# POLAROGRAPHY OF ARSENIC

## III. NATURE OF THE MAXIMA ON THE POLAROGRAMS OF ACID SOLUTIONS OF TRIVALENT ARSENIC

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Depending on the acid concentration, up to three different maxima, rarely observed simultaneously, appear on the polarogram of As(3+). The middle maximum called the basic maximum, has the greatest height at an acid concentration of 1-3 N. It decreases both when the acid concentration is increased and when it is reduced. It has been proposed that the liberation of hydrogen is catalyzed by nondissociated molecules of arsenous acid $HAsO_2$. The drop in the current is associated with exhaustion of $HAsO_2$ in the layer of solution near the electrode as a result of reduction to $AsH_3$. The disappearance of the basic maximum in strongly acid solution is due to the conversion of $HAsO_2$ to $As^{3+}$ cations. Direct experiments have shown that neither elementary arsenic nor arsine catalyzes the liberation of hydrogen in the range of potentials of the basic maximum.

The second wave of trivalent arsenic in acid solutions contains little-studied maxima. It is known only that one of them is eliminated by introducing surface-active substances into the solution, such as gelatin and methylene blue [1]. Information useful to establish the nature of the maximum is to be found in the studies of Khlopin [2-5], in which the liberation of gaseous hydrogen at the potentials of the maximum is described, and the absence of movements of the solution close to the drop is noted. Consequently, this phenomenon is not related to the so-called polarographic maxima, and it should be ascribed to the catalytic evolution of hydrogen. It remains unclear what valence state of arsenic catalyzes the discharging of hydroxonium ions. And yet, the maximum of arsenic can be used for analytical purposes, and a knowledge of the principles of its appearance is essential for finding the optimum conditions for analytical determinations.

In the first communication of this series [6] it was already noted that the catalytic activity can be associated in principle with any of the following trivalent states of arsenic: with the original trivalent arsenic, with elementary arsenic, arising as a result of the secondary reaction of As(3+) with $AsH_3$, and with arsine [6, 7].

This communication presents the results of some experiments conducted to attempt to establish the nature of the catalytically active state of arsenic. The experimental procedure was as before [6, 7].

## RESULTS AND DISCUSSION

The shape and position of the maxima depend greatly on the acid concentration, just like the reduction waves of trivalent arsenic themselves. Figure 1 shows a series of polarograms of As(3+) of constant concentration in the presence of various contents of sulfuric acid, beginning with an almost neutral solution without additions of sulfuric acid and ending with highly concentrated solutions of ~30 N sulfuric acid. A qualitatively analogous picture is observed in solutions of other mineral acids (HCl, $HClO_4$, $HNO_3$, $H_3PO_4$), but precisely sulfuric acid is taken as an illustration, since in this case the maximum variations of the acid concentration are possible.

Figure 1 shows that in weakly acid solutions (curve 2-4) and in the most highly concentrated solutions of sulfuric acid (curves 16-17) there are no maxima. When small quantities of sulfuric acid are introduced into the

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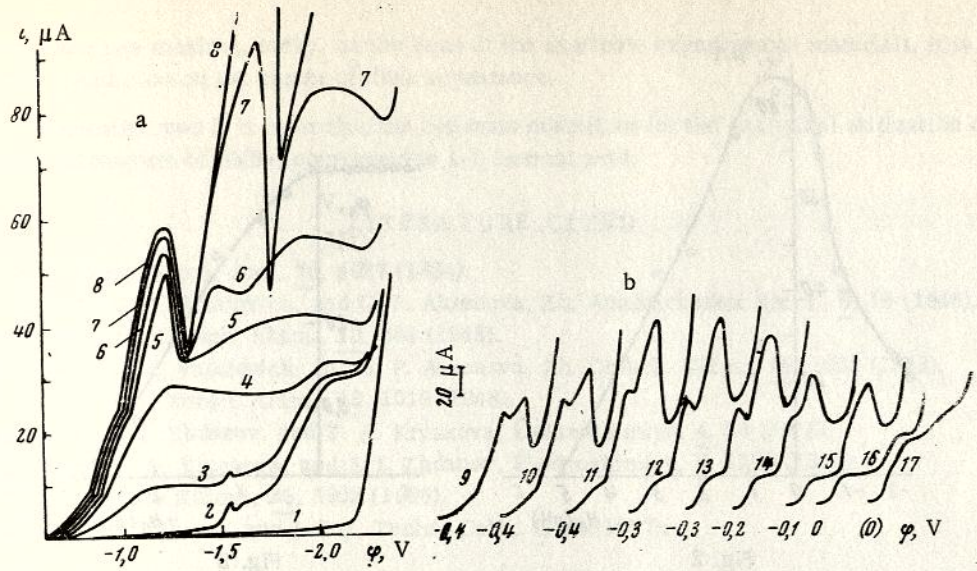



Fig. 1. Influence of the sulfuric acid concentration on the polarogram of trivalent arsenic, $10^{-3}$ M: a) $H_2SO_4$ concentration: 1 and 2) 0; 3) $8.84 \cdot 10^{-4}$; 4) $2.56 \cdot 10^{-3}$; 5) $4.13 \cdot 10^{-3}$; 6) $5.6 \cdot 10^{-3}$; 7) $8.26 \cdot 10^{-3}$; 8) 0.0106 N. 1) Background (0.1 N $Li_2SO_4$). Curves 1-8 are superimposed along the potential axis; b) $H_2SO_4$ concentration: 9) 0.089; 10) 0.28; 11) 0.815; 12) 3.0; 13) 5.0; 14) 9.2; 15) 12.3; 16) 18.0; 17) 32 N. Curves 12-17 are corrected for viscosity of the solution (the currents are increased $\sqrt{\eta}$ times). The initial potential is shown next to each curve.

initial, almost neutral solution of $Li_2SO_4$, a new wave arises, corresponding to the reduction of nondissociated molecules of arsenous acid [6] (curves 3-7, Fig. 1). Since hydrogen ions are required in this process, at the potentials of the limiting current of the new wave, an almost neutral medium is preserved close to the electrode; under these conditions a maximum does not arise. If, however, more sulfuric acid is added than is needed for the reduction of arsenous acid (this is evident from the appearance of the current of discharging of excess hydrogen ions at more negative potentials), then a maximum arises (curves 5-15). From this it may be concluded that either the catalyst lowers the overvoltage of the discharging of hydrogen ions and does not catalyze the discharging of water molecules, or the catalyst arises only in the presence of excess hydrogen ions in solution.

Depending on the acid concentration, three different maxima are observed on the polarogram of As(3+). Thus, on curves 6-8 there are already two maxima, the second of which rapidly becomes immeasurably great with increasing acid concentration, and for this reason is not visible on curves 9-15. Within the interval of $H_2SO_4$ concentrations 0.05-5 N, together with the maximum remaining on the polarogram, which we shall henceforth call the basic maximum, still another maximum of lower height is visible, situated at more positive potentials. The basic maximum disappears last when the acidity is further increased.

In a consideration of the causes of the appearance of maxima, it is also necessary to understand the principles relating the height and potential of the maximum to the acidity of the solutions. Figure 2 shows the dependence of the catalytic current in the basic maximum on the acidity function of sulfuric acid solution [8] (and on the pH in dilute solutions). The value of the catalytic current was found by deducting the diffusing limiting current of As(3+) in an almost neutral solution (curve 2 in Fig. 1) from the total current at the potential of the basic maximum, which was corrected for the change in the viscosity ($\eta$) of the solution by multiplying the measured value by $\sqrt{\eta}$. In this case two inaccuracies are introduced. Although the correction of the diffusion current by this method is justified, the correctness of this law for the catalytic current is not obvious. Moreover, in this method of determining the catalytic current, we do not consider the change in the diffusion coefficient of the discharging particle when its structure changes, i.e., in the transition from $AsO_2^-$ in weakly acid solutions (practically neutral) to $HAsO_2$ and $As^{3+}$ in acid and strongly acid solutions [6]. This is done for the reason that there is no other possibility, while a more accurate determination of the law is not essential.

Figure 2 shows that the catalytic current increases rapidly when the sulfuric acid concentration is increased to 1 N, while after 3 N it also decreases rapidly and disappears entirely in approximately 20 N $H_2SO_4$. If the increase in the catalytic current is determined primarily by the increase in the activity of hydrogen ions, its decrease must be related to some other factor.

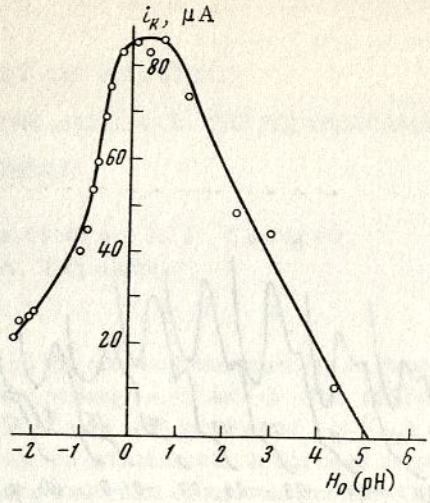



Fig. 2

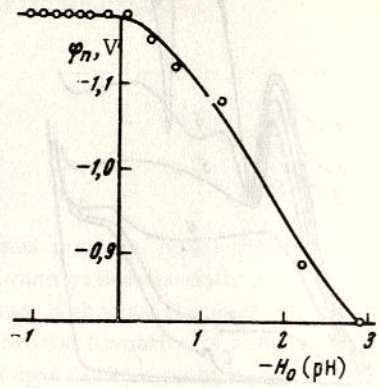



Fig. 3

Fig. 2. Dependence of the catalytic current in the basic maximum on the pH in weak solutions of $H_2SO_4$ and on the acidity function $H_0$ in concentrated solutions of $H_2SO_4$.

Fig. 3. Dependence of the potential of the basic maximum on the pH and $H_0$ of solutions of sulfuric acid.

Figure 3 shows the dependence of the potential of the basic maximum on the acidity function of the medium. The values of the potentials were corrected for the values of the diffusion potentials of the boundary saturated calomel electrode – x N $H_2SO_4$ [9]. Up to 1 N $H_2SO_4$, the potential of the maximum is practically independent of the acidity of the medium, while at a higher acidity it is sharply shifted in the anodic direction. Let us recall that the dependence of the half-wave potential of the first wave of As(3+) on the surface acid concentration also undergoes a substantial change in the same interval of $H_2SO_4$ concentrations, which has been attributed to the appearance of $As^{3+}$ cations [6]. The data presented may be explained if nondissociated molecules of arsenous acid $HAsO_2$ possess catalytic activity. Actually, the hump-like shape of the wave of the catalytic evolution of hydrogen with decreasing current may be associated with exhaustion of $HAsO_2$ in the layer near the electrode as the cathodic potential is increased. The decrease in the catalytic current in concentrated solutions of $H_2SO_4$ is easily explained by a decrease in the concentration of $HAsO_2$ as a result of their transition to $As^{3+}$ ions and a sharp facilitation of their reduction. For the same reason, the potential of the maximum is also rapidly shifted in the anodic direction under these conditions (Fig. 3).

We attempted to verify the catalytic activity of other states of arsenic (As and $AsH_3$) by direct experiments. In one of them a solution in 1 N $HClO_4$ was saturated with gaseous arsine, which was produced according to the reduction of As(3+) by metallic magnesium in hydrochloric acid. The polarograms of 1 N $HClO_4$ are entirely uniform in the cathodic portion before saturation and after saturation with arsine. The wave of arsine arises in the anodic portion.

In another experiment we attempted to detect catalytic activity of elementary arsenic. Suspensions of arsenic in 1 N $HClO_4$ were prepared by mechanical grinding of metallic arsenic. The arsenic powder was introduced directly into the cell. Most of the arsenic powder settled, but the finest fractions did not have time to settle, and its particles were in contact with a dropping mercury electrode. The polarogram of such a suspension contains waves and a maximum of As(3+), which appears in the solution as a result of the dissolution of arsenic oxide from the surface of the arsenic particles. Under these conditions the maximum of arsenic is not increased, i.e., it has the same height as though there were no elementary arsenic in the cell. If we measure the polarogram while mixing the suspension with gas, then all the currents increase, and although the current at the maximum increases to a somewhat greater degree than the diffusion limiting current, it does not increase so much as to conclude that this occurs precisely as a result of catalysis of the liberation of hydrogen by elementary arsenic. This experiment was also conducted in the following way. Elementary arsenic was produced in an atmosphere of inert gas directly in the cell according to the reaction of As(3+) with $AsH_3$. As this reaction proceeds, the waves of As(3+) and the maximum decrease almost to total disappearance. Thus, the catalytic action of elementary arsenic also could not be detected, which substantially confirms the hypothesis of catalysis of the liberation of hydrogen by arsenous acid.

As for the other two maxima, today, on the basis of the available experimental materials, it is difficult to draw any definite conclusion on the causes of their appearance.

From the aforementioned it is clear that the optimum conditions for the analytical utilization of the basic maximum on the polarogram of As(3+) correspond to 1-3 Normal acid.

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