Current reversal chronopotentiometry at the DME

Electrode reaction orders and sphericity effects

Angela Molina, Carmen Serna and Manuela López-Tenés
Laboratory of Physical Chemistry, University of Murcia, Espinardo, 30100 Murcia (Spain)
(Received 10 October 1989; in revised form 6 December 1989)

ABSTRACT

The effects of electrode curvature and reaction orders on E–t curves obtained in current reversal chronopotentiometry at a DME with a preceding blank period are analyzed. The influence of amalgam formation on the E–t curves and on the transition time corresponding to the reoxidation process is determined. The effect of concentration of the oxidized species on the reversibility of a higher order electrochemical reaction is discussed. Methods for determining reaction orders, kinetic parameters and the conditional (formal) potential are proposed. All the equations obtained previously in the literature for planar and spherical electrodes can be deduced from the results presented in this paper.

INTRODUCTION

The theory concerning a simple charge transfer reaction in current reversal chronopotentiometry (CRC) at a DME with a preceding blank period, has been developed in a previous paper [1], by using the expanding planar electrode model. The aim of the present paper is to extend that theory so that the sphericity of the electrode and the reaction orders are taken into account.

The electrode curvature should not be ignored when a current step is applied to the DME [2]. Moreover, the amalgamation, which has a considerable influence on the reverse curve, cannot be studied without considering the curvature effect. It is possible to determine the amalgam formation from measurements of the reverse transition time.

We have studied the influence of the cathodic and anodic reaction orders on potential–time curves and we have also analyzed how these curves are affected by the concentration of the oxidized species.

Methods are proposed for the calculation of reaction orders as well as kinetic parameters and the conditional formal standard potential, from measurements of
the forward and reverse transition times and the analysis of the potential–time curves, respectively. All the equations that appear in the literature for planar [1,3–11] and spherical [6,9,12–14] electrodes can be deduced from the general equations obtained in this paper.

**THEORY**

For a slow and higher order electrochemical reaction of the form

\[ a \, A + n \, e^{-\frac{k_w}{n} \, b} \, B \]

when a constant current \( I_0 \) is applied to the DME (necessarily after a blank period \( t_b \) [1]), the transition time, \( \tau \), and the \( E-\tau \) response can be obtained by making \( m = -1/6 \) and \( k = 0 \) in eqns. (27) and (28) in ref. 15.

If at time \( t_2 \) \( \leq \tau \) the current is reversed and the anodic process proceeds at a constant current \( I'_0 \), we may write for \( \tau > t_2 \)

\[ \tau = t_2 + t' \]

\[ \tau = t_2 + t_2 + t' \]

\[ \delta_i' = 0 \quad i = A \text{ or } B \]

where

\[ \delta_i' = \frac{\partial}{\partial \tau} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{g_i'^2}{2} \frac{\partial}{\partial r} \]

Under these conditions, the boundary value problem is given by:

(1) Both species soluble in the electrolyte solution:

\[ \begin{align*}
  \tau' &= 0, \quad r > r_0 \\
  \tau' &= 0, \quad r \rightarrow \infty \\
  \tau' &= 0, \quad r = r_0:
\end{align*} \]

\[ c_A = c_A(s_A, \xi_A, \lambda), \quad c_B = c_B(s_B, \xi_B, \lambda) \]

\[ c_A = c_A(s_A, \xi_A, \lambda), \quad c_B = c_B(s_B, \xi_B, \lambda) \]

\[ \left( \frac{\partial c_A}{\partial r} \right)_{r=r_0} = \left( \frac{\partial c_B}{\partial r} \right)_{r=r_0} = -\frac{I'_0}{nFA} \]

(2) Amalgam formation:

\[ \begin{align*}
  \tau' &= 0, \quad r > r_0 \\
  \tau' &= 0, \quad r \rightarrow \infty \\
  \tau' &= 0, \quad r = r_0:
\end{align*} \]

\[ c_A = c_A(s_A, \xi_A, \lambda), \quad c_B = c_B(s_B, \xi_B, \lambda) \]

\[ c_A = 0, \quad c_B = c_B(s_B, \xi_B, \lambda) \]

\[ c_A = 0, \quad c_B = 0 \]

\[ \left( \frac{\partial c_A}{\partial r} \right)_{r=r_0} = \left( \frac{\partial c_B}{\partial r} \right)_{r=r_0} = -\frac{I'_0}{nFA} \]

where \( c_A(s_A, \xi_A, \lambda, \beta), c_B(s_B, \xi_B, \lambda, \beta) \) and \( c_B(s_B, \xi_B, \lambda, \beta) \) are given in the Appendix.

Moreover, in both cases (1) and (2) the condition

\[ \frac{I'_0}{nFA} \left( \frac{\tau}{t_0} \right) = k_{oA}c_A^0 \left( \frac{r_0}{r'} \right) - k_{oA}c_A^0 \left( \frac{r_0}{r'} \right) \]

is fulfilled (see Notation and definitions).

By proceeding as an extension of the method followed in a previous paper [1] we obtain for the surface concentrations of species A and B, when \( t' > 0 \), the following expressions,

\[ \frac{c_A(r_0', t')}{c_A^0} = 1 - \left( \frac{\alpha n_e}{t'^{1/2}} \right) \left( t^{1/2}G(\beta, \xi_A) - (1 + Q)t^{1/2}G(\epsilon, \xi_A) \right) \]

\[ \frac{c_B(r_0', t')}{c_A^0} = \mu + \left( \gamma n_e/t'^{1/2} \right) \left( t^{1/2}G(\beta, \xi_B) - (1 + Q)t^{1/2}G(\epsilon, \xi_B) \right) \]

where

\[ \xi_i = \left( \frac{2(D_i)^{1/2}}{g_i^{1/2}} \right)^{1/3} \]

\[ \beta = \left( \frac{\epsilon}{t_b} \right)^{1/3} \]

\[ \xi_i' = \left( \frac{2(D_i)^{1/2}}{g_i^{1/2}} \right)^{1/3} \]

\[ \epsilon = \left( \frac{t'^{1/2}}{t_b} \right)^{1/3} \]

\[ N_i = \frac{2I_0/nFD_i^{1/2}}{A_i \phi_A^*} \]

\[ Q = I'_0/I_0 \]

\[ \mu = \frac{c_B^0}{c_A^0} \]

\[ \gamma = \left( \frac{D_A}{D_B} \right)^{1/2} \]

and the \( G \) function has the simple general form

\[ G(z, y_i) = F(z) - y_i F_i(z) + y_i^2 F_2(z) \]

\[ F(z) = \frac{1}{m^{1/2}} \left( 1 + \frac{1}{2} z^2 + \frac{1}{2} z^4 + \frac{1}{4} z^6 + \frac{1}{8} z^8 + \frac{1}{16} z^{12} + \ldots \right) \]

\[ F_i(z) = \frac{1}{2} \left( 1 + \frac{1}{2} z^2 + \frac{1}{3} z^3 + \frac{1}{4} z^4 + \ldots \right) \]

\[ F_2(z) = \frac{1}{6m^{1/2}} \left( 1 + \frac{3}{2} z^2 + \ldots \right) \]

where \( z \) refers to the variables \( \beta \) or \( \epsilon \) and \( y_i \) to \( \xi_i \) or \( \xi_i' \) (\( i = A \text{ or } B \)).

When the species B is amalgamated into the electrode, we must change \( \xi_B \) and \( \xi_B' \) to \( (-\xi_B) \) and \( (-\xi_B') \), respectively, in the \( G \) function (eqns. 11 and 20). This rule will be followed in all expressions in this paper.
The transition time for the reoxidation process, \( \tau' \), is given by

\[
(\tau')^{1/2} = \frac{\mu(t_1 + t_2 + \tau')^{3/2} + ybN_1(t_2 + \tau')^{1/2}G(\beta_b, \xi_b, \epsilon, \epsilon_b)}{ybN_1(1 + Q)G(\epsilon, \epsilon_b)}
\]

(24)

where \( \beta_b, \xi_b, \epsilon, \) and \( \epsilon_b \) are the values of variables \( \beta, \xi, \epsilon, \) and \( \epsilon_b \) for \( t' = \tau' \).

If the electrode reaction product is not present at the beginning of the electrolysis, eqn. (24) becomes

\[
\left( \frac{\tau'}{t_2 + \tau'} \right)^{1/2} = \frac{G(\beta_b, \xi_b, \epsilon)}{(1 + Q)G(\epsilon, \epsilon_b)}
\]

(25)

Under these conditions \( \tau' \) and, therefore, \( \tau'/t_2 \) are not dependent on the anodic order \( b \).

The potential-time functions are deduced by combining eqns. (9)-(11); thus we find

\[
\frac{QN_1D_k^{1/2}}{2\epsilon^{1/2}k_\epsilon^2} 10^{n\nu'} = 10^{n\nu}(c_\epsilon^{\nu'})^{b-1} \left\{ \mu + \frac{ybN_1}{t_2^{1/2}} \left[ t^{1/2}G(\beta, \xi_b) - (1 + Q)t^{1/2}G(\epsilon, \epsilon_b) \right] \right\}^b
\]

\[
- (c_\epsilon^{\nu'})^{a-1} \left\{ 1 - \frac{aN_1}{t_2^{1/2}} \left[ t^{1/2}G(\beta, \xi_b) - (1 + Q)t^{1/2}G(\epsilon, \epsilon_b) \right] \right\}^a
\]

(26)

where

\[ n(\nu') = (nF/RT) \ln(10)(E(\nu') - E_0^{\nu'}) \]

(27)

For a reversible process, eqn. (26) becomes

\[
\langle \nu(\tau') \rangle = E_0^{\nu'} + \frac{RT}{nF} \ln \left( \frac{c_\epsilon^{\nu'}}{t_2^{1/2}} \right)^{a-b} \times \left\{ \frac{t_2^{1/2} - aN_1}{t_2^{1/2} + ybN_1} \right\}^a \left\{ \frac{t_2^{1/2} - aN_1}{t_2^{1/2} + ybN_1} \right\}^b
\]

(28)

and for an irreversible one,

\[
\langle \nu(\tau') \rangle = E_0^{\nu'} + \frac{RT}{(1 - a)nF} \ln \frac{I_0}{nFA_0k_\epsilon^2(c_\epsilon^{\nu'})^b} + \frac{RT}{(1 - a)nF} \ln g'(\beta, \epsilon, \xi_b, \epsilon_b)
\]

(29)

\[
\langle \nu(\tau') \rangle = t_2^{1/3} \mu + ybN_1 \left[ t^{1/2}G(\beta, \xi_b) - (1 + Q)t^{1/2}G(\epsilon, \epsilon_b) \right]
\]

(30)

**Particular cases**

The general expressions obtained here for the transition times (eqn. 24) and potential-time curves (eqns. 26-30) at an expanding sphere electrode can be simplified in the following cases:

1. For an expanding plane electrode we have \( \xi = \xi' = 0 \). The introduction of this condition in all previous equations is equivalent to replacing the \( G \) function (eqn. 20) by the \( F \) function (eqn. 21). The expressions obtained in this way are the same as those derived in ref. 1 for \( a = b = 1 \).
2. For a stationary spherical electrode [6], we should take \( t_2 = t \) (i.e. \( \beta = \epsilon = 0 \)). This is equivalent to replacing the \( G \) function by a function \( E \) defined as

\[
E(z) = \frac{1}{\pi^{1/2}} - \frac{1}{4\pi} + \frac{1}{6\pi^{1/2}} z^2 - \ldots
\]

(31)

3. For a stationary plane electrode we have \( t_2 = t \) and \( \xi = \xi' = 0 \). In this case, when the species \( B \) is not present at the beginning of the electrolysis, eqn. (25) transforms into the equation obtained by Berzins and Dillahay [3] and Macero and Anderson [4].

For a reversible process with \( c_\epsilon^\nu = 0 \) and \( D_\lambda = D_\lambda \), eqn. (28) is identical to that deduced by Skillas and Welch [8]. Moreover, eqn. (29) (corresponding to an irreversible process), when \( b = 1 \) and \( t_2 = \tau \), is the same as that obtained by Anderson and Macero [5].

**RESULTS AND DISCUSSION**

From eqns. (24) and (25) it can be deduced that the amalgamation formation (which does not modify the transition time \( \tau \) of the forward process) has a remarkable effect on the reverse transition time, \( \tau' \). When the two species are soluble in the electrolyte solution (for any value of the variables \( Q, t_1, t_2 \) and \( \xi_b \)), from eqn. (25) we find (see Notation and definitions)

\[
R_{ES} < R_{EP}
\]

(32)

\( R_{ES} \) is the value of the ratio \( \tau'/t_2 \) when \( \xi_b = 0 \) (expanding sphere electrode model) and \( R_{EP} \) is the value of that ratio for \( \xi_b = 0 \) (expanding plane electrode model) [4].

On the other hand, when amalgamation takes place, eqn. (25) leads to

\[
(R_{ES})_{AM} > R_{EP}
\]

(33)

The different behaviour corresponding to eqns. (32) and (33) permits discrimination between the two previous cases, since \( R_{EP} \) is a function of \( Q \) and \( t_2 \) only.

In Fig. 1 we have plotted \( \tau'/t_2 \) vs. \( t_2 \) for several values of the parameter \( \xi_b \). From these curves it can be seen that eqns. (32) and (33) hold. These curves do not depend on the reaction orders \( a \) and \( b \), as can be deduced from eqn. (25) (for \( t_2 < \tau \)). We also show in Fig. 1 the curve corresponding to a stationary plane electrode \( (\tau'/t_2 = 1/Q(Q + 2)) \) [4]. As can be observed (I, curves b and c),
when both species are soluble in the electrolyte solution we have, for small values of $t_2$, 
\[ R_{ES} < R_p \]  
(i)

The range of values of $t_2$ for which expression (i) is valid decreases when $\xi_{0,b}$ gets smaller. For the values of $t_2$ out of this range the contrary inequality holds 
\[ R_{ES} > R_p \]  
(ii)

This peculiar behaviour is the result, for a given value of $t_2$, of two opposite effects: the sphericity ($\xi_{0,b}$), which tends to decrease $\tau'$, and the expansion of the electrode, which tends to increase $\tau'$. So, for a stationary spherical electrode, in which the second effect is not present, for any value of $t_2$, 
\[ R_{SS} < R_p \]  
(iii)

is fulfilled [13], where $R_{SS}$ is the value of the ratio $\tau'/t_2$ calculated for a stationary spherical electrode (eqn. 31). For this electrode, when the amalgamation takes place, we obtain 
\[ (R_{ES})_{Am} > R_p \]  
(iv)

The reaction orders $a$ and $b$ can be determined from measurements of $\tau$ and $\tau'$ when species B is present at the start of the electrolysis. In order to achieve this, we first rewrite eqn. (27) of ref. 15 with $m = -1/6$, $k = 0$ and eqn. (24) (this paper) as 
\[ J(\tau) = 1/aN_s \]  
(34)

\[ L(\tau') = 1/bN_R \]  
(35)

where 
\[ J(\tau) = \left( 1^{1/2}/(1 + \tau)^{1/6} \right) G(\beta_x, \xi_{\text{a,r}}) \]  
(36)

\[ L(\tau') = \left( 1/Q \right) G(\epsilon_{\text{r}}, \xi_{\text{b,r}}) - \left( t_2 + \tau' \right)^{1/2} G(\beta_x, \xi_{\text{b,r}}) \]  
(37)

\[ N_R = 2I_s/nFD_0^2A_0\rho^2 \]  
(38)

Then, $a$ and $b$ can be determined by plotting $J(\tau)$ vs. $1/N_s$ and $L(\tau')$ vs. $1/N_R$.

In Figs. 2 and 3 we show the effect of the electrode curvature on the $E-t$ curves ($\Delta E = E(t) - E_0^0$ vs. $t$), for $a = b = 1$ and when the two species are soluble in the electrolyte solution. As shown in Fig. 2, this effect increases with $t_2$ in the forward and the reverse curves. Furthermore, for $t_2 = t$ the effect increases with the blank period $t_1$ (Fig. 3).

The normalized $E-t$ curves ($\Delta E$ vs. $t/\tau'$) corresponding to a reversible process at $N_R$ and $Q$ fixed and with $\mu = 0$, are shown in Fig. 4. As can be observed, for $a = 1$ and $b = 2$, an increase in $\tau'$ results in a shift of the forward and reverse curves to more negative potentials. The effect is the opposite for $a = 2$ and $b = 1$. It
should be noted that for \( a = b \), under the same conditions as before, the curves do not depend on \( c_\alpha^* \), as can be deduced from eqn. (28).

In Fig. 5 we show the effect of amalgam formation on the \( E-t \) curves for reversible, quasi-reversible and irreversible processes with \( a = b = 1 \). The effect of the amalgamation on the forward curve is small, and decreases with \( k_0 \), while the change in the reverse curve is very noticeable, being maximal for \( t = t_2 + t' \), and is basically independent of the reversibility of the process.

Figures 6–8 show the influence of \( c_\alpha^* \) on the reversibility of the process. From these curves and from eqns. (26)–(30) we can deduce that a process with \( k_0 = 10^{-2} \) cm s\(^{-1}\) mM\(^{-1}\) \( \cdot \) mol\(^{-1}\), \( D_A = D_B = 10^{-5} \) cm\(^2\) s\(^{-1}\), \( \alpha = 0.5 \), which is considered typically as quasi-reversible for \( a = b = 1 \), can be considered reversible for \( c_\alpha^* \geq 10 \) mM (eqn. 28) and irreversible for \( c_\alpha^* < 0.01 \) mM (eqn. 29) when \( a = 1, b = 2 \) or \( a = 2, b = 1 \). In the case \( a = b = 2 \) (Fig. 8) the process can also be considered reversible for \( c_\alpha^* > 10 \) mM and irreversible for \( c_\alpha^* < 0.1 \) mM. The total time scale used in Figs. 6–8 goes up to 1.7 s.

Once \( a \) and \( b \) have been determined, a generalization of the method followed in ref. 1 allows calculation of the values of \( \alpha, \xi_\alpha^* \) and \( E_\alpha^* \). So, we carry out a linear regression analysis of \( E(t) \) vs. \( t \) (cathodic process) and of \( E(t') \) vs. \( t' \) (anodic process), where the \( g \) and \( g' \) functions are defined as

\[
\frac{\Delta E}{\Delta t} = g(\beta, \xi_\alpha, \xi_\beta) \quad \text{(cathodic process)}
\]

\[
\frac{\Delta E}{\Delta t'} = g'(\beta, \xi_\alpha, \xi_\beta) \quad \text{(anodic process)}
\]
Finally, we obtain

\[ P_A = RT/aNF \]  \hspace{1cm} (41)

\[ P_B = -RT/(1 - a)nF \]  \hspace{1cm} (42)

\[ \ln k_e^* = a \left[ (O_B - O_A)/P_B + \ln Q \right] + \ln \left( I_n/nFA_0(c^*_e)^2 \right) \]  \hspace{1cm} (43)

\[ E_{e}^* = -aO_A + (1 - a)O_B - aP_B \ln Q + (b - a)\alpha P_B \ln c^*_e \]  \hspace{1cm} (44)

where \( P_i \) and \( O_i \) are the slopes and the intercepts, respectively. The index \( i \) is equal to A or B for the cathodic and anodic processes, respectively.

CONCLUSIONS

The mathematical treatment used in this work has proved to be very suitable for the problem under study. It has allowed us to study a higher order electrochemical reaction in CRC at a DME, considering the more realistic model of an expanding sphere. The consideration of this model has made possible an analysis of the effects of amalgamation on the E-i curves by using the CRC technique. We have also proposed methods for the determination of reaction orders and kinetic parameters. This is of great interest, since the case \( a = 2, b = 1 \) leads to a divergent solution when controlled potential techniques [16] are used. Finally, the analysis of the double layer charge effects is usually not simple [17] and they have not been considered in this work.

ACKNOWLEDGEMENTS

The authors greatly appreciate the financial support of the Dirección General de Investigación Científica y Técnica (Project No. PB87-0700) and also of the Dirección Regional de Educación y Universidad de la Comunidad Autónoma de la Región de Murcia (Project No. PCT89/19). We also acknowledge the critical reading of this manuscript by Dr. Rafael Chucón (University of Murcia).

APPENDIX

The expressions corresponding to the concentration of species A and B (obtained when a constant cathodic current \( I_0 \) is applied to the DME) are given by:

(1) Solution soluble product

\[ c_A(s_A, \xi_A, \chi, \beta) = c^*_A + \chi \beta^2 \sum_{n=0}^{\infty} \sum_{i=0}^{2} \phi_{i,1,3n+2}^e(s_A) \xi_i \beta^{3n} \]  \hspace{1cm} (A1)

\[ c_B(s_B, \xi_B, \chi, \beta) = c^*_B + \chi \beta^2 \sum_{n=0}^{\infty} \sum_{i=0}^{2} \phi_{i,1,3n+2}^e(s_B) \xi_i \beta^{3n} \]  \hspace{1cm} (A2)

(2) Amalgam formation

In this case, \( c_A(s_A, \xi_A, \chi, \beta) \) does not differ from the preceding eqn. (A1). However, \( c_B \) is given by

\[ c_{B\text{amal}}(s_B, \xi_B, \chi, \beta) = c^*_B + \chi \beta^2 \sum_{n=0}^{\infty} \sum_{i=0}^{2} \phi_{i,1,3n+2}^a(s_B) \xi_i \beta^{3n} \]  \hspace{1cm} (A3)

where superscripts "-" or "+" in functions \( \sigma \) and \( \phi \) relate to the Koutecky functions used [18,19] and

\[ s_i = (r - r_i)/2(D_i t)^{1/2} \]  \hspace{1cm} (A4)

\[ \chi = aN_i t^{-1/6} \]  \hspace{1cm} (A5)

The expressions for the functions \( \phi_{i,1,3n+2}^e(s_A) \) and \( \phi_{i,1,3n+2}^a(s_B) \) can be obtained from eqns. (A10)–(A20) in ref. 15, by making \( m = -1/6 \), \( k = 0 \) and also taking into account eqns. (A39)–(A44) in the same work. Moreover, for the \( \phi_{i,1,3n+2}^a(s_B) \) functions we find

\[ \phi_{i,1,3n+2}^a(s_B) = -\gamma p \phi_{i,1,3n+2}^a(s_B) \]  \hspace{1cm} (i = 0, 2 \hspace{1cm} n \geq 0) \]  \hspace{1cm} (A6)

and for \( i = 1 \)

\[ \phi_{1,1,3n+2}^a(s_B) = -\gamma p c_A/4 \left\{ 2 \psi_0^e(s_B) - \psi_1^e(s_B) \right\} \]  \hspace{1cm} (A7)

\[ \phi_{1,1,3n+2}^a(s_B) = -\gamma p c_A^e \left\{ \frac{2}{3n+2} \frac{2}{n+1/2} e^{-n} \left[ 61 s_B - 18 s_B \right] + 272 \psi_0^e(s_B) - 780 \psi_1^e(s_B) \right\} \]  \hspace{1cm} (A8)

\[ \phi_{1,1,3n+2}^a(s_B) = -\gamma p c_A^{e+} \left\{ \frac{2}{3n+2} \frac{2}{n+1/2} e^{-n} \left[ 61 s_B - 18 s_B \right] + 272 \psi_0^e(s_B) - 780 \psi_1^e(s_B) \right\} \]  \hspace{1cm} (A9)

At the electrode surface (\( s_i = 0 \))

\[ \phi_{i,1,3n+2}^a(0) = (-1)^{i+1} \gamma p \phi_{i,1,3n+2}^a(0) \]  \hspace{1cm} (i = 0, 1, 2) \hspace{1cm} (A10)

is fulfilled.

NOTATION AND DEFINITIONS

- \( a, b \) : cathodic and anodic reaction orders
- \( k_{\text{red}} \) : electron transfer rate constant for the reducing (cathodic) reaction
  \[ k_{\text{red}} = k_0 \exp(-anF/RT) \]  \hspace{1cm} (E(t) - E^o)
- \( k_{\text{ox}} \) : electron transfer rate constant for the oxidizing (anodic) reaction
  \[ k_{\text{ox}} = k_0 \exp((a' + b')nF/RT) \]  \hspace{1cm} (E(t) - E^o)
- \( k_0' \) : conditional rate constant of an electrode reaction (see ref. 20)
- \( E_{c}^\circ' \) : conditional (formal) potential on the concentration scale of the electrode reaction (see refs. 20 and 21)
\[ E(t) \]  
\[ \alpha, \alpha' \]  
\[ \Sigma \]  
\[ t_1 \]  
\[ t_2 \]  
\[ t' \]  
\[ t = t_2 + t' \]  
\[ t_a = t_1 + t \]  
\[ I_0, I_0' \]  
\[ D_i \]  
\[ r \]  
\[ r_0 \]  
\[ g (3m_{\text{Hg}}/4\pi d)^{1/3} \]  
\[ m_{\text{Hg}} d \]  
\[ A(t) \]  
\[ A_0 \]  
\[ A_1 \]  
\[ Q = I_0/I_0' \]  
\[ \tau_0, \tau' \]  
\[ \xi_{0,1} = \xi_{1,0}' \]  
\[ \xi_{0}, \xi_{1}' \]  
\[ R_{\text{ES}}(R_{\text{ES}})_\text{Am} \]  
\[ R_{\text{EP}} \]  
\[ R_p \]  
\[ R_{\text{SS}}(R_{\text{SS}})_\text{Am} \]  

REFERENCES