THE REDUCTION OF ARSENIC ACID AND ARSENATES TO ARSINE AT THE MERCURY CATHODE. PART I.

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The electrolytic reduction of arsenates and arsenites has been thoroughly investigated by a number of authors[1] from the analytical standpoint. In these investigations, the quantities involved in the reduction were small, fractions of a milligram of elemental arsenic; it has been shown by many workers[2] that the mercury electrode gives the best results. It has been suggested by Sand and Hackford[1] and by Harkins[3] who used the Marsh method that the efficiency of this electrode is partially due to its cathodic overpotential. Thomson[1] considered the efficiency of reduction independent of overpotential and current density. The influence of current density in the literature has been considered of no importance, and in fact has not in most cases been mentioned.

The present work was undertaken to discover the potential changes which take place at mercury and other electrodes during the reduction in acid solutions of varying concentration with respect to arsenic content, the relation between current density and reduction capacity, and the effect of the addition of metallic salts to the electrolyte upon the yield of arsine.

The majority of the solutions used contained quantities of elemental arsenic in the quinquevalent state which were much greater than have been examined before, namely from 13·8 mg. to 82·6 mg.

Experimental.

The electrolytic cell was a porous pot of 50 c.c. capacity and contained in all the experiments 40 c.c. of electrolyte. This was closed with a rubber stopper, through which passed two tubes, one to admit hydrogen when necessary and the other to carry off the products of electrolysis. In the centre of the stopper was fitted a cork, through which passed the tube which allowed the arsenic solution to pass to the cathode and also the tube carrying the mercury, as shown in Fig. 1. The cork was used so that in closing the cell, the relative position of the capillary and the surface of the mercury would remain unaltered. The mercury was held in a cup at the end of the tube. The anode was platinum gauze stretched around the pot on the outside. The pot was placed in a beaker of 50 c.c. capacity. The electrolytic gas was led from the cell through an inch of water in a test

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[1] Thorpe, *J. Chem. Soc.*, **83**, 974, 1903; Sand and Hackford, *ibid.*, **85**, 1018, 1904; Thomson, *Chem. News*, **99**, 157, 1909, etc.

[2] Ramberg, *Lunds. Univ. Arrskr. N.F.*, (2) **21**, 1, 1918; Aumonier, *J.S.C.I.*, **46**, 341, 1927, etc.

[3] *J. Amer. Chem. Soc.*, **32**, 518, 1910.

tube, so as to rid the gas of acid spray and then into a U tube of neutral calcium chloride, which had been prepared by allowing crystalline calcium chloride to stand in a vacuum desiccator for two days. The quantity of arsine in the gas was determined in three ways :

(*a*) by passing the gas through a heated silica tube of 3 mm. bore,
(*b*) by passing the gas through $N/10$ iodine solution,
(*c*) by passing the gas into an absorption bulb containing $N/4$ silver nitrate solution.

Concordant results were obtained by these methods.

Before each experiment, pure mercury was placed in the cup and the capillary so adjusted as to just touch the surface of the mercury. The test solution containing the arsenic was placed in a small dropping funnel, which led to the mercury surface. Thus the test solution was sprayed on to the cathode for times (referred to later as the " capillary times ") which varied according to the size of the capillary (from 20 to 80 minutes). The cathode was thereby offered good facilities for reducing the arsenic solution.

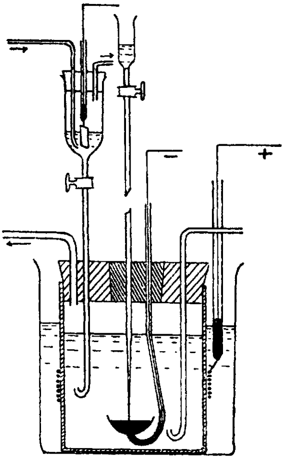

Fig. 1.

Where the commutator method was used for measuring the cathode potential, the cathode was connected alternately, 3000 times a minute, to the source of current and a potentiometer respectively by a rotatory commutator.[4] This enabled the overpotential of the electrode to be determined, measured against a hydrogen electrode working in the same solution.

In the experiments where other metals were used as cathodes, the mercury cup was replaced by a rectangular prism of the metal soldered on to a piece of copper wire, which passed through the cork. The largest face of the cathode was left exposed, the remainder and the copper wire inside the pot being coated with sealing wax. The capillary was pressed against the centre of the exposed face.

Commutator Experiments.

The object of these experiments, in which $2N$ sulphuric acid was the electrolyte and the test solutions were 10 c.c. of $2N$ sulphuric acid containing 20·8 mg. or 82·6 mg. of quinquevalent arsenic, was to determine the potential changes at the mercury cathode during the time when the reduction was taking place, measurement being made every minute.

Observations.—(1) During each experiment the commutator overpotential decreased from the value of that of mercury in $2N$ sulphuric acid, namely 0·920 V. to 0·450 V. (± 40 mV.). The rate of decrease was approximately independent of the rate at which the arsenic flowed on to the cathode. This is shown in Fig 2, which shows the relation between overpotential and time for three experiments, where the test solution was introduced in 35, 19 and 9 minutes respectively. From this it will be seen that a decrease of 0·5 V. is affected in 13, 9 and 8·5 minutes respectively.

(2) It would appear that by this method arsenic is deposited on the mercury surface in sufficient quantity to reduce the commutator over-

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[4] Sand, Grant, and Lloyd, *J. Chem. Soc.*, 378, 1927.

potential to the value of that for an arsenic cathode in the same solution when arsine is being liberated.[5] The decreasing overpotential during the period when the current is interrupted apparently only permits the arsenic acid to be reduced to elemental arsenic.

(3) No arsine was produced when $2N$ sodium sulphate was used as electrolyte. This was surprising in view of the fact that the commutator overpotential of mercury in this solution was found to be very high, 1·54 V. at the commencement of the experiment and 65 mV. higher at the conclusion.

(4) Yields (calculated as weight of arsenic in the gas produced at the electrode in a given time) vary as the concentration of the test solution under the same experimental conditions.

(5) The percentage yields (*i.e.* the percentage of the elemental arsenic in the test solution which is produced as arsine) by the commutator method, *i.e.* with intermittent current, are small when compared with those obtained when uninterrupted current was used. The highest yield was 14·7 per cent. after electrolysis for 78 minutes in $2N$ sulphuric acid.

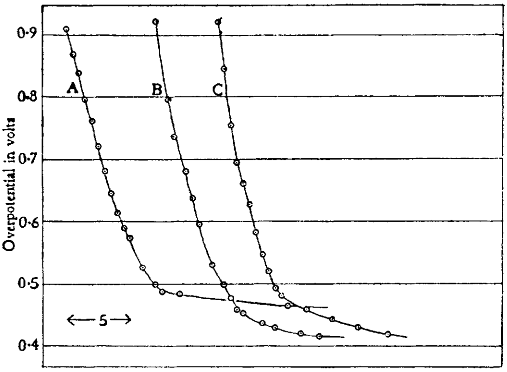

Fig. 2.—Overpotential in $2N H_2SO_4$, with time, test solution containing 8·26 mg. of arsenic as arsenic acid.

Curve A.—35 mins. capillary time.
" B.—19 mins. " "
" C.—9 mins. " "

Experiments with Uninterrupted Current.

(*a*) **Cathodes of Tin, Lead, Amalgamated Tin and Amalgamated Lead.**—These electrodes have high cathodic overpotentials of approximately the same value (1·2 V.), and have the advantage that they can be easily cleaned by scraping. Test solutions containing 180 mg. of elemental arsenic were used. The following observations were made.

(1) The percentage yields were found to be small (6 per cent. at 1350 ma/cm.^{2}), to vary with the current density and to be approximately the same for the four electrodes. There was some deposition of arsenic on the cathodes.

(2) The drop in overpotential during the experiments was smaller than in the case of the commutator experiments, *e.g.*, for amalgamated tin a drop of 235 mV. was noted after 60 minutes electrolysis.

(3) The effect of time on percentage yield is shown in Fig. 3. That the relationship is a linear one is apparently due to there being no considerable reduction in overpotential during the reduction.

(*b*) **The Mercury Cup Cathode.**—In the first place, experiments were conducted where 10 c.c. of test solution containing 20·8 mg. of quinquevalent arsenic were introduced into the pot before electrolysis and also in which similar test solutions were introduced to the surface of the cathode during the electrolysis. The latter method gave larger yields (*e.g.*, the

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[5] *Trans. Faraday Soc.*, **26**, 15, 1930.

yields at 1260 ma./cm.^{2} were 28·8 and 46·3 per cent. respectively), and the former method was abandoned.

The relation between current density and percentage yield of arsine is shown in Table I., 2*N* sulphuric being the electrolyte, 10 c.c. of 2*N* sulphuric acid containing 20·8 mg. of arsenic acid being the test solution and the capillary time 32 minutes.

TABLE I.

C.D. (in ma./cm.^{2}) .	70	280	560	700	840	1000	1120	1260
Percentage Yield .	5·9	15·0	22·5	27·0	33·0	33·4	34·5	32·8

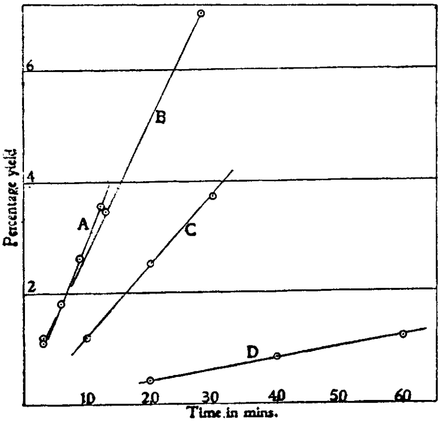

FIG. 3.—Relation between yield and time.
A.—Amalgamated lead at 1350 m.a./s.cm.
B.— ,, tin ,, 1250 ,,
C.— , lead ,, 810 ,,
D.— ,, tin ,, 290 ,,

The yields are approximately proportional to the current density, but at the higher current densities the heat produced during the electrolysis influences the yields.

Using 2*N* and 5*N* sulphuric acid, it was found that the latter electrolyte gave larger yields (32·2 and 48·6 per cent. respectively at 840 ma./cm.^{2}).

To show the effect of concentration of the test solutions upon the percentage yield, 10 c.c. of 5*N* sulphuric acid solutions containing 82·6, 61·9, 41·3, 20·8 and 13·8 mg. of arsenic respectively (in the proportion of 4, 3, 2, 1, 0·6 respectively) were used with a capillary time of 35 minutes at 1260 ma./cm.^{2} The results are shown in Table II.

TABLE II.

Weight of arsenic in 10 c.c. test solution . . .	13·8 mg.	20·8 mg.	41·3 mg.	61·9 mg.	82·6 mg.
Percentage yield . . .	79·5	57·1	51·5	48·8	47·9

It is observed that with increasing dilution of the arsenic acid solution the percentage yield is greater, this being more marked in the solution containing 13·8 mg. of arsenic per 10 c.c.

The reduction in overpotential, measured by the commutator method throughout the current densities used, was the same for the same concentration of arsenic acid in the test solution. The reductions are shown in Table III., the concentrations of the test solutions being stated as mg. of elemental arsenic per 10 c.c. Initially the overpotential of the mercury was 940 mV. and the current density 840 m.a./cm.^{2}

TABLE III.

Concentration of test solution . .	13·8	20·8	41·3	61·9	82·6
Decrease in overpotential in millivolts	100	250	350	450	500

Besides pure sulphuric acid solutions as electrolyte, the following solutions were used: 2*N* sodium sulphate and 2*N* sulphuric acid containing *N*/64 zinc sulphate.

Using $2N$ sodium sulphate as electrolyte, no arsine was produced, although the cathodic overpotential is very high at the value of 1·525 V. This is probably due to the formation of sodium arsenate at the cathode which is apparently not reducible cathodically to arsine.

The addition of zinc sulphate to the sulphuric acid electrolyte produced larger yields of arsine. Varying concentrations of zinc sulphate ($N/4$, $N/16$ and $N/64$ were used) had the same effect upon the yield. Table IV. shows the effect of the addition of zinc sulphate on the yields using 20·8 mg. of arsenic.

TABLE IV.

Electrolyte.	Percentage Yield at 700 ma./cm.^{2}	Percentage Yield at 840 ma./cm.^{2}
$2N$ H_2SO_4 . . .	35·1	69·2
$2N$ H_2SO_4 + $N/64$ $ZnSO_4$	58·6	89·0

At the same time it was observed that the overpotential was initially smaller than when pure sulphuric acid solutions were used (of value 830 mV.) and that the overpotential was not only maintained during the experiment but increased by 50 mV.

In place of pure mercury, some experiments were conducted, using zinc amalgam. This was made by electrolytically depositing zinc on mercury from a zinc sulphate solution till the amalgam contained 1 per. cent. of zinc by weight. The amalgam electrode was found to be more efficient than pure mercury as shown in Table V., and also during the experiments the decrease in overpotential was small, in no case greater than 50 mV. The test solution was 10 c.c. of sulphuric acid containing 20·8 mg. of elemental arsenic.

TABLE V.

C.D. in ma./cm.^{2}	Pure Mercury.	Zinc Amalgam.
840	32·2 per cent.	74·5 per cent.
1000	66·3 ,, ,,	87·0 ,, ,,

The efficiency of reduction, reckoned as percentage of hydrogen involved in the reduction of arsenic pentoxide to arsine during the electrolysis was calculated for all the experiments where pure acid electrolyte was used. Where zinc sulphate was used as well, the hydrogen was collected and the calculation then made. The maximum and minimum limits of the efficiencies are given in Table VI.

TABLE VI.—PERCENTAGE REDUCTION EFFICIENCIES.

Composition of 10 c.c. of Test Solution.	Minimum.	Maximum.
13·8 mg. As in $2N$ H_2SO_4	1·71 per cent.	3·89 per cent.
20·8 mg. ,, ,,	1·89 ,, ,,	7·60 ,, ,,
82·6 mg. ,, ,,	9·20 ,, ,,	14·1 ,, ,,
20·8 mg. ,, $2N$ Na_2SO_4	2·37 ,, ,,	11·12 ,, ,,

Summary and Conclusions.

Experiments have been conducted on the reduction of arsenic acid, using lead, tin, mercury, amalgamated lead and tin cathodes with a view to discover the potential changes involved and the yields of arsine produced. The test solution containing up to 180 mg. of elemental arsenic as arsenic acid has been admitted to the active cathode in periods varying from 20 to 60 minutes.

By a commutator method the overpotential has been shown to decrease by 0·5 Volt to a value representing the overpotential of arsenic, which suggests that some arsenic is deposited on the mercury cathode: analysis of the mercury cathode showed none, and that the quantity there is small is shown by the fact that when put into a pure sulphuric acid solution, the normal cathodic overpotential of mercury is quickly established.

Using uninterrupted current, the decrease in overpotential is found to be less and varies directly with increasing concentration of the arsenic acid in the test solution. In view of this decrease, the reduction of the whole of the arsenic acid in the concentrations used to arsine presents difficulty. Where the electrolyte contained zinc sulphate, the overpotential, although initially lower than that of mercury in pure acid, was maintained and even increased during electrolysis and a bigger yield of arsine was obtained. The decrease in the overpotential of the zinc amalgam cathode was small and the yield of arsine greater.

The efficiency of cathodes for reducing arsenic acid is not dependent on the overpotential alone, lead, tin not being so efficient as pure mercury at the same apparent current densities, although the overpotentials are approximately the same. Further, using a mercury cathode in $2N$ sodium sulphate produced no arsine although the commutator overpotential was very high, $-1{\cdot}525$ Volt. The catalytic action of the material of the cathode is also possibly an important factor.

The reduction is facilitated by increasing the current density, the strength of the acid electrolyte and the time of electrolysis. Also the quantity of arsine produced is larger the greater the concentration of the arsenic acid test solution, although the percentage yield is diminished.

The efficiency of the reduction process, reckoned as the percentage of hydrogen produced at the cathode which is converted to arsine, varied from to 1·71 per cent. to 14·1 per cent. under the best conditions.

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