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Abstract

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SELF-OSCILLATORY PROCESSES IN CERTAIN ELECTROCHEMICAL SYSTEMS

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Electrode reactions, as is well known, consist of a number of successive stages, such as diffusion, adsorption, and the electrochemical reaction proper. In some systems parallel reactions are possible, i.e., the simultaneous discharge of particles A and B, or the discharge of particles A and adsorption of particles B. The latter process is nonstationary. To each stage of the reaction one may assign a definite physical quantity. Thus, the diffusion stage is described by the concentration of particles near the electrode c (here "near" should be understood in a macroscopic sense), adsorption may be characterized by the surface concentration Γ, and the electrochemical reaction proper by the electrode potential φ. We shall call the number of degrees of freedom of an electrochemical system (or the order of the system) the number of variables $c, \Gamma, \varphi, \ldots$ necessary for a complete description of the behavior of the system in time. The question naturally arises of determining the number of degrees of freedom of various systems encountered experimentally. Usually, among several stages of a single reaction, one or two stages are slow, i.e., are characterized by a relatively small exchange current. For solving stationary problems it is sufficient to describe the system by means of quantities corresponding to the slow stages. For example, the reaction of cathodic hydrogen evolution on a mercury electrode from a 1 N HCl solution at a current density $i = 1 \cdot 10^{-4}$ A/cm^2 is completely described by the overvoltage η. In considering relaxation processes, neglect of some stages whose rate may be large sometimes leads to qualitative contradiction with experiment. Therefore, in solving the question of the number of degrees of freedom of a particular system, the ultimate criterion is experiment: if the choice of some single quantity as the defining variable does not lead to agreement with experiment, the model must be supplemented by introducing additional variables.

Let us consider the process of establishing a stationary state in a system with one degree of freedom. We write the law of conservation of the electrode charge in the form

$$\frac{dQ}{dt} = \frac{E-\varphi}{R} - j(\varphi), \tag{1}$$

where E is the applied voltage, R is the resistance of the external circuit, and $j(\varphi)$ is the polarization characteristic. In this equation $\dfrac{E-\varphi}{R}$ is the current in the external circuit, and $j(\varphi)$ is the reaction current. If

$$\frac{E-\varphi}{R} > j(\varphi),$$

the electrode charge Q increases with time. Introducing the constant capacitance of the electrode C, we can relate the change in charge dQ to the change in potential $d\varphi$, $dQ = C\,d\varphi$, and rewrite equation (1) in the form

$$C\frac{d\varphi}{dt} = \frac{E-\varphi}{R} - j(\varphi). \tag{2}$$

In the stationary state, $\frac{d\varphi}{dt} = 0$ and $\frac{E-\varphi_0}{R} = j(\varphi_0)$, where φ_0 is the stationary potential of the electrode. Dividing equation (2) by C and introducing the notation $\frac{1}{C}\left[\frac{E-\varphi}{R} - j(\varphi)\right] = F(\varphi)$, we obtain

$$\frac{d\varphi}{dt} = F(\varphi). \tag{3}$$

Equations of this kind have been studied in detail in the theory of oscillations (^{2}). Electrochemical systems described by equation (3) were studied by Franck (^{3}). Depending on the form of the function $F(\varphi)$, equation (3) may have one or another number of stationary states. In the presence of descending branches in the function $j(\varphi)$, the stationary states may be unstable. We shall be interested, however, not simply in the loss of stability, but in the possibility of a periodic process occurring in a system described by equation (3). Let us assume that equation (3) describes a periodic process. Then, for one and the same value of φ, the system must pass in opposite directions, i.e., with two different values of $d\varphi/dt$; that is, $F(\varphi)$ must be a multivalued function. The source of multivaluedness can only be $j(\varphi)$. If the polarization characteristic has an N-shaped form (Fig. 1a), then the function $F(\varphi)$ is single-valued everywhere and a periodic process is impossible. If, however, the polarization curve belongs to the S-type (Fig. 1b), then the function $F(\varphi)$ has a region of multivaluedness and a periodic process is possible in the system, the amplitude of which is determined by the depth of the loop. Such S-shaped characteristics have been little studied experimentally, and we shall confine ourselves to consideration of N-type curves.

Fig. 1

Oscillations during the ionization of hydrogen on a Pt electrode under passivity conditions have been described in the literature ($^{4-7}$). To describe the behavior

Fig. 1

Figure 1: Fig. 1

of such a system in time, equations (1)—(3) are no longer applicable, since the properties of the electrode depend substantially on the amount of chemisorbed anions or oxygen, and equilibrium with respect to the adsorbed particles is established slowly (^{8}). It may be said that the Pt electrode is a system with two degrees of freedom. As is known (^{1,9}), adsorbed atoms of hydrogen and oxygen take part in the formation of the potential jump at a Pt electrode. Accordingly, we shall consider the electrode potential as a single-valued function $\varphi(Q, \Gamma)$ of the charge of the metallic plate of the double layer Q and of the surface concentration of adsorbed substances Γ. The exchange current of the process of hydrogen adsorption is 10^3 times greater than the exchange current of oxygen adsorption. Consequently, it may be assumed that, at any value of Q, the surface concentration of hydrogen is at equilibrium, and the potential may be considered as a function of one variable Q or Γ_H, i.e., $\varphi = \varphi_1(Q)$ or $\varphi = \varphi_2(\Gamma_H)$. The process of adsorption—desorption of oxygen, as well as of anions, is irreversible (^{7,8}). The hysteresis loop is a consequence of the slowness with which equilibrium is established during oxygen adsorption. As the current is decreased, the loop diminishes. On the ascending branch $\Gamma < \Gamma_{\text{eq}}$, on the descending branch $\Gamma > \Gamma_{\text{eq}}$. From the fact of irreversibility it follows that the electrode potential in the region of adsorption of anions and oxygen is determined by the totality of two dynamic variables Q and Γ, which are no longer connected by an equilibrium relation. We shall base ourselves on the ideas (^{10}) according to which passivation in solutions containing adsorbing anions is caused by a decrease in the number of active sites of the electrode.

as a result of adsorption. Denote by Q the total charge of the metallic lining$^{(9)}$, and by Γ the surface concentration of anions (by anions we shall also mean OH^-). The total charge is $Q = q + \varepsilon$, where q is the free charge, compensated by the charges of the diffuse double layer, and ε is the "bound" charge, compensated by the adsorbed anions. Let us write the conservation law for the total charge

$$\frac{dQ}{dt} = \frac{E - \varphi}{R} - j(\varphi, \Gamma), \tag{4}$$

where $j(\varphi, \Gamma)$ is the hydrogen discharge current. Let us write the conservation law for Γ

$$\frac{d\Gamma}{dt} = I(\varphi, \Gamma). \tag{5}$$

In the stationary state $d\Gamma/dt = 0$, $I(\varphi, \Gamma) = 0$. Equation (5) describes the character of the change, with time, in the number of active sites on the surface. If one assumes that the number of active sites on the surface changes only as a result of adsorption—desorption of anions, then one may write $I(\varphi, \Gamma) = I_{\text{ad}} - I_{\text{d}}$. Very little is known about the form of the function $I(\varphi, \Gamma)$. Therefore, without making any assumptions about the function $I(\varphi, \Gamma)$, let us investigate what conditions it must satisfy in order for a self-oscillatory process to be possible at the electrode. If in (4) and (5) we pass to the variables φ, Γ, the system of equations takes the form

$$\frac{d\Gamma}{dt} = I(\varphi, \Gamma), \qquad C\frac{d\varphi}{dt} = \frac{E-\varphi}{R} - j(\varphi, \Gamma) - FI(\varphi, \Gamma). \tag{6}$$

Unlike systems with one degree of freedom, the equation for the potential includes the anion adsorption current. In the stationary state the adsorption current $I(\varphi, \Gamma) = 0$, and the current in the external circuit is equal to the hydrogen ionization current $j(\varphi_0, \Gamma_0)$. The stationary state is determined from the conditions

$$\frac{E-\varphi}{R} = j(\varphi, \Gamma), \qquad I(\varphi, \Gamma) = 0.$$

To investigate the stability of the stationary state φ_0, Γ_0, it is necessary to introduce small deviations from the stationary state $\overline{\varphi} = \varphi - \varphi_0$, $\overline{\Gamma} = \Gamma - \Gamma_0$. The investigation shows that the stationary state is unstable if the inequality

$$\frac{1}{C}\left[-\frac{1}{R} - \left(\frac{\partial j}{\partial \varphi}\right)_{\Gamma} - \left(\frac{\partial I}{\partial \varphi}\right)_{\Gamma} F\right] + \left(\frac{\partial I}{\partial \Gamma}\right)_{\varphi} > 0 \tag{7}$$

is satisfied.

The quantity $(\partial j/\partial\varphi)_{\Gamma}$ entering here is always positive, even for a falling static characteristic. The required inequality can be made to hold only if $(\partial I/\partial\varphi)_{\Gamma} < 0$ or $(\partial I/\partial\Gamma)_{\varphi} > 0$.

Instability of the stationary state still does not guarantee the possibility of oscillations. For a limit cycle to exist it is necessary that one more inequality be fulfilled:

$$\left[-\frac{1}{R} - \left(\frac{\partial j}{\partial \varphi}\right)_{\Gamma}\right]\left(\frac{\partial I}{\partial \Gamma}\right)_{\varphi} + \left(\frac{\partial j}{\partial \Gamma}\right)_{\varphi}\left(\frac{\partial I}{\partial \varphi}\right)_{\Gamma} > 0. \tag{8}$$

Let us note at once that the derivative $(\partial j/\partial\Gamma)_{\varphi} < 0$. Suppose that the derivative $(\partial I/\partial\varphi)_{\Gamma} > 0$. Then the product $(\partial j/\partial\Gamma)_{\varphi}(\partial I/\partial\varphi)_{\Gamma} < 0$, and in order for inequality (8) to be satisfied it is necessary that $(\partial I/\partial\Gamma)_{\varphi}$ be less than zero. But if $(\partial I/\partial\Gamma)_{\varphi} < 0$ and simultaneously $(\partial I/\partial\varphi)_{\Gamma} > 0$, then inequality (7) cannot be satisfied. Consequently, for oscillations to arise it is necessary that $(\partial I/\partial\varphi)_{\Gamma}$ be less than zero. In this case the sign of $(\partial I/\partial\Gamma)_{\varphi}$ may be arbitrary.

Let $(\partial I/\partial\Gamma)_\varphi < 0$. This is always true if there is no interaction between the adsorbed particles. Then from (7) we obtain

$$F\left|\left(\frac{\partial I}{\partial\varphi}\right)_\Gamma\right| > C\left|\left(\frac{\partial I}{\partial\Gamma}\right)_\varphi\right| + \frac{1}{R} + \left(\frac{\partial j}{\partial\varphi}\right)_\Gamma . \tag{9}$$

Condition (8) is then fulfilled automatically. Since $I'_\varphi < 0$ and $I'_\Gamma < 0$, $[d\Gamma/d\varphi]_{\text{static}} < 0$, i.e., oscillations can arise only near such a stationary state in whose vicinity the number of active sites increases with potential. On the static polarization curve, accordingly, an ascending segment should be observed in this range of potentials. A necessary condition for the occurrence of oscillations is the irreversibility of adsorption. Indeed, let the adsorption be reversible. Then it may be assumed that at any instant the concentration Γ is in equilibrium with respect to φ. The system of equations reduces to a single equation for the potential

$$C\frac{d\varphi}{dt} = \frac{E-\varphi}{R} - j(\varphi),$$

which has no oscillatory solutions. Comparison of the theory with experiment is somewhat difficult, since only in work (^{7}) is a polarization characteristic presented. The oscillations observed in that work did indeed occur in the region where the polarization curve rises. This rise, in the author's opinion, was caused by an increase in the number of active surface sites as a result of dissolution of platinum. Such a process is formally equivalent to the desorption of anions required by the theory. It would be much easier to test the theory on a liquid cathode with adsorbed organic matter, where the curve $\Gamma(\varphi)$ is known. Oscillations on solid electrodes in the presence of surface-active substances have been described in the literature (^{11}). It is interesting to note that, in these experiments, the oscillations were observed in the region of desorption, in agreement with the conclusions of the theory set out above.

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