inum-black electrode, the hydrogenation could be diffusion-controlled rather than kinetically controlled. This possibility was checked by determining the rate constant for cyclohexene at 0° as well as at 25°. Diffusion coefficients normally change 1% per degree centigrade, while reaction rates increase much more rapidly with temperature. The data in Table II for cyclohexene at 0 and 25° indicate that the change in rate is too large to be solely diffusion controlled. Furthermore, a change in hydrogen concentration on the catalytic surface causes a like change in the rate of reaction. If the reaction were diffusion controlled, no change in rate would be observed since the reaction must take place at the electrode.

An attempt was made to study benzene, but its reaction rate was too slow to be observable above the blank generation rate. Studies of styrene were also unsatisfactory because of low solubility and polymerization.

Summary.—Relative rates of hydrogenation can be determined rapidly and conveniently with this method. It should be emphasized that the concentrations of hydrogen are much lower than with conventional methods. Rate constants which are determined coulometrically may be of more interest than those evaluated by allowing the reaction to proceed to infinite time. By determining the rate of reaction at constant concentrations of reactants the problem of change of rate law with changes of concentration is avoided. The conditions are also more closely related to industrial continuous stream processes.

The limitations for applying the method are: 1, sufficient reactivity for the olefins; 2, sufficient solubility of the olefin; 3, sufficiently low vapor pressure for the olefin to prevent loss of sample. Highly active olefins may be studied by using lower concentrations of hydrogen, and comparing the generation rate with that of a known olefin at the lower concentration. Olefins of low reactivity cannot be studied because the concentrations of hydrogen are too low to produce sufficiently rapid reaction.

The method has applications other than in the determination of the relative reactivities of olefins. By studying the same olefin, the relative effective area of different samples of a given type of catalyst and the relative reactivities of different catalysts can be determined. In a similar way, the effects of different solvents might be studied.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Reduction at the Streaming Mercury Electrode. II. Current–Voltage Curves[1]

BY J. R. WEAVER AND R. W. PARRY

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A method has been developed for treating current–voltage curves obtained from steady-state measurements at the streaming mercury electrode. Applications to experimental curves using thallium, cadmium and lead ions for reversible reduction and zinc ion for irreversible reduction are shown. Rate constants for the reduction of aqueous solutions of zinc ion in several concentrations of potassium chloride are reported.

In a previous paper,[2] studies of the limiting steady-state current at the streaming electrode were reported with emphasis on factors causing deviations from the Rius equation.[3] In this paper current–voltage curves obtained from steady-state measurements will be considered. Because of the short time of contact between mercury and solution, a reduction process showing a tendency toward irreversibility should give a current–voltage curve with a greater deviation from the reversible form than it gives at the dropping electrode. The streaming electrode should thus prove particularly useful in investigating kinetic features of electrode processes, providing the current–voltage measurements can be properly interpreted.

A treatment for irreversible reduction at the streaming electrode has been given by Koryta.[4] Implicit in his derivation are the assumptions, first, that the physical characteristics of the stream are those of the hypothetical "ideal streaming electrode," *i.e.*, constant radius, constant surface velocity, and negligible effects from electrode curvature and velocity gradient; second, that the reduction potential does not vary with position on the stream; and third, that the effective length of the stream remains constant. Under these conditions an element of surface neither expands nor contracts as it moves forward on the electrode, and reduction occurs exactly as at a plane, stationary, constant-voltage electrode. For an element which has been in existence for t seconds, the current density, i, is given by[5–7]

$$i = nFCk \exp\left(\frac{k^2t}{K^2D}\right) \operatorname{erfc}\left(\frac{k}{K}\sqrt{\frac{t}{D}}\right) \qquad (1)$$

in which

$$K = \left[1 + \frac{k_b}{k}\sqrt{\frac{D}{D_r}}\right]^{-1} \qquad (2)$$

and C is the bulk concentration of the reducible species, k and k_b are the first-order, heterogeneous rate constants for the forward and reverse reactions, and D and D_r are the diffusion coefficients

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[1] Abstracted in part from a dissertation submitted by J. R. Weaver to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. R. Weaver and R. W. Parry, THIS JOURNAL, **76**, 6258 (1954).

[3] A. Rius, J. Llopis and S. Polo, *Anales real soc. Espan. fis. y quim.*, **45B**, 1039 (1949).

[4] J. Koryta, *Coll. Czech. Chem. Comm.*, **19**, 433 (1954).

[5] J. Koutecky and R. Brdicka, *ibid.*, **12**, 337 (1947).

[6] P. Delahay, THIS JOURNAL, **75**, 1430 (1953).

[7] D. M. H. Kern, *ibid.*, **75**, 2473 (1953).

of the reducible and reduced species. For an electrode of length L, surface velocity v, and radius r, the total current is

$$I = 2\pi rv\int_0^{L/v} i\,\mathrm{d}t = 4nFCr\sqrt{\pi DLvK}\,\left\{1 - \frac{\sqrt{\pi}}{2y}[1 - \exp(y^2)\,\mathrm{erfc}\,(y)]\right\} \quad (3)$$

where

$$y = \frac{k}{K}\sqrt{\frac{L}{Dv}} \quad (4)$$

For convenience the bracketed expression will be designated as $f(y)$

$$f(y) = 1 - \frac{\sqrt{\pi}}{2y}[1 - \exp(y^2)\,\mathrm{erfc}(y)] \quad (5)$$

and introducing the expression for the limiting current[2]

$$I_\mathrm{D} = 4nFCr\sqrt{\pi DLv} \quad (6)$$

equation 3 can be written as

$$\frac{I}{I_\mathrm{D}} = Kf(y) \quad (7)$$

This is the general equation for reduction at the constant voltage, ideal streaming electrode.

The distinguishing feature of reversible reduction is that, at every point on the reduction wave, y is sufficiently large for $f(y)$ to be unity within the experimental error of the measurements. Thus

$$\frac{I_\mathrm{rev}}{I_\mathrm{D}} = K \quad (8)$$

which for equilibrium conditions, is equivalent to

$$E = E_{1/2} - \frac{RT}{nF}\log_e\frac{I}{I_\mathrm{D} - I} \quad (9)$$

where $E_{1/2}$ is the conventional half-wave potential.

If K retains the equilibrium value for irreversible reduction as well, equation 7 may be written

$$\frac{I}{I_\mathrm{rev}} = f(y) \quad (10)$$

where I_rev is the current that would be drawn by the same electrode process if it were occurring reversibly, *e.g.*, if accelerated by catalysis. It appears, however, as pointed out in the final section, that this condition does not hold for the example of irreversible reduction studied in this investigation. In any case, for "totally irreversible" reduction, where the reverse process has ceased, one can write

$$\frac{I}{I_\mathrm{D}} = f(y) \quad (10a)$$

A tabulation of the function $f(y)$ is shown in Table V.

The Non-ideal, Constant-Voltage Electrode.—In order to investigate the effects on current–voltage curves which are attributable to deviations from "ideal" electrode behavior, the solution of the diffusion problem at a real streaming electrode was carried through in a manner similar to that given in the first paper of this series, but with the inclusion of a differential equation for diffusion of the reduced metal into the amalgam. For reversible reduction, the result obtained was

$$\frac{I_\mathrm{rev}}{I_\mathrm{D}} = K\{1 - (1 - K)A + \ldots\ldots\} \quad (11)$$

where A is given by

$$A = \sqrt{\frac{\pi LD}{v}}\left\{\frac{1}{4r}\left(1 + \sqrt{\frac{D_r}{D}}\right) + \frac{v_1}{8v}\left(1 + \gamma\sqrt{\frac{D_r}{D}}\right)\right\} \quad (12)$$

in which v_1 is the velocity gradient in the solution near the interface and γ is the ratio of the viscosity of the solution to that of mercury. For the log plot one obtains

$$\log_e\frac{I_\mathrm{rev}}{I_\mathrm{D} - I_\mathrm{rev}} = \log_e\frac{K}{1 - K} - A + \ldots \quad (13)$$

Three significant observations can be noted from these equations: (1) the factors which caused nearly all of the deviation of the limiting current from the Rius equation do not affect the shape of the reduction wave. This is shown by the fact that the principal term of equation 11 involves neither v nor r. An integral expression involving these quantities cancelled out upon division by I_D indicating that the effect of the variations in stream radius and surface velocity are, proportionately, the same at all points on the wave.[8] (2) In the expression for A, the first term in the bracket represents the contribution of the curvature of the electrode and the second of the velocity gradient. These two terms are of the same order of magnitude and, since v_1 is negative, they tend to cancel each other. For the stream used in this investigation, the second term in equation 11 contributed, at its maximum value, less than 1% to the current ratio. (3) The voltage-variable quantity K does not appear in the second term on the right-hand side of equation 13. This means that the correction term does not alter either the linearity or slope of the log plot. The only effect is a shift in the half-wave potential, which, for substances with diffusion coefficients of the order of 10^{-5} cm.^{2}/sec., is about 1 mv. in the negative direction.

It was concluded that for reversible reduction the departure from ideal behavior does not seriously alter the reduction wave, and that, for a fixed stream length, it is possible to define a hypothetical ideal electrode equivalent to the real electrode. The choice is not unique, since, as shown by equation 6 and the preceding discussion, all ideal electrodes with the same value for $r\sqrt{v}$ are equivalent, for reversible reduction.

At the opposite extreme from reversible reduction is the state that will be designated as "complete rate-control." It may be defined by the condition that $y << 1$, even when $K = 1$. $f(y)$ may then be approximated by

$$f(y) = \frac{\sqrt{\pi}}{2}y \quad (14)$$

and hence

$$I = 2\pi nFCkL\bar{r} \quad (15)$$

where $\bar{r}$ is the average stream radius. The velocity does not enter and, since there is no diffusion gradient, the curvature and shear factors likewise have no effect. Thus, for completely rate-controlled

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(8) The expression for A in equation 12 has been simplified by assuming v, v_1 and r constant. This is justified since the term involving A contributes less than 1% to the value of the current ratio. In the principal term of the solution v and r were, of course, considered variable.

reduction, all electrodes with the same average radius are equivalent.

From a consideration of these two limiting cases, one can find a hypothetical ideal electrode that is equivalent to the real electrode for both extremes, *viz.*, an electrode of constant radius equal to the average radius of the actual stream, and of constant velocity such that its limiting current is the same as that of the actual electrode over a fixed length. For the stream used in this investigation, the equivalent ideal electrode so determined had $r = 0.0051$ cm. and $v = 278$ cm./sec. for stream lengths in the neighborhood of 1 cm.

It does not follow strictly that the ideal electrode made equivalent to the real electrode for these two limiting cases will also be equivalent for general irreversible reduction. Since, however, in the intermediate case, the reaction tends to be rate-controlled at the base of the stream with diffusion-control becoming more significant as the interface moves farther out, the current will be affected most by the velocity in the upper part of the stream. This velocity lay between 278 and 283 cm./sec., a range of about 2%. Since the velocity never enters to a power greater than one-half, the error in using the value of 278 could not have been greater than 1%, *i.e.*

$$\sqrt{283/278} = 1.01$$

It was concluded from these considerations that the use of the ideal approximation introduces no appreciable error in the interpretation of current–voltage curves.

The Variable-voltage Electrode.—In all of the equations derived thus far, it has been assumed that the potential difference across the interface is constant. The object of this section is to present a method of treating the problem of diffusion to an electrode at which the potential varies from point to point according to a regular pattern. That such a variation actually occurs (Fig. 2) is evident from the fact that the variation in current density will cause a difference in the *IR* drop through the solution from the reference electrode to different parts of the stream and, consequently, a difference in the voltage across the interface.

A complete treatment of this effect would require a simultaneous solution of the diffusion problem and of the electric field problem in the cell. Because of lack of symmetry this was not attempted; instead, experimental data were introduced to assign a resistance value to each point on the stream surface. These data were obtained in the form of a conductance curve for the cell (Fig. 1) measured under conditions of approximately uniform current density. Details of the two methods used are given in the Experimental section. In making use of such data, two courses present themselves: first, the conductance for a given stream length and the total current for that length might be used to obtain an over-all resistance correction. This is the method ordinarily used at the dropping electrode when a single resistance value is applied, neglecting changes in resistance and current density during the life of the drop. Such use assumes that the effects of high and low current density equalize each other, an assumption shown by the subsequent discussion to be not entirely warranted, at least as far as the streaming electrode is concerned. The alternative procedure is to let the slope of the curve in Fig. 1 define a conductance (per unit length) for the solution around that point. The *IR* drop between this point and the reference electrode is considered to depend only on this conductance value and the current density at that point. This tends to exaggerate the influence of variable voltage, but is defensible on the grounds, first, that it will give an upper limit to the magnitude of the deviation from the constant voltage case, and second, it is a fairly good approximation since the converging lines of current flow around the cylindrical electrode cause a large part of the *IR* drop to occur close to the stream, and hence to be relatively independent of the current density at distant points on the electrode.

To the degree to which these approximations hold, it is possible, from the slope of the curve in Fig. 1, to obtain the *IR* drop between the reference electrode and every point on the streaming electrode for any arbitrary current density distribution. It is also possible, from the equations in the next paragraph, to obtain explicitly the dependence of the electrode potential on current density. For an actual electrode situation the sum of the *IR* drop and electrode potential is constant and is equal to the cell voltage. By the following trial and error process, a unique current density distribution satisfying a given set of conditions could be obtained: (1) an arbitrary, trial, reduction-current-density distribution was assumed; (2) from equations given below, the corresponding electrode-potential distribution was obtained; (3) using this potential distribution, the surface velocity of the stream at each point,[2] and Grahame's values for the capacitance of the double layer,[9] the current-density distribution of the charging current was obtained; (4) from the resistance data and the total current density distribution, the *IR* drop for every point on the electrode was found; (5) the assumed initial current density was adjusted until the sum of the *IR* drop and electrode potential was constant for the entire electrode.

The dependence of electrode potential on current-density was worked out as follows: at a plane, stationary electrode, the concentration of the reducible species at the electrode surface, $c_0(t)$, is related to the current density, $i(t)$, by the integral expression[10]

$$c_0(t) = C - \frac{1}{nF\sqrt{\pi D}} \int_0^t \frac{i(t')}{\sqrt{t - t'}}\, \mathrm{d}t' \qquad (16)$$

where t is the time during which reduction has been taking place and t' is the variable of integration. This equation was applied to the ideal streaming electrode by introducing for t and t'

$$t = \frac{z}{v},\ t' = \frac{z'}{v} \qquad (17)$$

where z is the distance coordinate parallel to the stream, and z' becomes the new variable of integra-

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(9) D. C. Grahame, This Journal, **71**, 2975 (1949).

(10) *Cf.* R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw Hill Book Co., N. Y., N. Y., 1944, p. 116.

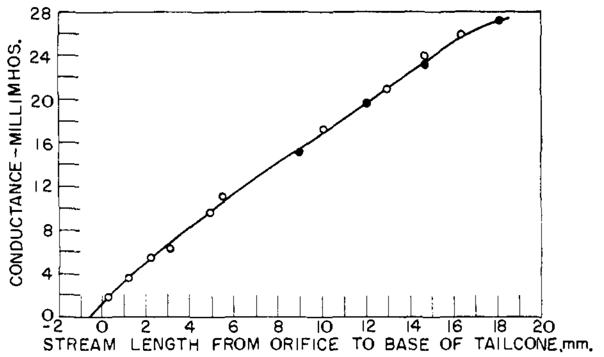


Fig. 1.—Cell conductance with 0.1 M KCl as determined by an alternating current method (●) and an oscillographic method (○).

tion. Inserting also the expression for the limiting current from equation 6 gives

$$c_0(z) = C\left[1 - \frac{4r\sqrt{L}}{I_D}\int_0^z \frac{i(z')}{\sqrt{z - z'}}\,dz'\right] \qquad (18)$$

The corresponding expression for the concentration of the reduced species at the interface is

$$c_r(z) = C\sqrt{\frac{D}{D_r}}\,\frac{4r\sqrt{L}}{I_D}\int_0^z \frac{i(z')}{\sqrt{z - z'}}\,dz' \qquad (19)$$

These equations depend only on diffusion and are independent of the type of electrode process. For reversible reduction, the electrode voltage was obtained from the Nernst equation in the form

$$E(z) = E_{1/2} - \frac{RT}{nF}\log_e\left[\frac{c_r(z)}{c_0(z)}\sqrt{\frac{D_r}{D}}\right] \qquad (20)$$

For irreversible reduction, a rate equation of the form

$$E(z) = -\frac{RT}{\alpha nF}\log_e \frac{i(z)}{nFk_0c_0(z)} \qquad (21)$$

with arbitrary values for α and k_0 was used. Equations 18, 19 and either 20 or 21 were used to obtain the electrode potential from the arbitrary current density distribution.

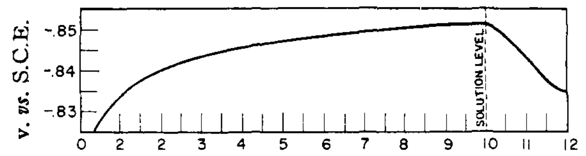
TABLE I

CALCULATED IR DROP IN 0.1 M KCl

(I_D = limiting current; I_r = reduction current; I_c = charging current; Δv = voltage correction)

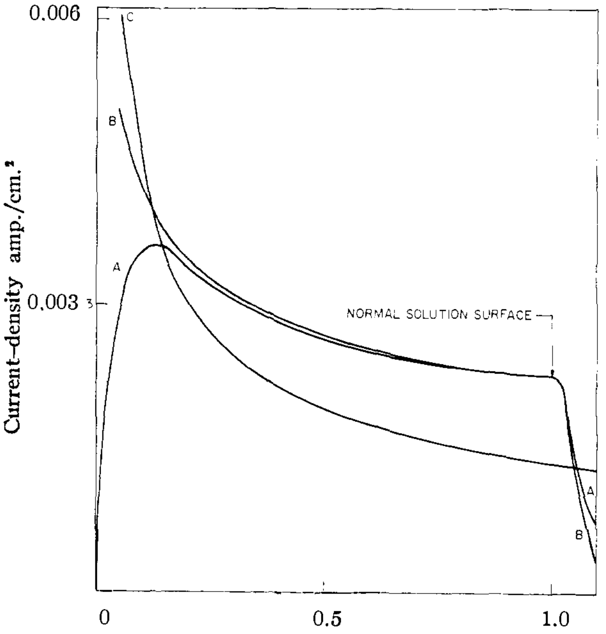
$E_{1/2}$ vs. S.C.E.	I_D, μamp.	I_r, μamp.	I_c, μamp.	Δv, mv.	$(I_r + I_c)/$ 17.0, mv.	$[I_r + (1/3)I_c]/$ 16.0, mv.
−0.420[a]	2000	1816	0	113	107	113
−0.850	2000	915	78	58	58	59
−0.450[a]	2000	636	0	38	37	40
−1.250	2000	220	141	15.5	21	16.7
−0.850	200	175	85	14.0	15	12.7
−1.100	200	139	120	11.3	15	11.2
−0.470[a]	200	83	0	4.5	4.9	5.2
−0.470[a]	200	44	0	2.6	2.6	2.8
−1.140	200	26.7	121	3.0	8.7	4.2
...	800	659	122	46	46	44
...	2000	993	118	63	65	64
...	2000	778	0	49	46	49
...	2000	90	0	6.1	5.3	5.6

[a] $E_{1/2}$ values selected such that reduction occurs at electrocapillary zero and charging current is negligible.



Distance from orifice, mm.

Fig. 2.—Variation in electrode potential with distance from the orifice for a typical reduction situation. (Calculated by the method described in the section on variable voltage electrode for $E_{1/2}$ = −0.850 v. vs. S.C.E., I_D = 2000 μ amp., E_{cell} = −0.906 v.; inert electrolyte, 0.1 M KCl.)



Distance from orifice, cm.

Fig. 3.—Calculated current density for A, the reduction current and B, the reduction and charging currents for a typical reduction situation: C, ideal, constant-voltage electrode (same conditions as Fig. 2.).

Figures 2 and 3 show one of the solutions obtained by the process just described. In general, the effect of variable voltage is to flatten the current-density curve. The charging current is concentrated at the base of the stream and tends to shift the reduction curve to the right.

The calculation was carried out for several sets of conditions with results as summarized in Table I. Each line of the table represents a particular solution of the problem corresponding to a single point on a current-voltage curve. In each case the length of the stream from the orifice to the base of the tail-cone was taken as 1 cm. The first nine calculations assume reversible reduction, while the last four are for irreversible cases. The half-wave potential and limiting current corresponding to the particular assumed conditions are given in the first two columns; the reduction current, I_r, and charging current, I_c, obtained by summing the current densities, as finally adjusted, over the one cm. length, follow; and the corresponding voltage correction, that is, the difference between the measured cell voltage and the potential of the constant-voltage electrode that would draw the same reduction current appears in the fifth column.

For comparison, the conventional resistance correction (ratio of the total current to the measured cell conductance for a stream length of one cm.) is shown in column 6. Differences may be ascribed to two factors: first, the conventional correction neglects the fact that the average *IR* drop should be weighted in favor of the high current–density region at the base of the stream, and second, that Δv, as calculated here, is not merely a resistance correction, but involves also the perturbation of the diffusion process by the variable electrode potential. These two effects tend to compensate each other, except for those cases where a large fraction of the total current is made up of the charging current. Since the charging current is concentrated almost entirely at the base of the stream, its effect is overcompensated by the diffusion process in the upper part of the stream.

An empirical modification of the conventional correction in the form

$$\Delta v \approx \frac{I_r + {}^1/_3 I_c}{16.0} \qquad (22)$$

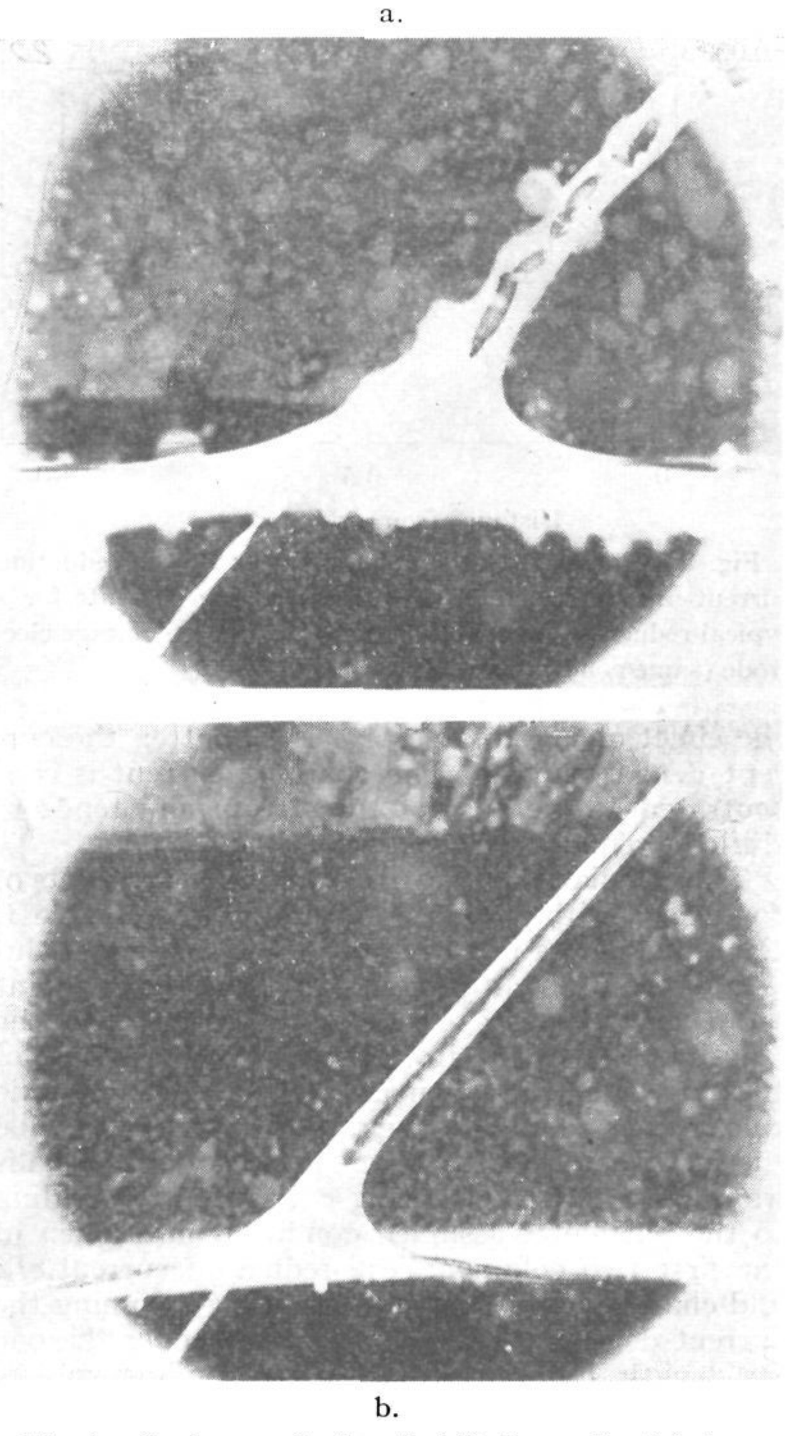


Fig. 4.—Shadowgraph of typical "tail cones": (a) stream beginning to break up below surface. Note incipient break-up of stream; (b) stream penetrates surface intact.

was found to agree within 2 mv. of all the calculated voltage correction, as shown in the last column of the table.

The constants in equation 22 are, of course, dependent on particular values for stream characteristics and reduction conditions. It is not known how the factor $^1/_3$ should vary for different streams other than that it should increase with decreasing stream length. The factor 16.0 can be generalized making the equation applicable to solutions other than 0.1 *M* KCl and to electrodes whose physical characteristics are not too widely different from those used here

$$\Delta v \approx (-\log r)\frac{I_r + {}^1/_3 I_c}{2.85\kappa L} \qquad (23)$$

where κ is the conductivity of the solution in millimhos/cm., r and L are in cm., I_r and I_c in microamps., and Δv in millivolts.

Tail-cone Correction.—One further characteristic of the stream requires consideration. In all of this investigation, Heyrovsky's original form of the streaming electrode in which the stream is directed upward at an angle breaking the surface of the solution was used.[11] At the surface the solution cones up around the stream forming a continuous sheath of aqueous liquid which will be designated as the "tail-cone." Depending on the position of stream break-up, the effective length of the stream as an electrode may depend on the actual stream length (Fig. 4a) or, if the stream remains intact through a sufficient length of the tail cone (Fig. 4b), on the electrical resistance of the aqueous sheath. The latter condition gives more consistent measurements, since it does not depend on maintaining a reproducible stream length, but the current will be expected to deviate from the theory developed thus far because of the difference in the relative amount of reduction occurring in the tail-cone.

An attempt was made to calculate the magnitude of this penetration effect by a modification of the numerical method described in the previous section. To obtain the *IR* drop between a point on the stream in the tail-cone and the reference electrode a different kind of approximation is required, since, in the tail-cone, current flow in a direction parallel to the stream becomes predominant. From cross-sectional area measurements obtained photographically for a typical tail cone, the resistance per unit length in 0.1 *M* KCl was calculated, with results as shown in Fig. 5. It was assumed that the product of this resistance and the current passing through the corresponding cross-section gave the rate of fall of potential in the parallel direction. As in the calculation of the voltage correction, the current density function was adjusted by a trial and error process until a consistent solution of the diffusion problem was obtained. Results were expressed in terms of the "penetration correction" defined as the ratio of the current entering the tail-cone to the reduction current in the main segment of the stream (below the normal solution level). Values for this quantity were calculated for several examples of reversible and irreversible reductions in both 0.1 and 0.9 *M* KCl as shown in

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(11) J. Heyrovsky and J. Forejt, *Z. physik. Chem.*, **193**, 77 (1944).

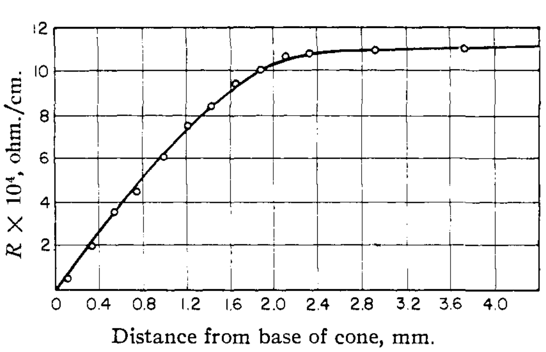

Fig. 5.—Resistance per unit length for a typical tail-cone as determined by measurements of the cross-sectional area.

Table II. Because of the approximations assumed in the calculations the accuracy of the absolute numerical values may be somewhat doubtful, but the comparative values are of significance. One notes that in addition to the expected increase as the voltage becomes more negative, the penetration: (1) increases with increasing solution conductivity; (2) decreases with increasing concentration of the reducible ion; (3) is greater for irreversible reduction than for reversible; and (4) approaches a limiting value as the cell potential becomes sufficiently negative. This limit is reached when the rate of fall of potential at the stream surface is so rapid that the charge released by the double layer (negative charging current) equals that needed for reduction. No more current is then drawn from the main body of solution. The values in parentheses are uncertain. If valid, they indicate that the penetration actually goes through a minimum in the neighborhood of the half-wave potential.

TABLE II

CALCULATED PENETRATION CORRECTION

REVERSIBLE REDUCTION ($n = 2$) (See Text)

	0.1 M KCl				0.9 M KCl		
$E - E_{1/2}$	I_D, μamp. 50	150	500	1000	500	1000	4000
+0.03			(0.07)		(0.11)		(0.12)
0	0.05	0.04	.03	0.03	.06	0.04	.04
− .03		.05			.06		
− .06					.09		
− .09	.06		.05		.11		.06
− .15					.13		
− ∞	.07	.07	.07	.07	.25	.25	.25

IRREVERSIBLE REDUCTION ($\alpha n = 0.4$)

	0.1 M KCl		0.9 M KCl	
k	I_D, μamp. 900	1500	3000	4500
0.0022		(0.15)		
.003	0.06			
.01	.05	.12		
.05	.05	.10	0.08	
.5	.04	.09		0.07
5	.05	.12		
∞	.07	.25	.25	.25

Experimental

The apparatus used for obtaining the current–voltage curves and photographic measurements was the same as previously described.[2] Since the cell was not constructed for use in a water-bath, temperature control was by room temperature. Temperature readings reported in the last section are probably correct to about ±0.5°.

The conductance measurements shown in Fig. 1 were determined by two independent methods. In the first of these, the a.c. impedance of the cell with only 0.1 M KCl present was analyzed at several d.c. levels using frequencies from 500 to 2000 cycles. As the frequency was varied, the cell behaved as a resistance and capacitance in series, and the resistance component showed no detectable variation with the d.c. level. Results are shown as the solid circles in Fig. 1.

In the second method, current in the form of a square pulse was passed through the cell, and the discontinuity in voltage at the end of each half cycle was observed on the oscilloscope. When sufficient bias was added to maintain the stream at the oxidation potential of mercury, the discontinuity could be accurately measured. All measurements were checked also at the potential of cadmium reduction in the presence of a high concentration of this ion. It was assumed that the electrode potential could not change instantaneously and that the discontinuity was equal to the IR drop.

The abscissa in Fig. 1 is the distance from the tip of the capillary to the point at which the stream would intersect the surface of the solution if there were no coning. A micrometer screw mounted in the cell and carrying a fine glass tip was used to measure the solution level. The angle of the stream was measured by supporting a meter stick in a position judged visually to be parallel to the stream.

Experimental Verification for Reversible Reduction.—It had been observed in preliminary studies that Cd^{++}, Tl^{+} and Pb^{++} in chloride solutions appeared to be reduced reversibly at the streaming electrode. The methods developed in the preceding sections were applied to curves for these ions with the following results.

As a test primarily of the voltage correction, current–voltage curves for four concentrations of Cd^{++} in 0.1 M KCl were compared as shown in Fig. 6. After correcting for the charging current, the data were plotted as the ratio of current to concentration, and corrections made for Δv according to equation 23, and for tail-cone penetration by interpolation in Table II. Since the smallest penetration correction for these curves, according to the table, should have been 0.03, the process was simplified by using only the correction in excess of this value. This does not alter the shape of curves since all points are affected in the same proportion. A curve having the theoretical shape (broken line) fits the corrected points (indicated by open circles) reasonably well.

A more stringent test of the penetration correction is provided by data from reduction of Cd^{++} in 0.9 M KCl, since the greater conductivity of the solution gives larger penetration values. For these solutions it was observed that the corrections shown in Table II needed to be increased by a factor of about 25% in order that the limiting current may reach a constant value and the curve for reversible reduction may have the theoretical shape. This result seemed to be observed consistently and apparently represents the effect of oversimplification in the calculation. The relative values obtained by the calculation appeared to be correct.

Log plots for Pb^{++}, Tl^{+} and Cd^{++} are shown in Fig. 7. Voltage corrections were made according to equation 23 and penetration corrections by interpolating in Table II and increasing the magnitude by 25%. The deviation at the base of the thallium curve appears to be reproducible and may be related to the fact that, for these points, the charging current and reduction current are in opposite directions, a situation not covered in the theoretical calculations. The slopes and half-wave

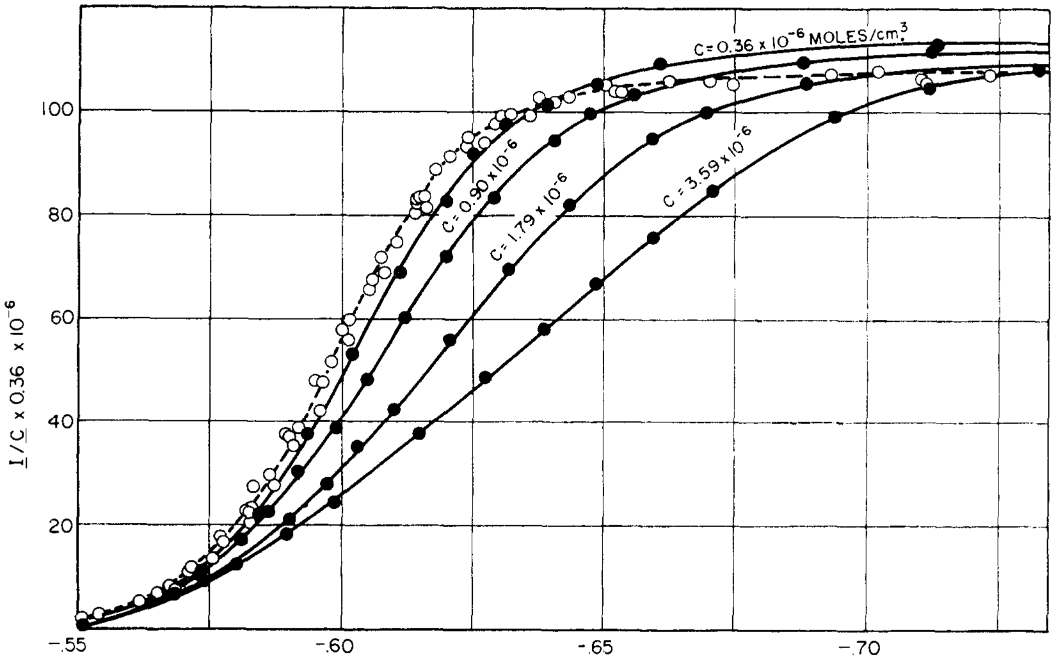

Fig. 6.—Current-voltage curves for Cd^{++} in 0.1 M KCl showing IR drop and penetration correction: C = concentration Cd^{++} g. ions/cm.³, L = 0.96 cm.; r = 0.0051 cm.; v = 278 cm./sec.

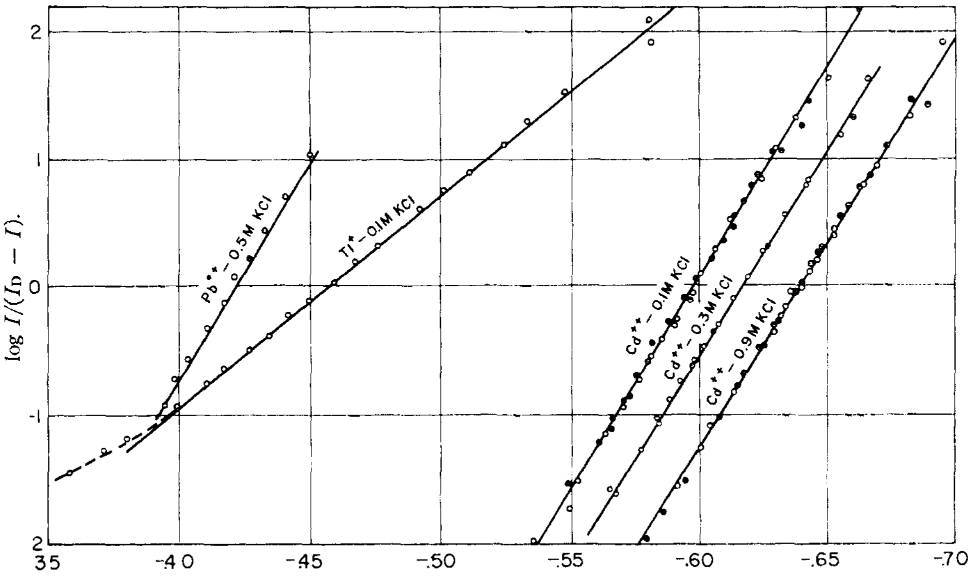

Fig. 7.—Log plots showing reversible reduction.

potentials with respect to the saturated calomel electrode are shown in Table III.

Table III

Reducible ion	Pb^{++}	Tl^{+}	Cd^{++}	Cd^{++}	Cd^{++}
Concn. of KCl, M	0.5	0.1	0.1	0.3	0.9
Reciprocal slope, mv.	30	61	30	31	30
Half-wave potential, v.	−0.421	−0.457	−0.598	−0.617	−0.639

The agreement with accepted values was considered satisfactory.

Application to Irreversible Reduction.—The reduction of Zn^{++} in chloride solution was studied as an example of a process that takes place irreversibly at the streaming electrode. A large number of current-voltage curves were taken in which the stream length, temperature and concentrations of the reducible ion and inert electrolyte were varied. The data were corrected for charging current voltage correction and tail-cone penetration as outlined.

In the first attempt at analysis it was assumed that polarographic half-wave potentials could be used to obtain the values of K needed in equation 7. It was found, however, that in every case the lower part of the reduction wave actually lies above the reversible curve with this half-wave potential. By shifting the half-wave potentials to more positive values until the base of the reversible curve coincided with the actual curve, an analysis could be made. In every case the plot of log k was straight in the region of totally irreversible reduction, but curved downward at the point where the reverse process became appreciable. This suggested that the effect of the reverse process was not properly accounted for in the constant K.

An alternative procedure, similar to that used by Audubert[12] in his studies of electrode kinetics, was then tried. It was assumed that: (1) K no longer retained the equilibrium value (equivalent to assuming the sum of the transfer coefficients for the forward and reverse processes is not unity), and (2) log k retained a constant slope and could be extrapolated from the region of totally irreversible reduction into the reverse process region. From the second assumption, the behavior of k_b (the rate constant for the reverse process) could be determined unambiguously. Eliminating K from equations 4 and 7 gave

$$\frac{y}{f(y)} = \frac{I_D}{I} k \sqrt{\frac{L}{Dv}} \tag{24}$$

Except for k which was obtained by extrapolation, the quantities on the right-hand side are all experimental. From Table V the unique value of y corresponding to this $y/f(y)$ ratio was found, and this value of y put back into equation 4 to obtain K, and thus k_b. Plots of log $[(k_b/k)\sqrt{D/D_r}]$ against voltage are shown in Fig. 8. The fact that straight lines are obtained shows that if the assumption that K must have the equilibrium value is discarded it is possible to describe the process in terms of two rate constants whose logarithms are both linear with voltage.

Excluding any speculation as to mechanism, the last approach is preferable since it permits the description of the electrode process in terms of four quantities which can be tabulated. A convenient set of quantities is αn, $(\alpha + \beta)n$, k_0 and E^* as defined by the equations

$$\log k = \log k_0 + \frac{\alpha n F(E^* - E)}{2.303RT} \tag{25}$$

$$\log \left[\frac{k_b}{k}\sqrt{\frac{D}{D_r}}\right] = \frac{(\alpha + \beta)nF(E - E^*)}{2.303RT} \tag{26}$$

where E^* is the intercept on the potential axis in Fig. 8, and k_0 is the rate constant of the reduction process at this potential. For the curves shown in Fig. 8 these quantities are shown in Table IV.

TABLE IV

SUMMARY OF RESULTS FOR REDUCTION OF Zn^{++} IN KCl

Concn. KCl, M	Temp., °C.	E^* (*vs.* S.C.E.)	$(\alpha + \beta)n$	αn	$k_0 \times 10^2$
0.9	24.5	−1.024	1.62	0.38	0.9
.3	25.5	−1.015	1.70	.44	1.4
.1	22	−1.012	1.56	.48	3.5
.1	29.5	−1.002	1.90	.54	5

Randles reports a value of 0.4×10^{-2} for the rate constant in 1 M KCl at the equilibrium potential of a dropping amalgam electrode.[13]

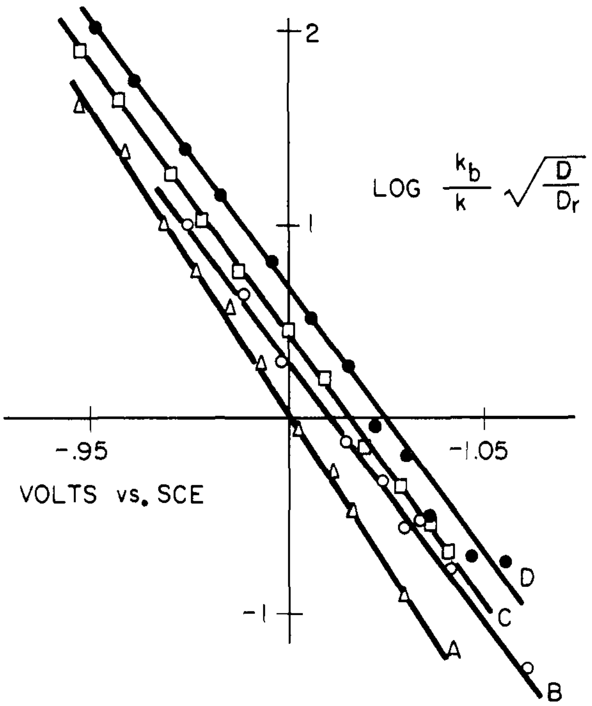

Fig. 8.—Test of rate equation with $\alpha + \beta$ less than unity. Concn. of KCl and temperature: A, 0.1 M, 29.5°; B, 0.1 M, 22°; C, 0.3 M, 25.5°; D, 0.9 M, 24.5°.

It may be observed that the mechanism proposed by Heyrovsky[14] to explain the irreversibility of Zn^{++} reduction when observed oscillographically can hardly account for the results reported here,

TABLE V

$$f(y) = 1 - \frac{\sqrt{\pi}}{2y}[1 - \exp(y^2)\text{erfc}(y)]$$

y	$f(y)$	y	$f(y)$
0.001	0.0009	0.80	0.434
.002	.0018	0.90	.465
.003	.0027	1.00	.493
.004	.0035	1.10	.518
.005	.0044	1.20	.541
.006	.0053	1.30	.562
.007	.0062	1.40	.581
.008	.0070	1.50	.599
.009	.0079	1.60	.616
.010	.0088	1.70	.631
.012	.0105	1.80	.645
.014	.0123	1.90	.659
.016	.0140	2.00	.671
.018	.0157	2.5	.720
.020	.0175	3.0	.758
.025	.0217	3.5	.786
.030	.0260	4.0	.809
.035	.0302	4.5	.827
.040	.0344	5.0	.842
.050	.0427	6.0	.866
.060	.0509	7.0	.884
.070	.0589	8.0	.897
.080	.0668	9.0	.908
.090	.0747	10.0	.916
.100	.0824	12	.930

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(12) R. Audubert, *Disc. Faraday Soc.*, **1**, 72 (1947).

(13) B. E. Conway, "Electrochemical Data," Elsevier Publishers, Inc., New York, N. Y., 1952, p. 356.

(14) J. Heyrovsky, *Disc. Faraday Soc.*, **1**, 212 (1947).

TABLE V (*Continued*)

y	$f(y)$	y	$f(y)$
.12	.0975	14	.939
.14	.1121	16	.947
.16	.1264	18	.952
.18	.1402	20	.957
.20	.1537	25	.966
.25	.186	30	.971
.30	.216	40	.978
.35	.244	50	.982
.40	.271	100	.991
.45	.296	200	.996
.50	.319	500	.998
.60	.362	1000	.999
.70	.400		

since, regardless of any interpretation of the reverse process, the region of total irreversibility definitely indicates a slow step in the reduction process. This is further supported by the observation that altering the effective stream length had no pronounced effect on the observed constants in Table IV. The poorest agreement for a threefold change in stream length was found in the case of the 0.9 *M* KCl solution, where the rate constant varied from about 0.8×10^{-2} to 1.1×10^{-2} cm./sec. This is in contrast to the very pronounced effect on the reaction rate of altering the concentration of inert electrolyte.

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

Kinetic Study of the Reduction of Chromium(VI) at Rotating Gold Microelectrodes

BY FREDERICK BAUMANN[1] AND IRVING SHAIN

RECEIVED MAY 23, 1956

The kinetics of the reduction of chromium(VI) at a rotating gold microelectrode were investigated. Equations were developed which permit the calculation of the rate of the electrode reaction from current-voltage curves, using solid electrodes in stirred solution. Over the range of hydrogen ion concentrations studied, the activated complex for this electrode reaction was found to have the composition $H_3CrO_4^x$, where x is the charge. A possible mechanism is postulated.

The reduction of chromium(VI) species at the dropping mercury electrode has been reported many times.[2-4] All of these studies were made in basic or weakly acidic solutions. The extension of these studies to lower *p*H values has not been possible because the rising portion of the current–voltage curve is shifted more positive than the anodic dissolution potential of mercury. It has not been possible to obtain a reduction wave for chromium(VI) on platinum electrodes since chromium(VI) in acid solution attacks platinum and the oxide film formed hinders the electrode reaction. However, gold electrodes were found suitable since they are resistant to attack by chromium(VI) species in acid solution.[5]

Although rotating solid microelectrodes have found many analytical applications, studies of the rising portion of the current–voltage curves obtained with these electrodes have not been very successful. Poor reproducibility, due to surface effects caused by oxide films and impurities, has hindered these studies. Since reproducible results can be obtained for the reduction of chromium(VI) in acid solution at rotating gold electrodes, a kinetic study was made of this reaction.

Theory

Delahay[6] has developed a unified theory of polarographic waves which rigorously treats polarographic waves regardless of the degree of irreversibility of the electrode process. This theory is applicable to the dropping mercury electrode where diffusion is the only mode of mass transfer. Using the approach of Delahay and Strassner,[7] an analogous theory for the case of electrodes of constant area in stirred solutions can be derived.

Consider the reduction of substance O to substance R in an electrode process involving n electrons, where R is soluble in the solution

$$O + ne = R$$

The current is given by

$$i = nFAf(x = 0) \qquad (1)$$

where F is the faraday, A is the area of the electrode and $f(x = 0)$ is the flux at the electrode surface. If the overvoltage is sufficiently high so that the effect of the backward reaction can be neglected, the flux can be equated to the concentration of O on the electrode surface and the rate at which it reacts. For a first-order reaction

$$f(x = 0) = kC_0 \qquad (2)$$

where C_0 is the concentration of the reactant at the electrode surface and k is the formal heterogeneous rate constant for the forward electrode reaction, expressed in centimeters/second. Combining equations 1 and 2

$$i = nFAkC_0 \qquad (3)$$

The concentration at the electrode surface can be related to the bulk concentration by[8]

$$C_0 = \frac{i_l - i}{i_l} C_0^0 \qquad (4)$$

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[1] Based on the Ph.D. thesis of Frederick Baumann, University of Wisconsin, 1956.

[2] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **62**, 852 (1940).

[3] T. Berzins and P. Delahay, *ibid.*, **75**, 5716 (1953).

[4] J. H. Green and A. Walkley, *Australian J. Chem.*, **8**, 51 (1955).

[5] F. Baumann and I. Shain, to be published.

[6] P. Delahay, THIS JOURNAL, **75**, 1430 (1953).

[7] P. Delahay and J. R. Strassner, *ibid.*, **73**, 5219 (1951).

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, p. 191.