to the electrode at a different rate than the symmetrical *trans* form. It follows that the migration current, and hence the limiting current, would be different for the *cis* ion than for the *trans*.[28]

The situation in the absence of supporting electrolyte is complicated by the formation of electrolyte (nitrite ions, for example) during the reduction, as well as by stirring effects associated with maxima which may not completely disappear even at more negative potentials. Absolute values for limiting currents are, therefore, not reproducible. Experimentally, the *cis*-dinitrotetramminecobalt(III) chloride has consistently given slightly higher limiting current values than the corresponding *trans* isomer in the absence of supporting electrolyte. The *trans* isomers of dinitrobisethylenediaminecobalt(III) nitrate and nitroisothiocyanatobisethylenediaminecobalt(III) chloride monohydrate have shown higher limiting currents than the corresponding *cis* forms.

It is apparent that difficulties inherent in the experimental method for study in the absence of supporting electrolyte may make the polarograph inadequate to measure accurately the differences in migration current which the theory suggests. On the basis of the present work, therefore, it is felt that polarographic reductions in the presence of supporting electrolyte show more promise in serving as an aid to differentiation between certain *cis* and *trans* isomers in solution.

(28) H. F. Holtzclaw, Jr., Ph.D. Thesis, University of Illinois, 1947.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA]

Measurement of Disproportionation Rates at the Dropping Mercury Electrode

BY E. F. ORLEMANN AND D. M. H. KERN[1]

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A theoretical study has been made of current increases at the dropping mercury electrode arising from disproportionation of the electrode product. A relationship is derived between this current increase, the diffusion current and the disproportionation rate constant, which reduces to a particularly simple form for small rates and depolarizer concentrations. In this case the rate constant is shown to be proportional to the slope of the plot i/i_d *vs.* i_d, where i is the observed limiting current and i_d the current due to diffusion alone. These conclusions were tested on the reduction of U(VI) to unstable U(V) in chloride and perchlorate solutions. Quantitative agreement with the theory was found in all the points tested with the exception of an anomaly observed in strongly acid chloride solutions. The experiments indicated that the theory permits the identification of a second-order reaction involving the electrode product, the discovery of the role of other ions in the reaction mechanism, and an estimate of the magnitude of the second-order disproportionation rate constant.

Introduction

At the dropping mercury electrode (d.m.e.) in acid solution, uranium(VI) is reduced to uranium (V) at potentials between −0.17 and −0.9 v. *vs.* the saturated calomel electrode (S.C.E.).[2] U(V) is unstable and disproportionates into U(VI) and U(IV) according to the rate law[3]

$$\frac{\mathrm{dU(V)}}{\mathrm{d}t} = -k'(\mathrm{H}^+)(\mathrm{U(V)})^2 \qquad (1)$$

A portion of the U(VI) from the disproportionation reaches the electrode and is reduced. The limiting current therefore has a reaction-controlled as well as a diffusion-controlled component. The increase in current beyond that corresponding to a one-electron diffusion-controlled reduction is a function of the rate of disproportionation.[2] In this paper a theoretically derived relationship between limiting current and the second-order rate constant has been sought, that is generally applicable to the case in which the primary electrode product is an oxidation state unstable with respect to disproportionation. The theory has been tested experimentally by applying it to the reduction of uranyl ion in acid solution. Since the formation of unstable intermediates at the d.m.e. is often postulated, the results obtained in this paper may be of use in permitting an estimate of the associated disproportionation rates. Related problems involving first-order reactions at the d.m.e. have been treated with varying degrees of rigor by Brdička[4] and co-workers, and Delahay.[5]

Theoretical

The Simultaneous Reaction and Diffusion Problem.—In this paper we are considering an electrode process of the type

$$\mathrm{A} + ne^- \longrightarrow \mathrm{B} \text{ or } \mathrm{A} \longrightarrow \mathrm{B} + ne^- \qquad (2a)$$

$$2\mathrm{B} \longrightarrow \mathrm{A} + \mathrm{C} \qquad (2b)$$

where C is an oxidation state which does not depolarize the electrode at the potential in question. The second reaction is second order with respect to B.

When the depolarizer concentration is affected by the decomposition of the electrode product, a reaction rate term must be included in the diffusion equations of species A and B, since the change of concentration with time is not dependent on diffusion alone. In our case the term involves the electrode product concentration, which must be solved for simultaneously.

Accordingly one arrives at the equations

$$\begin{aligned} \frac{\partial A}{\partial t} &= D_a \frac{\partial^2 A}{\partial x^2} + {}^1/_2 kB^2 \\ \frac{\partial B}{\partial t} &= D_b \frac{\partial^2 B}{\partial x^2} - kB^2 \end{aligned} \qquad (3)$$

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(1) Shell Fellow in Chemistry 1948–1949; Chemistry Department, Harvard University, Cambridge, Massachusetts.

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

(3) D. M. H. Kern and E. F. Orlemann, *ibid.*, **71**, 2102 (1949); K. A. Kraus, *et al.*, *ibid.*, **71**, 2510 (1949); H. G. Heal and J. Thomas, *Trans. Faraday Soc.*, **45**, 11 (1949).

(4) Brdička and collaborators, *Collection Czechoslov. Chem. Communs.*, **12**, 39, 138, 313, 337 (1947).

(5) P. Delahay, THIS JOURNAL, **73**, 4944 (1951).

the boundary conditions being the same as in the pure diffusion case.[6] Once these equations have been solved for A, $i(k,t)$ is easily found because of its simple relation to $(\partial A/\partial x)_{x=0}$.

A solution of these equations is unfortunately unobtainable in a convenient form.[7] The rigorous adaptation of these equations to the d.m.e. by the method of MacGillavry and Rideal[8] leads to equations of even greater complexity. It has accordingly been necessary to resort to approximate calculations based on a simplified model of the concentration gradients at the drop when both reaction and diffusion are taking place. This model is similar to that introduced by Wiesner[9] and Brdička[4] in their studies of first-order reactions.

The Concept of Reaction Volume.—Although B reacts over its entire diffusion gradient, the current is affected most by reaction occurring in the fraction of the gradient closest to the drop. This is true both because A produced in this region is in the most favorable position to be converted at the electrode, and because the concentration of B is greatest at the surface, falling rapidly at larger distances. It is convenient, then, to consider the reaction limited to a region around the drop, the product A from which is assumed to be entirely converted at the electrode. Further, this region is assumed to contain a homogeneous concentration $\bar{b}$ of electrode product averaged over the life of the drop; the continuous production of B in this region is balanced by (i) reaction according to equation (2b) and (ii) diffusion away from the outer edge of the reaction volume region.

In the absence of reaction, this diffusion away from the drop is given by the Ilkovic equation

$$\bar{\imath}_{\mathrm{d}} = 607\ nm^{2/3}T^{1/6}D_{\mathrm{b}}{}^{1/2}b = K_{\mathrm{b}}b \qquad (4)$$

where b is the surface concentration of electrode product and the other symbols have their usual significance. It is easily shown that b is time independent and equal to $\sqrt{D_{\mathrm{a}}/D_{\mathrm{b}}}$ × the bulk depolarizer concentration. In the presence of reaction this diffusion is assumed still to conform to the Ilkovic equation, except that b is replaced by $\bar{b}$.

The Solution Based on the Concept of Reaction Volume.—When reaction occurs, the average current $\bar{\imath}$ observed at the drop is made up of two parts. One part is the diffusion current $\bar{\imath}_{\mathrm{d}}$ resulting from the usual diffusion of A from the bulk of the solution. The remainder results from the diffusion to the surface of A that has been formed by reaction.

According to the concept of reaction volume then

$$\bar{\imath} - \bar{\imath}_{\mathrm{d}} = {}^1/_2 k\bar{b}^2 nFv \qquad (5)$$

where v is the reaction volume in liters, k the rate constant in (mmole/l.)$^{-1}$ sec.$^{-1}$, F is millicbs./mole, $\bar{\imath} - \bar{\imath}_{\mathrm{d}}$ in μamp., and $\bar{b}$ in mmole/l. A material balance of B leads to the equation

$$\bar{\imath} = k\bar{b}^2 nFv + K_{\mathrm{b}}\bar{b} \qquad (6)$$

where $\bar{\imath}$ is the rate of B formation and K_{b} is the Ilkovic constant. The terms on the right represent loss by reaction and diffusion, respectively.

The Calculation of v.—Let us suppose that reduction of a depolarizer of concentration A is initiated at zero time at a plane electrode, giving rise to a gradient of electrode product. This electrode product, of concentration B, then undergoes a reaction corresponding to equation (2b). In every layer of thickness dx parallel to the electrode a quantity ${}^1/_2 kB^2$ dx (assuming unit area) of A is formed per unit time. B itself is a function of x and t. Now we define a function $W(x,T-t)$ as the probability that a particle released at x at time t will reach the electrode within time T, where T and t are measured from the same origin. Then the total number of moles arriving at the electrode within time T because of reaction all along the diffusion gradient of B is given by

$$N = {}^1/_2 k \int_0^T \mathrm{d}t \int_0^\infty B^2(x,t)W(x,T-t)\,\mathrm{d}x \qquad (7)$$

A simple statistical derivation, based on the random flight distribution function for Brownian motion[10] yields for the probability function W the expression

$$W(x,t) = 1 - \frac{2}{\sqrt{\pi}}\int_0^{x/\sqrt{4D_{\mathrm{a}}t}} e^{-y^2}\,\mathrm{d}y \qquad (8)$$

We will assume that the function B, as in the previous section, can be represented by the expression for pure diffusion

$$B = b\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{x/\sqrt{4D_{\mathrm{b}}t}} e^{-y^2}\,\mathrm{d}y\right) \qquad (9)$$

corrected for depletion by reaction by the substitution of $\bar{b}$ for b. The effect of this substitution on B at very low and very high reaction rates can be determined by combining equations 5 and 6 to give

$$\bar{b} = [\bar{\imath} - 2(\bar{\imath} - \bar{\imath}_{\mathrm{d}})]/K_{\mathrm{b}}$$

At low rates, $\bar{\imath} = \bar{\imath}_{\mathrm{d}}$ and therefore $\bar{b} = b$. At high rates $\bar{\imath} = 2\bar{\imath}_{\mathrm{d}}$ and $\bar{b} = 0$. Thus the behavior of the corrected expression for B is seen to be satisfactory in these two limits.

In general the assumption that D_{a} and D_{b} are equal will introduce only a small error. After this simplification is made, it is apparent from equations (8) and (9) that the functions W and B differ only by a constant. Rather than carry out a numerical integration of equation (7), which would not give a general expression in terms of D and T, it is more satisfactory to substitute for W and B a simple function which behaves in approximately the same way. The function

$$F = 1 - \frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}\,\mathrm{d}y$$

departs from its initial slope only gradually, as shown in Fig. 1. It is consequently not unreasonable to substitute for the error function so simple a function as

$$f = 1 - (z/c) \qquad (10)$$

where c is the intercept on the z axis.

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(6) See I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1952, Chapter II.

(7) For a similar problem involving a first-order reaction, for which the authors give the complete solution, see J. Koutecky and R. Brdička, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

(8) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

(9) K. Wiesner, *Z. Elektrochem.*, **49**, 164 (1943).

(10) S. Chandrasekhar, *Rev. Modern Phys.*, **15**, 1 (1943).

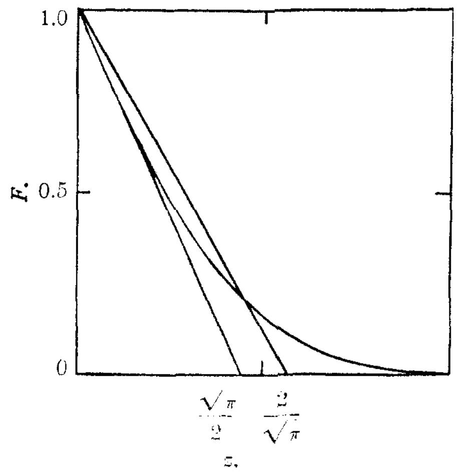

Fig. 1.—Approximations to the probability integral.

If this operation is carried out on the right-hand member of equation (7) and appropriate changes made in the limits so that no negative values of the integrand are included, a straightforward integration yields the result

$$N = 0.28c \times {}^1\!/_2 k\bar{b}^2 T^{3/2} D^{1/2} \qquad (11)$$

The best value for c lies between the intercept of the initial slope of the function F, and the intercept of the line enclosing the same area beneath it as the function F, *i.e.*, between $\sqrt{\pi}/2$ and $2/\sqrt{\pi}$. The former choice is clearly too small, the other too large because it effectively brings all the outlying probability and concentration regions into the space between the line and the F axis. The coefficient $0.28C$ in equation (11) is, respectively, 0.32 and 0.25 in the two cases. We will use the average value 0.28. Equation (11) gives the number of moles of reaction product that have reached a plane electrode of unit area by various times T. Differentiating with respect to time, we find for the instantaneous reaction component of the current at a plane surface of area s

$$i - i_d = nFs\frac{dN}{dt} = {}^1\!/_2 k\bar{b}^2 nFs \cdot {}^3\!/_2 \cdot 0.28\sqrt{Dt} \qquad (12)$$

Application to the D.M.E.—To transfer the above relation to the d.m.e., the growth of the drop and consequent increases of the diffusion gradient must be considered. Where pure diffusion is involved, rigorous treatment shows that the total flux of material is increased to $\sqrt{7/3}$ times that calculated for the plane surface of equal area. An increase is certain to occur when the current is partially reaction controlled also. Although the correction is probably too large, we shall assume that the same factor applies as in pure diffusion. The effective area of the d.m.e. in terms of the mercury flow rate m and the time t at 25° is then

$$s_t = \sqrt{7/3} \times 0.851 m^{2/3} t^{2/3} \qquad (13)$$

We shall also assume that the current observed on the galvanometer is the integrated average over the lifetime T of the drop. Now

$$\bar{i} - \bar{i}_d = \frac{1}{T}\int^T i\,dt - \frac{1}{T}\int^T i_d\,dt = \frac{1}{T}\int_0^T (i - i_d)\,dt \qquad (14)$$

Application of equation (12) to the d.m.e. in the light of equations (13) and (14) yields the relation

$$\bar{i} - \bar{i}_d = \frac{6}{13}(i - i_d)_T = {}^1\!/_2 nFk\bar{b}^2 s_T \times 0.30\sqrt{DT} \qquad (15)$$

Comparison of this result with equation (5) shows that the volume parameter v is equal to s_T 0.30 $\sqrt{DT}$. For ordinary values of D and T this corresponds to a shell of thickness *ca.* 10^{-3} cm. around the drop.

It now remains to reduce equations (5) and (6) to a form suitable for experimental verification. Eliminating $\bar{b}$ and using the expression for K_b given in equation (4), we arrive at the convenient relation

$$(\bar{i} - \bar{i}_d)^{-1/2} = \alpha(\bar{i}/[\bar{i} - \bar{i}_d] - 2) \qquad (16)$$

where

$$\alpha = \sqrt{0.2kT/K_b} \qquad (17)$$

As $\bar{i}$ approaches $\bar{i}_d$ equation (16) yields very uncertain values of α. For this limit, as α becomes small, a useful form of the equation is

$$\bar{i}/\bar{i}_d = \alpha^2\bar{i}_d + 1 \qquad (18)$$

A quantitative study of the uranyl limiting currents in perchlorate and chloride media has been undertaken, suitable for the testing of equations (16) and (18).

Experimental

Reagents.—Reagent grade uranyl nitrate was converted to the perchlorate and the chloride by evaporations with $HClO_4$ and HCl, respectively. Reagent grade $NaClO_4$ and $HClO_4$ were used without further purification. The 0.1 *M* uranyl stock solutions were obtained by diluting a 1 *M* solution with a diluent similar in composition to the supporting electrolyte. Thus the addition of depolarizer did not significantly change the composition of the supporting electrolyte, which was made up by volume to the desired ionic strength and hydrogen ion concentration. The uranium content of the stock solutions was determined gravimetrically as U_3O_8.

The Cell.—The cell used for the limiting current measurements had an internal mercury pool anode. The potential of the d.m.e. was measured against a S.C.E. *via* a salt bridge. Current voltage curves were obtained with a manual apparatus of the type described by Kolthoff and Lingane.[11] All measurements were made at 25 ± 0.05°.

Purified nitrogen was used to free both the supporting electrolyte and the depolarizer solutions of oxygen.

The Measurement of $\bar{i}$.[12]—The limiting current was measured after each successive addition of depolarizer to the supporting electrolyte at an applied potential of −0.5 v. *vs.* S.C.E. One or more drop-time measurements were made during each run. Zero point readings accompanied each current measurement. All currents are corrected for the residual current.

The Measurement of $\bar{i}_d$.—The pure diffusion current can be measured directly only in weakly acid solutions, where the disproportionation reaction is unimportant. For the chloride supporting electrolytes, $\bar{i}_d$ was measured at −0.5 v. in KCl solutions of the corresponding ionic strength but only 0.001 *M* in HCl. Under these conditions reaction did not contribute to the current as shown by the observed proportionality between current and concentration. It was assumed that the value of $\bar{i}_d$ was independent of the acidity.

An experimental verification of this assumption was obtained from wave-height measurements beyond −1.0 v. *vs.* S.C.E. in a 2 *M* HCl solution. At these potentials the current is always diffusion controlled, the result of a three electron reduction of U(VI) directly to U(III).[2] When this current was divided by 3 and corrected for changes in capillary characteristics with potential, the result checked with

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[11] See ref. 6, p. 297 ff.

[12] From now on all currents are the average currents as read from a damped galvanometer.

that found in slightly acid 2 M KCl at the lower voltage within 1%.

The identical method was used to determine i_d in 0.4 M perchlorate solutions. In 3.8 M perchlorate solutions, however, the diffusion coefficient increased with the proportion of $HClO_4$ to $NaClO_4$, because of the lower viscosity. For the two strongest acid solutions i_d was calculated from measurements in the solutions themselves at −1.05 v. as described above, made simultaneously with the limiting current measurement at −0.5 v.

When values of $i - i_d$ were determined for various volumes of added uranyl stock solution, care was taken to correct the value of i_d to the same volume, drop time, and galvanometer calibration as those of the i with which it was being compared. Volume and time corrections cannot be made on the limiting current itself, because it does not depend on these variables in a simple way.

Results

Test of Reaction Volume Model in Perchlorate Media.—Sodium perchlorate, perchloric acid solutions having a constant total perchlorate concentration of 3.8 M were investigated at six different concentrations of hydrogen ion from 0.03 to 3.7 M. At each acidity the U(VI) concentration was varied to give a set of limiting and diffusion current values determined as described in the previous section. The resultant data are shown in Fig. 2, where $1/\sqrt{i - i_d}$ is plotted *vs.* $i/(i - i_d)$ in accordance with equation (16), and i/i_d *vs.* i_d in accordance with the limiting form of this relation given in equation (18).

The fact that all of the curves in Fig. 2 are linear is evidence that the functional relationship between i and i_d of equation (16) is correct over a wide range of reaction rates. The average intercept of curves a, b, c and d on the abscissa is 2.2 rather than the value 2.0 predicted by equation (16). To the extent that this discrepancy is real it means that the assumption that all U(VI) formed in the defined "reaction volume" is reduced is not strictly valid. In our opinion the difference in observed and predicted intercepts raise no serious question as to the validity of the reaction volume model as a method of approach to this problem. It should be noted that the general test of equation (16) in this section does not concern the method of approximating the volume parameter v. The conclusion to be reached here is only that the reaction volume model is applicable to the case of disproportionation reactions without serious inconsistency in the results.

Investigation of the Current–Time Dependence. To check the dependence of current on time contained in equation (16), i and i_d were determined as functions of U(VI) concentration in 0.175 M HCl, 1.825 M KCl solutions using mercury pressures of 58 and 24 cm. on the capillary. In each case α was obtained by plotting $i/(i - i_d)$ *vs.* $(i - i_d)^{-1/2}$ and K was obtained as described in the experimental section. The drop times at each pressure were measured and the following results were obtained

T	K	α	$\alpha\sqrt{K/T}$
4.04	2.97	0.177	0.152
7.96	2.09	.303	.155

From the observed constancy of the quantity $\alpha\sqrt{K/T}$ it appears that the time dependence of the current found in equation (16) is correct.

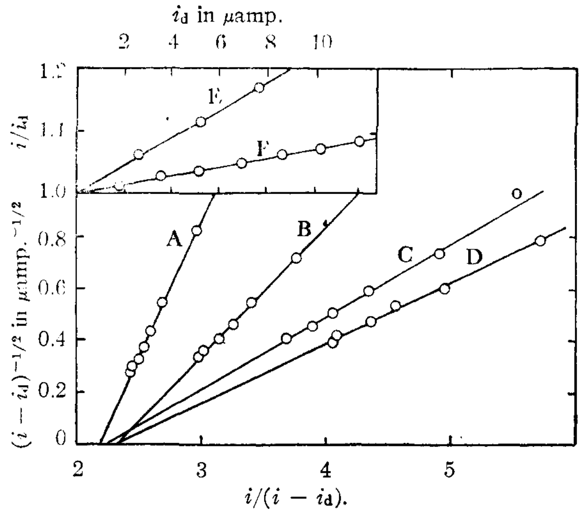

Fig. 2.—Current difference relation in 3.8 M perchlorate. Inset: i/i_d *vs.* i_d relation in 3.8 M perchlorate. Concentration H^+ is 3.68 in A; 0.92 in B; 0.331 in C; 0.170 in D; 0.068 in E; and 0.026 in F.

Dependence of Rate of Disproportionation on Acidity.—The slope of the curves in Fig. 2 is the parameter α where $\alpha = \sqrt{0.20\ kT/K_b}$. The diffusion current constant K_b of U(V) is equal to $\sqrt{D_b/D_a} \times K_a$. We have experimentally determined the value of K_a in the solutions used by the methods described in the experimental section. The value of $\sqrt{D_a/D_b}$ is essentially one.[3] The drop time T was determined in each run, and values of k, the apparent disproportionation rate constant, were calculated from the relation $k = \alpha^2K_a/0.20T$. From our previous study of U(V) we found that the rate of disproportionation is first order with respect to hydrogen ion, as expressed in equation 1. Therefore we should expect the quantity $k/(H^+)$ to be constant as the hydrogen ion concentration is varied. The data obtained in 3.8 M perchlorate solutions are summarized in Table I. From the data in the last column it is evident that the quantity $k/(H^+)$ is essentially constant as the hydrogen ion concentration varies from 0.26 to 3.68. The average value is 0.9 ± 0.1 (mmole/l.)$^{-1}$ sec.$^{-1}$.

TABLE I

CALCULATED DISPROPORTIONATION RATE CONSTANTS IN 3.8 M PERCHLORATE SOLUTIONS OF DIFFERENT ACIDITIES[a]

(H^+)	K, μamp./mmole	α, μamp.$^{-1/2}$	$k/(H^+)$, (mmole/l.)$^{-1}$ sec.$^{-1}$
3.68	2.86	1.04	0.95
0.92	2.67	0.485	.81
.331	2.64	.276	.72
.170	2.64	.231	.99
.068	2.64	.0217[b]	1.00
.026	2.64	.0072[b]	0.87

[a] T = 4.20 sec. [b] α^2 in μamp.$^{-1}$.

Comparison of Calculated and Observed Rates in Perchlorate Media.—The method previously described[3] was used to obtain direct measurements of the rate of disproportionation of U(V) in 3.8 M perchlorate solutions that were 0.025 and 0.026

M in hydrogen ion. The average value of $k/(\mathrm{H}^+)$ obtained was 1.80 ± 0.03 (mmole/l.)$^{-1}$ sec.$^{-1}$ compared to the calculated value of 0.9. Thus the rate constant calculated from the d.m.e. measurements is found to be too small by a factor of 2.0 in 3.8 M perchlorate media.

A similar comparison was made in 0.4 M perchlorate solution. From our previous study[3] in this medium, the directly determined value of $k/(\mathrm{H}^+)$ from 0.03 to 0.4 M hydrogen ion is 0.130 γ_{H^+} (mmole/l.)$^{-1}$ sec.$^{-1}$. In this solution $\gamma_{\mathrm{H}^+} = 0.75$; therefore $k/(\mathrm{H}^+)$ is 0.098 (mmole/l.)$^{-1}$ sec.$^{-1}$. The average value of $k/(\mathrm{H}^+)$ calculated by equation (16) from d.m.e. data in 0.4 M perchlorate solutions containing 0.333 and 0.405 M hydrogen ion was found to be 0.028 ± 0.001. The calculated result is therefore low by a factor of 3.5.

Tests of the Theory in 2 M KCl, HCl Solutions of Varying Acidity.—Six solutions containing a constant total HCl, KCl concentration of 2 M were prepared in which the concentration of hydrogen ion was varied from 0.0093 to 0.0573 M. At each hydrogen ion concentration i was determined as a function of U(VI) concentration. The quantities K and i_d were determined as described in the experimental section. Some of these data at low U(VI) concentrations are plotted in Fig. 3 to show the validity of the i/i_d *vs.* i_d relation. The data obtained and the calculated values of k and $k/(\mathrm{H}^+)$ are presented in Table II.

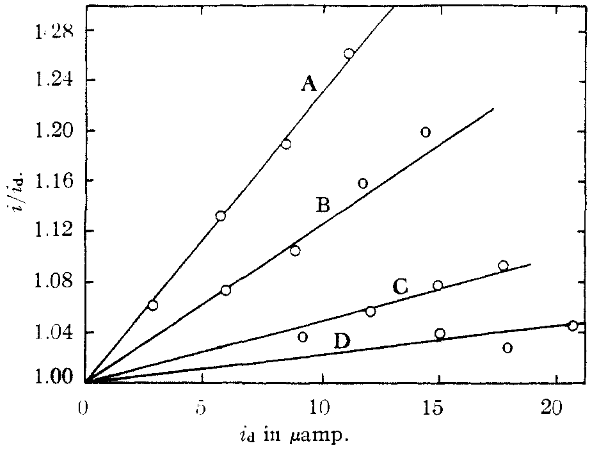

Fig. 3.—Plot of i/i_d *vs.* i_d in 2 M chloride + 0.0025 % gelatin. Molar concentration of H$^+$ is 0.175 in A; 0.090 in B; 0.037 in C; 0.018 in D.

TABLE II

CALCULATED DISPROPORTIONATION RATE CONSTANTS IN 2 M CHLORIDE SOLUTIONS OF VARIABLE ACIDITY[a]

(H$^+$)	α^2, μamp.$^{-1}$	k,(mmole/l.)$^{-1}$ sec.$^{-1}$	$k/(\mathrm{H}^+)$, (mmole/l.)$^{-1}$ sec.$^{-1}$
0.175	0.0239	0.084	0.48
.090	.0118	.0415	.46
.037	.0044	.0153	.41
.018	.0021	.0073	.41

[a] 0.0025% gelatin present; T = 4.20 sec.; K = 2.95 μamp./mmole.

The average value of $k/(\mathrm{H}^+)$ is 0.44 ± 0.03 (mmole/l.)$^{-1}$ sec.$^{-1}$. These results were obtained in the presence of 0.0025% gelatin which was later found to be unnecessary as a maximum suppressor. In gelatin-free solution the value of k was found to be about 35% higher. Direct determinations described in the following paragraph gave a value of 0.80 ± 0.05 (mmole/l.)$^{-1}$ sec.$^{-1}$ in the gelatin free medium. The results calculated from the d.m.e. data are therefore low by a factor of 1.33.

Direct determinations of k were made in the 2 M chloride solutions as indicated in connection with the perchlorate results with the exception of the following changes. The concentration of U(V) was followed by observing its diffusion current at −0.06 v. to eliminate interference from the mercury dissolution wave. Direct determinations of the residual current at this potential were not very reproducible. For each run therefore the residual current was introduced as a parameter that was adjusted to give a linear plot of i/i_d *vs.* time. This device was not necessary at the two lowest acidities. The results obtained were

(H$^+$)	0.0093	0.0206	0.042	0.0525	0.0573	0.0776
$k/(\mathrm{H}^+)$	.92	.73	.77	.80	.76	.86

Test of the Theory in 0.5 M KCl, HCl Solutions of Varying Acidity.—In 0.5 M chloride solutions of varying acidity plots of $i/(i - i_d)$ *vs.* $(i - i_d)^{-1/2}$ were linear in all cases. Table III contains the calculated values of $k/(\mathrm{H}^+)$ and the pertinent experimental data. The average calculated value of $k/(\mathrm{H}^+)$ is 0.044 ± 0.001 (mmole/l.)$^{-1}$ sec.$^{-1}$ which differs from the directly determined value of 0.175 ± 0.003 by a factor of 4.0.

TABLE III

CALCULATED DISPROPORTIONATION RATE CONSTANTS IN 0.5 M CHLORIDE SOLUTIONS OF DIFFERENT ACIDITIES[a]

(H$^+$)	α^2, μamp.$^{-1}$	k, (mmole/l.)$^{-1}$ sec.$^{-1}$	$k/(\mathrm{H}^+)$, (mmole/l.)$^{-1}$ sec.$^{-1}$
0.480	0.0057	0.0211	0.044
.215	.0027	.0102	.047
.188	.022	.0082	.044
.094	.00105	.0039	.042

[a] T = 3.99 sec.; K = 2.98 μamp./mmole.

The direct determinations were made as described in the perchlorate experiments except that the U(V) diffusion current was determined at −0.04 v. in order to avoid interference from the mercury dissolution wave. The results obtained were

(H$^+$)	0.230	0.100	0.060	0.040
$k/(\mathrm{H}^+)$	.175	.180	.168	.176

Anomalies in Chloride Media.—In chloride solutions of acidity greater than 0.5 it was found that i/i_d, instead of approaching the theoretical value unity as the depolarizer concentration was diminished, flattened out at a constant value for uranyl concentrations less than 0.5 millimolar. This value was 1.3 in 1 M HCl, 1.5 in 1.5 M HCl, and 1.75 in 2 M HCl. The unexpectedly large currents indicate an anomalously rapid decomposition of U(V), and one which is apparently first order rather than second order at low uranyl ion concentrations.

Significance of the Quantitative Results.—The directly determined rate constants and those obtained from d.m.e. data in various media are compared in Table IV.

TABLE IV

COMPARISON OF CALCULATED AND DIRECTLY MEASURED RATES IN VARIOUS MEDIA

Medium	Av. $k/(H^+)$ in (mmole/l.) $^{-1}$ sec. $^{-1}$ Calcd.	Directly measd.	Ratio
0.5 M Cl^-	0.044	0.175	4.0
2.0 M Cl^-	.49	.80	1.3
0.4 M ClO_4^-	.028	.098	3.5
3.8 M ClO_4^-	.89	1.81	2.0

The fact that the calculated rate constants are low by a factor varying from 4.0 to 1.3 suggests the possibility of improving the relationship contained in equation (16) by the introduction of an empirically determined factor provided a similar discrepancy is found in the study of other disproportionation rates. The present results do however show that equation (16) is essentially correct and that disproportionation rates can be determined to the correct order of magnitude. These results also show that it is incorrect to attempt reaction rate calculations by the arbitrary assumption of a few ångström units as the thickness of the effective reaction volume at the d.m.e.

It is of course possible that the observed discrepancies may be fundamentally more serious and reflect the fact that the calculated disproportionation rate is characteristic of reactions occurring at the surface of the drop where conditions may be quite different from those obtaining in the body of the solution. Because of this aspect of the problem the real significance of any reaction rates calculated from d.m.e. data is open to some question.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Rate Law and Mechanism for the Reaction of Cerium(IV) and Bromide Ion in Aqueous Sulfate Media[1,2]

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Cerium(IV) and bromide ion react in aqueous acidic sulfate media to form cerium(III) and bromine at a conveniently measurable rate. The reaction has been studied spectrophotometrically at 25°; the rate of reaction conforms to the rate equation $-[d(Ce^{IV})/dt] = [(Ce^{IV})/(SO_4^{=})]\{k_{12}'(Br^-)^2 + k_{11}'(Br^-)\}$. Since the dominant species of cerium(IV) in the solutions under consideration contains three sulfate ions and no bromide ions, the two important activated complexes have the compositions ($Ce(SO_4)_2Br_2^{=}$ and $Ce(SO_4)_2Br^-$. Activated complexes involving fewer than two sulfate ions are also important at the low end of the sulfate ion concentration range. Chloride ion catalysis is observed; an activated complex of the composition $Ce(SO_4)_2ClBr^{=}$ is important in chloride media. The presence of lithium ion accelerates the reaction noticeably. In the reaction of cerium(IV) and iodide ion in sulfate media with a pH value of approximately 3, a fraction of the oxidation, which increases with increasing acidity, occurs very rapidly; the remainder of the oxidation proceeds very slowly In such solutions there appears to be present some colloidal cerium(IV) species; it is assumed that it is this species which is responsible for the slow part of the reaction.

Equilibrium in the reaction of cerium(IV) and bromide ion to yield cerium(III) and bromine (or tribromide ion) in sulfuric acid media greatly favors the products. Using the oxidation potential values summarized by Latimer,[3] one calculates the value 7×10^{11} for the equilibrium quotient for the reaction

$$2Ce^{IV} + 2Br^- = 2Ce^{III} + Br_2(aq.)$$

in one molar sulfuric acid.[4] The rate of this unidirectional reaction is conveniently measurable at 25° over a wide range of concentration conditions. It has been possible to represent the rate data by a relatively simple rate law and this has been interpreted in terms of a reasonable mechanism.

Experimental Techniques and Results

Equipment and Reagents.—All spectrophotometric determinations were made using a Beckman Model DU spectrophotometer. The absorption of light by the reaction mixture was determined in cells with ground glass stoppers to prevent the loss of bromine. A thermostating arrangement for the cells was used. The temperature of the solutions was measured at the termination of each experiment. The average values of this temperature for the experiments of each series with the average deviation of the temperature in the several runs from this average value for each series were: 1, 25.4 ± 0.4°; 2, 25.1 ± 0.2°; 3, 25.0 ± 0.2°; 4, 25.0 ± 0.1°; 5, 25.3 ± 0.3°; 6, 25.0 ± 0.2°; 7, 25.0 ± 0.3°; 8, 24.6 ± 0.2°; 9, 24.4 ± 0.2°; 10, 25.0 ± 0.1°; 11, 25.0 ± 0.2°; 13, 25.3 ± 0.3°; 14, 25.9 ± 0.4°. Although the temperature control was not as good as might be desired, there was no evidence that the temperature variation was the most important source of error in this work.

All solutions were prepared using doubly distilled water; the second distillation was from an alkaline permanganate solution. The source of each reagent and the method of determination of its concentration is as follows: reagent grade sodium or potassium bromide was recrystallized and the stock solutions were standardized using silver nitrate; reagent grade sodium sulfate was recrystallized and standardized using a gravimetric barium sulfate determination; three different types of sources of ammonium sulfate were used, reagent grade material was weighed directly, reagent grade material was recrystallized and standardized gravimetrically, and a solution was prepared using ammonia and sulfuric acid solution; reagent grade lithium perchlorate was recrystallized once, twice, or three times and was standardized by conversion of an aliquot of the stock solution to the sulfate for direct weighing; reagent grade sodium perchlorate was recrystallized once or twice and determined by direct weighing of an aliquot of solution which had been heated to dryness; reagent grade sodium chloride was weighed directly or recrystallized and standardized using silver nitrate; the solution of cerium(IV) perchlorate in perchloric acid obtainable from G. F. Smith Chemical

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[3] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 60, 294.

[4] This calculation is an approximate one since the bromine-bromide potential which was used was the E^0 value and not the value for a one molar sulfuric acid solution.