} C_A Z_2 \left(\beta_2(0)(\beta_2) + \frac{\sqrt{\pi}}{2} \beta_2(0)(\beta_2) \xi_2 + \beta_2(0)(\beta_2) \xi_2^2\right) + \frac{\sqrt{\pi}}{2} \beta_2(0)(\beta_2) \xi_2 + \beta_2(0)(\beta_2) \xi_2^2 \right): \xi_1 \geq 1 \]

and, therefore, take into account the analogy between equations (7)-(10) and (17)-(20), we easily obtain:

\[
i_j = nFA(t_1) \sqrt{\frac{D}{\pi}} C_A \sum_{k=0}^{j} Z_k \left(\beta_2(0)(\beta_2) + \frac{\sqrt{\pi}}{2} \beta_2(0)(\beta_2) \xi_k + \beta_2(0)(\beta_2) \xi_k^2\right): \xi_1 \geq 1 \]

Equation (23) provides a general expression for the current corresponding to the application of any sequence of potential pulses, without any restriction regarding the duration of each pulse. Moreover, this equation is valid for any plane \((\xi_k = 0)\) or spherical electrode \((\xi_k \neq 0)\) whose area increases with an arbitrary power \(c\) of time.

In equation (23):

\[
\beta_k = \frac{t_{kj}}{t_{kj}}
\]

\[
t_{kj} = \sum_{m=k}^{j} t_m \quad \text{if} \quad k = j \quad t_{jj} = t_j \quad (25)
\]

and \(t_m\) is the duration of a pulse \(m\).

\[
\xi_1 = \frac{1}{r_0} \sqrt{\frac{4Dt_{1j}}{2\pi + 1}}
\]

\[
\xi_2 = \frac{2\sqrt{Dt_{1j}}}{r_0}
\]

\[
r_0 = cte \frac{\pi^{1/2}}{2}
\]

and

\[
\beta_2(0)(\beta_2) = \frac{1}{1 - (1 - \beta_2)^{2\pi + 1}}
\]

\[
\beta_2(1)(\beta_2) = \frac{3\pi (7\pi - 2) 128}{256} \beta_2^2 + \frac{(z - 4)(7z + 2)}{256} \beta_2^2 + \ldots
\]

\[
\beta_2(2)(\beta_2) = \frac{z(29z + 4)}{160} \beta_2^2 + \ldots
\]

For a DME \((z=2/3)\):

\[
\beta_2(0)(\beta_2) = \frac{7}{1 - (1 - \beta_2)^{3/2}}
\]

\[
\beta_2(1)(\beta_2) = \frac{1}{48} \beta_2^2 + \frac{25}{432} \beta_2^2 + \ldots
\]

\[
\beta_2(2)(\beta_2) = \frac{7}{72} \beta_2^2 + \ldots
\]

For a SMDE \((z=0)\):

\[
\beta_2(0)(\beta_2) = \beta_2(0)(\beta_2) = 1
\]

\[
\beta_2(0)(\beta_2) = 0 \quad \text{if} \quad n > 1
\]

\[
\text{In this last case, equation (23) is transformed to}
\]

\[
\frac{i_j}{nFAc_A} = \frac{\pi}{D} \sum_{m=1}^{j} Z_m \left(1 + \sqrt{\frac{\pi D}{r_0}}\right) = \frac{\left(1 + \sqrt{\frac{\pi D}{r_0}}\right)}{1 + K_j} + \sum_{m=1}^{j-1} \frac{t_m^{(1/2) - 1}}{1 + K_m}
\]

\[
= \left(1 + \sqrt{\frac{\pi D}{r_0}}\right) \frac{t_j^{(1/2) - 1}}{1 + K_j}
\]
Equation (31) is of great importance since, as can be observed, it clearly demonstrates that the sphericity of the static spherical electrode only affects the term corresponding to the last pulse of potential, $E_i$.

Aoki and co. [29] have obtained the solution for a sequence of pulses of equal duration corresponding to the square wave voltammetry technique. This solution is clearly a particular case of our equation (31). In the above reference, when the pulses are small, the authors cited obtain an approximate solution in which the influence of the sphericity and the potential can be separated into different functions (see equation (28) in reference 1). Equation (31) of this paper is a more general and simpler way of expressing the effect of sphericity on an arbitrary sequence of potential pulses of any duration.

Besides, for a single pulse, by making $k=j=1$, which implies that $β=1$ (see equation (24)), the following expressions hold:

\[
\begin{align*}
\theta_z &= \frac{3}{\pi} \sqrt{\frac{2z+1}{2z+1}} \\
\lambda_z &= \frac{2z+1}{5(z+4)} P_{1z}(z+1) \\
&= \frac{2z+1}{5(z+4)} \left[ \frac{73z^2 - 80z - 128}{2(z+1)} + 4(4-z)(2z+1) P_{1z}(z+1) \right]
\end{align*}
\]

(32)

So, from equation (24) with $k=j=1$ and equation (32) with $z=0$ we can easily deduce for a stationary sphere

\[
\frac{i_z}{nFAC_A} = \frac{1}{1 + K_1} \left( \frac{D_1}{\pi r_1^2} + \frac{D_2}{r_0^2} \right)
\]

(33)

which is the equation of Mc. Gillavy and Rideal [30] for spherical electrodes. In the same way, for a DME ($\varepsilon=2/3$) we obtain

\[
\frac{i_z}{nFAC_A} = \frac{1}{1 + K_1} \left( \frac{7D_1}{3\pi r_1^2} + 1 + 0.19 \frac{D_1}{r_0^2} + \frac{D_1}{r_0^2} \right)
\]

(34)

which is the equation of Koutecky [27] with second order spherical correction.

Note that while equation (33) is exact, equation (34) is a development in series of power of $\varepsilon_i = \sqrt{D_1 r_1 / r_0}$.

For cylindrical electrodes, by applying the superposition principle to the equations obtained in references 29 and 31 for a single pulse, and taking into account equations (14) and (17)-(20) in this paper, we obtain:

\[
\frac{i_z}{nFAC_A} = \frac{D}{r_0} \sum_{k=1}^{n} Z_k f_x(t_{yk})
\]

(35)

where the $f_x(t_{yk})$ function can be expressed such that

\[
f_x(t_{yk}) = \begin{cases} 
\frac{1}{\sqrt{\pi}} + 0.422 + 0.0675 \log(y) + \\
+0.0058 \operatorname{sgn}[(\log(y) - 1.47)^2] \left[ (\log(y) - 1.47)^2 ight] & \text{for } y < 1200 \\
\frac{2}{\ln(4y) - 2y} e^{-\frac{2}{\ln(4y) - 2y}} \left[ \left( \frac{\ln(4y) - 2y}{2y} \right)^{10.33} - 1 \right] & \text{for } y \geq 1200
\end{cases}
\]

(36)

with

\[
y = \frac{D t_{yk}}{r_0^2} \quad \text{and} \quad \gamma = 0.577216 = \text{Euler's constant}
\]

(37)

For any plane electrode increasing with an arbitrary power of time, it is similarly demonstrated that the superposition principle is fulfilled for
reversible processes whatever the value of $D_A$ and $D_B$ and if species $B$ is soluble in the electrolyte solution or in the electrode. Unfortunately, a plane electrode is not valid in detecting the amalgamation [32]. In this case, for any pulse $i$, the surface concentrations of $A$ and $B$ fulfill [4, 33]

$$
\frac{C'_i(x = 0)}{C_{iA}} = \frac{K_j}{1 + \gamma K_j},
$$

and we can write for pulse $j$:

$$
\frac{i_j}{nF\alpha(t_i)C_{iA}^2} = \left[ \frac{D_i}{\pi^{1/2}} \sum \frac{Z_i'}{1 + \gamma K_i} \right] h_i^{00}(\beta_i) (39)
$$

$$
Z_i' = \frac{1}{1 + \gamma K_i}, \quad Z_i'' = \frac{1}{1 + \gamma K_i} (40)
$$

Equations (23) and (38), both with $z=2/3$ or $z=0$, and equation (35) are the solutions which correspond to the response to the application of $j$ successive potential steps to a DME, to a static spherical or planar electrode and to a cylindrical electrode, respectively. The application of any of these equations to any multipulse technique is immediate [20].

2) Spherical electrodes with different diffusion coefficients and/or amalgam formation

Now, let us consider a reversible charge transfer process as given by scheme (1) when the diffusion coefficients of both species ($A$ and $B$) can take any value and when the reduced species ($B$) can be soluble in the electrolyte solution or in the electrode. The mass transport to a static spherical electrode (as the SMDE) is also determined by equations (1) with $\delta_0$ ($i = A$ or $B$) given by equation (2) with $z=0$. If these differential equations are solved by using the dimensionless parameter method when only the first order spherical correction is taken into account, we obtain the following results for the surface concentrations corresponding to the three first potential steps applied to the electrode [21, 22]

$$
C_1^j(\tau_0,t) = \frac{C_{iA}K_j}{1 + \gamma K_j} \left[ \frac{1 + (\tau_0/\tau)^{1/2}}{\sqrt{\tau}} \right] Z_i\xi_{1,A}
$$

$$
C_2^j(\tau_i,t) = \frac{C_{iA}K_j}{1 + \gamma K_j} \left[ \frac{1 + (\tau_0/\tau)^{1/2}}{\sqrt{\tau}} \right] \left( Z_i\xi_{1,A} + Z_i\xi_{2,A} \right)
$$

$$
C_3^j(\tau_i,t) = \frac{K_jC_{iA}}{1 + \gamma K_j} \left[ \frac{1 + (\tau_0/\tau)^{1/2}}{\sqrt{\tau}} \right] \left( Z_i\xi_{1,A} + Z_i\xi_{2,A} + Z_i\xi_{3,A} \right)
$$

$$
C_i^j(\tau_i,t) = C_i'(\tau_i,t)/K_j, \quad i = 1,2,3 (41)
$$

with

$$
\xi_{k,i} = \frac{2(D_iK_i)}{r_0}; \quad i = A \text{ or } B (42)
$$

and $Z_i'$ defined by equation (40).

As can be observed, in this case the surface concentrations are not independent of time, but their dependence on the different parameters $\xi_{k,i}$, which refer to the electrode sphericity in each pulse of potential $k$, is linear. This leads to the linearity of the problem not being lost and means that the superposition principle can be applied. The fact that the problem keeps its linearity when $D_A \neq D_B$ and/or species $B$ is amalgamated into the electrode is due to the use of the dimensionless parameters method which, since it adopts solutions in the form of series of powers in the different parameters, enables these solutions to be taken with only first order spherical corrections. If solutions are taken with higher order spherical corrections ($i$, e. if the terms of the series with exponents in $\xi_{k,i}$ higher than unity are taken into account), the problem
loses linearity and the superposition principle is not applicable.

Taking into account the above conditions and the results previously obtained for the current corresponding to the first three pulses by taking only the first order spherical correction [21, 22], we deduce the following expression for the current, \( I'_p \), corresponding to any step \( j \) of a sequence of a total of \( p \) potential steps \( (E_1, E_2, ..., E_p, ..., E_p) \) [23],

\[
\frac{I'_p}{nFAC_1\sqrt{D_1}/\pi} = I'_p = I'_p + Z'_j \left( \frac{1}{\sqrt{t'_p}} + \sqrt{\frac{\pi D_1}{r_0}} \Omega_j \right) + \\
+ \frac{(\gamma + 1)\sqrt{D_1}}{\gamma \rho_0} \sum_{k=1}^{p} Z'_k w \left( \frac{t'_k}{t'_p} \right) \text{ for } p \geq j \text{ and } j \geq 2
\]

(43)

and for \( j = 1 \)

\[
\frac{I'_1}{nFAC_1\sqrt{D_1}/\pi} = I'_1 = Z_1 \left( \frac{1}{\sqrt{t'_1}} + \sqrt{\frac{\pi D_1}{r_0}} \Omega_1 \right)
\]

(44)

where

\[
\Omega_j = \frac{1 + K_j}{1 + \gamma K_j}
\]

(45)

\[
t'_m = \sum_{s=1}^{p} t'_s
\]

(46)

\[
t'_m \equiv t'_p
\]

with \( t'_m \) being the duration of any potential step \( E'_m \).

\[
w \left( \frac{t'_p}{t'_m} \right) = \frac{2}{\sqrt{\pi}} \left[ \text{Arcsin} \left( \frac{t'_m}{\sqrt{t'_m}} \right) + \sqrt{\frac{t'_m-t'_p}{t'_p}} \right]
\]

(47)

In equation (43) and thenceforth, when two signs appear, the upper sign in any equation refers to a reaction product which is soluble in the electrolytic solution, whilst the lower sign corresponds to a product soluble in the electrode.

Equation (43), after some manipulations, takes the following more manageable form for the current corresponding to the step \( j \).

\[
I_j = \sum_{k=1}^{j} Z_k \left( \frac{1}{\sqrt{t_k}} + \sqrt{\frac{\pi D_k}{r_0}} \Omega_k \right) + \\
+ \frac{(\gamma + 1)\sqrt{D_k}}{\gamma \rho_0} \sum_{k=1}^{j} Z'_k S'_k
\]

(48)

with

\[
S'_k = \sum_{s=1}^{k} Z'_s w \left( \frac{t'_s}{t'_m} \right) \text{ for } k \geq 2
\]

(49)

\[
S'_1 = 0
\]

It is noticeable that the second term in equation (48) disappears when \( D_1=D_2 \) (\( \gamma = 1 \)) and both species are soluble in the electrolytic solution (upper sign). In this case equations (43) and (48) are applicable for any value of the electrode radius [23]. However, when amalgamation takes place and/or \( D_1 \neq D_2 \) these equations are only applicable if \( \sqrt{D_1 t}/r_0 \leq 0.23 \) (with \( t \) being the total time of electrolysis), due to the fact that only the first order spherical correction has been taken into account.

This solution is of great interest, since it can be applied to any multipulse electrochemical techniques (already designed or that might be designed in the future). The use of these multipulse techniques is very useful for the study of electrode processes and they are very sensitive to the presence of amalgamation. So, for example, equation (43) or (48) can be easily applied to cyclic staircase voltammetry (CSCV) by taking into account that in this technique all the potential steps have the same duration, \( \tau \), and the same height, \( \Delta E \), and by defining a dimensionless function of the current as [20, 23]

\[
\Phi_j = \frac{I_j}{\sqrt{\pi a}}
\]

(50)

with

\[
a = \frac{nFv}{RT}
\]

(51)

\[
v = \frac{\Delta E}{\tau}
\]
where \( v \) is the potential sweep rate.

![Graph showing cyclic staircase voltammetry for a plane electrode (solid line) and a spherical electrode (dotted line) with product soluble in the electrolytic solution (broken line) and amalgam formation (dotted line). In all cases \( \gamma = 0.8, n = 1, \Delta E = 10 \text{ mV}, \tau = 0.025 \text{ s} \) and \( E_0 = 250 \text{ mV} \).](image)

In Figure 1 we show three examples of equation (43) for \( \gamma = 0.8, n = 1, \Delta E = 10 \text{ mV}, \tau = 0.025 \text{ s} \) (\( \gamma = 400 \text{ mV/s} \)), with the initial and most positive potential being 250 mV and the most negative potential -250 mV. The solid line corresponds to the first voltammetric cycle for the case of a plane electrode (\( \xi_{ij} / \sqrt{t_u} \approx 0 \)). The broken line likewise corresponds to the case of a solution soluble product and \( \xi_{ij} / \sqrt{t_u} = 0.25 \text{ s}^{-1} \). As can be observed, a slight increase in current is appreciated in those sweeps tending towards negative potentials with respect to the solution corresponding to the plane electrode, and a decrease in absolute value of the current of those sweeps tending towards positive potentials. The dotted line corresponds to the case of amalgamation, with the same value of \( \xi_{ij} / \sqrt{t_u} \). As can be appreciated, in the first semi-cycle of potentials, the value of the current is very similar to that obtained for the case of a solution soluble product. However, we observe an appreciable increase in the absolute value of the current in the second semi-cycle, as compared to the two previous cases. This effect increases with the number of cycles.

![Graph showing cyclic square wave voltammetry for a plane electrode (solid line) and a spherical electrode (dotted line) with product soluble in the electrolytic solution (broken line) and amalgam formation (dotted line). In all cases \( \gamma = 0.8, n = 1, \tau = 2.5 \text{ ms} \) and \( E = 10 \text{ mV}, E_{am} = 25 \text{ mV} \) and \( E_i = +200 \text{ mV} \).](image)

An example of the application of cyclic square wave voltammetry (CSWV) is shown in Figure 2. In this figure, an amalgamation process
has been considered with $\tau=2.5$ ms, $E_i=10$ mV and $E_w=25$ mV, $\gamma=0.8$, $\xi_i/\sqrt{t_u}=0.5$ s$^{-1}$ with 200 mV being the initial potential and -202.5 mV being the most negative one. The current response obtained in this technique is given by

$$\Delta \Psi = \Psi_{j'} - \Psi_{j-1}$$

$$\Psi_j = I_j \sqrt{\tau}$$

The potential sequence is given by [34].

$$E_j = E_{init} - (j-1) \frac{E_w}{2} - \frac{[1-(-1)^{j-1}]}{4} \left( E_{sw} + \frac{E_w}{4} \right)$$

The solid line corresponds to the case of a plane electrode, while the broken line corresponds to the case of a solution soluble product with $\xi_s/\sqrt{t_u}=0.5$ s$^{-1}$. As can be observed, the signals are practically coincident in both cases. In the case of amalgamation (dotted line) the signal is always higher, in absolute value, than in the previous cases. A greater effect is observed in the sweep towards positive potentials. This phenomenon is similar to that already described in the case of CSVV.

Equation (50) can be also used in cyclic voltammetry introducing the condition $\Delta E \to 0$. In general, values of $|\Delta E|<0.01$ mV lead to a good agreement between both results [20].

**NOTATION**

- $A$: electrode area
- $C_i(r,t)$: concentration profiles of the $i$ species (with $i=A$ or $B$) when the $j$-th potential step is applied
- $\tilde{C}_i(r,t)$: partial solution of the concentration profiles corresponding to the application of the $j$-th potential step

**CURRENT CONTROLLED TECHNIQUES.**

For these techniques we have demonstrated that the superposition principle can be applied in order to obtain the analytical expressions for the response of the system when we consider the following cases:

b1) Single electrode processes in cyclic chronopotentiometry with different current time functions, which take place on plane or spherical electrodes with constant or variable area and also on tubular electrodes. In the case of spherical electrodes, the superposition principle has also been applied to the study of the amalgamation of the product [16, 35].

b2) Multistep electrode processes and systems with several components in chronopotentiometry with programmed current when the electrode process takes place on plane or
spherical electrodes with constant or variable area [17].

In both cases, the applicability of the superposition principle is independent of the method used in solving the problem, due to the fact that the solutions have been obtained by a procedure based only on the linearity of the operators and on the related boundary value problem.

The theoretical background for the above superposition principle applications are the following:

b1) Cyclic Chronopotentiometry with different current-time functions for different electrode geometries and different behaviours of the reaction product.

b1A) Cyclic Chronopotentiometry

Let us consider the following charge transfer reaction whose cathodic and anodic reaction orders $a$ and $b$ can take any positive value and are coincident with the stoichiometric coefficients for species $A$ and $B$ according to the scheme,

$$aA + ne^{-} \underset{k_f}{\overset{k_b}{\rightleftharpoons}} bB$$

(11)

$k_f$ and $k_b$ are the rate constants of forward (reduction) and backward (oxidation) processes.

In this section we will analyse the response of this electrode process in Cyclic Chronopotentiometry, which is a powerful electrochemical technique whose obtainable information is similar to that of cyclic voltammetry [15]. However, the mathematical treatment is simpler, primarily because the total flux at the electrode surface at any time is known and constant.

Cyclic Chronopotentiometry is based on the application of successive and alternating sign current steps to an electrode, in the manner indicated in the following scheme,

$$\begin{align*}
I_1 & \quad 0 \leq t_1 < \tau_1 \\
-I_2 & \quad 0 \leq t_2 < \tau_2 \\
& \quad \vdots \\
(-1)^{j+1}I_j & \quad 0 \leq t_j < \tau_j \\
& \quad \vdots \\
(-1)^{k+1}I_k & \quad 0 \leq t_k < \tau_k
\end{align*}$$

(55)

with $I_j$ ($1 \leq j \leq k$) being the absolute value of each current step applied; $t_j$ is the time during which a $j$ current step is applied and $\tau_j$ is the time in which the change in sign is produced, as well as the absolute value. For the sake of simplicity, we will suppose that each reversal of the current is produced precisely at the moment that the transition time corresponding to the reduction process $A$ (forward) or to the reoxidation process $B$ (backward) is reached.

Thus, initially a constant cathodic current $I_1$ is applied during $0 \leq t_1 < \tau_1$ (with $\tau_1$ being the first forward transition time). At time $\tau_1$ the current is changed to an anodic value $-I_2$ during $0 \leq t_2 < \tau_2$ (with $\tau_2$ being the first backward transition time). The above operations can be continued by giving a series of forward ($\tau_1, \tau_2, \ldots$) and backward ($\tau_2, \tau_3, \ldots$) transition times, with the total time being:

$$t = \tau_1 + \tau_2 + \ldots + \tau_{j-1} + t_j$$

(56)

To deduce the general expressions corresponding to the response of the process (11) with this technique, we will consider:

- Different types of electrodes: we will obtain the solutions corresponding to planar, spherical and tubular electrodes of constant area and also planar and spherical electrodes of variable area, as is the case of the dropping mercury electrode with the expanding plane electrode model and the expanding sphere electrode model.

- Different behaviours of the reaction product: We will consider the case where the
reaction product is soluble in the solution, as is the case in which the reaction product is soluble in the electrode (amalgam formation).

The mass transport is described by the differential equation system,

$$\hat{D}_AC_A = \hat{D}_BC_B = 0 \quad (57)$$

where $\hat{D}_i$ ($i=A$ or $B$) is the diffusion operator corresponding to Fick's second law, which is given by equation (2) for expanding spherical ($z=2/3$) or stationary spherical ($z=0$) electrodes and by equation (3) for tubular electrodes. The operators corresponding to the expanding plane electrode model for the DME and to the stationary plane electrode can be easily obtained from the general expression (2) [28, 32]. As the operators defined by equations (2) and (3) are linear, the system of differential equations (57) is also linear in all cases.

We will carry out the general development for the diffusion operator corresponding to the expanding sphere electrode model since, from the solutions obtained for the same, we can deduce those corresponding to the expanding plane electrode model for a DME and to the spherical and plane stationary electrodes, as particular cases. In the case of tubular electrodes, (equation (3)), the procedure followed is similar. For dynamic electrodes, the first current step $I_0$ must be used after a blank period $t_{bl}$. This blank period does not exist in the case of electrodes of constant area [36].

The boundary value problem corresponding to the first step current is given by,

a) Reaction product soluble in the electrolytic solution

$$t_i = 0; r = r_b \right \ C_i(r,t) = C_{i0} \quad t_i > 0; r \to \infty \right \ C_i^t(r,t) = C_{i0} \quad (58)$$

b) Reaction product soluble in the electrode (amalgam formation)

$$t_i = 0; r = r_b \right \ C_i(r,t) = C_{i0} \quad t_i > 0; r \to \infty \right \ C_i^t(r,t) = 0 \quad (59)$$

$$t_i = 0; r < r_b \right \ C_A(r,t) = 0 \quad t_i > 0; r \to -\infty \right \ C_A^0(r,t) = C_A^0 \quad t_i > 0; r = r_b$$

$$\left( \frac{D_A}{a} \frac{\partial C_A^t}{\partial r} \right)_{r=r_b} - \left( \frac{D_B}{b} \frac{\partial C_B}{\partial r} \right)_{r=r_b} = \frac{I_0}{\pi r_b A(t)} \quad (60)$$

with

$$A(t) = A_0 t_0^{2/3} \quad (61)$$

and $A_0$ being the electrode area for a DME when $t_0 = 1$ s [32].

The superscript which appears in the concentration of species $A$ and $B$ will refer to the number of the current step being considered.

The solutions for the concentration profiles of species $A$ and $B$, $C_A^t(r,t)$ and $C_B^t(r,t)$, when the first step current, $I_0$, is applied, have been previously obtained and their values for the electrode surface, $C_A^0(r_0,t)$ and $C_B^0(r_0,t)$, are given in equations (18) and (19) in reference [37] with $m = -1/6$.

At $t = r_1$, the current is reversed to an anodic value $-I_2$ during the interval $0 \leq t \leq r_2$ ($t = r_1 + r_2$), with the reoxidation of species $B$ being produced.

The study of the application of the two successive, alternating sign current steps constitutes an electrochemical technique of great interest; "Current Reversal Chronopotentiometry". This technique was introduced in 1953 by Delahay [38], who obtained the solutions corresponding to a plane electrode when both species are soluble in the electrolytic solution.

The solutions corresponding to the second current step for any of the operators described by equation (2). $C_A^t(r,t)$ and $C_B^t(r,t)$, can be expressed, due to the linearity of the equation system (57), in the following manner,

$$C_A^t(r,t) = C_A^0(r,t) + \varepsilon A(r,t)$$

$$C_B^t(r,t) = C_B^0(r,t) + \varepsilon B(r,t)$$

$$\begin{cases} t_i = 0; r < r_b \right \ C_A(r,t) = 0 \\ t_i > 0; r \to -\infty \right \ C_A^0(r,t) = C_A^0 \\ t_i > 0; r = r_b \end{cases}$$

$$\left( \frac{D_A}{a} \frac{\partial C_A^t}{\partial r} \right)_{r=r_b} - \left( \frac{D_B}{b} \frac{\partial C_B}{\partial r} \right)_{r=r_b} = \frac{I_0}{\pi r_b A(t)} \quad (60)$$

$$A(t) = A_0 t_0^{2/3} \quad (61)$$

$$t_i = 0; r \geq r_b \right \ C_A^t(r,t) = C_A^t$$

$$t_i > 0; r \to \infty \right \ C_B^t(r,t) = C_B^t$$

$$t_i = 0; r \geq r_b \right \ C_A(r,t) = C_A^0$$

$$t_i > 0; r \to \infty \right \ C_B(r,t) = 0$$

$$\begin{cases} t_i = 0; r < r_b \right \ C_A(r,t) = 0 \\ t_i > 0; r \to -\infty \right \ C_A^0(r,t) = C_A^0 \\ t_i > 0; r = r_b \end{cases}$$

$$\left( \frac{D_A}{a} \frac{\partial C_A^t}{\partial r} \right)_{r=r_b} - \left( \frac{D_B}{b} \frac{\partial C_B}{\partial r} \right)_{r=r_b} = \frac{I_0}{\pi r_b A(t)} \quad (60)$$

$$A(t) = A_0 t_0^{2/3} \quad (61)$$

$$t_i = 0; r \geq r_b \right \ C_A^t(r,t) = C_A^t$$

$$t_i > 0; r \to \infty \right \ C_B^t(r,t) = C_B^t$$

$$\begin{cases} t_i = 0; r < r_b \right \ C_A(r,t) = 0 \\ t_i > 0; r \to -\infty \right \ C_A^0(r,t) = C_A^0 \\ t_i > 0; r = r_b \end{cases}$$

$$\left( \frac{D_A}{a} \frac{\partial C_A^t}{\partial r} \right)_{r=r_b} - \left( \frac{D_B}{b} \frac{\partial C_B}{\partial r} \right)_{r=r_b} = \frac{I_0}{\pi r_b A(t)} \quad (60)$$

$$A(t) = A_0 t_0^{2/3} \quad (61)$$

$$t_i = 0; r \geq r_b \right \ C_A(r,t) = C_A^0$$

$$t_i > 0; r \to \infty \right \ C_B(r,t) = 0$$

$$\begin{cases} t_i = 0; r < r_b \right \ C_A(r,t) = 0 \\ t_i > 0; r \to -\infty \right \ C_A^0(r,t) = C_A^0 \\ t_i > 0; r = r_b \end{cases}$$

$$\left( \frac{D_A}{a} \frac{\partial C_A^t}{\partial r} \right)_{r=r_b} - \left( \frac{D_B}{b} \frac{\partial C_B}{\partial r} \right)_{r=r_b} = \frac{I_0}{\pi r_b A(t)} \quad (60)$$

$$A(t) = A_0 t_0^{2/3} \quad (61)$$
where $C_A^j(r, t)$ and $C_B^j(r, t)$ are the solutions found in reference [37] for the first step current and $\tilde{C}_A^j(r, t)$ and $\tilde{C}_B^j(r, t)$ are the new unknown quantities to be determined.

For this second current step, the boundary value problem, taking into account equations (58)-(61), can be expressed only in terms of the new unknown quantities $\tilde{C}_A^j(r, t)$ and $\tilde{C}_B^j(r, t)$, and is given by,

\begin{align}
    t_2 = 0; r \geq r_0 & \quad \tilde{C}_A^j(r, t) = \tilde{C}_A^0(r, t) = 0 \\
    t_2 > 0; r \to \pm \infty & \quad \tilde{C}_A^j(r, t) = \tilde{C}_A^j(r, t) \\
    t_2 > 0; r = r_0 & \quad \frac{D_A}{a} \left( \frac{\partial \tilde{C}_A^j}{\partial r} \right)_{r=r_0} = -\frac{D_B}{b} \left( \frac{\partial \tilde{C}_B^j}{\partial r} \right)_{r=r_0} \\
    & \quad + \frac{D_A}{a} \left( \frac{\partial \tilde{C}_A^j}{\partial r} \right)_{r=r_0} = -\frac{(I_1 + I_2)}{nFA(t)} \\
\end{align}

(64)

(65)

(66)

The solutions for this second current step, $C_A^j(r, t)$ and $C_B^j(r, t)$, have been obtained in a previous paper and their expression for the electrode surface, $\tilde{C}_A^j(r_0, t)$ and $\tilde{C}_B^j(r_0, t)$, is given in equations (10) and (11) of reference [39].

For the $j$-th current step $(-1)^{j+1} I_j$, we can express the solution in the form,

\begin{align}
    C_i^j(r, t) &= C_i^{j+1}(r, t) + \tilde{C}_i^j(r, t) \quad i = A \text{ or } B \\
    \text{where,} \\
    C_i^{j+1}(r, t) &= C_i(r, t) + \sum_{n=1}^{j+1} \tilde{C}_i^n(r, t) \\
\end{align}

(67)

And from equations (64)-(67) it is easy to demonstrate through induction that the boundary value problem for any current step $(-1)^{j+1} I_j$ with $j > 1$, is given by,

\begin{align}
    t_2 = 0; r \geq r_0 & \quad \tilde{C}_A^j(r, t) = \tilde{C}_A^j(r, t) = 0 \\
    t_2 > 0; r \to \pm \infty & \quad \tilde{C}_A^j(r, t) = \tilde{C}_A^j(r, t) \\
    t_2 > 0; r = r_0 & \quad \frac{D_A}{a} \left( \frac{\partial \tilde{C}_A^j}{\partial r} \right)_{r=r_0} = -\frac{D_B}{b} \left( \frac{\partial \tilde{C}_B^j}{\partial r} \right)_{r=r_0} \\
    & \quad + \frac{D_A}{a} \left( \frac{\partial \tilde{C}_A^j}{\partial r} \right)_{r=r_0} = -\frac{(I_1 + I_2)}{nFA(t)} \\
\end{align}

(68)

(69)

(70)

Since the boundary value problem can be expressed in a general form for any current step $(-1)^{j+1} I_j$, with $j > 1$, the surface concentrations of species $A$ and $B$ for any step can be expressed as a sum of $j$ terms. In these conditions the superposition principle is fulfilled and the following is obtained

\begin{align}
    \frac{C_A^j(r_0, t)}{C_A^0} &= 1 - \\
    & \quad -N_s a \frac{1}{t_s^{3/2}} \sum_{n=1}^{j} (-1)^{n+1} \frac{I_n}{I_1} H_n, a (1 + Q_n) \\
    \frac{C_B^j(r_0, t)}{C_A^0} &= C_B^0 + \\
    & \quad + b \gamma_{A,B} N_s \frac{1}{t_s^{3/2}} \sum_{n=1}^{j} (-1)^{n+1} \frac{I_n}{I_1} H_n, B (1 + Q_n) \\
\end{align}

(71)

(72)

with,

\begin{align}
    N_s &= \frac{2I_1}{nFA_D A_C} \\
    \gamma_{A,B} &= \sqrt{\frac{D_A}{D_B}} \\
    Q_n &= \frac{I_n - I_{n-1}}{I_n} \quad \text{if } n > 1 \\
    Q_1 &= 0 \\
\end{align}

(73)

(74)

(75)
$H_{n,j}$ (with $i = A$ or $B$) and $t_{n,j}$ are given by equations (A1) and (A4) respectively of the Appendix. When species $B$ is amalgamated into the electrode we must change $(\xi_{Bn})$ to $(-\xi_{Bn})$ in the $H_{n,s}$ series in equation (72) (see Appendix).

To obtain the transition time corresponding to the $j$-th current step, $(-1)^{n+1}I_j$, we must impose that the concentration of the species that is oxidised or reduced be zero in the surface of the electrode.

If $j$ is odd, a reduction process will take place. By imposing that $C_j'(r_0, r_1, + \ldots + r_j) = 0$ in (71), we obtain the transition time for the reduction of species $A$.

\[
\frac{(t_{n,p} + \tau_{n,j})^{2/3}}{\alpha N_s} = \sum_{n=1}^{j} (-1)^{n+1} \frac{I_n}{I_1} (r_{n,j})^{1/2} H_{n,A}(1 + Q_n)
\]  

(76)

If $j$ is even, an oxidation process will be produced. By imposing $C_j'(r_0, r_1, + \ldots + r_j) = 0$ in (72), we obtain analogously the previous case for the transition time corresponding to the oxidation of species $B$.

\[
-\frac{(t_{n,p} + \tau_{n,j})^{2/3}}{\beta Y_{A,B} N_s} = \frac{C_j}{C_B} \sum_{n=1}^{j} (-1)^{n+1} \frac{I_n}{I_1} (r_{n,j})^{1/2} H_{n,B}(1 + Q_n)
\]  

(77)

In these equations, $\tau_{n,j}$ is given by,

\[
\tau_{n,j} = \sum_{m=n}^{j} \tau_m
\]  

(78)

Equations (76) and (77) for the particular case of a stationary plane electrode ($r_0 \to \infty$ and $t_{n,p} \gg t$) of fixed area $A = A_{dp}^{2/3}$ coincide with those obtained by Herman and Bard (equations (8) and (9), respectively in reference 15). In the case of spherical electrodes equations (76) and (77) coincide with those deduced in reference 40 in the particular situation in which $j = 2$ (Current Reversal Chronopotentiometry).

From equations (71) and (72) for the surface concentrations obtained for an expanding spherical electrode model, it is possible to obtain those solutions corresponding to the expanding plane electrode model by making $r_0 \to \infty$ in the series $H_{n,s}$, of equations (71)-(72) and (76)-(77). If in the previous equations we make $t_{n,p} \gg t$, the expanding spherical electrode behaves like an electrode of constant area $A = A_{dp}^{2/3}$ (see NOTATION) making the series $H_{n,s}$ of equations (71)-(72) and (76)-(77) take the form given by equation (A7).

The general expression of the potential-time response corresponding to each current step can be easily obtained by introducing the expressions obtained for the surface concentrations (equations (71) and (72)) in the Butler-Volmer equation. So we deduce,

\[
\frac{I_j}{nFA_k} \frac{e^{\eta(t)}}{e^{\eta(t_0)}} = (-1)^{j+1} \left[ C_j'(r_0, t) \right]^p - \left[ C_j'(r_0, t) \right]^b \right]
\]

(79)

where,

\[
\eta(t) = \frac{nF}{RT} (E(t) - E^*)
\]  

(80)

Finally, the solution corresponding to tubular electrodes is obtained by substituting in (71)-(72) series $H_{n,s}$ for series given by equation (A9). To deduce the cyclic chronopotentiometric response in tubular electrodes (see equation (3)), we have taken into account the solution found by Aoki et al. for the application of a single current step [41] since we have shown that the superposition principle is fulfilled.

Figure 3 shows how the influence of the amalgam formation, which does not affect the first transition time $\tau_1$, makes the even transition times
increase in relation to those obtained when $B$ is soluble in the solution, the more so, the higher the number of the current steps applied. In the transition times corresponding to the reduction of $A$ for $j=3,5,...$, this effect is also obtained, but its origin is different. This behaviour can be used in the laboratory to characterise the amalgamation in a more conclusive manner than the proposal in reversal current chronopotentiometry, in which only two current step are applied.

**b1B) Cyclic Chronopotentiometry with a power current-time function**

In this case, we will apply successive and alternating sign power current-time functions in the manner indicated by the following scheme.

\[
\begin{align*}
I_1 t_1^\alpha & \quad 0 \leq t_1 < \tau_1 \\
-I_2 t_2^\beta & \quad 0 \leq t_2 < \tau_2 \\
& \quad \vdots \\
(-1)^{j+1} I_j t_j^\gamma & \quad 0 \leq t_j < \tau_j \\
& \quad \vdots \\
(-1)^{k+1} I_k t_k^\delta & \quad 0 \leq t_k < \tau_k
\end{align*}
\]  

(81)

to a stationary spherical electrode as the SMDE.

The solution of this problem is more complex. The solutions corresponding to the first power current-time function, $C_1(t_0, t)$ and $C_1(t_0, t)$, are given by the equations (18) and (19) of reference 37 with $t_0 \gg t$ and, by following a procedure similar to that of the case b1A, we obtain the following general expressions for the surface concentrations of species $A$ and $B$, $C_k(t_0, t)$, for any power current-time function $(-1)^{j+1} t_j^\gamma$ with $j > 1$ [16].

\[
\begin{align*}
\frac{C_1(t_0, t)}{C_2} = & \ 1 - \\
& -N_{e\beta} \sum_{n=1}^{j} (-1)^{n+1} I_1 t_1^{\eta+1/2} \left[ S_{n, A} - T_{n, A+1, A} \right] \\
\end{align*}
\]  

(82)

\[
\begin{align*}
\frac{C_2(t_0, t)}{C_1} = & \ \frac{C_1}{C_2} + \\
& +b_1 \gamma_{A,B} N_{e} \sum_{n=1}^{j} (-1)^{n+1} I_1 t_1^{\eta+1/2} \left[ S_{n, B} - T_{n, A+1, B} \right] \\
\end{align*}
\]  

(83)

$S_n$, and $T_{n+1, i}$, with $i=A$ or $B$ are given by equations (A10) and (A11) in the Appendix. For the case of a linear current-time function $(-1)^{j+1} t_j$ (see equation (81) with $\eta=1$) equations (82) and (83) are notably simplified. In the case of planar diffusion, these solutions coincide with
those obtained by Murray and Reilley for the case of two linear current-time functions (see equation (50) in reference 40).

The general expression of the potential-time response corresponding to each power current-time function can be obtained, as in the previous case, by introducing the expressions obtained for the surface concentrations (equations (82) and (83)) in the Butler-Volmer equation.

\[
\begin{align*}
I_1 e^{\alpha_1 t} & \quad 0 \leq t_1 < \tau_1 \\
-I_2 e^{\alpha_2 t} & \quad 0 \leq t_2 < \tau_2 \\
& \vdots \\
(-1)^{j-1} I_j e^{\alpha_j t} & \quad 0 \leq t_j < \tau_j \\
& \vdots \\
(-1)^{k-1} I_k e^{\alpha_k t} & \quad 0 \leq t_k < \tau_k 
\end{align*}
\]  

(84)

to a stationary spherical electrode as the SMDE.

Figure 4. Cyclic chronopotentiometry with a power current-time function. Influence of the exponent \( \alpha \) of the power current-time function on the potential-time curves for an irreversible process (\( k = 10^4 \text{ cm.s}^{-1} \)) corresponding to an SMDE. \( N_s = 2.5 \text{ s}^{-1/2} \), \( r_s = 0.06 \text{ cm} \), \( \alpha = 0.5 \). The values of the exponent of the power current-time function are: a) 0, b) 0.5 and c) 1. Other conditions as in Figure 5.

Figure 4 shows the cyclic potential-time response for an irreversible electrode process for three different values of the exponent of the power current-time function, given by equation (81). As can be noticed, the system behaves more and more irreversible when the exponent of \( t \) decreases (the cathodic branches of the curves are shifted to more negative potentials and the anodic ones to more positive potentials) as has been reported in previous papers [36].

b1C) Cyclic Chronopotentiometry with an exponential current-time function

In this case, we will apply the following exponential current-time function in an analogous way to the two previous cases,

\[
\begin{align*}
\frac{C_A'}{(r_0,t)} & = 1 - \\
-N_s & \sum_{n=1}^{N_s} (-1)^{n-1} \frac{\beta_n}{I_1} (t_n(t_{n+1}))^{1/2} (X_n + Q_n) M_{n,t} \\
\frac{C_D'}{(r_0,t)} & = C_A' + \\
+b & N_s \sum_{n=1}^{N_s} (-1)^{n-1} \frac{\beta_n}{I_1} (t_n(t_{n+1}))^{1/2} (X_n + Q_n) M_{n,B} 
\end{align*}
\]  

(85)

where

\[
\begin{align*}
X_n &= e^{\alpha r_n - 1} \quad \text{if } n > 1 \\
X_1 &= 1
\end{align*}
\]  

(87)
and with \( \tau_{n-1} \) being the transition time of the \((n-1)\) exponential current-time function applied. \( M_{ij} \) (with \( i=A \) or \( B \)) is given by equation (A16) in Appendix. \( Q_i \) is given by equation (72).

**b2) Multistep electrode processes and systems with several components in chronopotentiometry with programmed current**

**b2A) Multistep electrode processes in chronopotentiometry with programmed current**

Let us suppose that species \( O_i \) is reduced in \( k \) stages in line with the following scheme:

\[
\begin{align*}
O_i + n_i e^- & \rightleftharpoons O_i^0 & E_i^0 \\
O_i + n_2 e^- & \rightleftharpoons O_i^0 & E_i^0 \\
& \vdots & \\
O_i + n_i e^- & \rightleftharpoons O_i^0 & E_i^0 \\
& \vdots & \\
O_i + n_k e^- & \rightleftharpoons O_i^0 & E_i^0
\end{align*}
\]

(III)

Process (III) can only be studied with techniques using a programmed current for the case in which the reduction potentials for the individual charge transfer steps are sufficiently well separated for the chronopotentiometric response or potential-time curve to show perfectly defined \( k \) waves, each of which corresponds to individual steps in the overall process \([1, 2, 38, 42]\). In any other case the initial and boundary conditions of this problem cannot be reliably established in terms of time.

If we apply a cathodic current-time function \( I(t) \) of the form

\[
I(t) = I_0 t^u e^{-\alpha t} \quad \text{with} \quad I_0 > 0, \ u \geq -1/2, \ \forall \ alpha
\]

(88)

when \( O_i \) is the only species initially present in the solution - which contains an excess of any electrolyte so that transport through conduction need not be taken into account - mass transport from the bulk of the solution to the electrode surface, for process (III) is described by the differential equation system

\[
\hat{D}_{ij} \cdot C_{O_i} = 0 \quad \text{for} \quad i = 1, 2, \ldots, k + 1 \quad (89)
\]

where \( \hat{D}_{ij} \) is the diffusion transport operator given by Fick's second law given by equation (2) applied to species \( O_i \). As this operator is linear, the system of differential equations (89) is also linear in all cases \([28, 43]\).

In this section, we will consider the operator corresponding to a DME since it is the most complex and, it is possible to deduce the solutions which correspond to remaining, simpler models as particular cases of the solutions found for the DME.

We will suppose that using a function generator \([4]\) we apply the current-time function given by equation (88), which is reduced to a power function of time when \( \alpha = 0 \) \((I(t) = I_0 t^u)\), to an exponential function of time when \( u = 0 \) \((I(t) = I_0 e^{\alpha t})\), and to a current step or constant current when \( u = \alpha = 0 \) \((I(t) = I_0)\). In general, this current-time function must be used after a blank period, if it is applied to dynamic electrodes such as the DME. This blank period has no physical significance in stationary electrodes.

In order to analyse the response of process (III) to the application of a programmed current given by equation (88), we will suppose, as hitherto expounded, that the normal potentials corresponding to the different steps fulfil the condition

\[
E^0_{j-1} \ll E^0_j \ll E^0_{j+1} \quad (90)
\]

and that step \( j \) takes place during a time \( t_j (0 \leq t_j \leq \tau_{j+1}) \), with \( \tau_{j+1} \) being the transition time of species \( O_j \). When \( t_j = \tau_{j+1} \), the electrode surface concentration of species \( O_j \) becomes zero. We must keep in mind, moreover, that the reduction of
Superposition principle in the analysis of electrochemical techniques

with \( t \) given by equation (91). Henceforth, the superscript of the concentrations of different \( O_j \) species (with \( j=1, 2, ..., k+1 \)) refers to the number of the step being considered.

Taking into account that for any intermediate step \( j \geq 1 \), the condition

\[
C_{O_j}^j(t_0,t) = C_{O_{j+1}}^j(t_0,t) = \ldots = C_{O_{j+2}}^j(t_0,t) = 0 \quad (931)
\]

for the previous \( j \)-1 steps is fulfilled, since \( j \)-1 transition times have already been attached, it is easily demonstrated by induction that the boundary value problem is only dependent on the unknown quantities \( \tilde{C}_{O_j}^i \) (\( i=1, 2, ..., j+1 \)) and on the concentration of the species \( O_j \) in the previous step. These adopt the following general form for any intermediate step \( j \) with \( 3j \leq k \) and \( t \) given by equation (91)

\[
\begin{align*}
\begin{cases}
t_j = 0; r \geq r_0 & \\
t_j > 0; r \to \infty & \tilde{C}_{O_j}^i(r,t) = 0 \quad i = 1, \ldots, j+1
\end{cases}
\end{align*}
\]

\[
t_j > 0; r = r_0
\]

\[
\begin{align*}
& \tilde{C}_{O_j}^i(r_0,t) = 0 \quad i = 1, 2, \ldots, j-2 \\
& \tilde{C}_{O_{j+1}}^i(r_0,t) = -C_{O_{j+1}}^{j-1}(r_0,t) \\
& \sum_{i=1}^{j} D_{O_j} \int_{r=r_0}^{r_1} \frac{\tilde{C}_{O_j}^i}{\sigma} dr = 0 \quad (97)
\end{align*}
\]

Therefore, for \( j \geq 3 \), the superposition principle is fulfilled [28] since the general expressions of the boundary value problem for any step \( j \) with \( 3j \leq k \) (equations (94)-(98)) are identical to those for the third step, i.e. we have reduced a problem of \( k \) steps to one of independent \( k \) problems of only one step. Taking into account the solutions found for the first and second steps and conditions (94)-(98), we deduce that the
concentrations of the different species for j≥2 adopt the following, recurrent general expressions [35].

\[
C_j^i(r_0, t) = C_{j-1}^i(r_0, t) + \frac{D_{j-1}}{D_{j}} \frac{n_{j-1}}{n_j} C_{j-1}^i(r_0, t) G_{j-1, j}^i \tag{99}
\]

\[
C_{0,n}^j(r_0, t) = -\frac{D_{0,n}}{D_{0,m}} \frac{n_{j-1}}{n_j} C_{0,n-1}^j(r_0, t) G_{0,n}^j \tag{100}
\]

where

\[
G_{j, 0}^i, 0 = 1 - \left(1 - \frac{D_{j}}{D_{0}} \left[4 \left(\frac{D_{j}}{D_{0}} \frac{t_j}{r_0^2} \right) \left(1 - \left(\frac{1}{4} - \frac{1}{48} (\rho_j)^3 \right) \right) \right] \right) \left(\frac{t_j}{t_{t_{0j}} + \ldots + t_{t_{0,n_j}} + t_j} \right)^{\frac{3}{2}} \tag{101}
\]

\[
\rho_j = \left(\frac{t_j}{t_{t_{0j}} + \ldots + t_{t_{0,n_j}} + t_j} \right)^{\frac{3}{2}} \tag{102}
\]

In equation (101) \(i = 1, 2, \ldots, k-1\) and \(i = i+1\) or \(i = i+2\). For planar electrodes and for planar and spherical electrodes with \(D_j = D_{j+1} = \ldots = D_{j+n_j}\), we obtain,

\[
G_{j, 0}^i, 0 = 1 \tag{103}
\]

Owing to the simplicity of equations (99) and (100) and the ease of their calculation implied by their recurrent form, they offer important advantages in finding the concentrations of the different intermediate species and the different transition times. The determining of the transition time of the \(j\) step is immediate, since it suffices to make \(C_j^i(r_0, t) = 0\) in equation (99) with \(t = t_{t_{0j}} + t_{t_{02}} + \ldots + t_{t_{0j}}\).

b2B) Systems with several components in chronopotentiometry with programmed current.

The reaction scheme in this case is given by

\[
O_i + n_i e^- \rightarrow R_i \quad E_{i}^0
\]

\[
O_j + n_j e^- \rightarrow R_j \quad E_{j}^0
\]

\[
\vdots
\]

\[
O_l + n_l e^- \rightarrow R_l \quad E_{l}^0
\]

(IV)

Following a similar procedure to the above, it is possible to generalise the boundary value problem for any \(j>2\) step in the following way.

\[
t_j = 0; r \geq r_0
\]

\[
t_j > 0; r \to \infty
\]

\[
C_j^i(r, t) = C_j^i(r, t) = 0 \quad i = 1, \ldots, j
\]

\[
t_j > 0; r = r_0
\]

\[
C_j^i(r_0, t) = 0 \quad i = 1, 2, \ldots, j - 2
\]

\[
C_j^i(r_0, t) = -C_j^i(r_0, t)
\]

\[
\sum_{i=1}^{j} D_{ij} n_j \left(\frac{\partial C_j^i}{\partial r}\right)_{r=r_0} = 0 \tag{107}
\]

\[
D_{ij} \left(\frac{\partial C_j^i}{\partial r}\right)_{r=r_0} = -D_{ij} \left(\frac{\partial C_j^i}{\partial r}\right)_{r=r_0} \quad i = 1, 2, \ldots, j \tag{108}
\]

The solution to this problem is simpler than the previous one due to the absence of reaction intermediates which might complicate the overall process (see scheme IV). Under these conditions, the surface concentration expressions of species \(O_j\) and \(R_j\), \(C_j^i(r_0, t)\) and \(C_j^i(r_0, t)\), are given by [35],

\[
C_j^i(r_0, t) = C_{j-1}^i + \frac{D_{j-1}}{D_j} \frac{n_{j-1}}{n_j} C_{j-1}^i(r_0, t) G_{j-1, j}^i \tag{109}
\]
\[
C_i' (r_0, t) = \sqrt{\frac{D_{O_i}}{D_{O_j}}} \frac{C_{O_i} (r_0, t)}{n_j} \quad G_{O_i, ... h_j}
\]

(110)

\( G_{O_i, ... h_j} \) in equation (110) is also given by equation (98) by changing \( D_{O_i} \) for \( D_{O_j} \).

In the case of planar diffusion, these solutions coincide with those obtained by Kambara and Tachi [45].

**NOTATION**

- \( C_i' (r, t) \): concentration profiles of the \( i \) species (with \( i = A \) or \( B \)) for the \( j \)-th current-time function applied in cyclic chronopotentiometry with any current-time function.
- \( r_j \): \( j \)-th transition time in cyclic chronopotentiometry with any current-time function.
- \( a, b \): cathodic and anodic reaction orders respectively.
- \( k_f \) and \( k_b \): rate constants of forward and backward electrode processes.
- \( C_{O_j} (r, t) \): concentration profiles of species \( O_j \) in the \( j \)-th step (\( l \geq j \)) in multistep electrode processes or systems with several components.
- \( \tau_{O_j} \): transition time of species \( O_j \) for which the condition \( C_{O_j} (r_0, \tau_{O_j} + \ldots + \tau_{O_j}) = 0 \) is fulfilled.
- \( E_j^2 \): normal redox potential of the \( j \)-th step in multistep electrode processes or systems with several components.
- \( n_j \): number of electrons transferred in the \( j \)-th step in multistep electrode processes or systems with several components.
- \( D_{O_i} \): diffusion coefficient of species \( O_i \) in multistep electrode processes or systems with several components.
- \( t_j \): length of time of the application of the \( j \)-th current-time function or time during which the \( j \)-th step takes place in cyclic chronopotentiometry with any current-time function and in multistep electrode processes or systems with several components, respectively.
- \( t \): electrolysis time (elapsed between the beginning of the application of current and the measurement of the potential).
- \( r \): distance from the centre of the spherical electrode.
- \( r_0 \): radius for a DME.
- \( \tau_{BP} \): time-dependent electrode radius for an SMDE.
- \( t_w \): blank period used only for a DME.
- \( t_s \): total time (= \( t_{BP} + t \)).
- \( A(t) \): time-dependent electrode area of a DME (= \( \frac{A(t_{BP})}{t} \)).
- \( A \): electrode area (= \( \frac{A(t_{BP})}{t} \)) when \( t_{BP} \gg t \) (static spherical or planar electrodes).
- \( \text{DME} \): dropping mercury electrode.
- \( \text{SMDE} \): static mercury dropping electrode.

Other definitions are conventional.

**APPENDIX**

1) **Cyclic Chronopotentiometry**

The \( H_{n,i} \) series, with \( i = A \) or \( B \), in
equations (71) and (72) has a general expression which does not depend on the step current considered,

\[ H_{n,t} = F(\beta_n)\xi_n, F(\beta_n) + (\xi_n)^2 F_2(\beta_n) \]  

(A1)

where,

\[ \beta_n = \left( \frac{t_{n,t}}{t_{n,e} + t_{n,i}} \right)^{\frac{1}{3}} \]  

(A2)

\[ \xi_n = 2 \sqrt{D_f n} / \xi_0^{\frac{1}{3}} \]  

(A3)

\[ t_{n,i} = \sum \xi_n + t_i \]  

(A4)

\[ t_{n,t} = t_i \]

\[ F(\beta_n) = \frac{1}{2^{1/2}} \left( 1 + \frac{1}{9} \beta_n^2 + \frac{7}{270} \beta_n^4 + \frac{4}{567} \beta_n^6 + \frac{11}{5812} \beta_n^8 + \ldots \right) \]  

\[ F_1(\beta_n) = \frac{1}{4} \left( 1 + \frac{1}{4} \beta_n^2 + \frac{1}{16} \beta_n^4 + \frac{11}{5812} \beta_n^8 + \ldots \right) \]  

\[ F_2(\beta_n) = \frac{1}{6\pi^{1/2}} \left( 1 + \frac{2}{5} \beta_n^2 + \ldots \right) \]  

(A5)

with \( \xi \) being the electrode radius when \( t_{n} = 1 \) s [32].

Throughout this appendix, when two signs appear, the upper sign in any equations refers to a reaction product which is soluble in the electrolytic solution whilst the lower sign corresponds to a product which is amalgamated in the electrode (this is equivalent to change \((\xi_{+})\) to \((\xi_{-})\)).

**Particular cases of the \( H \)-series**

a) If \( r_0 \to \infty \) \((\xi_{n,e} = 0)\) the above expressions are simplified notably and become those corresponding to an expanding plane electrode. So, equation (A8) is simplified to

\[ H_{n,t} = F(\beta_n) \]  

(A6)

b) Making \( t_{n,t} \gg t_i \) in equations (A1) and (A2) we obtain the expressions corresponding to a static mercury dropping electrode (SMDE) of area \( A = A_{f_{n}} \). In this situation, equation (A8) becomes,

\[ H_{n,t} = \pm \frac{1}{\xi_{n,t}} \left[ 1 - \exp \left( \frac{\xi_{n,t}}{2} \right) \right] \left( 1 - \text{erf} \left( \frac{\xi_{n,t}}{2} \right) \right) \]  

(A7)

c) If \( r_0 \to \infty \) and \( t_{n,t} \gg t_i \), we deduce the equations corresponding to a stationary plane electrode of area \( A = A_{f_{n}} \) and equation (A8) is transformed to

\[ H_{n,t} = \frac{1}{\pi^{1/2}} \]  

(A8)

d) For a tubular electrode, the mathematical treatment for the first current step is given in reference [41] and for any current step \( i = 1 \) we deduce, taking into account that the superposition principle is fulfilled, that the series \( H_{n,i} \) in equations (71) and (72) is given by,

\[ H_{n,i} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{8} \xi_{n,i} \right) + \frac{1}{16} \xi_{n,i}^2 - \frac{3}{256} \xi_{n,i}^3 + \frac{21}{2560} \xi_{n,i}^4 - \frac{9}{4096} \xi_{n,i}^5 + \frac{3}{286720} \xi_{n,i}^6 + \ldots \]  

(A9)

2.) Cyclic chronopotentiometry with a power current-time function on a SMDE

The series \( S_{i,t} \) and \( T_{i,m,n,i} \), with \( i = A \) or \( B \), in equations (82) and (83) have the following expressions:

\[ S_{i,t} = \frac{1}{P_{2u+1}} \left( \frac{1}{2u+2} \right) \frac{\sqrt{D_f_{n,j}}}{r_0^2} + \frac{2}{(2u+3)P_{2n+1}} \frac{1}{r_0^2} \left( \frac{D_{f_{n,j}}}{r_0^2} \right)^{3/2} + \frac{4}{(2u+3)(2u+5)P_{2n+1}} \frac{D_{f_{n,j}}}{r_0^2} \pi \ldots \]  

(A10)
\[ T_{x+1,i} = \beta_0(\lambda_{n+1}) \beta_1(\lambda_{n+1}) \sqrt{D_{l(n+1),i}} + \]
\[ + \beta_3(\lambda_{n+1}) \frac{D_{l(n+1),i}}{r_0^3} + \beta_3(\lambda_{n+1}) \left( \frac{D_{l(n+1),i}}{r_0} \right)^{3/2} + \]
\[ + \beta_3(\lambda_{n+1}) \sum_{n < j} \left( \frac{D_{l(n+1),j}}{r_0} \right)^{3/2} \]

where,
\[ \lambda_{n+1} = \left( \frac{t_{x+1/2}}{t_{x+1}} \right)^{1/2} \tag{A11} \]

\[ R_0(x) = \frac{1}{\sqrt{\pi}} \left[ x - \frac{u}{3} x^3 + \frac{u(u-1)}{10} x^5 - \frac{u(u-1)(u-2)}{42} x^7 + \ldots \right] \]
\[ R_1(x) = \frac{1}{2} \sqrt{\frac{1}{3}} \left[ x - \frac{u}{5} x^3 + \frac{u(u-1)}{12} x^5 - \frac{u(u-1)(u-2)}{48} x^7 + \ldots \right] \]
\[ R_2(x) = \frac{2}{\sqrt{\pi}} \left[ x - \frac{u}{5} x^3 + \frac{u(u-1)}{14} x^5 - \frac{u(u-1)(u-2)}{54} x^7 + \ldots \right] \]
\[ R_3(x) = \frac{1}{\sqrt{3}} \left[ x - \frac{u}{5} x^3 + \frac{u(u-1)}{16} x^5 - \frac{u(u-1)(u-2)}{60} x^7 + \ldots \right] \]
\[ R_4(x) = \frac{4}{3} \sqrt{\frac{1}{5}} \left[ x - \frac{u}{5} x^3 + \frac{u(u-1)}{18} x^5 - \frac{u(u-1)(u-2)}{66} x^7 + \ldots \right] \tag{A12} \]

3.) Cyclic chronopotentometry with an exponential current-time function on a SMDE

The series \( M_{n+1} \), with \( i = A \) or \( B \), in equations (85) and (86) have the following expression:

\[ M_{n+1} = \sum_{k=0}^{\infty} \left( \frac{1}{r_{2k+1}} \right)^{1/2} \left( \frac{D_{l(n+1),j}}{r_0} \right)^{3/2} + \]
\[ + \frac{2}{(2k+3)(2k+5)^2} \frac{D_{l(n+1),j}^2}{r_0^2} + \frac{4}{(2k+3)(2k+5)^2} \frac{D_{l(n+1),j}^2}{r_0^2} + \ldots \]

where,
\[ \Omega_n = \omega t_{x+1} \tag{A13} \]

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