Polarographic Investigation of Rhenium Compounds. II. Oxidation of −1 Rhenium at the Dropping Electrode and the Potential of the Re+2–Re−1 Couple

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The reduction of perrhenate ion at the dropping mercury electrode has been discussed in a previous paper from this Laboratory,[1] in which evidence was presented that the −1 oxidation state of rhenium is produced at this electrode under certain conditions. The existence of −1 rhenium was discovered quite recently by Lundell and Knowles,[2] who obtained it by the reduction of perrhenate ion by amalgamated zinc in *cold* dilute sulfuric acid solutions from which air had been carefully excluded. The experiments of Lundell and Knowles were later confirmed by Tomiček and Tomiček.[3] Since the existence of Re−1 is of in-

terest from several points of view, and since very little is known about the potentials of the lower oxidation states of rhenium compounds, it seemed worth while to investigate the oxidation of solutions of −1 rhenium at the dropping electrode by the polarographic technique. This study has furnished some interesting information concerning the course of the oxidation of reduced rhenium solutions, and in particular it has supplied data which lead to a fairly accurate estimate of the potential of the Re+2–Re−1 couple in dilute sulfuric and perchloric acid solutions.

Experimental

Solutions of −1 rhenium were prepared by reducing perrhenate ion with amalgamated zinc in dilute sulfuric acid or perchloric acid. Lundell and Knowles[2] have shown that successful production of Re−1 requires the complete absence of oxygen and ice-cold solutions. In the present study it was necessary to work with moderately small volumes of quite dilute solutions since only a small quantity of potassium perrhenate was available, and it was also desired to perform the reductions in an initially dry reductor so that the concentrations of the solutions would remain unchanged. After numerous trials it was finally found that these conditions were fulfilled most satisfactorily by the reductor shown in Fig. 1.

Vacuum technique was employed to free the reductor and solutions from dissolved air, and the reductions were performed in an atmosphere of nitrogen that had been purified by passage over copper gauze at 500°. The reductor proper consisted of the double walled bulb B, the inner bulb of which (125 cc.) was about two-thirds filled with very pure 20-mesh amalgamated zinc. Previous to use the reductor was washed out with dilute sulfuric acid, water, and acetone, and was dried by evacuating to a pressure below 2 mm. for a few minutes. Pure nitrogen was then admitted. The potassium perrhenate solution to be reduced, contained in the 100-cc. reservoir bulb A, was freed from dissolved air by evacuating rapidly until boiling just began and then admitting nitrogen. This was repeated two or three times to ensure complete removal of air. Care was taken to minimize evaporation of water from the solution by evacuating very rapidly and maintaining vacuum for only a few seconds. The solution was then run into the reductor, which had previously been chilled to below 5° by passage of ice-water through the outer jacket. The volume of solution was such (50 cc.) that it covered the amalgamated zinc to a depth of less than a centimeter, and thus intimate contact was obtained between the two phases. Finally the reduced solution was run into the polarographic cell from the capillary delivery tube under an atmosphere of nitrogen, and with the cell
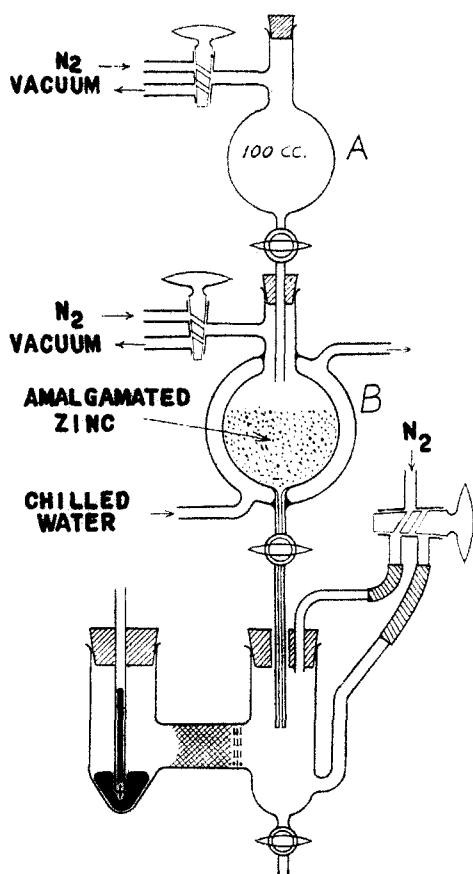

Fig. 1.—Zinc reductor and polarographic cell.

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

(2) G. E. F. Lundell and H. B. Knowles, *J. Research Nat. Bur. Standards*, 18, 629 (1937).

(3) O. Tomiček and F. Tomiček. *Coll. Czech. Chem. Commun.*, 11, 626 (1939).

in an ice- and water-bath at 0°. The reductor was then withdrawn and the capillary of the dropping electrode inserted through the same hole in the stopper, which was oversize to act as an exit for the nitrogen. The polarogram of the reduced solution was taken without delay, and, unless otherwise specified, at 0°.

The H-type polarographic cell that was used was similar to that previously described.[4] A medium porosity sintered glass disk (2-cm. diameter) was sealed into the cross tube as close as possible to the right-hand compartment, and this was backed with a plug of 4% agar gel containing 0.2 M sodium sulfate. This arrangement provides a good low resistance electrolytic contact between the two halves of the cell and at the same time effectively prevents streaming of one solution into the other. A mercury–mercurous sulfate electrode in the left-hand compartment, with 1 N sulfuric acid as electrolyte, was used as the working reference electrode of the cell. The potential of this electrode was measured at frequent intervals against a saturated calomel electrode, and all potential data are referred to the latter electrode as a standard.

The dropping electrode was of the same type described by Lingane and Laitinen,[4] and the rate of flow of mercury (m) was determined by means of the volumetric instrument described elsewhere.[5] It was found, as the average of a number of experiments, that the ratio of the rate of mercury flow at 25° to that at 0° was 1.075 in 2 N sulfuric acid. This corresponds to an average temperature coefficient for m of +0.0030 deg.$^{-1}$ between 0° and 25°. In most experiments the value of m was determined at 25° and divided by 1.075 to obtain its value at 0°.

Polarograms were recorded according to the usual technique[6] with a Sargent–Heyrovsky polarograph.

Standard solutions of potassium perrhenate (0.002 to 0.003 M) were prepared directly by weight from a pure sample of the salt (obtained from A. D. Mackay Co., New York) which had been dried at 110°.

Results and Discussion

In order to establish the fact that quantitative formation of −1 rhenium was actually obtained under the reduction conditions that were employed, several of the reduced solutions were titrated with a standard ceric sulfate solution. In preliminary experiments samples of the reduced solutions from the reductor were delivered under the surface of an excess of ferric sulfate solution in dilute sulfuric or perchloric acid, and the solution was then titrated with a standard ceric sulfate solution using o-phenanthroline ferrous sulfate ("Ferroin") as indicator. This procedure yielded unsatisfactory results because the rate of reaction of ceric ion with the reduced solution was surprisingly slow, even when the solutions were warmed to 40–50° prior to titration. These ob-

servations confirm the results of Geilmann and Wrigge,[7] who found that the oxidation of solutions of +3 and +4 rhenium by permanganate, dichromate and ceric ions is quite slow under certain conditions, particularly when substances, such as chloride ion, which form stable complexes with +4 rhenium are present. The following procedure was finally adopted and it led to correct results. The reduced solutions were run directly from the reductor into an excess of standard ceric sulfate solution *under an atmosphere of nitrogen*, and, after standing for at least fifteen minutes under nitrogen, the excess ceric ion was titrated back with a standard ferrous ammonium sulfate solution from a microburet, using Ferroin as indicator. Removal of air from the collecting ceric sulfate solution was found to be essential, and, when it was not done, low and erratic results were obtained, indicating that the rate of reaction of dissolved oxygen with the reduced rhenium compounds is more rapid than that of ceric ion with these compounds.

In order to determine the volume of the reduced solution taken for analysis, the collecting flask (Erlenmeyer flask with drawn out neck) was calibrated for total volume, and at the end of a titration the volume of water required to fill to the mark was measured. This volume was added to the known volumes of ceric solution and ferrous solution used, and the sum was subtracted from the total volume of the flask. The volume of the sample of reduced solution was known with an accuracy of ± 0.1 cc. The results are summarized in Table I.

TABLE I

OXIDATION STATE OF REDUCED RHENIUM SOLUTIONS

Solutions of potassium perrhenate in 2.0 N sulfuric acid reduced for 10 min. under nitrogen at a temperature near 5°.

KReO₄ Millimolar	Vol. reduced soln., cc.	0.01 N Ce(SO₄)₂, cc.	Equiv. Ce^{IV} per mole total rhenium
0.105	37.6	3.26	8.3
.209	33.3	5.28	7.6
.418	36.4	12.1	8.0
.836	35.2	23.0	7.8
			Av. 7.9

These results, which confirm the conclusions of Lundell and Knowles[2] and those of Tomiček and Tomiček,[3] show that, within the limits of the experimental error, 8 equivalents of ceric ion were required to oxidize the reduced solutions up to

(4) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, 11, 504 (1939).

(5) J. J. Lingane, *ibid.*, 14, 655 (1942).

(6) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(7) W. Geilmann and F. W. Wrigge, *Z. anorg. allgem. Chem.*, 222, 56 (1935).

perrhenate ion.   Hence there is no doubt that the solutions reduced under the present conditions contain all of the rhenium in the −1 oxidation state. No definite statement can yet be made concerning the actual ionic or molecular state of the −1 rhenium in these solutions, but since the chemistry of rhenium is similar in a number of respects to that of the halogens, it seems reasonable to assume that hydrorhenic acid is a strong acid and that the −1 rhenium is present as rhenide ion, Re⁻.

A typical polarogram of a reduced rhenium solution in dilute sulfuric acid at 0° is shown by curve 1 in Fig. 2.   In accordance with the usual conventions a negative sign is used to indicate anodic current (electroöxidation), and the sign prefixed to the potential of the dropping electrode, $E_{d.e.}$, signifies the polarity of this electrode with respect to the saturated calomel electrode.
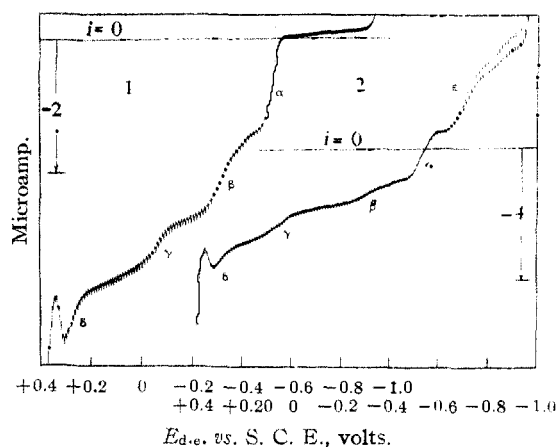

$E_{d.e.}$ vs. S. C. E., volts.

Fig. 2.—Curve 1: Polarogram of a 2.09 × 10⁻⁴ M solution of −1 rhenium in 2.0 N sulfuric acid at 0°. Curve 2: Polarogram obtained (at 0°) after partial oxidation by warming to 50° for sixty-five minutes in absence of oxygen.

It is seen that the polarogram (curve 1) consists of three distinct anodic waves, with half-wave potentials of −0.54, −0.3 and −0.05 v. vs. the S. C. E., which for the sake of convenient discussion will be referred to as α-, β-, and γ-waves, respectively. These waves correspond to oxidation of rhenide ion to successively higher oxidation states. The abrupt increase in cathodic current at about −0.9 v. results from the discharge of hydrogen ion, and the final increase in anodic current beginning at about +0.35 v. is caused by the oxidation of the mercury of the dropping electrode to mercurous ion. A fourth increase in anodic current, which at first glance appears to be the beginning of a fourth stage in the oxidation of the −1 rhenium, is also observable at +0.25 v. (δ in Fig. 2), and this is followed by an abrupt decrease in current just prior to the final anodic dissolution current of the mercury. Actually, data discussed below disprove the hypothesis that this δ-wave is the beginning of a fourth stage in the oxidation. Since mercurous perrhenate is only slightly soluble, we also considered the possibility that the δ-wave might be caused by the depolarization of the dropping electrode by perrhenate ion (formed in the preceding stage of the oxidation) according to the equation $2Hg + 2ReO_4^- = Hg_2(ReO_4)_2(s) + 2e$. However, this possibility was excluded by polarograms of solutions of potassium perrhenate itself in 1.8 N sulfuric acid which showed no indication of such a wave.

The abrupt decrease in current immediately preceding the anodic dissolution current of the mercury has been observed on the anodic waves of other substances, notably hydroquinone,[6,8] and it appears to be a rather general phenomenon in which the inception of the oxidation of the mercury itself inhibits the oxidation of other substances at the dropping electrode.

The significance of curve 2 in Fig. 2 is discussed in a following section.

A polarogram of a reduced rhenium solution in dilute perchloric acid is shown in Fig. 3. It possesses the same general features as the polaro-
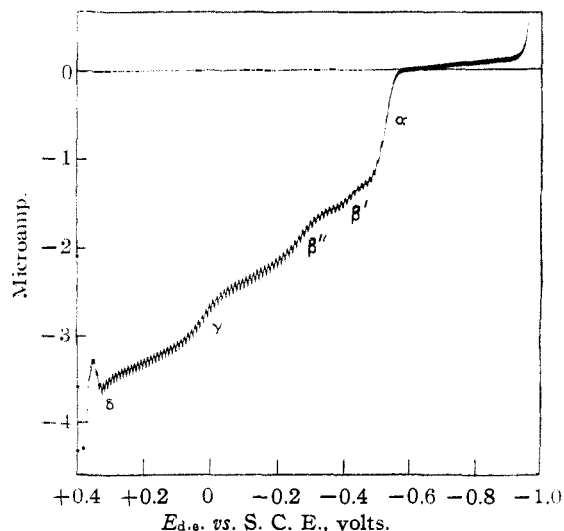

$E_{d.e.}$ vs. S. C. E., volts.

Fig. 3.—Polarogram of a 2.09 × 10⁻⁴ M solution of −1 rhenium in 1.2 N perchloric acid at 0°.

(8) O. H. Müller and J. P. Baumberger, Trans. Am. Electrochem. Soc., 71, 169, 181 (1937).

TABLE II
DIFFUSION CURRENT DATA FOR REDUCED RHENIUM SOLUTIONS

Polarograms were recorded at $0°$, and the diffusion currents have been corrected for the residual current and for the change of drop time—and hence current—with the potential of the dropping electrode. The α-, β-, and γ- diffusion currents were measured at ca. -0.45, -0.15, and $+0.2$ v., respectively, vs. the S. C. E. $m^2/st^{1/6} = 2.26$ mg.$^{2/3}$ sec.$^{-1/2}$ at $0°$ at -0.6 v. The values of i_d/C refer to the total, rather than separate, diffusion currents.

Re^{-1}, millimolar	i_d/C, microamp./mole/l.				Ratio			
	γ	β''	β'	α	γ	β''	β'	α
(a) In 1.0 N H$_2$SO$_4$; reduced for 30–60 min.								
0.151	14.4	11.5		6.0	1.25	1		0.52
.302	15.4	12.7		6.7	1.21	1		.53
.604	13.6	10.8		5.6	1.26	1		.52
Av.	14.5	11.7		6.1	1.24	1		0.52
(b) In 2.0 N H$_2$SO$_4$; reduced for 10 min.								
0.105	16.2	12.8		6.7	1.27	1		0.52
.209	17.0	13.3		6.9	1.28	1		.52
.836	14.9	11.6		5.5	1.29	1		.47
Av.	16.0	12.6		6.4	1.28	1		0.50
(c) In 1.2 N HClO$_4$; reduced for 5–10 min.								
0.209	15.3	11.4	7.7	5.9	1.34	1	0.68	0.52
.418	15.3	11.7	7.8	6.0	1.31	1	.67	.51

gram in dilute sulfuric acid, with the marked exception that instead of a single β-wave the two separate waves indicated in Fig. 3 by β' and β'' are obtained. The sum of these two waves is equal to that of the single β-wave in dilute sulfuric acid. The separate β'-wave is one-half the height of the separate β''-wave, or one-third the height of the α-wave (see Table II), and hence the electron change in the reaction responsible for the β'-wave must be one-third that for the α-wave. This point is important in the interpretation of the oxidation states to which the waves pertain (vide infra). There is some indication on the original polarograms that the β-wave in sulfuric acid medium is also composite in nature, but the two parts of the wave are not clearly separated as they are in perchloric acid medium.

A summary of diffusion current data for various concentrations of the reduced rhenium solutions in dilute sulfuric and perchloric acids at $0°$ is given in Table II.

The diffusion currents have been corrected for the residual current of the acid solution alone in each case. Since the diffusion current depends directly on the sixth root of the drop time,[6,9] and since the latter changes considerably over the potential range involved in the present measurements, a correction for this effect was also made. The requisite data for this correction were obtained by measuring the electrocapillary curve of

(9) 1. M. Kolthoff and E. F. Orlemann, THIS JOURNAL, 63, 2085 (1941).

mercury (drop time vs. $E_{d.e.}$) in 1.8 N sulfuric acid at $0°$. Values of $(t/t_{max.})^{1/6}$ obtained in this way at $+0.2$, -0.15 and -0.45 v. were 0.966, 0.992 and 1.00, respectively, and the maximum in the electrocapillary curve was at -0.58 v. The measured diffusion currents were referred to the value of the drop time at the electrocapillary maximum, $t_{max.}$, by dividing by the appropriate value of $(t/t_{max.})^{1/6}$.

From the data in Table II it is evident that the diffusion currents of all the anodic waves are directly proportional to the concentration of -1 rhenium, and hence are diffusion controlled. Since the values of i_d/C are essentially the same in dilute sulfuric and perchloric acids, it is clear that corresponding waves pertain to the same oxidation states in the two media. Although the precision of the data in Table II leaves something to be desired, there is no systematic trend in the values of i_d/C with concentration. It is believed that the variations observable in the values of i_d/C were caused by unequal amounts of evaporation of water from the solutions during the evacuation prior to reduction, in spite of the precautions that were taken to minimize this effect. Similar variations, probably due to the same cause, are noticeable in the data in Table I.

For the present purpose the ratio of the diffusion currents of the various waves is of more importance than their absolute values, and it is seen that the values of the ratios in the last columns of Table II are satisfactorily concordant. The rela-

tive heights of the anodic waves (*i. e.*, the ratios in Table II) are determined by the oxidation states to which the −1 rhenium is oxidized as each limiting current is attained. When a polarographic limiting current is diffusion controlled the ratio i_d/C is expressible by the Ilkovic equation[6,10]

$$i_d/C = knD^{1/2}m^{2/3}t^{1/6} \tag{1}$$

In this equation, i_d/C is the diffusion current constant (microamperes per millimole per liter), n is the number of electron equivalents per molar unit of the electrode reaction, D is the diffusion coefficient (cm.^{2} sec.$^{-1}$) of the substance that is being reduced or oxidized, m is the rate of mercury flow from the dropping electrode (mg. sec.$^{-1}$), t is the drop time (sec.), and k is a constant whose numerical value is 605 at 25° and 603 at 0°. Unfortunately this equation cannot be applied directly in the present case to determine the n-values of each of the anodic waves, because nothing is known about the diffusion coefficient of rhenide ion under the conditions of the present experiments. However, since the rhenium in these reduced solutions is present entirely in the −1 state, it will be evident that each of the diffusion currents results from the oxidation of the −1 rhenium from the same concentration to successively higher oxidation states, and therefore each is controlled by the rate of diffusion of the rhenide ion. Consequently the ratio of the *total* diffusion currents is the same as the ratio of the n-values of the various waves, and this ratio must be expressible as a ratio of simple integers. Furthermore, the maximum possible value of n is 8, for complete oxidation of rhenide ion to perrhenate ion.

It is immediately evident from the data in Table II, and the polarograms in Figs. 2 and 3, that the n-value for the α-wave is equal to that for the individual β-wave in dilute sulfuric acid, or equal to the combined n-values of the β'- and β''-waves in dilute perchloric acid. Furthermore, since the individual γ-wave is smaller than the individual α- or β-waves, the latter must each correspond to at least a 2-electron oxidation, but the sum of the α- and β-waves cannot correspond to more than a 6-electron change without exceeding the maximum possible n-value of 8 for the total combined diffusion currents. Hence the only patterns of n-values that need be considered are 8/6/3 and 5/4/2. The 8/6/3 pattern requires a ratio of

1.33/1/0.5, and the 5/4/2 pattern a ratio of 1.25/1/0.5, for the cumulative heights of the γ-, β- (or β' + β''), and α-waves. The average observed value of the ratio in dilute sulfuric acid is 1.26/1/0.51, whereas in dilute perchloric acid, with the β-wave resolved into its component β' and β'' parts, the observed ratio is 1.33/1/0.68/0.52. From Figs. 2 and 3 it is seen that the γ-diffusion current increases appreciably with increasing positive potential, even when proper allowance is made for the residual current and the effect of changing drop time with changing potential. Consequently, values for the ratio of the γ- to the β-diffusion current ranging from 1.25 to 1.33 can be obtained depending on the potential at which the γ-diffusion current is measured. The key to the correct pattern of n-values is found in the resolution of the β-wave into its component β' and β'' parts in dilute perchloric acid, and the fact that the individual β'-wave is only half the height of the individual β''-wave, or one-third the height of the α-wave. It seems reasonable to conclude that the correct pattern of n-values is 8/6/4/3. Hence the α-wave corresponds to oxidation of the −1 rhenium to the +2 state, the β'-wave to the +3 state, the β''-wave to the +5 state, and the γ-wave to complete oxidation to the +7 state (ReO$_4^-$).

In order to test the foregoing conclusion an amperometric titration[11] of a reduced rhenium solution with a standard solution of ammonium hexanitratocerate was carried out, with the result shown in Fig. 4. In this experiment a completely reduced rhenium solution was titrated with an air-free 0.01 N (NH$_4$)$_2$Ce(NO$_3$)$_6$ solution at 0°, and individual polarograms were recorded five to ten minutes after each addition of the ceric solution. Curve 1 in Fig. 4 is a polarogram of 35.0 cc. of the original reduced solution, and the other curves were recorded after successive additions of 3.00-cc. increments of the 0.01 N ceric solution, corresponding to the addition of 0, 2.0, 4.1, 6.2, 8.2, and 10.3 equivalents of oxidant for curves 1 to 6, respectively. It is seen that the anodic current, measured at a potential of +0.2 v. corresponding to the γ-diffusion current, decreased to zero after the addition of somewhat less than 8.2 equivalents of oxidant. The cathodic diffusion current obtained with larger amounts of the oxidant (curve 6) results from the

(10) D. Ilkovic, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934); *J. chim. phys.*, **35**, 129 (1938).

(11) See Ref. 6 for a discussion of the principles of amperometric titrations.

reduction of the excess ceric ion to the cerous state. This experiment constitutes conclusive proof that the correct pattern of n-values is 8/6/4/3, and that the -1 rhenium is completely oxidized to perrhenate ion at potentials at which the γ-diffusion current is attained.

It should be pointed out that the slow reaction of ceric ion with the reduced rhenium compounds should not seriously influence the validity of the conclusions that are drawn from this type of amperometric titration. Consider, for example, an extreme case in which the reaction between the oxidant and reductant is so very slow that it actually only proceeds to a slight extent during the time of a titration. At any point in the titration relatively large amounts of unreacted oxidant and reductant will then be present, and the net current will be the resultant of a cathodic current of the oxidant and an anodic current of the reductant, provided, as in the present case, that the measurements are made at a potential where both diffusion currents are separately attained with pure solutions of the oxidant and reductant. If the diffusion coefficients of the oxidant and reductant are equal, the *net* current will decrease to zero (corrected for the residual current) after an equivalent amount of oxidant has been added, just as if the reaction had been rapid and complete. This unique characteristic of amperometric oxidation–reduction titrations should permit their application to a number of reactions which cannot be followed by other methods that require the establishment of equilibrium conditions throughout the titration.

TABLE III

HALF-WAVE POTENTIALS OF REDUCED RHENIUM SOLUTIONS

The half-wave potentials were measured at $0°$, and are referred to the saturated calomel electrode at room temperature.

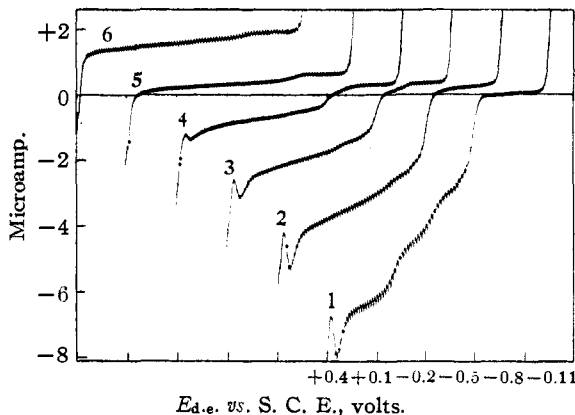| Re^{-1} Milli-molar	γ	$E_{1/2}$, vs. the S. C. E., v. β''	β'	α
		(a) In 1.0 N H$_2$SO$_4$		
0.151	-0.10	-0.34		-0.547
.302	.10	.34		.546
.604	.09	.33		.545
		(b) In 2.0 N H$_2$SO$_4$		
0.105	-0.07	-0.33		-0.524
.209	.06	.34		.540
.836	.04	.34		.536
		(c) In 1.2 N HClO$_4$		
0.209	$+0.03$	-0.26	-0.42	-0.542
.418	.03	.26	.42	.527
			Av.	-0.538 ± 7

Fig. 4.—Amperometric titration of -1 rhenium with ceric ion: 35.0 cc. of a 4.18×10^{-4} M solution of Re^{-1} in 1.2 N perchloric acid at $0°$ plus: (1) none, (2) 3.0 cc. (2.0 equiv.), (3) 6.0 cc. (4.1 equiv.), (4) 9.0 cc. (6.2 equiv.), (5) 12.0 cc. (8.2 equiv.), and (6) 15.0 cc. (10.3 equiv.) of 0.01 N (NH$_4$)$_2$Ce(NO$_3$)$_6$.

Data concerning the half-wave potentials of the reduced rhenium solutions are presented in Table III. The values pertaining to the sulfuric acid solutions in the β''-column refer to the single β-wave in these media, and it will be noted that these values are about midway between the half-wave potentials of the separate β'- and β''-waves in the 1.2 N perchloric acid solution. It will also be noted that the half-wave potential of the γ-wave is about 0.1 v. more positive in perchloric acid medium than in sulfuric acid solutions. It is evident that the half-wave potentials of all the waves are constant in a given medium and independent of the concentration of rhenium.

From the slopes of the β- and γ-waves it seems clear that the corresponding reactions do not proceed with thermodynamic reversibility at the dropping electrode. However, the slope of the α-wave indicates that the oxidation of Re^{-1} to Re^{+2} does approach reversibility. If this is actually the case, then the equation of the anodic α-wave should be[6]

$$E_{d.e.} = E_{1/2} - \frac{RT}{3F_y} \ln \frac{i_d - i}{i} \qquad (2)$$

where i is the anodic current at any point on the wave and i_d is the anodic diffusion current. The half-wave potential should be given by

$$E_{1/2} = E^0_{+2, -1} - \frac{RT}{3F_y} \ln \left(\frac{D_2}{D_1}\right)^{1/2} \qquad (3)$$

where $E^0_{+2, -1}$ is the reversible standard potential for the reaction written in the direction Re^{+2} + 3e = Re^{-1}, and D_2 and D_1 are, respectively, the diffusion coefficients of the Re^{+2} and Re^{-1}. Ac-

tually the second term in Eq. 3 is of very minor importance, and hence $E_{1/2}$ should be practically equal to $E^0_{+2,-1}$. From Eq. 2 the following relation should apply to the difference between the potentials at the one-fourth and three-fourths points on the α-wave at 0°, provided that the reaction proceeds reversibly

$$E_{3/4} - E_{1/4} = \frac{0.0546}{3} \log 9 = 0.017 \text{ v.} \quad (4)$$

From measurements of several polarograms in both dilute sulfuric and perchloric acids, the averaged observed difference between $E_{3/4}$ and $E_{1/4}$ was found to be 0.030 ± 3 v. It appears, therefore, that the oxidation of Re^{-1} to Re^{+2} does not occur with perfect thermodynamic reversibility. On the other hand, the observed slope of the α-wave is sufficiently close to the theoretical value to indicate that the degree of irreversibility cannot be very great. This is also evident from the character of the composite cathodic–anodic α-wave in partially oxidized solutions (curve 2 in Fig. 2), which displays a smooth transition from anodic to cathodic current without any pronounced inflection at the zero current point. Hence it seems safe to conclude that the reversible potential of the $Re^{+2} - Re^{-1}$ couple must be very nearly equal to the half-wave potential of the α-wave, namely, -0.54 v. vs. the S. C. E., or slightly more negative. Rhenide ion is thus a considerably stronger reducing agent than titanous ion, and is about equal to chromous ion in this respect.

In this connection it should be mentioned that Lundell and Knowles[2] performed a potentiometric titration of a solution of -1 rhenium in 1.8 N sulfuric acid with a standard permanganate solution, using a *platinum* indicator electrode. The titration curve they obtained showed only two points of inflection, the first after the addition of 2 equivalents of oxidant and the second after the addition of 8 equivalents. However, it is the author's experience from several such titrations with different oxidants that constant potential is established quite slowly, if at all, and since Lundell and Knowles apparently titrated rapidly the significance of the potential break after the addition of two equivalents of oxidant is doubtful and may well be fortuitous. It should be noted that a platinum indicator electrode cannot be expected to indicate the correct potential in a strongly acid solution of -1 rhenium, because the potential of the $Re^{+2}-Re^{-1}$ couple is consider-

ably more negative than the discharge potential of hydrogen ion on a platinum surface. Consequently, Re^{-1} will reduce hydrogen ion at the surface of a platinum electrode, the measured potential will lie between the hydrogen potential and that of the $Re^{+2}-Re^{-1}$ couple, and its actual value will depend on the rate of oxidation of Re^{-1} by hydrogen ion. This effect is evident from the titration curve given by Lundell and Knowles, in which the potential of the platinum indicator electrode was about -0.4 v. vs. the saturated calomel electrode at a point midway to the first break, or more than 0.1 v. more positive than the potential observed in the present study. The above conclusion is also borne out by the fact that quantitative deposition of metallic rhenium, with no indication of the formation of Re^{-1}, is obtained when strongly acid solutions of potassium perrhenate are reduced electrolytically at a platinum cathode under such conditions that hydrogen is simultaneously evolved.[2,12,13]

Lundell and Knowles[2] discovered that solutions of -1 rhenium in 1.8 N sulfuric acid were slowly oxidized, and acquired a straw-yellow color, when they were warmed to about 50° for thirty to sixty minutes in the absence of oxygen. They found that the partially oxidized solutions required 6 equivalents of permanganate for oxidation to perrhenate ion, and they concluded that the rhenium had been oxidized to the $+1$ state. These investigators passed pure carbon dioxide through the solutions during the warming process and discovered that the effluent gas contained a volatile sulfur compound which very likely was sulfur dioxide. Tomiček and Tomiček[3] have reported the evolution of hydrogen sulfide, as well as sulfur dioxide, from reduced rhenium solutions in sulfuric acid medium. It thus appears that sulfuric acid, or bisulfate ion, rather than hydrogen ion, is the oxidant responsible for the oxidation of the -1 rhenium under these conditions.

The experiments of Lundell and Knowles led to very concordant results and they leave no doubt that the *average* oxidation state of the rhenium in the warmed solutions was $+1$. However, a titration technique such as they employed does not prove that all of the rhenium in the partially oxidized solutions is present in a single oxidation state, and their results can be interpreted equally well by assuming that the partially oxidized solu-

(12) C. G. Fink and P. Deren. *Trans. Am. Electrochem. Soc.*, **66**, 471 (1934).

(13) O. Tomiček and F. Tomiček. *ibid.*, **76**, 105 (1939).

tions contained a mixture of two or more oxidation states in proportions that would be equivalent to an average oxidation state of $+1$. The polarograms obtained in the present study show no indication of a wave corresponding to the $+1$ state, which would lead one to expect that the $+1$ rhenium is unstable in respect to disproportionation into higher and lower states. In order to obtain further information on this point the experiment represented by curve 2 in Fig. 2 was performed. After the polarogram of the original reduced solution was recorded (curve 1 in Fig. 2), the solution was heated to $50°$ under an atmosphere of nitrogen for sixty-five minutes (the conditions employed by Lundell and Knowles) and it was then cooled back to $0°$ and curve 2 was recorded. The solution acquired the straw-yellow color reported by Lundell and Knowles. One marked effect of the warming process was the production of a new cathodic wave, designated by ϵ in Fig. 2. This wave increased to an abnormally great extent when the polarogram was recorded at $25°$ instead of $0°$, which is fairly good evidence that it is catalytic in nature and similar to the catalytic waves described in a previous paper.[1] It will be noted that the γ-wave in curve 2 has become quite extended, and inspection of the original polarogram shows that it is composite and consists of two parts. The diffusion currents (corrected for the residual current) of the partially oxidized solution are compared with those of the original solution in Table IV.

TABLE IV

COMPARISON OF ORIGINAL DIFFUSION CURRENTS WITH THOSE OF SOLUTION PARTIALLY OXIDIZED BY WARMING

| | i_d, microamp. | | |
	γ	β	α
Curve 1, Fig. 2.	3.55	2.73	1.42
Curve 2, Fig. 2	2.63	1.70	0.93[a]
Decrease, microamp.	0.92	1.03	0.49

[a] Anodic part of the α-wave. The cathodic part is equal to 0.50 microamp.

It is seen that the α-wave became approximately one-third cathodic and two-thirds anodic after warming, which indicates that two-thirds of the rhenium was still present as the Re^{-1} and the remainder in a higher oxidation state or states. The sum of the heights of the cathodic and anodic portions of the α-wave $(0.50 + 0.93 = 1.43$ microamp.$)$ is the same as the height of the original anodic α-wave.

The *cumulative* γ-diffusion current at $+0.2$ v.

decreased by 0.92 microamp., which is $0.92/3.55 = 0.26$, or one-fourth of its original value within the limit of accuracy of the measurements. Assuming for the sake of simplicity that the average diffusion coefficient of the rhenium compounds in the mixed oxidation states in the partially oxidized solution is the same as that of Re^{-1}, we conclude that the one-fourth decrease in the original 8-electron γ-diffusion current corresponds to a 2-electron oxidation. Hence the *average* oxidation state of the rhenium in the partially oxidized solution was $+1$; a value in agreement with the results that Lundell and Knowles obtained by direct oxidimetric titration.

From the data in Table IV it is seen that the *individual* height of the γ-wave of the partially oxidized solution $(2.63 - 1.70 = 0.93$ microamp.$)$ is the same, within the limits of the experimental error, with that of the original solution $(3.55 - 2.73 = 0.82$ microamp.$)$. On the other hand, the individual height of the β-wave decreased by about one-third from 1.31 microamp. $(2.73 - 1.42)$ to 0.77 microamp. $(1.70 - 0.93)$, and this decrease of 0.54 microamp. is equal to the cathodic portion of the α-wave. Since the height of the γ-wave, which corresponds to the oxidation of Re^{+5} to ReO_4^-, remained constant, it appears that none of the rhenium was present in an oxidation state higher than $+5$. The fact that the individual height of the β-wave, which results from the oxidation of Re^{+2} to Re^{+5}, decreased to about two-thirds of its original value indicates that part of the rhenium was present in an oxidation state greater than $+2$, because if only Re^{-1} and Re^{+2} had been present the height of the β-wave should not have differed markedly from its original value. It seems reasonable to conclude from these data that the partially oxidized solution still contained about two-thirds Re^{-1}, with the remainder of the rhenium present as Re^{+3}, Re^{+4} or Re^{+5}, or a mixture of these three. A more specific statement of the composition of such solutions must await the acquisition of more extensive data, which we expect from experiments now in progress in this Laboratory.

The existence of -1 rhenium raises an interesting question in regard to its electronic configuration. In the rhenium atom itself the first four quantum levels are completely filled, and the configuration of the outer fifth and sixth levels is $5s^2 5p^6 5d^5 6s^2$. Hence the addition of an electron to produce -1 rhenium could lead to either of the

configurations, (A) $5s^25p^65d^66s^2$, or (B) $5s^25p^66s^2-6p^6$. It is a significant and generally accepted fact that the negative oxidation states of all other elements involve the formation of stable s^2p^6 octets, and on this basis one is inclined to assign configuration B to Re^{-1}. This configuration, which requires the promotion of all of the original $5d$ electrons to the $6p$ orbital, would be in accord with the marked instability and strong reducing character of Re^{-1}.

Summary

A zinc reductor is described in which reduction can be performed conveniently at a controlled temperature and in the absence of oxygen. The fact that -1 rhenium is produced when ice-cold and air-free solutions of perrhenate ion in dilute sulfuric and perchloric acids are reduced with zinc has been confirmed by oxidimetric titration of the reduced solutions.

Polarograms of solutions of -1 rhenium in 1 to 2 N sulfuric acid at 0° display three anodic waves, whose half-wave potentials are (α) -0.54 v., (β) -0.34 v., and (γ) -0.07 v. vs. the saturated calomel electrode. A similar polarogram is obtained in 1 N perchloric acid with the following exceptions: (a) the β-wave is resolved into two separate waves, β' and β'', whose half-wave potentials are -0.42 and -0.26 v., and (b) the half- wave potential of the γ-wave is about 0.1 v. more positive than in sulfuric acid medium. Diffusion current data show that corresponding waves in the two media pertain to the same oxidation states and in both media the diffusion currents are directly proportional to the concentration of -1 rhenium. From the ratio of the heights of the various waves it is concluded that the α-wave results from the oxidation of -1 rhenium to the $+2$ state, the β'-wave to the $+3$ state, the β''-wave to the $+5$ state and the γ-wave to complete oxidation to the $+7$ state (ReO$_4^-$). This conclusion has been confirmed by amperometric titration of the reduced solutions with ceric ion. Evidence is presented which indicates that the reversible potential of the reaction Re^{+2} + 3 e = Re^{-1} is equal to, or slightly more negative than, -0.54 v. vs. the saturated calomel electrode in dilute sulfuric or perchloric acid medium at 0°.

Partially oxidized solutions, obtained by warming dilute sulfuric acid solutions of -1 rhenium to about 50° for an hour in the absence of oxygen, show an *average* oxidation state of $+1$. However, the polarogram of such a solution indicates that the rhenium is not actually present in the $+1$ state, but as a mixture of Re^{-1} and higher states in proportions that are equivalent to an average oxidation state of $+1$.

The Accommodation Coefficient of Mercury on Platinum and the Heat of Vaporization of Mercury

BY LLOYD B. THOMAS AND FRANCOIS G. OLMER

Introduction

We have been interested in applying the Pirani type pressure gage as a means of determining small total pressures of pure gases and as a means of following quantitatively the progress of gas reactions at low pressure. Such an application to mixtures in which some gaseous compounds are consumed and others produced requires an accurate knowledge of the free molecule heat conductivity of each gas from the surface of the specified filament material. This actual heat conductivity is conveniently expressed in terms of the calculated free molecule heat conductivity and the accommodation coefficient. Since there is available only an admittedly rough estimate of the accommodation coefficient of mercury[1] on platinum and since, in this case, pressures are established in equilibrium with liquid mercury and the measurements apparently lead to a precise method of determining the heat of vaporization which should be generally applicable, we are submitting this work under separate title.

Experimental

A diagram of the tube used is shown in Fig. 1. The filament consists of 31.5 cm. of 0.004 inch c. p. platinum wire (Bishop Company) hung in a loop from tungsten leads in a Pyrex tube 3.0 cm. in diameter. At a distance of 4.5 cm. from the ends of the filament, potential leads of 0.001 inch c. p. platinum wire of 3.0 cm. length are welded on the

(1) W. B. Mann, *Proc. Roy. Soc.* (London), **A146**, 786 (1934).