FREQUENCY OF AUTOOSCILLATIONS IN ELECTROLYTIC SYSTEMS

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(Presented by Academician A. N. Frumkin, June 20, 1962)
Translated from Doklady Akademii Nauk SSSR, Vol. 148, No. 1, pp. 136-139, January, 1963
Original article submitted June 14, 1962

Periodic oscillations generated in nonpassivated electrolytic systems with a falling characteristic [1-4] are discussed below. Autooscillation properties predicted by theory [3, 4] have been experimentally confirmed. The dependence of the autooscillation frequency on the system parameters (layer thickness $\underline{l}$ at the electrode, concentration $\underline{c}$ of the discharged substance, potential $\underline{v}$ applied to the terminals of the electric circuit embracing the electrolytic system to be studied and a series-connected resistance R was studied with reference to the above properties. The range of parameter values at which autooscillations occur, will be called the autooscillation range. If all parameters except one are fixed, the autooscillation range will be designated by $\Delta l, \Delta v$, etc.

We shall first simplify the derivation of the quantitative relationship without violating the essence of the phenomenon. Let us consider the effect which the capacitance of the electric double layer has on the oscillation period. This effect manifests itself in two ways. Firstly, jumps of the states with a low consumption to states with a high consumption of the discharging substance and vice versa, as occur in autooscillations, do not happen momentarily, but take finite times needed for overcharging the double layer. These times are approximately equal to or even shorter than [4] the time constant of the system. In calculating the period T, the capacitance C of the double layer can be neglected only if the time constant $\tau = RC$ of the system is much smaller than T. In practice, the T/τ ratio is, usually, of the order of 100-10. Secondly, the period is determined by the change (ΔQ) in the amount Q of substance in the layer near the electrode and by the rate at which this change is realized in the two stages of the oscillation. Some fraction δQ of the amount ΔQ participates in overcharging of the double layer, and the capacitance of the latter can be neglected only if δQ is small when compared with ΔQ. Using the known oscillation amplitude, it can be easily verified whether the above condition is satisfied; δQ usually amounts to 5-20% of ΔQ. Below, the two conditions are considered as satisfied.

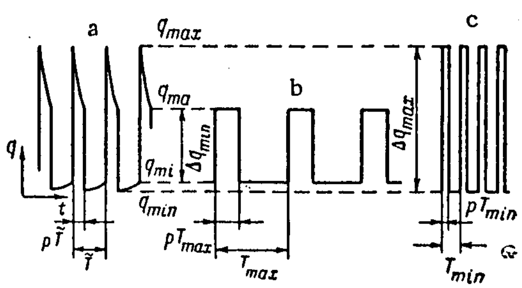

Fig. 1.

We shall further assume that the substances to be discharged are transported to the electrode by diffusion. This is realized when an excess of foreign electrolyte does not smooth out the falling region in the characteristic of the system. If no foreign electrolyte is present, the relationships derived below are only approximately valid. The time in which the concentration near the electrode $c = c(0, t)$ changes from one extreme value (for instance c_{max}) to the other (c_{min}) will be called the duration of the oscillation stage, in accordance with the autooscillation scheme in paper [3]. Let $\underline{p}$ be the ratio between the duration of the stage of maximum current ($\underline{c}$ falls) and the duration of the entire period T. Instead of the current density i(t), we shall consider the corresponding concentration gradient q(t) of the substance to be discharged:

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

(nF is the amount of electricity per mole, D the diffusion coefficient). The experimental values of c_{min}, c_{max}, q_{min}, q_{max} and also those of q_{mi} and q_{ma} in the periods preceding the transition from one oscillation stage to another (Fig. 1a) do not depend on the oscillation frequency, 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 of q_{min}, q_{max}, q_{mi}, and q_{ma} can be found directly from the experimental oscillogram. Sometimes it is difficult to distinguish the point corresponding to q_{ma} because of the extreme steepness of the current drop, whereas the points corresponding to q_{min}, q_{max} and q_{mi} are distinctly visible in $q(t)$ oscillograms.

We shall discuss one of the methods for determining q_{ma}. According to [3, 4], the conditions

$$\text{a)}\quad q_{ma} > (\bar{c} - c_{min})/l,$$
$$\text{b)}\quad q_{mi} < (c - c_{max})/l \qquad (2)$$

(the rate of discharge must predominate in the first stage and the rate of supply in the second) are necessary and sufficient for autooscillations to occur in the system. c_{min} and q_{ma} depend on $\underline{v}$ [3]. The value $v = v_\mu$ at which condition (2a) is violated by becoming an equality constitutes the left limit of the oscillation range Δv. Hence, $q_{ma}(v_\mu)$ is identical to the value $(c-c_{min})/l$ of the gradient in the stationary distribution. In consequence, the corresponding value of the stationary current, which is easily measured near the left boundary of Δv, also yields the value of $q_{ma}(v_\mu)$ when (1) is used. Now $q_{ma}(v)$ is easily determined at any $\underline{v}$ value within Δv; in fact, the left boundary of Δv can always be displaced to any given $\underline{v}$ by reducing l [4]. Knowledge of q_{mi} and q_{ma} makes it possible to distinguish the two oscillation stages in the current versus time oscillogram and permits a determination of $\underline{p}$.

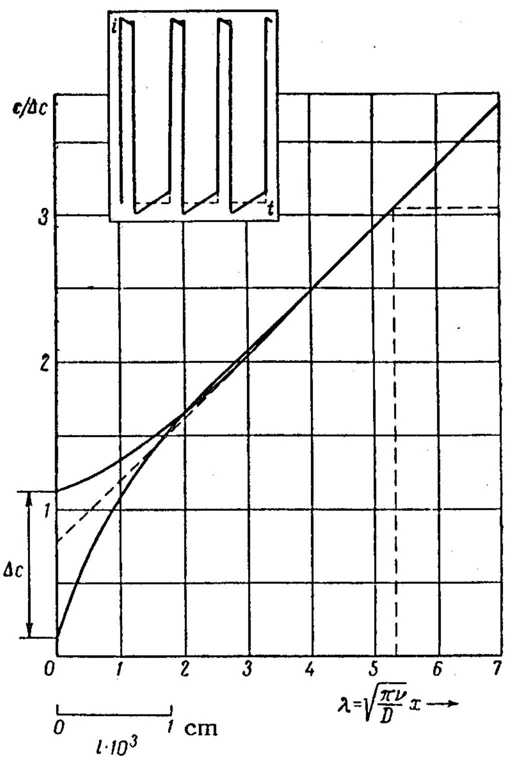

Fig. 2.

Let the values of q_{min}, q_{max}, q_{mi}, q_{ma}, $\Delta c = c_{max} - c_{min}$ and $\underline{p}$ be known for a given system. Then, the period T lies in between the periods T_{max} and T_{min} which would be shown by rectangular variations of the same Δc and $\underline{p}$ oscillating with amplitudes $\Delta q_{min} = q_{ma} - q_{mi}$ and $\Delta q_{max} = q_{max} - q_{min}$ (Fig. 1b, c). The following relationship holds for the frequency: Now we are faced with the problem how to determine $\nu(p)$ and, then, $l(p)$, we get the relation between ν and l in a parametric form.

The distribution $c(x, t)$ in the diffusion layer during autooscillation can be expressed as the sum of the stationary (linear) distribution with gradient q_{om} (the average of $q(t)$ over a period) and the variable concentration components $u(x, t)$:

$$u(x, t) = c(x, t) - \bar{c} + (l - x)\, q_{om}, \qquad (3)$$

$\Delta u = \Delta c$.

Omitting details, we shall give a schematic derivation of (p). First, the solution $u = f(x, t, \Delta q, p, \ )$ of the diffusion equation with boundary conditions

$$\partial u/\partial x\,(0, t) = q(t) - q_{om}, \qquad (A)$$
$$u(l, t) = 0. \qquad (B)$$

is found. Then, $u_{max} = \max(0, t) \equiv f(0, t_{max}, \Delta q, p, \nu)$, $u_{min} = \min u(0, t) \equiv f(0, t_{min}, \Delta_q, p, \nu)$ and $\Delta c = \Delta u = f(0, t_{max}, q, p, \nu) - f(0, t_{min}, \Delta q, p, \nu)$. are determined. Solving for ν, we thus find the desired result $\nu(p) = W(p, \Delta q, \Delta c)$. The amplitude $u(x, t)$ of the oscillations declines rapidly with the distance from the electrode surface ($x = 0$). The distribution $c(\lambda, t_{\substack{min\\max}})/\Delta c$, the stationary distribution (inclined straight line) and their difference $u(\lambda, t_{\substack{min\\max}})/\Delta u$ (the latter does not depend on q_{om} and is determined by $\underline{p}$ only) are shown in Fig. 2 for $p = 1/4$, $l = \infty$, $\bar{c} = \infty$, $\bar{c}/l = q_{om}$; already at $\lambda > 2$ $u(\lambda, t)/\Delta u \approx 0$, i.e., condition (B) is practically satisfied for finite l (the diffusion length was calculated with $D = 10^{-5}$ cm²/sec, $\nu = 10$ sec^{-1}). This case, where the effect of the right boundary ($x = 1$) can be neglected, is especially important for practice. It occurs at

$$\lambda_l = \sqrt{\pi\nu/D}\, l > 2, \quad 1/4 \leqslant p \leqslant 3/4. \qquad (4)$$

In the right-hand side of (3), l is still significant. Solving according to the above scheme for condition (4) gives the formula:

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

(Fig. 3a); $\varphi(0) = \varphi(1) = 0$, $\max\varphi(p) = \varphi(1/2) = 1{,}688254$. If condition (4) is violated, then (5) still gives the quantitative dependence of ν on p: $\nu(0) = \nu(1) = 0$; this is in agreement with the actual ν values. Using (5) and the inequality valid for the frequencies, we find for the frequency of autooscillations of arbitrary shape (Fig. 1a) that

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

Let us return now to the calculation of $l(p)$. We shall introduce the index m: $\alpha_m = (\alpha_{max} + \alpha_{min})/2$, where $\alpha = c, u, q$. From (3) it follows that $u_m = c_m - c + l\, q_{om}$ at $x = 0$. For the same conditions for which (5) was derived, it can be found that

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

(Fig. 3b). In the case of rectangular oscillations: $q_{om} = q_m + (2p - l)\Delta_q/2$. Using the equations for u_m and q_{om}, we get

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

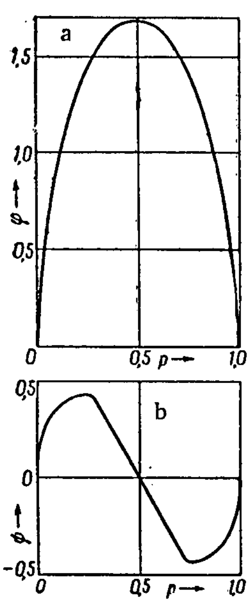

Fig. 3.

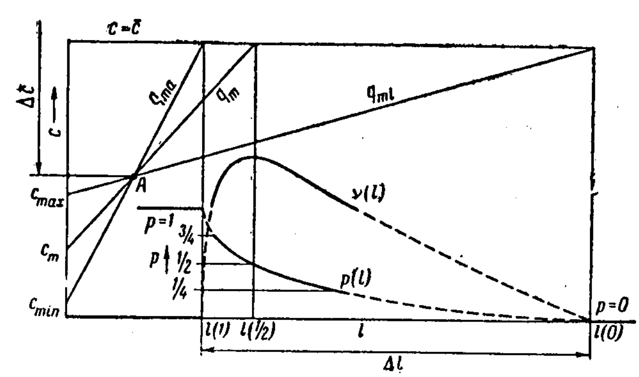

Fig. 4.

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

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

The boundaries of the Δc range are found in an analogous way: $c > (q_{ma}c_{max} - q_{mi}c_{min})/(q_{ma} - q_{mi}) = c_A$. In Fig. 4 it is shown how the ranges Δl and Δc are graphically constructed in (l, c) coordinates from q_{mi}, q_{ma}, c_{min}, c_{max}: c_A is the concentration at the intersection of the straight lines starting from the points (0, c_{min}) and (0, c_{max}) with slopes q_{ma} and q_{mi}, respectively. The relation between ν and l can be accurately constructed in the case of oscillations of rectangular shape. From (6) it follows that $\max\nu(p) = \nu(\frac{1}{2})$. From (8) it is found that $l(\frac{1}{2}) = (c - c_m)/q_m$; the corresponding straight line in Fig. 4 passes through the points (0, c_m) and A. The functions $p(l)$ and $\nu(l)$ are graphically determined by means of formulas (8), (5) and (9). So, near and beyond the boundaries of the Δl range, the autooscillation frequency ν is zero; within this region, the frequency at first rises from zero with decreasing l , attains a maximum and, then, drops again to zero. In the case of rectangular oscillations, the part (δl^+) of the Δl range where rises with decreasing l is larger than the part (δl^-) where it falls. In the case of oscilations of arbitrary shape (Fig. 1a), the frequency changes in the same way with l ; with increasing difference $q_{max} - q_{min}$, the inequality $\delta l^+ > \delta l^-$ becomes more pronounced.

The results obtained here are confirmed by experimental data. The function $\nu(l)$ at fixed $\underline{v}$ has the predicated shape ([4], Fig. 3a, b, c, d). By way of example we shall estimate the order of magnitude of the autooscillation frequency at a $\underline{v}$ value close to the right boundary of the Δv range in Fig. 3a of paper [4] by using inequality (6). A determination of the order of the frequency cannot be invalidated by such special features of the system considered [4] like absence of foreign electrolyte and nonuniform potential distribution along the electrode surface. From the oscillogram we find $\Delta q_{max} = 2.96 \cdot 10^{-3}$ mole/cm^4, $\Delta q_{min} = 1.33 \cdot 10^{-3}$ mole/cm^4 (the current density $i_{ma} = 3.72 \cdot 10^{-3}$ A/cm^2 corresponding to q_{ma} can be found by indirect methods one of which has been discussed above), p = 0.25. The Δc value for this case can be calculated from the ratio of the stationary current $i_0(v_\eta)$ at the left boundary of Δv to the maximum stationary current $i_0(v_m)$: $\Delta c(v_\eta) \approx \bar{c}[1 - i_0(v_\eta)/i_0(v_m)]$; in Fig. 3a of paper [4], c = $3.7 \cdot 10^{-6}$ mole/cm^3, $\Delta c \approx 3.7 \cdot 10^{-6}(1 - 0.6) = 1.48 \cdot 10^{-6}$ mole/cm^3, D = 10^{-5} cm^2/sec. Substituting these values in (6), we find: 2.2 Hz < ν < 10.7 Hz. The actual value is ν = 5.5 Hz (see Fig. 3 of paper [4]). Approximating l by the thickness of the diffusion layer near the rotating disc electrode [5] at ω = 5 rotations/sec, it is easily established that condition (4) is fulfilled.

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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.
