Self-Oscillations during the Reduction of the Anion $\mathrm{S}_2\mathrm{O}_8^{2-}$ on Mercury

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Abstract

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Self-Oscillations during the Reduction of the Anion $S_2O_8^{2-}$ on Mercury

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The literature describes numerous cases of the occurrence of oscillations of current and potential in electrochemical systems with a falling polarization characteristic. Usually, however, these processes are complicated by dissolution of the electrode or by the liberation of a solid phase. It seemed of interest to study oscillations in systems free from complications of this kind.

The object chosen for investigation was the reduction of the persulfate anion at a mercury cathode. $S_2O_8^{2-}$ belongs to the class of anions for which, in a certain range of potentials, a decrease in current density is observed with increasing cathodic polarization (^{1}). In an electrical circuit including this system, the authors indeed detected spontaneous oscillations of current and potential. The circuit consisted of a stabilized voltage source (a G KhI oscillographic polarograph or a battery with a rheochord bridge), a cell with a dropping mercury cathode and a reference electrode, and a series resistance introduced into the circuit. The investigations were carried out both at constant voltage at the terminals of the circuit and at a voltage varying linearly with time.

When studying processes on an oscillographic polarograph, it is expedient to change the electrode potential in such a direction that the reaction rate occurs under conditions of an excess of reacting substance in the near-electrode layer. Therefore, in studying the reduction of persulfate it is convenient to start from the region of current decrease and to study the positive branch of the polarization characteristic at a voltage whose absolute value decreases with time (Fig. 1). The beginning of this oscillogram (on the right) corresponds to a potential of -0.98 V (n.c.e.) and lies in the indicated region. As the voltage decreases (from right to left), oscillations of the current arise on the falling section of the polarization characteristic. With further decrease of the voltage the oscillations diminish in amplitude until they cease completely, after which the beam passes to the descending branch corresponding to the diffusion current (^{2}). When the voltage is decreased by a further 0.2 V, the current rises to the positive polarographic maximum. Since the resistance of the electrolyte is large, the current oscillations are accompanied by appreciable oscillations of the electrode potential. The decrease of amplitude from right to left (Fig. 1) is not evidence of damping of the oscillations with time, but is due to the dependence of the amplitude on the voltage at the terminals of the circuit.

If the change in voltage is stopped, then, with a sufficiently large series resistance in the circuit, undamped oscillations are established (Fig. 2). The time during which the oscillations can occur without damping is limited only by the lifetime of the electrode. When working with slowly dropping electrodes, this period reached 90 sec. The form of the oscillations at different amplitudes remains the same (Fig. 1, right to left): a very steep leading front, a brief halt at the maximum value of the current, greatly exceeding the diffusion···

Fig. 1. Oscillogram for $10^{-2}\,M\ K_2S_2O_8$. Rate of decrease of voltage 2.36 V/sec, voltage amplitude 0.61 V, initial voltage −1.0 V (s.c.e.). Time from the appearance of the drop to the application of the pulse: 3 sec.

Fig. 2. Oscillogram of self-oscillations in $10^{-2}\,M\ K_2S_2O_8$ at a voltage of −1.2 V (relative to anodic Hg)

Fig. 3. Oscillogram for $10^{-2}\,M\ K_2S_2O_8$. Rate of decrease of voltage 8.60 V/sec; the remaining conditions are the same as for Fig. 1.

the current in the absence of oscillations after the lapse of the same interval of time from the beginning of the decrease in voltage, a more gradual drop, and a plateau during which the current, rising slightly, remains below the diffusion current. The frequency of the self-oscillations depends on the experimental conditions. Under the conditions in which the oscillogram of Fig. 1 was recorded, the frequency of the oscillations with the greatest amplitude was 57.5 Hz, and with the smallest amplitude 175 Hz.

Summarizing the experimental material obtained in the study of self-oscillations in the mercury—persulfate solution system, the following may be noted:

1. A necessary condition for the occurrence of oscillations is a considerable series resistance (1-20 kΩ). It consists of the resistance of the solution and of a resistor connected in series in the circuit. If a third electrode is introduced into the cell and, in the oscillographic polarograph, connected to the grid of the compensator tube of the load resistance, then voltage control is replaced by control of the potential at the electrode, the series resistance loses its influence, and oscillations do not occur.

2. In those cases when the other conditions do not favor oscillations, the latter can be induced by increasing the rate of decrease of the voltage. Rates in the range 0-75 V/s were used.

3. Oscillations occur both on a growing dropping mercury electrode and on "stationary" mercury electrodes (the amalgamated end of a gold wire sealed into glass).

4. For oscillations it is essential that the current values in the region of the drop be sufficiently low. The presence in the solution of substances that accelerate the reaction in this region hinders the appearance of oscillations. Such an effect is produced by an excess of indifferent electrolyte and by mercury salts at a concentration comparable with the concentration of persulfate.

5. Prolonged electrolysis (1 h) leads to cessation of the oscillations. This is associated with a change in the composition of the solution and the appearance in it of mercury salts, formed at the anode and on the detaching drops. Artificial introduction of mercury salts into a fresh solution gives the same results.

6. When the series resistance is large (5–20 kΩ), oscillations occur even at constant voltage (Fig. 2). Their amplitude does not change with time.

7. The amplitude of oscillations at constant voltage is established immediately after that voltage is reached and does not depend on what the rate of voltage change was before it was stopped.

8. With increasing drop diameter, the amplitude decreases and, for diameter values greater than a certain critical value, becomes zero. The degree of change of the amplitude with the diameter and its critical value depend on the voltage at the terminals of the circuit.

9. After a short time has elapsed from the moment of detachment of the drop, under artificial stirring or at high series resistance, the behavior of the current during the decrease of voltage is as follows: at the beginning of the oscillation region the current rises, is delayed for several milliseconds, forming a zigzag, rises again, and remains on a sloping line corresponding to the positive polarographic maximum (the latter is confirmed by observation of the electrode under a microscope).

This behavior of the current is of interest because, under the conditions of the preceding points, the transition to the polarographic maximum occurs 0.20–0.25 V in the region positive of the oscillations. There are intermediate conditions under which oscillograms with premature and timely ascent to the maximum alternate. Two such oscillograms are superimposed in Fig. 3, from which the origin of the zigzag follows: it is the peak and part of the trailing front of the first oscillation.

10. The transition to the maximum at potentials positive of the oscillation region occurs without an intermediate stop. The transition potential

depends on the rate at which the voltage is decreased—with increasing rate, a delay in the onset of the rise is observed. The delay time at different rates of voltage decrease is the same, but depends on the potential from which the decrease begins.

The very fact of the delay is not a peculiarity of persulfate behavior; in a $10^{-2}M$ solution of $Pb(NO_3)_2$ with a normal polarization characteristic the authors observed the same phenomenon.

11. Gelatin present in the solution (0.05%) damps the oscillations at low rates of voltage change (2.36 V/sec, resistance box excluded from the circuit) and smooths them at higher rates (4.17; 8.60 V/sec).

Fig. 4

Figure 1: Fig. 4

Fig. 4. Oscillations in current-voltage coordinates (vertical straight lines) and current-potential coordinates (inclined lines): $10^{-2}M$ $K_2S_2O_8$, mercury outflow rate $6.54 \cdot 10^{-3}$ mm^3/sec, time from the appearance of the drop 6 sec. Series resistance 23 k ±5%.

12. With a small series resistance, the initial scan potential affects the oscillations. Its exit beyond the region of the falling branch favors damping of the oscillations.

13. Within a single scan, the oscillation frequency is inversely proportional to their amplitude,

$$\nu = k/a.$$

The duration of an oscillation increases with its amplitude. The proportionality coefficient for the conditions of Fig. 1 is $0.388 \cdot 10^{-2}$ a/sec.

14. The amplitude of the oscillations depends strongly on the voltage (Fig. 4). Replacement of the cations K^+, Na^+, NH_4^+ does not change the phenomenon.

In the main experiments, twice recrystallized reagents, twice distilled mercury and water were used; hydrogen was passed through for 4 hours. A number of experiments were carried out on the first drop, which made it possible to impart the required potential to the electrode before the mercury came into contact with the persulfate solution.

It has not yet been possible to construct a complete theory of the oscillations described. From analysis of the results obtained it follows that self-oscillations at the mercury electrode are associated with tangential motions of its surface. Observation under the microscope of particles suspended in the solution indicates that the motion has an oscillatory character and is directed from bottom to top at the leading front of the oscillation, followed by return. Surface displacements during the oscillations are more strongly expressed in the shielded part of the electrode, where they amount to several microns. The direct and reverse displacements are equal, so that, overall, the surface does not undergo significant displacement. The role of motion in the oscillation process follows from the properties listed in points 6 and 7. The stability of the amplitude over time is difficult, and the independence of it from the initial state of the near-electrode layer is impossible, to explain solely by diffusive supply of substance to the electrode. The inevitable zigzag during the early rise of the current to the polarographic maximum (point 9), in which the motion is directed, as is known, from top to bottom, confirms the supposition about the direction of surface motion in the first stage of the oscillation: in order to change direction, the surface must stop.

The mechanism by which the motions arise may be explained as follows. Nonuniform distribution of potential over the electrode surface when the surface is negatively charged leads to the creation, in the shielded part of the drop, of a higher surface tension. Apparently, this potential distribution, usual for a normal polarization characteristic, is preserved also for a falling one. Therefore, in the first stage of the oscillation the motion is directed toward the capillary. However, this motion differs from the motion at negative polarographic

at the maxima by the fact that it is nonstationary and occurs in short periodic pulses. The stopping and reversal of the direction of motion soon after its onset are probably connected with the possibility, in the case of a falling polarization characteristic, of a redistribution of potential over the surface of the drop. The motion of the surface accounts for the large values of the current at the peaks of the oscillations. At the leading front of the oscillation, substance is supplied to the electrode by convection. The cessation of motion corresponds to the onset of the current decline. The action of surface-active substances confirms this point of view. In the presence of gelatin the motion becomes less intense. The fact that gelatin, while completely stopping the motion at a positive polarographic maximum, only slows it during oscillations may possibly be explained by the difference in the regimes of the two motions (stationary and periodic).

Knowing the series resistance of the circuit and the dependence of the amplitude on the dc voltage (Fig. 4, thick vertical lines), one can construct the oscillation process in current-potential coordinates. At a given dc voltage, the current and potential oscillate while remaining on the thick inclined lines of Fig. 4. This scheme gives a simple explanation of some properties of the oscillations, in particular the dependence of the amplitude on the size of the electrode surface (p. 8): as the surface increases, the lower boundary of the oscillations rises. It is interesting that the peaks of the oscillations in current-potential coordinates lie on an almost vertical curve, whose abscissae are close to a potential of −0.6 V (N.C.E.). This shows that the end of the first stage is connected with a certain state that is communicated to the electrode in the region of the indicated potential. The investigation of the phenomena discovered is continuing.

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CITED LITERATURE

1. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, B. N. Kabanov, *Kinetics of Electrode Processes*, Moscow, 1952, p. 207.

2. Y. P. Gokhshtein, A. Y. Gokhshtein, Proc. Second Intern. Congress of Polarography, Cambridge, August 1959.

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