[CONTRIBUTION FROM PURDUE UNIVERSITY AND THE PURDUE RESEARCH FOUNDATION]

Oxidation Levels of Rhenium. II. Oxidation of Rhenide at the Dropping Mercury Electrode. Nature of the Rhenide Species in Hydrohalic Acid Media[1]

BY CHARLES L. RULFS[2a] AND PHILIP J. ELVING[2b]

The general character and behavior on polarographic oxidation of rhenide solutions in sulfuric, methanesulfonic, perchloric or phosphoric acids are fundamentally the same. Rhenium shows little tendency to exist in the intermediate (I), (II) or (III) states as independent species in aqueous media. The oxidation pattern at the dropping mercury electrode in dilute sulfuric acid involves the transition of Re (−I) to (I) at −0.50 v. *vs.* S.C.E., (I) to (II) at −0.27 and (II) to (III) at −0.02. The value of the (−I)/(I) couple at 25° and unit hydrogen ion activity is +0.230 *vs.* N.H.E.

The polarographic anodic curves found for rhenide in hydrochloric acid solution are less well-defined than in the other acid solutions. A definite cathodic wave appears in hydrochloric acid solution of rhenide, especially if the solution has aged for a short time; this phenomenon is common to rhenide solutions in all of the hydrohalic acids. Other lines of evidence were found to support the view that some specific type of complexation or compound formation must obtain for rhenide solutions in these media.

A polarographic study[3] of the oxidation of rhenide is of great interest from the standpoint of its potential contribution to a better understanding of the lower oxidation levels of rhenium, but several objections may be raised to the interpretation there placed on the waves.

We interpret the anodic waves obtained for rhenide solutions in dilute sulfuric acid as involving the (−I) to (I) oxidation at −0.50 v., the (I) to (II) oxidation at −0.27 v., and the (II) to (III) oxidation at −0.02 v. *vs.* S.C.E. There is some evidence that the wave at *ca.* +0.17 v. may involve oxidation of the (III) state and that the presence of a free (V) species results in a wave at *ca.* +0.09 v. The potentials applying to the various couples are summarized in Table I.

TABLE I

OXIDATION POTENTIALS OF RHENIUM COUPLES

Couple	E(N.H.E.),[a] v.
$Re^- = Re^+ + 2e$	+0.230
($2Re^- + H_2O = Re_2O + 2H^+ + 4e$	+ .13)
$Re^+ = Re^{+2} + e$	+ .02
$Re^{+2} = Re^{+3} + e$	− .23
(Re^{+3} oxidation	− .42, or more neg.)
(Re^{+5} oxidation	− .34, approx.)

[a] Potentials, other than the first given, apply specifically to 0.4 mM rhenide in 2 N H_2SO_4 at 15°.

The value for the (−I)/(I) couple of +0.230 v. *vs.* the N.H.E. (at unit hydrogen ion activity and 25°) is believed to be quite reliable. Values for the other couples apply specifically to 0.4 mM rhenide solutions in 2 N sulfuric acid at 15°; no thermodynamic significance is to be attached to these values in view of the irreversibility of the waves on which they are predicated.

The general character and behavior on oxidation of rhenide solutions in sulfuric, methanesulfonic, perchloric or phosphoric acids are fundamentally the same; the stability of rhenide is very limited in perchloric acid and the existence of the rhenium-(III) state as an intermediate species seems to be favored in phosphoric acid. Rhenium shows little tendency to exist in the intermediate (I), (II) or (III) states as independent species in aqueous media.

Rhenide solutions in the hydrohalogen acids evidence some unique properties in distinction to rhenide solutions in acids such as sulfuric. The cathodic polarographic wave and the distinctive absorption spectrum in HX media must be attributed to the existence of some unique species in this environment. The rate of formation of the rhenide species in hydrochloric acid has been measured. The formation of complexes with pyridine, thiocyanate ion and ethylenediamine is indicated, three molecules of pyridine being coördinated per rhenium atom.

Experimental

The apparatus and reagents employed were largely identical with that previously described.[4] The temperature for the rhenium oxidation experiments was 15.0 ± 0.2°. Rhenium pentachloride (Fairmount Chemical Company) was used to prepare rhenium trichloride by thermal decomposition in a nitrogen atmosphere[5]; the product was purified by resublimation under reduced pressure. The capillary constant, $m^{2/3} t^{1/6}$, is designated as k.

A small jacketed Jones reductor was employed to obtain rhenide solutions. Cold water was rapidly circulated through the jacket. The reductor tube, 1.2 cm. o.d. by 20 cm. long, contained a column, 1-cm. by 16-cm., of amalgamated 20- to 30-mesh zinc granules. The tube, which was used in an inclined position of 30° to the horizontal, had attached a stopcock at the lower end and a standard taper joint at the upper end. Into the joint was inserted the end of the right angle bended neck of a round-bottom flask. A tube was attached to the flask for the entry of nitrogen. About 25 ml. of perrhenate solution in the desired medium was placed in the flask. Air-free nitrogen was flushed through the entire assembly for at least 20 min. Careful rotation of the flask about the axis of the ground glass joint enabled the pressure of the nitrogen to force the solution through the reductor. The amount of flow was controlled by the degree of rotation of the flask, and the rate by the nitrogen pressure. A fresh zinc filling was necessary after every two or, at most, three runs. The first 5 to 10 ml. of solution was used for flushing and activating the reductor, after which the desired volume, usually only 10 ml., was passed. If this was to be polarographed at once, it was collected directly in a nitrogen-swept cell. In the amperometric runs, the rhenide solution of known concentration was admitted near the top of a narrow graduated tube which contained a Bunsen valve at the top and a stopcock at the bottom. A definite volume of the rhenide solution could then be run into the polarograph cell and mixed with a fixed volume of deaerated water containing the desired quantity of chemical oxidant. A positive pressure of nitrogen was always used for moving the solution since the employment of vacuum entails the danger of concentration change due to evaporation of water, loss of perrhenic acid or other volatile rhenium intermediates.

For the titration studies involving rhenide, a large Jones reductor, assembled from a 100-ml. buret and a condenser

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[1] Abstracted from the Ph.D. thesis of C. L. R., Purdue University, August, 1949.

[2] (a) University of Michigan, Ann Arbor, Michigan; (b) The Pennsylvania State College, State College, Pa.

[3] Lingane, THIS JOURNAL, **64**, 2182 (1942).

[4] Rulfs and Elving, *ibid.*, **73**, 3284 (1951).

[5] "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939.

TABLE II

PROPERTIES OF ANODIC RHENIDE WAVES IN SULFURIC ACID

Wave	$E_{1/2}$ 0.4 mM Re$^-$ in 2 N acid at 15°, v.	Shift in $E_{1/2}$ with			Slope of wave		Temp. coeff. of i_d (5 to 25°), %/°C.	Variation of i_d/h ratio for h = 33 and 62, and 28 and 67 cm., $i_d/h^{1/2}$ × 10^2
		Temp., 5 to 25°, v.	Re$^-$ concn., 0.2 to 1.0 mM, v.	H$^+$ concn., 0.8 to 4 N, v.	($E_{1/4}$ − $E_{3/4}$)	Remarks		
A	−0.505	+0.021	Nil	+0.019	0.029	Highly reproducible (±0.002)	3.2	22, 23 25, 27
A′	− .38	Not accurately readable			.06	Too small to be read accurately	1.2	4, 5 6, 9
B	− .268	+ .050	+ .045	+ .011	.050	Variable: 0.04 min., 0.08 max.	1.6	14, 14 15, 16
C	− .020	+ .01	+ .040	+ .046	.053	Variable: 0.03 min., 0.07 max.	2.5	10, 12 11, 11
D	+ .17	Not accurately readable			.04	Unsymmetrical about midpoint		

jacket, was employed, using water at 15° as coolant. The technique of using the assembly for perrhenate reduction was essentially that of Lundell and Knowles.[6] Reduced solutions were collected under an excess of ferric alum solution, treated with phosphoric acid and titrated with 0.05 N bichromate to a diphenylamine end-point.

A Beckman model DU spectrophotometer was employed in the absorption studies, using matched pairs of 1-cm. path, rectangular silica cells.

Nature of Rhenide Oxidation

General Character of Anodic Rhenide Waves.—Rhenide oxidation curves obtained in a sulfuric acid medium always had the general features shown in Fig. 1 when plotted from data obtained manually at 15°. Five distinct anodic waves were always observed, which will be designated as A, A′, B, G and D. These features concur with the α, β′, β″, γ and δ waves found by Lingane[3] except that the second wave (here called A′) apparently was not as clearly demarcated when automatically recorded at 0°. Rhenide curves in 2 N methanesulfonic acid were found to be identical in every respect with those obtained in 2 N sulfuric acid. The same pattern also resulted in 2 N perchloric acid, but difficulty was experienced in attaining and maintaining 100% reduction of the rhenium at 15°. The rhenide oxidations in a 1 M phosphoric acid solution follow an identical pattern except that the G-wave is displaced from its normal position of −0.02 v. in sulfuric acid to the more negative position of −0.21 v. The waves in sulfuric acid medium were studied with respect to all variables of probable significance; most of the characteristics observed should apply equally well to rhenide solutions in methanesulfonic, perchloric or phosphoric acids.

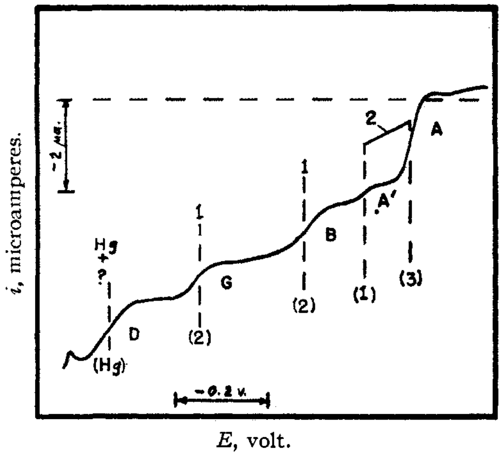

Fig. 1.—Rhenide curves in sulfuric acid: general appearance and nomenclature of the waves; the number of electrons involved per step is indicated according to the present study (above the curve) and according to Lingane[3] (in parentheses, below the curve).

$E_{1/2}$ values for the various waves are given in Table II. The A-wave exhibited only moderate shift with temperature or acidity and no shift with rhenide concentration in accord with the expected behavior for a reversible wave. The A′-wave is too small to be read with any significant precision. The B- and G-waves show significant shifts with temperature and with acidity, respectively; both are irreversible. The potential of the D-wave is somewhat variable.

An average value of 0.029 ± 0.002 v. was obtained for the slope of the A-wave (*i.e.*, for the slope of the usual "E *vs.* log. function of i" plot), which compares favorably with the theoretical value of 0.0275 v. for a reversible 2-electron process at 15°. The values for the A′- and D-waves are not readable with sufficient accuracy to warrant comment. The slopes of the B- and G-waves approximate the single-electron value of 0.055 v., but one cannot attach importance to this in view of the irreversibility of both waves. The averaged approximate relative magnitudes of the i_d/C values at 0.55 mM rhenide are 5.5 (A-wave), 0.7 (A′-wave), 6.2 (combined A-waves), 3.1 (B-wave) and 2.5 (G-wave). While none of the i_d temperature coefficients are notably abnormal for a diffusion-controlled process, the A-wave value of 3.2% is somewhat high while the A′-wave figure of 1.2% is slightly low; the variation of i_d with h for the A-, B- and G-waves seems to be in accord with that for true diffusion-controlled processes, while the A′-wave seems to follow some intermediate course.

On the basis of the foregoing, the following conclusions are at least tentatively established: (1) the A-wave is a reversible, 2-electron, diffusion-controlled process; (2) the A′-wave does not appear to

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[6] Lundell and Knowles, *J. Research Natl. Bur. Standards*, **18**, 629 (1937).

involve a pure diffusion process; (3) both the B- and G-waves appear to be irreversible; (4) the magnitude of the A′-wave is too small to justify its interpretation as even a full one-electron process; and (5) the B- and G-waves are each roughly one-half the size of the combined A-waves.

"Amperometric" Oxidation of Rhenide.—For brevity, use of the term amperometry will here be extended to apply to the process of recording the complete polarogram of a rhenide solution after the addition of each successive, one-equivalent increment of oxidant until 8 equivalents have been added. Only one polarogram for a particular equivalent oxidation level was attempted per run; the time requirement was too great to permit the determination of a complete curve after each of several successive additions of oxidant. Dilute oxidant solution was always added gradually to the rhenide solution with stirring, thus minimizing any possible effect of large local excesses of oxidant.

The curves of Fig. 2 represent the waves of successive "equivalent levels" from the rhenide to the perrhenate states as obtained on oxidation through successive stages with bichromate. The results are rather unusual and very difficult to interpret with absolute certainty. Apparently, some of the lower states must persist through several stages; this is truer of the rhenide itself than of any of the intermediate states. In this connection, the authors concur with Lingane's conclusion[3] that the (I) state obtained by warming rhenide solutions[6] is actually only an "equivalent plus one" state consisting of a mixture of rhenium species. The composition of such a solution seems to include some *bona fide* (I), a larger amount of rhenide, and either rhenium(III), -(IV) or both sufficient to balance the (−I).

The smoothness of the cathodic–anodic transition of the A-wave in partially oxidized solutions may be cited in further evidence of the reversibility of the initial step.

In light of the interpretation ultimately required for the curves, it can be noted that the (I) state has little tendency for independent existence as a species in solution in sulfuric acid. This remark is predicated on the fact that the B-wave remains only to the extent that the A-waves are present. It is probable from the present work and that of others[7,8] that a stabilized (I) species does exist in solution in hydrochloric acid media.

The large shift of the G-wave on the addition of one equivalent of oxidant and its disappearance after the addition of 2 equivalents are rather spectacular. If the G-wave is correctly interpreted as the (II) to (III) oxidation, the conclusion may be justified that the (III) state appears as a separate species in solution only when large amounts of lower oxidation states are present. Apparently, the (III) state is relatively unstable in solution and has little tendency to exist as a separate species, being analogous with manganese(III) in this respect. The negative shift in phosphate media implies a stabilization of the oxidation product of the G-wave, *i.e.*, the (III) state, in the presence of phosphate.

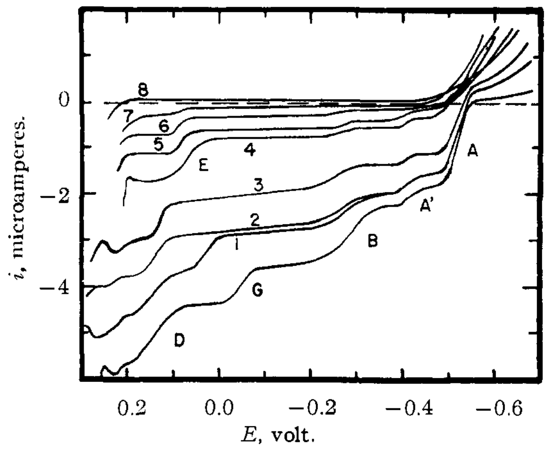

Fig. 2.—Amperometric oxidation of rhenide in sulfuric acid: 0.33 m*M* rhenide in 1.33 *N* acid (bottom curve) oxidized through successive "equivalent oxidation levels" by increments of bichromate to the perrhenate level (curve 8); $m^{2/3}t^{1/6}$ = 1.665 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.52 v., 1.670 at −0.26 v., and 1.684 at +0.05 v.

The appearance of the E-wave at later stages in the oxidation may be attributable to the existence of a free rhenium(V) species in solution at this point. There is some evidence from our work and that of Maun[8] that the oxidation potential for the (V)/(VII) couple may be more positive (Latimer convention) than those of the (IV)/(V) or (IV)/(VII) couples. Therefore, while the visible portion of the stepwise oxidation of rhenide does not include oxidations up to or beyond the (IV) state, it is nevertheless possible that rhenium(V) when present *in situ* may be oxidized in the available potential range. Amalgamated cadmium as a reductant for perrhenate in 6 to 8 *N* sulfuric acid gives an "equivalent (V) state" of rhenium (by titration); when diluted to 2 *N* acidity, such solutions show an anodic wave at *ca.* +0.09 v. Possibly the E-wave represents an oxidation of the (V) state.

The significance of the changes of the D-wave in amperometry with respect to rhenium processes is somewhat doubtful. It was found, however, that a similar wave exists at a corresponding potential *vs.* a mercurous sulfate reference electrode; the $E_{1/2}$ value of the latter wave is, unfortunately, only reproducible within ±0.03 v.

Interpretation of the Oxidation Pattern.—Numerous subsidiary lines of evidence have been presented in support of the interpretations which will now be drawn from more direct evidence.

Potassium hexachlororhenate(IV) in sulfuric acid media gave no anodic waves prior to *ca.* +0.2 v. where calomel discharge might be anticipated. To show that this result did not merely indicate the positive displacement of the true (IV) wave due to complexing, the more readily oxidized (IV) species noted by Maun[8] was also tested. Under a nitrogen atmosphere, hydrous rhenium dioxide was precipitated from a hexachlororhenate solution with base, dissolved in the minimum amount of hydrochloric acid, and appropriately diluted in air-free sulfuric acid. Immediate examination of such a solution showed no anodic waves prior to inception of a calomel wave at +0.18 v. Electrolysis of hexa-

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(7) Maun, private communication; Maun, Ph.D. thesis, California Institute of Technology, June, 1949.

(8) Maun and Davidson, THIS JOURNAL, **72**, 2254, 3509 (1950).

chlororhenate(IV) with a stationary platinum microelectrode *does* result in an anodic wave, but only at +0.5 v. Apparently, the pattern of anodic rhenide waves observed at the D.M.E. must involve oxidation of the rhenide to a level of (IV) or less.

Rhenium(III) chloride in sulfuric acid gave no anodic waves prior to the region of the D-wave. The $E_{1/2}$ varied between +0.14 and +0.17 v., but the wave seemed to be reasonably demarcated from the inception of the calomel discharge which follows at *ca.* +0.2 v. It appears likely that the D-wave may involve the (III) to (IV) step, and that none of the preceding anodic waves can involve rhenium levels higher than (III).

Unfortunately, the coulometric oxidation of a rhenide solution appears to involve an overvoltage phenomenon which does not permit the entirely unambiguous identification of a given potential setting with the potential of a specific wave. At potentials appreciably more negative than −0.2 v., no significant flow of current was obtained through the coulometer. At −0.2 v. a current-equivalent of 1.81 electrons was obtained; at −0.1 v., a figure of 1.97 electrons was found. It seems reasonable to identify the first result with the initial oxidation step, *i.e.*, the A-wave, and the second figure with the same process plus the second step (A′-wave). At the conclusion of runs of the second type, it was found that an insoluble brownish-black amorphous solid had separated. This material was insoluble in concentrated hydrochloric acid, contained rhenium, contained no more than incidental mercury, and resulted from a two-electron oxidation of rhenide. It seems logical to identify such a product with the suboxide.[9]

Apparently, the combined A-waves are to be interpreted as involving a two-electron oxidation of rhenide to rhenium(I), with the A′-wave resulting from the tendency for the formation of an insoluble (I) compound.

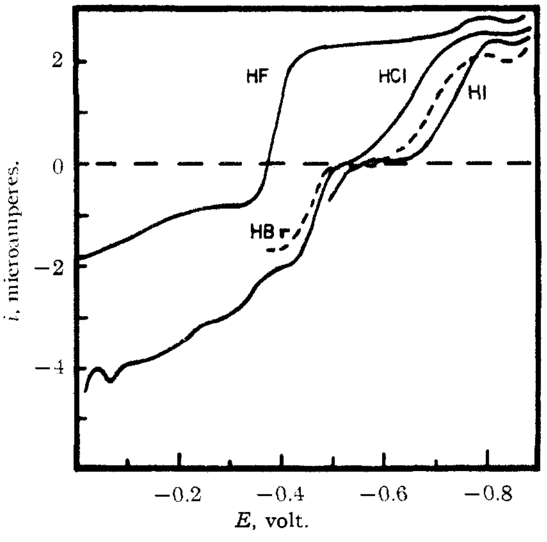

Fig. 3.—Polarography of rhenide in hydrohalic acids: 0.4 m*M* rhenide in 2.4 *N* acid solutions at 15°, *k* = 1.66 at −0.6 v.

The potential of the rhenium(−I)/(I) couple was approximately confirmed by chemical tests; 0.5 m*M* rhenide solutions in 2 *N* sulfuric acid were mixed with equal volumes of dilute solutions of the oxidized forms of various couples. It was found that rhenide in 1 *N* sulfuric acid at 15° will not reduce cobaltous ion but will reduce cuprous iodide. Accordingly, one may estimate the rhenide couple as lying intermediate between +0.28 v. and +0.19 v., or at *ca.* +0.23 ± 0.05 v. *vs.* the N.H.E. This agrees quite well with the polarographic half-wave potential for the A-wave of −0.505 v. *vs.* the S.C.E. (polarographic convention) or +0.26 v. *vs.* the N.H.E. (oxidation potential by Latimer convention).

Behavior of Rhenide in Hydrohalic Acid Media

Evidence for a Rhenide Complex in Hydrochloric Acid.—A distinction between the behavior of rhenide solutions in hydrochloric acid as compared to those in sulfuric acid is apparent from a quantitative study of the reduction of perrhenate to rhenide. In 0.7 to 7 *N* (2 to 20%) sulfuric acid, the maximum concentration of potassium perrhenate which could be quantitatively reduced to the rhenide state was 0.024 g. per 100 ml. or *ca.* 0.83 m*M*, while rhenide concentrations of at least 1.3 m*M* are attainable in 1.2 *N* (10%) hydrochloric acid; 2.6 m*M* rhenide is attainable with the addition of pyridinium chloride to the hydrochloric acid solutions.

A precise study of the various anodic rhenide waves obtained in hydrochloric acid is not possible since the definition of the B- and G-waves is extremely poor and the early inception of a large calomel discharge prevents the study of any waves more positive than *ca.* −0.1 v. The general appearance of the cathodic and anodic waves may be seen from the HCl curve of Fig. 3. Data from a typical run are given in Table III. The $E_{1/2}$ of the A-wave, −0.474 v., is not markedly different from that observed in sulfuric acid, −0.505 v. At unit activity of hydrogen ion in either acid, a potential of −0.485 v. applies at 15°. As in the media previously studied, the slope of the logarithmic plot of the A-wave, 0.031 v., agrees well with the theoretical value of 0.028 v. for a reversible 2-electron process. The slope of the B-wave approximates that of a one-electron process; the G-wave slope is definitely irreversible. The cathodic wave is highly irreversible. The cathodic and the A-waves are of approximately the same size indicating that the *n*-values for the two waves are the same, *i.e.*, 2. Both the B- and the G-waves are roughly one-half this size. An A′-wave does not appear in hydrochloric acid.

TABLE III

RHENIDE WAVES IN HYDROCHLORIC ACID

0.4 m*M* Re^- in 2.4 *N* HCl at 15°, *k* = 1.66 at −0.6 v.

Wave	$E_{1/2}$, v.	$(E_{1/4} - E_{3/4})$, v.	i_d, μa.
Cathodic	−0.657	0.090	2.32
A	− .474	.031	2.12
B	− .34	.053	0.92
C	− .17	.072	0.95

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[9] Young and Irvine, THIS JOURNAL, **59**, 2648 (1937).

The A-wave is probably again concerned with the oxidation step (−I) to (I). The absence of the A′-wave may reasonably be ascribed to a complexed (I) level such as $ReCl_x^{-(x-1)}$ instead of hydrous as Re_2O as in sulfuric acid. In this connection it may be noted that rhenide solutions in sulfuric acid on exposure to air, gradually turn yellow-brown and a dark solid separates; on the other hand, exposed solutions of rhenide in hydrochloric acid become clear yellow only on longer standing and no solid separates.

The cathodic wave is apparently diffusion-controlled since the variation of i_d with $h^{1/2}$ is constant to ±2% (*h*, 30 to 70 mm.) and the temperature coefficient of i_d is 2.2% (5 to 25°). As shown subsequently, a kinetic factor may also be involved but its effect is negligible due to the low rate of the process concerned (formation of the species producing the cathodic wave). The existence of a cathodic, *i.e.*, reduction, wave in a completely reduced rhenide solution is decidedly unexpected. The initial oxidation step (A-wave) in hydrochloric acid seems to differ in no significant manner from the comparable wave in sulfuric acid. The species present is apparently capable of being either oxidized or reduced.

Rhenide in the Four Hydrohalic Acids.—Similar cathodic waves (Table IV) exist in solutions of the other hydrohalic acids indicating the presence of comparable rhenium complexes. The anodic waves in hydrobromic acid are quite similar to those in hydrochloric acid. In hydroiodic acid the early inception of the mercurous iodide discharge will not permit an examination of the normal anodic rhenide waves. In hydrofluoric acid complete reduction to the rhenide state (as found by titration) is not attainable; apparently, one can only approach an average 7-electron reduction of perrhenate in the 2.4 *N* acid at 15°. It is notable that such anodic and cathodic portions of the wave as obtained in this medium occur at a single potential, presenting a smooth cathodic–anodic transition.

TABLE IV

HALF-WAVE POTENTIALS OF CATHODIC RHENIDE WAVES

0.4 m*M* Re^- in 2.4 *N* acid

Acid	HF	HCl	HBr
$E_{1/2}$, v.	−0.426	−0.657	−0.699
HI	HCl + pyr	HCl + NCS^-	HCl + en
−0.705	−0.700	−0.718	−0.780

Added complexing occurs in the presence of substances such as pyridine, as evidenced by the appearance of a second, more negative cathodic wave. On the assumption that 2 electrons are involved in each of the cathodic waves, it is possible to calculate from the shift in $E_{1/2}$ as a function of the pyridine concentration that 3 molecules of pyridine are coördinated per rhenium atom. The presence of large amounts of zinc ion (resulting from the Jones reductor) apparently does not vitiate the results, either because zinc is present in large and relatively constant excess or because any zinc–pyridine complexing in acid solution is comparatively weaker; a similar solution containing only zinc and pyridine in acid gives the cathodic zinc wave at the normal position of *ca.* one volt.

Comparable results are found with thiocyanate or ethylenediamine. With small amounts of ethylenediamine, however, some of the wave at −0.66 v. remains while the strongly bound *en*-complex reduces at −0.78 v.; however, all anodic waves are also reduced in size and remain only to the extent that the initial cathodic wave remains. Apparently, the complex resulting from ethylenediamine is so strongly bound as to resist oxidation, *i.e.*, to at least −0.1 v.

Rate of Formation of the Rhenide Complex in HCl.—As mentioned, the formation of the reducible species requires a finite period of time. Only a very modest cathodic wave is found on examining a freshly reduced rhenide solution in hydrochloric acid. Aging the solution under nitrogen for 30 or 40 minutes results in a larger cathodic wave, comparable in size with the A-wave.

A series of 3 runs at each of 2 temperatures, 15.8 and 25.0°, was conducted in which the rate of formation of the complex, as measured by the growth of the cathodic wave with time, was determined for 0.4 m*M* rhenide in 2.4 *N* hydrochloric acid. In one set of runs for each temperature the behavior of the A-wave with time was also followed as a criterion of the extent to which concurrent oxidation of rhenide was involved; oxidation did not become significant until after 60 minutes at 25° or 110 minutes at 15.8°. Plots of the data (i_d of the cathodic wave *vs.* time) defined reasonably smooth curves in every case. On the assumption that first order kinetics obtain, a replotting of the data as log i_d *vs.* time should yield a straight line relation. Such recalculation of the data does result in a straight line relation which is valid until the aforementioned time-limitation of oxidation is exceeded.

From the slopes of the straight line portions of the log-plots, one can evaluate first order specific rate constants of 0.0111 min.$^{-1}$ at 15.8° and 0.0191 min.$^{-1}$ at 25.0°. If one assumes rhenide and hydrochloric acid to be the reacting species, the reaction is to be interpreted as pseudo first order since 0.4 m*M* rhenide concentration in 2.4 *N* hydrochloric acid constitutes a small quantity of one reactant in the presence of a huge excess of the other.

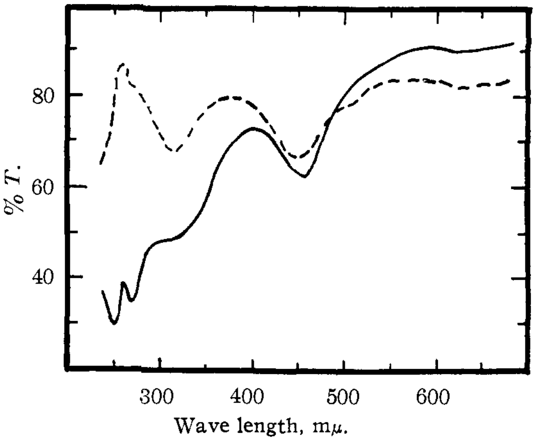

Fig. 4.—Rhenide absorption in two media: absorption spectra of 0.5 m*M* rhenide in 2 *N* sulfuric acid (dashed line) and 2 *N* hydrochloric acid (solid line) at 25°, 1 cm. path.

Absorption Spectrum of Complexed Rhenide.—The distinction between the rhenide state in sulfuric acid and that in hydrochloric acid might lead one to expect a difference in the ultraviolet absorption in the two cases and an experimental comparison of the rhenide absorption in the two media seemed worthwhile.

To this end, 0.5 m*M* rhenide solutions in the 2 *N* acids were prepared by reduction with amalgamated zinc. Comparison solutions of the 2 *N* acids containing no rhenium were contacted with zinc under comparable conditions. The solutions were aged in the covered absorption cells for *ca.* 30 minutes prior to reading. The absorption data were determined from 240 to 1050 mμ. At each wave length the instrument was set to read 100% transmission on the proper solvent before reading the transmission of the corresponding rhenide solution. Cross comparison of the solvents showed only small differences below 300 mμ and negligible differences above this region. The solutions were at 25° when read. Readings were taken every 5 mμ from 240 to 350 mμ, every 10 mμ from 350 to 500 mμ, every 20 mμ from 500 to 600 mμ, every 25 mμ from 600 to 900 mμ, and at 950, 1000 and 1050 mμ. The minimum usable slit width was employed throughout. The absorption curves (Fig. 4) show quite significant differences between the near ultraviolet absorption spectra of rhenide in sulfuric acid and in hydrochloric acid.

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WEST LAFAYETTE, IND. RECEIVED DECEMBER 7, 1950[10]

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[10] Original manuscript received August 6, 1949.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Silver Nitrate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND CLARENCE L. HILDRETH, JR.

The diffusion coefficient of silver nitrate has been determined by the conductometric method in dilute solutions. The results are found to be in agreement with the theory of Onsager and Fuoss.

The determination of the diffusion coefficient of silver nitrate contained in this communication supplements accurate results recently obtained with lithium, sodium[1] and potassium[2] chlorides and potassium nitrate.[3] The apparatus and experimental technique employed in these conductometric determinations has been described in detail[2] and requires no amplification. The results for silver nitrate contained in the second column of Table I are of comparable accuracy with those of the alkali halides and potassium nitrate.

TABLE I

THE OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS OF SILVER NITRATE IN WATER AT 25°

c	$\mathfrak{D} \times 10^5$ Observed	$\mathfrak{D} \times 10^5$ Calcd.
0.00000	...	(1.7675)
.00285	1.718	1.721
.00322	1.719	1.718
.00427	1.711	1.712
.00496	1.708	1.708
.00628	1.701	1.702

The values in the third column of this table were computed from the theoretical equations for a uni-univalent electrolyte[4,5,6]

$$\mathfrak{D} = 16.629 \times 10^{10} T (\overline{\mathfrak{M}}/c) \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c}\right) \quad (1)$$

where

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 1.0748 \left(\frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) - \frac{22.148}{\eta_0 (DT)^{1/2}} \frac{\sqrt{c}}{(1 + A'\sqrt{c})} \left(\frac{\lambda_1^0 - \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 + \frac{9.304 \times 10^7}{\eta_0 (DT)^2} c\phi(A'\sqrt{c}) \quad (2)$$

$\mathfrak{D}$ is the diffusion coefficient in cm.^{2} sec.,$^{-1}$ T the absolute temperature, c is in moles per liter, and $y_{\pm}$ is the activity coefficient of silver nitrate. D is the dielectric constant of water, η_0 its viscosity, and λ_1^0, and λ_2^0 are the equivalent ionic conductances of the silver and nitrate ions, respectively, at infinite dilution. $A'\sqrt{c}$ equals κa, where κ is the reciprocal radius of the ionic atmosphere and "a" is the mean distance of approach of the ions according to the Debye and Hückel theory. The exponential integral function of the theory $c\phi(A'\sqrt{c})$ may be interpolated from data given in tables.[5,6]

The activity coefficients obtained from isopiestic vapor pressure measurements by Robinson and Stokes[7] were employed to evaluate the thermodynamic term in equation (1) and the mean distance of approach of the ions, a. Utilizing the familiar Debye and Hückel equations, "a" was found to equal 3.03 Å. and consequently $A'\sqrt{c} = 0.995\sqrt{c}$. This procedure leads to the numerical equation for the thermodynamic term

$$\left(1 + c \frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{0.5862\sqrt{c}}{(1 + 0.995\sqrt{c})^2} - 0.2395c - c\psi(d) \quad (3)$$

estimated to be valid from 0 to 0.5 molar concentration. The numerical equation for the density term is

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[1] Harned and Hildreth, THIS JOURNAL, **73**, 650 (1951).

[2] Harned and Nuttall, *ibid.*, **69**, 736 (1947); **71**, 1460 (1949), Harned and Blake, *ibid.*, **72**, 2265 (1950).

[3] Harned and Hudson, *ibid.*, **73**, 652 (1951).

[4] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[5] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., pp. 178, 593.

[6] Harned, *Chem. Revs.*, **40**, 462 (1947).

[7] Robinson and Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).