also shifts the half-wave potential of tellurium from its normal value of -1.20 v. to nearly -1.4 v. With relatively small amounts of lead a maximum appears at the normal half-wave potential of the tellurium, but this fades out as the relative concentration of lead is increased. This shift of the half-wave potential of the tellurium is probably connected with the production of hydroxyl ion both by reaction 10 and by the reduction of hydrogen plumbite ion, $HPbO_2^- + H_2O + 2e^- = Pb + 3OH^-$, which results in a much larger concentration of hydroxyl ion at the electrode surface than in the body of the solution.

Summary

The polarographic characteristics of the +4 oxidation states of selenium and tellurium have been investigated over a wide range of *p*H and other conditions, and systematic data have been obtained for half-wave potentials and diffusion current constants. The reduction states of the various waves observed have been established conclusively by the coulometric analysis technique based on controlled potential electrolysis with a large mercury cathode.

In strongly acid medium and in buffered solutions above *p*H 8 the reduction of selenium(IV) proceeds all the way to the -2 state, but in buffered solutions of *p*H between 3 and 7 reduction stops at the elemental state.

In buffered solutions of *p*H between 0.4 and about 11 reduction of tellurium(IV) proceeds only to the element, but the wave observed in sodium hydroxide solutions does result from complete reduction to the -2 state.

The multiplicity of waves observed with both elements at low and intermediate *p*H values results from a combination of several factors, including reductions of the several ionization species of selenous and tellurous acids and the production of films of the elements on the surface of the dropping electrode. In the case of selenium one of the waves is a cathodic reflection of the anodic wave of selenide ion. No evidence of reduction to the +2 state has been obtained with either element.

The +6 states of selenium and tellurium are not reduced at the dropping electrode under any of the conditions investigated.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Electrolytic Oxidation of Arsenic(III) in Acid Solution[1]

BY WILLIAM MARSHALL MACNEVIN AND GEORGE LLOYD MARTIN[2,3]

This paper reports a study of the electrolytic oxidation of trivalent arsenic in acid solution. The purpose of the investigation was to determine whether conditions could be defined which would produce 100% efficient electrolytic conversion of trivalent to pentavalent arsenic.

Previous investigations of the electrolytic oxidation of As(III)[4,5,6,7,8] have dealt with the industrial preparation of arsenates. Alkaline media have been used almost entirely. One reason for this is that oxidation in excess of the current consumption occurs in alkaline solution if air is in contact with the cathode. Apparent current efficiencies of 150% have been obtained.[9,10] Metal impurities also increase the efficiency in alkaline solution in contact with air.[11]

Aleksyeev[4] reports that oxidation occurs in acid solution with lead dioxide anodes. Aleksyeev also states that a platinum electrode may be used for the oxidation in alkaline solution. The data are, however, insufficient to indicate the maximum efficiency obtainable and the absence of side reactions, or that a platinum electrode can be used in acid solution.

In the work described in the present paper, the effects of *p*H, current density and contact with air on the current efficiency have been determined. As will be seen, the current efficiency is low in the *p*H range 3–11, but quickly increases to 100% in strongly acid solutions.

Experimental

Current Measurement.—The electrolyses were conducted with d. c. current held constant within 1%. The current was measured by balancing the drop in potential across a standard resistance with a potentiometer using a recording galvanometer as a null point indicator. Corrections for the small fluctuations of the current were calculated from the galvanometer record. The time intervals were measured with a stop watch.

The Electrolysis Cell.—The cell for electrolysis was assembled using two 400 ml. beakers sealed together with a 20 mm. tube which had two sintered glass disks sealed into it at the ends. Thus the cell was divided into cathode,

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[1] From a thesis submitted by George Lloyd Martin to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree Doctor of Philosophy.

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[8] O. W. Brown, J. E. Hatfield and J. M. Church, *Trans. Electrochem. Soc.*, **70**, 323 (1936).

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[10] M. Janes, *ibid.*, **77**, 411 (1940).

[11] L. Lowenstein, U. S. Patent 2,375,933, May 15, 1945.

anode and bridge compartments. The bridge, in addition, had two 7 mm. tubes with stopcocks sealed into it. This provided a means of filling the bridge and of keeping it either under slight pressure during a run to prevent diffusion of the solutions from the electrode chambers, or under greater pressure when the anode chamber was being emptied. The bridge was kept filled with saturated potassium sulfate solution throughout the work. The cathode chamber was filled with potassium sulfate solution. A platinum cathode was used. The solution in the anode chamber was stirred steadily to reduce polarization effects. The temperature of the cell during electrolysis was not controlled. A thermometer was kept in the solution and the temperature was noted for each run.

Electrodes.—All oxidations were conducted with sand blasted platinum gauze electrodes of the type supplied for the Sargent–Slomin Electroanalyzer. The large electrode by geometric measurement had an apparent surface of 0.65 sq. dm. The small electrode had an apparent surface of 0.342 sq. dm. Due to the fact that the surfaces were sand blasted, the effective areas of both electrodes were probably larger than these values.

Buffer Solutions and *p*H Adjustments.—Standard buffer solutions were added to the arsenite solution to give the desired *p*H value. In most cases, the change of *p*H during electrolysis was 0.2–0.4 of a *p*H unit. This includes the change due to dilution as well as that due to electrolytic reaction.

All *p*H measurements were made with a Beckman Industrial Model M *p*H meter. The meter was calibrated regularly using standard buffer solutions. For measurement of *p*H values greater than 9.5, a Beckman High *p*H electrode was used.

The Determination of Arsenic(III).—The arsenic(III) was determined by titration with 0.1 *N* ceric sulfate using osmium tetroxide as catalyst and ferroin indicator according to the procedure developed by Gleu.[12] All solutions were made 1 *N* in sulfuric acid before titration. The buffers were shown to have no effect on the titration. The ceric sulfate solution was standardized against Primary Standard Arsenic Trioxide by the same procedure.

The Determination of Arsenic(V).—An adaptation of the method for arsenate given by Kolthoff and Furman[13] was used. This method uses the reduction of arsenate by iodide in acid solution followed by the determination of the iodine formed by thiosulfate titration. Kolthoff and Furman recommended a volume of 30 ml. of 4 *N* acid and 1 g. potassium iodide for 0.1 g. of arsenic pentoxide. The solution must be freed from air with bicarbonate.

The volume limitation could not be conveniently met in the solutions removed from the electrolytic cells. Thus it was necessary to establish the proper conditions for the determination of arsenate in these solutions. The volume used was 100 ml., and it was found that satisfactory results could be obtained by making the solution 6 *N* in sulfuric acid, using 2 g. of sodium carbonate for removing air, adding 6 g. of potassium iodide, and allowing it to stand at least thirty minutes before titrating with thiosulfate. The end-point was determined by adding carbon tetrachloride when the iodine was nearly gone and titrating until the organic layer was colorless.

The Method of Calculating the Current Efficiency.—On all the runs except those in which arsenic(V) was also determined, the current efficiency was based upon the difference between the amounts of arsenic(III) present before and after electrolysis. Stock solutions containing 0.020–0.025 g. arsenic trioxide/ml. were made up and the concentration determined by titration with standard ceric sulfate. Aliquots of these solutions were used for the electrolyses and the amount of arsenic trioxide present at the end was determined by ceric sulfate titration. The difference between the amount of arsenic trioxide present and the amount recovered was divided by the theoretical amount of arsenic trioxide oxidized as calculated from the number of coulombs passed. The arsenic (III) stock solutions were made up by dissolving the required amount of Primary Standard Arsenic Trioxide in dilute potassium hydroxide solution and making slightly acid with sulfuric acid. A small amount of reddish-brown precipitate appeared after the solution stood for some time and was filtered off before use. Reagent grade chemicals and distilled water were used throughout.

Air Oxidation of Arsenic(III) Solutions.—Runs to determine the effect of air oxidation were made by placing an electrode in a beaker containing an arsenic(III) solution prepared in exactly the same manner as the electrolysis solutions, and stirring the solution at the same rate and for the same length of time as the cell solutions. These solutions were then titrated to determine the change due to air oxidation.

Runs were also made under nitrogen in the electrolysis cell. A brass cap was constructed with sleeves for stirrer, electrode and gas inlet. The solution was outgassed with tank nitrogen for at least two hours before being placed in the cell, and the cell was swept for twenty minutes before electrolysis started.

Results and Discussion

The Effect of *p*H on the Current Efficiency.—The results of a series of runs in which the *p*H of the arsenic(III) solution was varied are given in Table I.

TABLE I

THE EFFECT OF CHANGING *p*H ON THE CURRENT EFFICIENCY

(0.5 g. As_2O_3 in 200 ml., apparent current density 0.123 amp. per. sq. dm., 50% oxidized, sand-blasted platinum electrode)

Temperature, °C.	*p*H	Current efficiency, %
23	(6 *N* H_2SO_4)	100.08
24	(1.25 *N* H_2SO_4)	99.80
21	(1.25 *N* H_2SO_4)	100.20
24	1.8	100.07
24	3.4	94.83
23	5.4	54.06
21	5.4	51.52
22	5.5	66.80
24	6.6	48.13
21	6.6	22.43
24	8.3	58.65
21	9.3	30.50
23	9.4	32.50
25	11.0	99.20
25	(1 *N* NaOH)	109.20
21	(1 *N* NaOH)	118.00

Examination of the data in Table I shows that the oxidation proceeds smoothly with 100% current efficiency in strongly acid solution. The efficiency decreases through the neutral range, reaches a minimum, and then increases and becomes greater than 100% in strongly alkaline solution.

The exact position of the minimum cannot be located from these data, since it was found that the reaction is quite sensitive to temperature changes through this range. For this reason, no attempt has been made to correlate the location of the minimum with a possible reaction mechanism.

From the equation for the reaction $HAsO_2 + 2H_2O = H_3AsO_4 + 2H^+ + 2e^-$, one would

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[12] L. Gleu, *Z. anal. Chem.*, **95**, 305 (1933).

[13] I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," Volume II, John Wiley and Sons, Inc., New York, N. Y., 1929, p. 350.

expect the oxidation to go more smoothly in alkaline solution. Brown, Hatfield and Church[8] state that an alkaline bicarbonate solution just acid to phenolphthalein (probably *p*H 7–8) is the best for carbon and platinum anodes, but cite no data comparing results in solutions of different *p*H.

The existence of the minimum in the current efficiency values indicates that the reaction probably proceeds by different mechanisms in acid and alkaline solutions. The high current efficiencies in acid solution have not been previously observed and indicate the possibility of preparing alkali free arsenic(V) solutions.

Electrolyses in acid solution in the presence and absence of air showed no detectable difference in the amount of oxidation produced. Catalytic oxidation by air which occurs up to one-third of the total oxidation in alkaline solution therefore does not occur in acid solution. The electrolytic oxidation is free from appreciable side reactions.

The Effect of Other Variables on the Oxidation Process.—The results of a study of the effect of changing the current density on the current efficiency are given in Table II.

TABLE II

THE EFFECT OF CHANGING CURRENT DENSITY ON THE CURRENT EFFICIENCY

Temperature 24° and sand-blasted platinum electrode, 1.25 *N* H_2SO_4

As_2O_3 per 200 ml., g.	Apparent current density, Amp./sq. dm.	Current efficiency, %
0.5	0.123	100.2
.5	.185	100.3
.5	.230	99.2
1.0	.230	100.4
0.5	.269	99.6
0.5	.307	99.1
1.0	.307	98.8

It is seen that the current efficiency begins to decrease as the current density increases above about 0.2 amp./sq. dm. From the figures obtained, the best value of the current density to use for quantitative electrolysis is the lowest one given, 0.123 amp./sq. dm. Use of this value gives a considerable margin of safety before side reactions, usually the evolution of oxygen, begin.

Taking 0.123 amp./sq. dm. as the optimum current density, the effect of changing the per cent. oxidation was investigated. The results are given in Table III.

TABLE III

THE EFFECT OF CHANGING THE PER CENT. OXIDATION ON THE CURRENT EFFICIENCY

0.5 g. As_2O_3 in 200 ml. 1.23 *N* H_2SO_4 current density 0.123 amp./sq. dm., sand blasted platinum electrode

Temperature, °C.	Oxidation, %	Current efficiency
24	51.0	99.80
21	50.4	100.20
26	74.9	99.75
30	85.2	99.82
30	95.5	99.65
30	98.0	98.36

These results show that the current efficiency remains high even when 90% of the arsenic(III) has been oxidized.

On seven runs the arsenic(V) produced was determined as well as the arsenic(III) consumed. The average difference was less than 0.3%, which is within the limits of error of the determinations. This agreement indicates the absence of intermediate oxidation stages.

Summary

1. The electrolytic oxidation of arsenic(III) at a platinum electrode has been shown to proceed at 100% current efficiency in strongly acidic solutions.

2. Air oxidation of arsenic(III) does not occur during electrolysis in acid solution.

3. The oxidation of arsenic(III) to arsenic(V) gives no indication of the presence of intermediate oxidation states.

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