to be a transformation of the solid dihydrate to a saturated aqueous solution of the anhydrous salt and anhydrous salt or from saturated solid solution of the dihydrate form to aqueous solution and saturated solid solution of the anhydrous form.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY, KNOLLS ATOMIC POWER LABORATORY]

The Polarography of Ruthenium(IV) in Perchloric Acid Solutions

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This work was undertaken to determine the stability of the lower valence states of ruthenium in non-complexing solutions. Well-developed polarograms were obtained for ruthenium(IV) which is reduced in three steps to ruthenium(II). The data indicate that the first two waves correspond to the reduction of two different hydrolysis species of ruthenium(IV) to ruthenium(III). On the third wave ruthenium(III) is reduced to ruthenium(II). The formal potentials for two ruthenium couples have been estimated.

Although there is a rather extensive literature on ruthenium, most of the published work is devoted to studies of the chloride and ammine complexes and to discussions of properties of solid compounds. Few quantitative data exist relative to the chemistry of non-complexed ruthenium in acid solutions, and in particular, very little work has been reported on the polarographic behavior of ruthenium. Herasymenko and Slendyk, although observing no reduction of ruthenium at the dropping mercury electrode, did report a catalytic effect on the discharge of hydrogen.[1] Later, Willis, using chloride complexes of ruthenium(III) and ruthenium(IV), was unable to obtain reduction at the dropping mercury electrode from acid or buffered solutions.[2] More recently Silverman, confining his attention to alkaline solutions, reported the first polarographic reductions of ruthenium(VI) and ruthenium(VII), both of which are unstable in acid solutions.[3]

During the course of our work several other investigators were studying the electrochemistry of the lower oxidation states of ruthenium in acid solutions. Turk[4] observed stepwise reduction of ruthenium(IV) at graphite and at platinum electrodes from perchloric, nitric, hydrochloric and sulfuric acid solutions, but a complete discussion of the data has not yet been published. Alkire[5] also obtained reproducible polarograms from nitric acid and acetate-buffered solutions of ruthenium(IV) using the dropping mercury electrode; the reduction waves observed were interpreted as being due to stepwise reduction to ruthenium(III) and then to ruthenium(II). Related experiments on the electrochemistry of ruthenium in perchloric acid solutions have been conducted by Wehner and Hindman.[6] From coulometric titration data they established upper and lower limits for the potential of the ruthenium(IV)–ruthenium(III) couple at 0°.

The present paper describes the polarographic behavior of ruthenium in a non-complexing medium. We have interpreted the observed stepwise reduction of ruthenium(IV) and estimated the formal potentials for the ruthenium(IV)–ruthenium(III) and the ruthenium(III)–ruthenium(II) couples.

Experimental

Preparation of Materials.—A stock solution of ruthenium(IV) in 1.0 *M* perchloric acid was prepared from ruthenium chloride by the following procedure. Chloride was first removed by repeated evaporation of a phosphoric acid solution. Potassium permanganate was then added to the hot solution and the ruthenium was oxidized to the tetroxide which was swept from the solution and collected in cold 1 *M* perchloric acid. The tetroxide was reduced to ruthenium(IV) with hydrogen peroxide, and the excess peroxide was destroyed by boiling the solution. Filtration of the solution through a fine, sintered-glass filter showed that no appreciable amount of insoluble ruthenium dioxide was formed during the preparation. In addition, dialysis of a portion of the filtered solution through a cellophane membrane indicated the absence of colloidal ruthenium.

The stock solution was analyzed for total ruthenium by a colorimetric method similar to that employed by Wehner and Hindman[6] in which the ruthenium is oxidized to the tetroxide and the optical density is measured at 385 mμ. Oxidation was accomplished at room temperature with about 200 mg. of periodic acid in 25 ml. of 1 *M* perchloric acid solution, and density values were measured on a Beckman model DU spectrophotometer. The calibration curves used for these determinations were obtained by using a ruthenium solution that had been standardized gravimetrically by hydrogen reduction of the ruthenium to the metal.[7] The over-all precision of the spectrophotometric measurements indicates that the stock solution in perchloric acid was 0.00554 *M* in ruthenium within an uncertainty of somewhat less than 1%.

The absorption spectrum of the reddish-brown stock solution in the range 400 to 700 mμ was in good agreement with that reported by Wehner and Hindman[6] for ruthenium(IV) in perchloric acid solution. But as a further check on the valence state, potentiometric titrations with chromous sulfate were performed in 6 *M* hydrochloric acid solutions.[8] The concentration of ruthenium obtained by this method was 0.00558 *M* which, on the basis of the original work, is considered accurate to within 1%. Because of the good agreement between the two standardization methods, the concentration of ruthenium(IV) in the stock solution was taken as the average, 0.00556 *M*.

The stock solution was also tested for the presence of chloride with silver nitrate. Interference from ruthenium(IV), because of its tendency to form stable chloride complexes, was eliminated by oxidation to the tetroxide with persulfate in the presence of silver ion as catalyst.[9] The

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[1] P. Herasymenko and I. Slendyk, *Collection Czechoslov. Chem. Commun.*, **5**, 479 (1933).

[2] J. B. Willis, THIS JOURNAL, **67**, 547 (1945).

[3] M. D. Silverman, Oak Ridge National Laboratory, Report CNL-37 (April, 1948), Report ORNL-286 (September, 1949).

[4] E. Turk, Argonne National Laboratory, Reports ANL-4292 (March 1949), 4329 (June 1949), 4372 (September 1949).

[5] G. J. Alkire, Hanford Engineering Works, Reports HW-13481 (June, 1949), 14026 (July, 1949).

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

[7] R. Gilchrist, *J. Research Natl. Bur. Standards*, **12**, 283 (1934).

[8] E. Zintl and P. Zaimis, *Ber.*, **60**, 842 (1927). These authors claim that the reaction involves reduction of ruthenium(III) to ruthenium(II), but W. R. Crowell and D. M. Yost, THIS JOURNAL, **50**, 374 (1928) have pointed out that the reaction involves reduction of ruthenium(IV) to ruthenium(III), and that in the original work an error was made in the valence state assigned to the starting material.

[9] P. Wehner, private communication.

TABLE I

HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS FOR POLAROGRAPHIC REDUCTION OF Ru(IV) IN $HClO_4$ SOLUTIONS

$(ClO_4^-) = 1$ *M* at $(H^+) = 0.1, 0.3, 1.0$ *M*; no maximum suppressor, $T = 25.0°$

(H^+)	(Ru)	Wave 1		Wave 2		Wave 3			
molar	millimolar	$E_{1/2}$[a]	I_1[b]	$E_{1/2}$[a]	I_2[b]	$E_{1/2}$[a]	I_3[b]	I_1/I_2	I_3/I_2
0.1	1.10	+0.57	0.57	+0.40	1.24	−0.14	2.30	0.46	1.85
.1	2.18	+ .56	.50	+ .40	1.22	− .14	2.35	.41	1.92
.3	1.10	+ .60	.74	+ .43	1.41	− .11	2.61	.52	1.85
.3	2.18	+ .60	.68	+ .43	1.42	− .13	2.62	.48	1.85
1.0	1.10	>+ .65	.94	+ .45	1.55	− .09	2.92	.60	1.88
1.0	2.18	>+ .65	.88	+ .45	1.51	− .10	2.89	.58	1.91
5.0	1.10	>+ .65	.99	?	1.43	− .10	2.98	.70	2.08
5.0	2.18	>+ .65	.99	?	1.45	− .10	2.99	.68	2.06

[a] $E_{1/2}$ in volts *vs.* the N.H.E. [b] $I = i_d/Cm^{2/3}t^{1/6} = 605\ nD^{1/2}$.

negative test for chloride in the stock solution obtained by this method implied a concentration of less than 10^{-4} *M* chloride.

Apparatus and Technique.—Polarograms were obtained automatically with a Sargent Model XII polarograph and manually with the circuit described by Lingane and Kolthoff.[10] A conventional H-type cell was used with a saturated mercurous sulfate reference electrode, and an agar plug saturated with potassium sulfate was used for the junction. The potentials were corrected to the normal hydrogen electrode scale using *E vs.* the N.H.E. for the saturated mercurous sulfate electrode equal to 0.65 volt. All measurements were made at 25 ± 0.05°. Purified nitrogen was used to displace dissolved oxygen from the solutions. No maximum suppressor was used.

The number of equivalents involved in certain of the polarographic reductions was determined by coulometric analysis at controlled potential[11] using an H-type diaphragm cell similar to that previously described.[12] The potential was controlled automatically by a circuit similar to that employed by Hickling.[13]

Results and Discussion

Typical polarograms for ruthenium(IV) are shown in Fig. 1. Three waves are associated with the reduction, and it is noted that the ruthenium catalyzes the hydrogen reduction wave. Although the first wave in Fig. 1 appears to merge with the dissolution wave for mercury, a distinct separation was observed on the polarograms which were obtained at the lower acidities. The diffusion current constants and the half-wave potentials for the three waves are summarized in Table I. The diffusion current constant is defined by the equation $I = i_d/(Cm^{2/3}\ t^{1/6}) = 605nD^{1/2}$, where i_d is the diffusion current, *C* is the concentration, *m* is the rate of flow of mercury from the capillary, *t* is the drop time, *n* is the number of electrons involved in the reduction, and *D* is the diffusion coefficient. All diffusion current constants are based on the total current associated with each wave. Both the half-wave potentials and the diffusion current constants are dependent on *p*H.

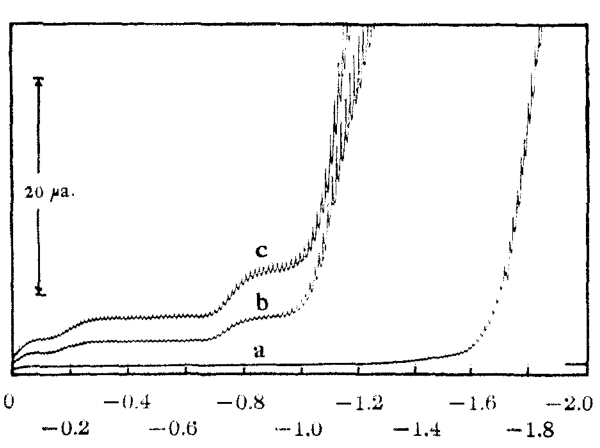

Fig. 1.—Polarograms for Ru(IV) in 1 *M* perchloric acid: (a), blank; (b), 1.10; (c), 2.18 millimolar Ru(IV).

Because of the relatively small variations reported in the literature for $D^{1/2}$ among the simpler ions, the number of electrons involved in a polarographic reduction is often estimated from a comparison of the observed diffusion current constant with those for reactions whose stoichiometry is known. Such a comparison of the data with data for several transition elements[14] indicates that the first wave corresponds to a partial reduction of ruthenium(IV) through less than 1 equivalent per mole. Similarly, on the second wave, reduction is completed to ruthenium(III) and on the third, to ruthenium(II).

The above estimates were confirmed in part by coulometric analysis at controlled potential. A solution of ruthenium(IV) in 1 *M* perchloric acid was electrolyzed successively at *E* = 0.58, 0.15 and −0.20 volt *vs.* the N.H.E., each potential lying near the mid-point of one of the three plateaus on the polarograms. The number of coulombs required for the first two reductions indicated partial reductions of 0.44 and 0.56 equivalent per mole on the first two steps, respectively, thereby confirming the hypothesis that reduction through one equivalent to ruthenium(III) is complete on the second polarographic wave. It has been indicated by Wehner and Hindman[6] that ruthenium(III) is oxidized by 1 *M* perchloric acid at room temperature. Although a similar behavior was observed during the present investigation, the rate of oxidation of the light yellow solution was not great enough to interfere beyond experimental error with the coulometric measurements.

The ratios of the diffusion current constants for the first and second waves are dependent on *p*H. This implies the separate reduction of two or more different hydrolysis species of ruthenium(IV). At present it is not possible to identify the individual

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[10] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

[11] J. J. Lingane, *ibid.*, **67**, 1916 (1945).

[12] J. J. Lingane and L. W. Niedrach, *ibid.*, **70**, 4115 (1948).

[13] A. Hickling, *Trans. Faraday Soc.*, **38**, 27 (1942).

[14] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

species involved, but the fact that the magnitude of the first wave increases with increasing acidity implies that the less hydrolyzed species are the more readily reduced. Turk[4] has independently arrived at a similar interpretation for the first two reduction waves which he obtained from perchloric acid solutions using a graphite electrode. Such a hypothesis is not without precedent since it is well known that the different ionization species of certain weak acids can produce separate reduction waves when the establishment of dissociation equilibria is slow compared to the life of a mercury droplet.[15,16] Further evidence for the presence of at least two ruthenium(IV) species in perchloric acid solutions was obtained by Wehner and Hindman[6] during the course of coulometric titrations of ruthenium(IV). These titrations were followed potentiometrically, and two breaks were found in the titration curve for reduction to ruthenium(III).

Coulometric analysis could not be used to establish the stoichiometry of the reaction on the third polarographic wave because the colorless reduction product was rapidly oxidized by the 1 *M* perchloric acid as shown by a positive test for chloride in the final solution. However, since it has been shown that reduction is complete to ruthenium(III) on the second wave, the ratio of 2 for the diffusion current constants for waves three and two shows quite clearly that the product on the third wave is ruthenium(II).

It is of interest to note that the actual reduction reaction on the third wave appears to be reversible. In the absence of polarographic waves for both the oxidized and reduced form of a material, a fair indication of the reversibility of a reaction at the dropping mercury electrode may be obtained from a plot of log $(i_d - i)/i$ *vs.* voltage, where i_d is the diffusion current and i is the current at a particular voltage on the wave. Reversibility is indicated if a linear plot having a slope of $0.059/n$ is obtained.[17] Such a plot for the third wave approximates a straight line with the proper slope of 0.059.

In conclusion it is of interest to estimate values for the potentials of the various ruthenium couples from the polarographic and chemical data. In the polarographic reduction from one valence state to another a simple relationship exists between the standard potential and the half-wave potential[17]

$$E_{1/2} = E^0 - 0.059/n \log D_{\text{ox.}}^{1/2}/D_{\text{red.}}^{1/2}$$

Since the ratio of $D_{\text{ox.}}^{1/2}$ to $D_{\text{red.}}^{1/2}$ will not differ greatly from unity, as a first approximation $E_{1/2} = E^0$. Any overvoltage that is involved in the reduction causes a shift of the half-wave potential to a more negative value, so that in the absence of rigorous proof that a reaction is reversible, the half-wave potential may be considered as a maximum negative value for the formal potential.

We have hypothesized a different half-wave potential for the reduction of two species of ruthenium (IV), the more highly hydrolyzed form having the larger overvoltage for the reduction. Under equilibrium conditions the two potentials must converge at some value equal to or more positive than the half-wave potential of the first wave. Therefore, only the most positive half-wave potential need be considered in the estimation of the formal potential.

On the basis of the above reasoning, the data in Table I establish $E^0 = +0.65$ volt *vs.* the N.H.E. as the lowest value for the reversible potential of the ruthenium(IV)–ruthenium(III) couple in 1 *M* perchloric acid. This value is in good agreement with the potential of 0.7 volt reported by Wehner and Hindman for the corresponding reduction at 0°.[6]

Evidence for the bracketing potential on the positive side was obtained from titration curves for the oxidation of ruthenium(III) to ruthenium(IV) by ceric perchlorate. The ruthenium(III) solutions used in these experiments were prepared by reduction of ruthenium(IV) with 0.1 weight per cent. bismuth amalgam. The amount of ceric perchlorate consumed in these titrations was low by about 6% because of the simultaneous oxidation of ruthenium(III) by perchloric acid. The titration curve, however, was sufficiently flat that a satisfactory estimate could be made of the potential at the point where the ruthenium(III) and ruthenium (IV) concentrations were equal. This potential was 0.85 volt *vs.* the N.H.E. and because the steady potentials were approached from the high side this may be considered as an upper limit to the formal potential for the ruthenium(IV)–ruthenium(III) couple. A similar value, 0.87 volt, was obtained by Wehner and Hindman as the lowest value of the potential for the oxidation of ruthenium(III) to ruthenium(IV) at 0°.

Because of the previously mentioned evidence for the reversibility of the third polarographic wave, −0.10 volt *vs.* the N.H.E. is considered a favorable value for the formal potential of the couple ruthenium(III) + e^- = ruthenium(II) at 25°.

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

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

[17] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1948.