General analytical solution for a reversible 1/2 response to a double potential step at spherical electrodes in the absence/presence of amalgamation effects

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The general rigorous theory corresponding to double potential step chronocoulometry for a reversible charge transfer reaction in a spherical electrode whose area increases with \( t \), where \( \zeta > 0 \), is presented. The static mercury drop electrode (\( \zeta = 0 \)) and the dropping mercury electrode (\( \zeta = 2/3 \)) are addressed specifically. The explicit equations for the current versus time response assuming unequal diffusion coefficients for the oxidized and reduced species are valid when the product is soluble in both the electrolytic solution and the electrode. Comparisons with previous general treatments in the literature are made. The theory is applied to the detection of amalgamation in RP and DNP techniques. Moreover, in this work we show the origin of errors appearing in some general treatments in the literature, these errors lead to physically meaningless results when amalgamation takes place.


On présente la théorie générale rigoureuse correspondant à la chronoamperméométrie avec une étape à double potentiel d'une réaction réversible de transfert de charge dans une électrode sphérique dont la surface augmente comme \( t \), où \( \zeta > 0 \). On examine d'une façon spécifique les cas des électrodes avec goutte de mercure statique (\( \zeta = 0 \)) et avec goutte de mercure tombante (\( \zeta = 2/3 \)). Les équations explicites pour le courant en fonction du temps de réponse, en supposant des coefficients de diffusions différents pour les espèces oxydées et réduites, sont valides lorsque le produit est soluble dans le solution électrolytique ainsi que dans l'électrode. On présente des comparaisons avec les traitements généraux rapportés précédemment dans la littérature. On applique la théorie à la détection d’amalgamation dans les techniques de RP et de DNP.

De plus, dans ce travail, on montre l’origine des erreurs qui apparaissent de quelques traitements généraux rapportés dans la littérature et qui, lorsqu’une amalgamation se produit, rendent les résultats physiquement sans signification.

[Traduit par la rédaction]

Introduction

In this paper we study the application of a double potential pulse to a reversible charge transfer process at stationary and nonstationary spherical electrodes. We consider the general case when the diffusion coefficients of the oxidized and reduced species are different, and the reduced species can dissolve in the electrolytic solution as well as in the electrode. In order to obtain an exact expression for the response corresponding to the second potential pulse, it is essential to consider the perturbation of the second pulse on the concentration profiles generated by the first potential pulse. Previous investigators (1, 2) have neglected this perturbation.

The difficulties in the calculation of the response to the second potential step for a spherical electrode arise from surface concentrations which are dependent on potential, diffusion coefficients, and time (3–5). Birke et al. (6) first reported that it was necessary to account for the variation of the concentration profiles obtained with the first pulse during the application of the second pulse. They found that this variation can be neglected only when both species are soluble and have equal diffusion coefficients.

The Koutecky approximation has been used when amalgamation is present (7), and the mathematical procedure developed in this work shows clearly that this approximation is valid for any value of the time of application of the second pulse. This can be easily verified from the analytic expressions obtained in this work for a Static Mercury Drop Electrode (SMDE) and a Dropping Mercury Electrode (DME). In the case of SMDE, the expression of \( i_2 \) is simple enough to permit direct match of the theoretical and experimental results. We have applied our equations to the study of double potential step chronocoulometry, and we have analyzed the influence of the electrode sphericity and amalgamation on the \( i-t \) response. The same considerations have been made for reverse pulse and differential normal pulse techniques. For reverse pulse techniques we have proposed a condition for the formation of amalgam based on measurements of the cathodic and anodic diffusion currents. Brumleve et al. (8) have used the reverse pulse technique to study the influence of spherical diffusion at a SMDE, for processes with and without amalgamation. They used numerical methods to obtain a complicated analytical solution for only the limiting current. Goodisman (5) solved the problem for a SMDE alone did not give explicit solutions that are directly applicable to double pulse techniques. The effect of amalgamation in differential pulse techniques has been studied experimentally for a DME (9) and a SMDE (10). These works clearly demonstrate the lack of a suitable theory that accounts quantitatively for the effect of amalgamation in double pulse techniques.

The equations derived in this paper are applied to double potential step chronoamperometry, reverse pulse (RP) and
differential normal pulse (DNP) techniques to analyze the influence of electrode sphericity and amalgamation on the i-t response. In RP, a criterion for the formation of amalgam based on the measurements of cathodic and anodic currents is proposed. Single pulse techniques including normal pulse (NP), dc voltammetry, or polarography are also considered. Our results do not differ from those previously reported (1, 3, 4, 11) because single pulse techniques do not suffer from the concentration perturbations that must be considered in double pulse methods.

**Theory**

Consider the following charge-transfer.

\[ A + ne^- \rightarrow B \]

Let us consider a spherical electrode with its area increasing as a power of time, \( q(t) = q_0 t^z \) (\( z = 0 \) for a SMDE and \( z = 2/3 \) for a DME), and a reversible charge transfer such that the potential is set at the value \( E_1 \) in the interval \( 0 \leq t \leq t_1 \) and stepped from \( E_1 \) to \( E_2 \) at the time \( t \geq t_1 \) (see Fig. 1). The current for each pulse will be called \( i_1 \) and \( i_2 \) respectively. See footnote 2 for notations.

The concentration profiles in the interval \( 0 \leq t \leq t_1 \) are given in ref. 1a.

\[ C_A^*(r, t) = C_A^*(s_1A, \xi_1A) = \rho_0(s_1A) + \xi_1A \rho_1(s_1A) \]

\[ \xi_1 = \xi_1^{10^{(r-1)/2}} \] (or eq. [5])

\[ \xi_2 = \xi_2 \sqrt{(2z + 1)B} \]

Time elapsed between the application of the first and second pulse

\[ t = t_1 + t_2 \]

Time elapsed between the second pulse application and the measurement of the current

\[ \gamma = \sqrt{\frac{D_A}{D_B}} \]

\[ K_i = \exp \left[ \frac{nF(E_i - E_0)}{RT} \right] \]

When two signs appear, the upper sign refers to a solution soluble product and the lower sign to amalgam formation. Other definitions are conventional.

**Fig. 1. Potential-time waveform and current-time response to a double potential step.**

\[ C_A^*(r, t) = C_A^*(s_1B, \xi_1B) = \phi_0(s_1B) + \xi_1B \phi_1(s_1B) \]

\[ s_1 = \sqrt{\frac{2z + 1}{4D_1t}(r - r_0)} \]

\[ i_1 = \sqrt{\frac{4D_1t}{2z + 1} \frac{1}{r_0}} \]

and where \( \rho_0(s_1A), \rho_1(s_1A), \phi_0(s_1B) \) and \( \phi_1(s_1B) \) are given in ref. 1a (eqs. [9]–[17]).

The concentration on the surface of the electrode are

\[ C_A^*(r_0, t) = A_1 + B_1 \xi_1A \]

\[ C_B^*(r_0, t) = C_A^*(s_1B, \xi_1B) \]

where we have taken

\[ A_1 = \frac{C_A^* K_i}{1 + \gamma K_i} \]

\[ B_1 = \frac{4(2z + 1)K_i}{(5z + 4)(1 + \gamma K_i)^2 \sqrt{\pi}} \]

If only the first order spherical correction is considered, the current has the expression (1a, 4a)

\[ i(t) = nFq(t) \sqrt{(2z + 1)D_A}{\xi_1A} \]

\[ i(t) = i_{DC} + \theta_2 \xi_2 \]

\[ \theta_2 = \frac{2(2z + 1)P_2}{(5z + 4)} \]

\[ \gamma = \frac{D_A}{D_B} \]

\[ K_i = \exp \left[ \frac{nF(E_i - E_0)}{RT} \right] \]

\[ \xi_1 = \xi_1^{10^{(r-1)/2}} \] (or eq. [5])

\[ \xi_2 = \xi_2 \sqrt{(2z + 1)B} \]
Throughout this paper the upper sign in any equation refers to a reaction product which is soluble in the electrolytic solution whilst the lower sign refers to a product soluble in the electrode (amalgam formation).

The theoretical analysis presented in this paper has been also carried out by taking into account the second order spherical correction. This highly increases the mathematical complexity, without significantly improving the results of the current in the second pulse of the potential, at least when \( \xi_1^{(2)} \leq 0.35 \) (see footnote 2 for notation). Therefore, to make our conclusions as clear as possible without invoking mathematical complexity, we only present our analysis on first order spherical correction.

It is important to note that the surface concentrations of species A and B are dependent on time (see eqs. [7], [8]). However, when \( \gamma = 1 \) and both species are soluble in the electrolytic solution the surface concentrations depend only on the applied potential \( E_1 \) (eqs. [7] and [10]) with upper sign), as is the case for plane electrodes (4, 5).

With \( t = t_1 + t_2 \) the boundary values in the interval \( 0 \leq t_2 \leq t_2 \) take the form

\[
\begin{align*}
\tilde{D}_A C_A(r, t) &= \tilde{D}_B C_B(r, t) = 0 \\
\tau_2 &= 0; \quad r = r_0 \\
\tau_2 &> 0; \quad r \to \pm \infty: \quad C_A^2(r, t) = C_B^0(r, t) = 0 \\
\tau_2 &> 0; \quad r = r_0: \quad C_A^2(r_0, t) = K_2 C_B^0(r_0, t) \\
\frac{i_2}{nFq(t)} &= D_A \left( \frac{\partial C_A}{\partial r} \right)_{r=r_0} = \mp D_B \left( \frac{\partial C_B}{\partial r} \right)_{r=r_0}
\end{align*}
\]

where the linear differential operator \( \tilde{D}_i \) \((i = A, B)\) is given by

\[
\tilde{D}_i = \frac{\partial}{\partial \tau_2} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{z r_0^3}{2 r^2 (t_1 + \tau_2)} \frac{\partial}{\partial r}
\]

The linearity of the differential equations involved means that we can search for a solution of the form

\[
\begin{align*}
C_A^2(r, t) &= C_A^2(r, t) + \tilde{C}_A(r, \tau_2) \\
C_B^2(r, t) &= C_B^2(r, t) + \tilde{C}_B(r, \tau_2)
\end{align*}
\]

where the new functions \( \tilde{C}_A(r, \tau_2) \) and \( \tilde{C}_B(r, \tau_2) \) are solutions of eq. [17] with null initial conditions (at \( \tau_2 = 0 \)) as it is immediately seen from eq. [18].

We seek a solution for the power series

\[
\begin{align*}
\tilde{C}_A(r, \tau_2) &= \sum_{i,j} \sigma_{ij}^{(2)}(s_{2A}) \xi_{ij}^{(2)} B^{(j-1)/2} \\
\tilde{C}_B(r, \tau_2) &= \sum_{i,j} \delta_{ij}^{(2)}(s_{2B}) \xi_{ij}^{(2)} B^{(j-1)/2}
\end{align*}
\]

Introducing these expressions into eq. [17] leads to the following set of ordinary differential equations for the coefficients \( \sigma_{ij}(s_{2A}) \) and \( \delta_{ij}(s_{2B}) \)

\[
\begin{align*}
\sigma'_{ij}(s_{2A}) + 2 s_{2A} \sigma_{ij}(s_{2A}) - 2 (i + j - 1) \sigma_{ij}(s_{2A}) &= \sum_{m+i+1=n} c_m \sigma_{ij}(s_{2A}) - \sum_{r_p=n} d_r \sigma_{ij}(s_{2A}) \\
- 2z \left( i + j - 3 \right) \Delta_i j = 2 (s_{2A}) \\
\delta'_{ij}(s_{2B}) + 2 s_{2B} \delta_{ij}(s_{2B}) - 2 (i + j - 1) \delta_{ij}(s_{2B}) &= \sum_{m+i+1=n} c_m \delta_{ij}(s_{2B}) - \sum_{r_p=n} d_r \delta_{ij}(s_{2B}) \\
- 2z \left( i + j - 3 \right) \delta_{ij} = 2 (s_{2A})
\end{align*}
\]

where

\[
\begin{align*}
c_m &= 2 (-1)^m (s_{2A})^m \\
c_m &= 0 \text{ for planar electrodes} \\
d_r &= 2z (-1)^{r+2} (s_{2A})^{r+1}
\end{align*}
\]

A rigorous treatment of the problem is complicated since the dimensionless parameters \( \xi_1 \) and \( \xi_2 \) (connected to the electrode sphericity during the first and second pulses, respectively) are not independent. In fact, they are linked as follows:

\[
\frac{\xi_2}{\xi_1} = \sqrt{2z + 1} \beta
\]

The appropriate boundary conditions for \( \sigma_{ij}(s_{2A}) \) and \( \delta_{ij}(s_{2B}) \) functions can be deduced from the initial conditions given in eq. [18], the boundary condition in eqs. [19]–[21] and also eq. [34]. Thus when \( s_{2A} = s_{2B} = 0 \):

\[
\begin{align*}
\sigma_{ij} = \delta_{ij} &= 0 & \forall \ i, j \\
\gamma^{(1)} \sigma'_{ij} &= \mp \delta'_{ij} & \forall \ i, j
\end{align*}
\]
\[ \sigma_{0,1} = -C_A^2 z_2 (1 + \gamma K_2) + K_2 \delta_{0,1} \]

\[ \gamma \sigma_{1,0} = -C_A^2 z_2 N_2 (1 + \gamma K_2) + K_2 \delta_{1,0} \]

\[ \gamma' \sigma_{i,j} = K_2 \delta_{i,j} \text{ unless } i = 1, j = 0 \text{ and } i = 0, j = 1 \]

\[ Z_2 = \frac{1}{1 + \gamma K_2} - \frac{1}{1 + \gamma K_1} \]

\[ N_2 = \frac{4 \sqrt{2} z + 1 (\gamma \mp 1)}{(5 z + 4)(1 + \gamma K_1) \sqrt{\pi}} \]

The expressions for \( \sigma_{i,j} (s^2 A) \) and \( \delta_{i,j} (s^2 B) \) are then obtained by the procedure developed in ref. 12, and are given in Appendix (eqs. [A3]–[A8], [A11]–[A22], and [A25]–[A33]).

The surface concentration of both species A and B during the second pulse, for an expanding spherical electrode, can now be found by substituting \( r = r_0 \) and eq. [A.23] in eqs. [23] and [24]. Then we obtain

\[ C^2_A (r_0, t) = \frac{C_A^2 K_2}{1 + \gamma K_2} \left( \gamma + \frac{4 (2 z + 1) (\gamma \mp 1)}{(5 z + 4)(1 + \gamma K_1) \sqrt{\pi}} \xi_{1 A} \right) \]

\[ + \frac{K_2 (\gamma \mp 1)}{(1 + \gamma K_2) \sqrt{\pi}} Q_2 (\beta) \xi_{2 A} \]

\[ C^2_B (r_0, t) = C^2_A (r_0, t) / K_2 \]

where

\[ Q_2 (\beta) = 1 - \frac{z (5 z + 2)}{48} \beta^2 + \frac{z (3 z^2 - 20 z - 8)}{240} \beta^3 \ldots \]

It is worth noting that if \( \gamma = 1 \) (i.e., \( D_A = D_B \)) and both species are soluble in the electrolytic solution (upper sign), \( C^2_A (r_0, t) \) and \( C^2_B (r_0, t) \) depend only on the applied potential \( E_0 \), for any type of electrode (\( z \geq 0 \)).

The current time response can also be immediately obtained from eqs. [21], [A9], and [A24].

\[ i_2 = i_1 (t) + n F A_0 \int_{\pi/2}^{\Delta A} C_A^2 Z_2 f_2 (\beta) \]

\[ + \frac{4 (2 z + 1) (\gamma \mp 1)}{(5 z + 4)(1 + \gamma K_1) \sqrt{\pi}} g_2 (\beta) \xi_{1 A} + \frac{\sqrt{\pi}}{2} \Omega_2 h_2 (\beta) \xi_{2 A} \]

where

\[ \Omega_2 = \frac{1 + K_2}{1 + \gamma K_2} \]

\[ f_2 (\beta) = \sqrt{\frac{(2 z + 1) \beta}{1 - (1 - \beta)^{2 z + 1}}} \]

\[ g_2 (\beta) = 1 + \frac{1}{2} \beta + \frac{2 z^2 + 2 z + 1}{24} \beta^2 + \frac{2 z^2 + 2 z + 1}{80} \beta^3 \ldots \]

\[ h_2 (\beta) = 1 - \frac{3 z (7 z + 2)}{128} \beta^2 + \frac{z (z - 4)(7 z + 2)}{256} \beta^3 \ldots \]

\( f_2 (\beta) \) and the series \( h_2 (\beta) \), in the particular case when \( z = 0 \) and \( z = 2/3 \), are coincident with the series \( h_0 (z, \tau) \) and \( h_1 (z, \tau) \) given by eqs. [42] and [43] in ref. 1a respectively (\( \tau \equiv \beta \)). On the other hand, the series \( g_2 (\beta) \) is a new series. It came about as a result of the disturbance on the surface concentrations deduced for the first pulse (\( C_1 (r_0, t) \) and \( C_A (r_0, t) \)) due to the application of the second pulse. Therefore, eq. [45] in this work does not coincide in general with eq. [41] in ref. 1a. Nevertheless, in the special case when \( \gamma = 1 \) and both species are soluble in the electrolytic solution, eq. [41] in ref. 1a (or eq. [36] in ref. 2) and our eq. [45] are the same; because in this particular case the surface concentrations of the electroactive couple are time-independent. On the other hand, if \( D_A \neq D_B \) or there is amalgam formation one should use our eq. [45] instead of the equations deduced in refs. 1a and 2.

The results expressed by eq. [45] simplify in the following cases:

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

\[ i_2 = i_1 (t) + n F A_0 \int_{\pi/2}^{\Delta A} C_A^2 Z_2 f_2 (\beta) \]

\[ + \frac{14 (\gamma \mp 1)}{11 (1 + \gamma K_1) \sqrt{\pi}} g_2 (\beta) \xi_{1 A} + \frac{\sqrt{\pi}}{2} \Omega_2 h_2 (\beta) \xi_{2 A} \]

where (13)

\[ f_2 (\beta) = \sqrt{\frac{7 \beta}{3 (1 - (1 - \beta)^{2/3})}} \]

\[ g_2 (\beta) = 1 + \frac{1}{2} \beta + \frac{29}{216} \beta^2 + \frac{29}{720} \beta^3 + \ldots \]

\[ h_2 (\beta) = 1 - \frac{5}{48} \beta^2 - \frac{25}{432} \beta^3 + \ldots \]

\( b \) \( z = 0 \) (SMDE)

\[ i_2 = i_1 (t) + n F A_0 \int_{\pi/2}^{\Delta A} C_A^2 Z_2 \]

\[ \times \left\{ 1 + \frac{(\gamma \mp 1)}{\sqrt{\pi} (1 + \gamma K_1)} g_0 (\beta) \xi_{1 A} + \frac{\sqrt{\pi}}{2} \Omega_2 \xi_{2 A} \right\} \]

where (14)

\[ g_0 (\beta) = 1 + \sum_{k=1}^{\infty} \frac{\beta^k (2 k - 1)!}{k! 2^{k-1} (k - 1)!(2 k - 1)^2} = \sqrt{\beta} \arcsin (\sqrt{\beta}) + \sqrt{1 - \beta} \]

\[ f_0 (\beta) = h_0 (\beta) = 1 \]

and eq. [54] takes the simpler form

\[ i_2 = i_1 (t) + n F A_0 C_A^2 \sqrt{\frac{\Delta A}{\pi}} \left( \frac{1}{1 + \gamma K_2} - \frac{1}{1 + \gamma K_1} \right) \]

\[ \times \left\{ \frac{1}{\sqrt{\beta} + (\gamma \mp 1)} \right\} \sqrt{\frac{\Delta A}{\pi}} \left( \frac{1}{2} \sqrt{1 - \beta} + \arcsin (\sqrt{\beta}) \right) \]

\[ + \frac{\sqrt{\pi} D_A}{r_0} \frac{1 \pm K_2}{1 + \gamma K_2} \]
Fig. 2. Influence of the amalgamation on $i/t_0$ recording for a double potential step at a SMDE (eq. [12] with $E_1 \to -\infty$ and [63]).

Fig. 3. Influence of sphericity on $i/t_0$ recording for a double potential step when the amalgamation takes place in a SMDE. The values of $\xi_{1A}^2$ in s$^{-1/2}$ are $(-\cdot) 0.15$, $(-\cdots) 0.25$, $(\cdots) 0.35$. Other conditions as in Fig. 2.

(c) $\xi_1 = \xi_2 = 0$ (expanding plane electrode)

\[ i_2 = i_1(t) + nFq(t) \frac{D_A}{n\pi_1} C_A^* Z_2 f_2(\beta) \]

(d) $\gamma = 1$ and the reduced species B soluble in the electrolytic solution (upper sign)

\[ i_2 = i_1(t) + nFq(t) \frac{D_A}{n\pi_2} C_A^* Z_2 \left( f_2(\beta) + \frac{\sqrt{\pi}}{2} \xi_2 h_2(\beta) \right) \]

Results and discussion

(A) $i-t$ curves

The $i-t$ response to a single pulse $E_2$ (normal pulse voltammetry or polarography) is directly obtained from eq. [45] by making $E_1 \to \infty$. In this case we have $K_1 \to \infty$, $i_1 \to 0$ and $Z_2 = 1/(1 + \gamma K_2)$, and therefore

\[ i_2 = i_N + nFq(t) \frac{D_A}{n\pi_1} C_A^* \left( \frac{1}{1 + \gamma K_2} \right) \]

\[ \times \left\{ f_2(\beta) + \frac{\sqrt{\pi}}{2} \xi_2 h_2(\beta) \right\} \]

If now we substitute $E_2 \equiv E_1$ (i.e. $\Omega_2 \equiv \Omega_1$), $t_1 \to 0$ (i.e. $\beta = 1$) and $\xi_2^2 A = \sqrt{2z + 1} \xi_2^2 A$ in eq. [60], it reduces to a dc response, as can be seen from eq. [12]. The following equations are therefore valid:

\[ f_2(\beta = 1) = \frac{\sqrt{2z + 1}}{\sqrt{7/3}} \]

\[ h_2(\beta = 1) = \frac{2}{\sqrt{\pi}} \theta \]

The behaviour of the $i_1-t$ and $i_2-t$ curves is very similar to that shown in Figs. 2-5 when $E_1 - E_0 \leq -2RT/nF$ and $E_2 - E_0 \geq 2RT/nF$.

Since the current $i_{tg2}$ is due to the oxidization of species B, which initially is not present in the solution, it is clear that

\[ i_{tg2} \to 0 \text{ when } t_2 \to +\infty \]

and this condition is verified both when B is soluble in the solution and when it produces amalgamation.

When $t_2 \to +\infty$ we have $\beta \to 1$, and therefore, by introducing eqs. [61] and [62] into eq. [63] we obtain (see also eqs. [52] and [53])

\[ g_c(\beta = 1) = \frac{\theta}{M_c} \left\{ \frac{\pi/2}{1.674} \right\} \]

These results can also be obtained from eqs. [52] and [53].
Fig. 4. Influence of the amalgamation on $i/i_0 - t$ recording for a double potential step in a DME (eq. [12] with $E_1 \to -\infty$ and [63]). $\xi_1^{(A)} = 0.2 \text{s}^{-1/6}$. (---) Planar electrode, (---) solution-soluble product, (---) amalgam formation. Other conditions as in Fig. 2.

Fig. 5. Influence of the first pulse duration on $i/i_0 - t$ recorder for a double potential step in a DME. $\gamma = 1.3$, $\xi_1^{(A)} = 0.3 \text{s}^{-1/6}$. The values of $t_1$ in s are (a) 1.0, (b) 1.5, (c) 2.0. Other conditions as in Fig. 3.

The Koutecky approximation (7) that we introduced in eq. [19] for amalgam formation works very well; this becomes apparent as in all cases:

\[ i_0 \leq 0 \text{ for } 0 < t_2 < +\infty \]  

However, in refs. 1 and 2 condition [68] is not fulfilled when the amalgamation takes place. This becomes clear in Figs. 3 and 4 (curves b) in ref. 1a, where $i_2$ suffers a change in sign for $t_2 > t_1$.

As shown in Figs. 2 and 4 SMDE and DME, respectively, the current $i_2$ is lower when amalgamation is present than when both species are soluble in the solution or for a plane electrode.

The effect of sphericity or a SMDE and the effect of the length of the first pulse, $t_1$, or a DME when species B amalgamates with the electrode are shown in Figs. 3 and 5, respectively.

Equation [63] has been used to explain the behaviour of the system Pb(II)/Pb(Hg) at a SMDE ($z = 0$). The applicability of eq. [63] corresponds to an experimental situation with $E_1 \ll E_0$ ($i_i = i_{DI}$ cathodic current) and $E_2 \gg E_0$ (i2 = iod anodic current). Under these conditions the system Pb(II)/Pb(Hg) has been studied by double potential step chronocoulometry (1b). The experimental results from the literature (see Fig. 5 in ref. 1b) are shown in Fig. 6 (circles). Other experimental conditions are given in the caption of Fig. 6. The continuous line in Fig. 6 corresponds to the results obtained from eq. [63] with $D_A = 8.1 \times 10^{-6} \text{cm}^2/\text{s} (D_{Pb(lb)})$ and $D_B = 1.33 \times 10^{-5} \text{cm}^2/\text{s} (D_{Pb(Hg)})$ (1a).

Following the procedure in ref. 1b, we have plotted $-i_{D2}/i_{D1}(t_1)$, where $i_{D1}(t_1)$ is the solution of eq. [12] for $E_1 \ll E_0$ and $t = t_1$. As it can be noticed, there is an excellent agreement between experimental and the results obtained from eq. [63]. It has been also included in Fig. 6 the theoretical predictions of the model presented in ref. 1a (dashed line). As is observed and stated in ref. 1b, that model leads to wrong results for electrode processes with amalgam formation. The reason is that the model does not take into account the perturbation of the second pulse on the concentration profiles generated by the first potential pulse.

(B) Reverse pulse techniques

Reverse pulse techniques (1, 2, 3, 8-10) are based on the choice $E_1 \to -\infty (K_1 \to 0)$ and a variable potential $E_2$. The current $i_{GP} = -i_2/i_{DC}$ can then be easily evaluated from eq.
An example of application of this technique is shown in Fig. 7. It can be seen that the effect of sphericity is quite remarkable, whether the reaction product is soluble in the electrolytic solution or if it amalgamates.

A criterion to determine if amalgamation occurs in a spherical electrode can be found by analyzing the limiting values of the cathodic, $i_{D1}$, and anodic, $i_{D2}$, currents. For the sake of simplicity we consider a SMDE ($z = 0$), and from eq. [12] with $K_1 = 0$ we have

$$i_{D1} = \sqrt{\beta} \left( 1 + \frac{\sqrt{\pi D_A t}}{r_0} \right)$$

where

$$i_{DC} = n F A_0 C^* \sqrt{\frac{D_A}{\pi r_2}}$$

Furthermore, from eqs. [63], [69], and [70]

$$-\frac{i_{D2} - i_{D1}}{i_{DC}} = 1 + \frac{\sqrt{\pi D_A t_2}}{r_0} \times \left\{ 1 + \frac{2 g_0(\beta)}{\pi \sqrt{\beta}} \left( \frac{\gamma + 1}{\gamma} \right) \right\}$$

this equation can also be written as

$$R = \frac{i_{D2} - i_{D1}^0}{i_{D1} - i_{D1}^0} = \frac{2 g_0(\beta)}{\pi \sqrt{\beta}} \left( \frac{\gamma + 1}{\gamma} \right)$$

where $i_{D1}^0$ and $i_{D2}^0$ are the limiting values of $i_{D1}$ and $i_{D2}$ when $r_0 \to \infty$ (planar electrode), respectively, given by (eqs. [69] and [63] with $r_0 \to \infty$)

$$i_{D1}^0 = i_{DC} \sqrt{\beta}$$

Therefore, eq. [72] gives the ratio between the contributions of sphericity to the first and second pulses. Since the bracket in eq. [74] fulfills the condition

$$0 \leq \left( \frac{2 g_0(\beta)}{\pi \sqrt{\beta}} - 1 \right) \leq \infty \quad \text{for } 1 \leq \beta \geq 0$$

we can make the following classification: (a) If $0 \leq R < (2 g_0(\beta)/\pi \sqrt{\beta} - 1)$, $B$ is soluble in solution and $\gamma \geq 1$; (b) If $R < 0$, $B$ is again soluble, and $\gamma < 1$; (c) If $R > (2 g_0(\beta)/\pi \sqrt{\beta} - 1)$, then amalgamation is present.

(C) Differential pulse techniques

These techniques are characterized because $\Delta E = E_2 - E_1$ is kept constant. A cathodic record is obtained if $\Delta E < 0$, and an anodic record if $\Delta E > 0$. The response is $I_{DNP} = (i_2 - i_1)/I_{DC}$, which is positive if $\Delta E < 0$ and negative if $\Delta E > 0$, respectively. From eq. [45] we deduce

$$I_{DNP} = \frac{\sqrt{2z + 1}}{1 + \gamma K_1} \left\{ r' \sqrt{\beta} \left[ 1 + \theta_0 \Omega_2 \xi_{1A}(t) \right] \right. \right.$$}

$$- r' \sqrt{\beta}/(1 - \beta) \left[ 1 + \theta_0 \Omega_2 \xi_{1A}(t) \right] \right.$$}

$$+ r' Z_2 \left( f_1(\beta) + \frac{4(2z + 1)(\gamma + 1)}{(5z + 4)(1 + \gamma K_1)\gamma \sqrt{\pi}} \right.$$}

$$\times g_2(\beta) \xi_{1A} + \frac{\sqrt{\pi}}{2} \Omega_2 h_2(\beta) \xi_{2A} \right)$$

A criterion for the analysis of electrode processes has been proposed by Birke et al. (6) on the basis of the ratio between
The influence of $\beta$ on the records obtained is shown in Fig. 9. In general, it can be said that amalgamation formation increases the current peaks, and also that they are shifted to more positive values of potential.

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Appendix

The differential equations [30] and [31] for $i = 0$ are simplified to

[A1] \[ \sigma^{(-)}_{0,j} (s_2 A) = 2 s_2 A \sigma^{(-)}_{0,j} (s_2 A) - 2(j - 1) \sigma^{(-)}_{0,j} (s_2 A) = -4 s_2 A \sigma^{(-)}_{0,j-2} (s_2 A) - 2(j - 3) \sigma^{(-)}_{0,j-2} (s_2 A) \]

[A2] \[ \delta^{(\mp)}_{0,j} (s_2 B) + 2 s_2 B \delta^{(\mp)}_{0,j} (s_2 B) - 2(j - 1) \delta^{(\mp)}_{0,j} (s_2 B) = -4 s_2 B \delta^{(\mp)}_{0,j-2} (s_2 B) - 2(j - 3) \delta^{(\mp)}_{0,j-2} \]

The solutions of these equations (corresponding to an expanding plane electrode of area $q(t) = q_0 t^2$) with the boundary value problem given by eqs. [36], [37], and [39] with $i = 0$, are

[A3] \[ \sigma^{(-)}_{0,2n} (s_2 A) = 0 \quad n = 0, 1, 2 \ldots \]

[A4] \[ \sigma^{(-)}_{0,1} (s_2 A) = -\Psi_{0,1}^{(-)} (s_2 A) C_A Z_2 \]

[A5] \[ \sigma^{(-)}_{0,3} (s_2 A) = \frac{z}{\sqrt{\pi}} s_2 A e^{-t_2 A^2} C_A Z_2 \]

[A6] \[ \sigma^{(-)}_{0,5} (s_2 A) = \frac{z}{2 \sqrt{\pi}} \left\{ \frac{z + 4}{6} - z (s_2 A)^2 \right\} s_2 A e^{-t_2 A^2} C_A Z_2 \]

[A7] \[ \sigma^{(-)}_{0,7} (s_2 A) = \frac{z}{6 \sqrt{\pi}} \left\{ \frac{4 - z^2}{4} - z (z + 2)(s_2 A)^2 + z^2 (s_2 A)^4 \right\} s_2 A e^{-t_2 A^2} C_A Z_2 \]
\[ \sigma_{0,0}^{(2)}(s_2\Lambda) = \frac{z}{24\sqrt{\pi}} \left\{ \frac{96 - 32z - 56z^2 - 3z^3}{40} - \frac{z(8 - z)(5z + 8)}{12} \right\} \frac{z}{(s_2\Lambda)^2} + \frac{z^3(5z + 8)}{2} \frac{z^3}{(s_2\Lambda)^2} - \frac{z^3(5z + 8)}{2} \frac{z^3}{(s_2\Lambda)^2} \right\} \frac{2}{s_2\Lambda e^{-i2\Lambda} C_\Lambda Z_2} \]

These functions hold

\[ \sum_{n=0}^{\infty} \sigma_{0,2n+1}^{(2)}(0)\beta^n = \frac{2C_\Lambda Z_2}{\sqrt{\pi}} f_1(\beta) \]

where

\[ f_1(\beta) = 1 + \frac{z}{2} \beta + \frac{z(z + 4)}{24} \beta^2 + \frac{z(2 + z)(2 - z)}{48} \beta^3 + \frac{z(96 - 32z - 56z^2 - 3z^3)}{1920} \beta^4 \]

This is equivalent to eq. [47] (13). Moreover

\[ \delta_{0,2n+1}^{(2)}(s_2\Lambda) = \mp \gamma \sigma_{0,2n+1}^{(2)}(s_2\Lambda) \quad \text{unless } n = 0 \]

\[ \delta_{0,1}^{(2)}(s_2\Lambda) = -\gamma \sigma_{0,1}^{(2)}(s_2\Lambda) \]

For \( \lambda = 1 \) (first order spherical correction) eqs. [30] and [31] become

\[ \sigma_{1,0}^{(2)}(s_2\Lambda) + 2s_2\Lambda \sigma_{1,0}^{(2)}(s_2\Lambda) - 2j\sigma_{1,0}^{(2)}(s_2\Lambda) = -2\sigma_{0,0}^{(2)}(s_2\Lambda) - 4z2\Lambda \sigma_{1,j}^{(2)}(s_2\Lambda) + 6z(s_2\Lambda)^2 \sigma_{0,j-2}^{(2)}(s_2\Lambda) \]

\[ = -(z + j - 3)\sigma_{1,j}^{(2)}(s_2\Lambda) \]

\[ \delta_{1,0}^{(2)}(s_2\Lambda) + 2s_2\Lambda \delta_{1,0}^{(2)}(s_2\Lambda) - 2j\delta_{1,0}^{(2)}(s_2\Lambda) = -2\delta_{0,0}^{(2)}(s_2\Lambda) - 4z2\Lambda \delta_{1,j}^{(2)}(s_2\Lambda) + 6z(s_2\Lambda)^2 \delta_{0,j-2}^{(2)}(s_2\Lambda) \]

\[ = -(z + j - 3)\delta_{1,j}^{(2)}(s_2\Lambda) \]

and the solutions are

\[ \sigma_{1,0}^{(2)}(s_2\Lambda) = -\frac{C_\Lambda Z_2 N_\gamma}{\gamma} \Psi^{(-)}(s_2\Lambda) \]

\[ \sigma_{1,0}^{(2)}(s_2\Lambda) = \frac{1}{\sqrt{\pi}} \left\{ e^{-i2\Lambda} - \Omega_2 \Psi^{(-)}(s_2\Lambda) \right\} C_\Lambda Z_2 \]

\[ \sigma_{1,2}^{(2)}(s_2\Lambda) = \left\{ \frac{z}{\sqrt{\pi}} s_2\Lambda e^{-i2\Lambda} - \frac{z - 1}{2} \left[ \Psi^{(-)}_0(s_2\Lambda) - \Psi^{(-)}_2(s_2\Lambda) \right] \right\} \frac{C_\Lambda Z_2 N_\gamma}{\gamma} \]

\[ \sigma_{1,3}^{(2)}(s_2\Lambda) = \frac{z}{2\sqrt{\pi}} \left\{ (\Omega_2 - 4s_2\Lambda)^2 e^{-i2\Lambda} - \Omega_2 [4\Psi^{(-)}_2(s_2\Lambda) - 2\Psi^{(-)}_4(s_2\Lambda)] \right\} \]

\[ \sigma_{1,4}^{(2)}(s_2\Lambda) = \left\{ \left( \frac{7z - 2}{6} - z(s_2\Lambda) \right) \frac{z}{\sqrt{\pi}} s_2\Lambda e^{-i2\Lambda} - \frac{(z - 1)(5z + 1)}{8} \left[ \Psi^{(-)}_0(s_2\Lambda) - 2\Psi^{(-)}_2(s_2\Lambda) + \Psi^{(-)}_4(s_2\Lambda) \right] \right\} \frac{C_\Lambda Z_2 N_\gamma}{\gamma} \]

\[ \sigma_{1,5}^{(2)}(s_2\Lambda) = \left\{ \left( \frac{2(13z + 4)\Omega_2 - 5z - 2}{24} - \frac{17z + 14 + 6\Omega_2}{12} \right) s_2\Lambda e^{-i2\Lambda} \right\} \frac{z}{2\sqrt{\pi}} \frac{z}{(s_2\Lambda)^2} + 3z(s_2\Lambda)^4 \]

\[ - \frac{(7z + 2)\Omega_2}{8}(6\Psi^{(-)}_2(s_2\Lambda) - 8\Psi^{(-)}_4(s_2\Lambda) + 3\Psi^{(-)}_6(s_2\Lambda)) \]

\[ + \frac{3\Psi^{(-)}_6(s_2\Lambda)}{\gamma} \]

\[ \sigma_{1,6}^{(2)}(s_2\Lambda) = \left\{ \left( \frac{3z^2 - z - 1}{4} - \frac{z(5z + 1)}{6} s_2\Lambda^2 + \frac{z^2}{3} s_2\Lambda^4 \right) \right\} \frac{z}{\sqrt{\pi}} s_2\Lambda e^{-i2\Lambda} \frac{(z - 1)(5z + 1)(3z + 1)}{16} \left[ \Psi^{(-)}_0(s_2\Lambda) \right] \]

\[ - 3\Psi^{(-)}_2(s_2\Lambda) + 3\Psi^{(-)}_4(s_2\Lambda) + \Psi^{(-)}_6(s_2\Lambda) \right\} \frac{C_\Lambda Z_2 N_\gamma}{\gamma} \]
\[ \sigma_{i,j}^{(s_2A)}(s_2A) = \frac{\gamma}{8\sqrt{\pi}} \left\{ \left( \frac{3z^2 - 20z - 8 + 5(33z^2 + 22z + 4)\Omega_2}{30} + \frac{59z^2 - 50z - 64 - 2z(35\gamma + 20)\Omega_2}{30} \right) (-s_2A)^2 \\
+ \frac{z(25z + 22) + 2z^2\gamma\Omega_2}{3} (-s_2A)^4 - \frac{16z^2}{3} (-s_2A)^4 \right\} e^{-(-s_2A)^2} - \frac{(7z + 2)(11z + 4)\gamma\Omega_2}{4} \\
\times \left( 2\Psi_1^{-}(s_2A) - \frac{43z + 16}{11z + 4} \Psi_3^{-}(s_2A) + 3\Psi_5^{-}(s_2A) - \frac{4}{5} \Psi_7^{-}(s_2A) \right) \right\} C_\lambda Z_2 \]

These functions have the following relationships:

\[ \sum_{n=0} \left( \sigma_{i,2n}(0)\beta^{2n-1/2} \right) = \frac{C_\lambda Z_2 N_\gamma}{\gamma \sqrt{\beta}} g_\gamma(\beta) \]

\[ \sum_{n=0} \left( \sigma_{i,2n+1}(0)\beta^n \right) = \frac{C_\lambda \sqrt{\pi}}{\pi} g_\gamma(\beta) \]

\[ \sum_{n=0} \left( \sigma_{i,2n}(0)\beta^{2n-1/2} \right) = \frac{C_\lambda Z_2 N_\gamma}{\gamma \sqrt{\beta}} h_\gamma(\beta) \]

\[ \sum_{n=0} \left( \sigma_{i,2n+1}(0)\beta^n \right) = C_\lambda Z_2 \Omega_2 h_\gamma(\beta) \]

where \( g_\gamma(\beta) \) and \( h_\gamma(\beta) \) are given by eqs. [48] and [49], respectively. Moreover

\[ \delta_1^{(s_2B)} = -\gamma^2 \sigma_{i,j}^{(s_2B)} \]

\[ \delta_{i,0}^{(s_2B)} = \gamma C_\lambda Z_2 N_\gamma \Psi_0^{(s_2B)} \]

\[ \delta_{i,1}^{(s_2B)} = \frac{1}{\sqrt{\pi}} \left\{ e^{-(-s_2B)^2} + \gamma\Omega_2 \Psi_1^{(s_2B)} \right\} \gamma C_\lambda Z_2 \]

\[ \delta_{i,2}^{(s_2B)} = \left\{ \frac{z}{2\sqrt{\pi}} s_2Be^{-(-s_2B)^2} + \frac{z - 1}{2} [\Psi_0^{(s_2B)} - \Psi_2^{(s_2B)}] \right\} \gamma C_\lambda Z_2 N_\gamma \]

\[ \delta_{i,3}^{(s_2B)} = \left\{ \frac{7z - 2}{6} - z(s_2B)^2 \right\} \frac{2}{\sqrt{\pi}} s_2Be^{-(-s_2B)^2} + \frac{(z - 1)(5z + 1)}{8} [\Psi_0^{(s_2B)} - 2\Psi_2^{(s_2B)}] \right\} \gamma C_\lambda Z_2 N_\gamma \]

\[ \delta_{i,4}^{(s_2B)} = \left\{ \frac{2(13z + 4)\gamma\Omega_2 + 5z + 2}{24} - \frac{17z + 14 - 6z\gamma\Omega_2}{12} (s_2B)^2 + \frac{7z + 2}{8} \Omega_2 \right\} \frac{6}{\sqrt{\pi}} \Psi_2^{(s_2B)} \]

\[ \delta_{i,5}^{(s_2B)} = \frac{z}{2\sqrt{\pi}} \left\{ \left( \frac{3z^2 - 20z - 8 + 5(33z^2 + 22z + 4)\gamma\Omega_2}{30} + \frac{59z^2 - 50z - 64 - 2z(35\gamma + 20)\gamma\Omega_2}{30} \right) s_2Be^{-(-s_2B)^2} + \frac{(z - 1)(5z + 1)(3z + 1)}{16} \Psi_0^{(s_2B)} \right\} \gamma C_\lambda Z_2 N_\gamma \]

\[ \delta_{i,6}^{(s_2B)} = \frac{z}{8\sqrt{\pi}} \left\{ \left( \frac{3z^2 - 20z - 8 + 5(33z^2 + 22z + 4)\gamma\Omega_2}{30} + \frac{59z^2 - 50z - 64 - 2z(35\gamma + 20)\gamma\Omega_2}{30} \right) s_2Be^{-(-s_2B)^2} + \frac{(z - 1)(5z + 1)(3z + 1)}{16} \Psi_0^{(s_2B)} \right\} \gamma C_\lambda Z_2 N_\gamma \]

\[ \delta_{i,7}^{(s_2B)} = \frac{z}{8\sqrt{\pi}} \left\{ \left( \frac{3z^2 - 20z - 8 + 5(33z^2 + 22z + 4)\gamma\Omega_2}{30} + \frac{59z^2 - 50z - 64 - 2z(35\gamma + 20)\gamma\Omega_2}{30} \right) s_2Be^{-(-s_2B)^2} + \frac{(z - 1)(5z + 1)(3z + 1)}{16} \Psi_0^{(s_2B)} \right\} \gamma C_\lambda Z_2 N_\gamma \]