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CURRENT REVERSAL CHRONOPOTENTIOMETRY AT SPHERICAL ELECTRODES

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ABSTRACT

A general study on current reversal chronopotentiometry at spherical electrodes (as are the hanging mercury drop electrode or the static mercury drop electrode) is carried out. The effects of amalgam formation, insolubility of reaction product and electrode curvature on the potential time functions are presented. The value of the ratio τ'/t_2 (where τ' is the transition time in the reverse step and t_2 is the previous electrolysis time) can be used as diagnostic criterion to detect amalgamation or insoluble product formation. Methods to determine kinetic parameters and the formal standard potential of the electroactive couple in all the possible behaviours of the reduced species are proposed.

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1. INTRODUCTION

The theory for a charge transfer reaction in current reversal chronopotentiometry (CRC) at spherical electrodes has been developed only for the transition times [1-3] and with the following additional restrictions 1) both species (the oxidized and the reduced one) are soluble in the electrolyte solution, 2) the product of the electrode reaction is not present at the beginning of the experiment and 3) equal forward and reverse currents.

In this paper, we have carried out the general study of the potential time response related to a slow charge transfer reaction with CRC at the above mentioned electrode. Besides, we have taken into account the three possible situations for the behaviour of the product of the electrode reaction (a) soluble in the electrolyte solution, (b) soluble in the electrode (amalgam formation) and (c) insoluble. The different behaviour of the potential time functions obtained in each case, has allowed us to develop a simple and easy method to discriminate between the above situations. This method is based in the measurement of the transition time corresponding to the reverse step, τ', in relation to the previous electrolysis time, t_2, and we have applied it to three experimental systems which include the three possibilities: $Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$, $Tl^+/Tl(Hg)$ and $I^-/Hg_2I_2(sol)$.

On the other hand, the sphericity and electrolysis time effects on the forward and reverse response have been considered. Finally, for an irreversible process, by extension of the method proposed in reference 4, it is possible to determine the kinetic parameters and the formal standard potential of the electroactive couple in all cases.

2. BASIC CONSIDERATIONS

a) Both species, the oxidized, A, *and the reduced one,* B, *are soluble in the electrolyte solution.*

For a slow charge transfer reaction, when a constant current is applied to the stationary spherical electrode, the surface concentrations of the oxidized species (A) and the reduced one (B) can be deduced by making w=0 in equations (27)-(28) of reference 5. So, we obtain

$$\frac{C_A(r_0,t)}{C_A^*} = 1 - N_e t^{1/2} E(\xi_A) \tag{1}$$

$$\frac{C_B(r_0,t)}{C_A^*} = \mu + N_e \gamma t^{1/2} E(\xi_B) \tag{2}$$

$$\xi_i = \frac{2\sqrt{D_i t}}{r_0} \tag{3}$$

$$\mu = \frac{C_B^*}{C_A^*} \tag{4}$$

$$N_e = \frac{2I_0}{nFAD_A^{1/2}C_A^*} \tag{5}$$

$$\gamma = \sqrt{D_A/D_B} \tag{6}$$

The E-function is defined in the following general form

$$E(z) = \frac{1}{\sqrt{\pi}} - \frac{1}{4}z + \frac{1}{6\sqrt{\pi}}z^2 - \frac{1}{32}z^3 + \frac{1}{60\sqrt{\pi}}z^4 - \ldots \tag{7}$$

and the transition time, τ

$$\frac{1}{N_e} = \frac{\tau^{1/2}}{\sqrt{\pi}} - \frac{D_A^{1/2}}{2r_0}\tau + \frac{2D_A}{3\sqrt{\pi}r_0^2}\tau^{3/2} - \frac{D_A^{3/2}}{4r_0^3}\tau^2 + \frac{4D_A^2}{15\sqrt{\pi}r_0^4}\tau^{5/2} \ldots \tag{8}$$

If the current is reversed at time t_2 ($t_2 \leq \tau$), the boundary value problem is given by

---

$$t' = 0 \quad r \geq r_0 \qquad C_A = C_A(s_A,\xi_A)\ ,\ C_B = 0 \tag{27}$$

$$t' > 0 \quad \begin{cases} r \to \infty & C_A(r,t') = C_A(s_A,\xi_A) \quad (28) \\ r \to -\infty & C_B(r,t') = C_B(s_B,\xi_B) \quad (29) \end{cases}$$

$$t' > 0 \quad r = r_0 \qquad D_A\left(\frac{\partial C_A}{\partial r}\right)_{r=r_0} = D_B\left(\frac{\partial C_B}{\partial r}\right)_{r=r_0} = -\frac{I_0'}{nFA} \tag{30}$$

where $C_A(s_A,\xi_A)$ and $C_B(s_B,\xi_B)$ are given by eqns. (24) and (54) in reference 5 (making w=0).

The procedure of derivation followed, using these new conditions, differs slightly from that adopted in the preceding section, and all expresions obtained here are identical to the preceding ones if we replace ξ_B by $-\xi_B$ and ξ_B' by $-\xi_B'$.

c) The product B is insoluble.

1.- Reduction process

$$\left.\begin{array}{ll} t = 0 & r \geq r_0 \\ t > 0 & r \to \infty \end{array}\right\} \qquad C_A = C_A^* \qquad C_B = 0 \tag{31}$$

$$t > 0 \quad r = r_0 \qquad D_A\left(\frac{\partial C_A}{\partial r}\right)_{r=r_0} = \frac{I_0}{nFA} \tag{32}$$

$$C_B(r=r_0) = 1 \tag{33}$$

we obtain the following expressions for the surface concentrations of A and B

$$\frac{C_A(r_0,t')}{C_A^*} = 1 - N_e\left\{(t_2+t')^{1/2}E(\xi_A) - (1+Q)(t')^{1/2}E(\xi_A')\right\} \quad (16)$$

$$\frac{C_B(r_0,t')}{C_A^*} = \mu + \gamma N_e\left\{(t_2+t')^{1/2}E(\xi_B) - (1+Q)(t')^{1/2}E(\xi_B')\right\} \quad (17)$$

$$Q = \frac{I_0'}{I_0} \quad (18)$$

from eqn. (17) we deduce for the transition time the following expression

$$(\tau')^{1/2} = \frac{\mu + \gamma N_e(t_2+\tau')^{1/2}E(\xi_B,\tau')}{\gamma N_e(1+Q)E(\xi_B',\tau')} \quad (19)$$

where $\xi_{B,\tau'}$ and $\xi'_{B,\tau'}$ are the values of the variables ξ_B and ξ_B' for $t = t_2+\tau'$ and $t' = \tau'$, respectively.

If the species B is not present at the beginning of the electrolysis, eqn. (19) becomes

$$(\tau')^{1/2} = \frac{(t_2+\tau')^{1/2}E(\xi_B,\tau')}{(1+Q)E(\xi_B',\tau')} \quad (20)$$

This equation is equivalent, in the particular case Q = 1 to that obtained by Murray and Reilley [1]. Therefore, eqns. (19)-(20) are transformed into the corresponding to a stationary plane electrode if we make $r_0 \rightarrow \infty$ [1,6,7].

On the other hand, eqn. (19) may be rewritten in polarographic units (τ' and t_2 s, D_B cm^{2}s^{-1}, r_0 cm, C_A^* mM, I_0 μA) at as

$$(\tau')^{1/2} = \frac{1}{(1+Q)E(\xi_B',\tau')}\left\{\frac{606327\mu n r_0^2\sqrt{D_A}\,C_A^*}{\gamma I_0} + (t_2+\tau')^{1/2}E(\xi_B,\tau')\right\} \quad (21)$$

Potential time functions

The potential time functions of the forward process (reduction of A) are described by eqns. (41)-(50) in reference 4. For the reoxidation process, these functions may be obtained by inserting eqns. (16) and (17) in eqn. (13), so we deduce

$$\theta_0^{-1/2}QN_e10^{\alpha\eta(t')} = 10^{\eta(t')}\left\{\mu + \gamma N_e\left[(t_2+t')^{1/2}E(\xi_B) - (1+Q)(t')^{1/2}E(\xi_B')\right]\right\} - \left\{1 - N_e\left[(t_2+t')^{1/2}E(\xi_A) - (1+Q)(t')^{1/2}E(\xi_A')\right]\right\} \quad (22)$$

HEWLETT-PACKARD-AMEL 862/D recorder . The transition time, τ', was assumed to be that at which a sudden jump in the reverse curve was observed . In all cases the transition times measured in several experiments under the same conditions were reproducible to better than 0.01 s. In order to avoid distortion in the curves by non-faradaic processes, relatively concentrated solutions ($>10^{-3}$ M) were used [10].

A Hanging Mercury Drop electrode (METRHOM EA 290) was used as working electrode. We used a 5×10^{-2}M stock solution of $Fe(NO_3)_3$, $TlNO_3$ or KI, to which $K_2C_2O_4$ (pH = 4.5) or KNO_3 were added. The electrode reference was SCE and the measurements were performed at 25°C. The description of the rest of the experimental procedures used in this work can be found in reference 9.

4. RESULTS AND DISCUSSION

Figure 1 shows the dependence of the ratio τ'/t_2 on t_2 for a stationary spherical electrode (as are the hanging mercury drop electrode, HMDE, or the static mercury drop electrode, SMDE) when $\mu = 0$ (eqn. (20)) for three values of the ratio between the reverse and direct current, Q. We have represented in this graph the situation in which both species are soluble in the electrolyte solution (a) as well as that in which the product is amalgamated into the electrode (b). As can be observed, in the former case, it is fulfilled the inequality (eqn. 20)

$$\hat{\delta} C_A = \hat{\delta} C_B = 0 \qquad (9)$$

$$\hat{\delta} = \frac{\partial}{\partial t'} - D_i\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r}\right) \qquad (10)$$

$$\left.\begin{array}{ll} t' = 0 & r \geq r_0 \\ t' > 0 & r \rightarrow \infty \end{array}\right\} \qquad C_A = C_A(s_A, \xi_A)\ ,\ C_B = C_B(s_B, \xi_B) \qquad (11)$$

$$t' > 0 \quad r = r_0 \qquad D_A\left(\frac{\partial C_A}{\partial r}\right)_{r=r_0} = -D_B\left(\frac{\partial C_B}{\partial r}\right)_{r=r_0} = -\frac{I'_0}{nFA} \qquad (12)$$

$$\frac{I'_0}{nFA} = k_b C_B(r_0, t') - k_f C_A(r_0, t') \qquad (13)$$

where $t = t_2 + t'$ and $C_A(s_A, \xi_a)$ and $C_B(s_B, \xi_B)$ are given by equations (24)-(25) in reference 5.

The equations (9) can be solved by using of the dimensionless variables

$$s'_i = \frac{r - r_0}{2\sqrt{D_i t'}} \qquad (14)$$

$$\xi'_i = \frac{2\sqrt{D_i t'}}{r_0} \qquad (15)$$

and adopting similar procedures to those in references 4 and 5, 2.- Reoxidation process

$$\left.\begin{array}{ll} t' = 0 & r \geq r_0 \\ t' > 0 & r \rightarrow \infty \end{array}\right\} \qquad C_A = C_A(s_A, \xi_A) \;,\; C_B = 0 \qquad (34)$$

$$t' > 0 \quad r = r_0 \qquad D_A\left(\frac{\partial C_A}{\partial r}\right)_{r=r_0} = -\frac{I'_0}{nFA} \qquad (35)$$

$$C_B(r=r_0) = 1 \qquad (36)$$

Under these conditions, the eqn. (8), corresponding to the transition time of the reduction of species A remains valid, while the transition time for the reoxidation of B, τ', fulfills, obviously

$$\frac{\tau'}{t_2} = \frac{1}{Q} \qquad (37)$$

This last relation is valid, evidently, for any type of electrode, stationary or not.

The potential time functions adopt the following general form

1.- Reduction process

$$10^{\eta(t)}\left\{\theta_0^{-1/2} N_e C_A^* 10^{(\alpha-1)\eta(t)} + 1\right\} = C_A^*\left\{1 - N_e t^{1/2} E(\xi_A)\right\} \qquad (38)$$

$$\eta(t) = \frac{nF}{RT\ln 10}\left[E(t) - E^0\right] \qquad (39)$$

2.- Reoxidation process

$$10^{\eta(t')}\left\{1 - \theta_0^{-1/2} Q N_e C_A^* 10^{(\alpha-1)\eta(t')}\right\} =$$

$$C_A^*\left\{1 - N_e (t_2+t')^{1/2} E(\xi_A) + N_e (1+Q)(t')^{1/2} E(\xi'_A)\right\} \qquad (40)$$

where $\eta(t')$ is given by eqn.(24).

For a reversible process eqn. (40) is simplified to

$$E(t') = E^0 + \frac{RT}{nF} \ln C_A^*\left\{1 - N_e (t_2+t')^{1/2} E(\xi_A) + \right.$$

$$\left. + N_e (1+Q)(t')^{1/2} E(\xi'_A)\right\} \qquad (41)$$

and for an irreversible one, eqn. (40) becomes

$$E = E^0 + \frac{RT}{(1-\alpha)nF} \ln \frac{I'_0}{nFAk_s} \qquad (42)$$

3. EXPERIMENTAL

E-t curves were obtained with an AMEL 553 potentiostat-galvanostat (modulated by an AMEL 565 square wave generator) and a NICOLET Explorer III digital oscilloscope. Hard copies of the E-t curves were obtained with a where

$$\theta_0 = 4k_s^2/D_A \qquad (23)$$

$$\eta(t') = \frac{nF}{RT\ln 10}\left[E(t') - E^0\right] \qquad (24)$$

For a reversible process ($k_s \rightarrow \infty$), eqn. (22) is transformed to

$$\eta(t') = \log \frac{1 - N_e\left[(t_2+t')^{1/2}E(\xi_A) - (1+Q)(t')^{1/2}E(\xi_A')\right]}{\mu + \gamma N_e\left[(t_2+t')^{1/2}E(\xi_B) - (1+Q)(t')^{1/2}E(\xi_B')\right]} \qquad (25)$$

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

$$\eta(t') = \frac{1}{1-\alpha}\log \frac{\theta_0^{-1/2}RN_e}{\mu + \gamma N_e\left[(t_2+t')^{1/2}E(\xi_B)-(1+Q)(t')^{1/2}E(\xi_B')\right]} \qquad (26)$$

If $r_0 \rightarrow \infty$, eqn. (22), (25) and (26) are equivalent to that obtained by Delahay and Berzins [6] and Macero and Anderson [7,8] for a stationary plane electrode.

b) Amalgamation of product B

In this case, we must rewrite the boundary conditions for the reoxidation processes as follows,

We have obtained in all cases a great number of chronopotentiograms (an example is shown in fig. 3) by using different values of I_0, I_0', t_2 and C_A^*. As can be observed, a very good agreement between experimental results and theoretical predictions is observed.

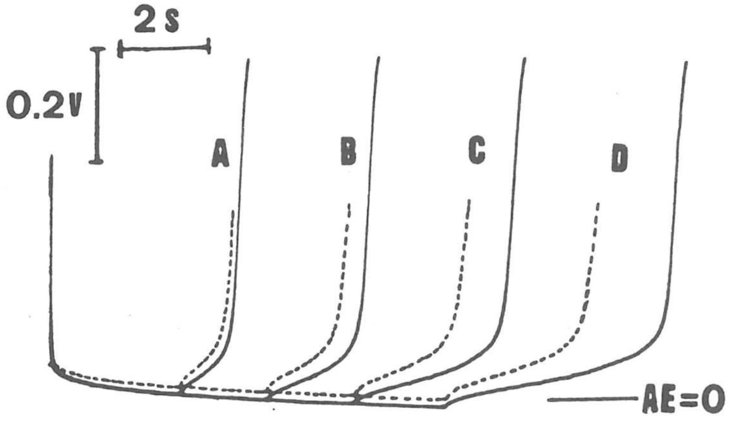

Figure 3.- Comparison between experimental potential-time curves obtained with and without amalgam formation. Tl^+ 3 mM in 0.2 M KNO_3 (——) and $Fe(C_2O_4)_3^{3-}$ 3 mM in 0.2 M $K_2C_2O_4$ (----). HMDE. r_0 = 0.042 cm. $I_0 = I_0'$ = 3 μA. The values of t_2 (s) are: A) 3; B) 5; C) 7; D) 9. $E^0(Tl^+/Tl(Hg))$ = - 0.458 V and $E^0(Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-})$ = -0.248 V.

In figs. 4 and 5 we have plotted ΔE ($=E(t)-E^0$) vs t with $\mu = 0$ and $t_2 = \tau$ for reversible (fig. 4), quasireversible and irreversible (fig. 5) processes. From these curves, we may deduce that the amalgamation effect (which originates the shifting of both, the forward and reverse, curves to more negative potentials) influences more strongly the reverse response than the forward one. Moreover, in the forward curve, this influence decreases when k_s diminishes, while the reverse response is practically independent on k_s. This behaviour is due

Finally, if species B is insoluble, independently of the type of electrode selected, it is fulfilled (eqn.(37))

$$(c) \qquad \frac{\tau'}{t_2} = \frac{1}{Q}$$

This different behaviour of the ratio τ'/t_2 can be used as diagnostic criterion in order to distinguish between the above possibilities. From the experimental point of view, the use of the HMDE has came upon the problem of the scarce reproducibility of its radius. Tipically, an uncertainty to 2-3% in the electrode radius is found, which leads to an uncertainty of 15% or larger in the transition time of the forward step (eqn. (8)). However (see figure 2), if the current is reversed at time $t_2 < \tau$, the same uncertainty in the electrode radius drives to deviations lower than 0.3% in τ'. This makes to reversal current chronopotentiometry with the HMDE largely applicable experimentally.

From figures 1 and 2 we may also deduce that, for the (a) and (b) situations, a decrease of r_0, and/or Q, and an increase of t_2 have the effect to emphasize the spherical nature of diffusion. Therefore, only when the span of time of the experiment is sufficiently short, we can approximate the ratio τ'/t_2 to that obtained in a linear diffusion problem [6,7]. Moreover, the relative error commited by using of this simplification diminishes slowly when Q increases. So, for example, if $Q \geq 1/3$ and $r_0 = 0.05$ cm, the relative error commited is lower than 6% in all cases, if $t_2 < 0.4$ s.

In tables I-III the practical application of eqns. (37), (43) and (44) is shown. In these tables we compare the experimental measurements of τ'/t_2 carried out for the systems $Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$, $Tl^-/Tl(Hg)$ and $I^-/Hg_2I_{2(sol)}$, which fulfill, respectively, the (a), (b) and (c) conditions. The values of the diffusion coefficients have been taken from literature [11-13].

Table I

Comparison between the values of the ratio τ'/t_2 computed from eqn. (20) (see also eqn. (43)), $(\tau'/t_2)_{cal}$, with those obtained from experimental E-t curves, $(\tau'/t_2)_{exp}$, for the system $Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$ in 0.2 M $K_2C_2O_4$ (pH = 4.5). HMDE. r_0= 0.042 cm. $C^*_{Fe(C_2O_4)_3^{3-}}$ = 2 mM, $C_{Fe(C_2O_4)_3^{4-}}$ = 0, $D_{Fe(C_2O_4)_3^{4-}}$ = $6.2\times10^{-6} cm^2 s^{-1}$[11].

I_0, µA	I'_0, µA	t_2, s	$(\tau'/t_2)_{cal}$	$(\tau'/t_2)_{exp}$
6.0	2.0	1.00	1.18	1.18
6.0	2.0	1.50	1.16	1.16
6.0	2.0	2.00	1.14	1.13
6.0	2.0	2.50	1.12	1.12
5.0	2.5	1.00	0.74	0.73
5.0	2.5	2.00	0.71	0.71
5.0	2.5	3.00	0.70	0.70
5.0	2.5	4.00	0.68	0.68
5.0	5.0	1.00	0.31	0.31
5.0	5.0	2.00	0.30	0.30
5.0	5.0	3.00	0.29	0.29
5.0	5.0	4.00	0.28	0.28

and for the reverse one, in the a) and b) situations

$$E(t') = E^0 + \frac{RT}{(1-\alpha)nF}\ln\frac{I'_0}{nFAC^*_AK_s} - \frac{RT}{(1-\alpha)nF}\ln g'_e(t',\xi'_B) \quad (47)$$

where, if both species are soluble in the electrolyte solution,

$$g'_e(t',\xi_B,\xi'_B) = \mu + \frac{2I_0}{nFA\sqrt{D_A}C^*_A}\left\{(t_2+t')^{1/2}E(\xi_B) - (1+Q)(t')^{1/2}E(\xi'_B)\right\} \quad (48)$$

and, if amalgamation takes place,

$$g'_e(t',\xi_B,\xi'_B) = \mu + \frac{2I_0}{nFA\sqrt{D_A}C^*_A}\left\{(t_2+t')^{1/2}E(-\xi_B) - (1+Q)(t')^{1/2}E(-\xi'_B)\right\} \quad (49)$$

From the slopes and intercepts of the plots of E(t) vs ln $g_e(t,\xi_B)$ and E(t') vs ln $g'_e(t',\xi_B,\xi'_B)$ we can deduce the above mentioned parameters, obtaining

$$\alpha = \frac{RT}{nFP_A} \quad (50)$$

or

$$(a) \quad \frac{\tau'}{t_2} < \frac{1}{Q(Q+2)} \quad (43)$$

In the particular case Q = 1, this result agrees with that obtained from eqn. (44) in reference 1 and has been experimentally proved by Murray and Gross [2].

When B is amalgamated into the electrode, from eqn. (20) (by changing ξ_B and ξ'_B by $-\xi_B$ and $-\xi'_B$) we obtain (see figure 1)

$$(b) \quad \frac{\tau'}{t_2} > \frac{1}{Q(Q+2)} \quad (44)$$

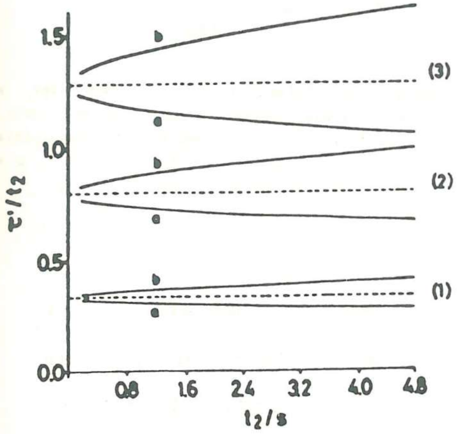

Figure 1.- Dependence of τ'/t_2 on t_2 (eqn. (20)). $\mu = 0$, $D_B = 10^{-5}$ cm^{2}s^{-1}, $r_0 = 0.05$ cm: (a) species B is soluble in the electrolyte solution, (b) amalgam formation. The values of Q are (1) 1; (2) 1/2; (3) 1/3. The dashed lines are the corresponding to an stationary plane electrode.

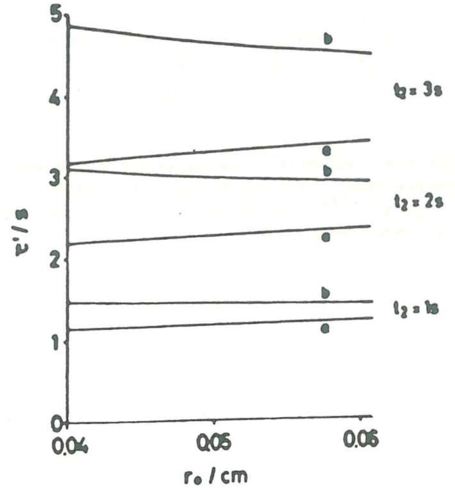

Figure 2.- Dependence of τ' on r_0 (eqn. (20)). Q = 1. The values of t_2 (s) are shown on the curves. Other conditions as in Figure 1.

to the fact that the effect of the amalgam formation on the reoxidation process is maximum in t' = τ', and, therefore, is not substantially affected by the kinetics of the process.

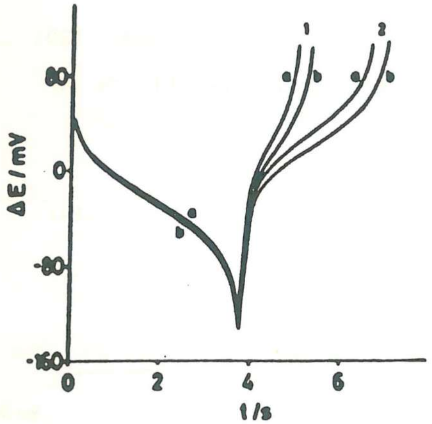

Figure 4.- Potential-time curves for a reversible process (eqn. (25)) n = 1, $\gamma = 1$, T = 298 K, $t_2 = \tau$. $N_e = 1\ s^{-1/2}$. The values of Q are (1) 1; (2) 1/2;. Other conditions as in Figure 1.

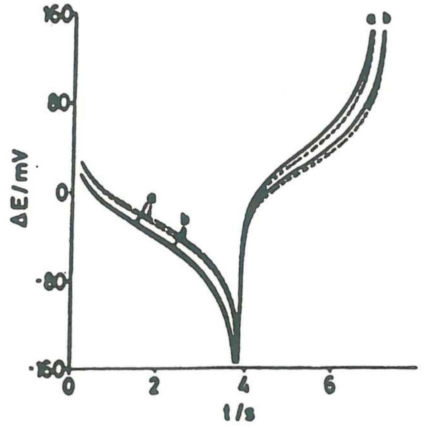

Figure 5.- Potential time curves for a quasirreversible process (eqns. (22) and (26)). $k_s = 5{\times}10^{-3}\ cm\ s^{-1}$ (- - -), and for an irreversible one, $k_s = 5{\times}10^{-5}\ cm\ s^{-1}$ (——). $N_e = 1\ s^{-1/2}$, Q = 1/2. Other conditions as in Figure 3.

On the other hand, the effect of kinetic parameters α and k_s on these curves is qualitatively similar to that described in references 4 and 8. In the case of insoluble product formation, (see figure 6) the charge transfer reaction behaves reversibly for values of k_s up to 10^{-3}cm.s^{-1}, while behaves as totally irreversible for values of k_s lower than 10^{-6}cm.s^{-1}. In this last case, according to eqn.(42), the reverse curve is time independent.

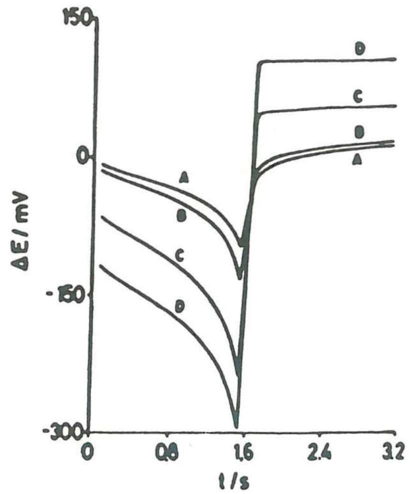

Figure 6.- Potential time curves in the case of insoluble product formation (eqns. (38) and (40)). The values of k_s (cm s^{-1}) are (A) 10^3; (B) 10^{-4}; (C) 10^{-6}; (D) 10^{-7}. $N_e = 1.5\ s^{-1/2}$, Q = 1. Other conditions as in Figure 3.

Finally, for an irreversible process, it is possible to obtain accurate values of α, k_s and E^0 in all the possible behaviours of the reduction product (in an extension of the method proposed in reference 4 for both species soluble in the electrolyte solution). So, for the forward process, we may write

$$E(t) = E^0 + \frac{RT}{\alpha nF} \ln \frac{nFAC_A^* k_s}{I_0} + \frac{RT}{\alpha nF} \ln g_e(t,\xi_A) \qquad (45)$$

where

$$g_e(t,\xi_A) = 1 - \frac{2I_0 t^{1/2} E(\xi_A)}{nFA\sqrt{D_A}\,C_A^*} \qquad (46)$$

Table II

Comparison between the values of the ratio τ'/t_2 computed from eqn. (20) modified to amalgam formation (see also eqn. (44)), $(\tau'/t_2)_{cal}$, with those obtained from experimental E-t curves, $(\tau'/t_2)_{exp}$, for the system $Tl^+/Tl(Hg)$ in 0.2 M KNO_3. HMDE, r_0= 0.042 cm. $C^*_{Tl^+}$ = 2mM, $C^*_{Tl(Hg)}$ = 0, $D_{Tl(Hg)} = 0.95\times10^{-5}$ cm^2s^{-1}[12,13].

I_0, μA	I'_0, μA	t_2, s	$(\tau'/t_2)_{cal}$	$(\tau'/t_2)_{exp}$
9.0	3.0	0.50	1.39	1.40
9.0	3.0	1.00	1.44	1.44
9.0	3.0	2.00	1.52	1.52
9.0	3.0	4.00	1.64	1.65
10.0	5.0	0.75	0.88	0.88
10.0	5.0	1.50	0.91	0.91
10.0	5.0	2.50	0.95	0.95
10.0	5.0	3.25	0.98	0.98
6.0	6.0	1.00	0.37	0.37
6.0	6.0	2.00	0.39	0.39
6.0	6.0	3.00	0.40	0.40
6.0	6.0	5.00	0.42	0.41

Table III

Comparison between the values of the ratio τ'/t_2 computed from eqn. (37), $(\tau'/t_2)_{cal}$, with those obtained from experimental E-t curves, $(\tau'/t_2)_{exp}$, for the system I^-/Hg_2I_2 in 0.2 M KNO_3. HMDE, r_0= 0.042 cm. $C^*_{I^-}$ = 2 mM.

I_0, μA	I'_0, μA	t_2, s	$(\tau'/t_2)_{cal}$	$(\tau'/t_2)_{exp}$
5.0	5.0	1.00	1.00	1.00
5.0	5.0	2.00	1.00	0.98
5.0	5.0	3.00	1.00	0.98
5.0	1.0	2.00	5.00	5.05
5.0	2.0	2.00	2.50	2.48
5.0	7.5	2.00	0.67	0.65
3.0	4.0	2.00	0.75	0.74
30.0	4.0	0.30	7.50	7.50

$$1 - \alpha = - \frac{RT}{nFP_B} \qquad (51)$$

and

$$\ln k_s = \frac{RT}{nFP_A} \left(\frac{O_B - O_A}{P_B} + \ln Q \right) + \ln \frac{I_0}{nFAC^*_A} \qquad (52)$$

$$E^0 = \frac{P_BO_A - P_AO_B - P_AP_B \ln R}{P_B - P_A} \qquad (53)$$

where O_i and P_i are the intercepts and slopes for the cathodic (i = A) and anodic (i = B) processes, respectively.

In the situation c), we may calculate α and k_s from the intercept and slope of the plot of E(t) vs $\ln g_e(t,\xi_A)$ in the forward curve (see eqns. (45), (46)), while E^0 must be calculated from eqn. (42).

5. CONCLUSIONS

We have developed the theory concerning a slow charge transfer process in current reversal chronopotentiometry with a stationary spherical electrode . We have considered three different situations for the reaction product. The effects of amalgamation (which cannot be taken into account in plane electrodes) and of the formation of an insoluble product on the potential-time curves are discussed. A procedure is given to discriminate between these different situations from measurements of the ratio τ'/t_2, which depends only on r_0, D_B

and Q. The different behavior of τ'/t_2 in each case is more remarkable for increasing values of t_2, whereas it is slightly affected by r_0. All these features allow us to carry out the discrimination with a minimal error, since t_2 can be modified in a long range. Finally, we have proposed methods to determine kinetic and thermodynamic parameters in the three above mentioned situations.

NOMENCLATURE

r_0	radius of spherical electrode
A	area of spherical electrode
I_0, I'_0	forward and reverse constant currents, respectively
t_2	time elapsed between the beginning of electrolysis and current reversal application.
t'	time elapsed between current-reversal application and measurement of the potential.
τ, τ'	transition times of reduction and reoxidation processes, respectively
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

Other definitions are conventional.

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