

crease falls well inside the limits of experimental error, so that the gross behavior described by equation 8 cannot be separated into heat and probability effects.

The form of equation 8 was chosen as the simplest one which describes the change in  $f_0$  in the experimental region from  $N_W = 0$  to  $N_W = 0.5$ . Since  $f_0$  changes by only about 25% throughout this region, one need not expect the form to be of significance. It was, therefore, interesting to find that in the products of solvolysis of *t*-butyl nitrate at 25.0° in aqueous dioxane as determined by Lucas and Hammett<sup>10</sup> the olefin fractions, which changed by more than a factor of 5 in the experimental region from  $N_W = 0.620$  to  $N_W = 0.205$ , obey an equation of the same form, *i.e.*

$$f_0(t\text{-BuNO}_3 \text{ in aq. diox. at } 25^\circ) = \frac{1}{1 + 26.9N_W^2} \quad (10)$$

Equation 10 is a one parameter equation since, in this solvent system,  $f_0^0$ , the fraction of olefin formed at  $N_W = 0$ , must be equal to unity.

In the solvent of composition  $N_W = 0.765$ , these authors measured olefin fractions at 0.3 and 10.0°. Solution of equation 10 at  $N_W = 0.765$  (*i.e.*, outside the 25° experimental range) yields a value of  $f_0$  which is compatible with the measurements at lower temperatures; that is, with increasing temperature the rate of the elimination reaction increases relative to that for the substitution reaction, and the increase is accounted for by a differ-

(10) G. R. Lucas and L. P. Hammett, *THIS JOURNAL*, **64**, 1928 (1942).

ence of about 2500 cal. in the heats of activation of the two reactions.

In their analyses for olefin in the presence of *t*-butyl nitrate, Lucas and Hammett had to correct for the amount of olefin produced during the very rapid hydrolysis of *t*-butyl nitrate in their aqueous analytical solution. They found that 2.99% of the *t*-butyl nitrate was converted to olefin under their experimental conditions, whereas equation 10 predicts 3.58% olefin formation in pure water at 25.0°. (The temperature of their analytical work was not given.)

Interpreted as a conventional concentration function, equation 10 means that the transition state for alcohol formation contains two more water molecules than the transition state for the elimination reaction. Such an interpretation then implies that in the methanol-water system there would be at least four analogous transition states leading to substitution, for every transition state en route to elimination, *i.e.*, one having two additional methanol molecules, one having two additional water molecules, and two others, each of which contained an additional methanol molecule and an additional water molecule. Thus, equation 8 would be an oversimplification.

The rates of solvolysis of *t*-butyl chloride in aqueous methanol which have been presented in a previous paper<sup>2</sup> and the product compositions as presented in this paper will be discussed in a later paper after further pertinent data have been presented.

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## Reduction at the Streaming Mercury Electrode. I. The Limiting Current<sup>1</sup>

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Solutions of the diffusion problem applicable to steady state reduction at the streaming mercury electrode are presented, with special attention being given to the influence of stream contraction and expansion, and variable liquid velocity. Experimental methods are described for the photographic determination of stream diameter and solution flow. The surface velocity of the stream was calculated from measurements of the charging current. Verification of the theory is shown by experimental measurements of the reduction current for several ions.

The streaming mercury electrode has been used rather extensively in recent years as a substitute for the dropping electrode in certain forms of polarography.<sup>2-6</sup> For rate studies, the streaming electrode has several distinct advantages, chief of which is the higher overvoltage due to the greater current density. In addition, the effect of impurities is minimized by the rapid renewal of the mercury surface, the interfacial area is constant, and in the majority of cases there are no maxima. Disad-

vantages in its use are the large amount of mercury consumed, the difficulty of obtaining the actual length, radius and surface velocity of the stream, and the variation of the potential drop across the interface on different parts of the electrode caused by variation in the *IR* drop through the solution.

In this paper the results of measurements of the limiting steady-state current at the streaming electrode will be discussed with particular reference to the effects of variable radius and surface velocity. Current-voltage curves will be presented in subsequent papers.

### Theoretical

The fundamental equation for the limiting current at the streaming electrode was derived by Rius, Llopis and Polo<sup>5</sup> as

$$I_d = 4nFC \sqrt{\frac{mLD}{d}} \quad (1)$$

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

(3) (a) A. Rius and J. Llopis, *Anales real soc. Espan. fis. y quim.*, **42**, 617 (1946); (b) A. Rius and M. J. Molera, *ibid.*, **43**, 1074 (1947).

(4) A. Rius, J. Llopis and S. Polo, *ibid.*, **45**, [B] 501 (1949).

(5) A. Rius, J. Llopis and S. Polo, *ibid.*, **45**, [B] 1039 (1949).

(6) J. W. Loveland and P. J. Elving, *J. Phys. Chem.*, **56**, 250 (1952).

where  $m$  is the mass of mercury flowing from the capillary in unit time,  $L$  is the length of the electrode over which reduction occurs,  $d$  is the density of mercury,  $C$  is the bulk concentration of the reducible species,  $D$  is its diffusion coefficient,  $n$  is its reduction valence, and  $F$  is the faraday. Experimental confirmation of this equation has been reported by Rius and co-workers<sup>5</sup> and by P. Valenta.<sup>7</sup> The conditions under which equation (1) is strictly applicable are that (1) the radius of the stream is uniform, (2) the velocity of the mercury and of the adjacent solution is uniform over the entire cross-section of the stream and of the diffusion layer, and (3) the thickness of the diffusion layer is very small compared to the radius of the stream. Because studies of the physical characteristics of a number of streams (as described below) showed rather large deviations from these limitations, a more generalized form of equation 1 applicable under less restrictive conditions was derived as follows.

In a moving medium, the diffusion equation in vector notation has the form<sup>8</sup>

$$D\nabla^2c - \vec{v} \cdot \nabla c = \frac{\partial c}{\partial t} \quad (2)$$

where  $c$  is the concentration of the diffusing species,  $D$  is its diffusion coefficient, the vector  $v$  is the velocity of the moving medium, and  $t$  is time. The velocity satisfies the equation

$$\nabla \cdot \vec{v} = 0 \quad (3)$$

In applying these equations to the problem of diffusion to a streaming electrode at constant potential, it will be assumed, first, that the process has reached a steady state and consequently the right-side of equation 2 is zero; second, that the concentration and velocity functions are cylindrically symmetrical; and third, that diffusion occurs essentially in the radial direction only. The first assumption will be valid if the stirring effect of the stream produces a smooth flow of solution, *i.e.*, a velocity which, at any point in space, is constant with time. The second requires in addition that the stream be round (though not necessarily of uniform radius throughout its length) and that the effect of natural convection be negligible compared to that of the forced convection. There may be a rotational motion of the solution, but it must be uniform around the stream. The third assumption implies that the flow is sufficiently rapid that appreciable concentration changes in a direction parallel to the stream axis will occur only over a distance that is very large compared to the thickness of the diffusion layer. With these simplifications, equations 2 and 3, expressed in cylindrical coordinates, become<sup>9</sup>

$$D \left[ \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right] - u \frac{\partial c}{\partial r} - v \frac{\partial c}{\partial z} = 0 \quad (r_0 < r < \infty) \quad (4)$$

$$\frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial v}{\partial z} = 0 \quad (r_0 < r < \infty) \quad (5)$$

where  $r$  is the radial distance from the center of the stream,  $z$  is the distance measured along the stream

from the point at which it emerges from the capillary,  $u$  and  $v$  are the velocity components of the medium in the  $r$  and  $z$  directions, respectively, and  $r_0$  is the radius of the stream (considered to be a function of  $z$  but not of  $t$ ). Although the concentration gradient has been assumed to have only a very small component in the  $z$  direction as compared to the  $r$  direction, the last term on the left-hand side of (4) is not negligible because of the large magnitude of  $v$  as compared to  $u$ .

It is convenient to define the coordinate  $x$  as the radial distance measured from the surface of the stream. Thus

$$x = r - r_0(z) \quad (6)$$

Transforming equations 4 and 5 from  $r$  and  $z$  to  $x$  and  $z$  as independent variables gives

$$D \left[ \frac{\partial^2 c}{\partial x^2} + \frac{1}{r_0 + x} \frac{\partial c}{\partial x} \right] + \left[ v \frac{dr_0}{dz} - u \right] \frac{\partial c}{\partial x} - v \frac{\partial c}{\partial z} = 0 \quad (7)$$

$$\frac{\partial u}{\partial x} + \frac{u}{r_0 + x} + \frac{\partial v}{\partial z} - \frac{dr_0}{dz} \frac{\partial v}{\partial x} = 0 \quad (8)$$

The velocity components  $u$  and  $v$  evaluated at the stream surface must satisfy the boundary condition

$$u(0, z) = v(0, z) \frac{dr_0}{dz} \quad (9)$$

while the concentration, for the case of the limiting current, must satisfy the conditions

$$c(\infty, z) = C \quad (10)$$

$$c(0, z) = 0 \quad (11)$$

$$c(x, 0) = C \quad (12)$$

where  $C$  represents the bulk concentration of the reducible species. A complete statement of the hydrodynamic problem would include, in addition to these equations, the equations of motion for the medium and additional boundary conditions involving the velocity. The equations given constitute a complete boundary value problem, however, if  $v(x, z)$  and  $r_0(z)$  are considered to be known. Experimental methods for determining these quantities from photographic and charging current measurements will be described.

A solution can be obtained by writing  $u$ ,  $v$  and  $1/(r_0 + x)$  as power series in  $x$

$$u = u_0 + u_1x + u_2x^2 + \dots \quad (13)$$

$$v = v_0 + v_1x + v_2x^2 + \dots \quad (14)$$

$$\frac{1}{r_0 + x} = \frac{1}{r_0} - \frac{x}{r_0^2} + \frac{x^2}{r_0^3} - \dots \quad (15)$$

where the coefficients  $u_0$ ,  $v_0$ ,  $u_1$ , etc., are functions of  $z$ . It follows from equations 8 and 9 that

$$u_0 = v_0 \frac{dr_0}{dz}$$

$$u_1 = \left( v_1 - \frac{v_0}{r_0} \right) \frac{dr_0}{dz} - \frac{dv_0}{dz}$$

$$u_2 = \left( v_2 - \frac{v_1}{2r_0} + \frac{v_0}{r_0^2} \right) \frac{dr_0}{dz} + \frac{1}{2r_0} \frac{dv_0}{dz} - \frac{1}{2} \frac{dv_1}{dz} \quad (16)$$

A solution can then be written in the form

$$c = C \left[ \operatorname{erf}(xZ) + (f_1x + f_2x^2 + \dots) \operatorname{erfc}(xZ) + \frac{2}{\sqrt{\pi}} (g_1x + g_2x^2 + \dots) \exp(-x^2Z^2) \right] \quad (17)$$

(7) P. Valenta, *Collection Czechoslov. Chem. Commun.*, **16**, 239 (1951).

(8) J. N. Agar, *Disc. Faraday Soc.*, **1**, 26 (1947).

(9) Cf. equation 2 of reference 5.

where  $Z$  is the expression

$$Z = \frac{r_0 v_0}{2} \left[ D \int_0^z r_0^2 v_0 dz \right]^{-1/2} \quad (18)$$

and the coefficients  $f_1, f_2, g_1$ , etc., can be evaluated to any desired degree of accuracy as functions of the radius and the velocity coefficients,  $v_0, v_1$ , etc. To a first approximation

$$\begin{aligned} f_1 &= \frac{1}{2r_0} + \frac{v_1}{4v_0}, f_2 = f_3 = \dots = 0 \\ g_1 &= 0, g_2 = \frac{v_1}{4v_0} Z, g_3 = g_4 = \dots = 0 \end{aligned} \quad (19)$$

A second approximation yielded expressions for the coefficients in the first series up to  $f_3$  and in the second to  $g_5$ , while the third approximation ran to  $f_5$  and  $g_3$ . These higher approximations made no appreciable contribution to the value for the current (less than 0.1% for the streams studied). The current density at any point on the electrode is thus given by

$$\begin{aligned} i &= nFD \left( \frac{\partial c}{\partial x} \right)_{(x=0)} = nFDC \left[ \frac{2}{\sqrt{\pi}} Z + f_1 + \frac{2}{\sqrt{\pi}} g_1 \right] \\ &= nFDC \left[ \frac{2}{\sqrt{\pi}} Z + \frac{1}{2r_0} + \frac{v_1}{4v_0} + \dots \right] \end{aligned} \quad (20)$$

and, finally, the total current by

$$\begin{aligned} I &= 2\pi \int_0^L r_0 i dz = 2\pi nFDC \left[ \frac{2}{\sqrt{\pi}} \int_0^L r_0 Z dz + \right. \\ &\quad \left. \frac{L}{2} + \frac{1}{4} \int_0^L \frac{v_1 r_0}{v_0} dz + \dots \right] \end{aligned} \quad (21)$$

A comparison of the magnitudes of the terms in this expression for a typical stream is shown in Table II. Tracing the origin of each of the terms in the bracket, it is found that the second term arises from the curvature of the electrode,<sup>10</sup> while the third term represents the effect of the "shear velocity" or velocity gradient in the diffusion layer. If the surface velocity  $v_0$  and stream radius  $r_0$  are constant, the first term reduces to  $2r_0 \sqrt{v_0 L / \pi D}$  and, neglecting the second and third terms

$$I = 4nFCr_0 \sqrt{\pi D v_0 L} \quad (22)$$

This will be termed the equation for the limiting current at an "ideal" streaming electrode. If, in addition, the velocity of mercury flow is constant throughout the interior of the stream as well as at the surface, equation 22 reduces to equation 1. As shown in Table II the principal deviations from Rius' equation are due to the difference between surface velocity and average velocity as caused by the drag of the solution on the stream.

### Experimental

The electrode and cell used in this investigation were similar to the earlier form of the streaming electrode used by Heyrovsky.<sup>11</sup> The polarizable electrode was a stream of mercury 0.1 to 0.25 mm. in diameter ejected upward through the solution at an angle of about 30 degrees from the vertical. The stream broke the surface of the solution and was collected in a separate part of the electrode vessel along with a considerable volume of entrained solution. A few strands of glass wool laid over the barrier between the collecting trap and the main chamber of the cell prevented droplets of mercury from "floating" back over the barrier and allowed a more uniform rate of return of the solution. A micrometer screw with a fine tip was mounted in the cell for measure-

ment of the solution level. Duplicate readings agreed within a few thousandths of a centimeter. The current carrying anode was a mercury pool in the bottom of the vessel, but to avoid the error of polarization at the surface of the pool, the voltage measurements were taken between the stream and a saturated calomel electrode. Flexible connections were made with Tygon tubing. Nitrogen purified by  $\text{CrCl}_2$  was used for de-oxygenating the solutions.

The capillaries used to produce the stream were drawn from Pyrex glass tubing (mostly 3 mm.) and were examined under the microscope for roundness before using. It was considered desirable to have square, thin-walled tips in order that the flow of solution toward the stream might be uniform and as unhampered as possible. In most of the capillaries used, the length of the tapered section was about 10 mm.

Solutions were prepared in most cases using analytical grade reagents without further purification. For several runs recrystallized KCl and water that had been redistilled in Pyrex were used, but no difference was noted in the current reading. Current measurements were obtained using  $\text{Cd}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Hg}_2^{+2}$  and  $\text{Tl}^{+1}$  as the reducible ions and KCl or  $\text{KNO}_3$  as supporting electrolyte. The smallest ratio of the concentrations of supporting electrolyte to reducible ion was 35:1, but in most cases the ratio was of the order of 100:1. The diffusion current was taken as the difference between the steady current readings with reducible ion present and with supporting electrolyte only, at an electrode potential 0.1 to 0.2 volt more negative than the half-wave potential of the ion.

To study the stream photographically, the capillaries were inserted in a special cell under conditions similar to those in the electrolytic cell except that the solution was not de-oxygenated. Shadowgraphs were taken on lantern slide plates at three different magnifications using 158, 72 and 45 mm. objectives, with two different light sources, a spark emanating from a small hole and having a duration of about 30 microseconds, and a stroboscopic unit with a flash of about 200 microseconds. Distances on the plate were measured by two different observers using a comparator equipped with a microscope. Duplicate readings on a good stream image agreed within 0.002 mm. distance on the plate or about 0.2% of a stream diameter. Readings of the diameter on the same stream on different plates taken under the same conditions agreed to within 0.5 to 1.0%. It was observed that the measured diameters were affected by variations in the light source and in the conditions of development of the plates. To obtain reliable values for absolute stream diameters a platinum wire of approximately the same size as the mercury stream was inserted in the cell and photographed in precisely the same way as the stream. The actual diameter of the wire was measured by Professor W. W. Gilbert of the Engineering College of the University of Michigan, using a Doall Comparator Gauge. Stream roundness was checked by rotating the capillary between photographs.

To observe the motion of the solution near the stream, aluminum dust was added to the solution and photographs taken with the cell illuminated from the front. The path of a moving particle in the focal plane of the camera appeared as a clearly-visible fine line from the length of which the speed of the solution could be estimated.

### Results and Discussion

**Stream Diameter.**—The variation in the diameter of a typical stream with distance from the tip of the capillary is shown in Fig. 1a. Measurements were obtained on streams from nine different capillaries ranging in diameter from 0.092 to 0.236 mm. All followed a similar pattern, *i.e.*, an initial contraction of 3–4% followed by a gradual enlargement of as much as 10%. When ejected into air instead of water, the contraction remained the same but the enlargement did not occur, indicating the importance of the drag of the solution on the stream flow. Increasing the mercury head decreased the rate of enlargement, but produced no observable change in the minimum diameter. Although the break-up point of the stream was af-

(10) Cf. equation 5, reference 5.

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

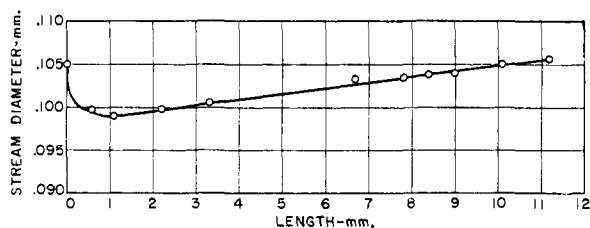


Fig. 1a.—Variation in stream diameter with distance from tip of the capillary.

ected by applied potential, there was no measurable effect of potential on diameter.

**Surface Velocity.**—Because of the drag of the solution on the mercury, the surface of the stream should move more slowly than the interior. Figure 1b shows a comparison of the average velocity of the stream as calculated from the mass flow rate and radius, and the surface velocity obtained from measurements of the “charging current,” *i.e.*, the current drawn by the cell with only inert electrolyte present (0.1 *M* KCl). Assuming no reduction this current must be a measure of the rate at which charge is carried out of the system by the double layer. Stream photographs of the region where the stream breaks the surface showed a coning of the solution, the cone narrowing down to a sheath of liquid around the stream. Under certain conditions this sheath disappeared,<sup>12</sup> and when this occurred, the charging current dropped abruptly to zero. Normally the cone and sheath remained intact, and the cell drew a current which varied with potential in direct proportion to the values given by Grahame for the specific charge density of the double layer.<sup>13</sup> From these observations it was concluded that reduction was actually negligible, and that the current, at a fixed potential, could be used to calculate the surface velocity near the point where the stream entered the sheath. Velocity changes beyond this point would not affect the measured current because of the high electrical resistance of the sheath. The effective cut-off point was calculated from the shape of the cone and, it was found, could be taken as that point which was separated from the main body of solution by a resistance of 5,000 ohms through the cone and sheath.

**Solution Flow.**—As observed by the paths of aluminum particles in the solution, the region of moving liquid was well defined, increasing in size with distance from the tip of the capillary and reaching a thickness, when the stream was long, of as much as 1 mm., or over 100 times the width of the calculated diffusion layer. The flow appeared smooth and reproducible, although no paths were observed in the high velocity region close to the stream, perhaps because of aluminum particles being swept into the mercury. By extrapolating to the known value of  $v_0$ , estimates of  $v_1$  and an upper limit for  $v_2$  were obtained as shown in Table I.

**The Limiting Current.**—From these data on stream properties the terms in equation 21 can be evaluated. For the stream whose characteristics are shown in Fig. 1 and Table I, the calculated val-

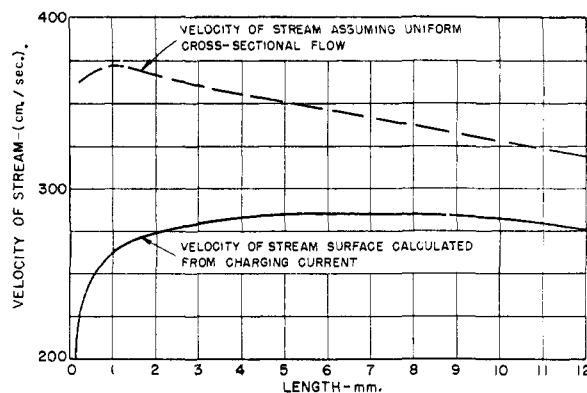


Fig. 1b.—A comparison of the surface velocity and the average cross-sectional velocity of the mercury stream.

TABLE I  
COEFFICIENTS IN EQUATION FOR SOLUTION VELOCITY AS ESTIMATED PHOTOGRAPHICALLY

$z$ , cm.	$v_1$ , <sup>a</sup> sec. <sup>-1</sup>	$v_2$ , <sup>a</sup> cm. <sup>-1</sup> sec. <sup>-1</sup>
0.1	$-13 \times 10^4$	
0.3	$-8 \times 10^4$	$<2 \times 10^7$
1.0	$-4 \times 10^4$	

<sup>a</sup> See equation 14.

ues for the three terms of the equation and for the total current according to equations 21, 1 and 22 when  $D = 10^{-5}$  cm.<sup>2</sup>/sec.,  $C = 10^{-3}$  g. ions/l. and  $n = 1$  are shown in Table II. For equation 22 in which  $v_0$  and  $v_0$  are to be considered constant, the values of 0.0051 cm. and 278 cm./sec., respectively, were used to compute the current. Several significant conclusions are evident from the table. The two small terms in equation 21 essentially cancel each other. This is a fortunate circumstance, since, in view of the definition of  $Z$  from equation 18, the diffusion coefficient enters in the first term in the same way (to the one-half power) as it does in the Rius equation and in the “ideal” equation. The relative deviation of the actual current from the values given by these latter two equations is thus dependent on stream characteristics alone and is independent of the reducible ion.

TABLE II  
COMPARISON OF EQUATIONS FOR LIMITING CURRENT

Stream length, mm.	Terms in eq. 21			Cor. eq. 21,	Rius' eq. 1,	“Ideal” eq. 22,
	$\mu$ amp.	$\mu$ amp.	$\mu$ amp.	$\mu$ amp.	$\mu$ amp.	$\mu$ amp.
1	52	0.3	-0.5	52	65	58
2	76	0.6	-0.8	76	92	82
3	95	0.9	-1.1	95	112	100
4	111	1.2	-1.3	111	130	116
5	125	1.5	-1.5	125	145	130
6	138	1.8	-1.7	138	159	142
7	150	2.1	-1.8	151	172	153
8	162	2.4	-2.0	162	184	164
9	172	2.7	-2.1	173	195	174
10	182	3.0	-2.2	183	205	183
11	192	3.3	-2.3	193	215	192
12	201	3.6	-2.4	202	225	200

The “ideal” equation 22 differs much less from the complete equation 21 than does the Rius equation 1. Since both the ideal equation and the Rius equation give a linear relationship between  $I$  and

(12) See reference 7.

(13) D. C. Grahame, *THIS JOURNAL*, **71**, 2975 (1949).

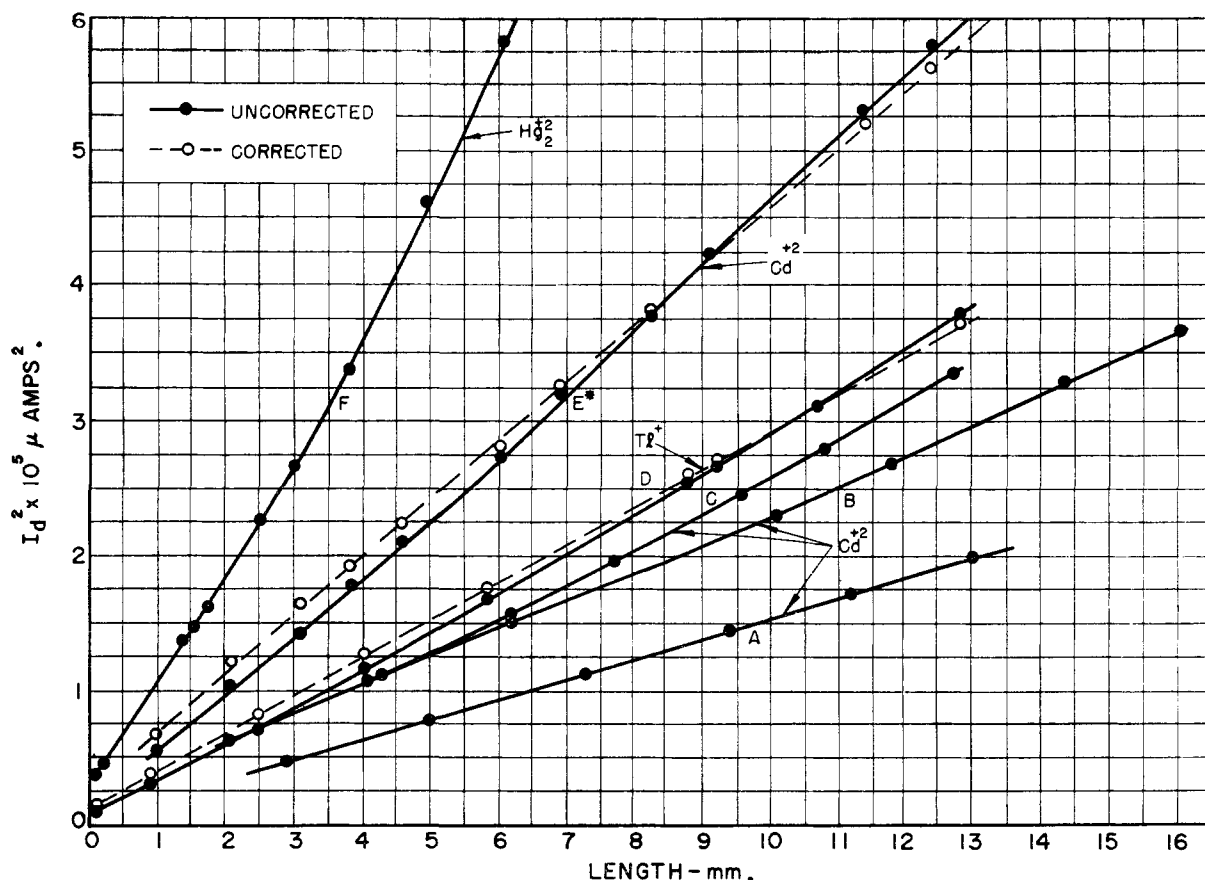


Fig. 2.—The square of the limiting current *versus* effective stream length for reduction at a streaming mercury electrode.

<sup>a</sup> To get curve E on this figure a new vertical scale was necessary. The actual scale for curve E only can be obtained by multiplying all readings on the vertical axis by 20.

Curve	Reducible ion	Concn. of reducible ion, g. ions/l.	Inert electrolyte	Dia. of capillary tip, mm.	Hg head cm.
A	Cd <sup>++</sup>	$0.8 \times 10^{-3}$	0.1 M KNO <sub>3</sub>	0.125	68
B	Cd <sup>++</sup>	$0.8 \times 10^{-3}$	0.1 M KNO <sub>3</sub>	.164	60
C	Cd <sup>++</sup>	$0.9 \times 10^{-3}$	1.0 M KNO <sub>3</sub>	.125	68
D	Tl <sup>+</sup>	$2.0 \times 10^{-3}$	0.1 M KCl	.105	95
E <sup>a</sup>	Cd <sup>++</sup>	$9.0 \times 10^{-3}$	1.0 M KCl	.105	95
F	Hg <sub>2</sub> <sup>++</sup>	$2.5 \times 10^{-3}$	1.0 M KNO <sub>3</sub>	.130	75

$\sqrt{L}$ , it is evident that this relationship is not necessarily a check on the validity of the Rius equation for a particular stream. The required condition for a straight line is that the product  $r_0^2 v_0$  be constant. From Fig. 1b it appears that the stream is approaching this condition, and that for a smaller stream in which the velocity pattern is compressed to the left,  $r_0^2 v_0$  would be sufficiently constant over a considerable length of the stream to give a straight plot for  $I$  vs.  $\sqrt{L}$  even though the difference between the surface velocity and average velocity was appreciable. For this reason, diffusion coefficients calculated from the Rius equation would be expected to be too small.

Figure 2 shows the experimental limiting current for several electrodes and solutions plotted as the square of the current against the distance from the tip of the capillary to the point at which the stream and surface of the solution would intersect if there were no coning. The effective length is some-

what greater than this because of penetration of the "tail cone," but studies of the shape of the cone and of the volume of solution carried into the trap indicate that this penetration would be very nearly linear with stream length and thus have no effect on the linearity of the curves. The data for curves D and E are shown corrected according to the ratios of equation 22 to equation 21 as calculated in Table II. Straight lines are obtained, although, because of the penetration effect just mentioned, they do not pass through the origin. If there were any appreciable turbulence in the liquid motion in the region of the diffusion layer, one would expect the current to vary more nearly as the first power rather than as the square root of the stream length. The curves in Fig. 2 illustrating the square root dependence thus serve as a verification of the assumptions on which the theoretical development was based.

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