

TABLE I  
REDUCTION OF 1 mM  $\text{Co}(\text{NH}_3)_6^{++}$  IN VARIOUS SUPPORTING  
ELECTROLYTES

Electrode I: Monovalent Anions		Concn., $M$	$\eta^{1/2}$ (19)	$i_d$ , $\mu\text{a.}$	$i_d \cdot \eta^{1/2}$	$E_{1/2}$ , v. S.C.E.
1	NaCl	1.0	1.047	3.59	3.75	-0.193
2	CaCl <sub>2</sub>	1.0	1.073	3.31	3.55	-.220
3	Na benzoate	1.0	1.285	2.68	3.41	-.300
4	NaClO <sub>4</sub>	1.0	1.023	3.56	3.65	-.240
5	NH <sub>4</sub> NO <sub>3</sub>	1.0	0.985	3.63	3.57	-.250
6	Na acetate	1.0	1.180	3.00	3.54	-.345
7	NaOH	0.5	1.051	3.53	3.71	-.355
8	CoCl <sub>2</sub>	1.0	1.097	3.13	3.43	-.195
Divalent anions						
9	Na tartr.	1.0	1.155	2.22	2.57	-0.380
10	Na <sub>2</sub> SO <sub>4</sub>	0.7	1.074	2.95	3.17	-.450
11	Na <sub>2</sub> SO <sub>4</sub>	1.0	1.110	2.64	2.94	-.465
12	CoSO <sub>4</sub>	1.0	1.163	2.43	2.82	-.440
13	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.0	1.055	2.96	3.12	-.465
14	K <sub>2</sub> SO <sub>4</sub>	0.7	1.036	3.09	3.20	-.465
15	H <sub>2</sub> SO <sub>4</sub>	1.0	1.043	3.19	3.33	-.385
16	Na <sub>2</sub> SO <sub>4</sub>	0.1	1.01	3.20	3.24	-.430
17	Na <sub>2</sub> CO <sub>3</sub>	0.5	1.135	2.82	3.20	-.455
18	MgSO <sub>4</sub>	1.0	1.170	2.24	2.63	-.452
Trivalent anions						
19	Na <sub>3</sub> citrate	1.0	1.175	1.75	2.06	-0.350

(19) N. W. Lange, "Handbook of Chemistry," 6th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1581.

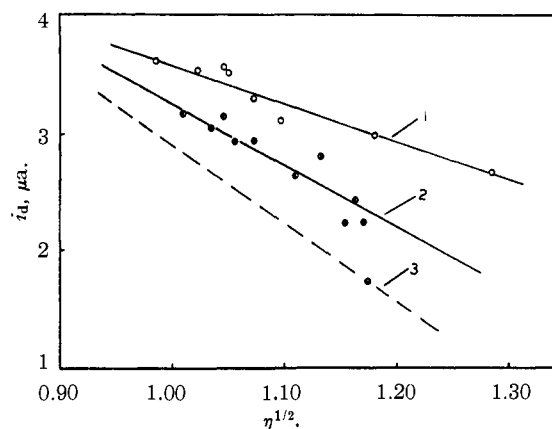


Fig. 5.—The diffusion current of a mM hexamminecobalt (III) plotted versus  $\eta^{1/2}$  of various supporting electrolytes with electrode I.

super complexing but that the change of the ionic strength also affects the potential. Keeping the ionic strength practically constant ( $\mu = 1$ ) with potassium nitrate an addition of 0.1 M potassium sulfate shifted the potential only 25 mv. whereas the shift was 170 mv. if the supporting electrolyte consisted of only sulfate.

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## Electrolytic Reduction of Perrhenate. I. Studies in Perchloric, Ethanesulfonic, Trifluoroacetic and Hydrochloric Acids

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Perrhenate solutions are reduced cathodically in trifluoroacetic or ethanesulfonic acids to insoluble oxide deposits. Perchloric acid is catalytically reduced at a cathode in the presence of perrhenate. In the presence of rhenium a mercury cathode is depolarized with consequent hydrogen evolution in both trifluoroacetic and hydrochloric acids. Conditions are given for the preparation of pure Re(IV) and Re(V) solutions in hydrochloric acid. Absorption spectra of these oxidation states in hydrochloric acid are given. Equilibria between the complex species present in hydrochloric acid solutions of Re(V) are rapidly established but only slowly in Re(IV) solutions. Re(V) can be quantitatively oxidized to perrhenate in hydrochloric acid while Re(IV) cannot.

Both polarographic and electrolytic studies of perrhenate reduction in different media have been reported.<sup>1-4</sup> The polarographic wave found in 2-4 M perchloric or hydrochloric acid has been interpreted as a reduction of perrhenate to Re(IV).<sup>1,2</sup> Rulfs and Elving, however, pointed out that the temperature coefficient of the diffusion current is not that of a diffusion controlled process and hence a value of three for the electron change would only be found at 25°. In addition, an attempt by these authors to electrolytically reduce Re(VII) in perchloric acid led to a continuous process which they attributed to the concurrent reduction of hydrogen ion.

According to Schmid<sup>3</sup> the electrolytic reduction of perrhenate in 6 M hydrochloric acid at a mercury cathode gives a yellow-green solution from which the Re(IV) salt,  $\text{K}_2\text{ReCl}_6$ , may be isolated. Further prolonged reduction gave an olive-green solution which he said was Re(III). Jakob and Jezowska<sup>4</sup> reported that the reduction in 6-10 M hydrochloric acid at either a Pd or platinized Pt electrode gives Re(V) solutions from which the salt,  $\text{K}_2\text{ReOCl}_5$ , can be isolated.

Although both the Re(IV) and Re(V) states have been obtained in hydrochloric acid by reduction with reagents such as stannous chloride,<sup>4-7</sup> studies

(1) J. J. Lingane, *THIS JOURNAL*, **64**, 1001 (1942).

(2) C. L. Rulfs and P. J. Elving, *ibid.*, **73**, 3284 (1951).

(3) H. Schmid, *Z. anorg. allgem. Chem.*, **212**, 187 (1933).

(4) N. F. Jakob and B. Jezowska, *ibid.*, **214**, 337 (1933).

(5) E. K. Maun and N. Davidson, *THIS JOURNAL*, **72**, 2254 (1950).

(6) H. Holemann, *Z. anorg. allgem. Chem.*, **217**, 105 (1934); **220**, 33 (1934); **235**, 1 (1937).

(7) S. Tribalat, *Compt. rend.*, **220**, 881 (1945); **222**, 1388 (1946); **223**, 34 (1946).

of the properties of these states are hindered to some extent by the presence of the reagent cations. An investigation of the controlled potential reduction<sup>8</sup> of Re(VII) was undertaken with a twofold purpose: first, to definitely establish which lower states of rhenium are obtained by reduction in different media and, second, to obtain pure solutions of these states to be used in a further investigation of their properties.

It has been shown that the continuous electrolysis occurring in perchloric acid solution is due to the catalytic reduction of the perchlorate ion. In the relatively non-complexing ethanesulfonic and trifluoroacetic acids reduction results primarily in the formation of insoluble electrode deposits. Pure Re(IV) and Re(V) solutions may be prepared in hydrochloric acid solutions of different concentrations. The preparation of lower states than Re(IV) is hindered by the fact that a mercury cathode is depolarized with respect to hydrogen evolution in the presence of rhenium.

### Experimental

**Materials.**—Solutions of perrhenic acid in the various acid media were prepared by appropriate dilution of a 0.482 *M* solution of perrhenic acid which had been prepared in the following manner. Potassium perrhenate, obtained from the Department of Chemistry of the University of Tennessee, was recrystallized twice from triply distilled water, dried, and reduced to metal in a silica boat in a hydrogen stream at approximately 400°. The reduction was accomplished in three successive treatments, the first lasting four hours and the others two hours each. After each period at 400° the product was cooled in the hydrogen stream, suspended in water, filtered, and washed free of alkali. Approximately 9 g. of the metal was oxidized with 80 ml. of 30% hydrogen peroxide in a modification of the procedure described by Dobbins and Colehour.<sup>9</sup> The peroxide was added in portions of about 5 ml. each, and the mixture was heated to reflux at frequent intervals. After the final addition of peroxide the solution was refluxed for several hours and then saturated with ozone at 50–60° for seven hours to remove the last traces of solid and color. The water-white solution was then purged with nitrogen at 60–70° for one hour, diluted to 100 ml., and centrifuged to remove a small amount of silica. The perrhenic acid content was established by titration with standard sodium hydroxide to the phenol red and phenolphthalein end-points. An aqueous dilution gave the value 3630 for the molar extinction coefficient of the intense perrhenate peak at 2275 Å.

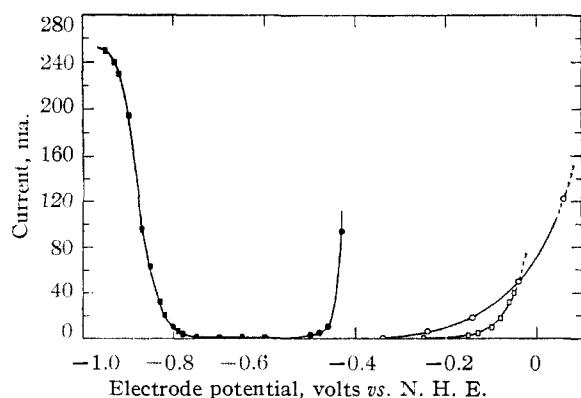


Fig. 1.—Current-potential behavior of: ●, 0.207 *M* HReO<sub>4</sub> in 6 *M* HClO<sub>4</sub>; ○, 0.0916 *M* HReO<sub>4</sub> in 4 *M* HCl; □, 0.0436 *M* HReO<sub>4</sub> in 8 *M* HCl; ■, 0.0436 *M* Re(V) in 8 *M* HCl.

(8) P. Wehner and J. C. Hindman, *THIS JOURNAL*, **72**, 3911 (1950).

(9) J. T. Dobbins and J. K. Colehour, *ibid.*, **56**, 2054 (1934).

Dilutions of the recrystallized potassium perrhenate gave the values 3630 in water and  $3610 \pm 10$  (average of three determinations) in 1 *M* perchloric acid.

The perchloric acid was 72% doubly vacuum distilled obtained from the G. Frederick Smith Chemical Co. Trifluoroacetic acid obtained from the Minnesota Mining and Manufacturing Co. was purified by double distillation. The ethanesulfonic acid obtained from Indoil Chemical Co. was doubly vacuum distilled.

**Apparatus.**—The electrolysis cells and the potentiostat were of the type previously described.<sup>8</sup> The oxidation state changes were determined with a gas coulometer. The reference electrodes used in the reduction were Pt(Cl<sub>2</sub>) in 4 *M* hydrochloric acid and Hg, Hg<sub>2</sub><sup>++</sup> in 6 *M* perchloric acid. A graphite anode was used in the experiments involving hydrochloric acid. Both the anode and cathode compartments were flushed continuously with prepurified nitrogen. For the electrolytic oxidation experiments a Pb, PbCl<sub>2</sub> reference electrode in 1 *M* hydrochloric acid was used. The potentials given in the paper are expressed as oxidation potentials with respect to the normal hydrogen electrode.

Spectrophotometric observations were made using a Cary Recording Spectrophotometer (marketed by the Applied Physics Corp., Pasadena, California). Unless otherwise stated the temperature of measurement was 25°.

### Results and Discussion

**Reductions in Non-complexing Acids.**—Attempts to prepare soluble lower states of rhenium in solutions of non-complexing acids by reduction of perrhenate at either platinum or mercury cathodes have been unsuccessful.

In 6.0 *M* perchloric acid at 25°, using a platinum cathode, the net reaction is the catalytic reduction of perchlorate to chloride ion. This was shown by the fact that after three faradays of current per mole of rhenium was passed through the solution spectral examination revealed that the perrhenate concentration was unchanged. The catholyte gave a strong chloride test. This behavior is similar to that exhibited by ruthenium.<sup>8</sup> A typical current-voltage curve is shown in Fig. 1. In concentrated rhenium solutions a black coating is obtained on the cathode at high current densities. This coating dissolves on decreasing the current or stopping the electrolysis to give a clear solution of perrhenate.

In the less easily reduced trifluoroacetic and ethanesulfonic acids reduction of perrhenate results in the formation of insoluble oxides. The same result is obtained in either 6 *M* or 10 *M* trifluoroacetic acid at either mercury or platinum cathodes. In addition it is found that in 6 *M* trifluoroacetic acid at a mercury cathode hydrogen evolution begins near 0 volt. In the absence of rhenium gas evolution is not observed until +0.4 v. Rhenium is apparently an effective depolarizer for the mercury cathode.

In experiments in 5 *M* ethanesulfonic acid, the oxide prepared by reduction at potentials more negative than 0 volt dissolved in hydrochloric acid to give a deep amber solution. If, however, the reduction was carried out with concurrent evolution of hydrogen the deposit was partially insoluble, indicating that perhaps some rhenium metal is formed under these conditions.

At 25°, the currents obtained in reductions fell to very low values at measured oxidation numbers between +4 and +5. In an experiment in 6 *M* ethanesulfonic acid at 80–85° at a platinum cathode it was found possible to obtain a sharp end-point (current 0 milliamp.) by electrolyzing at -0.375 v. The oxidation state of the rhenium was 3.87, in-

dicating that the probable end-product in these reactions is  $\text{ReO}_2$ .

**Reductions in Hydrochloric Acid.**—It has been found possible to prepare relatively pure solutions of two of the lower states of rhenium in hydrochloric acid.

Reduction of 0.0916 *M* perrhenic acid in 4 *M* hydrochloric acid at a mercury cathode and 25° produces an olive-green solution. The end-point corresponds to an oxidation state of  $4.06 \pm 0.06$  (mean of three determinations). The current-voltage behavior is summarized in Fig. 1. The electrode is strongly polarized as shown by the fact that the current attainable at a given voltage setting rises markedly if the electrolysis is momentarily interrupted. Gas evolution is observed at the cathode at a potential of +0.06 v. Rhenium effectively depolarizes the mercury cathode in hydrochloric acid as well as in trifluoroacetic. Since under these experimental conditions the electrolyses must be completed at +0.01 to 0.02 v. considerable care is required to avoid running into the hydrogen discharge region.

The olive-green solutions of the rhenium(IV) prepared in the above experiments are obviously mixtures of different complex species since in each preparation the absorption spectra are only qualitatively similar. A typical spectrum is shown in Fig. 2. Furthermore, on standing, slow changes occur which increase the similarity of the spectrum to that found on dissolving potassium hexachlororhenate(IV). It is of interest to note that there is no evidence in these solutions of the "reactive" yellow-brown form of Re(IV) reported by Maun and Davidson.<sup>5</sup>

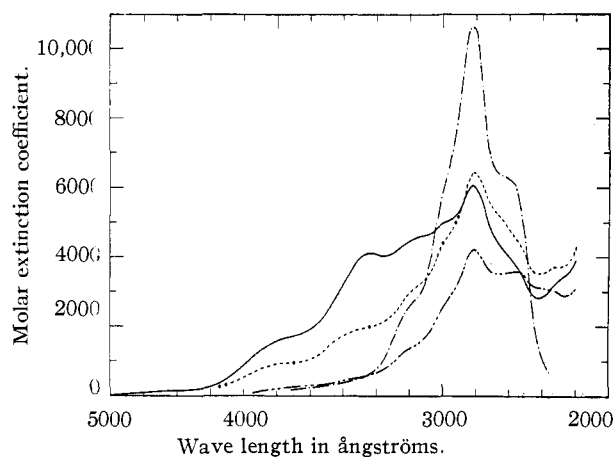


Fig. 2.—Re(IV) in hydrochloric acid: —, olive-green Re(IV) in 4 *M* HCl immediately after preparation; ---, same after storage for six months at room temperature; — · —, same after electrolytic oxidation to average oxidation state Re(4.37); ·····, potassium hexachlororhenate(IV) in 10 *M* HCl.

Attempts to prepare a lower state than Re(IV) by reduction at ice temperature in 4 *M* hydrochloric acid resulted in the partial formation of a reddish lower state that was highly unstable with respect to oxidation by hydrogen ion.

Reduction of perrhenic acid in 8 *M* hydrochloric acid at a platinum cathode and 25° yields a clear

light yellow-green solution. The average oxidation state obtained at a cathode potential of  $-0.08$  v. is  $4.96 \pm 0.03$  (mean of four determinations). The characteristics of the current-voltage curves are shown in Fig. 1. As in the case of the reductions to Re(IV), the electrodes are obviously highly polarized. No marked decrease in the overvoltage was found on electrolyzing at 50° although a sharper end-point was obtained (0 ma., oxidation state 5.00).

As initially prepared, Re(V) solutions all contain a small amount of a species absorbing at 4010 Å. In a few cases sufficient quantities of this species were present to give the solutions an amber or yellow-brown color. The apparent molar extinction coefficient at this wave length varied from 160 to 840 for different preparations. On standing this species disappears and the yellow-green equilibrium solution is obtained. This is characterized by the existence of two bands in the visible at 4800 and 4160 Å. (Fig. 3). The strong ultraviolet absorption band at 2410 Å. characteristic of Re(V) remains unaltered during this transformation (Fig. 4). The equilibrium Re(V) solution appears to be only slowly oxidized by air; in 10 *M* hydrochloric acid at room temperature only 3% was oxidized in fifty days.

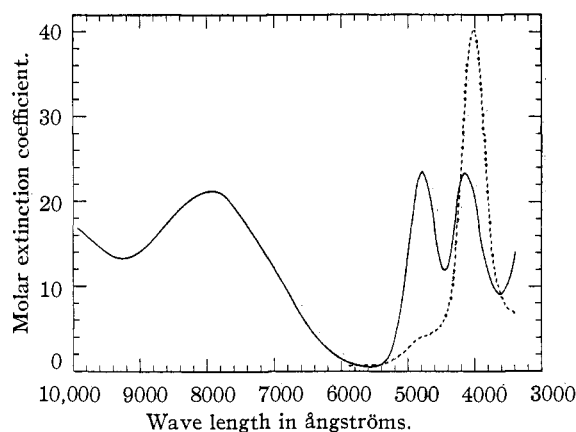


Fig. 3.—Spectra in hydrochloric acid: —, "equilibrium" Re(V) in 10 *M* HCl; ---, yellow-brown species believed to be Re(IV), in 8 *M* HCl, extinction coefficients initially four to twenty times greater than shown.

The question of the oxidation state of the yellow-brown species is of some interest since its absorption spectrum in the visible bears a qualitative resemblance to that reported by Maun and Davidson<sup>5</sup> for the "reactive" form of Re(IV). The largest amount of a species absorbing in this region was observed in a 10 *M* hydrochloric acid solution prepared by dissolving the black cathode deposit resulting from a reduction of perrhenate in 6 *M* sulfuric acid. The yellow-brown solution showed a sharp peak at 4040 Å. with a molar extinction coefficient of 6,400. The ultraviolet spectrum indicated the solution was predominantly Re(IV) admixed with some Re(V). Addition of sufficient perrhenate to this solution to raise the average oxidation state to +5 resulted in the rapid disappearance of the 4040 Å. band and the appearance of the typical absorption spectrum of a pure Re(V)

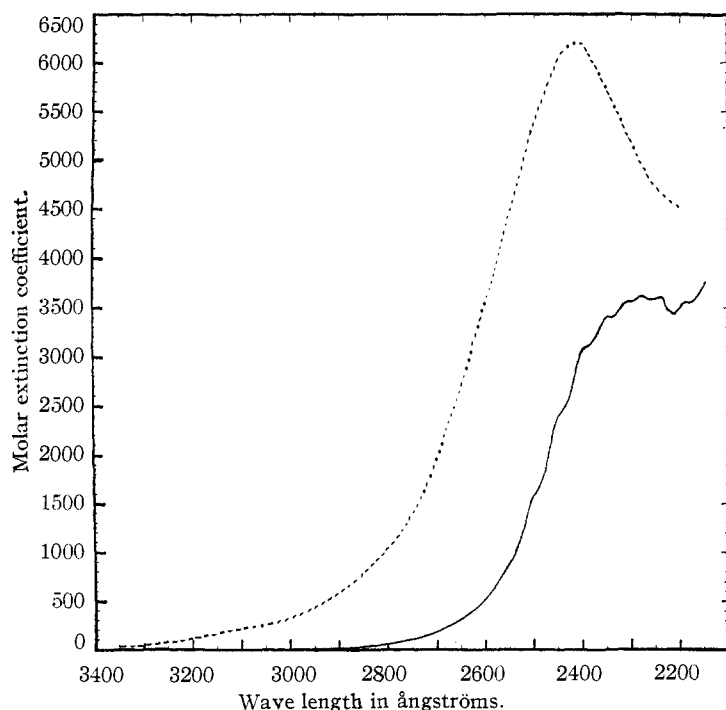


Fig. 4.—Spectra of Re(V) and Re(VII): —,  $\text{HReO}_4$  in water; ---, Re(V) in 10  $M$  HCl.

solution (Fig. 4). In the absence of perrhenate the yellow-brown species was stable, showing no change over a period of 4–5 days. These results strongly indicate that the yellow-brown species is Re(IV). Since different preparations had the visible maximum at wave lengths varying from 4010 to 4060 Å., it is probable that more than a single species is formed.

It is not surprising that some Re(IV) is produced in the preparation of Re(V) in 8  $M$  hydrochloric acid since the potential required to reduce perrhenate to Re(IV) is probably more negative than the potential actually used in the reduction. From the magnitude of the extinction coefficients observed in the rhenium(V) preparations it would appear that relatively small amounts of Re(IV) are produced in these reductions. Why the yellow-brown species are produced in the Re(V) preparations but are not observed in the Re(IV) preparations is not clear. It would have been expected that if these species are more highly oxygenated as suggested by Davidson and Maun,<sup>5</sup> an interpretation that is consistent with their preparation from cathode deposits, larger amounts would have been observed at lower acidities.

Examination of the effect of varying the acid concentration on the Re(V) solutions produced by the above procedure has revealed the following: (1) The solution typified by the twin peaks is apparently a mixture of species, as decreasing the acid concentration decreases the density of the 4800 Å. band faster than that of the 4160 Å. band. In 3.3  $M$  acid the 4800 peak is completely gone and the 4160 Å. band has decreased in magnitude and shifted to the ultraviolet. The visible spectrum obtained in 5  $M$  hydrochloric acid is qualitatively similar to that reported by Maun and Davidson.<sup>5</sup>

It would appear, therefore, that Re(V) does not exist in solution as a single species such as  $\text{ReOCl}_5^{--}$  as has been generally assumed.<sup>4,5</sup> (2) In addition to the essentially instantaneous changes observed in the dilution experiments described above, slow reactions also occur as the acid concentration is decreased from 5 to 3.3  $M$ . Spectral examination reveals that these changes may be correlated with the previously reported instability of Re(V) in low acid with respect to disproportionation into Re(IV) and Re(VII).<sup>7</sup>

If a mercury cathode is used in the reduction in 8  $M$  hydrochloric acid an immediate reaction with the cathode material is noted. If the reduction is carried to completion, an olive-green solution of oxidation state +4.11 is obtained and the mercurous chloride produced in the original reaction has been reconverted to mercury. The yellow-green oxidation state considered by Schmid<sup>8</sup> to be Re(IV) and the olive-green solution designated by him as Re(III) would appear to be correctly designated as Re(V) and Re(IV), respectively.

**The Oxidation of Re(IV) and Re(V) in Hydrochloric Acid.**—To garner further information about the ions present in hydrochloric acid solutions of these two oxidation states, attempts were made to electrolytically oxidize the Re(IV) and Re(V) solutions prepared in the above experiments.

The electrolysis results are in agreement with the spectrophotometric observations that the Re(IV) solutions contain a mixture of ionic species between which equilibrium is established only slowly. Oxidation of the Re(IV) solutions begins near a potential of  $-0.7$  v. Successive voltage increases up to the point of chlorine discharge ( $-1.05$ – $1.15$  v.) increase the current. However, complete oxidation is not possible at any potential below that for chlorine discharge. The species absorbing at longer wave lengths are preferentially oxidized (Fig. 2).

In contrast, Re(V) solutions when oxidized anodically give a current-voltage curve very much like that for a diffusion controlled reaction (Fig. 1). Quantitative oxidation to Re(VII) was obtained. The behavior of Re(V) is of interest in two respects: (1) The fact that the oxidation does not proceed in a stepwise manner similar to that of Re(IV) despite the evidence from the dilution experiments that Re(V) exists in these solutions as a mixture of ionic species confirms the conclusion that equilibria involving Re(V) complexes are established very rapidly. (2) The smoothness with which the oxidation proceeds, in contrast to the reduction process for producing Re(V), where activation polarization phenomena are obviously involved, suggests that the two processes proceed through different intermediates. One possibility would be that the reduction involves the formation of an oxide film on the cathode surface whose rate of dissolution is the rate determining process.