

MODELLING OF PULSATING DIFFUSIONAL BOUNDARY LAYERS—I.* A REVERSIBLE METAL–METAL ION ELECTROCHEMICAL REACTION UNDER SYMMETRIC SQUARE WAVE PERTURBING POTENTIALS AT A PLANE ELECTRODE

S. L. MARCHIANO,[†] L. REBOLLO NEIRA[‡] and A. J. ARVIA[†]

[†]Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina

[‡]Departamento de Física, Universidad Nacional de La Plata, Casilla de Correo 67 (1900) La Plata, Argentina

(Received 13 December 1988; in revised form 10 May 1988)

Abstract—The concentration profiles of reacting species at the electrode–solution interface under a periodic square wave perturbing potential are calculated by solving the diffusion equation for the case of a fast reversible metal–metal ion reaction. This situation is particularly interesting in the electrochemical faceting of metals. The model explains the dependence of current density and charge density on the frequency and number of cycles of the perturbing potential.

INTRODUCTION

Periodic perturbations, either current or potential have been used in electrochemistry in connection to electrochemical techniques such as ac voltammetry, and impedance measurements[1, 2] as well as electrolysis with a pulsating current[3–9]. The latter has been extensively used in pulse plating, electrodisolution (electrochemical shaping and polishing of metals) anodizing and *ac* corrosion processes. Pulsed current can produce considerable modifications on electrodeposits as far as the morphology, uniformity, compactness and adherence to the substrate are concerned. These effects are largely due to the influence of the periodic perturbation on the mass transport processes and accordingly, on the kinetics of the electrode reaction. The periodic perturbation produces a pulsating diffusional boundary layer wherein the concentrations of the ionic species oscillate with time near the electrode surface. This means that for instance, for a pulsating current the concentration and surface reaction overpotential depend not only on the magnitude but also on the frequency of the oscillating current.

Recently the application of periodic perturbing potentials under certain well-established conditions to various noble metal electrode has allowed study of the electrochemical faceting of those electrode surfaces[10–12]. Electrochemical faceting requires an anodic and a cathodic potential limit located at the negative and positive potential values, respectively, of the equilibrium potential of the corresponding metal–metal ion redox couple, to allow the electrodisolution and electrodeposition of the metal during the potential cycling. It has been demonstrated that the two processes are not exactly symmetric from the standpoint of the charge playing part in the oxidation–reduction cycles and this leads to an accumulation of dissolved metal in solution in the course of

the electrochemical treatment. This has been clearly proved by chemical analysis, rotating disc and ring–disc electrode techniques for various metals[13]. Therefore, the electrochemical faceting implies the build-up of concentration profiles related to the anodic and cathodic reactions, that is the existence of a pulsating diffusional boundary layer.

For process modelling let us firstly assume that the overall electrochemical reaction involves a redox process under ionic diffusion control in the solution phase. Hence, to solve this problem the analytical solution of the Fick's diffusion equation is required to obtain the concentration profile, current density and charge density at any cycle. This can be done exclusively on the basis of the pure diffusion equations because as the metal ion concentration initially is null and along the process is much smaller than the acid electrolyte concentration, migration effect can be neglected. Analogously, provided that the period of the perturbing potential is adequately chosen and the electrode size is sufficiently small, it is possible to suppose that convection and double layer effects can be also disregarded[14]. It is further assumed that the values of j_0 , the exchange current density for the metal–metal ion electrochemical reaction, is sufficiently large to avoid any activation polarization.

Furthermore, the perturbing potential is a periodic symmetric square wave potential for which the boundary conditions of the problem can be easily established.

The purpose of this work is to find out the dependence of the concentration profiles on frequency and number of cycles of the periodic potential and simplest electrochemical kinetic conditions.

MATHEMATICAL MODELLING

Let us consider that the following reaction takes place at a planar solid electrode (M) immersed in an

*Part II: *Electrochimica Acta*, Vol. 35, No. 1, pp. 215–223 (1989).

acid electrolyte:



Reaction (1) is assumed to be under diffusional control as the corresponding exchange current density value, j_0 , is large. Therefore, for a semi-infinite diffusion at a plane electrode the concentration profile of the reacting species, can be obtained by solving Fick's equation:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2}, \quad (2)$$

where c_i corresponds to the concentration of the M^{z+} species, its diffusion coefficient being D_i . The diffusion of M^{z+} takes place only along the x -axis, *ie* the direction perpendicular to the electrode surface. The electrode is subjected to a symmetric square wave perturbing potential at frequency $f = 1/T = 1/2\tau$, where T and τ being the period and half period, respectively. The upper, E_a , and the lower, E_c , potential limits are selected as, $E_a > E_r$ and $E_c < E_r$, E_r being the equilibrium potential of reaction (1). This perturbing potential brings about time-dependent boundary conditions to equation (2). Thus, the initial and boundary conditions are:

$$\begin{aligned} t=0 \quad c_i &= 0 \\ t > 0 \quad \begin{cases} x=0 & c_i = f(t) \\ x \rightarrow \infty & c_i = 0 \end{cases}, \end{aligned} \quad (3)$$

where:

$$\begin{cases} f(t) = c_i^* \text{ for } N \text{ odd} \\ f(t) = 0 \text{ for } N \text{ even} \end{cases}, \quad (4)$$

N is the number of halfcycles and t is given by the expression:

$$\begin{aligned} t &= (N-1)\tau + t' \\ 0 &< t' < \tau. \end{aligned} \quad (5)$$

Then, for the first anodic halfcycle ($N = 1$), the classic solution for equation (2) for the concentration profile is obtained:

$$c_i = c_i^* \left[1 - \operatorname{erf} \frac{x}{2(D_i t')^{1/2}} \right]. \quad (6)$$

As c_i^* represents the equilibrium concentration of soluble species at the electrode surface, its value for a completely reversible reaction depends on E_a , the applied potential, as given by Nernst's equation for a single phase metal of unit activity:

$$c_i^* = \exp \left[\frac{zF}{RT} (E_a - E_r^0) \right] \quad (7)$$

where E_r^0 is the standard potential of the reaction, and the others symbols have their usual meaning.

Taking into account the boundary conditions (3) to (4) the following general analytical solutions comes out from the calculation procedure worked out in the appendix.

For the anodic halfcycle (or odd halfcycles):

$$\begin{aligned} c_i(x, (N-1)\tau + t') &= \\ c_i^* \left\{ 1 + \sum_{k=1}^N (-1)^k \operatorname{erf} \left[\frac{x}{2\{D_i|(k-1)\tau + t'\}^{1/2}} \right] \right\}, \end{aligned} \quad (8)$$

and for the cathodic halfcycles (or even halfcycles):

$$c_i(x, (N-1)\tau + t') = c_i^* \left\{ \sum_{k=1}^N (-1)^{k+1} \operatorname{erf} \left[\frac{x}{2\{D_i|(k-1)\tau + t'\}^{1/2}} \right] \right\}. \quad (9)$$

From the concentration profiles given by equations (8) and (9) the corresponding fluxes of reacting species at the surface, expressed as anodic and cathodic current densities, j_a and j_c , respectively, and charge densities for the anodic and cathodic halfcycles, q_a and q_c , respectively, determined as a function of time and number of cycles can be immediately obtained. Thus:

$$\begin{aligned} j_a &= -z_i F D_i \left(\frac{\partial c_i}{\partial x} \right)_{x=0} \\ &= z_i F c_i^* D_i^{1/2} \pi^{-1/2} \sum_{k=1}^N (-1)^{k+1} \frac{1}{((k-1)\tau + t')^{1/2}}, \end{aligned} \quad (10)$$

and:

$$\begin{aligned} j_c &= z_i F D_i \left(\frac{\partial c_i}{\partial x} \right)_{x=0} \\ &= z_i F c_i^* D_i^{1/2} \pi^{-1/2} \sum_{k=1}^N (-1)^k \frac{1}{((k-1)\tau + t')^{1/2}}. \end{aligned} \quad (11)$$

From equations (10) and (11) the values of q_a and q_c for an interval of time τ , are calculated by integration as follows:

$$q_a = \left| \int_0^\tau j_a dt' \right|, \quad (12)$$

and:

$$q_c = \left| \int_0^\tau j_c dt' \right|. \quad (13)$$

Accordingly, the difference between q_a and q_c per cycle $\Delta q = q_a - q_c$ decreases progressively as the number of cycles increases, as given by the equation:

$$\begin{aligned} \Delta q &= z F \pi^{-1/2} D_i^{1/2} c_i^* \tau^{1/2} \\ &\times \sum_{k=1}^N (-1)^{k+1} \left(\sqrt{k+1} - \sqrt{k} \right). \end{aligned} \quad (14)$$

In this case, Δq , implies an accumulation of species M^{z+} in the solution per cycle. Likewise, the overall accumulation of charge, Δq_T , after N halfcycles results:

$$\Delta q_T = \sum_{k=1}^N (q_a - q_c) \quad (15)$$

BEHAVIOUR OF THE THEORETICAL MODEL

The theoretical model predicts certain critical functionalities, some of them relevant from the standpoint of a direct comparison to experimental data.

Let us firstly consider on the basis of the theoretical equations the behaviour of the concentration of the soluble species as a function of three independent variables, namely, the distance perpendicular to the electrode, the time elapsed from the initiation of each pulse, and the frequency of square wave perturbing potential.

The development of the concentration profile arising from the first anodic halfcycle, *ie* the initial halfcycle which produces through the reversible electrochemical reaction a source of diffusing species at $x=0$, is the classic one given by equation (6). The concentration profiles plotted as $c_i(x, t)/c_i^*$ vs x^* , where $x^* = 10x/x_{\max}$ and $x_{\max} = 4\sqrt{D_i\tau}$, is shown in Fig. 1a. Otherwise, the development of the concentration profiles resulting from the cathodic halfcycle subsequent to the first anodic halfcycle is depicted in Fig. 2a. According to the boundary conditions imposed by the model, these profiles (cathodic halfcycle), initiated at $c_i(x, t)/c_i^* = 0$, increase up to a maximum and reach again asymptotically $c_i(x, t)/c_i^* = 0$ when x^* increases. These profiles are broadened, the maximum $c_i(x, t)/c_i^*$ value decreases and appear at larger values of x^* as t' increases. This behaviour results in a crossing of profiles. These effects are related to the fact that the decrease of $c_i(x, t)/c_i^*$ with x^* becomes slower as t' increases.

The evolution of the concentration profile for each halfcycle during the subsequent cycles is considerably influenced by the preceding anodic and cathodic halfcycle. The greatest changes in the anodic profiles are produced in going from the first to the third cycle, and as the number of cycles further increases the whole profile tends asymptotically to the stationary profile, but the values of $c_i(x, t)/c_i^*$ continues to increase with N for large values of x^* . For a preset number of cycles, the inflexion points in Fig. 1b appear for greater

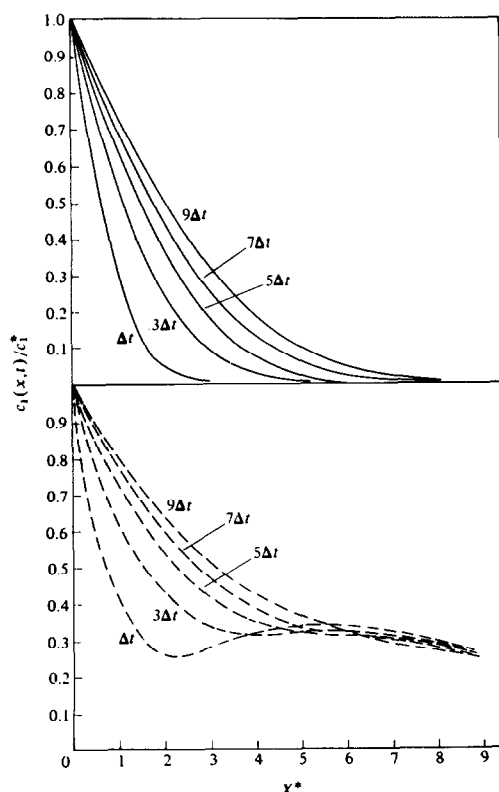


Fig. 1. Concentration profiles resulting from the model for the anodic halfcycles. $D_i = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; $\Delta t = \tau/10$. (a) 1st halfcycle (anodic); (b) 19th halfcycle (anodic)

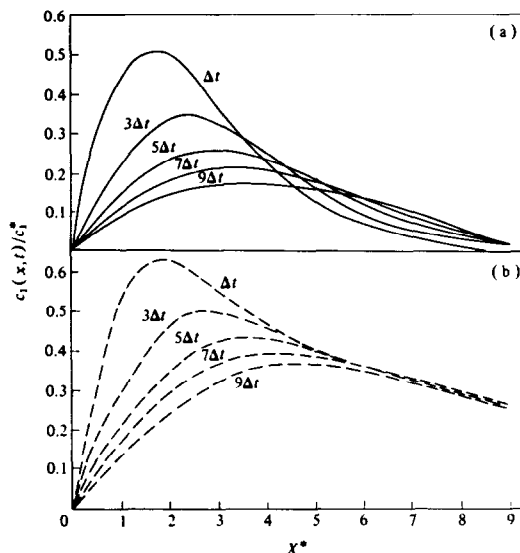


Fig. 2. Concentration profiles resulting from the model for the cathodic halfcycles. $D_i = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; $\Delta t = \tau/10$. (a) 2nd halfcycle (cathodic); (b) 20th halfcycle (cathodic).

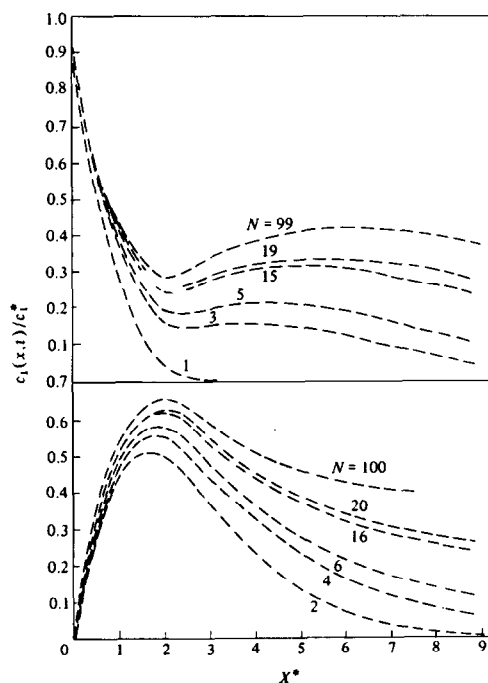


Fig. 3. Concentration profiles for $t = \Delta t$ for different cycles as identified by the numbers. (a) Anodic; (b) cathodic. $D_i = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; $\Delta t = \tau/10$.

values of x^* , as t' increases. Likewise, for a constant t' the inflexion points remain at the same x^* for any cycle as one should expect from the derivation of equations (8) and (9) with respect to x^* (Fig. 3a).

Analogously, the concentration profiles resulting during the sequence of cathodic halfcycles show up a shift of the $c_i(x, t)/c_i^*$ maximum value towards greater values of x^* with t' (Figs 2a and b). This shift with t' is

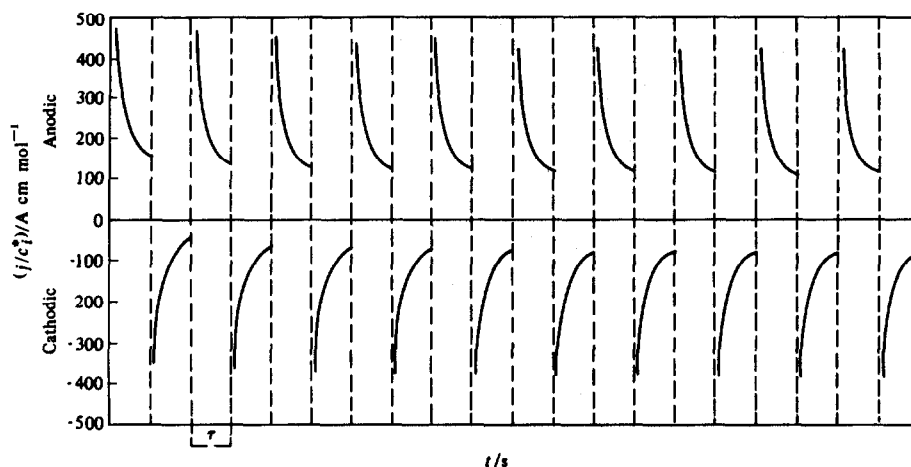


Fig. 4. Anodic and cathodic current transients for different halfcycles. $\tau = 0.1$ s.

independent whether the first cathodic halfcycle or a large number of cathodic halfcycles are considered. Likewise, for a constant t' , the maximal value of $c_i(x, t)/c_i^*$ changes slightly with x^* but its decay becomes smoother as N increases (Fig. 3b).

On the basis of the concentration profiles one can immediately derive the current transient behaviour associated with the reversible electrochemical reaction under the influence of the square wave perturbing potential. As shown in Fig. 4, the current transient either anodic or cathodic resulting during the corresponding halfcycle decay with time elapsed from the beginning of the halfcycle, but for a constant t' the cathodic current is smaller than the anodic one. This difference tends asymptotically to zero as the number of cycles, at a constant frequency, increases.

Similar relevant conclusions are accomplished for the charge resulting by integrating the current transients. Thus, the charge accumulated in each cycle decreases with N in the anodic halfcycles and increases with N in the cathodic halfcycles approaching asymptotically to a constant value as $N \rightarrow \infty$ (Fig. 5). Therefore, the charge difference, Δq_T , as given by equation (15) between anodic and cathodic charges, results in the increase in concentration of the soluble product in the bulk of the solution. The value of Δq_T depends on the number of cycles considered and on the frequency (Fig. 6). This means that Δq_T for a given time t , increases as f increases, although the opposite effect is observed when Δq per cycle is considered.

According to equation (7) all the calculated magnitudes should depend principally on the value of the anodic potential step, *ie* the potential at which the soluble species is produced. Equation (8) holds, in principle, for any anodic potential provided that $j_0 \rightarrow \infty$. Otherwise, the value of the cathodic potential step should approach $-\infty$ with respect to E_r to assure a null concentration of the reacting species at the electrode surface. When $j_0 \rightarrow \infty$ this situation can be asymptotically reached for relatively small values of E_c .

According to equation (8) when the potential step in the anodic half-cycle is considerably large, the value of c_i^* can exceed the solubility product of species accumulated in the electrolyte solution. Nevertheless, the

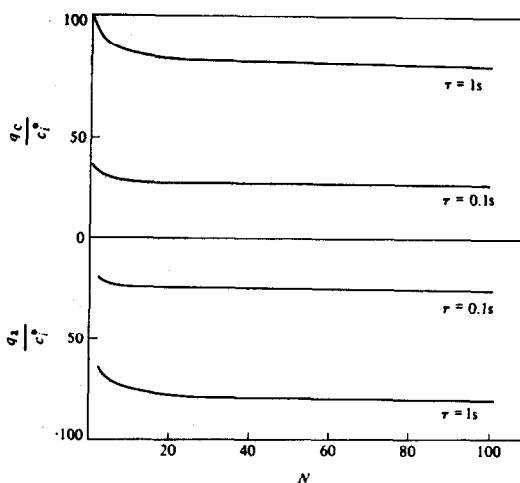


Fig. 5. Normalized charge densities ($q^* = q/c_i^*$) for anodic and cathodic halfcycles vs number of cycles: (●) $\tau = 0.1$ s; (×) $\tau = 1$ s.

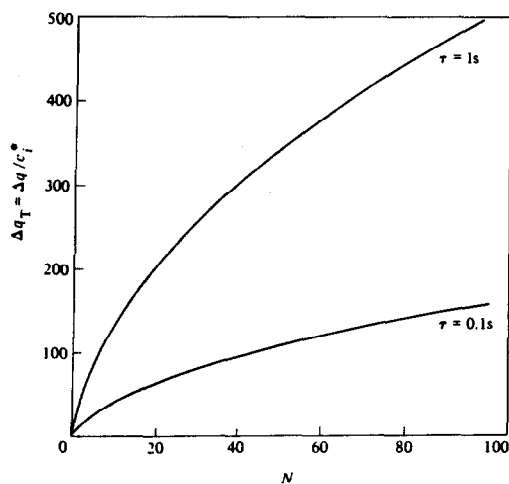


Fig. 6. $\Delta q_T = \Delta q/c_i^*$ vs N plot for different frequencies.

amount of accumulated product either as soluble species or insoluble species always is directly related to Δq_T . For a preset potential cycling time, the narrower the period (the greater the frequency) of the symmetric perturbing potential, the greater the accumulation of product in the solution.

CONCLUSION

Most of the experimental data related to the electrochemical faceting of metals concern with the conditions for developing certain morphologies. There is only one paper dealing with the accumulation of soluble palladium species in solution during the electrochemical faceting treatments of this metal. These results refer to a repetitive square wave potential treatment made either for constant potential limits at different frequencies or at a constant frequency and variable potential windows[13]. These results, particularly those obtained at the lower frequencies, offer possibilities for making a preliminary comparison with the prediction of the model. It is clear that in agreement with the model there is an accumulation of soluble palladium during cycling, as it should correspond to equation (15).

The amount of soluble palladium accumulated in solution as the average amount of palladium dissolved per cycle decreases according to $t^{-1/2}$, whereas the amount of metal dissolved per unit time increases with $t^{1/2}$. These dependences are in qualitative agreement with equation (15) derived from the model.

A more exhaustive experimental work based on various redox system particularly useful for testing mass transfer models has already been published[15].*

Acknowledgement—This research project was financially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires.

This work was partially supported by the Regional Program for the Scientific and Technological Development of the Organization of the American States.

REFERENCES

1. A. J. Bard and L. R. Faulkner, in *Electrochemical Methods*, Wiley, New York (1980).
2. E. Yeager and A. J. Salkin, in *Techniques of Electrochemistry*, Wiley, New York (1973).

3. A. R. Despic and K. I. Popov, *J. appl. Electrochem.* **1**, 275 (1971).
4. N. Ibl, J. Cl. Puipe and H. Angerer, *Surf. Technol.* **6**, 287 (1978).
5. K. Viswanathan and H. Y. Cheh, *J. appl. Electrochem.* **9**, 537 (1979).
6. N. Ibl, *Surf. Technol.* **10**, 81 (1980).
7. J. Cl. Puipe and N. Ibl, *J. appl. Electrochem.* **10**, 775 (1980).
8. D-T. Chin, *J. electrochem. Soc.* **130**, 1657 (1983).
9. C. Clerc and D. Landolt, *J. appl. Electrochem.* **17**, 1144 (1987).
10. R. M. Cerviño, W. E. Triaca and A. J. Arvia, *J. electrochem. Soc.* **132**, 266 (1984).
11. J. C. Canullo, W. E. Triaca and A. J. Arvia, *J. electroanal. Chem.* **175**, 337 (1984).
12. A. Visintin, J. C. Canullo, W. E. Triaca and A. J. Arvia, *J. electroanal. Chem.* **239**, 67 (1988).
13. C. L. Perdriel, E. Custidiano and A. J. Arvia, *J. electroanal. Chem.* **246**, 165 (1988).
14. P. Delahay, *New Instrumental Methods in Electrochemistry* (3rd edn), Interscience, New York (1962).
15. C. I. Elsner, C. L. Perdriel, S. L. Marchiano and A. J. Arvia, *Electrochim. Acta* **35**, 215 (1989).*

APPENDIX

The differential equation to be solved is:

$$D \frac{\partial^2 c(x, t)}{\partial x^2} = \frac{\partial c(x, t)}{\partial t}, \quad (1a)$$

with the boundary and initial conditions:

$$c(0, t) = f(t) \quad (2a)$$

$$c(x, 0) = 0, \quad (3a)$$

$$\lim_{x \rightarrow \infty} c(x, t) = 0. \quad (4a)$$

Applying the Laplace transform and taking into account the boundary conditions (2a) to (4a), one obtains:

$$g(x, s) = L\{c(x, t)\} = L\{c(0, t)\} \exp(-x\sqrt{s/D}), \quad (5a)$$

and by carrying out the anti-transform, and by using the convolution theorem, the following general equation results:

$$c(x, t) = \frac{x}{2\sqrt{DN}} \int_0^t f(u) \frac{\exp[-x^2/4D(t-u)]}{(t-u)^{3/2}} du, \quad (6a)$$

with $f(u) = f(t)$ as given by equations (3).

By integrating cycle by cycle [where $f(u) = c^*$ for odd cycles, and $f(u) = 0$ for even cycles] from the first cycle to the N cycle, and by considering $(k-1)\tau$ and τ as the integration limits, for each cycle (k) equations (8) and (9) are obtained.

*Modelling of pulsating diffusional boundary layers—II by C. I. Elsner, C. L. Perdriel, S. L. Marchiano and A. J. Arvia appeared in *Electrochimica Acta*, Vol. 35, No. 1.