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Abstract

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ON THE THEORY OF SELF-OSCILLATIONS IN ELECTROCHEMICAL SYSTEMS FREE FROM PASSIVATION AND HAVING A FALLING CHARACTERISTIC

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As was reported (^{1}), during the reduction of $S_2O_8^{2-}$ on dropping and stationary mercury electrodes, A. N. Frumkin and the author experimentally discovered and investigated periodic, undamped self-oscillations. Subsequently these oscillations were observed by A. N. Frumkin, O. A. Petrii, and N. V. Nikolaeva-Fedorovich (^{2}) in the case of the anions $PtCl_4^{2-}$, $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, and by the author in the case of $PtCl_6^{2-}$. However, no theory of these oscillations had been given. Most periodic phenomena in electrochemistry are connected with the appearance on the electrode of a passivating film or with the formation of a new phase. An essential contribution to the theory of these phenomena was made by the works of U. F. Franck (^{3,4}) and Yu. A. Chizmadzhev (^{5}). In the case considered here, there are no surface formations of this kind. Below a theory of the observed phenomenon is presented. It is based on two premises: (a) the characteristic $p(\varphi)$ of the system includes a falling segment; (b) the transfer of substance from the solution to the electrode surface is a slow process. In diffusion transfer, the decrease in concentration from its value $\overline{C}$ in the bulk of the solution to the value C at the surface occurs in a layer of finite thickness l. The conditions of its formation are determined by the geometry of the near-electrode space or by various stirring regimes (in the case of a dropping electrode, tangential oscillations of its surface are significant). The current density i and the electrode potential φ in irreversible electroreduction of anions are related by the relation (^{6}) $i = Cp(\varphi)$; $p(\varphi)$ is a single-valued positive differentiable function. The supporting electrolyte is present in the solution in such an amount that the falling segment on the polarization characteristic is preserved.

For the circuit of an electrolytic cell with a polarizable electrode of area S and a series resistance R, to the ends of which a voltage v is applied:

$$\text{a)}\quad ir + \varphi = v; \qquad \text{b)}\quad i = Cp(\varphi); \qquad \text{c)}\quad Cp(\varphi)r + \varphi = v, \tag{1}$$

where $r = RS$. The roots of equation (1c) determine the possible states of

Fig. 1

Figure 1: Fig. 1

the system. To a value of the near-electrode concentration $C = C_k = \text{const}$ fixed at some instant of time, generally speaking, several roots of (1c) may correspond and, consequently, several possible states of the system. Among the possible states there may be nonstationary states, i.e., such states for which (1c) is satisfied only at a given instant of time, as well as stationary states, for which (1c) is fulfilled at all times. Let us determine the number of the latter for $C = C_k$. In the stationary state, the concentration of the substance consumed in the electrode reaction is distributed linearly in the diffusion layer; in this case the current satisfies the condition

$$i = G(\overline{C} - C), \qquad [G = nFD/l], \tag{2}$$

where D is the diffusion coefficient, and nF is the amount of electricity per 1 mole of substance. Thus, among the possible states of the system corresponding to $C = C_k$, there can be no more than one stationary state. Further, from comparison of (1) and (2) it follows that, for given r and v, stationary states can be realized only at certain values of C.

Let us find these states. The dependence of i_0 (the subscript 0 indicates the stationary state) on φ is determined by eliminating C from (16) and (2):

$$i_0(\varphi) = G\bar{C}/[1 + G/p(\varphi)]. \tag{3}$$

Since i_0 must at the same time satisfy relation (1a), the possible stationary states (i_0, φ_0) are determined by the roots of

$$i_0(\varphi)r + \varphi = v, \tag{4}$$

which is one of the forms of combining (1a, b) and (2). If (4) has one root, then the stationary state of the system is unique. The dependence

Fig. 1

$i_0(\varphi)$ is usually obtained experimentally (a polarization curve with a platform) and serves here as the starting point for reasoning about a particular system. From this there follows a practical method for determining the possible stationary states. According to (4), they can be found as the points of intersection of the polarization curve with the straight line $i = (v - \varphi)/r$. If (i_0, φ_0) lies on the descending branch of $i_0(\varphi)$, then it also lies on the descending branch of $p(\varphi)$ (the platform on $i_0(\varphi)$ has a weakly expressed maximum at the same $\varphi_{\max}$ as $p(\varphi)$). From (3) it follows that $|i_0'(\varphi)| < |C_0(\varphi)p'(\varphi)|$. Since $p(\varphi) > 0$,

Fig. 2

Figure 2: Fig. 2

it also follows from (3) that $i_0(\varphi)$ is bounded. Let us consider the case of a single stationary state. Omitting, for brevity of exposition, the rigorous solution of the problem, which is obtained in the study of the integral diffusion equations in the case of an arbitrary function $p(\varphi)$, we give the following condition: the unique stationary state proves to be unstable if, for it, the inequality $C_0 p'(\varphi_0) < -(1/r)$ is satisfied.

The meaning of this condition, as well as the character of the oscillatory process, is explained in Fig. 1, where a concrete numerical example is given. The choice of conditional units C, i, and φ is clear from the figure. The quantities $p(\varphi)$, $G = 0.137$, and $\bar{C} = 7$ were specified. Then $i_0(\varphi)$ was determined from (3). The straight lines (1a) with the specified r and v are tangent above and below to the curves i_1 and i_3. They correspond to the critical concentrations $C_1 = C_{\max} = 2.67$, $C_3 = C_{\min} = 1.00$. The point of intersection of the straight line (1a) with the curve $i_0(\varphi)$ (dashed line) indicates the stationary state ($C_2 = C_0 = 1.41$). There are no other intersection points; therefore the stationary state O is unique. The inequality indicated above means: 1) that the point O is located on the descending portion of the curve $i_2(\varphi) = C_0 p(\varphi)$; 2) that at the point O the curve $i_2(\varphi)$ is directed more steeply than the straight line (1a). Such an arrangement of the curves $i = Cp(\varphi)$ relative to the straight line $ir + \varphi = v$ leads to the fact that, with increasing C, φ increases and i decreases. The region of potentials φ in which this arrangement of the curves is preserved is bounded by the potentials of the points

4 and 7, where the intersection changes into tangency. This region constitutes only part of the potential region of the falling branch of the function $p(\varphi)$ and, as is shown below, selects a portion of this function that does not operate during the oscillations. In order for oscillations to occur in the system, the point representing the state of the system must leave the "nonworking" portion. It can be shown that fulfillment of the instability condition given above ensures that the system leaves precisely the limits of the "nonworking" portion.

Fig. 2

The oscillations occur in the following way. Since the stationary state O is unstable and the system cannot remain for long on the "nonworking" portion, after some time it passes into state 1 on i_1 (or 4 on i_3). The consumption of substance (the ordinate of point 1) is less than its supply from the solution (for the concentration C_1 the stationary flux of substance is determined by the point of intersection of $i_1(\varphi)$ with $i_0(\varphi)$, which lies above point 1: for state 1 on the curve i_1, $(i_1)_1 < G(\bar{C} - C_1)$); the flux through the boundary $x = l$ corresponding to the concentration C_1 is higher than the stationary flux and, all the more, exceeds the consumption of substance at the boundary $x = 0$. Therefore C, and together with it the characteristic $i = Cp(\varphi)$, increases until tangency at point 1 ceases, after which the system passes into state 2 on the same characteristic. Here, conversely, the consumption of substance in the reaction exceeds its supply, and C gradually decreases from C to C_3; the state of the system gradually shifts along the straight line from point 2 to point 4. Here the consumption of substance is still large $((i_3)_4 > G(\bar{C} - C_3))$, $i_3(\varphi)$ and $i_0(\varphi)$ intersect below point 4), the characteristic $i = Cp(\varphi)$ continues to descend, and the system passes by a jump to point 5. The consumption drops sharply, C increases, and the system gradually moves from 5 to 7, after which the cycle $(1, 2—3—4, 5—6—7)$ repeats. In Fig. 1b the concentration distributions in the diffusion layer with distance x from the electrode surface are shown schematically. The stationary distributions, which would correspond to the critical near-electrode concentrations C_1 and C_3, are indicated by dashed lines. The shaded area is equal to the maximum change Q in the amount of substance in the diffusion layer during oscillations,

$$Q < \tfrac{1}{2}l(C_1 - C_3).$$

The concentration distributions are wave-like and in the course of the change may extend somewhat beyond the limits of this figure.

In Fig. 2 the cycle $(1, 2—3—4, 5—6—7)$ is shown in different coordinates. In Fig. 2a the state of the system is described by the point of intersection of the fixed curve $i/C = p(\varphi)$ with the straight line $i/C = (v - \varphi)/rC$, whose slope changes during the oscillation with the near-electrode concentration C. In this case the state of the system moves along a closed contour in the direction indicated by the arrow. The "nonworking" portion of the curve $p(\varphi)$ is drawn with a dashed line. As v decreases, the cycle contracts to the point e, and the oscillations cease. The cycle has no breaks at points 4 and 7; therefore in the $i - t$ plot they correspond to smooth transitions. The dependence of the breakaway currents (points 4, 7) and of the oscillation amplitude on v is shown in Fig. 2b. The mean currents in the upper part (I_1) and lower part (I_2) of the oscillation are determined by the function $p(\varphi)$. Therefore, for large l, the estimate

$$\tau_2/\tau_1 = (I_1 - I_0)/(I_0 - I_2),$$

is valid, where I_0 is the mean over an oscillation

current. Increasing l and decreasing $\bar{C}$ entail a decrease in I_0 and, consequently, an increase in the relative duration of that phase of the oscillation in which the current is small (τ_2), as well as an increase in the period $\tau_1 + \tau_2$. If, however, (4) has several roots in some region Δv (or Δr), then to this region in the coordinates $i—v$ $(i—r)$, under certain conditions, there may correspond a band in which there are no oscillations. This conclusion requires experimental verification.

Fig. 3. Curves $i—(v, t)$ at a voltage decreasing (from right to left) with time: a–$5 \cdot 10^{-3}$ M $K_2S_2O_8$ + 0.05% gelatin, dropping mercury electrode,

Fig. 3

Figure 3: Fig. 3

$S = 0.18$ mm^2, second electrode n.c.e., additional resistance $R_M = 0$, 1.3 V/sec; b–10^{-2} M $K_2S_2O_8$+10^{-3} M $CdSO_4$+0.05% gelatin, $S = 0.65$ mm^2, $R_M = 10$ k , the remaining conditions the same as in a; v–10^{-2} M $(NH_4)S_2O_8$, interference of oscillations occurring differently on different parts of the drop, periodic damping of the oscillations.

Conditions for the occurrence of the oscillatory process: 1) (i_0, φ_0) lies on the falling branch of the curve $i_0(\varphi)$, i.e. $|\varphi_0| > |\varphi_{\max}|$, where, for example, for $S_2O_8^{2-}$ $\varphi_{\max} \approx -0.35$ V (n.c.e.) (7); 2) (i_0, φ_0) is unique; this will always be the case if $\max|i_0'(\varphi)| < 1/r$; this can be achieved by simultaneously increasing $\bar{C}$ and l; 3) $|C_0 p'(\varphi_0)| > 1/r$. Since $|i_0'(\varphi)| < |C_0 p'(\varphi)|$, conditions 2) and 3) can be satisfied at once by choosing v and r so that $|i_0'(\varphi_0)| < 1/r < |C_0 p'(\varphi_0)|$.

The modifications of the self-oscillations that have been observed experimentally (Fig. 3a, b) agree with the facts established by the theory. Their properties become understandable (1), in particular the break from the peak of the oscillation to the polarographic maximum that occurs under certain conditions: the potential of the peak lies precisely in the region of the polarographic maximum. The distortions upon conversion from i—v to i—φ (1) are caused, as calculation of the potential distribution has shown, by neglect of the high resistance of the solution in the shielded part of the electrode. Introducing a large resistance in series with the cell diminishes the role of the solution resistance. As is clear from the foregoing, the shape of the electrode, and at low frequencies ($<$ 10 Hz) even the capacitance, are of no fundamental importance in the occurrence of the oscillations considered. In the absence of a supporting electrolyte, the scheme of the oscillations remains the same. According to calculations, the instability of the stationary state is not disturbed when a capacitance is introduced into the system. The period of oscillation at low frequencies exceeds the "time constant" of the system by more than a factor of 10.

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