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The Potential of the U(V), U(VI) couple and the Kinetics of U(V) Disproportionation in Perchlorate Media

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Kern, D.M.H.

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THE POTENTIAL OF THE U(V), U(VI) COUPLE AND THE KINETICS OF U(V) DISPROPORTIONATION IN PERCHLORATE MEDIA.

by

D. M. H. Kern and E. F. Orlemann

December 26, 1947

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December 26, 1947

ABSTRACT

1. Millimolar solutions of U(V) have been prepared by electrolysis of uranyl ion in sodium perchlorate, perchloric acid solutions and studied by means of the dropping mercury electrode. The U(V), U(VI) couple has been shown to be reversible.

2. The diffusion coefficient of UO_2^+ is 0.86×10^{-5} cm^2/sec in 0.4 M $NaClO_4$; that of UO_2^{++} is 0.68×10^{-5} cm^2/sec in 0.09 M $NaClO_4$, 0.01 M $HClO_4$ at 25°C.

3. In 0.01 to 0.5 M perchloric acid the U(V) species is UO_2^+ as shown by the fact that the potential of the couple

$$UO_2^+ = UO_2^{++} + 1e$$

is constant at -0.066 ± 2 v. at 25°C over this range of acidity in sodium perchlorate, perchloric acid solutions of ionic strength = 0.5.

4. In sodium perchlorate, perchloric acid mixtures of ionic strength, 0.4 the disproportionation of UO_2^+ at 25°C obeys the following law from $a_{H^+} = 0.01$ to 0.4 and from $[UO_2^+] = 10^{-5}$ to 10^{-3} M.

$$-\frac{d\,[UO_2^+]}{dt} = k_2 \cdot a_{H^+} \cdot [UO_2^+]^2$$

where $k_2 = 130 \pm 4$ (moles/l)$^{-1}$,(sec)$^{-1}$

5. The most probable mechanism for the disproportionation is:

$$UO_2^+ + H^+ = UOOH^{++}$$

$$UO_2^+ + UOOH^{++} \xrightarrow{k'2} UO_2^{++} + UOOH^+ \quad \text{(slow step)}$$

$$UOOH^+ \longrightarrow \text{stable U(IV) species}$$

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Results

Introduction

The disproportionation of pentavalent uranium into the four and six states in aqueous solutions has long been known to be rapid. Herasymenko[1] reported that the formation of U(V) and its rapid disproportionation could be detected during reduction of uranyl ion at the dropping mercury electrode (d.m.e.). His evidence for these conclusions was meager, but the formation and disproportion of U(V) at the dropping mercury electrode has been well established by the polarographic studies of Kolthoff and Harris[2] and the unpublished work of Heal. Heal[3] estimated the rate of disproportionation of U(V) by observing the rate at which a platinum electrode came to equilibrium after a small amount of U(V) was formed in a U(VI) solution. His data indicated that the rate of disproportionation in sulfate solutions was second order in U(V) and first order in hydrogen ion but the precision of the measurements was very limited.

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[1] P. Herasymenko, Trans. Faraday Soc. 24, 272, (1928)

[2] I. M. Kolthoff and W. E. Harris, J. Am. Chem. Soc. 68, 1175 (1946) 67, 1484 (1945).

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

In the present investigation millimolar solutions of U(V) have been prepared by a controlled reduction of U(VI) in sodium perchlorate, perchloric acid solutions at a mercury cathode; a method used previously by Kraus[4] in chloride media. The potential of the U(V), U(VI) couple and the rate of disproportionation of U(V) have been determined and used to establish the nature of the U(V) species in these solutions and the most probable mechanism of disproportionation.

Experimental

<u>Reagents</u> - Merck reagent grade uranyl nitrate was converted to the perchlorate by evaporations with perchloric acid, and also by precipitation of ammonium diuranate which was dissolved in perchloric acid, reprecipitated and again dissolved. 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 after they were found to be free of chloride.

<u>The Cell</u> - The electrolysis cell is shown in Figure 1. The volume of the anode compartment, 2.5 ml, was so small compared to the total solution volume of 250 ml that diffusion of material through the sintered glass disc after electrolysis

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[4] K. Kraus, MonN-194.

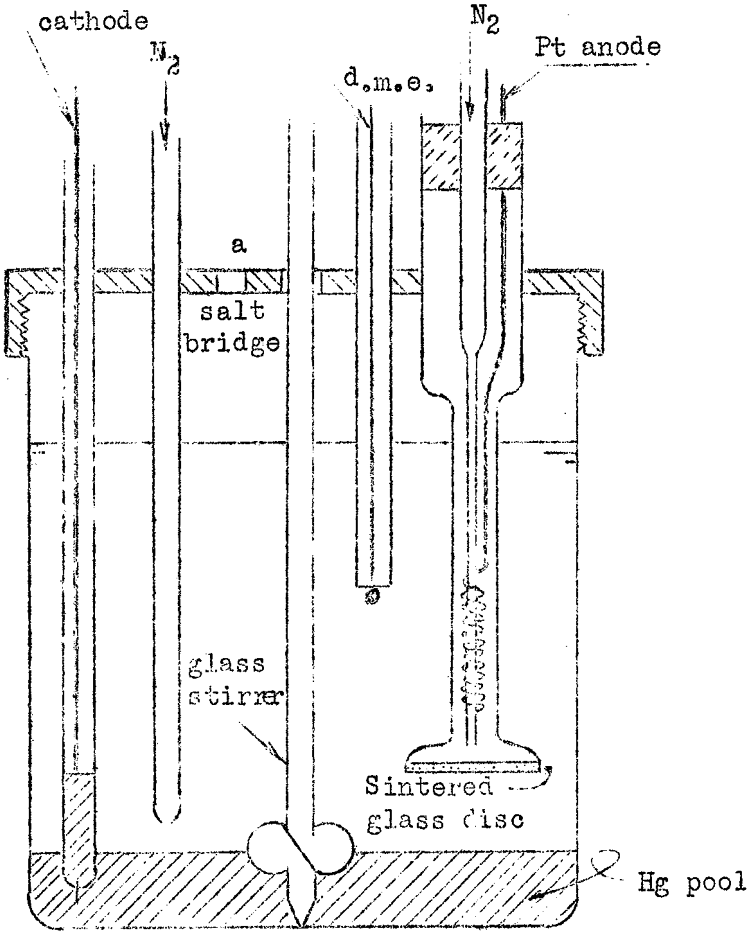

Fig. 1 Combined electrolysis and polarographic cell.

could be neglected. Current voltage (c.v.) curves could be obtained and the disproportionation of U(V) could be followed by means of the d.m.e. immediately after an electrolysis. Purified nitrogen or hydrogen was used to free the body of the solution from oxygen 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 about thirty minutes at an average rate of 18 milliamps. The 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[5]. Such electrolyses usually produced 0.001 M U(V). At higher acidities and/or higher uranyl concentrations, electrolysis is less efficient because of an increased rate of disproportionation of U(V).

Dropping Mercury Electrode Measurements - Current-voltage curves were obtained by means of a manual apparatus of the type described by Kolthoff and Lingane[6]. All measurements were made at a temperature of 25.00 ± .05°C. The value of

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

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

$m^{2/3}t^{1/6}$ for the capillary was 2.13 mg$^{2/3}$ sec$^{-1/2}$ (m = mass of Hg flowing per sec.; t = drop time) at a potential of + 0.1 v. against the S.C.E.

Results

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

In order to calculate U(V) concentrations from the observed currents the diffusion current constant was determined by amperometric titrations of U(V) with ferric ion in 0.4 M $NaClO_4$ solutions of pH 2.9 to 3.6. A standardized, air free, solution, about 0.02 M $Fe(NO_3)_3$, was added to about 250 ml of millimolar U(V) and the decrease in diffusion current of U(V) at 0.1 v. (v.s. the S.C.E.) was determined. The observed currents were corrected for the residual current, the change in volume, and the experimentally measured rate of decrease of current due to disproportionation. In Table I some of the data from a typical titration are given and the magnitude of the disproportionation correction can be seen.

TABLE I

AMPEROMETRIC TITRATION OF U(V) WITH FERRIC NITRATE IN 0.4 *M* SODIUM PERCHLORATE OF pH 3.1.

Fe(NO$_3$)$_3$ [a] added (ml)	Obs. i_d [b] (amps)	Corr. i_d [c] (amps)
0	1.87	1.87
1.945	1.30	1.32
4.082	0.71	0.73
5.560	0.27	0.30
6.434	0.03	0.06

[a] 0.01976 *M* solution added to 258 ml of U(V) at 25°C.

[b] Corrected for volume change and residual current.

[c] Additional correction due to disproportionation of U(V).

A typical plot of the corrected diffusion currents against the volume of added ferric nitrate is shown in Fig. 2. From this figure it is evident that the relation $i_d = K\,[U(V)]$ is followed. Experimental values of the diffusion current constant, K, in 0.4 M $NaClO_4$ at 25°C are as follows:

pH	2.9	3.1	3.6
K (amps$(m/mol/l)^{-1}$)	3.82	3.72	3.78

There is no trend with pH over this small interval and an average value for K of 3.77 ± 4μamps $(m.mol/l)^{-1}$ is found.

The Diffusion Coefficients of U(V) and U(VI) - The diffusion current constant is related to the diffusion coefficient, D, the rate of flow of mercury, m, the drop time, t, and the number of electrons transferred per molecule, n, by the Ilkovic equation:[7]

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[7] See reference 6 p. 55

$$K = 605\ n\ m^{2/3}\ t^{1/6}\ D^{1/2} \qquad (1)$$

Substitution of the experimental data into this equation leads to a value of $0.86 \pm .02 \times 10^{-5}$ $cm^2\ sec^{-1}$ for the diffusion coefficient of U(V) in 0.4 M $NaClO_4$ of pH 3 at 25°C.

Measurement of the diffusion currents of 1.8 and 3.6 $\times 10^{-3}$ M UO_2^{++} in 0.09 M $NaClO_4$, 0.01 M $HClO_4$ gave a value of 6.04 amps $(m.\ mol/l)^{-1}$ for the diffusion current constant and

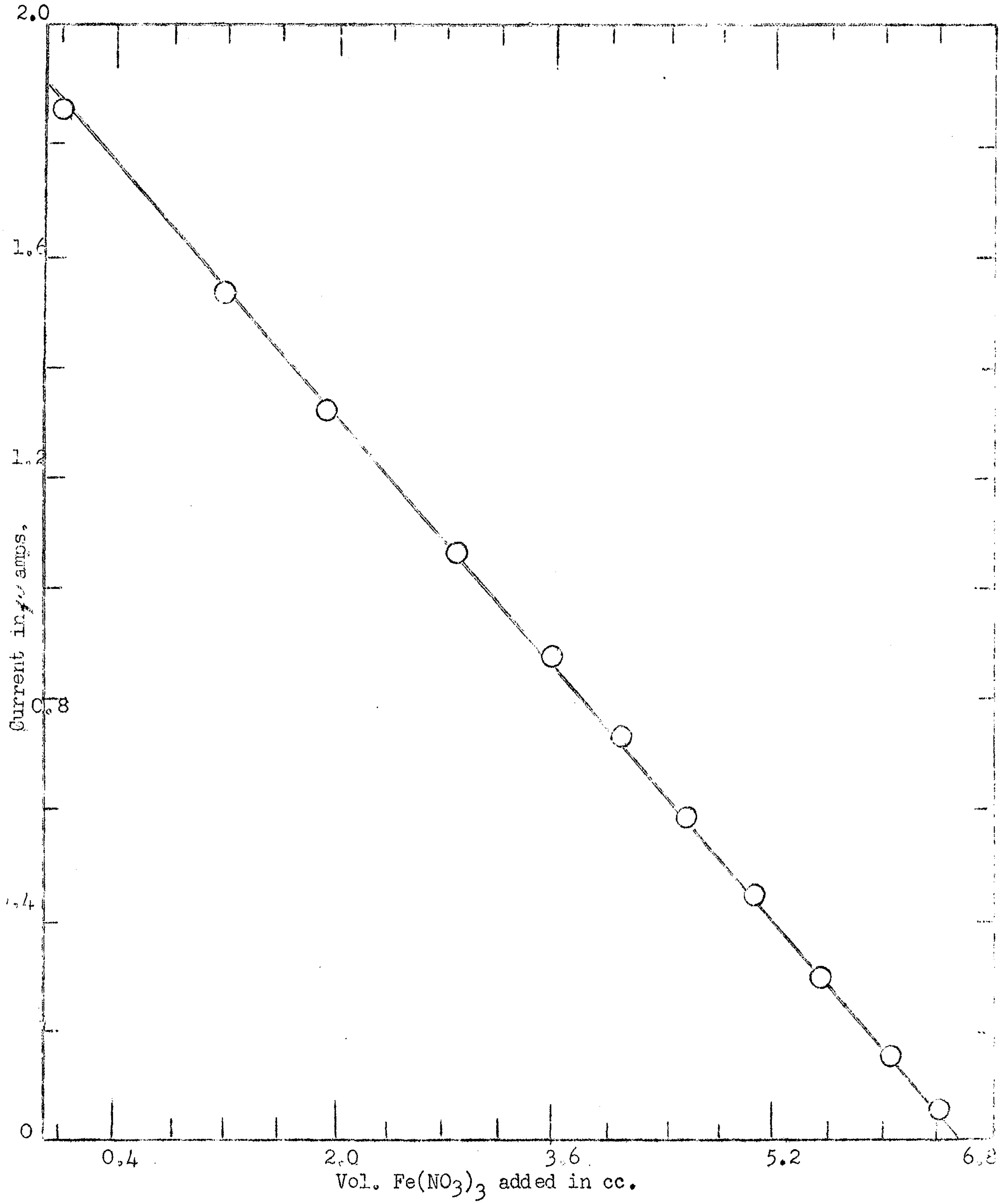

Fig. 2 Amperometric titration of U(V) with $Fe(NO_3)_3$

a calculated value of 0.68×10^{-5} cm^2 sec^{-1} for the diffusion coefficient of U(VI). Kolthoff and Harris[2] reported a value of 0.62×10^{-5} in 0.1 M KCl, 0.01 M HCl at 25°C. The difference between these values is probably due to some complexing by chloride ion in the latter case.

The fact that the diffusion coefficient of U(V) is about 25% larger than that of UO_2^{++} is consistent with the evidence that the U(V) species is UO_2^{+}.

The U(V), U(VI) Potential and The Effect of Hydrogen Ion. - In connection with the mechanism of U(V) disproportionation it was necessary to establish the nature of the U(V) species in perchlorate medium. To this end, the effect of hydrogen ion on the potential of the U(V), U(VI) couple was determined with the d.m.e. since U(V) disproportionates too rapidly to allow direct measurements except at very low acidities.

In the polarographic literature it is customary to have the cell reaction correspond to reduction at the d.m.e. and oxidation at the reference electrode. With this convention the current voltage equation for a reversible reduction of U(VI) to U(V) at 25°C is:[8]

$$E = E_{1/2} + 0.0591 \log (i_d - i)/i \qquad (2)$$

$$E_{1/2} = E^\circ + 0.0591 \log \frac{\gamma(VI)}{\gamma(V)} \left[\frac{D(V)}{D(VI)}\right]^{1/2} \qquad (3)$$

---

[8] See reference 6 p. 144

In these equations E° is the standard potential of the couple referred to a specified reference electrode; $E_{1/2}$ is the half-wave potential found when i equals one-half the diffusion current, i_d; the symbols (V) and (VI) refer to U(V) and U(VI), and the other symbols have their usual significance. Before these equations can be applied, it must be shown that the couple is reversible at the d.m.e., and that the disproportionation of U(V) does not contribute significantly to the U(VI) diffusion current. That the latter condition is met can be shown from the data in Table III. In the most severe case, (0.4 M $HClO_4$), the half life of millimolar U(V) is about twenty seconds as compared to the three second lifetime of a drop. That the couple is reversible is demonstrated by the c.v. curves of mixtures of U(V) and U(VI); the curve shown in Fig. 3 is a typical one. The curve in Fig. 3 is analyzed in Fig. 4, where log $(i_d-i)/i$ is plotted against E after shifting the current origin from zero to the U(V) diffusion current. The observed slope in Fig. 4 is 0.062 v. in satisfactory agreement with the theoretical value of 0.059 v. Equally important, Fig. 4 shows that the c.v. curve is continuous as the net process changes from an oxidation of U(V) to a reduction of U(VI). These two facts are definite proof that the couple is reversible at the dropping mercury electrode, and confirm the assumption of reversibility by previous investigators.[2,3] It should be noted that finding a linear relation of the theoretical slope, between E and log $(i_d-i)/i$,

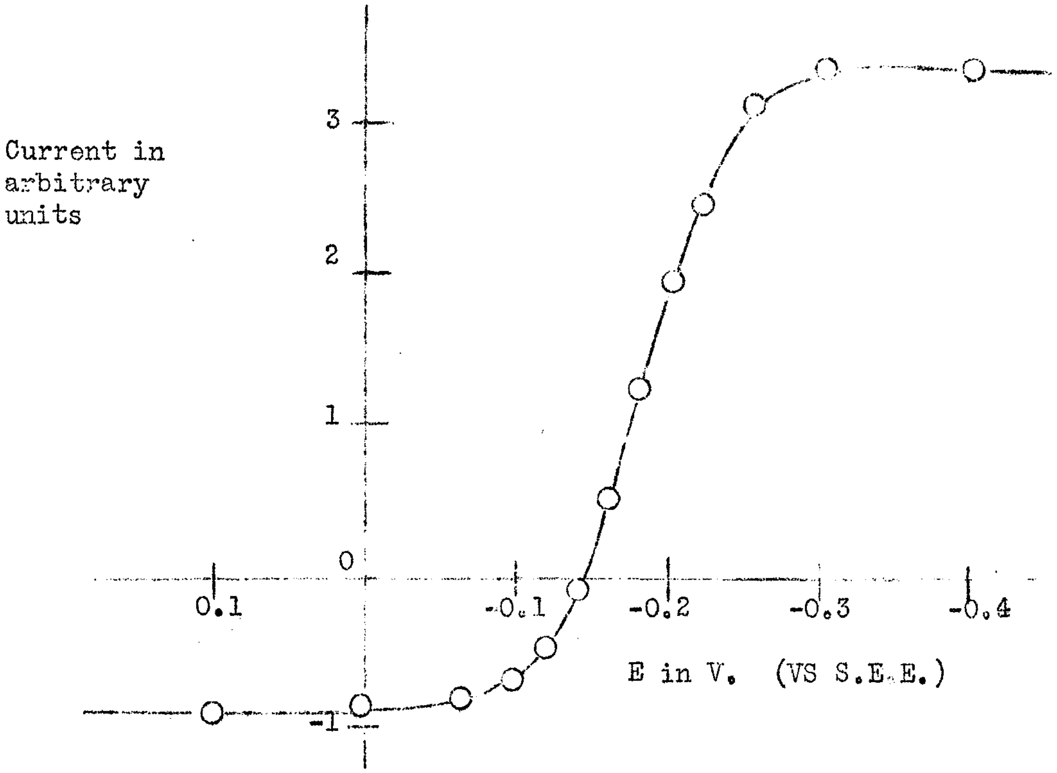

Fig. 3 - Typical c.v. curve of a solution containing U(V) and U(VI)

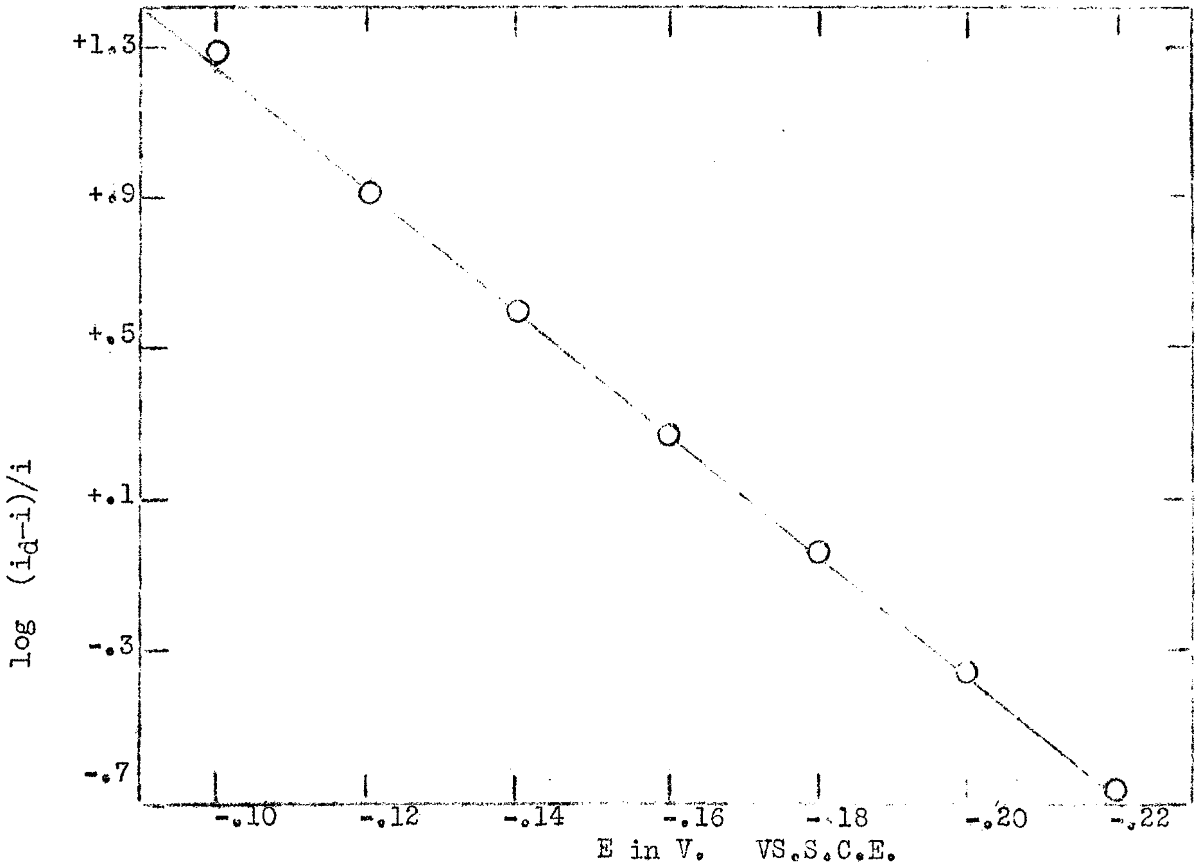

Fig. 6 Analysis of the C.V. curve of Fig.3.

for the c.v. curves of U(VI) alone is a necessary but not a sufficient condition for reversibility.

Current voltage curves of c.a. 0.002 M UO_2^{++} were obtained in sodium perchlorate, perchloric acid solutions of ionic strength 0.5. A mercury pool of large area served as an anode but a hydrogen electrode was used in the cell solution as a reference for all measurements of the potential of the d.m.e. In this way a possible iR correction was avoided and liquid junction potentials were eliminated. The latter were found to be serious from 0.1 - 0.5M $HClO_4$ when a S.C.E. reference electrode was tried. The observed $E_{1/2}$ values reported in Table II were obtained by plotting $\log(i_d-i)/i$ v.s. E, as in Fig. 4; they include the change in potential of the hydrogen electrode due to the change in pH of the solutions. The potential of the hydrogen electrode in each of these solutions was then calculated and subtracted from the observed $E_{1/2}$ to obtain values of $E_{1/2}$ v.s. the standard hydrogen electrode (column four of Table II). At the high acidities (0.1 - 0.5M $HClO_4$) the concentration of acid was determined by titration and a mean activity coefficient of 0.75 was used to calculate the corresponding hydrogen ion activities. The value 0.75 is an arbitrary average based on the data given by Latimer[9] in which it is found that $\gamma^{\pm}$ of perchloric acid changes from 0.80 to 0.76 in going from 0.1 to 0.5 M $HClO_4$ while that of sodium perchlorate changes from 0.67 to 0.76 in going from

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[9] W. M. Latimer, "Oxidation Potentials", Prentice Hall Inc. New York. 1938, p. 323.

0.4 to 0.1 M $NaClO_4$. The assumed activity coefficient affects: the apparent constancy of $E_{1/2}$ from 0.003 to 0.096 M $HClO_4$; the actual value of $E_{1/2}$ v.s. N.H.E. It does not alter the observed constancy of $E_{1/2}$ from 0.096 to 0.482 M $HClO_4$. An error of 10% in the assumed activity coefficient makes an error of 2.4 mv. in the reported value of $E_{1/2}$; we believe the value used is correct within 10%.

TABLE II

HALF-WAVE POTENTIAL OF U(VI) TO U(V) AT 25°C AND IONIC STRENGTH 0.5 IN $NaClO_4$, $HClO_4$ SOLUTIONS.

Obs. $E_{1/2}$ (v.)	$[HClO_4]$ M	a_{H^+}[a]	$E_{1/2}$(N.H.E.) (v.)
0.214		0.0028[b]	0.063
0.130	0.096	0.072	0.062
0.101	0.289	0.22	0.062
0.088	0.482	0.36	0.062

[a] See text for experimental meaning.

[b] Measured with a quinhydrone electrode instead of the hydrogen electrode.

Since the U(VI) species is known to be UO_2^{++} at these acidities[10], the couple has been shown to be reversible, and $E_{1/2}$ is independent of acidity, the principal U(V) species from 0.003 to 0.048 $\underline{M}$ $HClO_4$ must be UO_2^+ (or a hydrated UO_2^+).

Substitution of the value of $E_{1/2}$ and the previously given values of the diffusion coefficients of U(V) and U(VI) into equation (3) leads to the result:

$$UO_2^+ = UO_2^{++} + e$$

$$E^\circ(25^\circ C,\ N.H.E.) = -0.066 \pm 2 + 0.059 \log \frac{\gamma UO_2^+}{\gamma UO_2^{++}} \Bigg\} \text{in} \left\{ \begin{array}{l} NaClO_4 \\ HClO_4 \\ \mu = 0.5 \end{array} \right.$$

<u>Kinetics of Disproportionation of U(V)</u> - The acidity of sodium perchlorate, perchloric acid solutions of ionic strength 0.4 was varied from 0.02 to 0.4. The rate of disproportionation of U(V) was determined in these solutions by measuring the U(V) diffusion current at 0.1v. v.s. S.C.E. at thirty second intervals. After U(V) had been prepared by electrolysis of U(VI) in a slightly acid solution of the required sodium perchlorate concentration, the desired amount of oxygen free perchloric acid was added, and the solution was mixed by a stream of purified hydrogen or nitrogen. Oxygen reacts very rapidly with U(V); the rate is comparable to the rate of disproportionation of U(V) at the higher acidities. Since the U(V) concen-

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[10] W. E. Harris, Thesis, University of Minnesota, 1944. Also available as CC-2702.

tration was always millimolar or less, even traces of oxygen caused difficulty. At low acidities the initial U(V) concentration was only a fraction of millimolar to avoid changes of hydrogen ion concentration during the reaction. At high acidities, the initial measurements were made at small concentrations because the disproportionation was too fast to be followed until most of the U(V) reacted.

The amperometric titrations of U(V) previously described showed a linear dependence of the diffusion current on the U(V) concentration. In view of this fact, a linear relation between the reciprocal of the diffusion current and the time, observed for a typical run in Fig. 5, shows that the rate is proportional to the second power of the U(V) concentration. In all cases from 10^{-3} to 10^{-5} $\underline{M}$ UO_2^+ and from 0.02 to 0.5$\underline{M}$ $HClO_4$ this second order dependence was found. The observed rate constants corresponding to the expression:

$$-\frac{d(UO_2^+)}{dt} = k_2''(UO_2^+)^2$$

are tabulated in Table III. Unless otherwise indicated the hydrogen ion activities a_{H^+}, in column two were obtained from the observed potentials of a quinhydrone electrode and they have this experimental significance. The last column shows the first order dependence on the hydrogen ion activity.

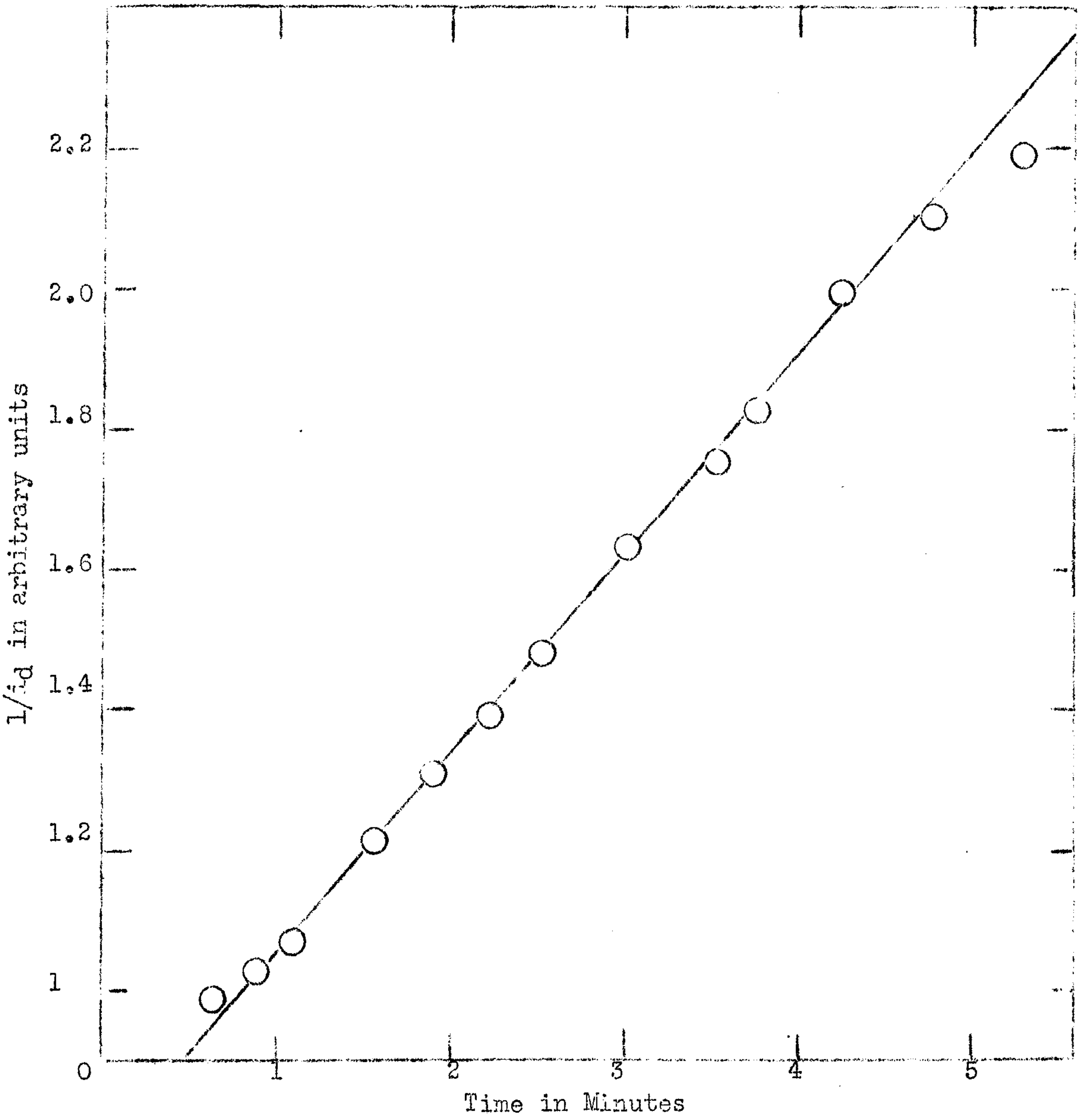

Fig. 5 Typical plot of the reciprocal of the U(V) diffusion current against time.

TABLE III

RATE OF DISPROPORTIONATION OF U(V) AT 25°C AND IONIC STRENGTH 0.4 IN $NaClO_4$, $HClO_4$ SOLUTIONS.

k_2'' $\left(\frac{\text{moles}}{\text{l}}\right)^{-1}$ sec^{-1}	a_{H^+}[c]	k_2''/a_{H^+} $\left(\frac{\text{moles}}{\text{l}}\right)^{-1}$ sec^{-1}
2.77	0.0216	128
4.69	0.0365	128
6.76	0.0555	122
9.64	0.0711	135
10.8	0.0843	128
25.9	0.197 [b]	131
35.2[a]	0.260 [b]	135
43.8[a]	0.318 [b]	137
40.5[a]	0.322 [b]	126
	Av.:	130 ± 4

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[a] Ionic Strength = 0.5

[b] Activity calculated as described in connection with Table II.

[c] See text for experimental significance.

The accuracy of the results is probably less than might be concluded from the precision.

From the data in Table III and the evidence that the U(V) species is UO_2^+ the observed rate law is:

$$-\frac{d\,(UO_2^+)}{dt} = k_2 \cdot a_{H^+} \cdot \left[UO_2^+\right]^2 \qquad (4)$$

$k_2 = 130 \pm 4$ (moles/l)$^{-1}$ sec^{-1} at 25.0°C in $NaClO_4$, $HClO_4$ of $\mu = 0.4$

The effect of ionic strength, over a limited range, is shown in Table IV. The rate of disproportionation was determined as before, but in 0.1 M $NaClO_4$ solutions of varying perchloric acid concentration.

TABLE IV

THE EFFECT OF IONIC STRENGTH ON THE RATE OF U(V) DISPROPORTIONATION IN $NaClO_4$, $HClO_4$ SOLUTIONS AT 25°C.

μ	k_2'' (moles/l)$^{-1}$sec^{-1}	a_{H^+}	k_2''/a_{H^+} (moles/l)$^{-1}$sec^{-1}
0.119	1.67	0.0214	78
0.137	3.08	0.0383	80
0.156	4.61	0.0577	80
0.174	6.41	0.0725	88
0.192	8.29	0.0852	97
0.281	18.9	0.158	120
0.40	--	0.02-0.3	130

The data in Table V show in increase in rate with an increase in ionic strength as would be predicted by the Brönsted theory for the proposed reaction mechanism in which the activated complex is $(UO_2\ UOOH)^{+++}$. However the experimentally possible ionic strength range is too high and too limited to permit a detailed analysis of this point.

<u>Mechanism of Disproportionation</u> - The most probable mechanism of disproportionation in acid perchlorate solutions is the following:

$$UO_2^+ + H^+ = UOOH^{++} \qquad (5)$$

$$UO_2^+ + UOOH^{++} \quad k_2' \quad UO_2^{++} + UOOH^+ \qquad (6)$$

$$UOOH^+ \quad \text{Stable U(IV) species} \qquad (7)$$

In calculating a rate law corresponding to this mechanism of disproportionation the reverse reaction can be neglected because the equilibrium concentration of U(V) is negligible. If we let K be the dissociation constant of $UOOH^+$, the above mechanism leads to the rate law:

$$-\frac{d\ UO_2{}^+}{dt} = \frac{k_2'}{K} \cdot a_{H^+} \cdot \left[UO_2{}^+\right]^2 \qquad (8)$$

Comparison with equation (4) shows that the experimentally observed k_2 is then approximately equal to k_2'/K. From the fact that the U(V), U(VI) potential was independent of hydrogen ion even in 0.5 M $HClO_4$ (see Table II) the value of K must be greater than 10. On this basis the value of k_2' must be greater than 1300 (moles/l)$^{-1}$sec^{-1} in the perchlorate solutions studied.

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