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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE STABILITY OF STATIONARY STATES OF ELECTROLYTIC SYSTEMS

(Presented by Academician A. N. Frumkin, 27 X 1962)

Nonstationary phenomena, in particular periodic phenomena, associated with the loss of stability of a stationary state have recently been discovered in electrolytic systems free from passivation ([1–5]). In the circuit of such a system the current i passes successively through the electrolyte (active resistance r) and the boundary (S) electrolyte–electrode, at which a substance A is discharged; in the simplest case this substance practically does not participate in the transfer of current through the electrolyte and is delivered to the electrode by diffusion (coefficient D) occurring in a layer of thickness l; $c(x,t)$ is the concentration of A at a distance x from an electrode of unit area at time t ($0 < x < l,\ t > 0$); $c(l,t) = \bar{c} = \text{const}$; $c_x(0,t) = i_e/nFD$, nF is the expenditure of electricity per 1 mole of A; the discharge current i_e depends on the jump φ of the potential at the boundary S: $i_e(\varphi) = cp(\varphi)$; $p(\varphi) > 0$ is a single-valued differentiable function, $c = c(0,t)$. The double electric layer at the boundary S has capacitance $q(\varphi)$. $i = i_e + i_q$, where $i_q = q\,d\varphi/dt$. The voltage at the ends of the circuit $v = \text{const}$; $ir + \varphi = v$.

1. Canonical form of the equation of stationary states. The stationary state $O(\varphi_0, c_0, i_0)$ (Fig. 1) is determined as follows ([3]): $i_q = 0$, $i_0 = i_e = (v - \varphi_0)/r = G(\bar{c} - c_0)$, where $G = nFD/l > 0$; φ_0 is a root of the equation $i_0(\varphi)r + \varphi = v$, where $i_0(\varphi) = G\bar{c}/[1 + G/p(\varphi)]$; $c_0 = c(\varphi_0)$, where $c(\varphi) = (v - \varphi)/rp(\varphi)$. Fixing the stationary state 0, introduce the quantity f

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

which will subsequently be denoted by $f(u)$, where $u = c - c_0$, or $f(\varphi)$. It is not difficult to verify that all stationary states of the system coincide with the roots of the equation $uf(u) = Gu$. Therefore, if the stationary state is unique, then $f(u) \neq G$ for any u (φ) not equal to 0 (φ_0). From (1)

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

where $\alpha = -(1 + c_0 p_0' r)$.

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The condition $f(\varphi_0) > 0$ is necessary and sufficient in order that, in the neighborhood $\mathfrak{B}$ of φ_0 ($\mathfrak{B} = \{\varphi : \ c'(\varphi) > 0\}$), the unique stationary state φ_0 satisfy $f(\varphi) > G$. **Sufficiency.** On the basis of (1) the existence is established of such φ_m and φ_n for which $f(\varphi)$ is continuous on (φ_m, φ_n) and $f(\varphi) \to +\infty$ as $\varphi \to \varphi_m + 0$, $\varphi \to \varphi_n - 0$; from the continuity of $f(\varphi)$ on (φ_m, φ_n) it follows that $f(\varphi) > G$ for $\varphi \in \{(\varphi_m, \varphi_n) \setminus \varphi_0\}$: otherwise ($f(\varphi) \leqslant G$) there would be at least one value $\varphi \in (\varphi_m, \varphi_n)$ not equal to φ_0, for which $f(\varphi) = G$, which contradicts the uniqueness of φ_0; the rest follows from $\mathfrak{B} \subset (\varphi_m, \varphi_n)$. **Necessity.** If $f(\varphi) > G$ in a neighborhood of φ_0, then $\lim f(\varphi \to \varphi_0) \geqslant G > 0$. If φ_0 is not unique, then it is possible that $0 < f(\varphi_0) < G$. According to (1), $f = f(\varphi)$ is single-valued; $f = f(u)$ may be multivalued, but as long as $\varphi \in \mathfrak{B}$, the functions

$f = f(\varphi)$ there corresponds a single-valued branch of the function $f = f(u)$, $u \in \{u : \varphi \in \mathfrak{B}\}$ ($u'(\varphi) = c'(\varphi) > 0$ for $\varphi \in \mathfrak{B}$). This branch $f(u)$ is used in Sec. 2.

2. Distributed system with a diffusion layer.

Consider the case $q = 0$, which is feasible in physical models of electrolytic systems. The problem $c_t = Dc_{xx}$ $(0 < x < l,\ t > 0)$; $c_x(0,t) = i/nFD$, $c(l,t) = \bar{c}$, $c(x,0) = c_0 + (c_x)_0 x + \nu(x)$, where $\nu(x) > 0$ is a small perturbation, by the substitution $u(x,t) = c(x,t) - c_0 - (c_x)_0 x$ and taking (1) into account, is reduced to the form $u_t = Du_{xx}$, $u_x(0,t) = -uf(u)/lG$, $u(l,t) = 0$, $u(x,0) = \nu(x)$. Using the corresponding source function $Q(x,\xi,t)$, we form an integral equation with respect to $u = u(0,t)$:

$$u = \int_0^l \nu(\xi) Q(0,\xi,t)\, d\xi - D \int_0^t u_x Q(0,0,t-\tau)\, d\tau =$$

$$= \eta(t) + \frac{D}{l} \int_0^t u \,\frac{f(u)}{G}\, K(t-\tau)\, d\tau, \tag{2}$$

$$K(t) = \frac{1}{\sqrt{D\pi t}} \left[1 + 2 \sum_{k=1}^{\infty} (-1)^k \exp\left(-\frac{(kl)^2}{Dt} \right) \right], \quad 0 < \eta(t) < \max \nu(\xi), \quad \eta(t \to \infty) \to 0.$$

Consider the solution of the auxiliary problem $\tilde{u}_t = D\tilde{u}_{xx}$, $\tilde{u}_x(0,t) = -h\tilde{u}(0,t)$, $\tilde{u}(l,t) = 0$, $\tilde{u}(x,0) = \nu(x)$. The eigenvalues μ to which the separation-of-variables method leads here are determined by the roots of the equation $h \tan lz = z$; $\sqrt{\mu} = z$. For $hl > 1$, along with real roots, it has purely imaginary ones: $z = \pm i\rho$, $\mu = -\rho^2$, which corresponds to an unbounded increase of $\tilde{u}(0,t)$. Let $hl = 1 + \sigma$, $\sigma > 0$, and $\nu(x) = \varepsilon[\exp \rho(2l - x) - \exp \rho x]/[\exp 2\rho l - 1] \leq \varepsilon$. Then $\tilde{u}(x,t) = \nu(x) \exp D\rho^2 t$, $\tilde{u}(0,t) = \varepsilon \exp D\rho^2 t$. At the same time, $\tilde{u}(0,t)$ satisfies the equation

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

Fig. 1. a–δ, $l = \text{const}$, $\alpha \neq \text{const}$; σ–α, $\delta = \text{const}$, $l \neq \text{const}$

Compare it and (2) as equations with kernels $(1+\sigma)K$ and $(f/G)K$. From the representation of their solutions by resolvents it follows that $f/G \geq 1+\sigma > 1$ is necessary and sufficient for $u \geq \tilde{u}$, i.e., the fulfillment of $f(\varphi) > G$, where $\varphi \in \mathfrak{B} \setminus \varphi_0$, guarantees not only the instability of φ_0, but also the departure of φ beyond the limits of $\mathfrak{B}$. If, however, $f(\varphi) \leq G$ in some neighborhood of φ_0, then the state φ_0 is stable. Hence, also from the property of $f(\varphi)$ found in the preceding item, it follows: the unique stationary state φ_0 is stable for $\alpha < 0$ and unstable for $\alpha > 0$. For $\alpha = 0$, either is possible; the question is resolved analogously, by comparing $f(\varphi)$ and G.

3. Distributed system with a diffusion layer and lumped parameters.

A. A system with a diffusion layer of thickness l and a capacitance $q \neq 0$, lumped at the point $x = 0$ (the conclusions do not change for a larger number of parameters, for example capacitance and inductance),

is described by the equation $c_t(x,t) = Dc_{xx}(x,t)$ $(0 < x < l,\ t > 0)$ with the conditions $c_x(0,t) = c(0,t)p(\varphi)/nFD$, $r[q(\varphi)\varphi_t(t) + c(0,t)p(\varphi)] + \varphi(t) = v$, $c(l,t) = \bar{c}$, $c(x,0) = c_0 + (c_x)_0 x + v(x)$. Let $p(\varphi) = p_0 + p_0'(\varphi - \varphi_0) + p_0''(\varphi-\varphi_0)^2 + \cdots$ and $1/q(\varphi) = 1/q_0 + (1/q)_0'(\varphi - \varphi_0) + \cdots$. In the new variables $u = c(x,t) - c_0 - (c_x)_0 x$, $m = \varphi - \varphi_0$, $\tau = t/rq_0$, $y = x/\sqrt{rq_0 D}$, $\lambda = l/\sqrt{rq_0 D}$, where τ, y are dimensionless, the problem takes the form:

$$\begin{gathered} dm/d\tau = \alpha m + \beta u + O_1(um)\big|_{y=0}, \qquad \partial u/\partial y = \gamma m + \delta u + O_2(um)\big|_{y=0}, \\ \partial u/\partial\tau = \partial^2 u/\partial y^2 \qquad (0 < y < \lambda,\ \tau > 0); \end{gathered} \tag{3}$$

$$\alpha = -(1 + c_0 p_0' r), \qquad \beta = -rp_0, \qquad \gamma = \sqrt{rq_0 D}\, c_0 p_0'/nFD,$$

$$\delta = \sqrt{rq_0 D}\, p_0/nFD > 0.$$

We shall denote the linearized problem (without the terms O_1 and O_2) by (3L).

It is not difficult to establish the following fact: *in the case of an electrolytic (or similar) system the coefficients $\alpha, \beta, \gamma, \delta$ are connected by the relation*: $\beta\gamma - \alpha\delta = \delta$. Transform the expression for δ, multiplying and dividing it by $l(\bar{c} - c_0)$:

$$\delta = \{p_0 c_0[(\bar{c}/c_0) - 1]/[nFD(\bar{c} - c_0)/l]\}\sqrt{rq_0 D}/l.$$

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Since $p_0 c_0 = i_0 = nFD(\bar{c} - c_0)/l$, it follows that $\delta = (\chi - 1)/\lambda$, where $\chi = \bar{c}/c_0$.

B. Let us investigate the stability of the trivial solution of (3L). We use the integral representation ((2), first equality), in which one should put $t = \tau,\ l = \lambda,\ D = 1$. We apply to it and to the first two equations of (3L) the Laplace transform. Eliminating $\mathcal{L}\{m(\tau)\}$ and finding $\mathcal{L}\{K(\tau)\} = \operatorname{th}(\lambda\sqrt{s})/\sqrt{s}$, we obtain

$$a(s) = \mathcal{L}\{u(0,\tau)\} = \frac{(s-\alpha)\xi(s) - \gamma m(+0)\operatorname{th}(\lambda\sqrt{s})/\sqrt{s}}{\dfrac{\delta}{\sqrt{s}}(s+\omega)\left(\dfrac{\sqrt{s}}{\delta}\dfrac{s-\alpha}{s+\omega} + \operatorname{th}\lambda\sqrt{s}\right)} =$$

$$= \frac{\tilde{b}(s)}{\tilde{w}(\sqrt{s},\lambda)} = \frac{b(s)}{w(\sqrt{s},\lambda)}.$$

where

$$\tilde{w}(z,\lambda) = \frac{1}{z}\left(\frac{z}{\delta}\frac{z^2-\alpha}{z^2+\omega} + \operatorname{th}\lambda z\right), \qquad w(z,\lambda) = \frac{1}{z}\,[g(z)e^{\lambda z} - g(-z)e^{-\lambda z}],$$

$\omega = (\beta\gamma - \alpha\delta)/\delta, \qquad g(z) = z^3 + \delta z^2 - \alpha z + \omega\delta; \qquad \alpha, \delta, \omega, \lambda$ are real, $\qquad \xi(s) = \mathcal{L}\{\eta(t)\}$.

$a(s)$ is single-valued and is a sum of transforms; for sufficiently large $\operatorname{Re} s > N$,

$$\left|\sqrt{s}(s-\alpha)/(s+\omega)\delta\right| > |\operatorname{th}\lambda\sqrt{s}|,$$

therefore $a(s)$ is regular for $\operatorname{Re} s > N$; $a(s) \to 0$ uniformly with respect to $\arg s$ for $|s| = (k\pi/\lambda)^2$ and $k \to \infty$. Then [6]

$$u(0,\tau) = \dots + \operatorname{res}_{s_k} a(s)\exp s_k\tau + \cdots,$$

where the residues are taken at s_k, which are zeros of $w(\sqrt{s},\lambda)$. $u(0,\tau)$ is bounded if $\operatorname{Re} s_k \le 0$, i.e. $z_k = \sqrt{s_k} \in \mathfrak{P} = \{z :\ |\arg z| < \pi/4\}$. Thus, *for the stability of the solution $u(y,\tau) \equiv 0,\ m(\tau) \equiv 0$ of the system (3L), it is necessary and sufficient that the domain $\mathfrak{P} = \{z :\ |\arg z| < \pi/4\}$ contain no zeros of* $w(z,\lambda)$. Replacing $m(\tau)$ in system (3) by a vector function, and also changing the type of condition for u at the boundary $y = 0$, is reflected in the degree of the polynomial $g(z)$; $-g(-z)$ coincides with the characteristic polynomial introduced by A. N. Tikhonov when considering the case $\lambda = \infty$ [7].

C. Together with a zero $z = z_0$, zeros of the function $w(z,\lambda)$ are also $-z_0,\ \bar{z}_0,\ -\bar{z}_0$. The equation $w(z,\lambda) = 0$ in implicit form specifies the dependence $z = z(\lambda)$, and $dz/d\lambda$ has a discontinuity at the λ' s corresponding to multiple zeros of $w(z,\lambda)$. Let z_g be one of the zeros of $g(z)$, $\operatorname{Re} z_g > 0$ (if there are no such zeros, then the solution $u \equiv 0$ is certainly stable). Denote by $z(\lambda)$ (or $z(\lambda,\alpha)$) the zero of the function $w(z,\lambda)$ corresponding to z_g: $z(\lambda) \to z_g$ as $\lambda \to \infty$. For $0 < \lambda < \infty$, besides the zeros $z(\lambda)$, $w(z,\lambda)$ has purely imaginary zeros, which do not affect the stability of the solution $u \equiv 0$. For

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Fig. 2.

Figure 1: Fig. 2.

for small λ

$$z(\lambda) \sim \sqrt{(\alpha - \delta\omega\lambda)/(1 + \delta\lambda)}; \qquad (dz/d\lambda)_{z=\sqrt{\alpha}} = -\delta(\alpha + \omega)/2\sqrt{\alpha};$$

$z(\lambda) \to \sqrt{\alpha}$ as $\lambda \to 0$. Thus, for $\alpha > 0$ and sufficiently small λ, $z(\lambda) \in \mathfrak{P}$, and the solution $u \equiv 0$ is unstable. The position of the curve $z(\lambda)$ in the z-plane depends on the parameters α, δ, and ω. Further, let $\delta > 0$, $\omega = 1$, in accordance with (3) and the relation $\beta\gamma - \alpha\delta = \delta$. For various fixed α, consider the change of $z(\lambda)$ as λ decreases from ∞ to 0, $z = z(\lambda, \alpha)$ (Fig. 2, $\delta = 1/30$, $\omega = 1$; the trajectories of the zeros of $w(z, \lambda)$ are shown by heavy lines). Segments of the curve $z(\lambda, \alpha)$ that fall into the region $\mathfrak{P}$ (hatched) correspond to those values of λ for which $u \equiv 0$ is unstable. 1) $\alpha = 0$; as λ decreases from ∞ to 0, the curve $z(\lambda, 0)$ first unwinds asymptotically about the point $z(\infty, 0)$, then ($\lambda_m = 2.90$) reaches the imaginary axis and descends along it to $z(0, 0) = 0$ ($\lambda_0 = \alpha/\omega\delta = 0$); for $\alpha < 0$, $u \equiv 0$ is asymptotically stable for any $0 < \lambda < \infty$. 2) $\alpha = 0.1$; the point $z(\infty; 0.1)$ and part of the spiral ($7.3 < \lambda < \infty$) are located in $\mathfrak{P}$; at $\lambda = 7.3$, $z(\lambda)$ leaves $\mathfrak{P}$, reaches the imaginary axis ($\lambda_m = 3.66$), descends along it to $z = 0$ ($\lambda_0 = \alpha/\omega\delta = 3.00$) and, having entered $\mathfrak{P}$ again, along the real axis reaches $z(0; \alpha) = \sqrt{\alpha} = 0.316$; thus, for $\alpha = 0.1$, $u \equiv 0$ is unstable for $0 < \lambda < 3.0$ and $7.3 < \lambda < \infty$, while $u \equiv 0$ is asymptotically stable for $3.0 < \lambda < 7.3$. As the point $z(\infty, \alpha)$ approaches, with changing α, the boundary of $\mathfrak{P}$ (the line $\operatorname{Im} z = \operatorname{Re} z$), the number of alternating intervals of stability and instability in the region $0 < \lambda < \infty$ increases without bound. 3) $\alpha = 0.2$; the entire 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 $0 \leqslant \lambda < \infty$ and remains so under a further increase of α. Thus, there exists an intermediate region of values of the parameters α and δ in which, as the thickness of the near-electrode layer l decreases, the stability of the fixed stationary state $u \equiv 0$ alternates with its instability.

Fig. 2.

$$w(z, \lambda) = \frac{1}{z}\left[g(z)e^{\lambda z} - g(-z)e^{-\lambda z}\right] = 0;$$

$$g(z) = z^3 + \delta z^2 - \alpha z + \omega\delta; \quad \omega = 1;$$

$$\delta = 1/30; \quad \alpha = 0,\ 1/10,\ 2/10$$

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Some differences between systems without capacitance (Sec. 2) and with capacitance (Sec. 3): a) in the former, the stationary state can be stabilized by decreasing l ($u \equiv 0$ is stable if $f(0) < G = nFD/l$); b) for complex $z(\infty, \alpha) \in \mathfrak{P}$ and sufficiently large l, in the system with capacitance (Sec. 3), u leaves the stationary state by oscillating.

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1. A. Ya. Gokhshtein, A. N. Frumkin, DAN, **132**, 388 (1960).
2. A. N. Frumkin, O. A. Petrii, N. V. Nikolaeva-Fedorovich, DAN, **136**, 1158 (1961).
3. A. Ya. Gokhshtein, DAN, **140**, 1114 (1961).
4. A. Ya. Gokhshtein, A. N. Frumkin, DAN, **144**, 821 (1962).
5. A. Ya. Gokhshtein, DAN, **148**, 148 (1963).
6. M. A. Lavrent' ev, B. V. Shabat, *Methods of the Theory of Functions of a Complex Variable*, Moscow, 1958.
7. A. N. Tikhonov, *Matem. sborn.*, **26**, 35 (1950).

Note: Figure translations are in progress. See original paper for figures.

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