

# THE STABILITY OF THE STATIONARY STATES OF ELECTROLYTIC SYSTEMS

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Nonstationary period effects resulting from breakdown in the stability of the stationary state have recently been observed in nonpassivated electrolytic systems [1-5]. The circuit current,  $i$ , of such system passes successively through

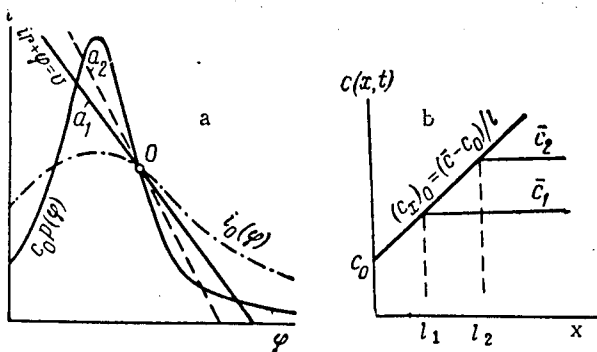


Fig. 1. a)  $\delta, l = \text{const}, \alpha \neq \text{const}$ ; b)  $\alpha, \delta = \text{const}, l \neq \text{const}$ .

by  $q(\varphi)$ .  $i = i_e + i_q$ , where  $i_q = qd\varphi/dt$ . The potential difference at the ends of the circuit,  $v$ , will be considered constant and  $ir + \varphi = v$ .

**1. Canonical Form of the Stationary State Equation.** The stationary state,  $0(\varphi_0, c_0, i_0)$  (Fig. 1) is determined by the following conditions [3]:  $i_q = 0$ ,  $i_0 = i_e = (v - \varphi_0)/r = G(\bar{c} - c_0)$ , where  $G = nFD/l > 0$ ;  $\varphi_0$  being a root of the equation  $i_0(\varphi)r + \varphi = v$ , in which  $i_0(\varphi) = G\bar{c}/[1 + G/p(\varphi)]$ ;  $c_0 = c(\varphi_0)$ , and  $c(\varphi) = (v - \varphi)/rp(\varphi)$ . Having fixed the stationary state  $0$ , we will now introduce a quantity  $f$  defined by

$$f = -\frac{i - i_0}{c - c_0} = -\frac{(v - \varphi)/r - (v - \varphi_0)/r}{c(\varphi) - c(\varphi_0)} = \frac{1}{r} \frac{\varphi - \varphi_0}{c(\varphi) - c(\varphi_0)}, \quad (1)$$

this will be designated as  $f(u)$ , where  $u = c - c_0$ , or as  $f(\varphi)$ . It can be readily shown that the stationary states of the system are marked out by the roots of the equation  $uf(u) = Gu$ . In the case of a unique stationary state,  $f(u) \neq G$  for

any  $u(\varphi)$  other than  $0(\varphi_0)$ . It follows from Eq. (1) that

$$= -(1 + c_0 p'_0 r).$$

$$f(\varphi_0) = \frac{1}{r} \frac{1}{c'(\varphi_0)} = -\frac{p(\varphi_0)}{1 + c_0 p'_0(\varphi_0) r} = \frac{p(\varphi_0)}{\alpha},$$

where  $\alpha$

$f(\varphi_0) > 0$  is a necessary and sufficient condition that the inequality  $f(\varphi) > G$  apply in the neighborhood  $\mathfrak{B} \setminus \varphi_0$  ( $\mathfrak{B} = \{\varphi : c'(\varphi) > 0\}$ ) of a unique stationary state. **Sufficiency.** Equations (1) can be used to show the existence of values  $\varphi_m$  and  $\varphi_n$  such that  $f(\varphi)$  is continuous over the interval  $(\varphi_m, \varphi_n)$  and  $f(\varphi) \rightarrow \infty$  when  $\varphi \rightarrow \varphi_m + 0$ , and  $\varphi \rightarrow \varphi_n - 0$ . The continuity of  $f(\varphi)$  over  $(\varphi_m, \varphi_n)$  implies that  $f(\varphi) > G$  when  $\varphi \in (\varphi_m, \varphi_n) \setminus \varphi_0$ . In the contrary case ( $f(\varphi) \leq G$ ) there would be at least one value of  $\varphi \in (\varphi_m, \varphi_n)$  differing from  $\varphi_0$  for which  $f(\varphi) = G$  and this would contradict the fact that  $\varphi_0$  is unique. The rest follows from the fact that  $\mathfrak{B} \subset (\varphi_m, \varphi_n)$ . **Necessity.** If  $f(\varphi) > G$  in the neighborhood of  $\varphi_0$ , it then follows that  $\lim_{\varphi \rightarrow \varphi_0} f(\varphi) \geq G > 0$ . If  $\varphi_0$  is not unique, there is a possibility that  $0 < f(\varphi_0) < G$ .

The function  $f = f(\varphi)$  is single-valued, according to Eq. (1). The function  $f = f(u)$  may not be single-valued, but as long as  $\varphi \in \mathfrak{B}$ ,  $f = f(\varphi)$  will correspond to the single-valued branch of  $f = f(u)$ ,  $u \in \{u: \varphi \in \mathfrak{B}\}$  [ $u'(\varphi) = c'(\varphi) > 0$  when  $\varphi \in \mathfrak{B}$ ]. This branch of  $f(u)$  will be used in Section 2.

**2. Distributed System with Diffusion Layer.** We will consider the case  $q=0$ , which may arise in physical models of the electrolytic system. The problem  $c_t = Dc_{xx}$  ( $0 < x < l$ ,  $t > 0$ ),  $c_x(0, t) = i/nFD$ ,  $c(l, t) = c$ ,  $c(x, 0) = c_0 + (c_x)_0 x + v(x)$ , where  $v(x) > 0$  is a small perturbation, can be reduced to the form  $u_t = Du_{xx}$ ,  $u_x(0, t) = -uf(u)/lG$ ,  $u(l, t) = 0$ ,  $u(x, 0) = v(x)$  by introducing the change in variable  $u(x, t) = c(x, t) - c_0 - (c_x)_0 x$  and taking account of Eq. (1). The associated source function  $Q(x, \xi, t)$  can be used to set up an integral equation in  $u = u(0, t)$ :

$$\begin{aligned} u &= \int_0^t v(\xi) Q(0, \xi, t) d\xi - D \int_0^t u_x Q(0, 0, t - \tau) d\tau = \\ &= \eta(t) + \frac{D}{l} \int_0^t u \frac{f(u)}{G} K(t - \tau) d\tau, \end{aligned} \quad (2)$$

$K(t) = \frac{1}{\sqrt{D\pi t}} \left[ 1 + 2 \sum_{k=1}^{\infty} (-1)^k \exp - \frac{(kl)^2}{Dt} \right]$ ,  $0 < \eta(t) < \max v(\xi)$ ,  $\eta(t \rightarrow \infty) \rightarrow 0$ . We will not consider the solution of the companion problem  $\tilde{u}_t = D\tilde{u}_{xx}$ ,  $\tilde{u}_x(0, t) = -h\tilde{u}(0, t)$ ,  $\tilde{u}(l, t) = 0$ ,  $\tilde{u}(x, 0) = v(x)$ . Separation of variables leads to characteristic values,  $\mu$ , determined as the roots of the equation  $h \tan lz = z$ ;  $\sqrt{\mu} = z$ . There will be not only real roots but purely imaginary roots as well when  $hl > 1$ ;  $z = \pm i\rho$ ,  $\mu = -\rho^2$ , these corresponding to unlimited increase of the function  $\tilde{u}(0, t)$ . Let  $hl = 1 + \sigma$ ,  $\sigma > 0$ , and  $v(x) = \varepsilon [\exp \rho(2l - x) - \exp \rho x] / [\exp 2\rho l - 1] \leq \varepsilon$ . Then  $\tilde{u}(x, t) = v(x) \exp D\rho^2 t$ ,  $\tilde{u}(0, t) = \varepsilon \exp D\rho^2 t$ . The function  $\tilde{u}(0, t)$  must also satisfy the equation

$$\tilde{u} = \eta(t) + (1 + \sigma) \frac{D}{l} \int_0^t \tilde{u} K(t - \tau) d\tau.$$

We will compare this relation and (2) as equations with kernels  $(1 + \sigma)K$  and  $(f/G)K$ . A representation of solutions through resolvents shows that  $f/G \geq 1 + \sigma > 1$  is a necessary and sufficient condition for  $u \geq \tilde{u}$ , that is to say that  $f(\varphi) > G$ , where  $\varphi \in \mathfrak{B} \setminus \varphi_0$ , assures instability of  $\varphi_0$  with passage of  $\varphi$  beyond the limits of  $\mathfrak{B}$ . The state  $\varphi_0$  is stable if  $f(\varphi) \leq G$  within a certain neighborhood of  $\varphi_0$ . From this and the property of  $f(\varphi)$  developed in the preceding Section it follows that a unique stationary state  $\varphi_0$  is stable when  $\alpha < 0$  and unstable when  $\alpha > 0$ . Both possibilities are open when  $\alpha = 0$ ; the problem is then to be solved by a similar comparison of  $f(\varphi)$  and  $G$ .

**3. Distributed System with Diffusion Layer and Lumped Parameters.** A. A system with a diffusion layer of depth  $l$  and non-null capacitance  $q$  concentrated at the point  $x=0$  (the treatment would be the same for a greater number of parameters, capacitance and inductance, for example) is described by the equation  $c_t(x, t) = Dc_{xx}(x, t)$  ( $0 < x < l$ ,  $t > 0$ ) with the conditions  $c_x(0, t) = c(0, t) p(\varphi)/nFD$ ,  $[q(\varphi)\varphi_t(t) + c(0, t) p(\varphi)] + \varphi(t) = v$ ,  $c(l, t) = c$ ,  $c(x, 0) = c_0 + (c_x)_0 x + v(x)$ . Let  $p(\varphi) = p_0 + p_0(\varphi - \varphi_0) + p_0(\varphi - \varphi_0)^2 + \dots$  and  $1/q(\varphi) = 1/q_0 + (1/q')(\varphi - \varphi_0) + \dots$ . In the new variables,  $u = c(x, t) - c_0 - (c_x)_0 x$ ,  $m = \varphi - \varphi_0$ ,  $\tau = t/\tau_0$ ,  $y = x/\sqrt{\tau_0 D}$ ,  $\lambda = l/\sqrt{\tau_0 D}$ , where  $\tau$  and  $y$  are dimensionless, the problem takes the form:

$$\begin{aligned} dm/d\tau &= \alpha m + \beta u + O_1(um)|_{y=0}, & \partial u/\partial y &= \gamma m + \delta u + O_2(um)|_{y=0}, \\ \partial u/\partial \tau &= \partial^2 u/\partial y^2 & (0 < y < \lambda, \tau > 0); \\ \alpha &= -(1 + c_0 \rho_0'), & \beta &= -r\rho_0, & \gamma &= \sqrt{r q_0 D} c_0 \rho_0' / nFD, \\ \delta &= \sqrt{r q_0 D} \rho_0 / nFD > 0. \end{aligned} \quad (3)$$

The linearized problem obtained by eliminating the members  $O_1$  and  $O_2$  will be designated as 3L).

It is readily shown that a relation of type  $\beta\gamma - \alpha\delta = \delta$  applies to the variables  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  in an electrolytic system or in any system similar to an electrolytic system. The expression for  $\delta$  will now be multiplied and divided by  $l(\bar{c} - c_0)$ : to obtain  $\delta = \{ p_0 c_0 [(\bar{c}/c_0) - 1] / [nFD(\bar{c} - c_0)/l] \} \sqrt{\tau_0 D}/l$ . Since  $p_0 c_0 = i_0 = nFD(\bar{c} - c_0)/l$ , it follows that  $\delta = (\chi - 1)/\lambda$  where  $\chi \triangleq \bar{c}/c_0$ .

B. We will investigate the trivial solution of (3L). We will make use of the integral representation (Eq. (2), first equality) with the substitutions  $t = \tau$ ,  $l = \lambda$ ,  $D = 1$ . To this and the first two equations of (3L) we will now apply Laplace transforms. After eliminating  $\mathfrak{L}\{m(\tau)\}$  and finding that  $\mathfrak{L}\{K(\tau)\} = \text{th}(\lambda \sqrt{s}) / \sqrt{s}$ , one obtains

$$a(s) = \mathfrak{L}\{u(0, \tau)\} = \frac{(s - \alpha)\zeta(s) - \gamma m(+0) \text{th}(\lambda \sqrt{s}) / \sqrt{s}}{\frac{\delta}{\sqrt{s}}(s + \omega) \left( \frac{\sqrt{s}}{\delta} \frac{s - \alpha}{s + \omega} + \text{th} \lambda \sqrt{s} \right)} = \frac{\tilde{b}(s)}{\tilde{\omega}(\sqrt{s}, \lambda)} = \frac{b(s)}{\omega(\sqrt{s}, \lambda)}$$

Here,  $\tilde{\omega}(z, \lambda) = \frac{1}{z} \left( \frac{z}{\delta} \frac{z^2 - \alpha}{z^2 + \omega} + \text{th} \lambda z \right)$ ,  $\omega(z, \lambda) = \frac{1}{z} [g(z) e^{\lambda z} - g(-z) e^{-\lambda z}]$ ,  $\omega = (\beta\gamma - \alpha\delta) / \delta$ ,  $g(z) = z^3 + \delta z^2 - \alpha z + \omega\delta$ ;  $\alpha, \delta, \omega$ , and  $\lambda$  are real and  $\zeta(s) = \mathfrak{L}\{\eta(t)\}$ . The function  $a(s)$  is a single-valued sum of transforms. Since at sufficiently large  $\text{Re } s > N \sqrt{s}$  ( $(s + \omega)\delta > |\text{th} \lambda \sqrt{s}|$ ), it follows that  $a(s)$  is regular when  $\text{Re } s > N$ ; and that  $a(s) \rightarrow 0$  is uniform in  $\arg s$  when  $|s| = (k\pi/\lambda)^2$  and  $k \rightarrow \infty$ . Then [6]  $u(0, \tau) = \dots + \text{res}_{s_k} a(s) \exp s_k \tau + \dots$ , where residues are taken relative to the  $s_k$  which are zeros of  $\omega(\sqrt{s}, \lambda)$ . The function  $u(0, \tau)$  is bounded when  $\text{Re } s_k \leq 0$ , i.e., when  $z_k = \sqrt{s_k} \in \mathfrak{P} = \{z: |\arg z| < \pi/4\}$ . Thus a necessary and sufficient condition for stability

of the solutions  $u(y, \tau) \equiv 0$  and  $m(\tau) \equiv 0$  of the system (3L) is that the region  $\mathfrak{P} = \{z: |\arg z| < \pi/4\}$  contain none of the zeros of  $w(z, \lambda)$ . Replacement of  $m(\tau)$  in system (3) by a vector function and alteration of the condition on  $\underline{u}$  at the  $y=0$  boundary would affect the order of the polynomial  $g(z)$ ;  $-g(-z)$  is identical with the characteristic polynomial introduced by A. N. Tikhonov in his treatment of the case  $\lambda = \infty$  [7].

C. Not only  $z = z_0$ , but also  $-z_0$ ,  $\bar{z}_0$ , and  $-\bar{z}_0$  are zeros of the function  $w(z, \lambda)$ . The equation  $\lambda(z, \lambda) = 0$  gives the implicit form of the relation  $z = z(\lambda)$ ,  $dz/d\lambda$  showing discontinuities at  $\lambda$  values corresponding to multiple zeros of  $w(z, \lambda)$ . Let  $z_g$  be one of the zeros of  $g(z)$  and  $\text{Re } z_g > 0$  (it is clear that the solution  $u \equiv 0$  is stable if there are no such zeros). We will designate by  $z(\lambda)$  [or  $z(\lambda, \alpha)$ ] the zero of the function  $w(z, \lambda)$  corresponding to  $z_g$ :  $z(\lambda) \rightarrow z_g$  when  $\lambda \rightarrow \infty$ . The function  $w(z, \lambda)$  has not only the zeros  $z(\lambda)$  but also certain purely imaginary zeros as well when  $0 < \lambda < \infty$  but these have no effect on the stability of the solution  $u = 0$ . At small values of  $\lambda$ ,  $\lambda z(\lambda) \sim \sqrt{(\alpha - \delta\omega\lambda) / (1 + \delta\lambda)}$ ;

$$\left( \frac{dz}{d\lambda} \right)_{z=\sqrt{\alpha}} = -\delta(\alpha + \omega) / 2\sqrt{\alpha}; \text{ and } z(\lambda) \rightarrow \sqrt{\alpha} \text{ when } \lambda \rightarrow 0. \text{ Thus when } \alpha > 0 \text{ and the value of } \lambda \text{ is sufficiently small, } \lambda z(\lambda) \in \mathfrak{P}, \text{ and the solution } u \equiv 0 \text{ is unstable.}$$

The position of the  $z(\lambda)$  curve in the  $z$  plane depends on the parameters  $\alpha, \delta, \omega$ . Furthermore (3) and the relation  $\beta\gamma - \alpha\delta = \delta$  show that  $\omega = 1$  when  $\delta > 0$ . We will consider the change in  $z(\lambda)$  as  $\lambda$  diminishes from  $\infty$  to 0 at fixed  $\alpha$ ,  $z = z(\lambda, \alpha)$  (Fig. 2, where  $\delta = 1/30$ ,  $\omega = 1$ , and the trajectory of the zeros of  $w(z, \lambda)$  is shown by the full curves). The segments of the  $z(\lambda, \alpha)$  curves falling in the  $\mathfrak{P}$  region (hatched) correspond to those values of  $\lambda$  for which the solution  $u \equiv 0$  is unstable. 1)  $\alpha = 0$ ; as  $\lambda$  diminishes from  $\infty$  to 0, the curve  $z(\lambda, 0)$  at first asymptotically spirals around the point  $z(\infty, 0)$ , then meets the axis of imaginaries at  $\lambda_m = 2.90$  and runs along it to  $z(0, 0) = 0$  ( $\lambda_0 = \alpha/\omega\delta = 0$ ). When  $\alpha \leq 0$ ,  $u \equiv 0$  is asymptotically stable for any  $0 < \lambda \leq \infty$ . 2)  $\alpha = 0.1$ ; the point  $z(\infty, 0.1)$  and part of the signal ( $7.3 < \lambda < \infty$ ) are located in  $\mathfrak{P}$ . At  $\lambda = 7.3$   $z(\lambda)$  passes out of  $\mathfrak{P}$ , meets the axis of imaginaries at  $\lambda_m = 3.66$ , moves along it to  $z = 0$  ( $\lambda_0 = \alpha/\omega\delta = 3.00$ ) and, entering  $\mathfrak{P}$ , once more, moves along the axis of reals to  $z(0, \alpha) = \sqrt{\alpha} = 0.316$ . Thus for  $\alpha = 0.1$ ,  $u \equiv 0$  is unstable for  $0 < \lambda < 3.0$  and  $7.3 < \lambda < \infty$ , and asymptotically stable for  $3.0 < \lambda < 7.3$ . The number of successive intervals of stability and instability in the region  $0 < \lambda < \infty$  increases indefinitely as  $\alpha$  varies and the point  $z(\infty, \alpha)$  approaches the boundary of  $\mathfrak{P}$  (the line  $\text{Im } z = \text{Re } z$ ). 3)  $\alpha = 0.2$ ; the entire segment of the curve  $z(\lambda, 0.2)$  from the asymptotic point  $z(\infty, 0.2)$  to  $z(0, 0.2) = \sqrt{0.2} = 0.447$  is located in  $\mathfrak{P}$ ;  $u \equiv 0$  is unstable for any  $0 \leq \lambda \leq \infty$  and remains so with further increase in  $\alpha$ . Thus there is an intermediate region of values of the parameters  $\alpha$  and  $\delta$  in which stability and instability in a fixed stationary state  $u \equiv 0$  alternate as the depth of the pre-electrode layer,  $l$ , is reduced.

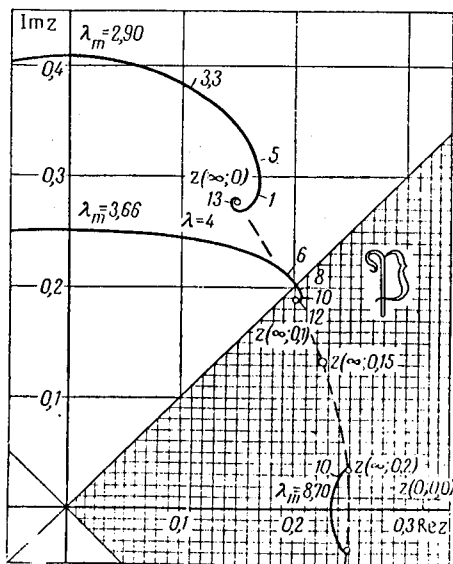


Fig. 2.  $w(z, \lambda) = (1/z) [g(z) e^{\lambda z} - g(-z) e^{-\lambda z}] = 0$ ;  $g(z) = z^3 + \delta z^2 - \alpha z + \omega\delta$ ;  $\omega = 1$ ;  $\delta = 1/30$ ;  $\alpha = 0, 1/10, 2/10$ .

There are certain differences in systems without capacitance (Section 2) and systems with capacitance (Section 3): a) In the first, the stationary state can be stabilized by reducing  $l$  ( $u \equiv 0$  is stable if  $f(0) < G = nFD/l$ ; b) with complex values  $z(\infty, \alpha) \in \mathfrak{P}$  and sufficiently large  $l$  in a system with capacitance (Section 3),  $u$  begins to vibrate and passes out of the stationary state.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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