[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarography of Selenium and Tellurium. II. The +4 States

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The polarographic behavior of the −2 states of selenium and tellurium has been discussed in a preceding paper.[2] The present paper is concerned with the polarography of the +4 states of these elements.

The only previous study is that of Schwaer and Suchy,[3] who observed three waves for selenium (IV) and tellurium(IV) in 1 *N* hydrochloric acid which they attributed to reduction to the +2, elemental, and −2 oxidation states. In very dilute solutions the first and second waves merged into one, which Schwaer and Suchy concluded was due to reduction to the elemental states. We observed an additional wave to those reported by Schwaer and Suchy in acid medium, and have been unable to confirm their hypothesis that one of the waves results from reduction to the +2 state.

With ammoniacal buffers Schwaer and Suchy observed a single well-developed wave with both selenium(IV) and tellurium(IV), which they concluded was due to reduction to the elemental state in both cases. Our experiments confirm this conclusion only in the case of tellurium, and we have found that the reduction of selenium(IV) proceeds completely to the −2 state in ammoniacal media.

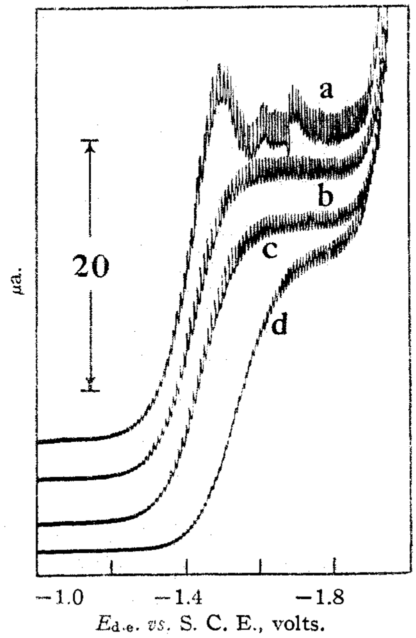

Fig. 1.—Polarograms of 1.5 millimolar selenium(IV) in 1 *M* ammonium chloride–ammonia at *p*H 8.0 with (a) 0, (b) 0.001, (c) 0.003 and (d) 0.01% gelatin.

Schwaer and Suchy found that tellurium(IV) is reduced from an approximately neutral tartrate solution, and they recommended this medium for the simultaneous determination of copper, bismuth and tellurium. They also observed that tellurium(IV) produces a wave in strongly alkaline solution, but selenium(IV) does not. The reduction product in alkaline medium was not identified.

In this investigation the polarographic characteristics of selenium(IV) and tellurium(IV) have been studied over a wide range of conditions, and the reduction states have been established conclusively by the coulometric analysis technique[4] based on controlled potential electrolysis with a large mercury cathode.

Results and Discussion

The preparation of the pure selenium dioxide and tellurium dioxide used, and the technique of the coulometric and polarographic measurements, have been described in previous papers.[2,5]

Selenium.—The polarograms in Fig. 1 demonstrate the influence of gelatin on the selenium(IV) wave in ammoniacal medium. Decreasing the ammonium chloride concentration from 1 to 0.1 *M* at constant *p*H causes a slight negative shift of the half-wave potential, and the wave remains well developed when 0.001 to 0.003% gelatin is present. The *p*H of the solution may vary from 8.0 to 9.5, but at greater *p*H the wave shifts to a more negative potential and merges with the final current rise, and when the *p*H of the ammoniacal supporting electrolyte is smaller than about 8 additional ill-developed waves appear. The most satisfactory supporting electrolyte is 1 *M* ammonium chloride containing not more than 0.003% gelatin and ammonia to adjust the *p*H to 8.0 to 9.5. Under these conditions the diffusion current is directly proportional to the concentration of selenium(IV) as shown by the data in Table I. The half-wave potential is independent of the selenium(IV) concentration at a constant *p*H, but shifts to more negative values with increasing *p*H.

The reduction state in ammoniacal medium (1 *M* ammonium chloride and ammonia to *p*H 8.0) was established by electrolyzing a 1.59 millimolar solution of selenium(IV) with a large mercury cathode whose potential was maintained at −1.65 v. *vs.* S. C. E. by an automatic

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[1] Allied Chemical and Dye Corporation Fellow, 1947–1948.

[2] J. J. Lingane and L. W. Niedrach, THIS JOURNAL, **70**, 4115 (1948).

[3] L. Schwaer and K. Suchy, *Coll. Czechoslov. Chem. Commun.*, **7**, 25 (1935).

[4] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945); *Anal. Chim. Acta*, in press (1948).

[5] J. J. Lingane and L. W. Niedrach, *ibid.*, **70**, 1997 (1948).

TABLE I

+4 SELENIUM IN AMMONIACAL BUFFERS (0.003% GELATIN) AT 25°

$m^{2/3}t^{1/6} = 1.450$ mg.$^{2/3}$ sec.$^{-1/2}$

Buffer	*p*H	Se(IV) millimolar	$E_{1/2}$ volts *vs.* S. C. E.	i_d microamp.	$i_d/Cm^{2/3}t^{1/6}$
1 *M* NH_4Cl	6.9	1.00	−1.39	16.2	11.2
	8.4	0.199	−1.46	3.28	11.4
		.500	−1.46	8.07	11.13
		.73	−1.45	11.6	11.0
		.73	−1.44	11.7	11.1
		1.000	−1.46	16.10	11.10
		2.000	−1.44	31.63	10.92
	9.4	0.199	−1.53	3.20	11.1
		0.500	−1.53	7.95	10.97
		1.000	−1.53	16.04	11.06
		2.000	−1.52	31.74	10.96
0.1 *M* NH_4Cl	6.8	0.990	−1.50	17.18	11.96
	8.2	1.000	−1.56	17.18	11.86
	9.2	0.92	−1.64	15.39	11.1
	10.0	0.81	−1.73	13.0	11.0
1 *M* NH_4-Tartrate	7.9	2.04	−1.40	28.4	9.8
	9.4	2.04	−1.53	29.4	10.2
0.1 *M* NH_4-Tartrate	9.4	2.04	−1.59	29.6	10.2

potentiostat.[6] The quantity of electricity passed was determined by a hydrogen–oxygen coulometer, and was found to correspond to 6 electrons per mole of selenium(IV). Thus at *p*H 8.0 the reduction proceeds to the −2 state, according to

$$HSeO_3^- + 6H^+ + 6e^- = HSe^- + 3H_2O \quad (1)$$

The change in current with time during the controlled potential coulometric electrolysis is shown in Fig. 2. Soon after the start the solution showed a light pink coloration which gradually deepened to a bright red as the current decreased to the minimum. The current then increased rapidly and the color of the solution changed to orange. After passing through the maximum the current decreased continuously while the color became less intense and finally the solution became colorless. Although no solid phase was observed, the red color was undoubtedly due to colloidal selenium. Since in a controlled potential reduction the current at any instant is directly proportional to the momentary concentration of the electroreducible substance, the minimum and maximum in Fig. 2 are readily understandable. The −2 selenium formed in the primary electrode reaction 1 reacted with the remaining +4 compound and precipitated the element, $HSO_3^- + 2HSe^- + 3H^+ = 3Se + 3H_2O$. When all the +4 compound had been reduced in this manner, the current went through the minimum. The slow reduction of the element then produced −2 selenium which dissolved the element as polyselenide, xSe + Se^{--} = Se_x^{--}. The current increased until all the element had dissolved, and then decreased finally as the polyselenide was reduced.

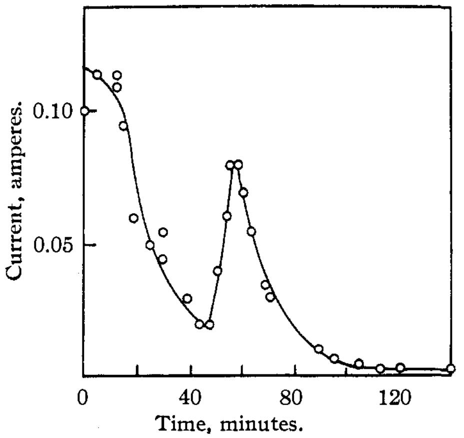

Fig. 2.—Current-time curve during coulometric reduction of 1.59 millimolar selenium(IV) in 1 *M* ammonium chloride–ammonia at *p*H 8.0 with potential of large mercury cathode at −1.65 v. *vs.* S. C. E.

Polarograms recorded at various stages of the electrolysis confirmed the absence of −2 selenium when the +4 compound was present. A polarogram obtained with the final clear and colorless solution, agreed with those for −2 selenium.[2]

The effect of *p*H from 0 to 14 is illustrated by

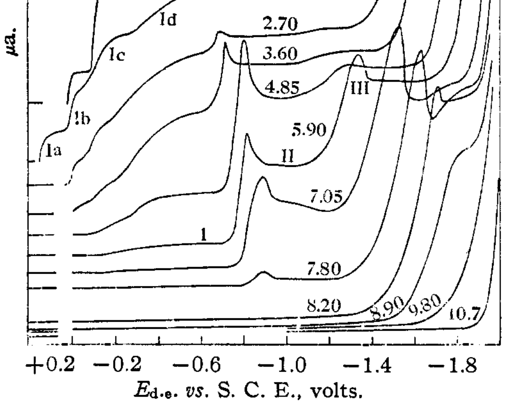

Fig. 3.—Tracings of polarograms of 1 millimolar +4 selenium at the various *p*H values indicated for each curve. The galvanometer zero for each curve is indicated by the short lines on the left ordinate. At low *p*H, hydrochloric acid and citrate buffers were used, at intermediate *p*H, phosphate buffers, and borate and carbonate buffers were used for the alkaline region. No gelatin or other maximum suppressor was present.

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[6] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **17**, 332 (1945).

the tracings of automatically recorded polarograms in Fig. 3. The solutions used were 1 millimolar in +4 selenium and contained no maximum suppressor. No specific effects of the buffer constituents were found upon comparing polarograms obtained in the ranges where the buffers overlapped.

The presence of three major waves is illustrated by the polarograms at *p*H 4.85 and 5.90 in Fig. 3. The first of these is resolved into several additional waves in the lower *p*H range.

Moderate amounts of gelatin eliminated the maxima from all waves; however, at the higher *p*H as little as 0.001% suppressed the wave III quite markedly, while in hydrochloric acid (*p*H 0.01) wave II is sensitive to gelatin.

In 1 *N* hydrochloric acid the three waves mentioned by Schwaer and Suchy were found, and the effects of the selenium(IV) concentration on their form was confirmed. A fourth wave at the very start of the polarogram in 1 *N* hydrochloric is also observable, which indicates that the reduction potential of selenium(IV) is more positive than the dissolution potential of mercury in 1 *N* hydrochloric acid.

The effects of selenium(IV) concentration at *p*H 1.63 are illustrated in Fig. 4. Several additional steps develop as the concentration of selenium(IV) is increased. At higher values of *p*H the additional steps do not appear and the general form does not change with the selenium (IV) concentration.

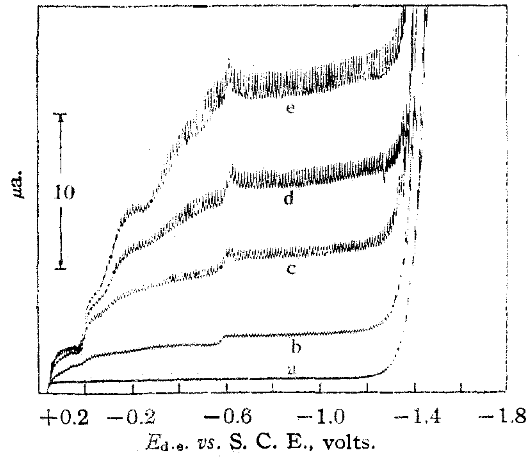

Fig. 4.—Polarograms of (a) 0, (b) 0.199, (c) 0.61, (d) 1.00 and (e) 1.50 millimolar selenium(IV) in 0.5 *M* citric acid at *p*H 1.63.

Figure 5 shows polarograms of selenium(IV) in unbuffered potassium chloride and ammonium chloride. In potassium chloride at *p*H 3.3 reduction begins but normal development of the waves is prevented by the increasing *p*H at the electrode surface as hydrogen ion is consumed. In neutral potassium chloride (curve b) the production of hydroxide ion at the surface of the mercury drops completely inhibits the reduction until the potential exceeds about −1.6 v. In the unbuffered ammonium chloride solutions (curves c and d) nearly normal waves are obtained because the hydrogen ion required for the reduction is furnished by ammonium ion, and the resultant production of ammonia buffers the solution at the electrode surface and prevents the *p*H from increasing.

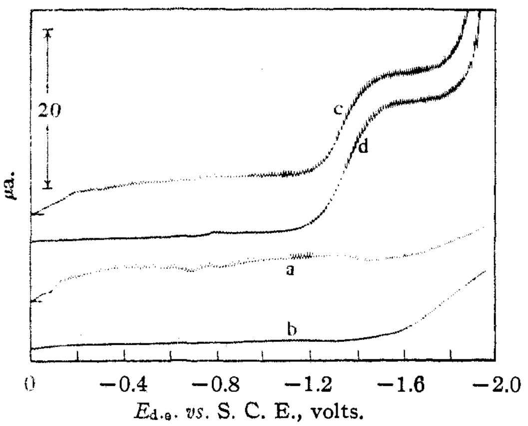

Fig. 5.—Polarograms of 1 millimolar selenium(IV) in (a) 1 *M* potassium chloride at *p*H 3.3, (b) 1 *M* potassium chloride at *p*H 7.2, (c) 1 *M* ammonium chloride at *p*H 3.2 and (d) 1 *M* ammonium chloride at *p*H 6.2. All solutions contained 0.003% gelatin.

The absence of anodic waves under all conditions shows that oxidation of +4 selenium to the +6 state does not occur at the dropping electrode. Furthermore, in agreement with Schwaer and Suchy, we found no reduction waves for either +6 selenium or +6 tellurium at any *p*H.

The complexity of the cathodic waves in Fig. 3 is due in part to stepwise reduction and it also suggests the reduction at different potentials of the different species formed by the dissociation of selenous acid. It is well known that the different ionization species of certain weak acids can produce separate reduction waves when the establishment of dissociation equilibrium is slow compared to the drop time.[7,8,9] Brdicka and his collaborators[10,11] have recently developed quantitative relations by means of which the several wave heights observed in such cases can be correlated with the rate constants involved in the establishment of the dissociation equilibria.

The upper graph in Fig. 6 shows the *total* diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ as a function of *p*H, and the solid curves in the lower graph show the observed *relative* heights of waves I, II and III as a function of *p*H. The dotted curves in the lower graph of Fig. 6 show the

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[7] N. H. Furman and C. E. Bricker, THIS JOURNAL, **64**, 660 (1942).

[8] P. Herasymenko, *Z. Elektrochem.*, **34**, 129 (1928).

[9] L. Meites, Ph.D. Thesis, Harvard University, 1947.

[10] R. Brdicka and K. Weisner, *Coll. Czech. Chem. Commun.*, **12**, 138 (1947).

[11] J. Koutecky and R. Brdicka, *ibid.*, **12**, 337 (1947).

relative proportions of the three species H_2SO_3, $HSeO_3^-$, and $SeO_3^=$ as a function of *p*H, and they were computed using the values 2.4×10^{-3} and 4.8×10^{-9} for the dissociation constants of selenous acid.[12]

There is seen to be approximate agreement of the shapes of the curves for the relative heights of the three waves and the relative equilibrium concentrations of the H_2SeO_3, $HSeO_3^-$, and $SeO_3^=$, which might be regarded as evidence that the three main waves result from reduction of the three different species. However, there are two facts which indicate that this is not a satisfactory interpretation. In the first place the change of the total diffusion current constant with *p*H shown by the upper curve in Fig. 6 is much too large to be attributed to different diffusion coefficients of the three species, and it points to a different reduction product, involving fewer electrons, at intermediate *p*H values. Since the coulometric analyses conclusively prove that reduction proceeds all the way to −2 selenium ($n = 6$) at *p*H 8.0 and above, and since the total diffusion current constant at small *p*H values is of the same order of magnitude as at high *p*H, the reduction at low *p*H must also involve 6 electrons. The diffusion current constants at intermediate *p*H are very nearly two-thirds of the extreme values, indicating a 4-electron reduction at *p*H values between about 3 and 7. Secondly, the cathodic half-wave potentials of wave II are the same (within 0.03 v.) at all *p*H values as the half-wave potentials of the *anodic* wave of −2 selenium discussed in a previous paper.[2] This anodic wave was shown[2] to result from the reaction

$$Hg + H_2Se = HgSe + 2H^+ + 2e \qquad (2)$$

at small *p*H values, and to the analogous reactions involving HSe^- and $Se^=$ at intermediate and high *p*H, and the observed anodic half-wave potentials agreed very well with values computed from the standard potential of reaction 2 and the ionization constants of hydroselenic acid over the entire *p*H range. Wave II is thus the cathodic reflection of the anodic wave of −2 selenium.

It is evident, therefore, that wave I cannot be due to a net reduction to −2 selenium because at potentials more positive than wave II the −2 selenium depolarizes the dropping electrode anodically according to reaction 2. We believe that the *primary* electrode reaction at potentials more positive than wave II (*i. e.*, on wave I) is a 6-electron reduction producing −2 selenium according to

$$H_2SeO_3 + 6e + 6H^+ = H_2Se + 3H_2O \qquad (3)$$

and this is followed by the 2-electron anodic reaction 2. The *net* result is a 4-electron reduction in which mercuric selenide is the final product

$$H_2SeO_3 + 4e^- + 4H^+ + Hg = HgSe + 3H_2O \qquad (4)$$

This interpretation of wave I was confirmed by coulometric reduction of a 1 millimolar solution of selenium(IV) in a citrate buffer of *p*H 1.6. The potential of the large mercury cathode was maintained constant at −0.45 v. *vs.* S. C. E., a value corresponding to the top of wave I at this *p*H (see Fig. 3), and the coulometer reading corresponded to a 4-electron reduction. The reduction product was a black solid which qualitative tests showed to be a mercury compound (*i. e.*, mercuric selenide).

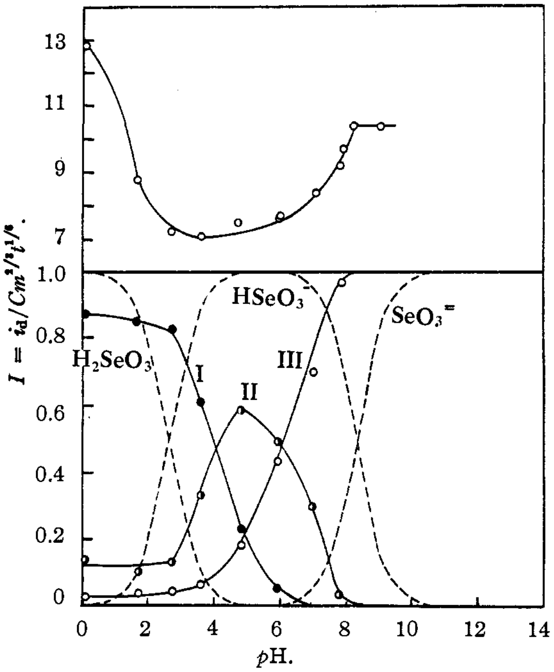

Fig. 6.—The upper curve shows the variation of the *total* diffusion current constant of 1 millimolar selenium(IV) with *p*H. The solid curves in the lower graph are the *relative* observed heights of the main waves I, II and III, and the dashed curves show the relative equilibrium concentrations of H_2SeO_3 (left), $HSeO_3^-$ (middle) and $SeO_3^=$ (right), calculated from the dissociation constants of selenous acid.

The fact that at potentials more negative than the half-wave potential of wave II the anodic reaction 2 is excluded, and yet at intermediate *p*H values the *total* diffusion current constant corresponds to only a 4-electron reduction, is, we believe, due to the formation of elemental selenium. The −2 selenium produced by the primary reaction 3 diffuses away from the electrode surface and reacts in the diffusion layer with the incoming hydrogen selenite ion to precipitate elemental selenium

$$HSeO_3^- + 2H_2Se + H^+ = 3Se + 3H_2O \qquad (5)$$

Since it is known from the coulometric electrolyses that elemental selenium is only slowly reduced (see Fig. 2), and since it is formed in the diffusion layer at some distance from the electrode surface,

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[12] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall Inc., New York, N. Y., 1944.

the *net* reaction at intermediate *p*H is the 4-electron reduction

$$HSeO_3^- + 4e^- + 5H^+ = Se + 3H_2O \qquad (6)$$

At a *p*H of 8 or above, and at low *p*H values, reaction 5 (or the analogous reactions involving H_2SeO_3, $SeO_3^=$, $HSe^=$ and $Se^=$) proceeds so slowly that no appreciable formation of elemental selenium occurs during the drop life, and the final product is −2 selenium.

No evidence has been obtained at any *p*H for the reduction to +2 selenium postulated by Schwaer and Suchy.

At *p*H values below 8 the diffusion current quotients i_d/C of the separate waves, as well as that of the total wave, were found to vary significantly with the concentration of +4 selenium. For example at *p*H = 5.0 the value of $i_d/(C\, m^{2/3}t^{1/6})$ for the total wave decreased from 10.5 and 8.5 when the concentration of selenium(IV) was increased from 0.2 to 2 millimolar. Hence supporting electrolytes of *p*H smaller than about 8 are not suitable for practical analytical purposes.

Copper and Selenium.—Since copper and selenium frequently occur together their simultaneous polarographic determination in ammoniacal medium was investigated. As shown in Fig. 7, polarograms of ammoniacal mixtures of +2 copper and +4 selenium display the familiar double wave which results from the stepwise reduction of the tetramminocupric ion, followed by the well-developed selenium wave.

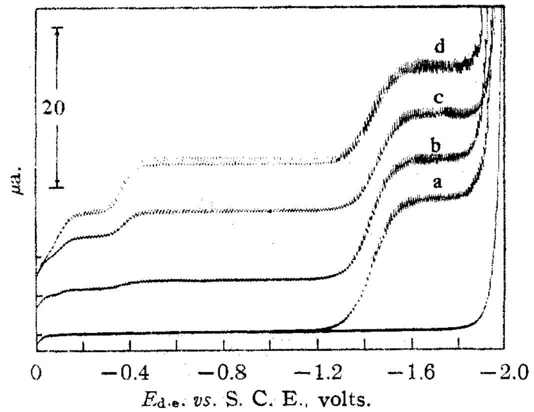

Fig. 7.—Polarograms of 1 millimolar selenium(IV) in 1 *M* ammonium chloride-ammonia at *p*H 8.4 with (a) 0, (b) 0.302, (c) 1.00 and (d) 2.00 millimolar copper(II). Gelatin (0.003%) was used as maximum suppressor. The galvanometer zero for each curve is indicated by the short marks on the left-hand ordinate.

Although the waves of both elements are well developed their analytical application is complicated by the fact that the height of the selenium wave decreases markedly with increasing concentration of copper. With 1.00 and 2.00 millimolar copper the height of the selenium wave in Fig. 7 is only 72 and 75% of its value in the absence of copper. This interesting effect is not due to a decreased diffusion current of the selenium, but rather to a smaller contribution of copper to the total diffusion current at potentials at which selenium(IV) is reduced. The −2 selenium formed at the electrode surface reacts with the incoming tetramminocupric ion in the diffusion layer, precipitating cupric selenide

$$Cu(NH_3)_4^{++} + Se^= = CuSe + 4NH_3 \qquad (7)$$

and the contribution of copper to the total diffusion current is correspondingly diminished. Since 6 electrons are involved in the formation of each selenide ion, but the reduction of the copper complex requires only 2 electrons, it is evident that if the diffusion coefficients of copper(II) and selenium(IV) were the same, then increasing the concentration of copper should decrease the apparent height of the selenium wave only until the molar concentrations of copper and selenium are equal. At this point the apparent height of the selenium wave alone should be two-thirds of its original value. The observed selenium wave height (72%) is slightly larger than two-thirds its original value because the diffusion coefficient of the tetramminocupric ion is somewhat larger than that of selenium(IV), and also because the precipitation of cupric selenide is not quite complete. With still larger concentrations of copper the apparent height of the selenium wave should remain constant, and this is the observed result. In other words, the *total* diffusion current at the potential of the selenium wave (−1.6 to −1.8 v.) remains practically constant until the quantity $CD^{1/2}$ for copper exceeds that for the tellurium, and then increases in direct proportion to the increased copper concentration.

Correction for this effect is complicated by the fact that the precipitation of cupric selenide is not quite complete, and hence in practical work the correction will have to be determined empirically. This same effect will doubtless also be observed with other metals that form insoluble selenides.

Tellurium.—The low solubility of tellurium dioxide in neutral and acid solutions limits the choice of supporting electrolytes for experiments at *p*H less than 7. It was found that the solubility in acid medium is greatly increased by the presence of citrate or tartrate, apparently because of the formation of telluryl citrate complexes, and in citrate media it is possible to work with concentrations of tellurium(IV) up to about 5 millimolar. Tellurium dioxide is freely soluble in ammoniacal and alkaline media.

Figure 8 shows tracings of polarograms of 1 millimolar tellurium(IV) in 0.5 *M* citrate buffers of *p*H between 0.4 and 6.88. Maximum suppressors such as methyl red, thymol blue, α-naphthol and thiourea are without effect, and even gelatin up to 0.01% does not eliminate the very large maximum.

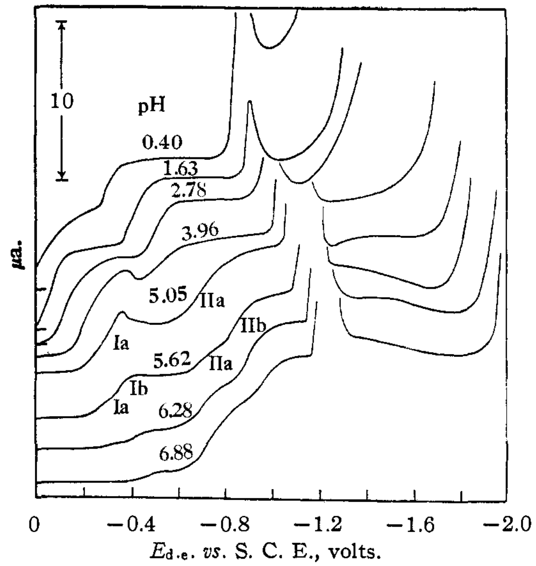

Fig. 8.—Polarograms of 1 millimolar +4 tellurium in 0.5 *M* citrate buffers at the *p*H values indicated for each curve. No maximum suppressor was present.

There are two main waves preceding the large maximum, and these are best developed at *p*H values between 0.4 and 3. The approximate equality of the heights of these two waves with 1 millimolar tellurium(IV) up to about *p*H 5 is purely fortuitous, and does not correspond to stepwise reduction, nor to the intermediate production of +2 tellurium. For example, with a citrate buffer of *p*H 1.63 only a single wave preceding the maximum is observed when the concentration of tellurium(IV) is smaller than about 0.4 millimolar. With increasing tellurium(IV) concentration the second wave at −0.4 v. develops, but the first wave retains a virtually constant height. With 3 millimolar tellurium(IV) the second wave height becomes nearly four times the height of the first wave. At *p*H 1.63, the *total* diffusion current measured at −0.6 to −0.8 v. was strictly proportional to the concentration of tellurium(IV) between 0.1 and 3 millimolar, with $i_d/(C\ m^{2/3}t^{1/6})$ equal to 5.72 ± 0.07. The diffusion current constant increases from 4.8 at at *p*H of 0.4 to a maximal value of 5.75 at about *p*H 2, and then gradually decreases to 4.8 as the *p*H is increased to 7.

The virtual constancy of the first wave height with increasing concentration of tellurium(IV) suggests the formation of a film of reduction product (elemental tellurium) on the electrode surface which inhibits further reduction until the potential exceeds about −0.4 v.

Coulometric analysis at −0.65 v. showed that the total double wave at *p*H 1.63 results from a 4-electron reduction to elemental tellurium

$$H_2TeO_3 + 4e^- + 4H^+ = Te + 3H_2O \qquad (8)$$

Since the change in the total diffusion current constant is not very great between *p*H 0.4 and 7, it is evident that the total wave over this *p*H range is due to reduction to the element.

At *p*H values between 5.5 and 7.0 additional poorly defined waves are observable before the maximum. These may be due in part to reduction to the +2 state, but film formation and reduction of the different ionization species of tellurous acid are probably more important factors.

In ammoniacal medium only one very well developed wave appears as shown in Fig. 9. In two coulometric reductions with the potential of the large mercury cathode at −0.90 v. *vs.* S.C.E. the coulometer reading corresponded to 4.07 and 3.95 electrons per mole of tellurium (IV) reduced, proving that the wave results from reduction to the element.

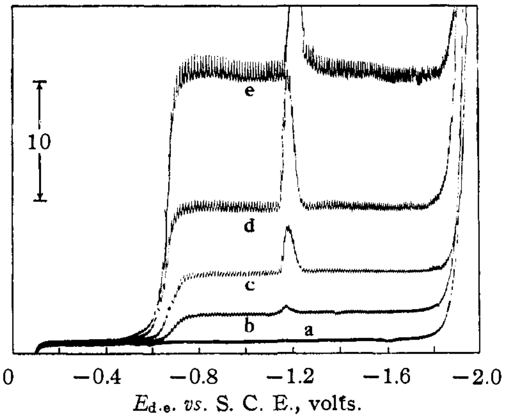

Fig. 9.—Polarograms of (a) 0, (b) 0.202, (c) 0.500, (d) 1.00 and (e) 2.00 millimolar tellurium(IV) in 1 *M* ammonium chloride–ammonia at *p*H 9.4 in the presence of 0.003% gelatin.

The polarographic characteristics in ammoniacal buffers are summarized in Table II. All the solutions contained 0.003% gelatin. The values of $i_d/(Cm^{2/3}t^{1/6})$ in the last column display a

TABLE II

+4 TELLURIUM IN AMMONIACAL BUFFERS AT 25°

Buffer	*p*H	*C*, millimolar	$E_{1/2}$ *vs.* S.C.E.	i_d, microamp.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
1 *M* NH_4Cl	8.4	0.202		2.37	7.75
		0.500	−0.64	5.83	7.72
		1.000	− .63	11.40	7.54
		2.000	− .62	22.48	7.43
	9.4	0.202	− .69	2.43	7.95
		0.500	− .67	6.04	7.99
		1.000	− .66	11.74	7.76
		2.000	− .66	22.44	7.75
1 *M* NH_4 Tartrate	9.3	0.083	− .72	0.85	6.7
		1.67	− .68	15.4	6.1
	10.0	0.083	− .80	0.80	6.3
		1.67	− .77	15.8	6.3
0.1 *M* NH_4 Tartrate	9.0	0.083	− .76	0.98	7.8
		1.67	− .76	18.9	7.5
	10.0	0.083	− .83	0.92	7.3
		1.67	− .79	18.1	7.2

small but significant decrease with increasing concentration of tellurium(IV) at any given *p*H, the trend being less pronounced the higher the *p*H. Thus the diffusion current is not strictly proportional to *C* over a wide range of concentrations, but the discrepancy is small.

Single well developed waves were also obtained in borate and carbonate buffers between *p*H 7.8 and 11.1. The half-wave potentials at a given *p*H are somewhat more negative in borate and carbonate buffers than in ammoniacal medium. For example, at *p*H 9.4 the half-wave potentials in 0.5 *M* carbonate and borate buffers were −0.87 v. and −0.88 v., respectively, compared to −0.68 v. in 1 *M* ammonium chloride–ammonia at the same *p*H. The half-wave potential of the alkaline wave shifts markedly to more negative values with increasing *p*H; in 0.5 *M* borate buffers of *p*H 7.8, 8.8, 10.5 and 11.1 the values were *seriatim* −0.74, −0.84, −0.96 and −1.18 v. *vs.* S.C.E.

In 0.1 and 1 *M* sodium hydroxide in the presence of gelatin, a very well developed single wave is obtained as shown in Fig. 10. Without gelatin a small prewave precedes the main wave, but this is completely eliminated with 0.01% gelatin. The half-wave potentials in 0.1 and 1 *M* sodium hydroxide in the presence of 0.003% gelatin are −1.22 v. and −1.19 v., respectively. It is interesting to note that these values are very close to the standard potential (−1.21 v. with 1 millimolar tellurium) of the couple $Te + 2e = Te^{=}$ (see ref. 2). This indicates that the reduction proceeds all the way to −2 tellurium and that the $Te \rightarrow Te^{=}$ stage is the potential determining step.

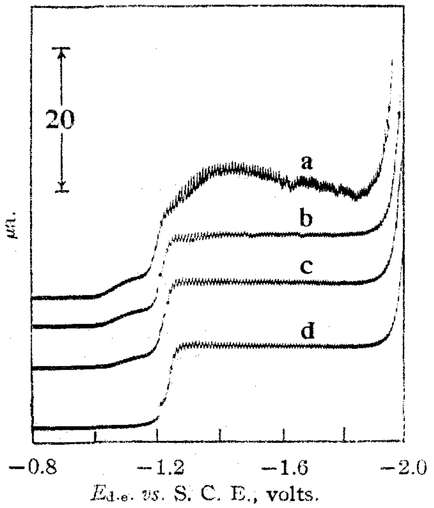

Fig. 10.—Polarograms of 0.837 millimolar tellurium(IV) in 1 *M* sodium hydroxide with (a) 0, (b) 0.001, (c) 0.003 and (d) 0.01% gelatin.

That reduction in sodium hydroxide medium proceeds to −2 tellurium, according to

$$TeO_3^{=} + 3H_2O + 6e^{-} = Te^{=} + 6OH^{-} \quad (9)$$

was verified by the coulometric technique. A 1.37 millimolar solution of tellurium(IV) in 1 *M* sodium hydroxide was reduced with the potential of the large mercury cathode at −1.60 v. *vs.* S.C.E. The coulometer reading after the current decreased to zero corresponded to 5.97 electrons per mole of tellurium(IV) reduced. The current decreased from an initial value of 135 milliamp. to less than 1 milliamp., showing that reduction at this potential proceeds with 100% current efficiency. The current–time curve during this reduction had the same shape as that for the reduction of selenium(IV) shown in Fig. 2. During the first stage of the electrolysis elemental tellurium precipitated, then dissolved to form deep violet polytelluride ion, and the latter was finally completely reduced to colorless telluride ion.

The data in Table III show that $i_d/(C\,m^{2/3}t^{1/6})$ for tellurium(IV) in 1 *M* sodium hydroxide shows a significant variation with concentration. The trend is smaller with 0.003% gelatin than with either 0.001 or 0.01%. In the former case i_d is a linear function of *C* to ±1% over the concentration range 0.2 to about 2.8 millimolar.

TABLE III

DIFFUSION CURRENT CONSTANT OF +4 TELLURIUM IN 1 *M* SODIUM HYDROXIDE AT 25°

C, millimolar	*i*, microamp.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	*C*, millimolar	*i*, microamp.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
0.001% gelatin			0.334	4.70	9.75
0.0837	1.17	9.7	.500	7.03	9.75
.1674	2.37	9.8	.834	11.67	9.70
.3344	4.92	10.18	1.169	16.62	9.85
.502	7.46	10.32	1.668	23.34	9.70
.837	11.66	9.65	2.167	30.48	9.75
1.172	16.78	9.92	2.835	39.37	9.62
1.674	23.72	9.82	3.335	44.08	9.16
2.175	30.24	9.64	0.010% gelatin		
2.845	36.13	8.81	0.0839	0.86	7.1
3.344	40.32	8.35	.1672	2.14	8.9
0.003% gelatin			.335	4.32	8.92
0.0834	1.12	9.3	.839	11.62	9.60
.1668	2.32	9.6	1.677	23.65	9.77
			3.34	46.31	9.60

Since +4 selenium does not produce a wave in 1 *M* sodium hydroxide this is a most suitable supporting electrolyte for the determination of tellurium in the presence of selenium, especially when selenium predominates. As Schwaer and Suchy[3] pointed out, an ammoniacal supporting electrolyte is useful for the simultaneous determination of both elements, the wave of tellurium preceding that of selenium by about 0.8 v.

A most striking feature of the polarograms of +4 tellurium is the very large maximum which appears in the diffusion current plateau at all *p*H values in all the supporting electrolytes, except sodium hydroxide. This maximum is unusual in that it occurs after the diffusion current plateau has been reached, or in the middle of the plateau in ammoniacal media and in borate and carbonate buffers, rather than as an extension of the rising part of the wave as in the case of ordinary maxima. The maximum is also exceptionally indifferent to the usual maximum suppressors. Significantly the potential at which the maximum develops coincides at all *p*H values with the half-wave potential of the *anodic* wave of the reaction $\text{Te}^{=} = \text{Te} + 2e^-$ discussed in a preceding paper.[2] It is also significant that the only medium in which the maximum is absent is 1 *M* sodium hydroxide, which is probably related to the fact that the cathodic tellurium(IV) wave occurs at almost exactly the same potential as the anodic $\text{Te}^{=}$ wave in this medium.[2] The occurrence of the maximum is thus intimately related to the $\text{Te}^{=}$–Te couple.

Apparently the rising part of the maximum reflects the beginning of reduction of the tellurium(IV) to the −2 state, but when this starts the normal diffusion layer at the surface of the mercury drops, is disrupted, and a vigorous stirring action ensues which causes the current to rise to a very large value. Observations under the microscope revealed the formation of a brown turbidity (elemental tellurium) as a succession of bands which expanded radially from the drop. At potentials before the maximum, as well as after it, the deposited tellurium formed an adherent coating on the drop and no streaming or turbidity near the drop was observed. The band pattern suggests a rhythmically recurrent process during the drop life. A likely mechanism is that the $\text{Te}^{=}$ which forms partially dissolves the adherent tellurium deposit, forming polytelluride ion in the diffusion layer and freeing part of the electrode surface. Part of the relatively large concentration of polytelluride ion formed near the electrode surface is rapidly reduced to $\text{Te}^{=}$, causing a large surge of current, and part of it diffuses outward from the electrode and reacts with tellurium(IV) to precipitate elemental tellurium and produce the observed bands. The combination of these processes and the resultant density gradients disturbs the diffusion layer and produces stirring which accelerates the transfer of tellurium(IV) to the electrode surface. The reduction of the enhanced concentration of tellurium(IV) to elemental tellurium proceeds at a faster rate than its reduction to $\text{Te}^{=}$, and than the reaction between the elemental tellurium and $\text{Te}^{=}$, so that the adherent tellurium coating tends to reform, the current surge decreases, and the diffusion layer begins to reestablish itself until the formation of polytelluride again catches up with the decreased rate of reduction of tellurium(IV). The cycle then repeats. The fact that at a slightly more negative potential these processes abruptly cease, so that the current falls to the original value corresponding to only a 4-electron reduction, remains to be explained.

Tellurium in Presence of Other Metals.—Metals which produce polarographic waves preceding that of tellurium(IV) and which form insoluble tellurides exert a pronounced suppressing effect on the apparent height of the tellurium wave in strongly alkaline medium. This effect, which is analogous to the suppressive action of copper on the selenium wave, is illustrated by the polarograms in Fig. 11 of mixtures of lead and tellurium in 1 *M* sodium hydroxide. The first wave at −0.76 v. is the normal wave due to reduction of the hydrogen plumbite ion, and the second is that for the reduction of tellurium(IV) to telluride ion.

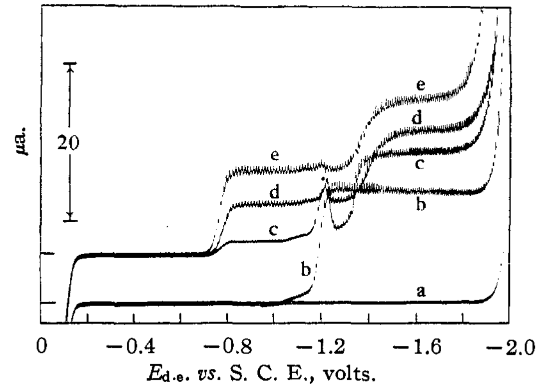

Fig. 11.—Polarograms of 1 millimolar tellurium(IV) in 1 *M* sodium hydroxide containing 0.003% gelatin with (a) 0, (b) 0.30, (c) 1.20 and (e) 2.00 millimolar lead ion added.

Amounts of lead up to the point where the product $CD^{1/2}$ for the plumbite ion becomes equal to this product for the tellurium(IV) produce no increase in the *total* diffusion current between −1.5 and −1.8 v., but the apparent height of the tellurium wave decreases. With larger amounts of lead the height of the tellurium wave remains constant and the *total* diffusion current increases in direct proportion to the excess lead added. These phenomena are due to the fact that the telluride ion produced at the electrode surface reacts in the diffusion layer with the incoming hydrogen plumbite ion to precipitate lead telluride

$$\text{Te}^{=} + \text{HPbO}_2^- + \text{H}_2\text{O} = \text{PbTe} + 3\text{OH}^- \quad (10)$$

Hence the hydrogen plumbite ion cannot contribute to the total diffusion current until its flux at the electrode (proportional to $CD^{1/2}$) exceeds the flux of +4 tellurium. Because the reduction of tellurium(IV) requires 6 electrons, and that of the plumbite ion only 2 electrons, it is to be expected that the apparent height of the tellurium wave will decrease only to $^2/_3$ of its original value, and this is precisely what we observed. With 1 millimolar tellurium the apparent height of the tellurium wave was 81, 69, 68 and 66% of its original value when the respective concentrations of lead were 0.30, 0.70, 1.20 and 2.00 millimolar. The same effect was produced by copper and mixtures of copper and lead.

From Fig. 11 it is seen that addition of lead 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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[4] D. Aleksyeev, *J. Russ. Phys.-Chem. Soc.*, **41, 1155** (1909).

[5] S. J. Lloyd and A. M. Kennedy, *Trans. Am. Inst. Chem. Engrs.*, **16**, 29 (1924).

[6] S. J. Lloyd and A. M. Kennedy, *Chem. & Met. Eng.*, **32**, 624 (1925).

[7] O. A. Essin, *Z. Elektrochem.*, **35**, 234 (1929).

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

[9] G. W. Heise, *Trans. Electrochem. Soc.*, **75**, 147 (1932).

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

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