
**POTENTIAL-TIME RESPONSE FOR SEVERAL TYPES
OF PROGRAMMED CURRENT AT MOST USUAL ELECTRODES.
THEORETICAL STUDY OF CE AND EC MECHANISMS**

Angela MOLINA* and Manuela LÓPEZ-TENÉS

*Laboratory of Physical Chemistry,
University of Murcia, Espinardo 30100 Murcia, Spain*

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

A theoretical study of the potential-time response corresponding to the CE and EC mechanisms at the DME by using non linear perturbation functions with the general form $I(t) = I_0 t^u e^{wt}$ and $I(t) = I_0(t_1 + t)^v$ is presented. Equations for the potential-time curves and for the transition times have been derived by taking into account the sphericity of the electrode. Methods for determining heterogeneous and homogeneous kinetic parameters are proposed. The expressions corresponding to a null blank period, to an expanding plane electrode and to spherical and plane stationary electrodes, can be deduced as particular cases of the equations obtained in this work.

We have previously developed the theory concerning the use of several non linear current-time functions (ctf's) at the dropping mercury electrode (DME), for charge transfer reactions (ctr's)^{1,2}. The aim of this work is the application of that theory to the study of the CE and EC mechanisms with different electrodes. The ctf's used can be divided into two types. First, functions which are the product of an exponential by a power, i.e., $I(t) = I_0 t^u e^{wt}$ (the power law current and the exponential law current are obtained as particular cases of this general function). Secondly, power law functions of the total time, $I(t) = I_0 t_s^v$. The broad class of ctf's used in this paper can be applied to any type of dependent-time area electrodes by using, necessarily, a preceding blank period t_1 (ref.¹).

For all the perturbations considered, we have deduced the concentration profiles $C_i(r, t)$, the surface concentrations $C_i(r_0, t)$ and the E/t response concerning both processes, assuming the expanding sphere electrode model (ESE) for the DME. The response corresponding to any stationary spherical electrode (SSE) and for any stationary plane electrode (SPE) can be deduced as particular cases of our equations.

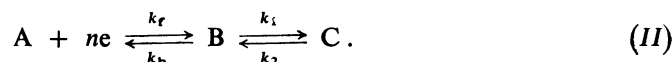
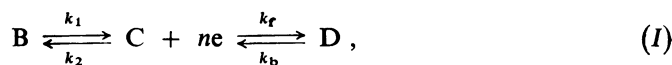
When the blank period t_1 is null, and the ctf has the simplified form $I(t) = I_0 t^u$, our equations are coincident with those deduced by Gálvez et al.³⁻⁵. For an expanding plane electrode (EPE), and when the diffusion coefficients of all the species

are equal, our equations are equivalent to those recently obtained by Kant and Rangarajan⁶ for power law currents.

Finally, methods for the calculation of kinetic parameters of the homogeneous and heterogeneous steps are also proposed.

FORMULATION OF THE PROBLEM

The schemes corresponding to the CE and EC mechanisms are, respectively



The boundary value problem (bvp) associated to process (I), neglecting double layer effects, is given by

$$\delta_B C_B = -\delta_C C_C = -k_1 C_B + k_2 C_C, \quad (1)$$

$$\delta_D C_D = 0, \quad (2)$$

$$\left. \begin{array}{l} t = 0, \quad r > r_0 \\ t > 0, \quad r \rightarrow \infty \end{array} \right\} C_B = C_B^*, \quad C_C = C_C^*, \quad C_D = C_D^*, \quad (3)$$

$$t > 0, \quad r = r_0:$$

$$D_C \left(\frac{\partial C_C}{\partial r} \right)_{r=r_0} = -D_D \left(\frac{\partial C_D}{\partial r} \right)_{r=r_0} = \frac{I(t)}{nFA(t_s)}, \quad (4)$$

$$D_B \left(\frac{\partial C_B}{\partial r} \right)_{r=r_0} = 0, \quad (5)$$

$$\frac{I(t)}{nFA(t_s)} = k_f C_C(r_0, t) - k_b C_D(r_0, t). \quad (6)$$

The bvp corresponding to process (II) can be obtained by changing D for A in Eqs (2)–(4), C for B and $I(t)$ for $-I(t)$ in Eq. (4), B for C in Eq. (5), and finally C for A and D for B in Eq. (6).

δ_i is the operator corresponding to an ESE (ref.⁷)

$$\delta_i = \frac{\partial}{\partial t} - D_i \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{a^3}{3r^2} \frac{\partial}{\partial r} \quad (7)$$

and D_i is the diffusion coefficient of species i .

We have supposed for the processes (I) and (II) respectively

$$\left. \begin{aligned} D_B &= D_C \neq D_D \\ D_A &\neq D_C = D_C \end{aligned} \right\} \quad (8)$$

We will consider the following general forms for the ctf applied to the DME after a blank period t_1 .

1) Power-exponential law current of time

$$I(t) = I_0 t^u e^{wt} \quad u \geq -1/2, \forall w$$

1a) power law current of time

$$I(t) = I_0 t^u, \quad u \geq -1/2$$

1b) exponential law current of time

$$I(t) = I_0 e^{wt}, \quad \forall w$$

2) Power law current of total time t_s

$$I(t_s) = I_0 t_s^v, \quad \forall v$$

A discussion of the values of the exponents u , w and v can be found in refs^{1,2}.

CASE 1: POWER-EXPONENTIAL LAW CURRENT

Using the transformations

$$\zeta = C_B + C_C \quad (9)$$

$$\Phi_1 = (C_B - KC_C) e^{kt} \quad (10)$$

Eqs (1) and (2) are transformed into (process (I))

$$\delta_C \zeta = \delta_B \Phi_1 = \delta_D C_D = 0. \quad (11)$$

For process (II) we must change D for A in Eq. (11).

By introducing the variables

$$s_i = \frac{r - r_0}{2(D_i t)^{1/2}}, \quad \xi_i = \frac{2(D_i t)^{1/2}}{at_s^{1/3}} \quad (12), (13)$$

$$\beta_1 = \left(\frac{t}{t_s}\right)^{1/3}, \quad \chi_1 = kt, \quad \Omega = wt \quad (14), (15), (16)$$

we can deduce equations of the concentration profiles, as shown in Appendix I (Eqs (A1)–(A3)), and also the expressions for the surface concentrations corresponding to a CE process, which are

$$\frac{C_C(r_0, t)}{\zeta^*} = \frac{1}{1+K} \left\{ 1 - \frac{N_{CE} t^{m+2/3}}{t_s^{2/3}} [S_m(\zeta_C, \beta_1, \Omega) + K T_m(\zeta_C, \chi_1, \beta_1, \Omega)] \right\}, \quad (17)$$

$$\frac{C_D(r_0, t)}{\zeta^*} = \mu_{CE} + \frac{\gamma_{CE} N_{CE} t^{m+2/3}}{t_s^{2/3}} S_m(\zeta_D, \beta_1, \Omega). \quad (18)$$

For an EC mechanism we find

$$\frac{C_A(r_0, t)}{C_A^*} = 1 - \frac{N_{EC} t^{m+2/3}}{t_s^{2/3}} S_m(\zeta_A, \beta_1, \Omega), \quad (19)$$

$$\frac{C_B(r_0, t)}{C_A^*} = \frac{1}{1+K} \left\{ K \mu_{EC} + \frac{\gamma_{EC} N_{EC} t^{m+2/3}}{t_s^{2/3}} [K S_m(\zeta_C, \beta_1, \Omega) + T_m(\zeta_C, \chi_1, \beta_1, \Omega)] \right\}, \quad (20)$$

where

$$m = u - 1/6 \quad (21)$$

$$\gamma_{CE} = \left(\frac{D_C}{D_D}\right)^{1/2}, \quad \mu_{CE} = \frac{C_D^*}{\zeta^*}, \quad N_{CE} = \frac{2I_0}{nFD_C^{1/2} A_0 \zeta^*} \quad (22)$$

$$\gamma_{EC} = \left(\frac{D_A}{D_B}\right)^{1/2}, \quad \mu_{EC} = \frac{\zeta^*}{C_A^*}, \quad N_{EC} = \frac{2I_0}{nFD_A^{1/2} A_0 C_A^*} \quad (23)$$

and the series S_m and T_m are defined in Appendix I.

The transition time corresponding to a CE mechanism is deduced from Eq. (17)

$$\tau^{m+2/3} = \frac{(t_1 + \tau)^{2/3}}{N_{CE} [S_m(\zeta_{C,\tau}, \beta_{1,\tau}, \Omega_\tau) + K T_m(\zeta_{C,\tau}, \chi_{1,\tau}, \beta_{1,\tau}, \Omega_\tau)]}, \quad (24)$$

where $\zeta_{C,\tau}$, $\chi_{1,\tau}$, $\beta_{1,\tau}$ and Ω_τ are the values of these variables for $t = \tau$.

The potential–time functions (ptf's) can be deduced inserting Eqs (17) and (18)

in Eq. (6)

$$\begin{aligned}
 & N_{\text{CE}} t^{m+2/3} \Theta_{\text{CE}}(t)^{-1/2} e^{\Omega} 10^{2\eta(t)} = \\
 & = \frac{1}{1+K} \left\{ t_s^{2/3} - N_{\text{CE}} t^{m+2/3} [S_m(\xi_{\text{C}}, \beta_1, \Omega) + K T_m(\xi_{\text{C}}, \chi_1, \beta_1, \Omega)] \right\} - \\
 & \quad - 10^{\eta(t)} \{ \mu_{\text{CE}} t_s^{2/3} + \gamma_{\text{CE}} N_{\text{CE}} t^{m+2/3} S_m(\xi_{\text{D}}, \beta_1, \Omega) \}, \quad (25)
 \end{aligned}$$

$$\Theta_{\text{CE}}(t)^{-1/2} = \frac{D_{\text{C}}^{1/2}}{2k_s t^{1/2}}, \quad (26)$$

$$\eta(t) = \frac{nF}{RT \ln 10} (E(t) - E^0). \quad (27)$$

For a reversible ctr ($k_s \gg 1$), Eq. (25) takes the more simple form

$$\eta(t) = \log \frac{t_s^{2/3} - N_{\text{CE}} t^{m+2/3} [S_m(\xi_{\text{C}}, \beta_1, \Omega) + K T_m(\xi_{\text{C}}, \chi_1, \beta_1, \Omega)]}{(1+K) [\mu_{\text{CE}} t_s^{2/3} + \gamma_{\text{CE}} N_{\text{CE}} t^{m+2/3} S_m(\xi_{\text{D}}, \beta_1, \Omega)]} \quad (28)$$

and for an irreversible one ($k_s \ll 1$)

$$\eta(t) = \frac{1}{\alpha} \log \frac{t_s^{2/3} - N_{\text{CE}} t^{m+2/3} [S_m(\xi_{\text{C}}, \beta_1, \Omega) + K T_m(\xi_{\text{C}}, \chi_1, \beta_1, \Omega)]}{(1+K) N_{\text{CE}} t^{m+2/3} \Theta_{\text{CE}}(t)^{-1/2} e^{\Omega}}. \quad (29)$$

The transition time deduced for an EC process from Eq. (19) is, as it is well known, identical to that obtained for an E process¹, and the ptf's can be deduced by substituting Eqs (19) and (20) in Eq. (6). Then, we obtain

$$\begin{aligned}
 & N_{\text{EC}} t^{m+2/3} \Theta_{\text{EC}}(t)^{-1/2} e^{\Omega} 10^{2\eta(t)} = t_s^{2/3} - N_{\text{EC}} t^{m+2/3} S_m(\xi_{\text{A}}, \beta_1, \Omega) - \\
 & - \frac{10^{\eta(t)}}{1+K} \{ K \mu_{\text{EC}} t_s^{2/3} + \gamma_{\text{EC}} N_{\text{EC}} t^{m+2/3} [K S_m(\xi_{\text{C}}, \beta_1, \Omega) + T_m(\xi_{\text{C}}, \chi_1, \beta_1, \Omega)] \}, \quad (30)
 \end{aligned}$$

$$\Theta_{\text{EC}}(t)^{-1/2} = \frac{D_{\text{A}}^{1/2}}{2k_s t^{1/2}}. \quad (31)$$

The ptf for an irreversible ctr is clearly coincident to that obtained for an E process¹.

Power Law Current (*I*_a)

The equations corresponding to this case can be obtained by making $q = 0$ in the series S_m and T_m (Eqs (A19) and (A20)).

Exponential Law Current (1b)

Now, we can deduce the corresponding expressions by making $m = -1/6$ ($u = 0$) in the series S_m and T_m (Eqs (A19) and (A20)).

CASE 2: POWER LAW CURRENT OF THE TOTAL TIME t_s

The method used in this case differs from that used in the three preceding cases. Now we should introduce a new variable Φ_2 defined as

$$\Phi_2 = (C_B - KC_C) e^{kt_s} \quad (32)$$

instead of the variable Φ defined in Eq. (10). Furthermore, the dimensionless parameter Ω disappears, and instead of the variables β_1 and χ_1 we must introduce the variables β_2 and χ_2 , respectively, given by

$$\beta_2 = \left(\frac{t}{t_s}\right)^{1/2}, \quad \chi_2 = kt_s. \quad (33), (34)$$

In this way, we obtain the Eqs (B5)–(B8) in Appendix II for the surface concentrations.

RESULTS AND DISCUSSION

The equations obtained in this paper allow us to carry out a complete analysis of the CE and EC processes using ctf's corresponding to cases 1 and 2 (see the preceding section). These equations give the concentration profiles (Eqs (A1)–(A3) and (B1)–(B3)) and the surface concentrations (Eqs (17)–(20) and (B5)–(B8)). Here, we will only employ the equations corresponding to surface concentrations for the study of the E/t response obtained in the CE and EC processes. The analysis of concentration profiles $C_i(r, t)$ requires a separate study and is not dealt with here.

GENERAL ASPECTS OF THE EQUATIONS

The E/t response for the CE and EC processes deduced for a ctf corresponding to case 1 depends on the series S_m and T_m (Eqs (A19) and (A20)), while that corresponding to case 2 depends on the series V_m and W_m (Eqs (B9) and (B10)).

The series S_m and V_m are the same as those deduced for an E process in both cases (Eqs (A19) and (B9)). The series T_m and W_m have been obtained in this paper, they have upper and lower limits and satisfy the inequalities

$$0 \leq T_m(\xi_i, \chi_1, \Omega) \leq S_m(\xi_i, \beta_1, \Omega), \quad (35)$$

$$0 \leq W_m(\xi_i, \chi_2, \beta_2) \leq V_m(\xi_i, \beta_2). \quad (36)$$

For large values of χ_1 or χ_2 the series T_m and W_m are slowly convergent. In these conditions, we may apply the steady state approximation⁸, and proceeding as in a previous paper³ we deduce

$$T_m(\xi_i, \chi_1, \beta_1, \Omega) = \frac{e^{\Omega}}{2\chi_1^{1/2}} \quad \chi_1 \gg 1. \quad (37)$$

$$W_m(\xi_i, \chi_2, \beta_2) = \frac{1}{2\beta_2\chi_2^{1/2}} \quad \chi_2 \gg 1. \quad (38)$$

In Fig. 1 we have plotted T_m vs χ_1 when $\Omega = 0$ (case 1a), for an EPE ($\xi_c = 0$) corresponding to two limit situations: $t_1 = 0$ ($\beta_1 = 1$) and $t_1 \gg t$ ($\beta_1 = 0$) (curves a and b), and for an ESE ($\xi_c = 0.2 \text{ s}^{-1/6}$) with the same values of β_1 (curves c and d). It should be noticed that the influence of β_1 and ξ_c on T_m is small.

The influence of Ω and m on T_m (case 1) is clearly shown in Fig. 2. It can be deduced from the curves that Eq. (35) holds.

From the general equations (17)–(20) and (B5)–(B8) it is possible to deduce those corresponding to a great number of special situations, some of which have already been described in the literature.

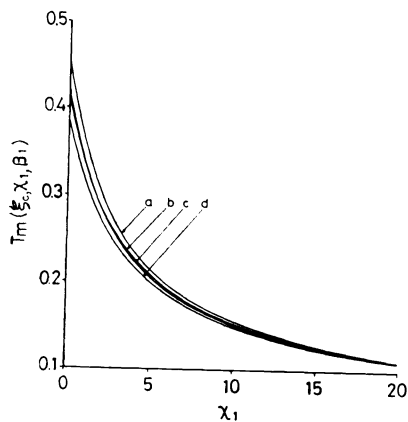


FIG. 1

Dependence of $T_m(\xi_c, \chi_1, \beta_1, \Omega)$ on χ_1 (Eq. (A20)) for the case 1a) with $m = 1/2$. The values of ξ_c and β_1 are, respectively: a 0.0, 1.0; b 0.0, 0.0; c 0.2, 1.0; d 0.2, 0.0

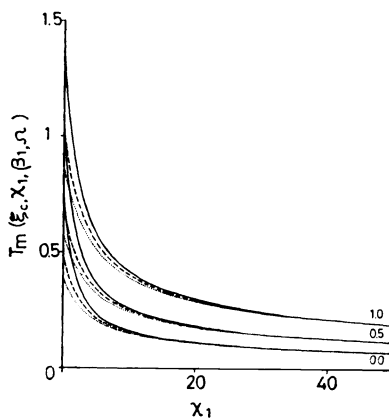


FIG. 2

Dependence of $T_m(\xi_c, \chi_1, \beta_1, \Omega)$ on χ_1 (Eq. (A20)) for the case 1. The values of Ω are shown on the curves. The values of m are: $-1/2$ (—); $1/6$ (---); $5/6$ (···). $\xi_c = 0$, $\beta_1^3 = 0.5$

a) *Null Blank Period*

In these conditions $\beta_1 = \beta_2 = 1$, $\chi_1 = \chi_2$, and the Eqs (A19) and (A20) for $w = 0$ and $u \geq 1/6$ are equivalent to Eqs (B9) and (B10) for $v \geq 1/6$. Moreover, we have the following relationships

$$S_m(\xi_C, \beta_1 = 1, \Omega = 0) = V_m(\xi_C, \beta_2 = 1) = \frac{(3/7)^{1/2} G_m(0, t)}{P_{6m/7}}, \quad (39)$$

$$T_m(\xi_C, \chi_1, \beta_1 = 1, \Omega = 0) = W_m(\xi_C, \chi_2, \beta_2 = 1) = \frac{(3/7)^{1/2} G_{m,e}(\chi)}{P_{6m/7}}, \quad (40)$$

where the functions $G_{m,e}(\chi)$ and $g_m(0, t)$ are given by Eqs (A1) and (A2) in ref.⁴, where there is no blank period (see also curves a and c in Fig. 1).

b) *Current Step $I(t) = I_0$*

This situation can be obtained from cases 1 and/or 2 by making $w = 0$ and $u = 0$ ($m = -1/6$) and/or $v = 0$ ($m = -1/6$), respectively. In these conditions we deduce (Eqs (A19)–(A20) and (B9)–(B10))

$$S_{-1/6}(\xi_C, \beta_1) = V_{-1/6}(\xi_C, \beta_2), \quad (41)$$

$$T_{-1/6}(\xi_C, \chi_1, \beta_1) = W_{-1/6}(\xi_C, \chi_2, \beta_2), \quad (42)$$

where

$$\chi_2 = \frac{\chi_1}{\beta_2^2}. \quad (43)$$

c) *Expanding Plane Electrode Model*

We can deduce the equations corresponding to this particular situation by making $\xi_i = 0$ in all the expressions in this paper. This model has recently been studied by Kant and Rangarajan⁶, for ctf's corresponding only to cases 1a) and 2 of this paper, and with the additioned assumption that the diffusion coefficients of all species are equal. In these conditions, our equations are equivalent to those deduced by these authors (see also Table I).

d) *Stationary Electrodes*

The DME, considered as an EPE ($\xi_i = 0$) or as an ESE ($\xi_i \neq 0$), can be transformed into a stationary electrode of area $A = A_0 t_1^{2/3}$ by making $t_1 \gg t$ (i.e. $\beta_1 = \beta_2 = 0$, curves b and d in Fig. 1). In this situation, the E/t response is much simple, and can be compared with that given in ref.⁹ and in the reviews of CE and EC mechanisms in refs^{10,11}.

TRANSITION TIMES

In Table I we show the values obtained for transition times corresponding to a CE mechanism for an EPE ($\xi_{0,C} = 0$) and for an ESE ($\xi_{0,C} \neq 0$), for a ctf corresponding to the case 1a) and for different values of u and t_1 . We have selected the same conditions as in Table II in ref.⁶ to compare. As can be observed, the values of τ_p agree with those obtained in this reference. We can also deduce that the sphericity effects are important and they increase strongly when u decreases.

Table II shows the transition times τ_p and τ calculated for a ctf corresponding to case 2. For this ctf, when $v = 2/3$ (the density of current remains constant) the

TABLE I

Comparison between the transition times obtained from Eqs (24) and (37) when $w = 0$ (case 1a) for an expanding plane electrode, τ_p ($\xi_{0,C} = 0$) and for an expanding sphere electrode, τ_e ($\xi_{0,C} = 0.15 \text{ s}^{-1/6}$), $N_{CE} = 2.7 \text{ s}^{-m}$, $K = 1$, $k = 25 \text{ s}^{-1}$, (—) $N_{CE} < (N_{CE})_{\min}$

u	$t_1 = 0.5$		$t_1 = 1$		$t_1 = 1.5$		$t_1 = 2$		$t_1 = 2.5$	
	τ_p	τ_e	τ_p	τ_e	τ_p	τ_e	τ_p	τ_e	τ_p	τ_e
1	0.983	1.024	1.189	1.232	1.352	1.392	1.487	1.532	1.609	1.657
2/3	0.849	0.904	1.137	1.202	1.366	1.436	1.566	1.643	1.746	1.830
1/2	0.726	0.787	1.076	1.157	1.362	1.456	1.616	1.726	1.849	1.972
1/3	0.541	0.598	0.961	1.062	1.334	1.467	1.676	1.847	2.001	2.205
1/6	0.294	0.328	0.742	0.853	1.233	1.436	1.745	2.065	2.271	2.721
0	0.079	0.085	0.378	0.442	0.928	1.218	1.801	3.420	3.200	—
-1/30	0.053	0.057	0.296	0.344	0.819	1.120	1.799	—	—	—

TABLE II

Comparison between the transition times obtained from Eqs (B5) and (38) (case 2) for an expanding plane electrode, τ_p ($\xi_{0,C} = 0$) and for an expanding sphere electrode, τ_e ($\xi_{0,C} = 0.15 \text{ s}^{-1/6}$), $N_{CE} = 2.4 \text{ s}^{-m}$, $K = 1$, $k = 10 \text{ s}^{-1}$

v	$t_1 = 1$		$t_1 = 1.5$		$t_1 = 2$		$t_1 = 2.5$	
	τ_p	τ_e	τ_p	τ_e	τ_p	τ_e	τ_p	τ_e
1	0.187	0.197	0.125	0.130	0.090	0.093	0.068	0.069
2/3	0.219	0.234	0.216	0.228	0.215	0.225	0.214	0.224
1/2	0.241	0.259	0.290	0.311	0.331	0.353	0.365	0.389
1/3	0.270	0.295	0.404	0.442	0.528	0.579	0.644	0.707
1/6	0.312	0.348	0.607	0.700	0.938	1.104	1.292	1.548

effect of t_1 on τ_p and τ is minimal. The sphericity effects are qualitatively similar to those described for Table I.

The effects of reversibility (K) and rate constants (k) of the chemical reaction on the transition times are similar to those described in refs^{3,6}.

Equations (17) and (B5) can be rewritten as

$$\frac{(1 + K) C_C(r_0, t)}{\zeta^* N_s} = \frac{1}{N_{CE}} - H_m(\xi_C, \chi_1, \beta_1, \Omega), \quad (44)$$

$$\frac{(1 + K) C_C(r_0, t)}{\zeta^* N_s} = \frac{1}{N_{CE}} - H_m(\xi_C, \chi_2, \beta_2), \quad (45)$$

where

$$H_m(\xi_C, \chi_1, \beta_1, \Omega) = \frac{t^{m+2/3}}{t_s^{2/3}} [S_m(\xi_C, \beta_1, \Omega) + KT_m(\xi_C, \chi_1, \beta_1, \Omega)], \quad (46)$$

$$H_m(\xi_C, \chi_2, \beta_2) = \frac{t^{1/2}}{t_s^{1/2-m}} [V_m(\xi_C, \beta_2) + KW_m(\xi_C, \chi_2, \beta_2)]. \quad (47)$$

In the same way as for an E process, a study of the behaviour of the function H with t permits us to determine the interval of existence of the transition time τ , corresponding to a CE process. In Fig. 3 we have plotted H vs t for a ctf with $w = 0.15 \text{ s}^{-1}$ and $u = -1/3$ (case 1). In this situation there always exists a transition time, but it presents a jump discontinuity with N_{CE} (ref.¹). It can be observed that the jump increases with k (i.e. as a CE process becomes an E process). In general, the variation of H with t is qualitatively similar to that described in refs^{1,2} for an E process, and when an N_{CE} minimal exists, its value diminishes when k gets smaller.

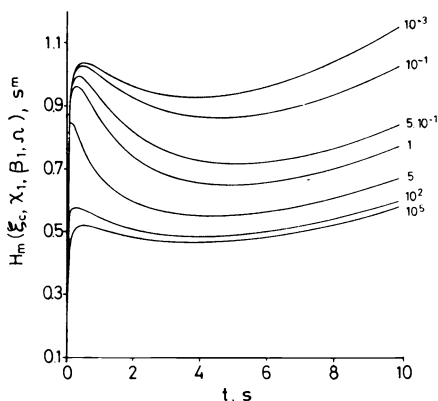


FIG. 3
Dependence of $H_m(\xi_C, \chi_1, \beta_1, \Omega)$ on t for a CE process (Eq. (46)) for the case 1 with $w = 0.15 \text{ s}^{-1}$ and $m = -1/2$. $\xi_{0,c} = 0.15 \text{ s}^{-1/6}$, $t_1 = 1 \text{ s}$, $K = 1$. The values of k (in s^{-1}) are shown on the curves

Finally, when $u = -1/2$ and for any value of w (case 1) there exists an N_{CE} maximal, which is given by

$$(N_{CE})_{\max} = \frac{2t_1^{2/3}}{(1+K)\pi^{1/2}} \quad (48)$$

It is also possible to determine K for a CE process by following a similar procedure to that described in refs^{3,12}. So, from Eq. (24) we find

$$\lim_{I_0 \rightarrow \infty} (I_0 \tau^{m+2/3}) = \frac{nFAD_C^{1/2} \zeta^* p_{(6m+4)/3}}{2(1+K)} \quad (49)$$

The existence of a blank time t_1 is of great interest for the determination of K , since, if $t_1 = 0$ (ref.³), the current density necessary for Eq. (49) to be fulfilled is quite high (it should be noticed that τ becomes smaller as I_0 increases).

Once K is determined, the rate constants k_1 and k_2 can be obtained from the working curves plotted in Figs 4 and 5. In these figures, we have represented $(\tau/\tau_d)^m Y$ vs χ_1 for several values of K , with Y being

$$Y = \left(\frac{\beta_{1,\tau_d}}{\beta_{1,\tau}} \right)^2 \frac{S_m(\xi_{C,\tau}, \beta_{1,\tau}, \Omega_\tau)}{S_m(\xi_{C,\tau_d}, \beta_{1,\tau_d}, \Omega_{\tau_d})} \quad (50)$$

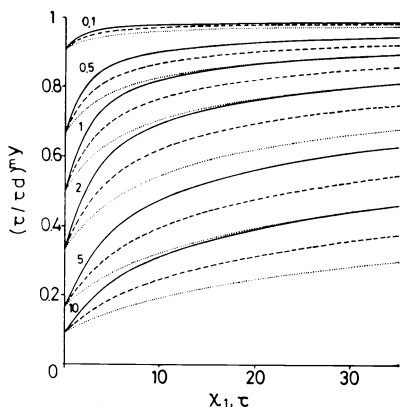


FIG. 4

Dependence of $(\tau/\tau_d)^m Y$ on $\chi_{1,\tau}$ (Eq. (50)) for the case 1a) with $m = -1/2$ (—); $m = 0$ (---); $m = 1$ (···). $\xi_{C,\tau} = 0.2$, $\beta_{1,\tau}^3 = 0.5$. The values of K are shown on the curves

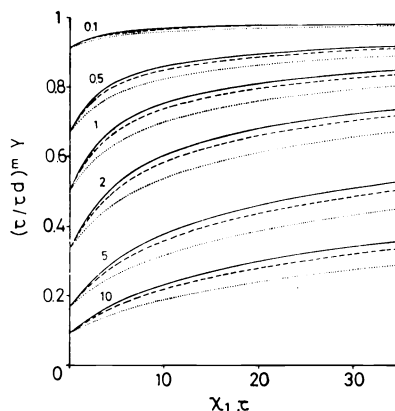


FIG. 5

Dependence of $(\tau/\tau_d)^m Y$ on $\chi_{1,\tau}$ (Eq. (50)) for the case 1 with $m = -1/2$ and $\Omega_\tau = -0.5$ (—); $\Omega_\tau = -0.1$ (---); $\Omega_\tau = 1$ (···). $\beta_{1,\tau}^3 = 0.7$. Other conditions as in Fig. 4

ξ_{C,τ_d} , β_{1,τ_d} and Ω_{τ_d} are the values of these variables for $t = \tau_d$ (see Symbols). Figures 4 and 5 show the influence of m and Ω_{τ} on these curves. The influence of $\xi_{C,\tau}$ and $\beta_{1,\tau}$ is very weak and the range of the rate constants that can be determined does not differ from that indicated in ref.³

The transition time deduced for an EC mechanism is identical to that corresponding to an E process, and the situation has already been discussed in refs^{1,2}.

POTENTIAL-TIME CURVES

Figure 6 shows the sphericity effects on the E/t curves obtained for a CE process with a ctf of the type 1a) for two different values of the blank period. In general, these effects increase with t and are more important when the exponents u and w (case 1), or v (case 2) decrease. Figure 7 shows the dependence of the E/t curves on K for a reversible ctr. The influence of k_s (Eq. (25)) is similar to that described in refs^{1,2}.

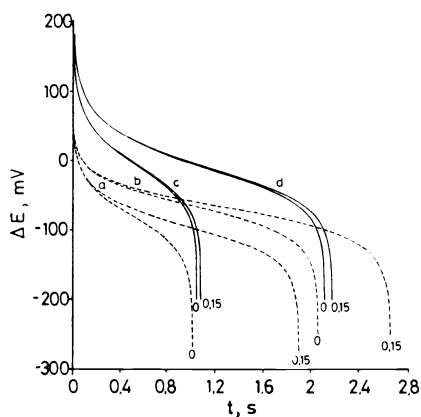


FIG. 6

Electrode curvature effects on the potential-time curves corresponding to a CE process when $k_s \gg 1$ (Eq. (28)) for the case 1 with $w = 0.1 \text{ s}^{-1}$ and $u = 1$ (—); $u = 0$ (---). The values of t_1 (in s) and N_{CE} (in s^{-m}) are, respectively: a 1.0, 1.6; b 2.0, 1.85; c 1.0, 2.0; d 2.0, 1.15. $T = 298 \text{ K}$, $n = 1$, $\gamma_{CE} = 1$, $\mu_{CE} = 0$, $k = 10 \text{ s}^{-1}$, $K = 2$. The values of $\xi_{0,C}$ (in $\text{s}^{-1/6}$) are shown on the curves

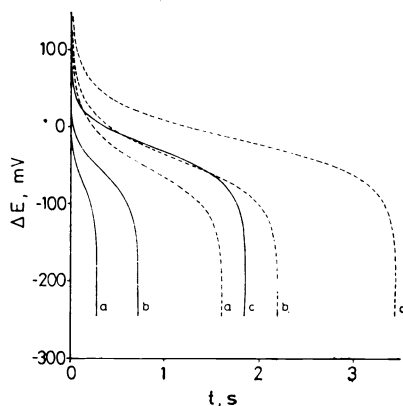


FIG. 7

Potential-time curves corresponding to a CE process when $k_s \gg 1$ (Eq. (28)) for the case 1 a with $u = 2/3$ (—) and for the case 2 with $v = 2/3$ (---). $\xi_{0,C} = 0.15 \text{ s}^{-1/6}$, $t_1 = 1 \text{ s}$, $N_{CE} = 1.5 \text{ s}^{-1/2}$, $k_1 = 10 \text{ s}^{-1}$. The values of K are: a 7.0, b 3.0, c 0.1. Other conditions as in Fig. 6

When the ctr is irreversible, we deduce from Eq. (29)

$$\Delta E = \frac{RT}{\alpha nF} \ln \frac{nFA_0 k_s \zeta^*}{(1+K)I_0} + \frac{RT}{\alpha nF} \ln g(\zeta_c, \chi_1, \beta_1, \Omega), \quad (51)$$

where

$$g(\zeta_c, \chi_1, \beta_1, \Omega) = \frac{e^{-\Omega}}{t_1^{m+1/6}} \{t_1^{2/3} - N_{CE} t_1^{m+2/3} [S_m(\zeta_c, \beta_1, \Omega) + KT_m(\zeta_c, \chi_1, \beta_1, \Omega)]\} \quad (52)$$

and the values of α and k_s can be obtained through a linear regression of ΔE vs $\ln g(\zeta_c, \chi_1, \beta_1, \Omega)$. Moreover, if we take into account the influence of exponents u and w on the reversibility of the ctr (ref.¹) it is possible to determine values of $k_s \leq \leq 10^{-2} \text{ cm s}^{-1}$ by using this procedure.

For an EC process, it is not possible to deduce the constants K and k from measurements of transition times. However, from the E/t curves corresponding to a reversible ctr and when $\zeta^* \neq 0$ it is possible to estimate the value of K by an extrapolation at zero time. In these conditions, from Eq. (30) we obtain

$$E(t \rightarrow 0) - E^0 = \frac{RT}{nF} \ln \frac{(1+K) [2t_1^{2/3} - N_{EC} \pi^{1/2}]}{2K\mu_{EC} t_1^{2/3} + \gamma_{EC} N_{EC} \pi^{1/2} (1+K)} \quad u = -1/2, \quad (53)$$

$$E(t \rightarrow 0) - E^0 = \frac{RT}{nF} \ln \frac{1+K}{K\mu_{EC}} \quad u > -1/2. \quad (54)$$

We have represented these curves in Fig. 8 for $u = -1/2$ and different values of K . It is also possible to determine k_1 and k_2 in the way indicated in ref.⁵ for $t_1 = 0$.

Finally, the dependence of E/t curves (Eq. (30)) on k_s is shown in Fig. 9. We have plotted the chronopotentiograms corresponding to $\alpha = 0.5$ and five different values of k_s . These curves are shifted to more negative potentials when k_s decreases. Furthermore, when $k_s \leq 10^{-3} \text{ cm s}^{-1}$ the process becomes totally irreversible, and therefore the corresponding E/t curves are coincident to those obtained for an E process. In these conditions we can determine α and k_s in the way indicated in refs^{1,2}.

CONCLUSION

We have analyzed the responses corresponding to CE and EC mechanisms when a broad class of ctr's, included in cases 1 and 2, is applied to the DME. The model chosen for this electrode is that of an expanding sphere (ESE). The electrode sphericity effects, which are maximal at the transition time, cannot be neglected when the

exponents of the ctf's diminish. All the expressions obtained previously in the literature for CE and EC processes in chronopotentiometry with power or exponential currents for planar and spherical electrodes can be deduced as particular cases of our equations. The use of ctf's corresponding to case 1 is of great interest, since they show very different behaviour depending on the relative sign of exponents u and w . We also propose methods for determining homogeneous and heterogeneous kinetic parameters by using any of the ctf's analyzed in this paper.

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APPENDIX I

Case 1. Power-Exponential Law Current

By using the transformations given by expressions (12)–(16) and supposing that ζ , Φ and C_D have the form

$$\zeta(r, t) = \zeta^* + \sum_{h,i,j,q=0} \varrho_{h,i,j,q}(s_C) \xi_C^h \chi_1^{im} \beta_1^j \Omega^q, \quad (A1)$$

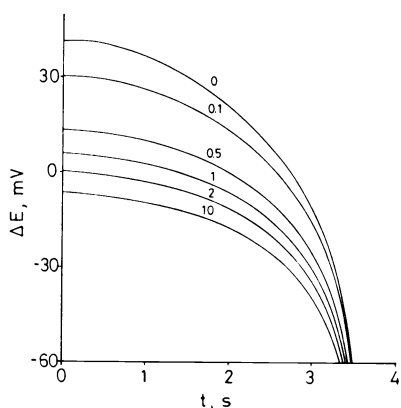


FIG. 8

Potential-time curves corresponding to an EC process when $k_s \gg 1$ (Eq. (30)) for the case 1 with $w = 1 \text{ s}^{-1}$ and $u = -1/2$. $N_{EC} = 0.3 \text{ s}^{2/3}$, $t_1 = 2 \text{ s}$, $\gamma_{EC} = 1$, $\mu_{EC} = 1$, $k = 0.5 \text{ s}^{-1}$. The values of K are shown on the curves. Other conditions as in Fig. 7

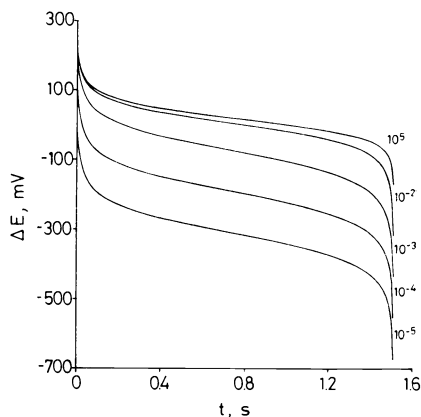


FIG. 9

Dependence of potential-time curves corresponding to an EC process on k_s (Eq. (30)) for the case 1 with $w = -0.1 \text{ s}^{-1}$ and $u = 1$. $N_{EC} = 3 \text{ s}^{-5/6}$, $D_A = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $k = 100 \text{ s}^{-1}$, $K = 1$. The values of k_s (in cm s^{-1}) are shown on the curves. Other conditions as in Fig. 7

$$\Phi(r, t) = \sum_{h,i,j,q=0} \delta_{h,i,j,q}(s_C) \zeta_C^h \chi_1^{i+m} \beta_1^j \Omega^q, \quad (A2)$$

$$C_D(r, t) = C_D^* + \sum_{h,i,j,q=0} \sigma_{h,i,j,q}(s_D) \zeta_D^h \chi_1^{im} \beta_1^j \Omega^q. \quad (A3)$$

Equation (11) is transformed into

$$\begin{aligned} \varrho''_{h,i,j,q}(s_C) + 2s_C \varrho'_{h,i,j,q}(s_C) - 2 \left(\frac{3h + 6mi + 2j + 6q}{3} \right) \varrho_{h,i,j,q}(s_C) = \\ = - \left\{ \sum_{f+g+1=h} c_f \varrho'_{g,i,j,q}(s_C) + \sum_{r+y=h} d_r \varrho'_{y,i,j-3,q}(s_C) + \right. \\ \left. + \frac{4}{3}(h+j-3) \varrho_{h,i,j-3,q}(s_C) \right\}, \end{aligned} \quad (A4)$$

$$\begin{aligned} \delta''_{h,i,j,q}(s_C) + 2s_C \delta'_{h,i,j,q}(s_C) - 2 \left(\frac{3h + 6(m+i) + 2j + 6q}{3} \right) \delta_{h,i,j,q}(s_C) = \\ = - \left\{ \sum_{f+g+1=h} c_f \delta'_{g,i,j,q}(s_C) + \sum_{r+y=h} d_r \delta'_{y,i,j-3,q}(s_C) + \right. \\ \left. + \frac{4}{3}(h+j-3) \delta_{h,i,j-3,q}(s_C) \right\}, \end{aligned} \quad (A5)$$

$$\begin{aligned} \sigma''_{h,i,j,q}(s_D) + 2s_D \sigma'_{h,i,j,q}(s_D) - 2 \left(\frac{3h + 6mi + 2j + 6q}{3} \right) \sigma_{h,i,j,q}(s_D) = \\ = - \left\{ \sum_{f+g+1=h} c_f \sigma'_{g,i,j,q}(s_D) + \sum_{r+y=h} d_r \sigma'_{y,i,j-3,q}(s_D) + \right. \\ \left. + \frac{4}{3}(h+j-3) \sigma_{h,i,j-3,q}(s_D) \right\}, \end{aligned} \quad (A6)$$

where

$$c_f = 2(-1)^f s_i^f, \quad (A7)$$

$$d_r = \frac{4}{3}(-1)^r (r+2) s_i^{r+1}. \quad (A8)$$

For an EC mechanism we must change D for A in Eqs (A3) and (A6).

The bvp corresponding to a CE process (Eqs (1)–(6)) is transformed into

$s_i \rightarrow \infty$:

$$\varrho_{h,i,j,q}(s_C) = \delta_{h,i,j,q}(s_C) = \sigma_{h,i,j,q}(s_D) = 0, \quad h, i, j, q \geq 0 \quad (A9)$$

$s_i = 0$:

$$\gamma_{CE}^{h+1} \varrho'_{h,i,j,q}(0) = -\sigma'_{h,i,j,q}(0) \quad (A10)$$

$$\varrho'_{h,i,j,q}(0) = 0 \quad \text{unless } h = 0, i = 1, j = 2 \quad (A11)$$

$$\sigma'_{0,1,2,q}(0) = \frac{\zeta^* N_s}{k^m q!} \quad q \geq 0 \quad (A12)$$

$$\delta'_{0,i,2,q}(0) = -K \frac{\zeta^* N_s}{k^m q! i!} \quad q, i \geq 0. \quad (A13)$$

Moreover

$$\sigma_{h,1,j,q}(s_D) = -\gamma_{CE} \varrho_{h,1,j,q}(s_D), \quad (A14)$$

$$\delta_{h,i,j,q}(s_C) = -\frac{K}{i!} \varrho_{h,i,j,q}(s_C). \quad (A15)$$

By following a similar procedure to that indicated in refs^{1,2} we have deduced the functions $\varrho_{h,1,j,q}(s_D)$ and $\varrho_{h,i,j,q}(s_C)$ which are identical to the $\sigma_{h,1,j,q}(s_i)$ ($i = D$ or C) functions obtained in ref.¹ for an E process (Eqs (A10)–(A18) in this reference) if we change C_A^* for $\zeta^* N_{CE}/k^m$. Moreover, for deducing the $\varrho_{h,i,j,q}(s_C)$ functions we must also change m for $(m + i)$ in the mentioned equations in ref.¹. Therefore, the concentration profiles (Eqs (A1)–(A3)) are determined totally.

The Eqs (A1)–(A3) are simplified at the electrode surface ($r = r_0$) to

$$\zeta(r_0, t) = \zeta^* [1 - t^m N_s \beta_1^2 S_m(\xi_C, \beta_1, \Omega)], \quad (A16)$$

$$\Phi(r_0, t) = K \zeta^* t^m N_s \beta_1^2 T_m(\xi_C, \chi_1, \beta_1, \Omega), \quad (A17)$$

$$C_D(r_0, t) = C_D^* + \gamma \zeta^* t^m N_s \beta_1^2 S_m(\xi_D, \beta_1, \Omega) \quad (A18)$$

with

$$S_m(\xi_i, \beta_1, \Omega) = \sum_{q=0} \left\{ \frac{J(m, q, \beta_1)}{p_{m,q,4}} - \xi_i J_1(m, q, \beta_1) + \xi_i^2 \frac{J_2(m, q, \beta_1)}{p_{m,q,4}} \right\} \frac{\Omega^q}{q!}, \quad (A19)$$

$$T_m(\xi_C, \chi_1, \beta_1, \Omega) = \exp(-\chi_1) \sum_{i=0} S_{m+i}(\xi_C, \beta_1, \Omega) \frac{\chi_1^i}{i!}, \quad (A20)$$

where $p_{m,q,4}$, $J(m, q, \beta_1)$, $J_1(m, q, \beta_1)$ and $J_2(m, q, \beta_1)$ are defined by expressions (A25) and (A26) in ref.¹. From Eqs (A16)–(A18) and taking into account Eqs (9) and (10) we deduce the expressions (17) and (18) for the surface concentrations.

By following a similar procedure to that described for a CE process we find the Eqs (19) and (20) corresponding to the surface concentrations for an EC process.

APPENDIX II

Case 2. Power Law Current of the Total Time t_s

By taking into account the Eqs (1)–(8), (12)–(13) and (32)–(34), and supposing that ζ , Φ and C_D have the form

$$\zeta(r, t) = \zeta^* + \sum_{h,i,j=0} \varrho_{h,i,j}(s_C) \zeta_C^h \chi_2^{im} \beta_2^j, \quad (B1)$$

$$\Phi(r, t) = \sum_{h,i,j=0} \delta_{h,i,j}(s_C) \zeta_C^h \chi_2^{i+m} \beta_2^j, \quad (B2)$$

$$C_D(r, t) = C_D^* + \sum_{h,i,j=0} \sigma_{h,i,j}(s_D) \zeta_D^h \chi_2^{im} \beta_2^j, \quad (B3)$$

where

$$m = v - 1/6, \quad (B4)$$

we deduce the functions $\varrho_{h,i,j}(s_C)$, $\delta_{h,i,j}(s_C)$ and $\sigma_{h,i,j}(s_D)$ if we follow a similar procedure to that indicated in Appendix I and in ref.². The functions $\varrho_{h,1,j}(s_C)$ and $\varrho_{h,i,j}(s_C)$ are identical to the functions $\sigma_{h,1,j}(s_C)$ deduced in ref.² for an E process (Eqs (A2)–(A12) in this reference) if we write $\zeta^* N_{CE}/k^m$ instead of C_A^* . Moreover, for deducing the functions $\varrho_{h,i,j}(s_C)$ we must also change m for $(m + i)$ in the mentioned equations in ref.².

In this way, we have deduced the expressions corresponding to the surface concentrations of the species C and D for the CE process

$$\frac{C_C(r_0, t)}{\zeta^*} = \frac{1}{1 + K} \left\{ 1 - \frac{N_{CE} t^{1/2}}{t_s^{1/2-m}} [V_m(\zeta_C, \beta_2) + K W_m(\zeta_C, \chi_2, \beta_2)] \right\}, \quad (B5)$$

$$\frac{C_D(r_0, t)}{\zeta^*} = \mu_{CE} + \frac{\gamma_{CE} N_{CE} t^{1/2}}{t_s^{1/2-m}} V_m(\zeta_D, \beta_2). \quad (B6)$$

For an EC process, by following a similar procedure, we deduce

$$\frac{C_A(r_0, t)}{C_A^*} = 1 - \frac{N_{EC} t^{1/2}}{t_s^{1/2-m}} V_m(\xi_A, \beta_2), \quad (B7)$$

$$\frac{C_B(r_0, t)}{C_A^*} = \frac{1}{1 + K} \left\{ K \mu_{EC} + \frac{\gamma_{EC} N_{EC} t^{1/2}}{t_s^{1/2-m}} [K V_m(\xi_C, \beta_2) + W_m(\xi_C, \chi_2, \beta_2)] \right\} \quad (B8)$$

with

$$V_m(\xi_i, \beta_2) = F(m, \beta_2) - \xi_i F_1(m, \beta_2) - \xi_i F_2^2(m, \beta_2) \quad (B9)$$

$$W_m(\xi_i, \chi_2, \beta_2) = e^{-\chi_2} \sum_{i=0}^m V_{m+i}(\xi_i, \beta_2) \frac{\chi_2^i}{i!}, \quad (B10)$$

where $F(m, \beta_2)$, $F_1(m, \beta_2)$ and $F_2(m, \beta_2)$ are defined by Eqs (17), (19) and (21) in ref.².

Since the convergence of the W_m series is slightly slower than that corresponding to the T_m series (Eq. (A20)), in order to obtain accurate results, it is advisable to choose the values of τ in such a way that $\beta_2^2 \leq 0.5$. Moreover, we have calculated a sixth term, $G(m)$, in the $F(m, \beta_2)$ function which is given by

$$G(m) = \frac{6858432m^6 - 109734912m^5 + 622550400m^4 - 1757257980m^3}{64194923520} + \frac{2019452148m^2 - 582399888m + 214128635}{64194923520}. \quad (B11)$$

SYMBOLS

k_1, k_2	rate constants of the chemical reaction
K	equilibrium constant of the chemical reaction ($=k_2/k_1$)
k	$=k_1 + k_2$
k_f, k_b	heterogeneous rate constants of the forward and reverse charge transfer reactions
k_s	apparent heterogeneous rate constant of charge transfer at E^0
α	electron-transfer coefficient
$E(t)$	time-dependent electrode potential
E^0	formal standard potential of electroactive couple
ΔE	$=E(t) - E^0$
t	time elapsed between current application and measurement of the potential
t_1	blank period
t_s	total time ($=t_1 + t$)
τ_p	transition time for a CE process for an EPE
τ	transition time for a CE process for an ESE
τ_d	transition time for an E or EC process for an ESE
$I(t)$	time dependent faradaic current [$=I_0 t^u e^{wt}$, $u \geq -1/2$, $\forall w$ (case 1) or $=I_0 t_s^v$, $\forall v$ (case 2)]
I_0	value of $I(t)$ at $u = w = 0$ (case 1) or $v = 0$ (case 2)
m	$= [u - 1/6$ (case 1) or $v - 1/6$ (case 2)]
Ω	dimensionless parameter ($=wt$)
ξ_i	dimensionless spherical correction parameter
$\xi_{0,i}$	$= \xi_i t_s^{1/3} / t^{1/2}$
r	distance from the center of the electrode
r_0	electrode radius at time t_s
$A(t_s)$	time-dependent electrode area ($=A_0 t_s^{2/3}$)
A_0	electrode area at $t_s = 1s$ ($= (4\pi)^{1/3} (3m_{\text{Hg}}/d)^{2/3}$)
A	electrode area when $t_1 \gg t$ (stationary electrode) ($=A_0 t_1^{2/3}$)

a	$(3m_{\text{Hg}}/4\pi d)^{1/3}$
m_{Hg}, d	rate of flow and density of mercury
ESE	expanding spherical electrode
EPE	expanding plane electrode
SSE	stationary spherical electrode
SPE	stationary plane electrode
$C_i(r, t)$	concentration profile of species i (A, B, C or D)
$C_i(r_0, t)$	surface concentration of species i
C_i^*	bulk concentration of species i
ζ^*	$C_B^* + C_C^*$
p_j	$= 2\Gamma(1 + j/2)/\Gamma((1 + j)/2)$
Γ	gamma Euler function
	Other definitions are conventional.

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