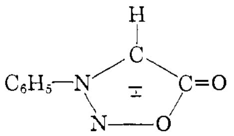
The band at 1241 cm.$^{-1}$, which may be assigned to the C–O stretching vibration according to Glusker, *et al.*,[4] increases in frequency upon complex formation. If the iodine molecule combines directly with the oxygen atom of the C–O bond, the band should decrease in frequency as is the case for the ether–iodine complex. The increase observed may be due to a secondary effect exerted by the neighboring C=O bond. The similarity of the K values indicates that the 1:1 complex is formed in this case also. The concentrations of the complex were estimated from the decrease in intensity of the C=O or C–O band of free methyl acetate, as indicated in the table.

If the complex is stabilized by the transfer of a lone-pair electron at the oxygen atom of the C=O group, it is very probable that the first ionization potential of the ester is due to the removal of this lone-pair electron.

Sydnone is a meso-ionic compound with the peculiar structure[16] shown below. As 3-phenylsydnone does not dissolve in non-polar solvents, the measurements were made on an acetonitrile solution. When iodine was added to the solution, the band at 1756 cm.$^{-1}$ assigned to the C=O stretching vibration shifts to 1749 cm.$^{-1}$, and the band at 843 cm.$^{-1}$, assigned to the C–O stretching vibration, shifts to 854 cm.$^{-1}$. These changes are due to the formation of the sydnone–iodine complex with the iodine attached to the oxygen atom of the C=O group, since the shifts are similar to those observed for the ester–iodine complex. No abnormal behavior was observed for the complex in spite of the peculiar structure of sydnone. The results obtained for the intensity of the C=O stretching band and the formation constant at about 30° are shown in Table VI.



3-phenylsydnone

TABLE VI

FREQUENCY AND INTENSITY OF THE C=O BAND OF 3-PHENYLSYDNONE AND OF THE SYDNONE–IODINE COMPLEX

	Initial concn. (mole/l.) Syd-none	Initial concn. (mole/l.) Io-dine	Complex (mole/l.)	ν_{max} (cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$A \times 10^{-4}$	K (l./mole) at ~30°
3-Phenyl sydnone				1756	14.8	10.8	
Complex	0.0321	0.150	0.0041	1749	19	14	1.0

From the fact that the formation constant of the sydnone–iodine complex is large, it seems likely that the first ionization potential of the sydnone is relatively small, although data on the entropy change with complex formation are unavailable.

Acknowledgment.—We are indebted to Professor M. Ohta of our Institute for the sample of 3-phenylsydnone.

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[16] For the meaning of the sign ± in this formula see W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, 307 (1949).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA

Faradaic Rectification with Control of Alternating Potential Variations—Application to Electrode Kinetics for Fast Processes

BY HIROAKOI MATSUDA[1] AND PAUL DELAHAY

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In this method, the potential of an electrode at which a fast charge transfer process occurs is varied about the equilibrium potential according to a sinusoidal function of time. The resulting alternating current includes a rectification component because of the asymmetry of the current-potential curve. An equation is derived for the faradaic rectification current and is compared with a previous result obtained on the assumption of current control for $t \to \infty$. A correction for the double layer structure in the solution of the boundary value problem also is derived.

Introduction

A faradaic rectification method for the kinetic study of electrode processes recently was developed by Barker[2,3] from an idea originally advanced by Doss and Agarwal.[4] The method is based on the rectification by an electrode reaction as a result of the asymmetry of its current-potential characteristic with respect to the equilibrium potential (except, of course, for the rare case of symmetry). Thus, a sinusoidal current causes the electrode potential to vary periodically about a mean potential which is different from the equilibrium potential without current. This shift in potential allows the kinetics of the electrode reaction to be studied. Doss and Agarwal[4] gave a theoretical analysis of the method for the particular case of reactants having equal concentrations and equal diffusion coefficients. Barker[3] and, independently, Vdovin[5] generalized this treatment. The former author also considered[3] processes with adsorption, slow electrode reactions, etc. These authors derived the shift of the mean potential on the assumption that there is control of the alternating current whereas in many instances the low impedance of the double layer capacity at the high frequencies (perhaps 1 megacycle per sec.) at which measurements are made results

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[1] Research Associate, 1958–1959; on leave from the Government Chemical Industrial Research Institute, Tokyo.

[2] G. C. Barker, *Anal. Chim. Acta*, **18**, 118 (1958).

[3] G. C. Barker, "Transactions of the Symposium on Electrode Processes, Philadelphia, 1959," E. Yeager ed., John Wiley and Sons, Inc., New York, N. Y., in course of publication.

[4] K. S. G. Doss and H. P. Agarwal, *Proc. Indian Acad. Sci.*, **39**, 263 (1951); **35A**, 45 (1952).

[5] Iu. A. Vdovin, *Doklady Akad. Nauk SSSR*, **120**, 554 (1958).

in control of the alternating voltage across the Faradaic impedance. Furthermore, correction for the double layer structure was not considered by previous workers in the solution of the boundary value problem. An analysis for voltage control and a correction for the double layer are given here.

Faradaic Rectification Current

Qualitative Discussion.—Consider the current–potential characteristic without concentration polarization for the electrode reaction O + ne = R, O and R being soluble species (Fig. 1), and assume that this curve is asymmetrical with respect to the equilibrium potential E_e. If the variation of the potential E about E_e is a sinusoidal function of time, there results an asymmetrical periodic current[6] and a net consumption of substance O or R (O in the case of Fig. 1). An aperiodic faradaic rectification current thus appears. As a result of the asymmetry of the alternating current, the concentrations of O at the electrode surface, $(C_O)_{x=0}$, decreases and that of R, $(C_R)_{x=0}$, increases. These concentration changes result (a) in a shift of E_e toward more negative (European convention) values and (b) in a progressive distortion of the current-potential curve (decrease of cathodic currents and increase of anodic currents) corresponding to $(C_O)_{x=0}$ and $(C_R)_{x=0}$ if such a curve could be determined without changes in $(C_O)_{x=0}$ and $(C_R)_{x=0}$ (Fig. 1, curves for $t_2 > t_1 > 0$). Changes in the current–potential curve and in E_e (there is now an anodic current at the initial E_e which compensates the effect of asymmetry) cause the net rectification to approach zero.

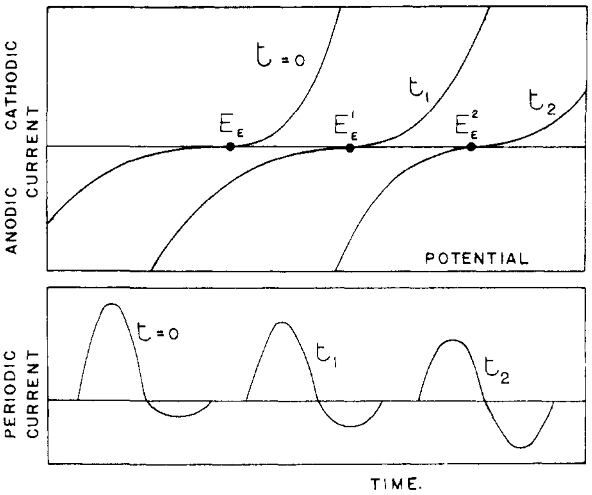

Fig. 1.—Progressive distortion of current-potential curves as a result of faradaic rectification with controlled variations of alternating potential. See text and footnote 6 in particular.

Since the faradaic rectification current depends on current–potential characteristics, it should be possible, at least in principle, to study electrode kinetics from the faradaic rectification with controlled variations of the alternating potential.

Quantitative Treatment.—The faradaic rectification current will be derived first without consideration of the double layer structure in the solution of the boundary value problem. Consider the electrode reaction, O + ne = R, involving soluble species, with mass transfer controlled by semi-infinite linear diffusion. The concentrations C_O and C_R are then solutions of Fick's equations, as written for substances O and R, for the conditions

$$C_0 = C_0{}^0,\ C_R = C_R{}^0 \text{ at } x \geqslant 0 \text{ and } t = 0$$

$$C_0 \longrightarrow C_0{}^0,\ C_R \longrightarrow C_R{}^0 \text{ for } x \longrightarrow \infty \text{ and } t \geqslant 0$$

$$D_0(\partial C_0/\partial x)_{x=0} = -D\,(\partial C_R/\partial x)_{x=0} = I(t)/nF \quad \text{for } x = 0 \text{ and } t > 0$$

x being the distance from the electrode, t the elapsed time, the C^0's the bulk concentrations of O and R, the D's the diffusion coefficients of O and R, and $I(t)$ the current density (which is a function of time).

By application of the Laplace transformation method one obtains these relationships between the concentrations at $x = 0$ and the current density

$$(C_0)_{x=0} = C_0{}^0 - D_0{}^{-1/2}\pi^{-1/2}\int_0^t \frac{I(y)/nF}{(t-y)^{1/2}}\,\mathrm{d}y \qquad (1)$$

$$(C_R)_{x=0} = C_R{}^0 + D_R{}^{-1/2}\pi^{-1/2}\int_0^t \frac{I(y)/nF}{(t-y)^{1/2}}\,\mathrm{d}y \qquad (2)$$

By introducing these values of the concentrations in the current–potential characteristic one obtains

$$I(t) = (I_0)_{\mathrm{ms}} \left\{ \left(\exp\left[-\frac{\alpha nF}{RT}(E-E_e)\right] - \exp\left[\frac{(1-\alpha)nF}{RT}(E-E_e)\right]\right) - \left(\frac{1}{C_0{}^0D_0{}^{1/2}}\exp\left[-\frac{\alpha nF}{RT}(E-E_e)\right] + \frac{1}{C_R{}^0D_R{}^{1/2}}\exp\left[\frac{(1-\alpha)nF}{RT}(E-E_e)\right]\right) \times \pi^{-1/2}\int_0^t \frac{I(y)/nF}{(t-y)^{1/2}}\,\mathrm{d}y \right\} \qquad (3)$$

where

$$(I_0)_{\mathrm{ms}} = nF(k_s)_{\mathrm{ms}}(C_O{}^0)^{1-\alpha}(C_R{}^0)^{\alpha} \qquad (4)$$

is the measured exchange current density (*i.e.*, not corrected for double layer effects), $(k_s)_{\mathrm{ms}}$ being the measured standard rate constant, and E_e the equilibrium potential for the bulk concentrations $C_O{}^0$ and $C_R{}^0$.

Equation 3 is solved in the Appendix for the particular case in which

$$E = E_e - \Delta E \sin \omega t \qquad (5)$$

and for steady-state for the periodic current components.[7] *This solution also holds only for* $\Delta E << RT/nF$ (*i.e.*, $\Delta E < 5$ mv. at room temperature) because expansion in series is limited to terms of the second order (see Appendix). The faradaic current density is the sum of a periodic component and the following aperiodic faradaic rectification component

$$I_{\mathrm{F.R.}} = nF\left(\frac{nF}{RT}\Delta E\right)^2 \left[\lambda \exp(\lambda^2 t)\operatorname{erfc}(\lambda t^{1/2}) \Big/ \left(\frac{1}{(C_O{}^0D_O{}^{1/2})} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\right]\psi \qquad (6)$$

with

$$\lambda = [(I_0)_{\mathrm{ms}}/nF]\,[(1/C_O{}^0D_O{}^{1/2}) + (1/C_R{}^0D_R{}^{1/2})] \qquad (7)$$

$$\psi = \frac{1}{4}\left\{(2\alpha - 1) - 2\,\frac{(\alpha/C_O{}^0D_O{}^{1/2}) - [(1-\alpha)/C_R{}^0D_R{}^{1/2}]}{(1/C_O{}^0D_O{}^{1/2}) + (1/C_R{}^0D_R{}^{1/2})} \times \frac{(1/\omega C_s)[R_s + (1/\omega C_s)]}{R_s{}^2 + (1/\omega C_s)^2}\right\} \qquad (8)$$

---

(6) The alternating current which is determined in part by diffusion of reactants *cannot* be determined by a simple graphic construction from the current-potential curve of Fig. 1.

(7) Transients die out after a few cycles in faradaic impedance measurements; see T. Berzins and P. Delahay, *Z. Elektrochem.*, **59**, 792 (1955).

$$R_s = \frac{RT}{nF}\left\{\frac{1}{(I_0)_{ms}} + \frac{1}{2^{1/2}nF\omega^{1/2}}\left(\frac{1}{C_O{}^0D_O{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\right\} \quad (9)$$

$$\frac{1}{\omega C_s} = \frac{RT}{nF}\left\{\frac{1}{2^{1/2}nF\omega^{1/2}}\left(\frac{1}{C_O{}^0D_O{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\right\} \quad (10)$$

The elements R_s and C_s are the components of the series equivalent circuit of the faradaic impedance. Note that R_s includes kinetic (term in $1/(I_0)_{ms}$) and diffusion components whereas $1/\omega C_s$ contains only diffusion terms. The rectification current of eq. 6 is positive or negative depending on the sign of ψ (eq. 8). A positive current corresponds to a net cathodic process according to the convention used in the writing of current–potential characteristics. One has $I_{F.R.} = 0$ for $\alpha = 0.5$ and $C_O{}^0D_O{}^{1/2} = C_R{}^0D_R{}^{1/2}$ since the current–potential curve is then symmetrical about E_e and rates of diffusion are the same for substances O and R.

In agreement with the foregoing qualitative discussion, the rectification current according to eq. 6 decreases continuously (Fig. 2).[8] For $\lambda t^{1/2} >> 1$ one has

$$I_{F.R.} = \pi^{-1/2}nF\left(\frac{nF}{RT}\Delta E\right)^2\left(\frac{1}{C_O{}^0D_O{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{/2}}\right)^{-1}\psi t^{-1/2} \quad (11)$$

and a plot of $I_{F.R.}$ *versus* $t^{-1/2}$ is linear. Conversely, one can show by expanding the error function in eq. 6 for small arguments that $I_{F.R.}$ decreases linearly with $t^{/2}$ for $\lambda t^{1/2} << 1$ and that the *extrapolated* value of $I_{F.R.}$ for $t = 0$ is

$$(I_{F.R.})_{t=0} = [(nF/RT)\Delta E]^2\cdot\psi\cdot(I_0)_{ms} \quad (12)$$

The rectification current depends on the frequency in view of the form of ψ (eq. 8). One has $\psi \rightarrow (\alpha/2) - {}^1/_4$ for $\omega \rightarrow \infty$; and the dependence of ψ, and consequently of $I_{F.R.}$, on ω is quite small at sufficiently high frequencies (Fig. 2). Interference resulting from the frequency dispersion of the double layer and, possibly, of the electrolyte conductivity should not be overlooked (variation of ΔE, etc.).

The shift in mean potential, $(nF/RT)\Delta E^2\psi$, for $t \rightarrow \infty$ is the same as the value derived by Barker[3] and by Vdovin[4] on the assumption of current control. Thus, for $t \rightarrow \infty$ analysis based on current control or alternating voltage control yields the same result.

Influence of the Double Layer in the Absence of Specific Adsorption

It was pointed out in previous investigations from this Laboratory[9] that the structure of the double layer must be considered in the solution of the boundary value problem for diffusion at the electrode. By transposition of our previous results one can write for the concentration of species *j* (O or R) in the plane of closest approach (compare with eq. 1 and 2)

$$C_j{}^* = \exp(-z_j F\varphi_0/RT)\{C_j{}^0 - (\pm I(t)/nF)(a_j/\kappa D_j) - D_j{}^{-1/2}\pi^{-1/2}\int_0^t \frac{(\pm I(y)/nF)}{(t-y)^{1/2}}\,dy\} \quad (13)$$

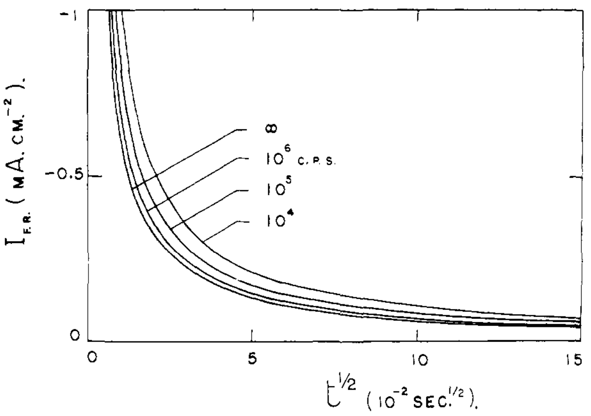

Fig. 2.—Variations of the faradaic rectification current density with $t^{1/2}$ for different frequencies. Data for the discharge for mercurous ion (1 m*M*) in 1 *M* perchloric acid at 25°[8]: $(I_0)_{ms} = 0.25$ amp. cm.$^{-2}$, $\alpha = 0.24$, $D_{Hg_2{}^{++}} = 0.91 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, $\Delta E = 5$ mv. Values of $(I_{F.R.})_{t=0}$ (eq. 12) are: −4.89, −5.42, −6.36, −7.82, ma. cm.$^{-2}$ for $f \rightarrow \infty$ and $f = 10^6, 10^5, 10^4$ c.p.s., respectively. Note that this system probably could not be studied below 10^5 c.p.s., and that curves for 10^5 and 10^4 c.p.s. are shown only to indicate the effect of frequency.

with

$$a_j = \frac{\exp[F(\pm|z_j| - |z|/2)|\varphi_0|/RT] - 1}{\pm|z_j/z| - (1/2)} - \frac{\exp[F(\mp|z_j| - |z|/2)|\varphi_0|/RT] - 1}{\mp(|z_j/z| - (1/2))} \quad (14)$$

where z_j is the valence of species j, z the valence of the supporting electrolyte (assumed to determine solely the double layer structure) and φ_0 the difference of potential across the diffuse double layer. The upper and lower signs in eq. 14 correspond to $z_j\varphi_0 > 0$ (repulsion of species j) and $z_j\varphi_0 < 0$ (attraction), respectively. By introducing the above expressions into the current-potential characteristic one has now instead of eq. 3

$$I(t) = (I_0)_{app}\left\{\left(\exp\left[-\frac{\alpha nF}{RT}(E - E_e)\right] - \exp\left[\frac{(1-\alpha)nF}{RT}(E - E_e)\right]\right) - \frac{I(t)}{nF}\left(\frac{a_O}{\kappa C_O{}^0D_O}\exp\left[-\frac{\alpha nF}{RT}(E - E_e)\right] + \frac{a_R}{\kappa C_R{}^0D_R}\exp\left[\frac{(1-\alpha)nF}{RT}(E - E_e)\right]\right) - \left(\frac{1}{C_O{}^0D_O{}^{1/2}}\exp\left[-\frac{\alpha nF}{RT}(E - E_e)\right] + \frac{1}{C_R{}^0D_R{}^{1/2}}\exp\left[\frac{(1-\alpha)nF}{RT}(E - E_e)\right]\right) \times \pi^{-1/2}\int_0^t \frac{I(y)/nF}{(t-y)^{1/2}}\,dy\right\} \quad (15)$$

where the *apparent* exchange current density is

$$(I_0)_{app} = I_0 \exp[(\alpha n - z_O)F\varphi_O/RT \quad (16)$$

and I_0, the exchange current density, is defined by eq. 4 in which a "true" standard rate constant k_s is substituted for $(k_s)_{ms}$.

By repeating the same calculations as above one concludes that eq. 6 for the rectification current is

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(8) Data taken from H. Matsuda, S. Oka and P. Delahay, THIS JOURNAL, **81**, 5077 (1959).

(9) (a) H. Matsuda and P. Delahay, *J. Phys. Chem.*, in course of publication; (b) H. Matsuda, *ibid.*, in course of publication.

still valid but that ψ is now given by

$$\psi = \frac{1}{4}\left\{(2\alpha - 1) - 2\,\frac{(\alpha/C_O{}^0D_0{}^{1/2}) - ([1-\alpha]/C_R{}^0D_R{}^{1/2})}{(1/C_0{}^0D_0{}^{1/2}) + (1/C_R{}^0D_R{}^{1/2})}\cdot \frac{(1/\omega C_s)[R_s + (1/\omega C_s)]}{R_s{}^2 + (1/\omega C_s)^2} - 2\,\frac{RT}{n^2F^2}\left(\frac{\alpha a_0}{\kappa C_O{}^0D_O} - \frac{(1-\alpha)a_R}{\kappa C_R{}^0D_R}\right)\frac{R_s}{R_s{}^2 + (1/\omega C_s)^2}\right\} \quad (17)$$

λ, R_s and C_s being given by eq. 7, 9 and 10, respectively, and $(I_0)_{ms}$ being

$$(I_0)_{ms} = \frac{(I_0)_{app}}{1 + [(I_0)_{app}/nF][(a_0/\kappa C_O{}^0D_O) + (a_R/\kappa C_R{}^0D_R)} \quad (18)$$

There κ is the reciprocal "thickness" of the diffuse double layer given by the Gouy–Chapman theory, *i.e.*

$$(1/\kappa) = (RT\epsilon/8\pi z^2F^2C_t)^{1/2} \quad (19)$$

with ϵ the dielectric constant, and C_t the sum of the concentrations of the $z - z$ supporting electrolytes.

The correction of eq. 18 is the same as for the double pulse galvanostatic method[9a] and faradaic impedance measurements,[9b] and our previous discussion can be transposed here without change. It should be noted that the derivation of eq. 15 involves a first order approximation and that *eq. 18 should not be applied when the second term in its denominator is either very large in comparison with unity or close to −1.*

It follows from eq. 17 that

$$(\psi)_{\omega\to\infty} = \frac{1}{4}\left\{(2\alpha - 1) - 2\,\frac{(I_0)_{ms}}{nF}\left[\frac{\alpha a_0}{\kappa C_O{}^0D_O} - \frac{(1-\alpha)a_R}{\kappa C_R{}^0D_R}\right]\right\} \quad (20)$$

The apparent transfer coefficient deduced from eq. 20 is somewhat in error when the last term in this equation is ignored. For instance, in the discharge of a metal ion attracted in the diffuse double layer ($a_O < 0$ and $a_R = 0$), the apparent transfer coefficient is too large.

Acknowledgment.—This investigation was supported by the Office of the Naval Research. We are indebted to Dr. G. C. Barker (Harwell, England) for comments on this paper.

Appendix

Derivation of Equation 6.—Equations 3 and 5 are combined, and the exponentials and the current density are expanded in a power series with respect to $(nF/RT)\Delta E$. Thus

$$\exp\left(\frac{\alpha nF}{RT}\,\Delta E \sin \omega t\right) = \sum_{p=0}^{\infty} \frac{\alpha^p}{p!} \sin^p \omega t \left(\frac{nF}{RT}\,\Delta E\right)^p \quad (21)$$

$$\exp\left[-\frac{(1-\alpha)nF}{RT}\,\Delta E \sin \omega t\right] = \sum_{p=0}^{\infty} (-1)^p\,\frac{(1-\alpha)^p}{p!}\sin^p \omega t\left(\frac{nF}{RT}\,\Delta E\right)^p \quad (22)$$

$$I(t) = \sum_{p=0}^{\infty} \phi_p(t)\left(\frac{nF}{RT}\,\Delta E\right)^p \quad (23)$$

By combining these equations with the current potential characteristic (combination of eq. 3 and 5) and equating the terms of the same order with respect to $(nF/RT)\Delta E$, one obtains this system of integral equations

$$\phi_p(t) = (I_0)_{ms}\left\{[\alpha^p - (-1)^p(1-\alpha)^p](1/p!)\sin^p \omega t - \frac{1}{nF}\sum_{r=0}^{p}\left(\frac{\alpha^r}{C_O{}^0D_O{}^{1/2}} + (-1)^r\,\frac{(1-\alpha)^r}{C_R{}^0D_R{}^{1/2}}\right)\frac{1}{r!}\sin^r \omega t \times \frac{1}{\pi^{1/2}}\int_0^t \frac{\phi_{p-r}(y)}{(t-y)^{1/2}}\,dy\right\},\ (p = 0,1,2,\ \ldots) \quad (24)$$

Solutions will be obtained for $p = 0$, 1 and 2. For $p = 0$, eq. 24 is

$$\phi_0(t) = [(I_0)_{ms}/nF]\left\{-\left(\frac{1}{C_0{}^0D_0{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\pi^{-1/2}\int_0^t \frac{\phi_0(y)}{(t-y)^{1/2}}\,dy\right\} \quad (25)$$

with the solution

$$\phi_0(t) = 0$$

For $p = 1$, eq. 24 can be transformed into

$$\phi_1(t) = (I_0)_{ms}\left\{\sin \omega t - \frac{1}{nF}\left(\frac{1}{C_O{}^0D_O{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\frac{1}{\pi^{1/2}}\int_0^t \frac{\phi_1(y)}{(t-y)^{1/2}}\,dy\right\} \quad (26)$$

This integral equation can be solved for the steady-state for the periodic current component ($\omega t \to \infty$) by putting

$$\phi_1(t) = A_1 \sin(\omega t + \delta_1) \quad (27)$$

A_1 and δ_1 being given by

$$\left.\begin{aligned} A_1 \sin \delta_1 &= \left(\frac{RT}{nF}\right)\frac{(1/\omega C_s)}{R_s{}^2 + (1/\omega C_s)^2} \\ A_1 \cos \delta_1 &= \left(\frac{RT}{nF}\right)\frac{R_s}{R_s{}^2 + (1/\omega C_s)^2}\end{aligned}\right\} \quad (28)$$

and R_s and C_s being the elements of the series equivalent circuit of the faradaic impedance given by eq. 9 and 10.

For $p = 2$ one has from eq. 24

$$\phi_2(t) = (I_0)_{ms}\left\{\frac{1}{2}(2\alpha - 1)\sin^2 \omega t - \left[\left(\frac{\alpha}{C_O{}^0D_O{}^{1/2}} - \frac{1-\alpha}{C_R{}^0D_R{}^{1/2}}\right)\Big/\left(\frac{1}{C_O{}^0D_O{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\right] \times [\sin^2\omega t - (\phi_1/(I_0)_{ms})\sin \omega t] - \frac{1}{nF}\left(\frac{1}{C_O{}^0D_O{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\frac{1}{\pi^{1/2}}\int_0^t \frac{\phi_2(y)}{(t-y)^{1/2}}\,dy\right\} \quad (29)$$

In the steady state for the periodic current component ($\omega t \to \infty$) one can put

$$\phi_2(t) = \overline{\phi_2}(t) + A_2 \sin(2\omega t + \delta_2) \quad (30)$$

By introducing eq. 27 and 30 into eq. 29 and retaining the terms which do not contain sin $2\omega t$ and cos $2\omega t$, one obtains

$$\overline{\phi_2}(t) = (I_0)_{ms}\left\{\psi - \frac{1}{nF}\left(\frac{1}{C_O{}^0D_O{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\frac{1}{\pi^{1/2}}\int_0^t \frac{\overline{\phi_2}(y)}{(t-y)^{1/2}}\,dy\right\} \quad (31)$$

Equation 31 is a Volterra integral equation of the second kind which can be solved easily by Laplace transformation. One has

$$\overline{\phi_2}(t) = nF\left[\lambda \exp(\lambda^2 t)\operatorname{erfc}(\lambda t^{1/2})\Big/\left(\frac{1}{C_O{}^0D_O{}^{1/2}} + \frac{1}{C_R{}^0D_R{}^{1/2}}\right)\right]\psi \quad (32)$$

where λ is defined by eq. 7.

Equation 6 for $I_{F.R.}$ is finally obtained by combination of eqs. 24, 30, 32.