ments must be due to the absence of inhibitors in our reaction solutions, since competitive inhibitors, at least, cause an increase in the apparent K_m.

The observed deviations from the Michaelis–Menten mechanism may have an explanation entirely different from the two-site hypothesis discussed above. Falconer and Taylor[10] noted certain anomalies in the solubility of pig liver esterase, which they attributed to the presence of two separate enzymes. But their observations, as well as the results presented here, may find an explanation in terms of a more or less continuous range of enzyme variation. Given the pronounced alteration in the enzyme's kinetic properties as it is purified,[7,8,11,12] it is not unreasonable to suppose that liver impurities clinging to the enzyme could result in several molecular species having different enzymatic parameters, whose assembly would then show deviations from the Michaelis–Menten kinetics. The existence of such rather firmly bound complex species is also suggested by the failure to crystallize any of the liver esterases, notwithstanding all attempts to purify them.

Thanks are due to the Rockefeller Foundation for financial aid which made this research possible.

(10) J. S. Falconer and D. B. Taylor, *Biochem. J.*, **40**, 831, 835 (1946).

(11) H. Sobotka and D. Glick, *J. Biol. Chem.*, **105**, 221 (1934).

(12) K. Gyotoku, *Biochem. Z.*, **193**, 18, 27 (1928).

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Diffusion Currents at Spherical Electrodes

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The theory of diffusion currents at microelectrodes has been extended to the case of spherical electrodes under conditions where the curvature of the electrode surface must be considered and where the applied voltage varies linearly with time. Theoretical current–voltage curves were constructed and compared with experimental results for the reduction of lead and thallous ions. The stationary spherical mercury electrode used in this work shows great promise as an analytical tool.

Diffusion currents at microelectrodes under conditions where the equations for linear diffusion apply have been studied by Randles,[2] Sevcik,[3] and Berzins and Delahay.[4] They showed that their equations apply to electrodes of any shape provided that the rate of voltage change is high and/or the electrode surface is large. However, when these conditions are not met and spherical or cylindrical microelectrodes are used, the curvature of the electrode surface must be considered in a theoretical treatment of the current–voltage relationships observed. Nicholson[5] studied the current–voltage curves obtained with cylindrical platinum microelectrodes. The development of stationary spherical mercury microelectrodes by Gerischer[6] and Berzins and Delahay[7] has made it possible to extend the theory to spherical electrodes.

Theory

Consider the reduction of a substance O to a substance R which is soluble in the solution or in the electrode. Further conditions are that the only way substance O can reach the electrode surface is through diffusion, that the electrode reaction is reversible, that the voltage varies linearly with time, and that the electrode is a sphere. The current flowing at the electrode will be a function of the flux of substance O at the electrode surface, which, under these conditions, will be determined by the general equation for spherical diffusion[8]

$$\frac{\partial C_o(r, t)}{\partial t} = D_o\left[\frac{\partial^2 C_o(r, t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_o(r, t)}{\partial r}\right] \qquad (1)$$

C_o is the concentration of substance O, r is the distance from the center of the electrode, t is the time, and D_o is the diffusion coefficient of substance O. This equation must be solved for certain initial and boundary conditions.

The initial conditions are that the concentration of substance O is uniform throughout the solution at zero time, and that the concentration of substance R is zero in the solution (or in the electrode, if an amalgam is formed) at zero time.

The first boundary condition is derived from the Nernst equation. If the voltage varies linearly with time

$$E = E_i - vt \qquad (2)$$

where E is the potential of the electrode, E_i is the potential at zero time, and v is the rate of voltage change. The negative sign indicates that the potential of the working electrode varies toward more cathodic potentials. Combining equation 2 and the Nernst equation[9]

$$\frac{C_o(r_0, t)}{C_R(r_0, t)} = \theta \exp(-\sigma t) \qquad (3)$$

where

$$\theta = \frac{f_R}{f_o} \exp\left[\frac{nF}{RT}(E_i - E^0)\right] \qquad (4)$$

and

$$\sigma = \frac{nF}{RT} v \qquad (5)$$

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(1) Based on the Ph.D. thesis of R. P. Frankenthal, 1956. Procter and Gamble Fellow 1954–1955.

(2) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948).

(3) A. Sevcik, *Collection Czechoslov. Chem. Communs.*, **13**, 349 (1948).

(4) T. Berzins and P. Delahay, THIS JOURNAL, **75**, 555 (1953).

(5) M. M. Nicholson, *ibid.*, **76**, 2539 (1954).

(6) H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953).

(7) T. Berzins and P. Delahay, THIS JOURNAL, **77**, 6448 (1955).

(8) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, p. 60.

(9) Ref. 8, pp. 116–117.

f_O and f_R are the activity coefficients of substances O and R, and since their evaluation is difficult, $E°$ will henceforth be considered the formal potential. C_R is the concentration of substance R, r_0 is the radius of the electrode, and all other terms have their usual significance.

The second boundary condition arises from the fact that the fluxes of the product and the reactant must be equal at the electrode surface

$$D_o \frac{\partial C_o(r_0, t)}{\partial r} + D_R \frac{\partial C_R(r_0, t)}{\partial r} = 0 \qquad (6)$$

The solution to equation 6 is given by Delahay[10]

$$C_o + kC_R = C_o° \qquad (7)$$

where $k = (D_R/D_O)^{1/2}$, D_R is the diffusion coefficient of the substance R, and C_O^0 is the bulk concentration of substance O.

Equation 1 was solved for the specified initial and boundary conditions by numerically solving the corresponding finite difference equation

$$\frac{C_o(r, t)}{C_O^0} = \frac{1}{2}\left\{\frac{C_o(r + \Delta r, t)}{C_O^0} + \frac{C_o(r - \Delta r, t)}{C_O^0} + \frac{2\Delta r}{r}\left[\frac{C_o(r + \Delta r, t)}{C_O^0} - \frac{C_o(r, t)}{C_O^0}\right]\right\} \qquad (8)$$

The method used to solve this equation is described in Scarborough[11] and is the same used by Randles[2] and Nicholson.[5] Equation 8 has been simplified by setting the condition that $(\Delta r)^2 = 2D_O\Delta t$, and by converting all concentration terms into concentration ratios.

The result of the numerical solution of this equation is a network of values of the concentration ratio $C_O(r,t)/C_O^0$ for various values of r and t. The differential of the concentration ratio at the electrode surface at any time t was obtained by fitting the concentration ratios at points (r_0, t), (r_1, t), and (r_2, t) to a parabola and differentiating the result.

The validity of the approximations depends on the size of Δr and Δt used in the calculations. Table I shows the values of $(\partial C_o(r_0,t)/C_O^0)/\partial r$ as a function of Δr (which of necessity determines Δt) at the peak of the current–voltage curve.

TABLE I

VARIATION OF THE CONCENTRATION GRADIENT AT THE ELECTRODE SURFACE AS Δr DECREASES

Δr, cm.	$\frac{\partial C_O(r_0, t)/C_O^0}{\partial r}$
0.003464	101.0 ± 0.1
0.002450	102.3 ± .1
0.001732	102.8 ± .1
0	103.3 ± .5[a]

[a] Extrapolated.

The true value of the differential is approached as Δr approaches zero; 103.3 was taken as the extrapolated value within 1%. Since all calculations in this work were made on the basis of Δr = 0.003464 cm., the results have been corrected by a factor of 103.3/101.0 = 1.02.

The values of the differential $\partial C_o(r_0,t)/C_O^0$ which were obtained could be used to determine the current flowing

$$i = nFAD_oC_O^0 \frac{\partial C_o(r_0, t)/C_O^0}{\partial r} \qquad (9)$$

provided Δr can be expressed in terms of the experimental parameters. From the first boundary condition (equation 3) and the condition $(\Delta r)^2 = 2D_o\Delta t$ which was set in the numerical solution of the finite difference equation

$$\Delta r = \left[\frac{2RTD_O\Delta\tau}{nFv}\right]^{1/2} \qquad (10)$$

where

$$\Delta\tau = \Delta\left[\ln \frac{C_O(r_0, t)}{C_R(r_0, t)}\right] = \frac{nF}{RT}(E_2 - E_1) \qquad (11)$$

Substituting equation 10 into equation 9 one obtains

$$i = \frac{n^{3/2}F^{3/2}AD_O{}^{1/2}v^{1/2}C_O^0}{(2RT\Delta\tau)^{1/2}}\,\partial C_O(r_0, t)/C_O^0 \qquad (12)$$

This equation can be used to construct theoretical current–voltage curves for any system if the experimental parameters n, A, D_O, v and C_O^0 are known. The differential term $\partial C_O(r_0,t)/C_O^0$ is a function of n, r_0, v and D_O which cannot be expressed explicitly. However, the effect of these parameters on the differential is the same as their effect on the finite difference equation 8 where $\Delta r/r$ is a function of n, r_0, v and D_O. Since $r = r_0 + m\Delta r$ where m is an integer

$$\frac{\Delta r}{r_0} = \frac{\Delta r/r_0}{1 + m(\Delta r/r_0)} \qquad (13)$$

and dividing equation 10 by r_0

$$\frac{\Delta r}{r_0} = \frac{1}{r_0}\left[\frac{2RTD_O\Delta\tau}{nFv}\right]^{1/2} \qquad (14)$$

Thus the differential is proportional to r_0^{-1}, $D_O{}^{1/2}$, $n^{-1/2}$ and $v^{-1/2}$.

As the function $(1/r_0)(D_O/nv)^{1/2}$ approaches zero, equation 12 should approach the Randles[2] equation for linear diffusion in the same manner that the Nicholson[5] equation for cylindrical diffusion does. Using a value of $\Delta\tau$ = 0.233, the differential of the concentration ratio at the peak of the current–voltage curve was calculated as a function of $(1/r_0)(D_O/nv)^{1/2}$.

TABLE II

THE DIFFERENTIAL OF THE CONCENTRATION RATIO AS A FUNCTION OF $(1/r_0)(D_O/nv)^{1/2}$ AT THE PEAK OF THE CURRENT–VOLTAGE CURVE

$(1/r_0)(D_O/nv)^{1/2}$	$\partial C_O(r_0, t)/C_O^0$
0.632	0.360
.420	.344
.316	.336
.032	.314
.003	.312
0	.311[a]
0	.310[b]
0	.306[c]

[a] Extrapolated. [b] Randles. [c] Nicholson.

The effect of the experimental parameters on the differential is shown graphically in Fig. 1 where values of the differential are shown for various values of $(E - E°)$. Substituting the value of $\Delta\tau$ and other constants into equation 12, leads to the expression, at 25°

$$i = 881n^{3/2}AD_O{}^{1/2}v^{1/2}C_O^0\,\partial C_O(r_0, t)/C_O^0 \text{ amperes} \qquad (15)$$

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(10) Ref. 9, pp. 53–54, 418–419.

(11) J. B. Scarborough, "Numerical Mathematical Analysis," The Johns Hopkins Press, Baltimore, Md., 1950, pp. 309–340.

TABLE III

THE DIFFERENTIAL OF THE CONCENTRATION RATIO AS A FUNCTION $(1/r_0)(D_O/nv)^{1/2}$ AND $(E - E^0)$

$E - E^0$ (mv.)	$(1/r_0)(D_O/nv)^{1/2}$						
	0.003	0.316	0.422	0.632	1.000	2.000	3.000
135	0.003	0.003	0.003	0.004	0.004	0.004	0.004
111	.008	.009	.009	.009	.009	.010	.011
87	.021	.022	.022	.023	.024	.026	.028
63	.049	.052	.053	.054	.056	.061	.066
51	.075	.078	.079	.081	.084	.093	.099
39	.109	.113	.115	.118	.124	.135	.146
27	.152	.159	.161	.166	.173	.191	.207
15	.201	.210	.213	.219	.230	.255	.278
3	.247	.261	.265	.274	.288	.322	.353
−9	.284	.302	.308	.318	.337	.382	.421
−21	.306	.328	.335	.348	.371	.426	.474
−33	.312	.336	.344	.360	.386	.451	.508
−39	.309	.335	.343	.360	.388	.457	.517
−45	.304	.332	.340	.357	.387	.460	.523
−57	.288	.318	.328	.346	.378	.457	.527
−69	.270	.301	.311	.331	.365	.447	.522
−81	.250	.282	.294	.314	.349	.437	.514
−93	.233	.266	.277	.299	.335	.426	.504
−105	.217	.250	.262	.283	.320	.412	.492
−117	.203	.237	.248	.271	.308	.401	.483

where A is in cm.^{2}, v is in volts/sec., C_O^0 is in moles/liter, and D_O is in cm.^{2}/sec. This equation can be used in conjunction with Fig. 1 to calculate theoretical current-voltage curves. For accurate work, a large scale reproduction of Fig. 1 would be necessary. The points for such a plot are given in Table III.

Shain and Crittenden[12] were placed in series with the cell. The IR drop across the load resistor was recorded as a function of time on a Leeds and Northrup Type G Speedomax recorder (10 mv. full scale). The cell resistance was measured with a Serfass Conductivity Bridge, Model RC-M15, and all results were corrected for the calculated IR drop.

The cell consisted of a 300-ml. beaker connected by a salt bridge containing the indifferent electrolyte to a saturated calomel reference electrode.

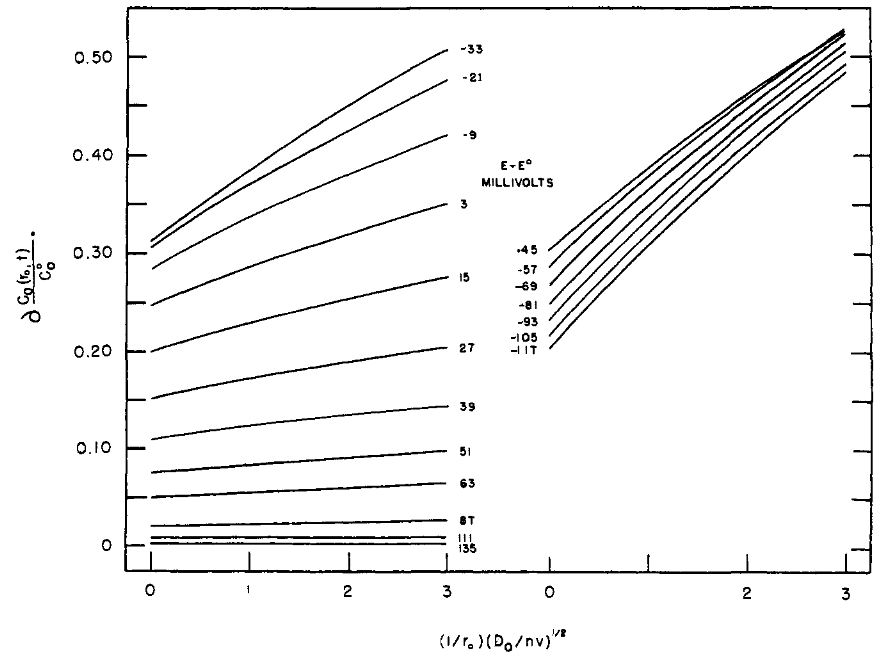

Fig. 1.—Values of the differential of the concentration ratios as a function of the experimental parameters, plotted at various potentials.

Experimental

Calculations.—All calculations were made on the International Business Machines Corporation, Type 650 Magnetic Drum Data-Processing Machine.

Apparatus.—A mechanical sweep generator, d.c. bias circuit and load resistor similar to the circuits described by

The working electrode was a gold wire (0.25 mm. diameter) soldered to a brass rod. The entire assembly was covered with sealing wax (Consolidated Electrodynamics Corp. No. 18792) and the wax was carved to expose only the

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[12] I. Shain and A. L. Crittenden, *Anal. Chem.*, **26**, 281 (1954).

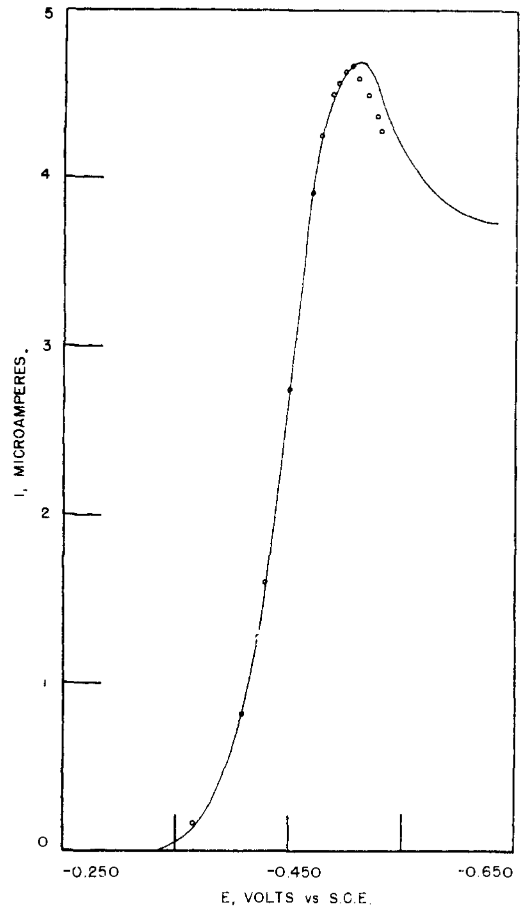

Fig. 2.—Current-voltage curve for the reduction of 1.00 m*M* Tl^+ in 0.1 *M* KCl: line, exptl.; points, theoretical.

tip of the gold wire. The mercury drops were obtained from an ordinary polarographic capillary assembly and were transferred to the gold wire with a Teflon scoop.

The radius and area of the mercury drops used for electrodes were calculated from the weight of a known number of drops. The radius of one drop was 0.046 cm., and the area was 0.027 cm.^{2}.

The cell and reference electrode were thermostated at 25.0°.

Materials.—All chemicals were reagent grade and were used without further purification. Solutions were prepared with doubly distilled water. Linde high purity nitrogen was passed through the cell for 10 minutes prior to recording a current-voltage curve and was also passed over the solution during the recording period. The nitrogen was used without further purification but was saturated with water vapor before it entered the cell.

Results and Discussion

Current-Voltage Curves.—The reduction of thallous and lead ions was studied using 0.1 *M* potassium chloride for the indifferent electrolyte. Figures 2 and 3 show experimental curves for 1 millimolar solutions of these ions. The points shown were calculated using Fig. 1 and equation 15. Values for the diffusion coefficients at infinite dilution[13] were used in these calculations. The lower currents observed for lead before the peak are due to a decrease in diffusion coefficient since lead chloride complexes are present[14] at these concentrations. The currents are higher than theory beyond the peak because of the convection caused by density gradients at the electrode surface. Spherical electrodes seem to be more sensitive to stirring effects of this sort than cylindrical electrodes.[5] The rate of voltage change used in these experiments was 0.01389 volt/sec.

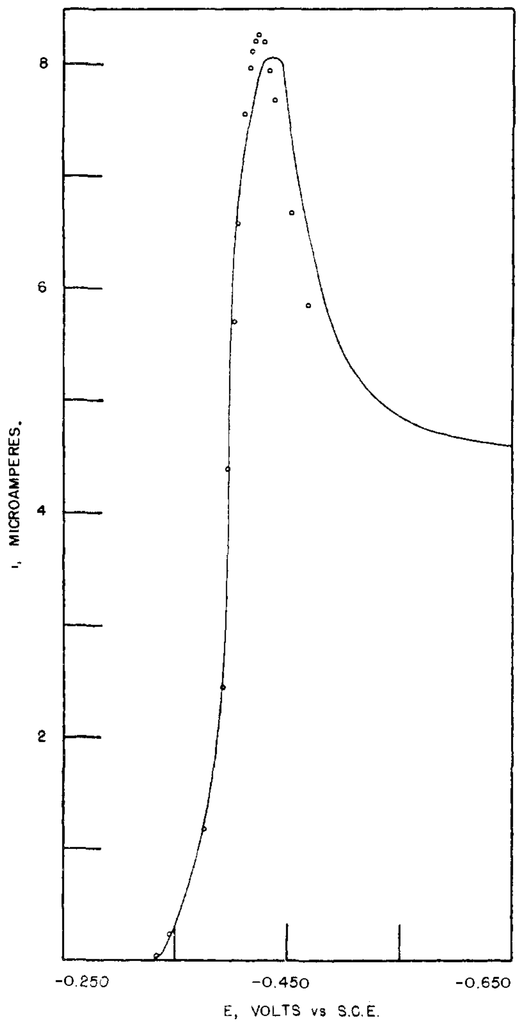

Fig. 3.—Current-voltage curve for the reduction of 1.00 m*M* Pb^{++} in 0.1 *M* KCl: line, exptl.; points, theoretical.

Current-Concentration Relationship.—Since the differential $\partial C_O(r_o,t)/C_O^0$ is independent of the bulk concentration of substance O, a linear relation between current and bulk concentration is predicted by equation 15 (Fig. 4). The lower peak current for lead at higher concentrations again indicates the decrease in D_O due to complex formation.

Effect of r_o.—The effect of the electrode radius was studied while holding the other experimental parameters constant by catching 2 or 3 drops of mercury on the gold wire electrode. Since only a very small gold surface was exposed, it was not possible to make very large electrodes. Current-voltage curves were obtained on 1 millimolar thallous solutions using 1 and 2 drops of mercury and on 0.6 millimolar lead solutions using 1 and 3 drops. The results are shown in Fig. 5 where the

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(13) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York, N. Y., 1952, p. 52.

(14) P. Papoff, L. Riccoboni and M. Caliumi, *Gazz. chim. ital.*, **85**, 69 (1955).

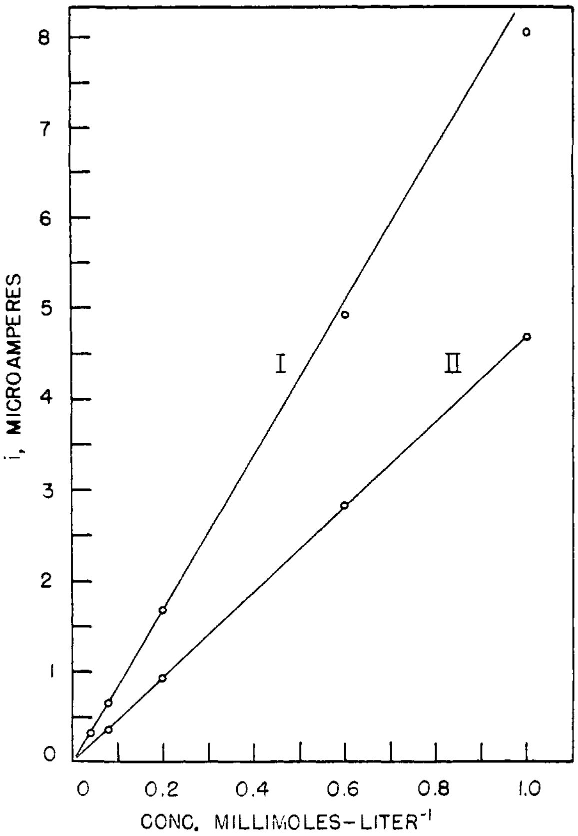

Fig. 4.—Peak current as a function of concentration: I, Pb^{++}; II, Tl^{+}; both in 0.1 M KCl.

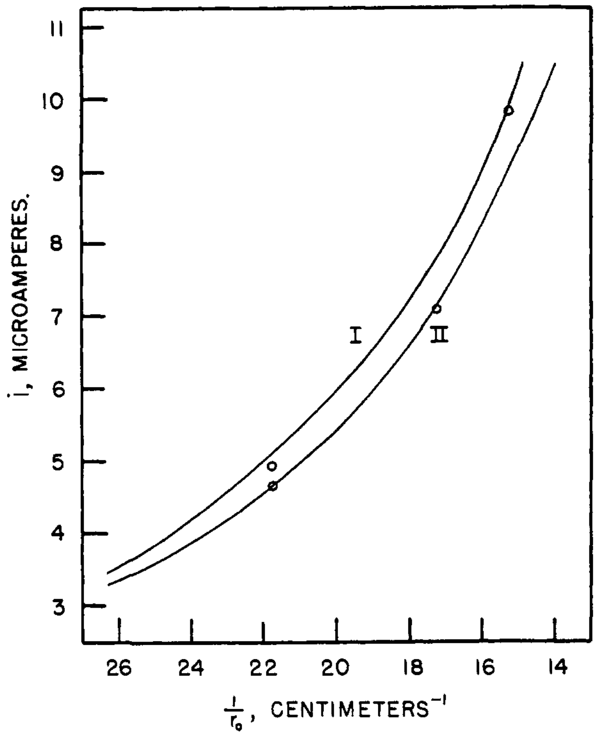

Fig. 5.—Peak current as a function of electrode radius: I, 0.60 mM Pb^{++}; II, 1.00 mM Tl^{+}; both in 0.1 M KCl; lines, theoretical; points, exptl.

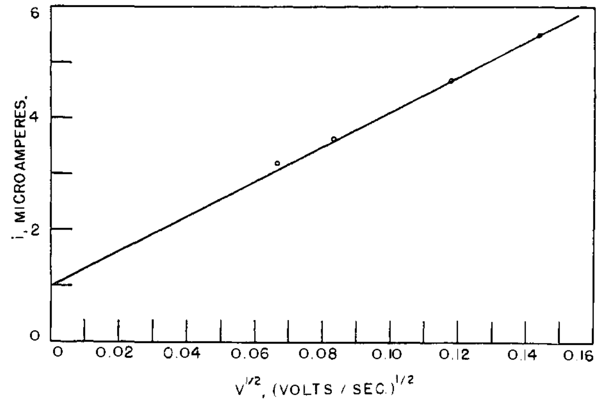

Fig. 6.—Peak current as a function of rate of voltage change, 1.00 mM Tl^{+} in 0.1 M KCl: line, theoretical; points, exptl.

lines were obtained from equation 15 and Fig. 1 and the points are experimental.

Effect of v.—Current–voltage curves were obtained for a 1 millimolar thallous solution at 4 different rates of voltage change. The results are shown in Fig. 6 where the line is theoretical and the points are experimental. The deviation at very low rates of voltage change is due to convection at the electrode surface. It should be noted in connection with Fig. 6 that convection becomes important at low rates of voltage change, and not at high rates as implied by Nicholson.[5]

Effect of n, D_O and D_R.—The independent variation of these parameters could not be studied. The effect of n and D_O can be seen in Fig. 1, however, and since accurate current–voltage curves were constructed for both one and two electron reactions involving ions with different diffusion coefficients, the theory is considered to hold satisfactorily. The value of D_R does not affect the peak current or the shape of the curve, but merely shifts the curve along the voltage axis, 30 mv. for each 10-fold change in D_R.

Conclusions.—The reproducibility of the current–voltage curves obtained with stationary spherical mercury electrodes is excellent. This fact combined with the ease and rapidity of obtaining curves indicates that this electrode will be extremely useful in analytical chemistry. A report on the analytical applications of this method is now in preparation.

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