POLAROGRAPHY OF ARSENIC

II. VERIFICATION OF THE MECHANISM OF THE REDUCTION OF TRIVALENT ARSENIC

E. G. Vasil'eva, S. I. Zhdanov, and T. A. Kryukova

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The formation of arsenide ions in the reduction of As(3+) in neutral solutions was demonstrated by the method of latent limiting currents. As a result of the formation of water-insoluble arsenides, the additivity of the reduction waves of As(3+) and ions of di- and trivalent metals (Cd^{2+}, Zn^{2+}, In^{3+}), when they are present together, is disrupted. The waves of Tl^{+} and As(3+) are additive, which indicates solubility of the thallium arsenide formed. In acid solutions the waves of Cd^{2+} and As(3+), as well as Hg^{2+} and As(3+), are additive. This is evidence that on the first wave of As(3+), mercury arsenide is formed as a result of a reaction with metallic mercury, and not with the Hg^{2+} and Cd^{2+} ions introduced into the solution. Experiments with a Kalousek switch indicated that mercury arsenide does not give any waves of "reverse" processes, which may be treated as a result of equality of the currents of reduction of mercury ions and oxidation of the components, contained in the mercury arsenide molecule. These same experiments have shown that arsine, detectable by the reaction with $AgNO_3$ according to the anodic wave corresponding to it, arises in acid solutions on the second wave of As(3+).

To select one of the two possible mechanisms of the reduction of As(3+) in acid solutions, experiments on preparative electrolysis at the potentials of the first wave of As(3+) were the deciding factor. In moderately acidic solutions (0.1 N), gaseous arsine is the product of electrolysis. The mechanism proposed in the previous communication is thereby confirmed. In strongly acid solutions (10 N), during electrolysis a mixture of arsine and elementary arsenic, arising as a result of a secondary chemical reaction of arsine with arsenite, is obtained.

The production of elementary arsenic is promoted by conditions accelerating the reaction of arsine wth arsenite (high temperature and increased concentrations of acid), prolonged electrolysis (low current densities), and conditions leading to an increase in the arsine concentration.

For analytical purposes, especially in the analysis of mixtures of As(3+) with certain di- and trivalent metals, acid solutions are convenient.

In our previous communication [1], we proposed a new scheme of the reduction of trivalent arsenic in acid solutions on a dropping mercury electrode. Under these conditions two waves of equal height are observed, which correspond to the summary transfer of six electrons:

$$As(3+) + 6e \rightarrow As(3-). \quad (1)$$

We have proposed that the doubling of the wave of As(3+) is associated not with the stepwise reduction of As(3+) to the elementary state and to arsine (at more negative potentials), as was believed, but with the anodic dissolution of mercury in the presence of an arsenide ion arising on the electrode. In accord with this scheme, a cathodic process (1) and anodic oxidation of mercury (2) proceed simultaneously at the potentials of the first wave:

$$3Hg + 2As(3-) = Hg_3As_2 + 6e \quad (2)$$

The summary reaction may be represented by the equation:

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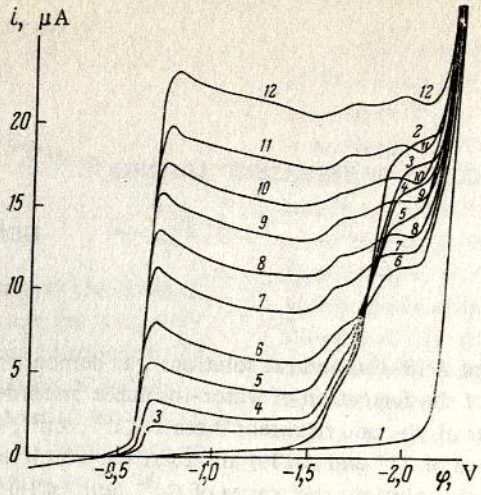


Fig. 1

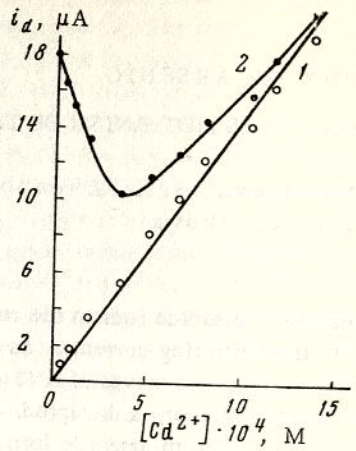


Fig. 2

Fig. 1. Influence of additions of Cd^{2+} on the polarogram of trivalent arsenic against a background of 0.1 M LiCl (1). Li_3AsO_3 concentration $5 \cdot 10^{-4}$ M. Cd^{2+} concentration: 2) 0; 3) $4.7 \cdot 10^{-5}$; 4) $9.3 \cdot 10^{-5}$; 5) $1.83 \cdot 10^{-4}$; 6) $3.53 \cdot 10^{-4}$; 7) $5.1 \cdot 10^{-4}$; 8) $6.6 \cdot 10^{-4}$; 9) $8.0 \cdot 10^{-4}$; 10) $1.05 \cdot 10^{-3}$; 11) $1.17 \cdot 10^{-3}$; 12) $1.38 \cdot 10^{-3}$ M.

Fig. 2. Dependences of the limiting current of Cd^{2+} at the potential of the limiting current of As(3+) (1) and summary limiting current of Cd^{2+} and As(3+) at the same potential (2) on the Cd^{2+} concentration at a constant concentration of As(3+) (according to the data of Fig. 1).

$$2As(3+) + 3Hg + 6e \rightarrow Hg_3As_2 \qquad (3)$$

At more negative potentials, Eq. (2) stops, and only Eq. (1) takes place.

The concepts of a stepwise reduction of trivalent arsenic, as has already been noted [1], contradict the data on preparative electrolysis of solutions of As(3+). Elementary arsenic is obtained only in the case of prolonged electrolysis (at low current densities). In accord with the new scheme, it arises as a result of a secondary slow chemical reaction:

$$As(3+) + As(3-) \rightarrow 2As. \qquad (4)$$

The experimental data supporting the new scheme were cited in our first communication. In this communication we cite the results of a supplementary verification of the proposed mechanism. Three methods were used for this purpose. The first is based on the disturbance of additivity of the reduction currents of As(3+) and heavy metal ions in the case of their joint presence as a result of the formation of arsenides of these metals, i.e., on the phenomenon of latent limiting currents [2-4]; the second is based on measurements with a Kalousek switch [5], permitting an identification of the reaction products according to the anodic waves of their oxidation; the third is based on preparative electrolysis with identification of the products.

The experimental technique was the same as in our previous communication, with the exception that the polarograms were recorded with an LP-60 electronic polarograph. Measurements with a Kalousek switch were conducted using a relay of new design [6].

EXPERIMENTAL RESULTS

I. Latent Limiting Currents

1. Neutral Solutions. In neutral solutions trivalent arsenic is reduced to arsine [Eq. (1)]. Therefore, the reduction currents of heavy metal and arsenic ions when they are both present together will not be additive under these conditions if arsine rapidly forms a water-insoluble arsenide with the heavy metal ions. To test this hypothesis we investigated the joint reduction of arsenide with Cd^{2+}, Zn^{2+}, In^{3+}, and Tl^{+} ions. It is known that cadmium, zinc, and indium arsenides are practically insoluble in water; we have been unable to find any information on the solubility of thallium arsenide.

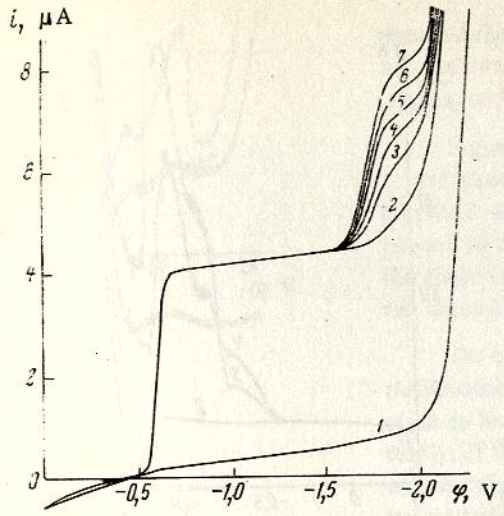


Fig. 3

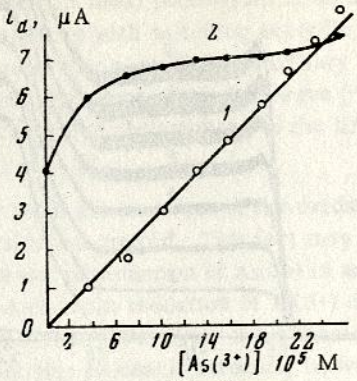


Fig. 4

Fig. 3. Influence of additions of As(3+) on the polarogram of Cd^{2+} against a background of 0.1 M LiCl (1); Cd^{2+} concentration $2.5 \cdot 10^{-4}$ M; As(3+) concentration: 2) 0, 3) $3.7 \cdot 10^{-5}$, 4) $7.1 \cdot 10^{-5}$, 5) $1.3 \cdot 10^{-4}$, 6) $1.9 \cdot 10^{-4}$, 7) $2.6 \cdot 10^{-4}$ M. Gelatin (0.01%) was introduced into the solution to suppress the maxima on the wave of Cd^{2+} (see Fig. 1).

Fig. 4. Dependences of the limiting current of As(3+) (1) (individual measurement) and the summary limiting current of As(3+) and Cd^{2+} on the concentration of As(3+) at a constant concentration of Cd^{2+} (according to the data of Fig. 3).

Figure 1 shows polarograms of solutions simultaneously containing arsenic and cadmium; the arsenic concentration was maintained strictly constant, while the cadmium concentration was increased (from curve 2 to curve 12). It is evident that the first additions of cadmium produce an appreciable decrease in the summary limiting current of cadmium and arsenic as a result of its increase, required by the additivity of the currents. Only in the presence of sufficiently large concentrations of cadmium does the decrease in the summary current cease, giving way to an increase in it.

Figure 2 presents a graph of the dependence of the summary limiting current on the cadmium concentration, constructed according to the data of Fig. 1. From Fig. 2 it is distinctly evident that the limiting currents of As(3+) and Cd^{2+} and are not additive. When the cadmium concentration is increased, the summary limiting current decreases, passes through a minimum, and again increases; moreover, under these conditions its value approaches the limiting current of cadmium alone.

Figures 3 and 4 correspond to the case when the cadmium concentration remained constant, while the arsenic concentration was increased. These data also distinctly reflect the interaction of the reduction product of trivalent arsenic with cadmium ions, leading to a decrease in the flux of cadmium ions to the electrode. Analogous data were obtained in an investigation of the joint reduction of Zn^{2+} and As(3+), as well as In^{3+} and As(3+).

In contrast to these cases, the reduction currents of Tl^{+} and As(3+) are entirely additive (Fig. 5). Consequently, thallium arsenide is sufficiently readily soluble in water, and the flux of thallium ions to the electrode is not reduced when thallium arsenide is formed.

The data presented in Figs. 1-4 cannot be used to find the composition of the arsenides formed according to the theory of latent limiting currents [2-4], since the dependence of the summary limiting current on the cadmium concentration (Fig. 2) or arsenic concentration (Fig. 4) at a constant concentration of the second component is not approximated by any ratio of the stoichiometric coefficients. The cause of this quite probably lies in the fact that the formation of insoluble arsenides leads not only to a decrease in the flux of metal ions, but also to a decrease in the rate of reduction as a result of adsorption and blockage of the electrode surface. The experiment shows that the distortion of the dependence of the summary limiting current on the concentration of one component is manifested to a lesser degree in the presence of more rapid dropping of mercury. This also indicates the presence of adsorption phenomena. It is extremely possible that a significant role is played by the rate of formation of the solid phase.

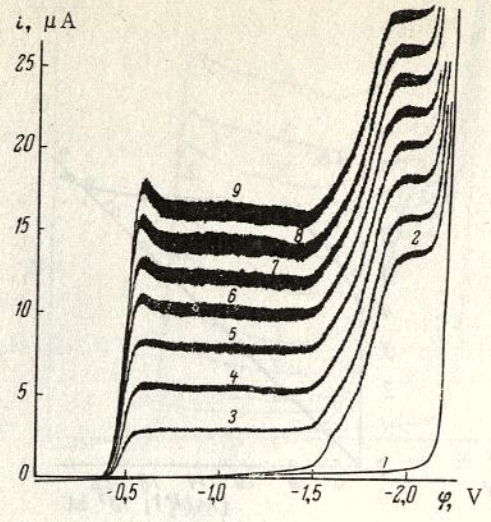


Fig. 5

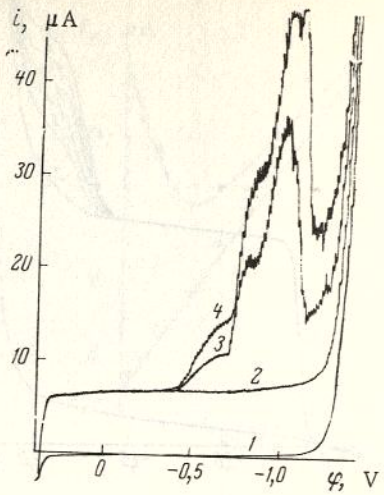


Fig. 6

Fig. 5. Influence of additions of Tl^+ on the polarogram of trivalent arsenic against a background of 0.1 M LiCl (1); Li_3AsO_3 concentration $5 \cdot 10^{-4}$ M; Tl^+ concentration: 2) 0, 3) $1.83 \cdot 10^{-4}$, 4) $3.5 \cdot 10^{-4}$, 5) $5.1 \cdot 10^{-4}$, 6) $6.6 \cdot 10^{-4}$, 7) $8 \cdot 10^{-4}$, 8) $9.3 \cdot 10^{-4}$, 9) $1.05 \cdot 10^{-3}$ M.

Fig. 6. Influence of additions of As(3+) on the polarogram of Hg^{2+} against a background of 1 M Li_2SO_4 and 1 N H_2SO_4 (1); Hg^{2+} concentration $1 \cdot 10^{-3}$ M; As(3+) concentration: 2) 0, 3) $3.5 \cdot 10^{-4}$, 4) $6.7 \cdot 10^{-4}$ M.

Under the conditions of formation of insoluble arsenides, maxima or irregular outbreaks of current are frequently observed on the polarograms, which are also encountered in an investigation of the behavior of suspensions of solid insoluble substances on the electrode [7]. These experiments indicate with a high degree of reliability that As(3-) is formed in the reduction of As(3+) in neutral solutions.

2. Acid Solutions. In the joint reduction of heavy metal and trivalent arsenic ions in acid solutions, in accord with the new scheme [1], two cases might be realized in principle, depending on the fate of As(3-). If mercury arsenide is formed according to the reaction with mercury ions (Fig. 2), then the currents of the reduction of the heavy metal and arsenic ions will be entirely additive. If, however, an arsenide of the heavy metal introduced into a solution of trivalent arsenic, for example, the same mercury or Cd^{2+}, is formed,

$$3Hg^{2+} + 2As(3-) \rightarrow Hg_3As_2 , \qquad (5)$$

then the stepwise character of the reduction of As(3+) should disappear, and the additivity of the currents will be disrupted. The currents should also be additive if the concepts of stepwise reduction of As(3+) in acid solutions are correct. Therefore, the second case (disruption of additivity of the waves) would be significant for diagnosing the mechanism.

The experiments show that the reduction currents of Hg^{2+} and As(3+) ions (Fig. 6), as well as Cd^{2+} and As(3+), are entirely additive. The limiting currents of arsenic in the presence of mercury ions are equal in magnitude to the limiting currents of arsenic in the absence of mercury ions (in an individual measurement). Consequently, the first case is realized, and the Hg^{2+} or Cd^{2+} ions do not enter into a reaction with As(3-). In the presence of Hg^{2+} ions as well, mercury arsenide is formed only during the anodic dissolution of metallic mercury. Consequently, from these data it still cannot be established according to which of the two mechanisms the reaction occurs.

II. Experiments with a Kalousek Switch

In experiments with a Kalousek switch, schemes III and IV were accomplished, in accord with the notations in [8]. The auxiliary constant potential was selected in such a way that it corresponded to the limiting current of the first or second wave of arsenic in the case of scheme III or the maximum positive value for scheme IV. The basic potential was slowly varied, as in the recording of the usual polarograms; moreover, the current was recorded during switching to the basic potential in scheme III or to the auxiliary potential in scheme IV. This current rep-

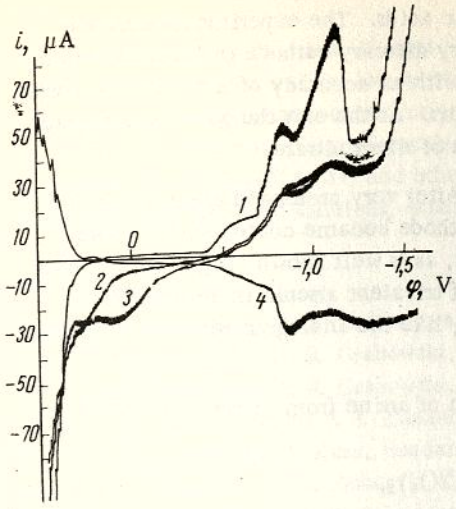


Fig. 7. Usual polarogram (1) and polarograms with switching according to Kalousek (2-4); $9 \cdot 10^{-4}$ M As(3+) against a background of 3 N H_2SO_4; 2) scheme III– auxiliary potential −0.65 V; 3) scheme III– auxiliary potential −1.0 V; 4) scheme IV – auxiliary potential +0.1 V.

resented the current of the reverse reaction of the product, which was obtained in the case of switching to the auxiliary potential (Hg_3As_2 on the first wave and AsH_3 on the second).

Figure 7 shows the usual polarogram of an acid solution (curve 1) and three polarograms with switching according to Kalousek (curves 2-4). In recording curve 2, the auxiliary potential corresponded to the limiting current of the first wave (−0.65 V), while in the recording of curve 3 it corresponded to the limiting current of the second wave (−1.0 V).

On curve 2 there are no waves of the oxidation of the reduction products of trivalent arsenic. This fact may correspond in principle to both schemes of reduction of As(3+) in acid medium. Actually, if the product of the reduction of As(3+) on the first wave is elementary arsenic, then most likely there should not be a wave of its oxidation, since this process is evidently irreversible. If, however, the product is mercury arsenide, then in the case of switching to the basic potential, both components of this compound will undergo electrode conversions with the participation of an equal number of electrons:

$$3Hg^{2+} + 6e \rightarrow 3Hg \quad (6)$$

$$2As(3-) \rightarrow 2As + 6e \quad (7)$$

$$\overline{Hg_3As_2 \rightarrow 3Hg + 2As} \quad (8)$$

so that the summary current will be equal to zero. Consequently, in this case no conclusion can be drawn on the nature of the reduction product of As(3+) from the absence of an oxidation current.

Curves 3 and 4 show the anodic wave of a product with half-wave potential about −0.05 V (saturated calomel electrode), arising on the second wave of As(3+), i.e., AsH_3. A wave with $E_{1/2}$ = +0.38 V (converted to the saturated calomel electrode) corresponds to the oxidation of AsH_3 in neutral medium according to the data of Vašak [9]. We should mention that this wave is situated very close to the anodic oxidation potential of mercury. If this wave corresponded to the oxidation of AsH_3, then in acid medium its $E_{1/2}$ would be even more positive, i.e., the wave generally would be impossible to observe. Vasak's assertion that this wave corresponds to oxidation with the participation of eight electrons is also incomprehensible. Therefore, in contrast to Vasak, we ascribed the wave observed in an experiment with a Kalousek switch to a different process, namely:

$$3Hg + 2AsH_3 \rightarrow Hg_3As_2 + 6H^+ + 6e \quad (9)$$

It might seen that the anodic wave should be observed in the same potential interval as the second cathodic wave of As(3+), since, in accord with our scheme, it corresponds to a conversion that in all probability is the reverse of Eq. (2). Actually, however, there is an essential difference between Eqs. (2) and (9). Molecular arsine participates in Eq. (9), while, as has already been proposed [1], Eq. (2) proceeds with the participation of the As(3-) anion. In other words, during switching of the potential from the auxiliary to the basic potential, the arsenide anion has time to react with hydrogen ions. This experiment shows that arsine is formed in acid solutions at the potentials of the second wave of As(3+).

An unexpected result was obtained in an experiment with a Kalousek switch and a neutral solution of trivalent arsenic. Under these conditions, one wave of As(3+) is observed on the usual polarogram, corresponding to a six-electron process, i.e., the reduction of As(3+) to As(3-) [reaction (1)]. On the polarogram recorded with a Kalousek switch [the auxiliary potential corresponded to the limiting current of the wave of As(3+)], there were no anodic waves, although the appearance of an anodic wave of Eq. (2) was expected. The cause of this anomaly is apparently the same as in acid solutions [see Eqs. (2) and (9)].

III. Preparative Electrolysis

Results permitting an unambiguous selection of one of the two possible mechanisms of the electrode processes on the first wave of trivalent arsenic in acid solution to be made were obtained by preparative electrolysis at a constant potential of the limiting current of the first wave. This experiment was conducted in moderately acid (0.1 N)

and strongly acid (10 N) solutions, using special-purity perchloric and sulfuric acids. The experiments were carried out in a polarographic cell. The reduction was conducted on a stationary mercury cathode (a layer of mercury on the bottom of the cell). The reduction potential was strictly controlled (with an accuracy of ±3 mV). A weak stream of inert gas was passed through the solution to mix it during electrolysis. At the exit the gas was analyzed qualitatively for arsine with a piece of paper moistened with a weak solution of silver nitrate.

In strongly acid solutions, arsine was practically not liberated at all. After very prolonged electrolysis (7 h), only a slight darkening of the paper was observed. At the same time, the cathode became coated with a loose, voluminous precipitate of elementary arsenic with a dark brown color, which, as is well known [10], is insoluble in mercury. It might seem that this experiment supports a stepwise reduction of trivalent arsenic in acid solutions. However, elementary arsenic can also be formed according to Eq. (4), which, like the analogous reaction of tellurite with telluride (11), is accelerated in acid solutions.

In moderately acid solutions (0.1 N), sufficiently acid for the liberation of arsine from mercury arsenide (in a long-term experiment) according to the reaction,

$$Hg_3As_2 + 6HClO_4 = 2AsH_3 + 3Hg(ClO_4)_2, \quad (10)$$

but insufficiently acid for Eq. (4) (formation of As) to occur, at the potentials of the limiting current of the first wave there is actually an intensive formation of arsine, while the surface of the mercury cathode remains clear. Consequently, under these conditions the following sequence of reactions takes place:

$$As(3+) + 6e \rightarrow As(3-) \quad (1)$$

$$Hg = Hg^{2+} + 2e \quad (11)$$

$$3Hg^{2+} + 2As(3-) \rightarrow Hg_3As_2 \quad (5)$$

$$Hg_3As_2 + 6H^+ \rightarrow AsH_3 + 3Hg^{2+} \quad (12)$$

$$Hg^{2+} + 2e \rightarrow Hg \quad (13)$$

and the only product is arsine. According to the concepts of stepwise reduction of trivalent arsenic in acid solutions, arsine should arise on the first wave.

The occurrence of Eq. (4) in strongly acid solution has been demonstrated as follows. A mixture of hydrogen with arsine, obtained in a separate vessel by the reduction of As(3+) with metallic magnesium in 1 N HCl, was passed through a solution of As(3+) in 8 N $HClO_4$. An abundant precipitate of elementary arsenic was rapidly isolated from the strongly acid solution.

DISCUSSION OF RESULTS

Thus, we succeeded in showing unambiguously that in acid solutions trivalent arsenic is not reduced in steps on a dropping mercury electrode. As(3-) is formed first.

The shape of the polarograms of trivalent arsenic in acid solutions can also be determined in principle by the rates of the chemical reactions (10) and (4). Both these reactions are accelerated when the acid concentration is increased. In strongly acid solutions, within the interval of potentials of the first reduction wave of As(3+), the final product [considering Eqs. (10) and (4)] may be elementary arsenic (if it is not further reduced at some distance from the electrode under the conditions of its formation). But in this case also the height of the wave, as before, will correspond to the transfer of three electrons per As(3+) particle. If, however, elementary arsenic is reduced further (at least partially), or if only Eq. (10) takes place, then in strongly acid solutions the first wave should rise somewhat at the expense of the second (i.e., at a constant height of the sum of the two waves). Such a phenomenon is actually observed in concentrated solutions of sulfuric acid. At the potentials of the second wave, Eqs. (1) and (4) can form a catalytic cycle when the following reaction takes place:

$$As + 3e \rightarrow As(3-) \quad (14)$$

However, the experiments show that this does not occur all the way up to the highest sulfuric acid concentrations. The cause of this may be the slowness of Eq. (14) (if it takes place at all under the conditions of polarography). Moreover, if this reaction did occur at an appreciable rate, elementary arsenic could not be accumulated under the conditions of preparative electrolysis.

On the basis of the experimental data presented, we can formulate conditions that should promote the production of elementary arsenic by electrolysis of acid solutions of As(3+). Since elementary arsenic is obtained as a

result of a secondary reaction (4), this process should be promoted by increased temperature and an increase in the acid concentration, as well as low current densities (prolonged electrolysis). It should also be mentioned that experiments on the simultaneous reduction of trivalent arsenic and other metals facilitate the selection of conditions for analytical determinations of metals and arsenics by a polarographic method when both are present. Since in most cases the waves of As(3+) and other metals are nonadditive in neutral solutions, while they are additive in acid solutions, precisely acid solutions, especially sulfuric acid solutions, are convenient for analytical determinations.

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