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The Anodic Dissolution of Tin¹

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Studies of the dissolution of tin either from a solid or from a liquid amalgam anode in aqueous solutions showed that, in the presence of chlorate or nitrate ion in electrolyte salts, the quantity of tin dissolved per faraday of electricity passed was greater than could be accounted for solely on the basis of anodic oxidation to the +2 state. This effect was accompanied by the appearance in the anode compartment, during electrolysis, of reduction products of the electrolyte anion; chlorate was reduced to chloride, and nitrate to nitrite ion, hydroxylamine, and ammonium ion. No such effects were observed for electrolyses in sodium chloride or sodium acetate solutions. A hypothesis based on the primary anodic production of tin(I), an intermediate susceptible to chemical oxidation to tin(II) by nitrate or chlorate, serves best to explain these results. Such a hypothesis is consistent with the observed effects of variation in current density or in duration of electrolysis, and of use of an interrupted current. Measurements of anode potential during some of the electrolyses yielded data which discredit any explanation involving undetected nonelectrolytic attack upon the tin.

Introduction

In 1911, White,² in order to explain his observation of anomalously high current efficiencies for the anodic dissolution of tin metal into an aqueous sodium nitrate solution, postulated the anodic formation of univalent tin. He noted no anomalous effects, however, when tin was anodically dissolved in sodium chloride or sodium acetate solutions.

The present report describes a reinvestigation of these systems, as well as studies upon related ones. Electrolyses were carried out under various conditions, and effects were studied of current density, of an interrupted current, and of duration of electrolysis. The products appearing at the anode were analyzed, and during some of the electrolyses measurements were made of the anodic potential.

The electrolytic weight loss of the tin anodes is presented here in terms of the initial mean valence number, V_i , given by

$$V_i = \frac{\text{no. of faradays passed}}{\text{no. of g-atoms of metal dissolved electrolytically}} \quad (1)$$

If the weight loss of the anode is due solely to passage of the electrolytic current, and if no species other than tin are oxidized at the anode, the V_i value is seen to

represent the average charge per tin ion as these ions leave the electrode.

Materials and Procedures

A divided cell similar to that described in a recent paper from this laboratory³ was used for the electrolyses. The anode compartment held approximately 35 ml. of electrolyte. A sintered glass divider between electrode compartments permitted analysis of the contents of the anode compartment without interference by cathodic products. A flow of inert gas (nitrogen or helium) above the electrolyte prevented air oxidation of products formed during electrolysis. The cell was thermostated at 30°.

The power source was capable of delivering 250 volts d.c. from rectified and filtered a.c. On a cathode-ray oscilloscope the voltage showed no discernible fluctuations or undulations when delivering up to 0.1 amp. In some of the runs the current was intermittently interrupted by means of an electromagnetically activated vibrating contact. The interrupter allowed current to flow for 40% of the time, the interruptions occurring 60 times a second. In these cases the oscilloscope pattern revealed a very clean square wave. Since the interrupter mechanism operated only at 100 volts, the voltage fed to the electrolytic cell was regulated by means of a rheostat in series with the cell. Current was monitored with an ammeter, but the total quantity of electricity passed was measured by means of a silver coulometer in series with the electrolysis cell. Current density at the platinum cathode of the coulometer never exceeded 5 ma./cm.².

During some electrolyses the potential behavior of the tin anode was measured by comparison against a saturated potassium chloride-calomel reference electrode. Electrical contact between reference electrode and tin anode was established by

(1) Abstracted from part of a thesis submitted by Max L. Rumpel in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, University of Kansas, 1962.

(2) G. R. White, *J. Phys. Chem.*, **15**, 723 (1911).

(3) M. L. Rumpel, A. W. Davidson, and J. Kleinberg, *Inorg. Chem.*, **2**, 810 (1963).

means of a salt bridge which entered the anode compartment of the cell and terminated in a capillary tip which bore a glass fiber plug and was placed very close to the surface of the working anode. The potential was determined with a Rubicon Model 2730 null-current potentiometer which could directly measure potentials from zero to 1.6 volts. In some experiments, in order that the net potential might fall within the range of the instrument, it was necessary to place a 1.5-volt dry cell in series with the unknown potential, but with opposite polarity. The value of this "bucking" e.m.f. was frequently checked, and the actual potential of the tin anode-reference electrode pair was then taken as the sum of the measured net e.m.f. and the "bucking" e.m.f.

Except as otherwise noted, both electrodes in the electrolytic cell were of tin, in the form of sticks cast to 1-cm. diameter; the area of the anode was approximately 10 cm.². The reported upper limits of impurities in the tin were: arsenic, 0.001%; copper, 0.002%; iron, 0.005%; and lead, 0.02%. Prior to use the tin was rinsed in dilute hydrochloric acid and then in water, oven-dried, and weighed. As a check on nonelectrolytic corrosion, a weighed stick of tin was immersed in the anolyte; ordinarily this control sample was suspended next to the anode. Anode, cathode, and control were washed with water, 3 *M* hydrochloric acid, and then water again before being dried and weighed at the end of a run.

All chemicals used were of reagent quality. Distilled water was boiled and cooled under a stream of inert gas before use, and solutions were purged of dissolved oxygen by having nitrogen bubbled through them.

Tin(II) nitrate solution was prepared by treating tin(II) chloride solution with ammonia, repeatedly washing the precipitate to remove chloride ion and ammonia, and redissolving the solid in the stoichiometric quantity of 2 *M* nitric acid. In this preparation, the last traces of chloride ion could not be removed.

Quantitative analyses for tin(II), total tin, and ammonium ion were carried out for the anode compartment contents after each of several electrolyses in which sodium nitrate solutions were used as electrolyte. To avoid air oxidation of tin(II), it was necessary to work under inert gas while the anode chamber contents were removed, the anode metal was rinsed clean, precipitated tin(II) hydroxide was dissolved, and the resulting solution was diluted to a known volume. These manipulations were most effectively performed inside a large polyethylene bag which was fitted with plastic gloves cemented into the bag at the wrists. After the necessary equipment had been introduced, the mouth of the bag was closed about a rubber stopper, the interior was flushed with gas through inlet and outlet tubes which had been inserted through the stopper, and the necessary steps were taken, as just described, to obtain exactly 100 ml. of anolyte solution.

The first aliquot from the flask was drawn into a 20-ml. pipet (previously flushed with inert gas), by means of a bulb equipped for a flow of inert gas into the top of the pipet as its contents drained. The sample was thus introduced into a 250-ml. flask which also had previously been swept with inert gas. The aliquot was titrated with standard iodine solution and the result calculated as tin(II) ion.

Total tin in a 20-ml. aliquot of anolyte solution was determined for most of these runs by the method of Hillebrand and Lundell.⁴ Before analysis, nitrate ion was removed, usually by the addition of concentrated sulfuric acid and evaporation to fumes of sulfur trioxide. Lead metal was then added to reduce any tin(IV) to tin(II). The iodine solution used for titration of tin(II) was standardized against weighed samples of pure tin dissolved in hydrochloric acid.

A 50-ml. aliquot of the anolyte solution was made basic with sodium hydroxide solution and all ammonia thereby released was distilled into boric acid solution for titration with standard hydrochloric acid.

In a number of additional experiments a liquid tin amalgam

(containing about 0.12% of tin by weight), instead of solid tin, was used as anode in 10% sodium nitrate solution. The surface of the anode pool was about 20 cm.²; stick tin again served as cathode. Nonelectrolytic oxidation of the solution upon a similar pool of amalgam was found to be insignificant. In these electrolyses the quantity of tin lost from the anode by electrolytic dissolution was determined by adding to the entire anolyte the minute amount of finely divided black deposit formed on the anode, acidifying the solution with 3 *M* hydrochloric acid, and electroplating the tin with a Fisher electrometer. Qualitative tests on the anolyte were carried out on different runs from those used for *V*_i determinations.

Results

The results of 37 electrolyses with solid tin anodes and of 11 with liquid amalgam anodes are shown in Table I. Except as otherwise noted, the concentration of the electrolyte was about 10% by weight, the anodic current density was approximately 10 ma./cm.², and the time of electrolysis from 1.5 to 3.5 hr. The tin corrosion control samples suffered no significant weight loss during any of the electrolyses.

TABLE I
INITIAL MEAN VALENCE NUMBERS BY ANODIC DISSOLUTION OF TIN

Electrolyte	Notes	<i>V</i> _i
(A) Solid anodes		
NaCl		2.0
NaC ₂ H ₃ O ₂	Concn. 6% by wt.	2.0
SnCl ₂	Concn. 2 <i>M</i>	2.0
KClO ₃	Concn. 5% by wt.; 2 concordant trials	1.81
NaNO ₃	Mean of 17 trials; std. dev. ±0.02 unit	1.17
NaNO ₃	Time of electrolysis only 20 min.; mean of 2 trials	1.25
NaNO ₃	Current density only 1 ma./cm. ² ; mean of 2 trials	1.08
Sn(NO ₃) ₂	Concn. 2 <i>M</i>	1.33
NaC ₂ H ₃ O ₂ -NaNO ₃ mixture	Total concn. 9% by wt.; mean of 3 trials	1.17
KCl-NaNO ₃ mixture	Total concn. 10% by wt.	1.80
NaNO ₃	Intermittent current, 60 c.p.s., mean current density 9 ma./cm. ²	1.09
NaNO ₃	Intermittent current, 60 c.p.s., mean current density 4 ma./cm. ² ; mean of 4 trials	1.02
NaNO ₃	Current shut off manually for 15 of each 30 sec.	1.17
(B) Amalgam anodes		
NaNO ₃	Time of electrolysis 45 min.; mean of 5 trials	1.40
NaNO ₃	Current density 2.5 ma./cm. ² ; mean of 6 trials	1.27

Significantly, in every case where a *V*_i value below 2 was observed, chemical reduction of the electrolyte occurred. After electrolysis in potassium chlorate solution, chloride ion was found to be present in the anode compartment; after electrolysis in nitrate-containing electrolytes, qualitative tests on the anolyte revealed the presence of nitrite ion, hydroxylamine, and ammonium ion.

(4) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 293.

TABLE II

	QUANTITATIVE ANALYSIS OF ANOLYTE									
	10.80	10.23	8.33	8.62	10.69	8.25	6.98	6.72	6.63	6.86
Moles of Sn × 10 ³	10.80	10.23	8.33	8.62	10.69	8.25	6.98	6.72	6.63	6.86
Moles of Sn ²⁺ × 10 ³	8.94	8.37	6.79	7.24	9.00	5.92	5.74	5.44	5.48	5.60
Moles of NH ₃ × 10 ³	1.20	1.11	0.88	0.93	1.40	0.96	0.82	0.71	0.67 ^a	0.74

^a Possibly incomplete distillation of ammonia for analysis.

A closer investigation of the materials in the anode compartment after electrolysis in 10% sodium nitrate solution showed that the nitrite ion produced during electrolysis disappeared when the anolyte was stirred. The bottom of the anode chamber contained a precipitate of hydrous tin(II) oxide after electrolysis, and the pH of the originally neutral anolyte had decreased to ~2. Control tests showed that such a hydrous tin(II) oxide slurry reduced nitrite ion in acid solution to hydroxylamine, but did not affect nitrate ion or hydroxylamine itself.

Because of interference of other nitrogen compounds, direct quantitative determination of hydroxylamine in the anolyte could not be accomplished. Determinations of total tin, tin(II), and total ammonia were, however, carried out for several electrolyses. Results are presented in Table II.

For the first four electrolyses presented in the table, the figure for total tin was taken as equal to the weight of tin metal dissolved anodically. For succeeding trials, total tin was determined by analysis of the anolyte solution. Since it is estimated that 98% recovery of anolyte for analysis was achieved, the tabulated values of total tin for the first four trials are slightly too high.

Potential measurements on the tin anode were carried out in 2 M sodium nitrate, 1 M tin(II) nitrate, 2 M tin(II) chloride, 0.4 M potassium chlorate, and 2 M sodium acetate solutions. Current densities in the neighborhood of 10 ma./cm.² were used. The V_i values were the same, within experimental error, as those reported above.

The observed potential behavior in a given solution may be classed as either "normal" or "abnormal." In "normal" behavior, which was observed in the sodium nitrate, potassium chlorate, and tin(II) chloride solutions, the anodic potential measured during electrolysis was only slightly (*ca.* 100 mv.) more noble than the constant reversible tin metal-tin(II) potential that was attained as soon as electrolysis was terminated.

In "abnormal" behavior, the anodic potential during electrolysis was found not only to be far more noble than the reversible potential, but also to fluctuate erratically. In this case the potential was very sensitive to vibration of the cell, even after electrolysis had been terminated. The fluctuations mentioned were far too large to be accounted for by increased random error of measurement due to decreased sensitivity of the null-current device. At the end of the electrolysis, the potential generally remained somewhat more noble than the reversible tin metal-tin(II) value.

Such "abnormal" potential behavior was especially marked in tin(II) nitrate solutions, in which the reduction potential during electrolysis never fell below +2.5 volts *vs.* a normal hydrogen electrode. No gas evolution, however, was observed at the anode. Less markedly "abnormal" behavior was observed in sodium acetate solution. When a small amount of concentrated nitric acid was added to a sodium nitrate solution, the anodic potential behavior became "abnormal."

Discussion

On the basis of experiments on the anodic corrosion of steel, it has been suggested by Marsh and Schaschl⁵ that the weight loss of a metal during anodic dissolution may sometimes be due, in part, to a spallation of microscopic "chunks" of the metal from the anode surface. This phenomenon, reported by Straumanis and Mathis⁶ to occur also in the anodic dissolution of beryllium in neutral sodium chloride solutions, has been cited by these authors as an explanation of the low V_i values observed in such dissolution,⁷ since, when this "chunk effect" contributes to the dissolution of the anode, the apparent faradaic weight loss would be expected to be anomalously high. The chunk effect, it is claimed, would not necessarily be accompanied by visible deposition of finely divided metal, since the relatively high surface area of the chunks would lead to their rapid destruction by chemical reaction with the electrolyte.

In order for the results reported in this paper for solid anodes to be explicable in terms of the chunk effect theory, the rate of mass loss by spallation would have to be assumed to be quite reproducible from experiment to experiment—a hypothesis which is improbable for varying conditions of electrolysis. The rate of mass loss from a given anode by spallation must, for example, be a function of instantaneous current density,⁵ regardless of the wave form used. With a square wave current, the rate of mass loss by spallation should correspond to the current density at the square wave peak, which in our experiments was approximately 2.5 times the average current density. Yet V_i values in sodium nitrate solution are not in accord with this hypothesis. A steady current density of 10 ma./cm.² gave a faradaic yield ($1/V_i$) of 0.855, whereas with a square wave of average current

(5) G. A. Marsh and E. Schaschl, *J. Electrochem. Soc.*, **107**, 960 (1960).

(6) M. E. Straumanis and D. E. Mathis, *ibid.*, **109**, 434 (1962).

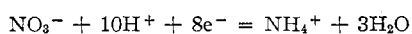
(7) B. D. Laughlin, J. Kleinberg, and A. W. Davidson, *J. Am. Chem. Soc.*, **78**, 559 (1956).

density 4 ma./cm.² (peak current density 10 ma./cm.² when current flowed) a $1/V_i$ value of 0.98 was obtained.

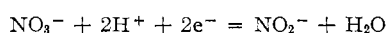
In the case of amalgam electrodes, the chunk effect hypothesis appears to be quite inapplicable.

The concept of negative "difference effect"⁸ has been applied by Straumanis^{9,10} to explain the anomalous faradaic yields in anodic dissolution by postulation of an increased rate of chemical (nonelectrolytic) corrosion of the anodically polarized metal. According to this theory, a protective surface film initially present on the anode is broken down by the electrolytic current, leaving the metal surface available for chemical attack by oxidizing agents in the electrolyte. The formation of reduction products of the electrolyte in the anode compartment during electrolysis can, it is true, be predicted on the basis of this theory. However, the appearance of *unusual* reduction products, such as the ammonium ion which was observed here, as *major* products in the reaction cannot readily be accounted for in this way, nor is it in accord with the theory that V_i values less than unity have never been observed.

The potential measurements described above offer further contradiction to the negative difference effect theory. "Normal" anode potential behavior may plausibly be attributed to activation polarization of the metal during the passage of current, without assumption of the presence of a surface film. "Abnormal" potential behavior, on the other hand, is best explained in terms of a surface film which causes the anode to become partially passive (although not to such an extent as to bring about electrolytic oxidation of other species besides tin metal). The presence of such a film would account for the decreased potentiometric sensitivity which was observed to accompany "abnormal" behavior. The iR drop in the electrolysis circuit brought about by the adherent film would explain the absence of oxygen evolution at the solution side of the film, despite the high polarization of the anode metal. Yet lowered V_i values were observed both in the systems exhibiting "normal" potential behavior and in those characterized as "abnormal." Moreover, a lowered V_i was found even in tin(II) nitrate solutions, where the potential of the anodically polarized metal remained above +2.5 volts. This means that it is thermodynamically impossible for nitrate ion to bring about chemical oxidation of the tin metal unless the reduction potential for nitrate ion at the tin surface is in excess of +2.5 volts. The standard reduction potential, however, for each of the half reactions



and



is +0.9 volt. When the approximate concentrations of the various species are taken into account calculated potentials become -0.2 volt for the conversion $\text{NO}_3^- \rightarrow$

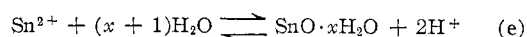
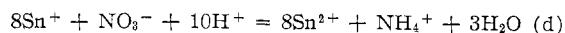
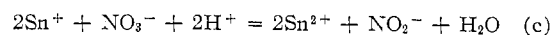
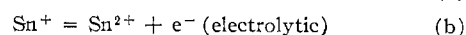
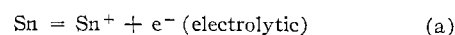
NH_4^+ , and +0.8 volt for the conversion $\text{NO}_3^- \rightarrow \text{NO}_2^-$. Even though overpotential effects have been neglected in their calculation, these values fall far short of the requisite +2.5 volts.

If it is postulated that the first step in the anodic oxidation of tin is the production of a univalent ionic species, all of the observations may be explained. For systems in which tin shows a V_i of two in anodic dissolution, it is to be supposed that all of the univalent intermediate returns to the anode, there to be oxidized electrolytically to the +2 state. However, when a chemical oxidizing agent, such as nitrate or chlorate, is present, part of the univalent tin is oxidized chemically (nonelectrolytically). In such a case, the measured V_i value must be less than 2 and will approach the more closely to unity the more successfully this chemical reaction competes with the further electrolytic oxidation of the univalent intermediate. This is the same general mechanism that has previously been proposed to explain anomalously low V_i values found in the anodic dissolution of other metals.¹¹

Whenever a low V_i is found, it is to be expected that reduction products of the electrolyte will appear in the anode compartment of the electrolysis cell. Moreover, in view of the probable high reactivity of such a univalent intermediate, the appearance of unusual reduction products in major quantities is not surprising.

According to this hypothesis, the V_i value is not directly related to the presence or absence of a surface film. Thus, the occurrence of "abnormal" potential behavior, which appears to be caused by a surface film on the anode, would not be expected to coincide with the incidence of a lowered V_i .

The observations for electrolyses in sodium nitrate solutions may be explained in detail by the reaction scheme shown below, which is based upon the primary anodic production of unipositive tin.



According to this mechanism, if 71% of the total quantity of electricity produces Sn^+ which is chemically oxidized by paths c and d, while the other 29% produces tin(II) cation by consecutive reactions a and b, the measured V_i will be 1.17. The more successful reactions c and d compete with reaction b at the anode surface, the lower will be the V_i . The appearance of hydrous tin(II) oxide is accounted for by reaction e, which is the pH-determining reaction for the anolyte. Reaction f goes to completion when the anolyte is stirred.

If it is assumed that during subsequent procedure

(8) A. Thiel and J. Eckell, *Z. Elektrochem.*, **33**, 370 (1927).

(9) M. E. Straumanis, *J. Electrochem. Soc.*, **105**, 284 (1958).

(10) M. E. Straumanis, *ibid.*, **108**, 1087 (1961).

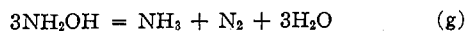
(11) D. T. Sorensen, A. W. Davidson, and J. Kleinberg, *J. Inorg. Nucl. Chem.*, **13**, 64 (1960).

TABLE III
 COMPARISON OF V_i VALUES FROM EQ. 1 AND EQ. 8

V_i from eq. 1	1.16	1.16	1.17	1.13	1.12	1.16	1.17	1.19	1.19	1.18
V_i from eq. 8	1.17	1.19	1.22	1.19	1.00	1.16	1.12	1.22	1.25 ^a	1.20

^a Possibly incomplete distillation of ammonia for analysis.

for ammonia analysis, the hydroxylamine decomposes according to the equation¹²



then purely stoichiometric considerations allow the derivation of an equation giving the V_i value in terms of the analytically determined numbers of moles of total tin (n_{Sn}), tin(II), and evolved ammonia. Let the number of moles of species i which are involved in reaction j of the proposed mechanistic sequence be symbolized by n_{ij}^j . We note first that

$$n_{\text{Sn}^{2+}}^a = n_{\text{Sn}} = n_{\text{Sn}^{2+}}^b + n_{\text{Sn}^{2+}}^c + n_{\text{Sn}^{2+}}^d \quad (2)$$

and that

$$V_i = \frac{\text{total no. of faradays transferred at anode}}{\text{total no. of g.-atoms of tin dissolved}} = \frac{n_{\text{Sn}^{2+}}^a + n_{\text{Sn}^{2+}}^b}{n_{\text{Sn}^{2+}}^b} = \frac{n_{\text{Sn}} + n_{\text{Sn}^{2+}}^b}{n_{\text{Sn}}} \quad (3)$$

Upon combination of eq. 2 and 3 so as to eliminate $n_{\text{Sn}^{2+}}^b$ we obtain

$$V_i = \frac{2n_{\text{Sn}} - n_{\text{Sn}^{2+}}^c - n_{\text{Sn}^{2+}}^d}{n_{\text{Sn}}} \quad (4)$$

From consideration of reaction d, we find $n_{\text{NH}_4^+}^d = 1/8 n_{\text{Sn}^{2+}}^d$, and from reactions c, f, and g, $n_{\text{NH}_3}^c = 1/6 n_{\text{Sn}^{2+}}^c$. Therefore the total ammonia as determined by analysis, n_{NH_3} , is given by

$$n_{\text{NH}_3} = 1/8 n_{\text{Sn}^{2+}}^d + 1/6 n_{\text{Sn}^{2+}}^c \quad (5)$$

The value of $n_{\text{SnO}_2 \cdot 2\text{H}_2\text{O}}^f$ is the difference between the analytically determined total tin and tin(II), $n_{\text{Sn}} - n_{\text{Sn}^{2+}}$. From eq. c and f we find also that $n_{\text{SnO}_2 \cdot 2\text{H}_2\text{O}}^f = n_{\text{Sn}^{2+}}^c$. Therefore

$$n_{\text{Sn}^{2+}}^c = n_{\text{Sn}} - n_{\text{Sn}^{2+}} \quad (6)$$

Substitution of eq. 6 into eq. 5 gives

$$n_{\text{NH}_3} = 8n_{\text{Sn}} - 4/3 n_{\text{Sn}^{2+}} + 4/3 n_{\text{Sn}^{2+}} \quad (7)$$

Now eq. 6 and 7 may be substituted into eq. 4 to give the desired relationship

$$V_i = \frac{7n_{\text{Sn}} - n_{\text{Sn}^{2+}} - 24n_{\text{NH}_3}}{3n_{\text{Sn}}} \quad (8)$$

Table III gives the results of the application of this equation to the analytical data from Table II. The calculated V_i values are compared with the V_i values which were obtained from eq. 1. The agreement between the two V_i values shows that the postulated reaction sequence is fully consistent with what is known of the reaction stoichiometry.

Our observations on the variation of V_i values with conditions of electrolysis may also be explained in terms of the postulated mechanism. Before electrolysis is begun, the electrolyte is neutral, but as electroly-

sis proceeds, the pH of the solution soon reaches a quite steady value of ~ 2 . This increase in hydrogen ion concentration would be expected greatly to increase the rates of reactions c and d and cause the V_i to drop to a steady value. Because the measured V_i is a time-weighted average of the instantaneous mean valence values of the anodically produced tin species, the V_i should drop with time. If the total time of electrolysis is very long compared to the time for the pH to reach a steady state, the measured V_i should closely approach its limiting value. On the other hand, if the time of electrolysis is not much longer than the time required to reach this steady state, the time-weighted average of the mean valence should be greater than the limiting value. The observed variation of the measured V_i with time of electrolysis follows this pattern.

As electrolysis proceeds, nitrate ion must become somewhat depleted, because of reactions c and d, in a thin layer of solution near the anode. The steady-state value of the nitrate ion concentration in this thin layer would be expected to decrease with rising current density. Thus the average unreacted lifetime of Sn^{2+} with respect to chemical oxidation should increase with increasing current density. The lifetime of Sn^{2+} with respect to oxidation by reaction b, however, should not be affected by current density. It might be expected, therefore, that the V_i should increase with increasing current density, as was shown experimentally.

The above considerations should still hold for electrolysis with an interrupted instead of a steady direct current. It may be noted that the elevation of the V_i with increased current density, as just discussed, was observed also in the interrupted current experiments. As an additional effect, however, the Sn^{2+} that remains when current is interrupted should be oxidized, during the interval, exclusively by paths c and d. This accounts for the observation of substantial lowerings of the V_i values when an interrupted current is used, provided that the frequency of interruption is sufficiently great so that a significant proportion of the short-lived Sn^{2+} has path b denied it.

It appears to the writers, then, that the phenomena observed when tin is dissolved anodically in aqueous solutions containing nitrate are more readily accounted for by the lowered-valence theory than by other current hypotheses. The lowered-valence theory serves also to explain observations on potassium chlorate solutions, which need not be discussed in detail.

Acknowledgment.—M. L. R. takes this opportunity to thank the National Science Foundation for Fellowships received while this work was in progress. This work was supported mainly by the General Research

(12) J. Kleinberg, W. J. Argersinger, Jr., and E. Griswold, "Inorganic Chemistry," D. C. Heath and Co., Boston, Mass., 1960, p. 390.

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CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES,
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Electrolytic Preparation of Tellurides

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The compounds CuTe, ZnTe, SnTe, PbTe, and Bi₂Te₃ were prepared by electrolysis with tellurium cathodes and metal anodes in ammonium acetate acid buffer solutions. The tellurides were formed by homogeneous reaction between metal cations and telluride ions in the bulk of the solutions. GeTe, Ag₂Te, SnTe, and ZnTe were also prepared by adding metal salt solutions to electrolytically generated telluride solutions. X-Ray measurements indicated that stoichiometric SnTe is formed in contrast to extensive nonstoichiometry possible in compounds prepared at elevated temperatures. Also, GeTe prepared at room temperature was shown to have a somewhat smaller trigonal distortion than observed in GeTe preparations quenched from higher temperatures. In addition, a low temperature CuTe phase was observed which transformed to the previously reported orthorhombic phase on annealing above 250°.

Introduction

Direct union of the elements either by melting or by sintering compacted powders is the most commonly used method of preparing tellurides and other semi-conducting compounds. In either case high temperatures are required. As the compounds are cooled, the electronic system comes to equilibrium at room temperature, but the motion of lattice defects and the diffusion of atoms is very slow below about one-half the absolute melting temperature. Thus the lattice defect concentration and the chemical composition of compounds prepared in this way are characteristic of some ill-defined high temperature.

The preparation of such nonstoichiometric compounds by alternate methods at low temperature can give products with equilibrium defect concentrations and can reveal new low temperature structures. The study of such compounds may contribute considerable information to solid state chemistry and, in particular, to the study of semiconductors.

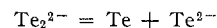
Apart from these considerations there may be practical disadvantages to the direct reaction of the elements. For example, very high temperatures may be necessary to effect reactions, high vapor pressures may be encountered, and peritectic reactions may interfere. In this paper a convenient electrolytic method for preparing tellurides from aqueous solution at room temperature will be described.

Previous Methods.—In the older literature Tibbals¹ reported the preparation of tellurides by allowing solutions of Na₂Te to react with metal acetates; Brukl² used hydrogen telluride gas which was prepared by hydrolyzing Al₂Te₃. More recently, Nitsche³ gave a method in which powdered tellurium was reduced by

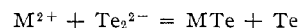
aluminum powder in aqueous ammonia solutions and allowed to react with Zn, Cd, and Hg ammonia complexes. The preparation of tellurides by reaction between fine particle tellurium and fine particle metals formed by hydrazine reduction of ionic solutions was reported by Kulifay.⁴

Electrolytic Preparation.—In the present study electrolytic reactions were used. Telluride ions were formed by cathodic dissolution of tellurium in acid solution. It was generally possible to introduce the metal ions into solution by simultaneous anodic dissolution of the metal by passing current between a tellurium cathode and a metal anode through an acid electrolyte. The electrodes dissolve cleanly and the tellurides are formed by ionic reaction in the bulk of the solution. In cases where metal ions are not conveniently generated by anodic dissolution, they are added as salt solutions to the electrolytically generated telluride ion solutions.

Knowledge of the products formed on cathodic dissolution of tellurium is essential to control the purity of the products. The pH of the electrolyte is a controlling factor since the equilibrium in the reaction



is maintained and the acid dissociation constants of H₂Te ($K_1 = 2.27 \times 10^{-3}$ and $K_2 = 6.9 \times 10^{-13}$) are smaller than those for H₂Te₂.⁵ Although the equilibrium constant for the disproportionation reaction written above is 2×10^{-4} , disproportionation becomes favorable, *i.e.*, hydrogen telluride ion becomes the predominant tellurium species, at pH values less than approximately 9.⁵ Metal tellurides formed from solutions containing ditelluride ion are contaminated with tellurium, the net reaction being



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