

the calculated value by a large factor which again averages about 10. (Note: the sum of the logarithms of the deviations of the experimental from the calculated k_1 values for each series of simple complexes must equal zero because $(k_1 k_2 k_3)^{1/3} = k_{av.}$) It may therefore be expected that the unsaturated mixed complex, MX_Y , will include the deviations involving k_1 and k_2 of the simple complexes and will show considerable positive deviations, or "enhancements." The saturated complexes, MX_2Y and MX_Y_2 , will include the negative deviation associated with k_3 and should exhibit

net deviations or enhancements considerably smaller, by about a factor of 10, than the unsaturated complex. The data for the mixed complexes of nickel support these predictions almost quantitatively,^{19,30} and the data for cadmium are in qualitative agreement.

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Polarographic Characteristics of Osmium. II. The +6 and +4 States

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Information is presented regarding the oxidation-reduction behaviors of +6 and +4 osmium in sodium hydroxide media and of +6 osmium in mineral acid solutions, both at dropping mercury electrodes and at large stirred mercury electrodes.

Introduction

Very little information has been available regarding the polarographic behaviors of the lower oxidation states of osmium. Crowell, Heyrovsky and Engelkemeir² reported that +6 osmium gave a double wave in a saturated calcium hydroxide medium and ascribed this to the reduction scheme $VI \rightarrow IV \rightarrow III$. Willis,³ Ruis and Molera⁴ and Meites⁵ studied the behaviors of +6, +3, and +2 osmium in cyanide media.

The work described here was undertaken in order to supplement this scanty information, to obtain further data bearing on the question of the possible existence of +5 osmium in alkaline media, which had been inferred from previous experiments,⁵ and to provide a basis for the design of electroanalytical methods for the determination of osmium.

Experimental

The apparatus and techniques employed were described in the first paper of this series.³

Solutions of osmium tetroxide were assayed by coulometry at controlled potential, employing the previously described four-electron reduction on the plateau of the total double wave in a cyanide supporting electrolyte. Solutions of +6 osmium were prepared by the quantitative electroreduction of osmium tetroxide in dilute sodium hydroxide media at a mercury cathode whose potential was maintained at -0.35 v. vs. s.c.e. Solutions of +4 osmium were prepared similarly but at a working-electrode potential of -1.00 v. vs. s.c.e.

Although a silver-silver chloride reference electrode⁶ occasionally was used in carrying out controlled-potential electrolyses, all potentials are referred to the usual saturated calomel electrode. All diffusion current constants

are given in $\mu\text{amp./mmole/l./mg.}^{2/3}\text{sec.}^{-1/2}$ and are calculated from the difference between the total current on the plateau of the wave in question and the separately measured residual current at the same potential.

Results and Discussion

+6 Osmium in Sodium Hydroxide Media.—Polarograms of +6 osmium in solutions containing more than about 0.5 F sodium hydroxide consist of two waves, as shown by Fig. 1. Their half-wave potentials are constant and equal to -0.596 ± 0.009 v. and -1.521 ± 0.015 v. at sodium hydroxide concentrations varying from 0.1 to 9.4 F . These values are in good agreement with those (-0.61 ± 0.01 v. and -1.51 ± 0.02 v.) previously reported for the second and third waves of +8 osmium in similar media. In the absence of a maximum suppressor, there is also an anomalous wave at about -1.3 v., which is displaced to -1.7 v. by the addition of 0.002% Triton X-100 (cf. Fig. 1). The total diffusion current constants of the waves at various sodium hydroxide concentrations are given in Table I.

TABLE I
DIFFUSION CURRENT CONSTANTS OF +6 OSMIUM IN SODIUM HYDROXIDE MEDIA

| [NaOH] F | I_1 | I_2 | $I_{17}^{1/2}$ | I_2/I_1 |
|---------------|-------------------|-----------------|----------------|-----------|
| 0.098 | 2.83 ± 0.05^a | 6.79 ± 0.13 | 8.6 | 2.40 |
| 0.25 | $2.65 \pm .11^a$ | $5.2 \pm .1$ | 8.1 | 1.96 |
| 1.0 | $2.69 \pm .05$ | $4.85 \pm .09$ | 8.9 | 1.80 |
| 3.8 | $2.05 \pm .04$ | $3.41 \pm .06$ | 10.2 | 1.66 |
| 9.4 | $1.06 \pm .02$ | $1.45 \pm .09$ | 9.8 | 1.37 |

Mean 9.1 ± 0.7

^a Total diffusion current constant for a poorly resolved doublet wave.

The decrease of the diffusion current constant of the first wave with increasing sodium hydroxide concentration is due to the increasing viscosity of the solution, as is shown by the near constancy of the product $I_{17}^{1/2}$. The variation of the ratio I_2/I_1 ,

(1) This paper is based on a thesis submitted by Richard E. Cover to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the M.S. degree in June, 1960.

(2) W. R. Crowell, J. Heyrovsky and D. W. Engelkemeir, *J. Am. Chem. Soc.*, **63**, 2888 (1941).

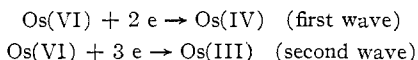
(3) J. B. Willis, *ibid.*, **67**, 547 (1945).

(4) A. Ruis and M. J. Molera, *Anales real soc. espan. fis. y quim. (Madrid)*, **45B**, 1151 (1949).

(5) L. Meites, *J. Am. Chem. Soc.*, **79**, 4631 (1957).

(6) L. Meites and S. A. Moros, *Anal. Chem.*, **31**, 23 (1959).

on the other hand, is largely and probably even entirely due to the effect of sodium hydroxide concentration on the height of the anomalous wave, which is included in the calculated value of I_2 . As is also true for the corresponding waves of +8 osmium,⁵ the value of this ratio becomes essentially equal to 1.5 at high sodium hydroxide concentrations. This indicates that the reduction scheme is



This interpretation of the first wave is confirmed by the coulometric data shown in Table II. Small

TABLE II

COULOMETRIC n -VALUES FOR THE FIRST WAVE OF +6 OSMIUM IN SODIUM HYDROXIDE MEDIA

| [NaOH], F | $E_{w.e.} = -1.00$ v. vs. s.c.e. | | n |
|-------------|----------------------------------|------------------------|-----------------|
| | +6 Osmium, micromoles | Microfaradays consumed | |
| 0.25 | 37.1 | 74.68 | 2.01 |
| 1.0 | 44.6 | 88.63 | 1.99 |
| 3.8 | 27.4 | 55.70 | 2.03 |
| | | 55.63 | 2.03 |
| | 41.3 | 84.11 | 2.04 |
| | 44.6 | 88.22 | 1.98 |
| 9.4 | 44.6 | 95.26 | 2.14 |
| | | Mean | 2.03 ± 0.03 |

background corrections⁶ were necessary in the 0.25 and 1 F sodium hydroxide solutions, but in 3.8 F sodium hydroxide the final electrolysis current was indetectably small at the potential employed.

The phenomena encountered in attempts to confirm the n -value of 3 assigned to the second wave by carrying out controlled-potential coulometric measurements at potentials on its plateau are described below.

The ratio between the diffusion current constant of the first wave of +6 osmium (Table I) and that previously reported⁵ for the first wave of +8 osmium shows no detectable trend with sodium hydroxide concentration but remains equal to 0.73 ± 0.07 over the range from 0.25 F to 9.4 F sodium hydroxide. Since each of these waves represents a 2-electron reduction, this ratio of I -values must be essentially equal to the corresponding ratio of the square roots of the diffusion coefficients, $(D_6/D_8)^{1/2}$. It therefore reflects a difference in mobility between the predominant species of +6 osmium and the monohydrogenosmate(VIII) ion, which is the principal constituent of +8 osmium solutions in this range of alkalities and ionic strengths.⁷

In 9.4 F sodium hydroxide the value of $E_{3/4} - E_{1/4}$ for the first wave of +6 osmium is -27.3 mv., which is in good agreement with the expected value, -28.2 mv., for a reversible 2-electron reduction at 25°. The behavior of this parameter at lower hydroxide concentrations is shown in Table III. In 0.1 and 0.25 F sodium hydroxide the wave divides into two poorly resolved portions of very roughly equal heights. In view of this

(7) R. D. Sauerbrunn and E. B. Sandell, *J. Am. Chem. Soc.*, **75**, 4170 (1953).

TABLE III

HALF-WAVE POTENTIALS AND VALUES OF THE PARAMETER $E_{3/4} - E_{1/4}$ FOR THE WAVES OF +6 OSMIUM IN SODIUM HYDROXIDE SOLUTIONS

| [NaOH], F | First wave (\rightarrow Os(IV)) | | Second wave (\rightarrow Os(III)) | |
|-------------|------------------------------------|---------------------------|--------------------------------------|---------------------------|
| | $E_{1/2}$, v. | $E_{3/4} - E_{1/4}$, mv. | $E_{1/2}$, v. | $E_{3/4} - E_{1/4}$, mv. |
| 0.098 | -0.610 | -62 | -1.511 | -45 |
| | - .839 | -83 | | |
| 0.25 | - .612 | -48 | -1.506 | -61 |
| | - .776 | -91 | | |
| 1.0 | - .605 | -78 | -1.543 | -81 |
| 3.8 | - .583 | -58 | -1.507 | -46 |
| 9.4 | - .601 | -27.3 | -1.513 | -45 |

poor resolution, the value of $E_{3/4} - E_{1/4}$ for the first wave of the doublet (*cf.* Table III) is essentially equal to the value, -56.4 mv., that would be expected if it corresponded to a reversible 1-electron process. Since, in addition, its half-wave potential appears to be independent of hydroxyl-ion concentration, it is believed to reflect the occurrence of the half-reaction $\text{OsO}_4^{2-} + e = \text{OsO}_4^{-3}$. The second wave of the doublet shifts rapidly toward more negative potentials as the hydroxyl-ion concentration decreases: thus the increase of $E_{3/4} - E_{1/4}$ as the sodium hydroxide concentration is decreased from 9.4 to 1 F may be ascribed to an incipient division of the first wave into this doublet. The second wave of the doublet is clearly irreversible. It is believed to correspond to the reduction of +6 osmium directly to the +4 state at a rate that is increased by increasing the hydroxyl-ion concentration.

The height of the first wave of the doublet is actually always greater than one-half, and is usually more nearly two-thirds, of the total height of the doublet. Data on the effect of mercury pressure on its height show that its behavior is intermediate between those of diffusion-controlled and kinetic waves. Finally, controlled-potential electrolysis at a potential on its plateau yields +4 osmium, rather than the +5 osmium that would be expected on the basis of the above half-reaction. From these facts it appears that the +5 osmium initially formed at the electrode surface disproportionates into +4 and +6 osmium. The reduction of the +6 osmium thus regenerated causes the current to increase beyond the expected value for a 1-electron reduction to the +5 state, and the magnitude of this increase shows that the disproportionation of +5 osmium in these relatively weakly alkaline solutions is quite rapid. In 4 to 10 F sodium hydroxide +5 osmium is much more stable, as is shown below. Results in qualitative agreement with this picture are obtained by chronoamperometric measurements during controlled-potential electrolysis at a potential on the plateau of the first wave; these results, together with their quantitative interpretation, will be published elsewhere.

+4 Osmium in Sodium Hydroxide Media.—A typical polarogram of +4 osmium in a moderately concentrated sodium hydroxide solution is shown in Fig. 2. It consists of two cathodic and two anodic waves. The second cathodic wave has a half-wave potential of -1.497 ± 0.014 v.

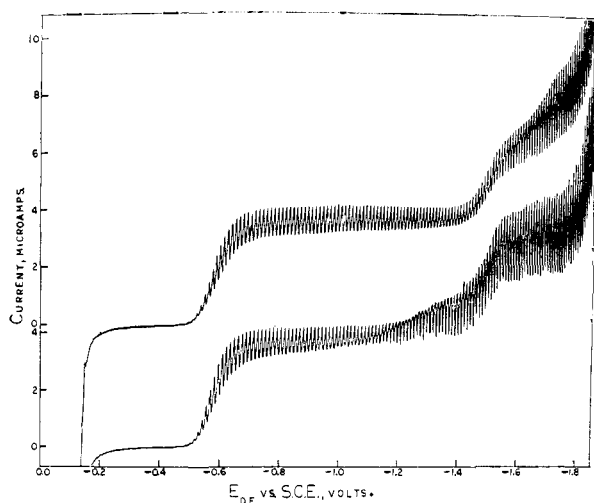


Fig. 1.—Polarograms of 0.825 mM +6 osmium in 3.8 *F* sodium hydroxide, alone (lower curve) and in the presence of 0.002% Triton X-100 (upper curve).

over the range of sodium hydroxide concentrations from 0.1 to 9.4 *F*. This is essentially identical with that of the last wave on a polarogram of either +6 or +8 osmium, and therefore this wave must represent a 1-electron reduction of the osmium to the +3 state. The ratio of the diffusion current constant of this wave to that for the over-all 3-electron reduction of +6 osmium in 3.8 or 9.4 *F* sodium hydroxide (where, as is shown by Table I, the anomalous contribution to the +6 osmium wave is nearly completely suppressed) is 0.533 ± 0.014 . The fact that this is greater than the ratio (1/3) of the *n*-values assigned to these waves must reflect a greater mobility of the +4 osmium species. On the other hand, in 9.5 ± 0.2 *F* sodium hydroxide the value of I/n for the total cathodic wave of +4 osmium ($= 0.79/1$) is not very much greater than that for the first wave of +8 osmium ($= 1.32/2$), which lends further support to the assignment of the value $n = 1$ to the total cathodic wave of +4 osmium. The diffusion coefficients calculated from the relationship $D = (I/607 n)^2$ are $D_6 = 0.76 \times 10^{-6}$, $D_3 = 1.18 \times 10^{-6}$ and $D_4 = 1.69 \times 10^{-6}$ cm.²/sec., all in 9.5 ± 0.2 *F* sodium hydroxide.

The value of $E_{3/4} - E_{1/4}$ for the second cathodic wave of +4 osmium (Table IV) at any sodium hydroxide concentration is nearly identical with that for the corresponding wave of +6 osmium (Table III) but is much smaller than for +8 osmium.⁵ Apparently the reduction of the latter to the +3 state proceeds *via* an intermediate that is different from the stable form of +4 osmium in these media.

The total anodic diffusion current constant of +4 osmium is numerically exactly equal to the total cathodic diffusion current constant in 3.8 and 9.4 *F* sodium hydroxide. Hence +4 osmium is oxidized only to the +5 state at the dropping electrode in these media. Nevertheless, controlled-potential coulometry on the plateau of the total anodic wave gives $n = -2.07 \pm 0.02$. It is evident that +5 osmium disproportionates in concentrated as well as in dilute sodium hydroxide

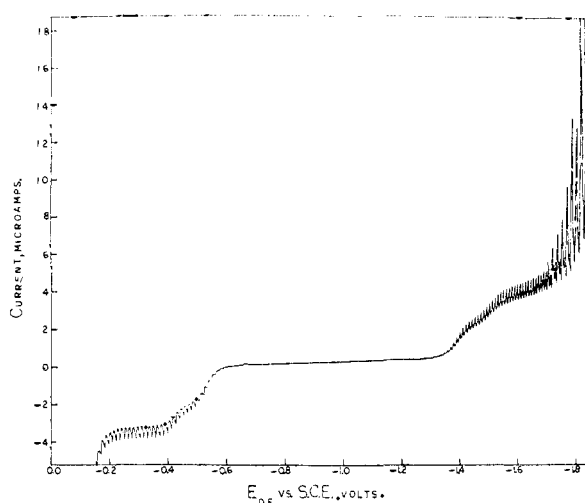


Fig. 2.—Polarogram of 0.893 mM +4 osmium in 3.8 *F* sodium hydroxide.

media. Its relative stability in the more concentrated media is shown not only by the agreement between the wave height measured and that expected for a 1-electron oxidation but also by the fact that the total anodic wave was found to be entirely diffusion-controlled. Similar apparent discrepancies between polarographic and controlled-potential coulometric *n*-values have been shown to exist in the reductions of +6 uranium^{8,9} and of *p*-N,N-dimethylaminoazobenzene.¹⁰

Although +5 osmium disproportionates more slowly at higher than at lower sodium hydroxide concentrations, it is not formed on reducing +6 osmium in concentrated sodium hydroxide solutions because reduction to the +4 state proceeds more rapidly. At lower sodium hydroxide concentrations the data on +4 and +6 osmium are in agreement regarding the moderately rapid disproportionation of the +5 osmium that is formed from both.

This effect of hydroxyl-ion concentration on the rate of disproportionation of +5 osmium is shown by the behavior of the ratio, I_a/I_c , of the over-all anodic and cathodic diffusion current constants of +4 osmium. Whereas, as was stated above, this ratio is equal to -1.00 in 9.4 or 3.8 *F* sodium hydroxide, it is -1.35 in 1.0 *F* sodium hydroxide. This corresponds to the oxidation of about 35% of the +4 osmium to the +6 state during the lifetime of a drop, which is of the same order as the extent of disproportionation indicated by the ratio of wave heights for the doublet wave of +6 osmium in dilute sodium hydroxide solutions.

In 0.1 *F* sodium hydroxide, on the other hand, the ratio I_a/I_c is only -0.64. The variation of I_a with changing sodium hydroxide concentration, which is described in detail by Table IV, is attributable to the changing viscosity of the solution: the product $I_c \eta^{1/2}$ is essentially constant from 0.1 to 9.4 *F* sodium hydroxide. The de-

(8) P. Herasymenko, *Trans. Faraday Soc.*, **46**, 272 (1928); W. E. Harris and I. M. Kolthoff, *J. Am. Chem. Soc.*, **68**, 1175 (1946).

(9) L. Meites and J. H. McGlotten, unpublished experiments.

(10) H. A. Laitinen and W. J. Kneip, *ibid.*, **78**, 736 (1957).

crease of I_a/I_0 at low hydroxide concentrations must therefore reflect an anomaly in the behavior of I_a . Since the above ratio corresponds to an n -value of only -0.6 , only a portion of the osmium is oxidized despite the relatively rapid disproportionation of $+5$ osmium in these dilute sodium hydroxide solutions. Hence a precipitate must form which contains osmium in some oxidation state below $+6$ (probably $+4$ and $+5$). This was confirmed by controlled-potential electrolyses: in a typical experiment with $2.8 \text{ mM} +4$ osmium in 0.2 F sodium hydroxide, controlled-potential oxidation at -0.25 v. gave a black precipitate and an n -value of only -1.63 . In 3.8 F sodium hydroxide, however, the solution remains clear throughout and n -values very close to -2 are obtained. A precipitate is observed in 0.2 F sodium hydroxide only if the total osmium concentration exceeds about 0.5 mM . The behavior of the diffusion current constant data indicates that the solubility in 0.1 F sodium hydroxide is even smaller.

Data on the effect of mercury pressure show that the first cathodic wave of $+4$ osmium is entirely kinetic in nature, so that it must correspond to the reduction of some species whose equilibrium concentration is negligibly small but which is formed from the principal species at the drop surface. The half-wave potential of this kinetic wave varies slightly with sodium hydroxide concentration, as is shown in Table IV. Except in 9.4 F sodium hydroxide, however, it is always so close to the second cathodic wave that its characteristics cannot be measured accurately. In 9.4 F sodium hydroxide its wave height was 0.22 times that of the total cathodic wave with the capillary employed; the mean of the corresponding ratios in 0.1 to 1 F sodium hydroxide was 0.18 ± 0.05 . Though the latter value is not very precise, it is clear that the rate of the chemical transformation involved is not sensibly affected by changes in the hydroxyl-ion concentration.

The doublet anodic wave shown in Fig. 2 appears only at the higher concentrations of sodium hydroxide: in 0.1 to 1 F sodium hydroxide only a single anodic wave is observed. Its half-wave potential shifts rapidly ($\Delta E_{1/2}/\Delta \log [\text{OH}^-] = \text{ca. } -80 \text{ mv.}$) to more negative values with increasing hydroxyl-ion concentration. The value of $E_{1/2} - E_{1/4}$ for this single anodic wave is constant and equal to $+44.5 \pm 0.8 \text{ mv.}$ over the range from 0.1 to 1 F sodium hydroxide; this value is consistent with the proposed mechanism (oxidation to $+5$ osmium followed by relatively fast disproportionation and partial precipitation).

The anodic waves of $+4$ osmium in sodium hydroxide media appear to provide the best available approach to the polarographic determination of this element. Relatively concentrated sodium hydroxide solutions should be used for this purpose to avoid the complications that would certainly result from the disproportionation and precipitation that occur at lower alkalinities.

Curve a of Fig. 3 shows the data obtained when an alkaline solution of $+4$ osmium was electrolyzed at a potential on the plateau of its over-all cathodic wave in an attempt to confirm the n -value ($= 1$)

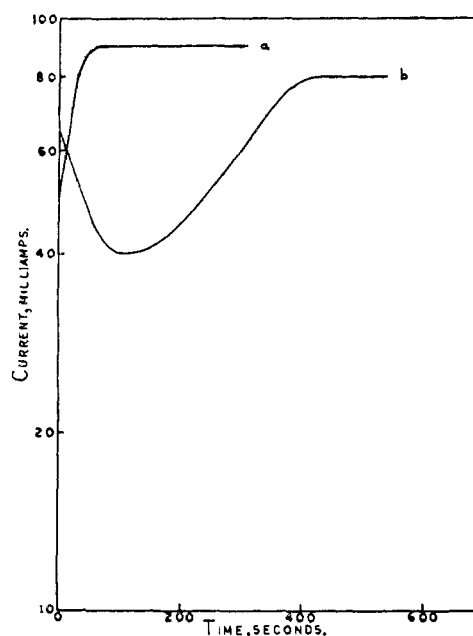


Fig. 3.—Logarithmic chronoamperograms for reductions of (a) 41.3 micromoles of $+4$ osmium and (b) 27.4 micromoles of $+6$ osmium in 50 ml. of 3.8 F sodium hydroxide with a mercury cathode at a potential of $-1.65 \text{ v. vs. s.c.e.}$

assigned here to the process occurring at that potential. Instead of decreasing exponentially with time in the usual fashion, the current increased from the very start of the electrolysis and rapidly approached a value that was nearly twice as large as that at the start. This cannot be explained by any mechanism that is confined to the solution phase: for example, even if the reaction $\text{Os(III)} + \text{H}_2\text{O} \rightarrow \text{Os(IV)} + \frac{1}{2} \text{H}_2 + \text{OH}^-$ were instantaneous (which is belied by the magnitude of the over-all cathodic diffusion current constant under these conditions), the current would only remain equal to its original value. To explain the increase, it is necessary to assume that the reduction of $+4$ osmium to the $+3$ state occurs at potentials

TABLE IV
POLAROGRAPHIC CHARACTERISTICS OF $+4$ OSMIUM IN SODIUM HYDROXIDE MEDIA
The half-wave potentials of anodic waves are enclosed in parentheses.

| [NaOH], F | $E_{1/2}$, v. vs. s.c.e. | I | $E_{1/4} - E_{1/2}$, mv. | Oxidation state of product |
|--------------|---------------------------------|--------------------|------------------------------|-------------------------------|
| 0.098 | (-0.405) | -1.30 ± 0.03 | + 43.2 | V + VI (pptn.) |
| | -1.2 | (0.23) | -100 | |
| | -1.485 | $2.03 \pm .04$ | - 57.8 | III |
| 0.25 | (-0.440) | $-2.37 \pm .04$ | + 44.5 | V + VI (pptn.) |
| | -1.30 | (0.75) | -100 | |
| | -1.501 | $2.89 \pm .06$ | - 57.2 | III |
| 1.0 | (-0.485) | $-2.52 \pm .05$ | + 45.8 | V + VI |
| | -1.33 | (0.53) | -100 | |
| | -1.520 | $1.87 \pm .03$ | - 53.4 | III |
| 3.8 | (-0.443) | $-1.77 \pm .06$ | + 48 | V |
| | (-0.548) | $-1.03 \pm .02$ | + 40 | V (part) |
| | -1.399 | $1.00 \pm .04$ | - 45 | III (part) |
| | -1.506 | $1.77 \pm .13$ | - 40 | III |
| 9.4 | (-0.501) | -0.796 ± 0.015 | + 36 | V |
| | (-0.585) | $-.332 \pm .005$ | + 46 | V (part) |
| | -1.059 | $.183 \pm .020$ | - 88 | III (part) |
| | -1.476 | $.793 \pm .034$ | - 41.3 | III |

TABLE V

DIFFUSION CURRENT CONSTANTS OF +6 OSMIUM IN HYDROCHLORIC AND SULFURIC ACID SOLUTIONS

The second column gives the diffusion current constant of +6 osmium in the supporting electrolyte named in the first column. The third column gives the diffusion current constant of +8 osmium in a similar supporting electrolyte whose composition is specified in the fourth column. The fifth column gives the ratio of the diffusion current constant for +6 to that for +8 osmium.

| Supporting electrolyte | I_6 | I_8 | Medium | I_6/I_8 |
|--|---------------------------|-------------|---|---------------------|
| HCl 1.1 <i>F</i> | 4.77 ± 0.23 | 9.59 ± 0.04 | 1.0 <i>F</i> HCl | 0.498 |
| 9.1 <i>F</i> | (4.12 ± .11) ^a | 11.8 ± .5 | 12 <i>F</i> HCl | (.350) ^a |
| H ₂ SO ₄ , 0.21 <i>F</i> | 3.40 ± .25 | 8.5 ± .4 | 0.5 <i>F</i> H ₂ SO ₄ | .400 |
| 1.9 <i>F</i> | 3.55 ± .04 | 8.5 ± .4 | 0.5 <i>F</i> H ₂ SO ₄ | .417 |
| | | | Mean | 0.438 ± 0.04 |

^a Believed to be too low and excluded from average; see text.

where the further reduction to the metal proceeds at a small but appreciable rate and that the metal thus formed decreases the overpotential for the evolution of hydrogen on the electrode and thus leads to an increase of the electrolysis current. This interpretation is consistent with the fact that the value of $E_{3/4} - E_{1/4}$ for the second cathodic wave is smaller than that expected for a reversible 1-electron reduction to +3 osmium. Though the rate of increase of current is fairly high on the time scale of a controlled-potential electrolysis, it is small compared to the frequency of renewal of the drops at a dropping electrode. The accumulation of metallic osmium at the surface of a mercury drop in a polarographic experiment is consequently sufficiently slow that the increased rate of reduction of water caused by its presence does not produce a perceptible effect on the diffusion current observed.

Generally similar phenomena are encountered in reducing +6 osmium under the same conditions (Fig. 3, curve b). In this case, however, the current decreases initially, and coulograms show that the minimum current flows when about 2.4 faradays of electricity have been consumed per mole of osmium. As this figure doubtless includes some contribution from the accelerated reduction of water, it seems probable that the minimum actually corresponds to the point at which substantially all of the osmium is present in the +4 state. This suggests that the accumulation of metallic osmium at the electrode surface is prevented by the occurrence of the reaction $\text{Os} + \text{Os(VI)} \rightarrow 2 \text{Os(III)}$ as long as any +6 osmium remains in the bulk of the solutions.

The polarographic characteristics of +4 osmium in sodium hydroxide media are summarized for convenient reference in Table IV.

+6 Osmium in Mineral Acid Media.—In sulfuric and hydrochloric acid solutions, +6 osmium gives a single well-defined cathodic wave which rises from zero applied potential. The height of the wave is always diffusion-controlled. Coulometry at controlled potential gives $n = 2.92 \pm 0.03$, indicating that the reduction proceeds directly to the +3 state. This is in agreement with the fact that +8 osmium undergoes a 5-electron reduction in these media.⁵ The dif-

fusion current constants of +6 osmium in several acidic media are given in Table V. The value in 9 *F* hydrochloric acid is probably somewhat low because of volatilization of chlorine from the solutions; this was found to occur very rapidly during deaeration with nitrogen and must have taken place to some extent during the few seconds for which nitrogen was passed into the solution to stir it after addition of the stock +6 osmium solution. Otherwise the values are generally parallel to those for +8 osmium. The ratio of n -values for the waves of these substances is 3/5, whereas the mean ratio of I -values (excluding the value for 9 *F* hydrochloric acid) is 0.438 ± 0.04 . Hence the ratio $(D_6/D_8)^{1/2}$ is 0.73 ± 0.07 , which is precisely equal to that obtained in sodium hydroxide media.

Summary

Polarograms of +6 osmium in solutions containing more than about 0.5 *F* sodium hydroxide consist of two cathodic waves which represent stepwise reduction to the +4 and +3 states. Polarograms of +4 osmium in the same media consist of a poorly resolved double anodic wave which corresponds to oxidation to the +5 state, a kinetic cathodic wave representing the reduction (to the +3 state) of a portion of the osmium which undergoes a chemical transformation into a more easily reducible species in the bulk of the solution, and a second cathodic wave which is due to the reduction of the remainder of the osmium to the +3 state and which also includes a small contribution from the accelerated reduction of water because of the deposition of a trace of metallic osmium in the mercury and the consequent decrease of the overpotential for hydrogen evolution. At lower concentrations of sodium hydroxide the first cathodic wave of +6 osmium divides into a poorly resolved doublet whose first portion reflects the transient formation of +5 osmium, while the behavior of the anodic wave of +4 osmium shows that the rate of disproportionation of +5 osmium is increased by decreasing the hydroxyl-ion concentration and that there is also some precipitation of osmium in an oxidation state lower than +6. In mineral acid media +6 osmium is reduced directly to the +3 state at mercury electrodes.