A PERIODIC SOLUTION OF THE DIFFUSION EQUATION

N. N. Kochina

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Under some circumstances, autooscillations can arise in an electrochemical system with decreasing characteristics [1–3]. A method for finding the polarization curve $P = P(\vartheta)$ (here ϑ is the electrode potential, $P = i / c(0, t)$, where i is the current density, and c(0, t) is the mass concentration at the electrode surface), if the distribution in time of the current density is given, is proposed in [1]. In the numerical solution of this problem, which is considered below, considerable computational difficulties were encountered.

§1. It is assumed in [1] that the quantity $\chi(t)$, proportional to the current density, is a known periodic function of the time t with period T:

$$\chi(t) = \begin{cases} \psi(t) & \text{when } \alpha + kT \leqslant t \leqslant \beta + kT \\ \varphi(t) & \text{when } \beta + kT \leqslant t \leqslant \gamma + kT \end{cases} \quad (k = 0, \pm 1, \pm 2, \ldots)$$

$$(\alpha = {}^1/_2\, pT,\ \beta = -{}^1/_2\, pT + T,\ \gamma = {}^1/_2\, pT + T,$$

$$0 < p < 1,\ \psi(t) < 0,\ \varphi(t) > 0), \tag{1.1}$$

and with the help of the Duhamel formula [4], convergent series were obtained for the function u(x, t), the periodic solution of the diffusion equation (D is the diffusion coefficient)

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} \tag{1.2}$$

with the boundary condition

$$\frac{\partial u(0, t)}{\partial x} = \chi(t) \tag{1.3}$$

in the semi-infinite region $x \geq 0$. The matter concentration c(x, t) is related to u(x, t) by the equation

$$u(x, t) = [c(x, t) - c_0 - (c^\circ - c_0)x / l]Gl$$

(here c_0, c°, l, and G are some constants [1]). The function $\chi(t)$ must now satisfy certain requirements [1].

When the function $\chi(t)$ is known and the formulas (1.1) are given, the solution of Eq. (1.2) with the condition (1.3) gives us

$$u(0, t) = \begin{cases} u_1(0, t) & \text{when } \alpha + kT \leqslant t \leqslant \beta + kT \\ u_2(0, t) & \text{when } \beta + kT \leqslant t \leqslant \gamma + kT \end{cases} (k = 0, \pm 1, \pm 2, \ldots). \tag{1.4}$$

It is now easy to find the parametric representation of the characteristic $P(\vartheta)$, which consists, for the values of ϑ which correspond to the autooscillation cycle and include the region of the characteristic maximum, of the two pieces $P_1(\vartheta)$ and $P_2(\vartheta)$, i.e. [1],

$$P_1 = \frac{Gl(\psi(t) + A)}{u_1(0, t) + c_0}, \qquad v - \vartheta = Glr(\psi(t) + A),$$

$$P_2 = \frac{Gl(\varphi(t) + A)}{u_2(0, t) + c_0}, \qquad v - \vartheta = Glr(\varphi(t) + A),$$

$$(v, r, A = \text{const}). \tag{1.5}$$

The series $u_1(0, t)$ and $u_2(0, t)$ now have the following forms:

$$u_1(0, t) = -\left(\frac{D}{\pi}\right)^{1/2} \left\{J_1 + \sum_{j=1}^{\infty} (J_{2j} + J_{2j+1})\right\}, \tag{1.6}$$

$$u_2(0, t) = -\left(\frac{D}{\pi}\right)^{1/2} \left\{I_1 + \sum_{j=1}^{\infty} (I_{2j} + I_{2j+1})\right\}. \tag{1.7}$$

Here

$$J_1 = \int_\alpha^t \frac{\psi(\sigma)\, d\sigma}{\sqrt{t - \sigma}}, \qquad J_{2j} = \int_\beta^\gamma \frac{\varphi(\sigma)\, d\sigma}{\sqrt{t + jT - \sigma}},$$

$$J_{2j+1} = \int_\alpha^\beta \frac{\psi(\sigma)\, d\sigma}{\sqrt{t + jT - \sigma}}, \tag{1.8}$$

$$I_1 = \int_\beta^t \frac{\varphi(\sigma)\, d\sigma}{\sqrt{t - \sigma}}, \qquad I_{2j} = \int_\gamma^{\beta + T} \frac{\psi(\sigma)\, d\sigma}{\sqrt{t + jT - \sigma}},$$

$$I_{2j+1} = \int_\beta^\gamma \frac{\varphi(\sigma)\, d\sigma}{\sqrt{t + jT - \sigma}}. \tag{1.9}$$

Formulas (1.6) and (1.9) were obtained, after some transformations, from Eqs. (2.3)–(2.5) of [1].

Clearly, if in the formulas (1.8) we replace α by β, β by γ, γ by $\beta + T$, $\psi(\sigma)$ by $\varphi(\sigma)$, and $\varphi(\sigma)$ by $\psi(\sigma)$, then Eq. (1.6) passes over into Eq. (1.7). Thus the numerical computation of the functions $u_1(0, t)$ and $u_2(0, t)$ can both be carried out by the same program, with only the input data being changed. Accordingly, we shall consider below only the means of finding a numerical solution of Eq. (1.6), where the notation (1.8) is used. Technical difficulties arise only in finding the solution of Eq. (1.6), since when $u_1(0, t)$ has been determined, the characteristic $P_1(\vartheta)$ can easily be calculated from the formulas (1.5). These difficulties are twofold.

In the first place, if the functions $\psi(t)$ and $\varphi(t)$, which appear in Eq. (1.8) have some sort of complicated form, then approximate integration formulas must be used to calculate the integrals (1.8); the direct calculation of these integrals is often a laborious process, requiring a great deal of machine time.

In the second place, the series (1.6), using the notation (1.8), converges very slowly; this is an alternating series, each term of which is of order $j^{-1/2}$, and the computation time from the formula (1.6) would be very large.

In order to avoid these difficulties, we transform the integrals (1.8) into a new form, and we shall further make use of asymptotic formulas to calculate them at large values of j.

§2. We now show how the calculation is carried out in the case in which the functions $\varphi(t)$ and $\psi(t)$ are given by

$$\varphi(t) = a + b(\gamma - t)^s + g(t - \beta)^{1/2},$$

$$\psi(t) = e + d(\beta - t)^q + f(t - \alpha)^{1/2}, \tag{2.1}$$

$$(a > 0,\ b > 0,\ g < 0,\ {}^1/_2 < s < 1,\ e < 0,$$

$$d < 0,\ f > 0,\ {}^1/_2 < q < 1).$$

Here these constants are such that the relations (4.2)–(4.4) and (2.15)–(2.16) of [1] are to be satisfied.

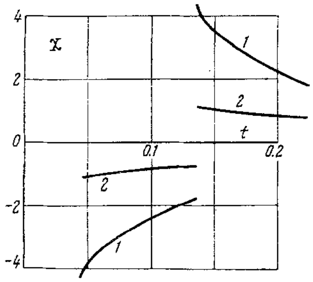

Fig. 1

Let us set

$$\varphi(t) = \varphi_1(t) + \varphi_2(t), \qquad \psi(t) = \psi_1(t) + \psi_2(t). \qquad (2.2)$$

Here

$$\varphi_1(t) = a + g(t-\beta)^{1/2}, \quad \psi_1(t) = e + f(t-\alpha)^{1/2} \qquad (2.3)$$

$$\varphi_2(t) = b(\gamma - t)^s, \qquad \psi_2(t) = d(\beta - t)^q. \qquad (2.4)$$

Substituting (2.2) into Eq. (1.8), we see that, using the notation of Eqs. (2.1)–(2.4), each of the integrals of Eq. (1.8) separates into two parts:

$$J_1 = J_{1,1} + J_{1,2},$$

$$J_{2j} = J_{2j,1} + J_{2j,2}, \qquad J_{2j+1} = J_{2j+1,1} + J_{2j+1,2}, \qquad (2.5)$$

$$J_{1,i} = \int_\alpha^t \frac{\psi_i(\sigma)\, d\sigma}{\sqrt{t-\sigma}},$$

$$J_{2j,i} = \int_\beta^\gamma \frac{\varphi_i(\sigma)\, d\sigma}{\sqrt{t+jT-\sigma}}, \qquad J_{2j+1,i} = \int_\alpha^\beta \frac{\psi_i(\sigma)\, d\sigma}{\sqrt{t+jT-\sigma}}, \qquad (2.6)$$

$$(i = 1, 2).$$

It is clear from Eq. (2.3) that the integrals (2.6), with i = 1, can be performed with elementary functions.

Let us now take up the integrals (2.6) with i = 2.

We first consider the expression $J_{1,2}$. It is easy to see that

$$J_{1,2}(\alpha) = 0, \qquad J_{1,2}(\beta) = \frac{d(\beta-\alpha)^{q+1/2}}{q+1/2}. \qquad (2.7)$$

Now let $\alpha < t < \beta$. In this case the integral $J_{1,2}$ is not taken in elementary functions; it is a conver-

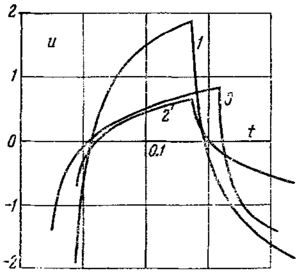

Fig. 2

gent improper integral, since the integrand becomes infinite at $\sigma = t$. Integrating by parts, we find that

$$J_{1,2} = 2d\left\{(\beta-\alpha)^q\sqrt{t-\alpha} - q\int_\alpha^t (\beta-\sigma)^{q-1}\sqrt{t-\sigma}\, d\sigma\right\}. \qquad (2.8)$$

Let us examine the following integral from Eq. (2.8):

$$J = \int_\alpha^t (\beta-\sigma)^{q-1}\sqrt{t-\sigma}\, d\sigma. \qquad (2.9)$$

At $\sigma = t$ the derivative of the integrand becomes infinite.

A method for the approximate calculation of integrals of this type is given in [5]. Assume that $\delta > -1$ and that it is not a positive integer. We introduce the notation

$$I = \int_a^b f(\sigma)\, d\sigma$$

$$(f(\sigma) = (\sigma_1 - \sigma)^\delta \varkappa(\sigma)). \qquad (2.10)$$

As in [5], we separate the function $f(\sigma)$ into two parts

$$f(\sigma) = f_1(\sigma) + f_2(\sigma)$$

$$\left(f_i(\sigma) = (\sigma_1 - \sigma)^\delta \varkappa_i(\sigma), \quad i = 1, 2\right), \qquad (2.11)$$

such that the function $f_1(\sigma)$ contains all the singularities of $f(\sigma)$, but is integrable in finite form, while the function $f_2(\sigma)$ has no singularities, and its integral can be

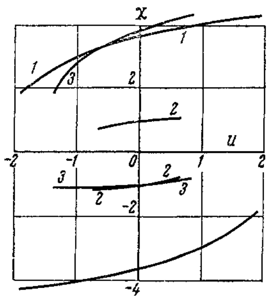

Fig. 3

found with the help of one of the numerical integration formulas (for example, the Simpson formula). The error ε in the Simpson formula is determined by the modulus of the fourth derivative of the integrand:

$$\varepsilon \leqslant \left(\frac{b-a}{2}\right)^5 \frac{M_4}{90 m^4}, \quad M_4 = \max|f^{\mathrm{IV}}(\sigma)| \quad (a \leqslant \sigma \leqslant b). \qquad (2.12)$$

Here 2m is the number of segments into which the interval of integration $a \le \sigma \le b$ is divided.

Therefore the function $f(\sigma)$ must be transformed so as to make the fourth derivative of the function $f_2(\sigma)$ equal to zero at $\sigma = \sigma_1$.

Comparing formulas (2.9) and (2.10), we see that in the case under consideration $\delta = 1/2$, $\sigma_1 = t$. Since $\alpha < t < \beta$, the function $\varkappa(\sigma) = (\beta - \sigma)^{q-1}$ has no singularities in the interval (α, t).

Separating out the first four terms in the Taylor series expansion of the function $\varkappa(\sigma)$ around the point

$\sigma = t$, we obtain

$$\varkappa_1(\sigma) = \sum_{m=0}^{3} \frac{1}{m!} \varkappa^{(m)}(t)(\sigma - t)^m,$$
$$\varkappa_2(\sigma) = \varkappa(\sigma) - \varkappa_1(\sigma). \quad (2.13)$$

Using Eqs. (2.9) and (2.13), we can write out the expression for the function $f_2(\sigma)$, which appears in Eq. (2.11):

$$f_2(\sigma) = \sqrt{t-\sigma}\Big\{(\beta-\sigma)^{q-1} - \sum_{m=0}^{3} a_m(q)(\beta-t)^{q-1-m}(\sigma-t)^m\Big\},$$
$$a_0(q) = 1,$$
$$a_m(q) = \frac{(-1)^m}{m!}(q-m)(q-m+1)\ldots(q-1) \quad (m \neq 0). \quad (2.14)$$

The integrals $J_{2j,2}$ and $J_{2j+1,2}$ are transformed similarly.

Let us now write down the final forms for the integrals J_1, J_{2j}, and J_{2j+1}:

$$J_1 = 2e\sqrt{t-\alpha} + \frac{\pi}{2} f(t-\alpha) + 2d\Big\{(\beta-\alpha)^q \times \sqrt{t-\alpha} - 2q(\beta-t)^{q-1}(t-\alpha)^{3/2} \times \Big[\frac{1}{3} + \sum_{m=1}^{3} \frac{(q-m)(q-m+1)\ldots(q-1)}{m!\,(2m+3)}\Big(\frac{t-\alpha}{\beta-t}\Big)^m\Big] - q\int_\alpha^t f_2(\sigma)\,d\sigma\Big\} \quad (\alpha < t < \beta),$$
$$J_1(\alpha) = 0,$$
$$J_1(\beta) = 2e\sqrt{\beta-\alpha} + \frac{\pi}{2} f(\beta-\alpha) + \frac{d(\beta-\alpha)^{q+1/2}}{q+1/2}. \quad (2.15)$$

Here $f_2(\sigma)$ is given by formula (2.14),

$$J_{2j} = 2a[\sqrt{\tau-\beta} - \sqrt{\tau-\gamma}] + g\Big\{-\sqrt{(\gamma-\beta)(\tau-\gamma)} + \frac{1}{2}(\tau-\beta)\Big[\frac{\pi}{2} - \arcsin\Big(\frac{\tau+\beta-2\gamma}{\tau-\beta}\Big)\Big]\Big\} + b\Big\{\frac{(\gamma-\beta)^{s+1}}{s+1}\frac{1}{\sqrt{\tau-\gamma}} + \sum_{m=2}^{4} \frac{(-1)^{m+1}(\gamma-\beta)^{s+m}(2m-3)(2m-5)\ldots1}{2^{m-1}(m-1)!\,(s+m)(\tau-\gamma)^{m-1/2}} + \int_\beta^\gamma f_2^{(2j)}(\sigma)\,d\sigma\Big\}$$
$$(\tau = t + jT,\ \tau \neq \alpha + T),$$
$$J_2(\alpha) = 2a\sqrt{\gamma-\beta} + \frac{\pi}{2} g(\gamma-\beta) + \frac{b(\gamma-\beta)^{s+1/2}}{s+1/2},$$
$$f_2^{(2j)}(\sigma) = b(\gamma-\sigma)^s\Big\{\frac{1}{\sqrt{\tau-\sigma}} - \frac{1}{\sqrt{\tau-\gamma}} - \sum_{m=1}^{3} \frac{(2m-1)(2m-3)\ldots1\,(\sigma-\gamma)^m}{m!\,2^m(\tau-\gamma)^{m+1/2}}\Big\}. \quad (2.16)$$

The expressions for the integral $J_{2j+1,2}$ and the function $f_2^{(2j+1)}(\sigma)$ can be obtained from the first and third formulas of Eq. (2.16) if we replace a by e, g by f, s by q, b by d, β by α, and γ by β.

§3. At large values of j we make use of asymptotic expansions of the integrals J_{2j} and J_{2j+1}, as defined by Eq. (1.8).

Introducing the notation

$$x^2 = (jT)^{-1} \quad (3.1)$$

and expanding the function $[1 + x^2(t-\sigma)]^{1/2}$ in a Maclaurin series around the value x = 0 with a remainder term, we obtain from Eq. (1.8)

$$J_{2j} = \sum_{n=0}^{l} \frac{(-1)^n\,1\cdot3\ldots(2n-1)}{2^n\cdot n!} x^{2n+1}\int_\beta^\gamma \varphi(\sigma)(t-\sigma)^n\,d\sigma + (-1)^{l+1}\frac{1\cdot3\ldots(2l+1)}{2^{l+1}(l+1)!} x^{2l+3}\int_\beta^\gamma \frac{\varphi(\sigma)(t-\sigma)^{l+1}\,d\sigma}{[1+\theta(t-\sigma)x^2]^{l+3/2}}$$
$$(0 < \theta < 1). \quad (3.2)$$

Here l is some positive integer. A formula analogous to Eq. (3.2) can also be written for the integral J_{2j+1}, defined by the third formula of Eq. (1.8). Adding together J_{2j} and J_{2j+1}, computing the integrals

$$\int_\beta^\gamma \varphi(\sigma)(t-\sigma)^n\,d\sigma,\quad \int_\alpha^\beta \psi(\sigma)(t-\sigma)^n\,d\sigma \quad (1 \leqslant n \leqslant l), \quad (3.3)$$

and, as was shown in [1], taking into account that

$$\int_\alpha^\beta \psi(\sigma)\,d\sigma + \int_\beta^\gamma \varphi(\sigma)\,d\sigma = 0. \quad (3.4)$$

and then returning to the previous notation of Eq. (3.1), from Eq. (3.2) and from the analogous formula for J_{2j+1} we find the following expression:

$$J_{2j} + J_{2j+1} = \sum_{n=1}^{l} f_{1/2(2n+1)}(jT)^{-(2n+1)/2} + R_{2j} + R_{2j+1}. \quad (3.5)$$

Here

$$f_{(2n+1)/2} = \sum_{j=1}^{n} b_j(A_{n+3/2-j} + A^*_{n+3/2-j})t^{j-1}$$
$$(n = 1, 2, \ldots l),$$
$$b_1 = 1,$$
$$b_j = \frac{(-1)^{j+1}}{2^{j-1}(j-1)!}(2n+3-2j)(2n+3-2j+2)\times(2n+3-2j+4)\ldots(2n-1) \quad (j \neq 1). \quad (3.6)$$

The quantity $A_{1/2(2m+1)}$ is given by the formula

$$A_{1/2(2m+1)} = \frac{1\cdot3\ldots(2m-1)}{2^m} \times \sum_{j=0}^{m} \frac{(-1)^j}{(m-j)!}[\gamma^{m-j}\Phi_{j+1}(\gamma) - \beta^{m-j}\Phi_{j+1}(\beta)]. \quad (3.7)$$

The functions $\Phi_i(\tau)$, defined on the interval $\beta \leq \tau \leq \gamma$, are given by

$$\Phi_i(\tau) = \frac{a\tau^i}{i!} +$$

$$+\frac{(-1)^i b}{(s+1)(s+2)\ldots(s+i)}(\gamma-\tau)^{s+i}+$$

$$+\frac{2^i g}{3\cdot 5\ldots(1+2i)}(\tau-\beta)^{1/2+i} \quad (i=1,2,\ldots,7). \qquad (3.8)$$

The quantity $A^*_{1/2(2m+1)}$ is defined by the formula which is obtained if in the expression (3.7) we replace γ by β, β by α, and the functions $\Phi_i(\tau)$ by the corresponding functions $\Phi_i^*(\tau)$, which in turn are given by (3.8) when we replace a by e, b by d, s by q, g by f γ by β, and β by α.

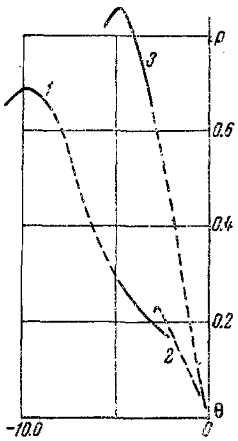

Fig. 4

In Eq. (3.5) $R_{2j} + R_{2j+1}$ is the remainder term, for which we obtain the following estimate:

$$|R_{2j}+R_{2j+1}| \leqslant \lambda(l)(jT)^{-l-3/2}. \qquad (3.9)$$

Here

$$\lambda(l)=\frac{1\cdot 3\ldots(2l+1)}{2^{l+1}(l+2)!}\times$$

$$\times\{\varphi(\beta)[(\gamma-\alpha)^{l+2}-(\beta-\alpha)^{l+2}]-\psi(\alpha)(\beta-\alpha)^{l+2}\}\cdot \qquad (3.10)$$

Let us now rewrite Eq. (1.6) in the form

$$u_1(0,t)=$$

$$=-\sqrt{\frac{D}{\pi}}\Big\{J_1+\sum_{j=1}^{j_0-1}(J_{2j}+J_{2j+1})+S_{j_0}+R_{j_0}\Big\}, \qquad (3.11)$$

$$S_{j_0}=\sum_{j=j_0}^{\infty}\sum_{n=1}^{l} f_{n+1/2}(jT)^{-n-1/2},$$

$$R_{j_0}=\sum_{j=j_0}^{\infty}(R_{2j}+R_{2j+1}). \qquad (3.12)$$

Here j_0 is some integer, which is defined below.

When the Riemann zeta-function is introduced into this discussion, it becomes easy to calculate the function S_{j_0} given in Eq. (3.12) and to choose the number j_0, such that for given ε and l, the remainder term R_{j_0} does not exceed ε:

$$|R_{j_0}| \leqslant \frac{\lambda(l)}{T^{l+3/2}(1-2^{-l-1/2})}\frac{1}{\left[2E\left(\frac{j_0}{2}\right)\right]^{l+1/2}} \leqslant \varepsilon. \qquad (3.13)$$

Here E(x) is the integer part of the number x.

In [7] are presented the results of calculations by the method proposed here for the function u(0, t) in the case of rectilinear oscillations, when $b = g = d = f \equiv 0$. In this case the parameter p takes the following values: 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875.

Figures 1–4 present the graphs of the functions $\chi(t)$, u(0, t), $\chi(u)$, and $p(\theta)$, where $p = P/Gl$, $\theta = (\vartheta - v)/Gl\tau$. The function $\chi(t)$ is calculated from Eq. (2.1), u(0, t) from Eq. (3.11), and $p(\theta)$ from Eq. (1.5). Curve 1 corresponds to the following values of the constants in the solution: p= 0.5, $a = -e = 3.87000$, $b = -d = 4.69923$, $g = -f = -6.89511$, $s = q = 0.93477$, $A = 6.555$, $c_0 = 14.884$; curve 2: $p = 0.5$, $a = -e = 0.96333$, $b = -d = 1.56644$, $g = -f = -0.67403$, $s = q = 0.93477$, $A = 1.695$, $c_0 = 11.654$; curve 3: $p = 0.25$, $a = 3.87000$, $b = 8.98298$, $g = -9.75116$, $e = -0.96333$, $d = -1.07228$, $f = 0.55034$, $s = q = 0.93477$, $A = 1.2$, $c_0 = 6$. The lowest curve in Fig. 3 corresponds to curve 1. The dashed lines in Fig. 4 show the segments of the characteristic $p(\theta)$ which do not correspond to the autooscillation cycle, but to the neighborhood of an unstable stationary state, and so cannot be calculated by the method proposed here. In each case considered here we have set T = 0.182 sec, $D = 10^{-5}$ cm^2/sec. The dimensions of the parameters used in the solution are as follows:

$$[u]=[c_0]=10^{-6}\ \mathrm{A/cm},$$

$$[\chi]=[A]=[a]=[e]=10^{-3}\ \mathrm{A/cm^2},$$

$$[b]=10^{-3}\ \mathrm{A/cm^2sec^s},\ [d]=10^{-3}\ \mathrm{A/cm^2sec^q},$$

$$[g]=[f]=10^{-3}\ \mathrm{A/cm^2sec^{1/2}};$$

the quantities s and q are dimensionless.

The results of the calculations with the constants used here agree with the experimental data of [3], and we have succeeded in calculating the maximum values of the characteristic $p(\theta)$, which cannot be done experimentally.

The computer program was written, and the calculations performed, by S. V. Dergacheva.

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