[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE ARGONNE NATIONAL LABORATORY]

The Potentials of the Uranium Three–Four and Five–Six Couples in Perchloric and Hydrochloric Acids

BY EVELYN S. KRITCHEVSKY AND J. C. HINDMAN

Recently Harris and Kolthoff[1,2,3] and Heal[4] have published results of their extensive researches on the behavior of uranium at the dropping mercury electrode. These authors agree that the first wave observed on the reduction of a uranium(VI) solution is due to the reversible reaction

$$UO_2^{++} + e^- \rightleftarrows UO_2^+ \qquad (1)$$

The second wave observed in uranium(VI) solutions is ascribed to a composite wave involving the reduction of U(V) to U(IV) and U(IV) to U(III). They report that the reduction U(V) to U(IV) is irreversible at the dropping electrode. With respect to the U(IV)–U(III) reduction, Harris and Kolthoff[1] concluded that the wave was irreversible. Heal[4] supported this view although he reported his polarograms more nearly satisfied the criteria for reversibility than did those of Harris and Kolthoff.

In connection with investigations of the ionic species present in solutions of elements in this region of the periodic table, Magnusson, LaChapelle and Hindman[5] found that the potential of the neptunium(III)–neptunium(IV) couple was reversible. Hindman[6] was also able to show that not only was the plutonium(III)–plutonium(IV) couple reversible but it was also independent of acid concentration above 0.3 molar, and that the Pu(IV) ion exists as the hydrated Pu^{+4} ion in perchloric acid solutions. It was considered highly likely that the larger U(IV) ion should also be U^{+4} in perchloric acid and in dilute hydrochloric acid solutions. The hydrogen ion independence of the U(IV)–U(III) potential at the dropping mercury electrode found by Harris and Kolthoff[1] could be interpreted in terms of a reduction of U^{+4} to U^{+3}. However, partially on the basis of the irreversibility of the couple, these authors concluded that the initial reaction at the dropping electrode was probably

$$UO^{++} + e^- \longrightarrow UO^+ \qquad (2)$$

or

$$UOOH^+ + e^- \longrightarrow UOOH \qquad (3)$$

with further reaction of the UO^+ or UOOH with hydrogen ion to give U^{+3}.

Although the results of the present research confirm the conclusion that the initial reduction of the uranyl ion at the dropping mercury electrode corresponds to reaction (1) above, they differ in that it has been found that the U(III)–U(IV) couple is also reversible and represented by the reaction

$$U^{+4} + e^- \rightleftarrows U^{+3} \qquad (4)$$

in acid chloride and perchlorate solutions. The present communication summarizes an extensive investigation of the polarographic behavior of uranium at the dropping mercury electrode.

Material

Uranyl Chloride.—Solid uranyl chloride monohydrate was prepared by the reaction of hydrogen chloride gas on uranium trioxide at room temperature for twenty-four-forty-eight hours.[7] The excess hydrogen chloride was removed by alternatingly flushing with air and pumping off the gases. A stock solution of approximately 0.125 molar uranyl chloride was prepared by dissolving the appropriate amount of solid. Analysis of the solution gave a Cl/U ratio of 1.995.

Uranium Tetrachloride.—The solid uranium tetrachloride was material of high purity furnished by C. A. Kraus of Brown University. Stock solutions were prepared by dissolving the appropriate amount of solid in air-free 0.1 molar hydrochloric acid to make a 0.125 molar solution. All polarograms were run within two hours of the preparation of these stock solutions because anomalies were noticed when using older stock solutions. One stock solution of 0.25 *M* uranium tetrachloride in 10 molar hydrochloric acid was also prepared.

Uranium Trichloride.—The pure solid, furnished by C. A. Kraus of Brown University was added directly to the air-free supporting electrolyte. In certain cases a solution of uranium trichloride was prepared by electrolysis of an air-free 0.001 *M* uranium tetrachloride solution in the polarograph cell.

$UO_2(ClO_4)_2 \cdot xH_2O$.—The salt was prepared[8] by dissolution of freshly precipitated uranyl peroxide in perchloric acid, evaporating until the formation of crystals, recrystallizing twice from water, and drying *in vacuo* over sulfuric acid. The dry salt was found to contain 42.6% uranium. All of the uranyl perchlorate polarograms were made from solutions containing weighed amounts of the solid dissolved in the supporting electrolyte.

$U(ClO_4)_4$.—Solutions of $U(ClO_4)_4$ were made by the electrolytic reduction of uranyl perchlorate in 1 molar perchloric acid.

$U(ClO_4)_3$.—Solutions of $U(ClO_4)_3$ were made by the electrolytic reduction of uranyl perchlorate in 1 molar perchloric acid.

Miscellaneous.—The supporting electrolytes were made from weighed quantities of reagent grade salts and aliquots of standardized acids. The reagent sodium perchlorate was found to contain 27 parts per million NO_3^-. The data in Table I were obtained from nitrate-free solutions containing sodium perchlorate prepared by neutralization of perchloric acid with sodium hydroxide. Where the *p*H is reported it was determined with a Beckman Model G *p*H meter.

Experimental

All the polarograms in this work were obtained with a Sargent Model XX potentiometric pen chart recording

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[1] W. E. Harris and I. M. Kolthoff, THIS JOURNAL, **67**, 1484 (1945).

[2] I. M. Kolthoff and W. E. Harris, *ibid.*, **68**, 1175 (1946).

[3] W. E. Harris and I. M. Kolthoff, *ibid.*, **69**, 446 (1947).

[4] H. G. Heal, *Nature*, **157**, 225 (1946).

[5] L. B. Magnusson, T. J. LaChapelle and J. C. Hindman, CN-3053, June 28 (1945); to appear as paper No. 15.3, Vol. 14B of the National Nuclear Energy Series.

[6] J. C. Hindman, CN-2289, Nov. 1 (1944); to appear as Paper No. 4.4, Vol. 14B, of the National Nuclear Energy Series.

[7] C. A. Kraus, Brown University Report, A-360, p. 9, October 26 (1942).

[8] Gmelins, "Handbuch der anorganischen Chemie," "Uran," System Number 55, p. 136, Berlin, 1936.

polarograph calibrated according to the method of Lingane.[9] Electromotive force values in the vicinities of the half-wave potentials were determined with a Leeds and Northrup type K_2 potentiometer. These values are recorded in the figures in the parentheses along the abscissas of the polarograms. All values of half-wave potentials reported in this work have an experimental error of ± 0.004 v. This error includes any possible error due to the iR drop in the solution. An H-cell[10] was used with a sintered glass disc and an agar–agar plug separating the two compartments. A saturated potassium chloride agar bridge was used in all cases except where otherwise noted. Since precipitation of potassium perchlorate occurs in the potassium chloride bridge if the perchlorate concentration exceeds 0.1 molar and large and uncertain liquid junction potentials are observed, an ammonium chloride agar bridge was used for the perchlorate solutions with exception of measurements listed in Table I. Such a bridge is nearly as effective as the potassium chloride bridge in eliminating the liquid junction potential.[11]

TABLE I

EFFECT OF HYDROGEN ION CONCENTRATION ON THE BEHAVIOR OF U(VI) AT THE DROPPING MERCURY ELECTRODE IN CHLORIDE AND PERCHLORATE SOLUTIONS

Initial H^+ moles/liter	$E_{1/2}'$, volts	1/slope	$E_{1/2}''$, volts	i_d''/i_d'
HCl–KCl Solutions: 0.1 Molar Total Chloride Ion				
0.0[a]	−0.170	0.067	−0.86 and −1.06	0.80
2.5×10^{-4}	− .170	.068	−0.95 and −1.06	0.53
0.001	− .165	.058	−0.96	1.44
.01	− .174	.060	− .875	1.77
.10	− .176	.063	− .820	2 01
$HClO_4$–$NaClO_4$ Solutions: 0.1 Molar Perchlorate Ion				
0.0[b]	−0.23	0.123	−0.84	0.38
2.5×10^{-4}	− .178	.061	− .89	.29
0.001	− .175		− .939	.56
.01	− .175	.060	− .878	2.10
.10	− .175	.062	− .839	2.23

[a] Final pH 4.0. [b] Final pH 3.82.

In most cases a maximum suppressor was not found necessary, probably because of the agar in the salt bridge. A saturated calomel electrode was used as a reference electrode and as anode in one compartment of the cell.

Air was removed by bubbling pre-purified nitrogen through all solutions. Redistilled water was used exclusively and all measurements were carried out at 25.0 ± 0.2°.

The capillary used was a 20-cm. length of Corning marine barometer tubing. All values of the current reported have been corrected for the residual current.

Uranium(VI) solutions were reduced to uranium(IV) in a two-compartment cell connected by a porous glass disc. A 2-cm. diameter pool of mercury was the cathode and the anode was a spiral of platinum wire. In all the experiments the potential difference between the electrodes was about 9 volts and a current of about 0.9 ampere flowed. Because of the rapid oxidation of the U(III) when transferring the solution from one vessel to another the reductions to uranium(III) were performed in the polarograph cell using the same electrodes as described above. Twenty minutes was found to be sufficient to reduce U(VI) to U(IV) and a forty-minute reduction period was necessary to get U(III) in satisfactory yield.

I. Behavior of Uranium(VI) Solutions at the Dropping Mercury Electrode

Aliquots of 0.2 ml. of uranyl chloride stock solution and weighed samples of uranyl perchlorate were added to 25.0 ml. of the appropriate supporting electrolyte to make solutions *ca.* 1×10^{-3} molar in uranium(VI).

A typical polarogram of a uranyl perchlorate solution is given in Fig. 1. The half-wave potential and diffusion current of the first wave are designated $E_{1/2}'$ and i_d' and of the second wave $E_{1/2}''$ and i_d'', respectively.

The First Reduction Wave of the Uranyl Ion.—Analyses of the polarographic reduction wave were made by the equation of Heyrovsky and Ilkovic.[12]

$$E_{\text{d.e.}} = E_{1/2} - \frac{0.05915}{n} \log \frac{i}{i_d - i} \qquad (5)$$

The plot of log $i/(i_d - i)$ *vs.* $E_{\text{d.e.}}$, for the first wave of the polarogram in Fig. 1 gives a straight line with a value of 1/slope of 0.062, in reasonable agreement with the theoretical value of 0.059 for a one-electron reaction. The data in Tables I and II show that the theoretical value of 1/slope is found for both perchlorate and chloride solutions at acidities above 0.001 molar. It will also be noted from these data that the half-wave potential, $E_{1/2}'$, is the same and independent of acidity in both 0.1 molar perchlorate and 0.1 molar chloride solutions at acidities above 0.001 molar. Hydrolysis of the uranyl ion at low acidities is accompanied by a shift of the half-wave potential to a more negative value and a diminution in the diffusion current. As Table II shows, whereas the half-wave potential, $E_{1/2}'$, is independent of ionic strength in perchlorate solutions between 0.05 and 1.0 molar, shifting to a more positive value in 3.0 molar perchlorate, in chloride solutions the half-wave potential becomes more negative with in-

TABLE II

EFFECT OF SOLUTION CONCENTRATION ON THE BEHAVIOR OF URANIUM(VI) AT THE DROPPING MERCURY ELECTRODE

H^+, moles/liter	Anion, moles/liter	$E_{1/2}'$, volts	$E_{1/2}''$, volts	i_d''/i_d'
KCl–HCl Solutions—Varying Ionic Strength				
0.05	0.05	−0.164	−0.829	2.04
.05	.10	− .178	− .838	2.07
.05	.30	− .184	− .842	2.00
.05	1.0	− .188	− .848	1.88
.05	3.0	− .194	− .840	1.85
$NaClO_4$–$HClO_4$ Solutions—Varying Ionic Strength[a]				
0.05	0.05	−0.178	−0.890	2.06
.05	.10	− .176	− .863	2.15
.05	.30	− .183	− .860	2.09
.05	1.0	− .179	− .855	2.00
.05	3.0	− .167	− .822	1.95

[a] NH_4Cl-agar bridge; nitrate-free $NaClO_4$.

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[9] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).

[10] J. J. Lingane and H. A. Laitinen, *ibid.*, **11**, 504 (1939).

[11] C. N. Murray and S. F. Acree, *Bureau Standards J. Research*, **7**, 713 (1931).

[12] J. Heyrovsky and D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **1**, 198 (1935).

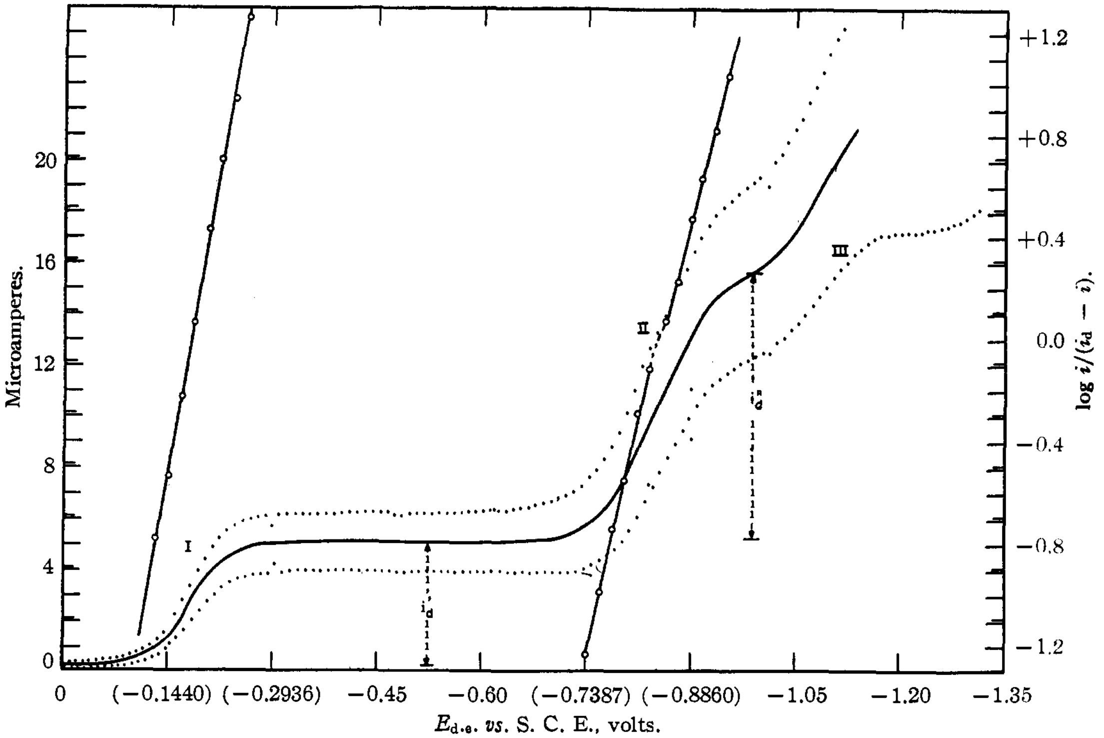

Fig. 1.—Polarogram of *ca.* 1 × 10^{-3} M U(VI) in 0.1 M $HClO_4$: I, the U(VI) reduction wave; II, the U(V)-U(IV)-U(III) reduction wave; III, the hydrogen discharge wave. The dotted lines represent the extent of the pen excursions of the recording polarograph. i_d' and i_d'' are the diffusion currents of the first and second waves, respectively.

creasing ionic strength. The potential shift in going from perchlorate to chloride solutions may be due to the formation of a weak chloro complex with the uranyl ion.

The Second Wave of the Uranyl Polarogram.—The second wave in the uranyl polarogram is well defined in solutions of greater acidity than 0.01 molar. The break in the plot of log $i/i_d - i$ *vs.* $E_{1/2}''$ shown in Fig. 1 shows that this wave is actually composed of two waves (corresponding to the reduction of U(VI) to U(V) and then U(V) to U(IV)) with half-wave potentials close together. The inflection is more marked in chloride than in perchlorate solutions. At low acidities the wave breaks up into two quite distinct waves. Our observations on the effect of acidity on the second wave are in essential agreement with those of Harris and Kolthoff[1] and Heal[13] with the exception that we found a very definite change in $E_{1/2}''$ with pH that takes place even at acidities of greater than 0.01 molar that would indicate that hydrogen ions are involved in one or both of the reductions. In addition, Heal[13] found the second wave to be completely gone in solutions of less than 0.001 molar hydrogen ion. We found that the discrepancy could be eliminated only on the addition of the maximum suppressors thymol or gelation to the solution. For example, Fig. 2 shows the data for a solution 0.001 molar in U(VI), 0.01 molar in H^+ and 0.09 molar in potassium chloride. It will be noted that the addition of 0.02% gelatin eliminates the second wave. Suppression of the hydrogen ion dependence was most pronounced when the maximum suppressor was in solution for a longer time than one-half hour or present in large concentrations, *i. e.*, 0.5%. It should also be noted that in a 0.01 molar hydrochloric acid, 0.1 molar chloride solution, the half-wave potential, $E_{1/2}''$ shifts from −0.875 to −0.95 volt on the addition of gelatin. This compares with the values of −0.92 and −1.0 volt reported by Harris and Kolthoff and by Heal, respectively.

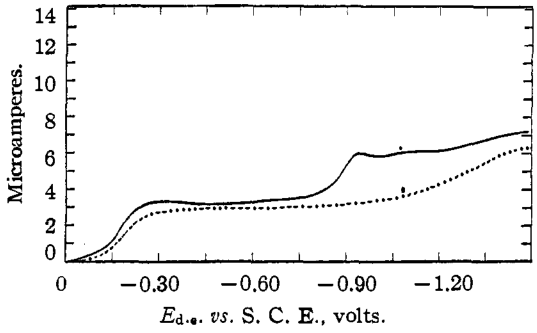

Fig. 2.—Polarogram of 10^{-3} M U(VI) in 0.01 M hydrochloric acid–0.09 M potassium chloride: A, without maximum suppressor; B, with 0.02% gelatin.

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[13] H. G. Heal, National Research Council, Montreal Laboratory, MC-95, October 20 (1944).

II. Behavior of Uranium(IV) Solutions at the Dropping Mercury Electrode

Aliquots of 0.200 ml. of uranium tetrachloride stock solutions 0.125 molar in hydrochloric acid were added to 25.0 ml. of appropriate supporting electrolyte to obtain the polarograms of the uranium tetrachloride–hydrochloric acid system. All polarograms were run within two hours of the preparation of the stock solution. Anomalies (to be discussed later) were observed if these stock solutions stood for longer periods. The perchlorate solutions were prepared both by addition of weighed amounts of uranium tetrachloride to the appropriate supporting electrolyte and by electrolytic reduction of uranyl solutions.

Analysis of the Wave.—Figure 3 is a typical example of a plot of log $i/i_d - i$ *vs.* $E_{d.e.}$ (equation 4) for a 0.001 molar U(IV), 0.05 molar hydrochloric acid solution. The value of 1/slope of 0.058 is in excellent agreement with the theoretical value for a one-electron reduction. The theoretical slope for a one-electron reaction is obtained in solutions of acidity greater than 0.01 molar. At lower acidities, the slope indicates that the reduction is no longer reversible. The diffusion current also progressively decreases as the hydrogen ion concentration falls below 0.01 molar.

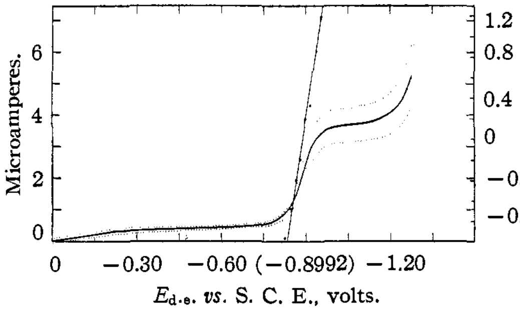

Fig. 3.—Polarogram of *ca.* 10^{-3} *M* uranium tetrachloride in 0.05 *M* hydrochloric acid–0.25 *M* potassium chloride solution: the dotted lines represent the extent of the pen excursions on the recording polarograph.

TABLE III

POLAROGRAPHIC BEHAVIOR OF U(IV) IN CHLORIDE SOLUTION. EFFECT OF HYDROGEN ION CONCENTRATION

Initial H^+, moles/liter	$E_{1/2}''$, volts	i_d'', microamperes	1/slope
	0.1 *M* Chloride Ion		
0[a]	−0.951	1.73	0.073[b]
.001	− .938	2.01	.073[b]
.003	− .922	2.55	.064
.01	− .906	2.84	.058
.05	− .888	2.75	.061
.10	− .885	2.94	.063
	1.0 *M* Chloride Ion		
0.001	−0.951	1.24	0.086[b]
.01	− .912	3.07	.062
.05	− .891	3.11	.065
.10	− .886	3.20	.065
.50	− .892	3.00	.065
1.0	− .891	2.82	.061

[a] Final *p*H 2.55. [b] Evidence of an anodic or oxidation wave.

Effect of Solution Composition of the Uranium(IV) Reduction Wave.—The effect of changing solution composition on the behavior of U(IV) at the dropping mercury electrode can be summarized as follows: (1) At constant ionic strength in both 0.1 and 1.0 molar chloride solutions, the half-wave potential, $E_{1/2}''$, becomes less negative with increasing acidity until the hydrogen ion concentration exceeds 0.01 molar when it becomes constant at about −0.89 v. (Table III). In very dilute acid solutions the cathodic U(IV) wave is almost gone while a well-defined anodic wave is observed. In Fig. 4 the polarogram for a 0.001 molar hydrochloric acid solution of U(IV) is shown. The anodic wave has a half-wave potential of −0.19 v. Analysis of the wave gives a value of 0.052 for the slope, which might indicate a reversible one-electron oxidation of one of the hydrolysis product of U(IV) to U(V). Changing the ionic strength from 0.05 to 3.0 molar by the addition of potassium chloride to a 0.05 *M* hydrochloric acid solution of U(IV) does not affect the half-wave potential. (2) As in the case of chloride solutions, decreasing the acidity in perchlorate solutions resulted in $E_{1/2}''$ becoming more negative, the diffusion current decreasing, and the slope departing from the theoretical value for a reversible one-electron reaction (Table IV). (3) The values of $E_{1/2}''$ both in 0.1 and 1.0 molar perchlorate solutions are more positive than in the corresponding chloride solutions. There is also a progressive shift of the halfwave potential to more negative values as the chloride to perchlorate ratio is increased in a mixed acid solution at one molar total acid concentration. This potential difference is somewhat greater than might be expected from a change in the activity coefficient ratio, $f_{U^{+4}}/f_{U^{+3}}$, and is probably attributable in part to the formation of a weak chloro complex of U(IV).

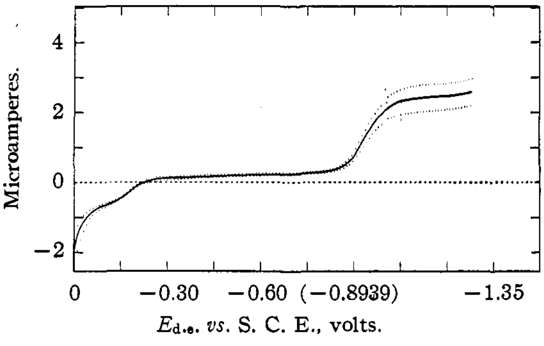

Fig. 4.—Polarogram of *ca.* 1×10^{-3} *M* U(IV) in 0.001 *M* hydrochloric acid–0.1 *M* potassium chloride solution: the dotted lines represent the extent of the pen excursions of the recording polarograph.

Effect of Standing and Acidity on the Polarographic Behavior of a Uranium(IV) Solution.—It was early noted that if polarograms were run on aliquots of a stock solution in dilute acid that had been standing overnight the reduction wave no longer had the theoretical slope for a reversible reaction although the half-wave potential had not changed significantly. Whereas in a series of experiments aliquots of a 0.125 *M* U(IV) solution in 0.1 *M* hydrochloric acid had an average value of 1/slope of 0.062 after twenty-four hours in duplicate experiments the average value of 1/slope had changed to 0.072. It would appear that the U (IV) hydrolyzes appreciably in the dilute acid, a process that is not immediately reversed on the addition of more concentrated acid. Solutions made in concentrated acid are more stable. Aliquots of stock solutions of 0.25 *M* U(IV) in 10 *M* hydrochloric acid had an average value of 1/slope of 0.060 after the stock had stood for seventy-two hours. Some of the difficulties observed by other workers in obtaining reversible waves may have been due to hydrolysis of their solutions.

TABLE IV

POLAROGRAPHIC BEHAVIOR OF URANIUM(IV) IN PERCHLORATE SOLUTIONS. EFFECT OF HYDROGEN ION CONCENTRATION

Initial H^+, moles/liter	$E_{1/2}$,$''^{a}$ volts	1/slope
	0.1 *N* Perchlorate Ion	
0.0^{b}	−0.921	0.094
.01	− .896	.066
.05	− .874	.064
.10	− .862	.064
	1.0 *N* Perchlorate Ion	
0.0^{c}	−0.910	...
.01	− $.881^{d}$	...
.05	− $.864^{d}$	...
.10	− $.863^{d}$	...
.50	− $.871^{d}$	...
1.00	− $.878^{d}$	...

[a] NH_4Cl–agar bridge. [b] *p*H 2.57 after run. [c] *p*H 1.92 after run. [d] Average of three runs which deviate from average less than ±0.005 volt.

III. Behavior of U(III) at the Dropping Mercury Electrode

According to Kolthoff and Lingane[14] if, in addition to a theoretical slope for a plot of long $i/i_d - i$ *vs.* $E_{d.e.}$, the half-wave potential of the oxidation wave of the reduced state is the same as the half-wave potential of the reduction wave of the oxidized state, the reaction is conclusively reversible. Analysis of the wave of polarograms of U(III) solutions prepared both by the dissolution of solid uranium trichloride in air-free 0.1 *M* hydrochloric acid and by the electrolysis of uranium tetrachloride in 1 *M* hydrochloric acid by a plot of $E_{d.e.}$ *vs.* log i-$(i_d)_a/(i_d)_c - i$ gives a straight line with an average value of 1/slope of 0.063 which is in good agreement with the theoretical value of 0.059. The anodic and cathodic currents form a smooth continuous curve with a half-wave potential identical with the value for the reduction of U(IV) (Table V). The U(III)–U(IV) reaction in hydrochloric acid thus satisfies both these criteria.

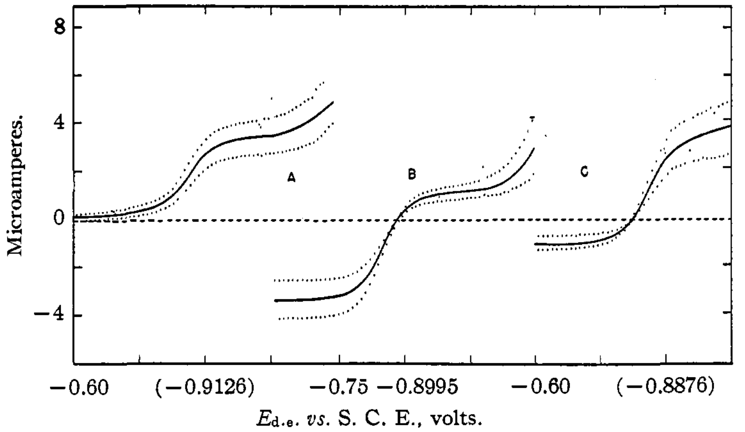

Fig. 5.—Polarograms of U(III) and U(IV) in perchlorate solutions: A, U(IV) in 1 *M* perchloric acid (from electrolysis of uranyl perchlorate solution); B, U(III) in 1 *M* perchloric acid (dissolution of solid uranium trichloride); C, U(III) in 1 *M* perchloric acid (electrolysis of uranium tetraperchlorate solution); the dotted lines represent the extent of the pen excursions of the recording polarograph.

Figure 5A is a polarogram of uranium (IV) perchlorate made by the electrolytic reduction of uranyl perchlorate in 1 *M* perchloric acid. Figure 5B is that of solid uranium trichloride dissolved in 1 *M* perchloric acid and Fig. 5C is that of uranium (III) perchlorate made by electrolytic reduction in 1 *M* perchloric acid. All three polarograms were run successively in the same cell. The half-wave potentials are the same in the three cases and the anodic and cathodic parts of the curves are continuous. The U(III)–U(IV) couple in 1 *M* perchloric acid therefore also satisfies the criteria of a reversible reaction.

The half-wave potentials of the U(III)–U(IV) couples in 1 molar hydrochloric and perchloric acids are compared in Table V.

IV. The Oxidation Potentials of the U(III)–U(IV) and U(V)–U(VI) Couples

With the conventions usually conformed to in polarographic literature, that the cell reaction corresponds to reduction at the dropping mercury electrode and oxidation at the reference electrode, the half-wave potential, $E_{1/2}$, is related to the stand-

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(14) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishing Co., New York, N. Y., 1941, pp. 153–159.

TABLE V

COMPARATIVE VALUES OF THE HALF-WAVE POTENTIALS OBTAINED IN 1 MOLAR PERCHLORIC AND HYDROCHLORIC ACID SOLUTIONS OF URANIUM(III) AND (IV)

Acid	Initial oxidation state	$E_{1/2}''$, volts	
HCl	+4	-0.891^c	
HCl	+4	$-\ .888^b$	
HCl	+3	$-\ .877$	av. -0.885
$HClO_4$	+4	$-\ .878^e$	
$HClO_4$	$+3^a$	$-\ .868$	
$HClO_4$	$+3^d$	$-\ .873$	av. -0.876

[a] By addition of UCl_3. [b] NH_4Cl–agar bridge. [c] KCl–agar bridge. [d] Produced by electrolytic reduction. [e] Average of three runs.

ard oxidation potential, E^0, of the couple referred to the specified reference electrode by the equation[15]

$$E_{1/2} = E^0 + 0.0591 \log f_{\text{ox}}/f_{\text{red}}(D_{\text{red}}/D_{\text{ox}})^{1/2} \quad (6)$$

where f_{ox} and f_{red} are the activity coefficients of the oxidized and reduced ions, respectively, and D_{ox} and D_{red} are their corresponding diffusion coefficients.

The Diffusion Coefficients of the Uranium Ions.—Using the values of the diffusion currents in microamperes per millimole per liter, the capillary constant $m^{2/3}t^{1/6}$, mg.$^{2/3}$ sec.$^{-1/2}$, substituted in the Ilkovic equation[16]

$$i_d = 605\, nD^{1/2}Cm^{2/3}t^{1/6} \quad (7)$$

values of the diffusion coefficients for the U(III), U(IV) and U(VI) ions have been calculated.

A value of $D_{UO_2^{++}} = 0.69 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ was found for a 0.09 *M* sodium perchlorate –0.01 *M* perchloric acid solution. This compares with the value of 0.68×10^{-5} cm.^{2} sec.$^{-1}$ for 0.09 *M* sodium perchlorate, 0.01 *M* perchloric acid solutions reported by Kern and Orlemann[17] and the value of 0.62×10^{-5} cm.^{2} sec.$^{-1}$ for 0.09 *M* potassium chloride, 0.01 *M* hydrochloric acid solutions reported by Harris and Kolthoff.[1] The diffusion currents were measured at -0.5 volt. The diffusion coefficients of U^{+3} and U^{+4} in 0.1 *M* perchloric acid were found to be $D_{U^{+3}} = 0.65 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ and $D_{U^{+4}} = 0.66 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, respectively. The uranium(III) concentrations were computed from the ratio of the diffusion currents of U(III) and U(IV), measured consecutively at -0.5 and -1.1 volts, respectively, and the total uranium concentrations obtained from the uranium(IV) diffusion current after oxidation of the uranium(III).

The Formal Oxidation Potentials.—For the calculation of the formal potential of the uranium(V)–uranium(VI) couple in perchloric acid the value of the diffusion coefficient of uranium(V) reported by Kern and Orlemann was used.[16] A redetermination of this constant was deemed unnecessary in view of the agreement found for $D_{UO_2^{++}}$ in the two investigations and the fact that Kraus[18] also reported that $D_{UO_2^{++}}$ and $D_{UO_2^{+}}$ are practically the same. Since in general the diffusion coefficients change little with change in salt concentration[19] and their ratios should change even less; neglect of any corrections for this effect should introduce an error of not more than one millivolt.

Since the activity coefficients, f_{ox} and f_{red}, of the different ions cannot be estimated with any accuracy at this time, a formal electrode potential is defined by

$$E_f = -E^0 + 0.0591 \log f_{\text{ox}}/f_{\text{red}} = E_{1/2} - \log (D_{\text{red}}/D_{\text{ox}})^{1/2} \quad (8)$$

For the reaction

$$UO_2^{+} \rightleftarrows UO_2^{++} + e^- \quad (9)$$

the formal potential in 0.1 molar perchlorate solution, at 25° is -0.067 ± 0.004 v. For a 1.0 molar perchlorate solution at 25° the potential is -0.063 ± 0.004 v. These values compare with the potential of -0.066 v. reported by Kern and Orlemann[17] for 0.5 molar perchlorate solutions. For the reaction

$$U^{+3} \rightleftarrows U^{+4} + e^- \quad (10)$$

the formal potential in 1.0 molar perchloric acid solutions at 25° is $+0.631 \pm 0.005$ v. The values from the data of Harris and Kolthoff[1] are $+0.68$ v. for both 0.1 molar and 1.0 molar perchloric acid. These more positive values deviate in the direction expected from their reported irreversibility for the couple. The formal potential in 1 *M* hydrochloric acid is calculated to be $+0.640 \pm 0.005$ v. This value compares with a potential of 0.69 v. estimated from the data of Heal[13] and the value of 0.633 volt reported from a single experiment by Howland and Magnusson[20] from potential measurements of the couple by classical e. m. f. methods. It should also be noted that these authors found the couple to be reversible over a twentyfold change in the ratio of U(IV) to U(III).

Summary

The uranium(III)–uranium(IV) couple has been shown to be reversible at the dropping mercury electrode. From the hydrogen ion independence of the couple it is concluded that the ionic species are U^{+3} and U^{+4} in acid solutions. The reaction

$$U^{+3} \rightleftarrows U^{+4} + e^-$$

has a formal oxidation potential of $+0.631 \pm 0.005$ v. in 1.0 *M* perchloric acid and $+0.640 \pm 0.005$ v. in 1 *M* hydrochloric acid at 25°. The difference in potential between the chloride and

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[15] Reference 14, pp. 157–159.

[16] Reference 14, p. 38.

[17] D. M. H. Kern and E. F. Orlemann, UCRL-26, Dec. 26 (1947); THIS JOURNAL, **71**, 2102 (1949).

[18] K. A. Kraus, MonN-194, Clinton Laboratories, Nov. 11, 1946.

[19] Reference 14, p. 52.

[20] J. J. Howland and L. B. Magnusson, Manhattan Project Report, CN-2888, May 9 (1945); to be published in the Collected Papers of the Uranium Volume of the Plutonium Project Record of the National Nuclear Energy Series.

perchlorate solutions is attributed in part to the formation of a weak chloride complex of U(IV).

The potential of the reaction

$$UO_2^+ \rightleftarrows UO_2^{++} + e^-$$

is −0.063 ± 0.004 v. in 1 *M* perchloric acid at 25°. Chloride ion also appears to form a weak complex with the uranyl ion.

The reduction of UO_2^+ at the dropping mercury electrode is hydrogen ion dependent in the absence of the maximum suppressors thymol and gelatin.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Potential of the Uranium(V), Uranium(VI) Couple and the Kinetics of Uranium (V) Disproportionation in Perchlorate Media[1,2]

BY D. M. H. KERN AND E. F. ORLEMANN

Introduction

The disproportionation of pentavalent uranium into the four and six states in aqueous solutions has long been known to be very rapid. Herasymenko[3] reported that the formation and disproportionation of uranium(V) could be detected during reduction of uranyl ion at the dropping mercury electrode (d. m. e.). His evidence for these conclusions was meager, but they have since been completely confirmed by the polarographic studies of Kolthoff and Harris[4] and the unpublished work of Heal.[5] Heal estimated the rate of disproportionation of uranium(V) by observing the rate at which a platinum electrode came to equilibrium after a small amount of uranium(V) was formed in a uranium(VI) solution; his data indicated that the rate of disproportionation in sulfate solutions was second order in uranium(V) and first order in hydrogen ion, but the precision of the measurements was very limited.

In the present investigation millimolar solutions of uranium(V) have been prepared by a controlled reduction of uranium(VI) in sodium perchlorate, perchloric acid solutions at a mercury cathode, a method used previously by Kraus[6] in chloride media. The potentials of the uranium(V), uranium (VI) couple and the rate of disproportionation of uranium(V) have been determined in solutions of varying acidity, and these measurements have served to establish the nature of the uranium(V) species and the most probable mechanism of disproportionation in these solutions.

Experimental

Reagents.—Merck reagent grade uranyl nitrate was converted to the perchlorate by evaporation with perchloric acid, and also by precipitation of ammonium diuranate, which was dissolved in perchloric acid, reprecipitated, and redissolved. The uranium content of the stock solutions was determined gravimetrically as (U_3O_8).

Reagent grade sodium perchlorate and perchloric acid were used without further purification; they were found to be free of chloride.

The Cell.—The electrolysis cell is shown in Fig. 1. The volume of the anode compartment, 2.5 ml., was sufficiently small compared to the total solution volume of 250 ml. so that diffusion of material through the sintered glass disc after electrolysis could be neglected. Thus current voltage (c. v.) curves could be obtained and the disproportionation of uranium(V) could be followed by means of the d.m.e. in the cathode compartment immediately after an electrolysis. Purified nitrogen or hydrogen was used to free the body of the solution of air and to sweep oxygen out of the anode compartment during electrolysis.

Electrolysis Procedure.—Solutions containing 0.1 to 0.5 *M* $NaClO_4$, 0.002 *M* $UO_2(ClO_4)_2$ and about 0.002 *M* $HClO_4$ were freed of oxygen and electrolyzed for thirty minutes or less at a rate of between twenty and forty milliamps. The vigorously stirred mercury cathode was maintained at a potential of −0.55 v. against a saturated calomel reference electrode (S. C. E.) by an adaptation of the potential controlling device described by Lingane.[7] Such electrolyses usually produced 0.001 *M* uranium(V).

Dropping Mercury Electrode Measurements.—Current-voltage curves were obtained with a manual apparatus of the type described by Kolthoff and Lingane.[8] All measurements were made at a temperature of 25.00 ± 0.05°.

Results

Diffusion Current Constant of Uranium(V).—In the kinetic studies, the uranium(V) concentrations were obtained from the diffusion currents of the uranium(V) oxidation wave at the d. m. e. A well-defined diffusion current region is available for such measurements as shown in Fig. 3.

In order to calculate uranium(V) concentrations from the observed currents, the diffusion current constant was determined by amperometric titrations of uranium(V) with ferric ion. An air-free solution of 0.02074 *M* $Fe(ClO_4)_3$, was added in small amounts to 250 ml. of millimolar uranium(V) in a 0.4 *M* $NaClO_4$ solution and the decrease in the diffusion current of uranium(V) at +0.1 v. (*vs.* the S.C.E.) was determined. The ob-

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[1] This paper is based on work performed under Contract Number W-7405-eng-48B with the Atomic Energy Commission in connection with the Radiation Laboratory of the University of California, Berkeley, California.

[2] Presented at the Symposium on the Transuranic Elements at the meeting of the American Chemical Society, Chicago, Illinois, April, 1948.

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[4] I. M. Kolthoff and W. E. Harris, THIS JOURNAL, **68**, 1175 (1946); **67**, 1484 (1945).

[5] H. G. Heal, *Nature*, **157**, 225 (1946), and private communications.

[6] K. A. Kraus, private communication.

[7] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **17**, 332 (1945).

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 215 ff.