

THE OVERPOTENTIAL OF ARSENIC AND THE YIELDS OF ARSINE AT AN ARSENIC CATHODE IN ACID SOLUTIONS.

BY WILLIAM VERNON LLOYD, M.Sc., A.I.C.

(Received 16th September, 1929.)

The overpotential of arsenic has been studied by many workers,¹ but in no case has a compact solid arsenic cathode been used. Such a cathode has been used in the present work, which is a continuation of the investigation of the overpotential of the Group 5b elements.²

Experimental.

The experimental arrangements were similar to those used in the previous work on antimony.² Pure arsenic was used for the cathodes and pieces which had comparatively large plane surfaces were specially selected, such surfaces being formed during the purification of the element. Thick copper wire was soldered to these cathodes and only the plane surfaces were left exposed, the wire, solder, and remainder

¹ Grube, *Z. Elektrochem.*, **30**, 517, 1924; Marquis, *J. Amer. Chem. Soc.*, **42**, 1569, 1920.

² Sand, Grant, and Lloyd, *J. Chem. Soc.*, 378, 1927.

16 OVERPOTENTIAL OF ARSENIC AND YIELDS OF ARSINE

of the cathode in the porous pot being covered with sealing wax. The electrolytic gas passed from the pot through two calcium chloride tubes, an empty capillary silica tube suitable for heating, a set of absorption bulbs containing silver nitrate solution and then into a nitrometer.

Various strengths of sulphuric, hydrochloric, phosphoric, oxalic, and tartaric acids were used.

Connection to the hydrogen electrode working in the same solution as that in the porous pot was made by means of a capillary, pressed against the test electrode. The exposed areas of the cathodes were from 0.8 to 1.55 cm.² Except where otherwise stated, the cathode surface was polished with Oakey's Grade F emery paper before each experiment.

Commutator overpotentials were measured by the specially designed commutator, which has been described (*loc. cit.*) and by the Whetham commutator, which gave average overpotentials corresponding to an interval of 0.0059 second after interruption of the polarising current.

Results.—A. The Overpotential of Arsenic.

From an examination of the values obtained in acid electrolytes the following are to be noted:

1. The overpotentials by the commutator methods are not so reproducible as those of antimony and bismuth. Under similar conditions, variations of as much as ± 3 centivolts were noted. This is apparently due to the influence of the formation of Arsine.

2. The overpotentials produced by initial polarisation by currents corresponding to low current densities reach high values which are not

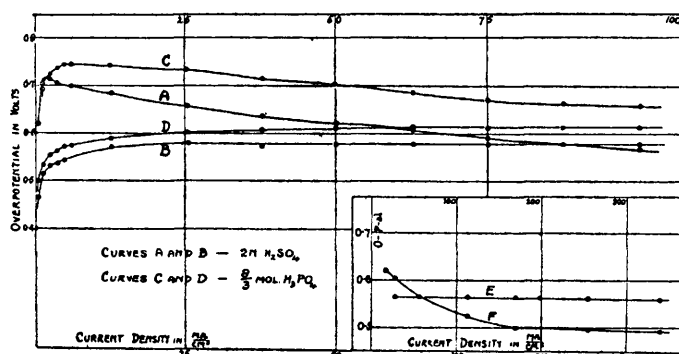


FIG. 1.

maintained at higher current densities, indicating a high state of supersaturation at the cathode at the low current densities used. Such high overpotentials were obtained by initial polarisation with a current corresponding to a current density of 0.2 ma./cm.² after a period of one hour's electrolysis, but not produced by electrolysis at a current corresponding to 8.0 ma./cm.² Fig. 1(a) shows the relation between commutator overpotential and current density for two typical examples. Curves A and B refer to 2N H₂SO₄ and C and D to 4/3 molar H₃PO₄ solutions, A and C showing the high state of supersaturation at low current densities and the decrease in commutator overpotential with increasing current density. Curves B and D, obtained by initial polar-

isation at a current density of 8 ma./cm², are similar to those always obtained by the commutator method for antimony² and bismuth³ where a maximum overpotential is maintained over a wide range of current densities.

3. This constant maximum commutator overpotential (as in the cases of antimony and bismuth) decreases slightly for the highest current densities used, this decrease having been ascribed to heating effects. This decrease for current densities varying from 25 to 150 ma./cm.² was but a few millivolts for all solutions.

4. The maintenance of this maximum commutator overpotential is dependent on whether arsine is being produced at the cathode. When arsine is produced (conditions for which are shown below) there is a very appreciable decrease in the commutator overpotential with increasing current density, as is shown in Fig. 1(b) for 4*N* H₂SO₄ solution. Curve *E* shows a decrease of a few millivolts over a range of from 28 to 336 ma./cm.² when no arsine is being evolved and curve *F* the considerable decrease when the hydride is being formed.

5. Unsteadiness was noted in the potentiometric readings and in the polarising current as shown by the ammeter when the evolution of arsine occurred.

6. A longer period is required to obtain the maximum constant overpotential at any current density, when electrolysis is initially started, than in the cases of antimony and bismuth, 45 to 60 minutes being necessary.

7. The average commutator overpotential, where there is no high degree of supersaturation and no arsine is being evolved, is in acid solutions 0.6 volts approximately: this value corresponds to the average polarisation during an interval of 0.0059 second after the interruption of the current.

8. By the special commutator, the "decay" curves shown in Fig. 2 were obtained, when no arsine was being produced electrolytically. These are similar to those found for antimony and bismuth.

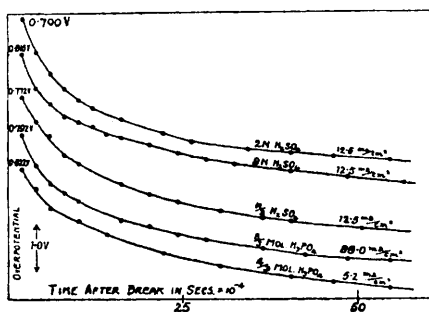


FIG. 2.

B. The Production of Arsine Electrolytically.

During these experiments, three products were formed at the cathode: (a) a slight black suspension, which is probably arsenic; (b) the brown arsenic hydride (AsH₃), and (c) arsine; (b) and (c) are produced at the same time.

Sulphuric, oxalic, tartaric, and hydrochloric acids in varying strengths were used and in the case of the latter, sulphuric acid was used in the anodic compartment outside the pot.

The arsine was estimated by passing the dried electrolytic gas through a silica tube of 3 mm. bore, which was heated to low red heat in two places as far apart as possible, and weighing the arsenic formed by decomposition. The absence of blackening when the gas subsequently

³ *Trans. Far. Soc.*, **25**, 525, 1929.

18 OVERPOTENTIAL OF ARSENIC AND YIELDS OF ARSINE

passed through a silver nitrate solution showed that all the arsine had been decomposed. The arsine was calculated in volume percentage of the total electrolytic gas, 100 c.c. of hydrogen being collected in all cases.

The following results were obtained :

1. When the cathode was polished before an experiment, electrolysis had to be maintained for at least 30 minutes before any appreciable quantity of arsine was produced. The cathode then appeared to break down under the electrical pressure, arsine was evolved and the cathode became pitted and silvery in appearance. For example, at a current density of 336 ma./cm.² 1.5 per cent of arsine was formed electrolytically in 8N H₂SO₄ solution, but after 30 minutes electrolysis in the same solution 16.8 per cent. was obtained. After polishing the cathode again, 1 per cent. was produced.

2. Currents corresponding to current densities of from 262 to 1700 ma./cm.² were employed as continuous current and as current interrupted by the commutator. Both methods gave similar results and approximate percentages are given in Table I., sulphuric acid being the electrolyte.

TABLE I.

Current density .	300	1200	1700 ma./cm. ²
Per cent. yield .	20	50	22

These values are averages of those obtained when the cathode was in the "active" condition. The quantity of brown hydride is greater at the higher current densities. The lower percentage yield at the higher current densities is probably due to the heating of the solution.

3. Neither the particular acid used, nor its strength appears to affect the percentage yield considerably when the cathode is "active," as is shown in Table II.

TABLE II.

Electrolyte .	8N H ₂ SO ₄	4N H ₂ SO ₄	N H ₂ SO ₄	N/4 H ₂ SO ₄	N HCl
Per cent. yield	22.2	17.0	18.5	18.5	18.0

4. The highest percentage yield of arsine was obtained in 4N HCl solution using alternating current by the method described by Sand and Lloyd ⁴ with anodic and cathodic current densities of 44 and 525 ma./cm.² respectively, when a yield of 60 per cent. was obtained.

Summary.

1. The commutator method shows that arsenic when initially polarised at low current densities exhibits a high overpotential not maintained at higher current densities. When no arsine is being formed, a maximum overpotential is obtained as in the cases of antimony and bismuth.

2. With continued electrolysis, an arsenic cathode passes into an "active" state when arsine is evolved. In this "active" state, a considerable decrease is noted in the maximum commutator overpotential with increasing current density.

3. For sulphuric, hydrochloric, phosphoric, and tartaric acids the percentage of arsine produced electrolytically at a given current density is approximately independent of the acid used, and of its strength.

The author wishes to express his thanks to Dr. Sand for his interest and advice during the course of this work.

⁴ *J. Chem. Soc.*, 2971, 1926.