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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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On the Frequency of Self-Oscillations in Electrolytic Systems

(Presented by Academician A. N. Frumkin, 20 VI 1962)

Periodic self-oscillations arising in electrolytic systems, free from passivation, with a descending characteristic are considered below ([1–4]). The properties of self-oscillations following from the theory ([3,4]) have been confirmed experimentally. On the basis of these properties, the present work investigates the dependence of the frequency of self-oscillations on the parameters of the system (l (the thickness of the near-electrode layer with concentration c of the discharging substance in the volume of the electrolyte, the voltage v applied to the ends of the electric circuit into which the electrolytic system under study is connected in series with a resistance R). We shall call the oscillation region the set of those values of the parameters at which self-oscillations occur. If all parameters except one are fixed, then the oscillation region will be denoted Δl, Δv, etc.

Fig. 1

Let us make several remarks that will make it possible, without affecting the substance of the phenomenon, to simplify the derivation of quantitative relations. Consider the influence of the capacitance of the double electric layer on the period of oscillations. It manifests itself in two ways. First, the jumps of the system, occurring during self-oscillations, from a state with a low consumption to a state with a high consumption of the discharging substance and back are not instantaneous, but occur over finite time intervals required for recharging the double layer. They are approximately equal to or even less than ([4]) the time constant of the system. In calculating the period T, the capacitance C of the double layer may be neglected only when the time constant $\tau = RC$ of the system is much smaller than T. In practice, usually T/τ is of the order of 100–10. Second, the period is determined by the change (ΔQ) in the quantity Q of substance in the near-electrode layer and by the rate at which this change takes place in both stages of the oscillation. A certain fraction δQ of the quantity ΔQ participates in recharging the double layer, and its capacitance may be neglected only if δQ is small in comparison with ΔQ. Fulfillment of this condition is not

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difficult to verify, using the known amplitude of the potential oscillations and the mean value of the double-layer capacitance; usually δQ amounts to $5 \div 20\%$ of ΔQ. Below, both conditions are assumed to be fulfilled.

Next we shall assume that delivery of the discharging substance to the electrode occurs by diffusion. This is realized when an excess of supporting electrolyte does not smooth the descending segment on the characteristic of the system. In the absence of supporting electrolyte, the relations obtained below are valid with a certain approximation. In accordance with the scheme of self-oscillations ([3]), we shall call the duration of an oscillation stage the time during which the near-electrode concentration $c = c(0,t)$ changes from one of the extreme values (for example, $c_{\max}$) to the other ($c_{\min}$). Let p be the ratio of the duration of the high-current stage (c decreases)

over the entire period T. Instead of the current density $i(t)$, we shall consider the corresponding concentration gradient $q(t)$ of the discharging substance,

$$q(t) = \partial c/\partial x(0,t) = i(t)/nFD \tag{1}$$

(nF is the amount of electricity per mole, D is the diffusion coefficient). The experimental values $c_{\min}, c_{\max}, q_{\min}, q_{\max}$, as well as the values q_{mi} and q_{ma}, preceding in time the transitions from one stage of the oscillation to another (Fig. 1a), do not depend on the frequency of the oscillations and are determined only by the characteristic of the system and by the parameters $v, r = RS$ (S is the electrode area) ([3]). The values $q_{\min}, q_{\max}, q_{mi}$, and q_{ma} can be determined directly from the experimental oscillogram. Whereas the points corresponding to $q_{\min}, q_{\max}$, and q_{mi} are clearly expressed on the oscillograms $q(t)$, the point corresponding to q_{ma} is sometimes difficult to identify because of the high steepness of the current drop.

We shall indicate one method for determining q_{ma}. According to ([3], [4]), the conditions

$$\begin{aligned} &\text{a)} \quad q_{ma} > (\bar{c} - c_{\min})/l, \\ &\text{b)} \quad q_{mi} < (\bar{c} - c_{\max})/l. \end{aligned} \tag{2}$$

(the predominance of the rate of consumption in the first stage and the rate of supply in the second) are necessary and sufficient for a self-oscillatory process to occur in the system. $c_{\min}$ and q_{ma} depend on v ([3]). The value $v = v_\mu$, at which (2a) is violated, turning into an equality, serves as the left boundary of the oscillation region Δv. Thus $q_{ma}(v_\mu)$ coincides with the value of the gradient $(\bar{c} - c_{\min})/l$ for the stationary distribution. Therefore the value of the stationary current, which is easily observed experimentally near the left boundary of Δv, gives, with the aid of (1), the value $q_{ma}(v_\mu)$. It is now easy to determine $q_{ma}(v)$ for any v lying within Δv; indeed, by decreasing l one can always achieve a shift of the left boundary of Δv to a prescribed v ([4]). Knowledge of q_{mi} and q_{ma}

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Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

makes it possible to distinguish on the current-time oscillogram both stages of the oscillation and to determine p.

Fig. 2

Let, for the given system, the values $q_{\min}, q_{\max}, q_{mi}, q_{ma}, \Delta c = c_{\max} - c_{\min}$, and p be known. Then the period T of self-oscillations in the given system is bounded between the periods $T_{\max}$ and $T_{\min}$ that would be possessed, at the same Δc and p, by rectangular oscillations with amplitudes $\Delta q_{\min} = q_{ma} - q_{mi}$ and $\Delta q_{\max} = q_{\max} - q_{\min}$ (Fig. 1b, c). For the frequency, $1/T_{\max} = \nu_{\min} < \tilde{\nu} < \nu_{\max} = 1/T_{\min}$. We have arrived at the problem: for rectangular oscillations, given Δq and Δc, determine $\nu(p)$. Having found $\nu(p)$, and then $l(p)$, we shall establish, in parametric form, the relation between ν and l.

The distribution $c(x,t)$ in the diffusion layer during self-oscillations can be represented as the sum of the stationary (linear) distribution

with a gradient q_{0m} equal to the mean over a period of $q(t)$, and the variable component of the concentration $u(x,t)$,

$$u(x,t) = c(x,t) - \bar{c} + (l - x)q_{0m}, \tag{3}$$

$\Delta u = \Delta c$.

Omitting the detailed derivation of $\nu(p)$, we give its scheme. First one finds the solution $u = f(x, t, \Delta q, p, \nu)$ of the diffusion equation with the conditions

$$\partial u/\partial x(0,t) = q(t) - q_{0m}, \tag{A}$$

$$u(l,t) = 0. \tag{B}$$

Then one determines $u_{\max} = \max u(0,t) \equiv f(0, t_{\max}, \Delta q, p, \nu)$, $u_{\min} = \min u(0,t) \equiv f(0, t_{\min}, \Delta q, p, \nu)$

Fig. 3

Fig. 4

and

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Fig. 4

Figure 4: Fig. 4

$$\Delta c = \Delta u = f(0, t_{\max}, \Delta q, p, \nu) - f(0, t_{\min}, \Delta q, p, \nu).$$

Expressing ν from this, we obtain the desired result $\nu(p) = W(p, \Delta q, \Delta c)$. The amplitude of the oscillations $u(x,t)$ rapidly decreases with distance from the electrode surface ($x = 0$).

In Fig. 2, for the case $p = 1/4,\ l = \infty,\ \bar{c} = \infty,\ \bar{c}/l = q_{0m}$, there are shown the distributions $c(\lambda, t_{\min}^{\max})/\Delta c$, the stationary distribution (the inclined straight line), and the difference between them $u(\lambda, t_{\min}^{\max})/\Delta u$, which does not depend on q_{0m} and is determined only by the value of p; already at $\lambda > 2$, $u(\lambda, t)/\Delta u \simeq 0$, i.e., condition (B) is practically satisfied for finite l (the scale l is calculated for $D = 10^{-5}$ cm^2/sec, $\nu = 10$ sec^{-1}). This case, when the influence of the right-hand boundary ($x = l$) may be neglected, is especially important for practice. It occurs when

$$\lambda_l = \sqrt{\pi\nu/D}\, l > 2, \qquad 1/4 \le p \le 3/4. \tag{4}$$

In the right-hand side of (3), l retains its meaning. The solution according to the scheme indicated above, under condition (4), leads to the formula

$$\nu(p) = 4\frac{D}{\pi}\left[\frac{\varphi(p)}{\pi}\frac{\Delta q}{\Delta c}\right]^2, \qquad \text{where} \quad \varphi(p) = \sum_{n=1}^{\infty}\frac{\sin^2(\pi n p)}{n^{3/2}}. \tag{5}$$

(Fig. 3a); $\varphi(0) = \varphi(1) = 0,\ \max\varphi(p) = \varphi(1/2) = 1.688254$. If condition (4) is violated, then (5) nevertheless continues to convey qualitatively the dependence of ν on p: $\nu(0) = \nu(1) = 0$; this coincides with the true values of ν. Using (5) and the inequality for the frequencies, we obtain for the frequency of self-oscillations of arbitrary form (Fig. 1a)

$$4\frac{D}{\pi}\left[\frac{\varphi(p)}{\pi}\frac{\Delta q_{\min}}{\Delta c}\right]^2 < \tilde{\nu}(p) < 4\frac{D}{\pi}\left[\frac{\varphi(p)}{\pi}\frac{\Delta q_{\max}}{\Delta c}\right]^2. \tag{6}$$

Let us turn to the calculation of $l(p)$. Introduce the index m: $\alpha_m = (\alpha_{\max} + \alpha_{\min})/2$, where $\alpha = c, u, q$. From (3), at $x = 0$, $u_m = c_m - \bar{c} + l q_{0m}$. For the same condi-

for which (5) was derived, one can obtain

$$u_m = -\frac{1}{2}\frac{\psi(p)}{\varphi(p)}\Delta c, \quad \text{where } \psi(p) = \frac{1}{2}\sum_{n=1}^{\infty}\frac{\sin(2\pi n p)}{n^{3/2}} \tag{7}$$

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(Fig. 3b). For rectangular oscillations $q_{0m} = q_m + (2p-1)\Delta q/2$. Taking into account the expressions for u_m and q_{0m}, we find

$$l(p) = \left[\bar{c} - c_m - \frac{\psi(p)}{\varphi(p)}\frac{\Delta c}{2}\right] \Big/ \left[q_m + (2p-1)\frac{\Delta q}{2}\right]. \tag{8}$$

According to the definition of p, the values $l(0)$ and $l(1)$ are the boundaries of the oscillation region Δl. Their exact values are easily found, for oscillations of arbitrary form, from conditions (2):

$$l(1) = (\bar{c} - c_{\min})/q_{ma} < l < (\bar{c} - c_{\max})/q_{mi} = l(0). \tag{9}$$

The boundary of the region $\Delta\bar{c}$ is found analogously: $\bar{c} > (q_{ma}c_{\max} - q_{mi}c_{\min})/(q_{ma} - q_{mi}) = c_A$. In Fig. 4, in the coordinates $(l, \bar{c})$, the construction of the regions Δl and $\Delta\bar{c}$ is shown from the values $q_{mi}, q_{ma}, c_{\min}, c_{\max}$; c_A is the concentration at the intersection of straight lines issuing from the points $(0, c_{\min})$ and $(0, c_{\max})$ with gradients q_{ma} and q_{mi}. The dependence of ν on l can be constructed exactly for the case of rectangular oscillations. From (6), $\max \nu(p) = \nu(1/2)$. From (8), $l(1/2) = (\bar{c} - c_m)/q_m$; the corresponding straight line in Fig. 4 passes through the points $(0, c_m)$ and A. By formulas (8), (5), and (9), the dependences $p(l)$ and $\nu(l)$ are constructed. Thus, outside the region Δl and on its boundaries, the frequency of self-oscillations ν is equal to zero; inside the region Δl, as l decreases, the frequency first increases from zero, reaches a maximum, and then again falls to zero. For rectangular oscillations, that part (δl^+) of the region Δl in which, as l decreases, ν increases is greater than the part (δl^-) where ν decreases. For oscillations of arbitrary form (Fig. 1a), the character of the change of ν with l is the same; with increasing difference $q_{\max} - q_{ma}$, the inequality $\delta l^+ > \delta l^-$ is strengthened.

The results obtained here are confirmed by experimental data. The dependence $\nu(l)$ at fixed v has the character described above ([4], Fig. 3a, b, c, d). As an example, let us estimate, with the aid of (6), the order of magnitude of the self-oscillation frequency at a value of v close to the right boundary of the region Δv in Fig. 3a from [4]. Determining the order of the frequency may be hindered by such features of the given system [4] as the absence of a supporting electrolyte and the nonuniform distribution of potential over the electrode surface. From the oscillogram we have $\Delta q_{\max} = 2.96 \cdot 10^{-3}$ mol/cm^4, $\Delta q_{\min} = 1.33 \cdot 10^{-3}$ mol/cm^4 (the current density corresponding to q_{ma}, $i_{ma} = 3.72 \cdot 10^{-3}$ A/cm^2, can be obtained by indirect methods, one of which was described above), $p = 0.25$. The value of Δc in this case can be calculated from the ratio of the stationary current $i_0(v_n)$ at the right boundary of Δv to the maximum stationary current $i_0(v_m)$: $\Delta c(v_n) \approx \bar{c}[1 - i_0(v_n)/i_0(v_m)]$; for Fig. 3a from [4], $\bar{c} = 3.7 \cdot 10^{-6}$ mol/cm^3, $\Delta c \approx 3.7 \cdot 10^{-6}(1 - 0.6) = 1.48 \cdot 10^{-6}$ mol/cm^3, $D = 10^{-5}$ cm^2/sec. Substituting these values into (6), we obtain 2.2 Hz $< \tilde{\nu} <$ 10.7 Hz. The true value is $\nu = 5.5$ Hz (see Fig. 3 from [4]). Estimating approximately l as the thickness

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of the diffusion layer on a rotating disk electrode [5] at $\omega = 5$ rev/sec, it is not difficult to establish that condition (4) is satisfied.

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