

TABLE II  
 X-RAY DIFFRACTION DATA ON SULFUR SAMPLES

Monoclinic after 24 hr. <i>d</i> ( <i>I</i> / <i>I</i> <sub>1</sub> )		Pure orthorhombic <sup>2</sup> <i>d</i> ( <i>I</i> / <i>I</i> <sub>1</sub> )		Monoclinic after 24 hr. <i>d</i> ( <i>I</i> / <i>I</i> <sub>1</sub> )		Pure orthorhombic <sup>2</sup> <i>d</i> ( <i>I</i> / <i>I</i> <sub>1</sub> )	
		7.62	6			1.959	5
		5.75	10	1.906	25	1.901	8
		4.17	1	1.829	6	1.823	8
4.11	14	4.06	16			1.783	3
3.90	100	3.85	100	1.760	7	1.757	7
		3.56	7	1.726	12	1.725	13
3.48	37	3.45	19			1.696	6
3.36	38	3.34	31			1.668	1
3.24	76	3.22	39	1.649	8	1.649	3
3.14	59	3.11	21			1.622	8
		3.09	15	1.607	12	1.604	5
		2.85	15			1.561	2
		2.68	3			1.535	3
2.63	8	2.62	11	1.531	8	1.529	2
		2.57	5			1.499	1
		2.50	9			1.474	3
2.43	54	2.43	10			1.457	2
2.39	10	2.38	9			1.437	4
		2.29	4			1.418	4
2.15	8	2.14	3			1.388	2
2.13	16	2.11	14			1.351	3
1.996	35	1.988	3			1.305	2
						1.279	2

not be expected for the two samples for the same reason.

In view of the recent experiments of Hartshorne and co-workers on the rate of transformation of monoclinic to rhombic sulfur,<sup>13</sup> it would appear certain that the conversion to orthorhombic sulfur should be complete in 24 hr. It would seem possible that the rate of this conversion may be increased by the X-ray irradiation. It has been shown that this is the case for the transformation

(13) N. H. Hartshorne and M. Thackray, *J. Chem. Soc.*, 2122 (1957), and earlier papers.

of plastic sulfur to the rhombic form<sup>14</sup> and more recently it has been reported that rhombohedral sulfur (S<sub>6</sub>) is converted to a mixture of plastic and orthorhombic sulfur on exposure to X-rays.<sup>15</sup>

In some further experiments in which crystallization of the melted sample was induced by various methods (touching with a spatula, tapping the side of the holder, etc.) various anomalous patterns were obtained which could not be indexed as completely, using the monoclinic cell constants. We have not yet been able to assess completely the significance of these results. Whenever the sample was allowed to crystallize undisturbed, however, reproducible patterns were obtained.

**Acknowledgment.**—The authors express their appreciation to the Texas Gulf Sulphur Co., Newgulf, Texas for a fellowship to J. S. K. in partial support of this work.

### Experimental

Sulfur was purified by the method used in the previous paper.<sup>2</sup> Diffraction patterns were obtained on a North American Philips X-ray diffractometer using Cu K $\alpha$  radiation. In the tables, *d* is the interplanar spacing in Å. calculated from the Bragg law:  $d = \lambda/2 \sin \theta$  where  $\lambda$  is the wave length of radiation used = 1.540 Å. and  $\theta$  is the angle of diffraction. (*I*/*I*<sub>1</sub>) is the relative intensity in % based on the most intense line taken as 100 where *I*<sub>1</sub> is the strongest line and *I* is the intensity of the respective line.

Values for  $Q_{\text{obsd}}$  were obtained from the relationship<sup>16a</sup>:  $Q_{\text{obsd}} = 1/d^2$ . The following relationship for monoclinic crystals (second setting) was used to compute  $Q_{\text{obsd}}$  values<sup>16b</sup>

$$Q_{\text{calcd}} = (1/d_{hkl})^2 = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta}$$

where  $a = 10.90$ ,  $b = 10.96$ ,  $c = 11.02$  and  $\beta = 83^\circ 16'$  as given by Burwell.<sup>6</sup>

(14) H. Müller and E. Schmid, *Monatsh. Chem.*, **85**, 719 (1954).

(15) J. Donohue, A. Caron and E. Goldish, *Nature*, **182**, 518 (1958).

(16) D. V. Azaroff and M. J. Buerger, "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, (a) p. 274, (b) p. 49.

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## Voltammetry with Linearly Varying Potential: Case of Irreversible Waves at Spherical Electrodes

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RECEIVED SEPTEMBER 20, 1958

The theory of voltammetry with linearly varying potential has been extended to the case of irreversible electrode reactions at spherical electrodes. Theoretical current-voltage curves were constructed from the results of a numerical calculation which assumed a first-order electrode reaction occurring at potentials where the rate of the back reaction is negligible. The curves make it possible to determine the kinetic parameters of the electrode reaction from an experimental irreversible wave. Effect of variation of any of the experimental parameters was also considered. The theory was checked by comparison with current-voltage curves obtained for the reduction of iodate ion.

In the course of recent work on the analytical applications of the hanging mercury drop electrode using the techniques of voltammetry with linearly varying potential,<sup>2-4</sup> irreversible reactions were encountered which could not be interpreted by the theory for diffusion currents at spherical

electrodes developed by Frankenthal and Shain<sup>5</sup> and by Reinmuth.<sup>6</sup> These irreversible waves are characterized by peaks which are lower and which span an unusually wide range of potentials. Both of these effects are drawbacks from an analytical point of view. The fact that these kinetic effects can be observed, however, indicates that the method may be of use in the investigation of slow electrode processes.

(1) Based in part on the Ph.D. thesis of Richard D. DeMars, University of Wisconsin, 1958. General Electric Fellow, 1957-1958.

(2) J. W. Ross, R. D. DeMars and I. Shain, *Anal. Chem.*, **28**, 1768 (1956).

(3) R. D. DeMars and I. Shain, *ibid.*, **29**, 1825 (1957).

(4) K. J. Martin and I. Shain, *ibid.*, **30**, 1808 (1958).

(5) R. P. Frankenthal and I. Shain, *THIS JOURNAL*, **76**, 2969 (1956).

(6) W. H. Reinmuth, *ibid.*, **79**, 6358 (1957).

Delahay<sup>7</sup> has treated these irreversible waves obtained with voltammetry with linearly varying potential for the case of a plane electrode. This theory can be applied to a spherical electrode, provided that the rate of voltage change is fast enough. At the lower rates of voltage change normally used in analytical work, the spherical nature of the electrode must be considered.

### Theory

Consider the first-order reduction of a substance O to a substance R, under the conditions that the only way substance O can reach the electrode surface is by means of diffusion, that the voltage varies linearly with time, that the electrode is a sphere and that the rate of the back reaction (oxidation of R) is negligibly low at potentials where the forward reaction proceeds. 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<sup>8</sup>

$$\frac{\partial C_0(r,t)}{\partial t} = D_0 \left[ \frac{\partial^2 C_0(r,t)}{\partial r^2} + \frac{2}{r} \left( \frac{\partial C_0(r,t)}{\partial r} \right) \right] \quad (1)$$

where  $C_0$  is the concentration of substance O at the electrode surface,  $r$  is the distance from the center of the electrode,  $t$  is the time and  $D_0$  is the diffusion coefficient of substance O. This equation must be solved for certain initial and boundary conditions.

The initial condition is that the concentration of substance O is uniform throughout the solution at time zero

$$C_0(r,t) = C_0^* \text{ at } t = 0 \quad (2)$$

where  $C_0^*$  is the bulk concentration of substance O.

The first boundary condition follows from the assumption that semi-infinite diffusion takes place

$$C_0(r,t) \rightarrow C_0^* \text{ as } r \rightarrow \infty \quad (3)$$

The second boundary condition equates the flux of substance O at the electrode surface to the rate of the electrode reaction

$$D_0 \frac{\partial C_0(r,t)}{\partial r} = k_t C_0(r,t) \text{ at } r = r_0 \quad (4)$$

The rate constant is a function of potential<sup>9</sup>

$$k_t = k_s \exp \left[ - \frac{\alpha n_a F}{RT} (E - E^0) \right] \quad (5)$$

where  $k_s$  is the rate constant at a potential equal to  $E^0$ , the standard electrode potential for the oxidation-reduction couple involved in the rate-determining step,  $n_a$  is the number of electrons involved in the rate-determining step,  $\alpha$  is the electron transfer coefficient and  $R$ ,  $T$  and  $F$  have the usual significance.

The potential, in turn, is a function of time

$$E = E_i - vt \quad (6)$$

where  $E$  is the electrode potential,  $E_i$  is the potential at zero time and  $v$  is the rate of voltage change in volts per second. Thus, the second boundary condition becomes (at  $r = r_0$ )

$$D_0 \left( \frac{\partial C_0(r,t)}{\partial r} \right) = C_0(r,t) k_s \exp \left[ - \frac{\alpha n_a F}{RT} (E_i - E^0 - vt) \right] \quad (7)$$

**Method of Solution.**—The presence of the product of two time dependent terms on the right

(7) P. Delahay, *THIS JOURNAL*, **75**, 1190 (1953).

(8) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 58.

(9) Ref. 8, p. 60.

side of equation 7 prevents the application of the Laplace Transform to this problem.<sup>10</sup> The application of the numerical method used by Delahay for plane electrodes<sup>7</sup> leads, in this case, to a complex numerical integration in two variables. A finite difference method thus was chosen as the most promising way to obtain a solution to this problem. A central difference method developed by Crank and Nicholson<sup>11,12</sup> was used here. The details will be found in the Appendix.

The results of this type of calculation are numerical values of a function of the concentration of substance O at the electrode surface at various times. These data are obtained in terms of the non-dimensional variables  $U$ ,  $X$  and  $T$  where

$$U = \frac{C_0(r,t)}{C_0^*} (1 + X) \quad (8)$$

$$X = \frac{r - r_0}{r_0} \quad (9)$$

$$T = \frac{D_0 t}{r_0^2} \quad (10)$$

The current then can be calculated from equation 7 which now has the form

$$i = nFA C_0^* k_s \exp \left[ - \frac{\alpha n_a F}{RT} (E_i - E^0) \right] U(O,T) \exp \left( \frac{\alpha n_a F v t}{RT} \right) \quad (11)$$

The term  $U(O,T)$ , a function of the concentration of substance O at the electrode surface, decreases with time. Simultaneously, the exponential increases in value, and the result is the characteristic peaked current voltage curve. Typical results of such a calculation are shown in Fig. 1.

### Experimental

**Calculations.**—All calculations for the theoretical current voltage curves were made on the International Business Machines Corporation Type 704 Electronic Data Processing Machine.<sup>13</sup> All theoretical calculations are based on a set of standard values for the various parameters and, unless otherwise indicated, the experimental results have been reduced to the same basis:  $r_0 = 0.0600$  cm.,  $D_0 = 1.00 \times 10^{-5}$  cm.<sup>2</sup>/sec.,  $k_s = 1.00 \times 10^{-5}$  cm./sec.,  $\alpha n_a = 0.50$  and  $v = 0.030$  volt/sec. ( $E_i - E^0$ ) was arbitrarily selected equal to  $+0.200$  volt.

**Apparatus.**—The cell assembly, sweep generator, d.c. bias and load resistor circuits were the same as used previously.<sup>2</sup> The voltage drop across the load resistor was recorded directly as a function of time on a Leeds and Northrup Type G Speedomax recorder (1 mv. full scale, 1 second response). The cell and reference electrode were thermostated at  $25.0 \pm 0.1^\circ$  for all work.

**Materials.**—All chemicals were reagent grade and were used without further purification. Solutions were prepared with triply distilled water. In each case the solution contained 0.1 M potassium chloride as indifferent electrolyte and was buffered to pH 4.7 with 0.1 M acetic acid–0.1 M sodium acetate; to pH 7.2 with 0.1 M sodium dihydrogen phosphate–0.1 M disodium hydrogen phosphate; or to pH 12.3 with 0.1 M disodium hydrogen phosphate–0.1 M trisodium phosphate. Linde high purity nitrogen was used to remove oxygen from the solutions.

### Results and Discussion

The equation defining the theoretical current-voltage curves (equation 11) contains the product

(10) R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Co., New York, N. Y., 1944.

(11) J. Crank, "The Mathematics of Diffusion," Oxford University Press, London, 1956, p. 189–190.

(12) J. Crank and P. Nicholson, *Proc. Cambridge Phil. Soc.*, **43**, 50 (1947).

(13) The use of computer facilities donated to the University of Wisconsin by International Business Machines Corporation through the Midwest Universities Research Association is gratefully acknowledged.

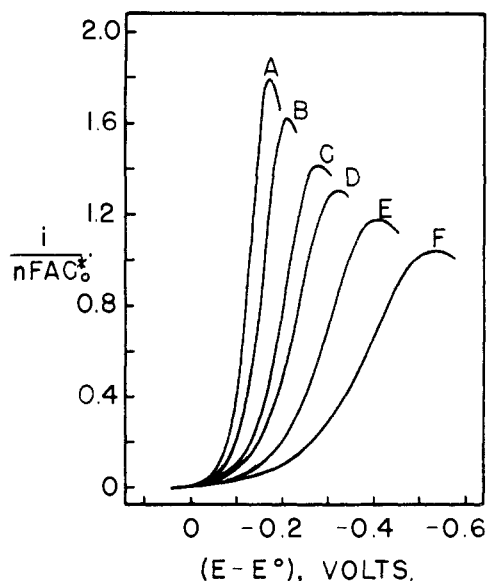


Fig. 1.—Theoretical curves of the function  $i/nFAC^*_o$  vs. potential at various values of  $\alpha n_a Fv/RT$ .

For all curves,  $i$  is in microamperes, and  $C^*_o$  in moles/liter.

Curve	$\alpha n_a$	$\alpha n_a Fv/RT$
A	1.0	1.1680
B	0.8	0.9345
C	.6	.7009
D	.5	.5804
E	.4	.4672
F	.3	.3504

of several terms which are complex functions of each other. Thus, a change in any one term will result in a complex variation of the current, and it is not possible to obtain an equation for the current-voltage curve which will permit an unambiguous calculation of the kinetic parameters or the current. It is necessary to determine these quantities for a given system by means of a comparison of the experimental curves with theoretical curves calculated at various values of the parameters.

**Shape and Position of the Current-Voltage Curve.**—By plotting the data as the function  $i/nFAC^*_o$  versus potential, equation 11 indicates that the shape of the curve and its position on the potential axis will be determined by the quantity

$$U(O,T)k_s \exp \left[ -\frac{\alpha n_a F}{RT} (E_i - E^0) \right] \exp \left( \frac{\alpha n_a Fvt}{RT} \right)$$

If an initial potential is selected which is sufficiently anodic, variations of  $\alpha n_a$  in the term  $\exp \left[ -\frac{\alpha n_a F}{RT} (E_i - E^0) \right]$  will have little effect on the shape of the current-voltage curve and will result only in a shift along the potential axis. Similarly, changes in  $k_s$  will merely shift the curve along the potential axis (provided  $k_s$  is less than about  $10^{-3}$  cm./sec. as originally assumed when the back reaction was ignored).

The shape of the curve is determined by the quantity  $U(O,T) \exp(\alpha n_a Fvt/RT)$ . Although  $U(O,T)$  is a function of the radius of the electrode, the diffusion coefficient of substance O, and each term in the exponential, the shape of the curve is determined primarily by the exponential. Thus  $\alpha n_a$  can be determined for an experimental system by a comparison of the experimental curves with the

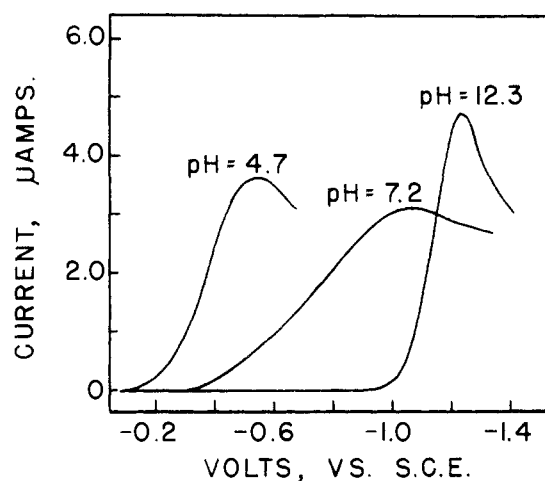


Fig. 2.—Experimental current-voltage curves for the reduction of  $1.00 \times 10^{-4} M$  iodate;  $v = 0.030$  volt/sec.,  $r_0 = 0.0676$  cm.

theoretical curves. A typical set of theoretical curves required for such a comparison is shown in Fig. 1, where, for the sake of demonstration, values of the exponential were chosen corresponding to particular values of  $\alpha n_a$ . For accurate work, large scale reproductions of Fig. 1 would be required, with curves plotted at much closer values of the exponential.<sup>14</sup> It should be noted that these curves are valid only for the particular values of the experimental parameters stated.

**Determination of the Kinetic Parameters for the Reduction of Iodate.**—The reduction of iodate ion serves as an excellent example of the effect of  $\alpha n_a$  on the shape of the current-voltage curve. Experimental curves (Fig. 2) show the effect of the changing kinetic parameters. In each case the iodate concentration was  $1.00 \times 10^{-4} M$ . By replotting these curves as the function  $i/nFAC^*_o$  against potential and comparing them to curves similar to Fig. 1, three values of  $\alpha n_a$  were obtained (Table I). For comparison, values of  $\alpha n_a$  obtained by Delahay<sup>15</sup> using a polarographic method are included. The value of the diffusion coefficient used to calculate  $\alpha n_a$  was  $1.09 \times 10^{-5}$  cm.<sup>2</sup>/sec.<sup>16</sup>

TABLE I  
 $\alpha n_a$  FOR THE REDUCTION OF IODATE AS A FUNCTION OF pH

pH	$\alpha n_a Fv/RT$	$\alpha n_a$ calcd.	$\alpha n_a$ Delahay
4.06			0.53
4.72	0.466	0.39	
6.03			.28
7.21	.304	.26	
7.82			.31
11.6			.63
12.3	.806	.69	

Obviously, the reduction of a substance as complex as iodate cannot be represented at any pH by the simple first-order reaction mechanism used in this derivation. For this reason, it is not possible

(14) Tables have been prepared containing values of  $i/nFAC^*_o$  as a function of potential for 24 values of  $\alpha n_a Fv/RT$ . Copies of this and other tables of pertinent information may be obtained on request from the senior author.

(15) P. Delahay, *THIS JOURNAL*, **73**, 5219 (1951).

(16) L. Meites, "Polarographic Techniques," Interscience Publishers, New York, N. Y., 1955, pp. 265-266.

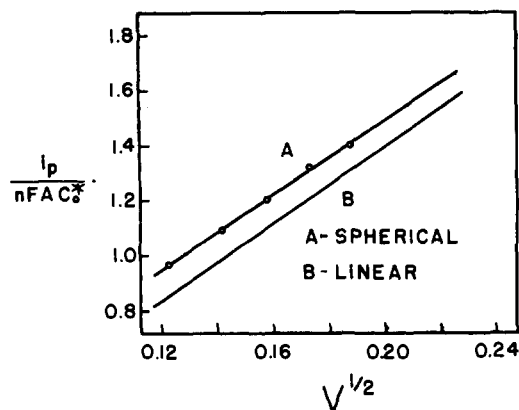


Fig. 3.— $i_p/nFAC^*v^{1/2}$  as a function of  $v^{1/2}$  for plane and spherical electrodes. Lines, theoretical; points, experimental for the reduction of  $1.00 \times 10^{-4} M$  iodate at a  $pH$  of 4.7.

to draw any conclusions regarding possible mechanisms for the electrode reaction from the value of  $\alpha n_a$  or its variation with  $pH$ . However, it was found that the experimental current-voltage curves could be exactly superimposed on the theoretical current-voltage curves calculated for the indicated values of  $\alpha n_a$ . Thus, these kinetic complications apparently have little effect on the shape of the current-voltage curves in this case.

**Effect of Rate of Voltage Change.**—Equation 11 indicates that varying the rate of voltage change will have the same effect as varying  $\alpha n_a$ . Thus Fig. 1 illustrates equally well the decrease in peak current and shift in potential encountered as  $v$  decreases, provided all other terms are held constant. In order to check the theoretical calculations, a series of current-voltage curves for the reduction of iodate ion at a  $pH$  of 4.7 were obtained at various rates of voltage change. The results are summarized in Fig. 3, curve A, where the line is theoretical and the points are experimental.

At faster rates of voltage change, the current should approach that for the same reaction at a plane electrode (Fig. 3, curve B). However, the convergence is not very rapid and  $v$  must be increased to the order of 3 volts per second in order for the error to be less than 1% when applying the theory for plane electrodes<sup>7</sup> to spherical electrodes of reasonable dimensions.

**Effect of Electrode Area and Radius.**—Since the area of a hanging mercury drop electrode cannot be varied without simultaneously varying the radius, the effect cannot be determined explicitly because of the dependence of  $U(O,T)$  on the radius and must be obtained by means of calculations such as outlined in the Appendix. The variation of the peak current with  $1/r_0$  for the reduction of iodate is shown in Fig. 4, where the line is theoretical and the points are experimental. The change in current for a given change in radius is less than that observed for a reversible system, as expected from the lower currents observed in general for these slow electrode reactions.

**Comparison to the Irreversible Case Involving Plane Electrodes.**—If the area of the electrode is held constant while the radius is increased, the current at a spherical electrode should approach that

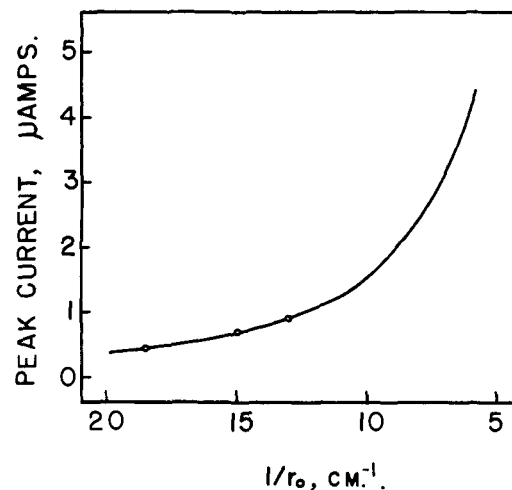


Fig. 4.—Peak current as a function of  $1/r_0$ , with variable area. Line, theoretical; points, experimental for the reduction of  $1.00 \times 10^{-4} M$  iodate at a  $pH$  of 4.7.

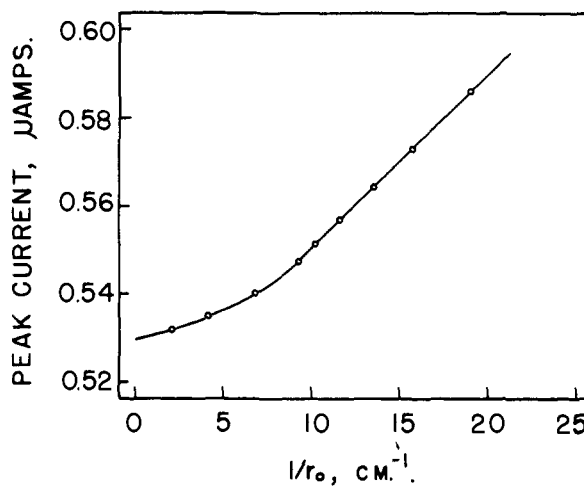


Fig. 5.—Theoretical peak current as a function of  $1/r_0$ , electrode area held constant.

for a plane electrode. Figure 5 shows a plot of peak current for a theoretical irreversible system against  $1/r_0$  with the area of the electrode held constant. The extrapolated value at  $1/r_0 = 0$  (i.e., a plane electrode) agrees with the value calculated for the same system at a plane electrode using Delahay's equation<sup>7</sup> to within 0.4%.

These data are also of use in construction of theoretical current-voltage curves for a real system. The curves in Fig. 1 were based on an electrode radius of 0.0600 cm. Since in a real case one has little control over the exact size of the electrode when choosing capillaries, it is necessary to convert all the points used to construct Fig. 1 to real values corresponding to the actual electrode radius. This may be done by obtaining the ratio of peak currents corresponding to the actual radius and 0.0600 cm. from Fig. 5 and then multiplying either the points of Fig. 1 or the experimental data by the appropriate value to convert all information to the same basis. For accurate work, a large scale reproduction of Fig. 5 would be required.<sup>14</sup>

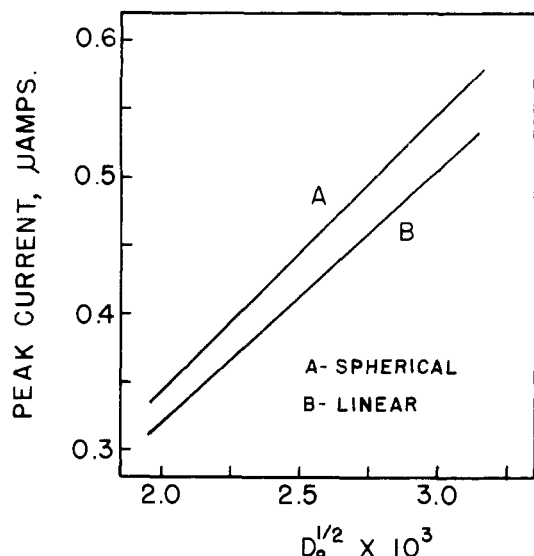


Fig. 6.—Theoretical peak current as a function of  $D_0^{1/2}$  for plane and spherical electrodes.

**Effect of Diffusion Coefficient.**—The current is also a complicated function of the diffusion coefficient, since  $U(O, T)$  is a function of the diffusion coefficient. Since the data in Fig. 1 are all based on a diffusion coefficient of  $1.00 \times 10^{-5}$  cm.<sup>2</sup>/sec., it is again necessary to convert all points to values for a real system by obtaining a ratio of peak currents corresponding to  $1.00 \times 10^{-5}$  and the actual diffusion coefficient and then reducing all data to the same basis. This ratio can be obtained from Fig. 6, where, for comparison, the variation of current with  $D^{1/2}$  for a plane electrode is included. For accurate work a large scale reproduction of curve A of Fig. 6 would be required.<sup>14</sup>

**Current-Concentration Relation.**—As expected (equation 11) the peak current is a linear function of the concentration, although the sensitivity is much lower than would have been expected had no kinetic effects been present. Table II demonstrates the linearity between peak current and concentration, and, at the same time, indicates the general reproducibility of these irreversible waves.

TABLE II  
PEAK CURRENT AS A FUNCTION OF CONCENTRATION FOR THE  
REDUCTION OF IODATE AT pH 4.7

Concn., moles/l.	Peak current, <sup>a</sup> μamp.	Av. % dev., %	$i_p$ / concn. <sup>b</sup>
$1.00 \times 10^{-4}$	3.83	0.8	38.3
$5.00 \times 10^{-5}$	1.86	.6	37.3
$2.00 \times 10^{-5}$	0.750	.6	37.5
$1.00 \times 10^{-5}$	.381	1.0	38.1
$5.00 \times 10^{-6}$	.184	1.4	37.2

<sup>a</sup> Average and average deviation of six determinations.  
<sup>b</sup> Microamperes/millimole/liter.

### Conclusion

The use of the method of voltammetry with linearly varying potential for the investigation of slow electrode processes is rather cumbersome, due to the lack of an explicit relation between all kinetic and experimental parameters. On the other hand, it is very easy to obtain the experimental data, since all kinetic information required can be taken from one current-voltage curve.

In addition, the theory presented here makes it possible to assess the effect of these kinetic parameters on the analytical applications of voltammetry with linearly varying potential, thus making the method an even more valuable analytical technique.

### Appendix

After transformation of the equations in terms of the new variables  $U$ ,  $X$  and  $T$  (eq. 8, 9 and 10) the problem becomes

$$\frac{\partial U}{\partial T} = \frac{\partial^2 U}{\partial X^2}, \quad r > r_0, \quad T > 0 \quad (12)$$

$$U = X + 1, \quad X > 0, \quad T = 0 \quad (13)$$

$$U \rightarrow \infty \text{ as } X \rightarrow \infty, \quad T > 0 \quad (14)$$

$$\frac{\partial U}{\partial X} = U[1 + Z \exp(YT)], \quad x = 0, \quad T > 0 \quad (15)$$

where

$$Z = \frac{k_s r_0}{D_0} \exp \left[ -\frac{\alpha n_a F}{RT} (E_t - E^0) \right] \quad (16)$$

and

$$Y = \frac{\alpha n_a F}{RT} \frac{r_0^2 V}{D_0} \quad (17)$$

Replacing both differentials in equation 12 by central differences at  $T + 1/2 \Delta T$  for the interval  $T + \Delta T$ ,<sup>11</sup> one obtains

$$U(X, T + \Delta T) = \frac{1}{4} [U(X + \Delta X, T + \Delta T) + U(X + \Delta X, T) + U(X - \Delta X, T + \Delta T) + U(X - \Delta X, T)] \quad (18)$$

This equation holds under the restriction that  $\Delta T/(\Delta X)^2 = 1$  and will be valid for all points in a rectangular  $X$  and  $T$  network except those points that lie on a boundary, provided  $\Delta X$  and  $\Delta T$  remain small enough.

The boundary points in the  $X$  direction can be determined by extending the network far enough so that the value of  $U$  does not change during the electrolysis. Representing this distance by  $m\Delta X$ , where  $m$  is a sufficiently large integer, each boundary point in the  $X$  direction will be of the form

$$U(m\Delta X, T) = 1 + m\Delta X \quad (19)$$

The boundary points in the  $T$  direction can be obtained by expressing equation 15 as a central difference in  $X$  and  $T$  and again in  $X$  and  $T + \Delta T$ . Combining these equations with equation 18 one obtains

$$U(O, T + \Delta T) = \frac{U(\Delta X, T + \Delta T) + U(\Delta X, T) - \Delta X U(O, T)[1 + Z \exp(YT)]}{2 + \Delta X \{1 + Z \exp[Y(T + \Delta T)]\}} \quad (20)$$

Each boundary point at  $X = 0$  will be of this form.

The problem now is to determine  $U$  as a function of  $X$  and  $T$  on a rectangular  $X$  and  $T$  network. For each increment in  $T$  there will be  $m$  simultaneous equations of which one will have the form of equation 19, one the form of equation 20 and  $m - 2$  the form of equation 18.

The procedure is started by calculating the points on the  $T = 0$  boundary using equation 13, obtaining values of  $U$  for the range  $X = 0$  to  $X = m\Delta X$ . Starting with these points, values of  $U$  on the  $T = T_1$  increment are guessed, using a quadratic extrapolation as a guide. The guessed values are then iterated using the formulas outlined above until all the answers along the  $T$  increment are self consistent. The procedure is

repeated until all the variations of  $X$  and  $T$  have been satisfied.

TABLE III

PEAK CURRENT AS A FUNCTION OF $\Delta T$			
$\Delta T \times 10^4$	$i_p$ ( $\mu\text{amp.}$ )	$\Delta i_p^a$	% error <sup>b</sup>
20.00	0.7440	0.1412	26.0
10.00	.8121	.0731	8.26
5.000	.8479	.0373	4.21
2.500	.8664	.0188	2.12
1.250	.8758	.0094	1.06
0.6250	.8805	.0047	0.53
0.3125	.8829	.0023	0.26
0.1563	.8841	.0011	0.13
0	.8852 <sup>c</sup>	0	0

<sup>a</sup> Difference between peak current at indicated value of  $\Delta T$  and peak current at  $\Delta T = 0$ . <sup>b</sup>  $(\Delta i_p/0.8852) \times 100\%$ . <sup>c</sup> Extrapolated.

This calculation is very time consuming and tedious and is not practical unless computer facili-

ties are available.<sup>17</sup> This is particularly so since the accuracy of the method depends on using small values of  $\Delta T$  to reduce the error. The convergence of the calculations for decreasing values of  $\Delta T$  was checked using the standard set of experimental and kinetic parameters (Table III).

As a compromise between accuracy and excessive machine time, a value of  $\Delta T = 0.3125 \times 10^{-4}$  was used in this work. The results can be considered accurate within about 0.3%.

**Acknowledgments.**—This work was supported in part by funds received from the United States Atomic Energy Commission under Contract No. AT(11-1)-64 and the Research Committee of the Graduate School of the University of Wisconsin with funds received from the Wisconsin Alumni Research Foundation.

(17) This problem was programmed for the IBM type 704 with the help of Mr. Lee F. Thompson of this Laboratory. It was Mr. Thompson's ability and patience which made this work possible.  
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[CONTRIBUTION NO. 1525 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY

## Conductance of Dilute Solutions of 1-1 Electrolytes<sup>1</sup>

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RECEIVED DECEMBER 24, 1958

The conductance of solutions of 1-1 electrolytes decreases with increasing concentration because the mobility of the ions is decreased due to the action of long range interionic forces and because the concentration of free ions decreases due to association increasing with concentration. A conductance equation based on these effects is derived; it is applicable to 1-1 electrolytes in solvents of dielectric constant greater than about 15, at concentrations up to that corresponding to  $\kappa a \approx 0.2$  ( $a$  = ionic diameter,  $\kappa$  = Debye-Hückel parameter). In solvents of high dielectric constant, the equation reduces to Onsager's limiting tangent while in solvents of low dielectric constant, it transforms into the classical Ostwald dilution law. In the intermediate range of dielectric constant, previously inaccessible to theoretical analysis, the equation describes conductance data in terms of three molecular parameters: the limiting conductance, the ion size and the association constant. Methods of applying the equation to experimental data are described.

The theory of the conductance of symmetrical electrolytes in dilute solutions now appears to be substantially complete; various parts of the derivation of the final equation are, however, scattered among a number of different publications.<sup>2-11</sup> The purpose of this paper is to present a summary derivation for the case of 1-1 electrolytes, unobscured by mathematical details, and to describe the analysis of conductance data by means of the theory.

Specific conductance, the experimentally observable quantity, is given by the ratio of current density to field strength  $X$  and is therefore proportion to  $\sum n_i e_i u_i$ , where  $n_i$  is the number of ions of species  $i$  per unit volume and  $e_i$  and  $u_i$  are, respectively, their charge and mobility. The equivalent conductance  $\Lambda$  is defined as the ratio of 1000 times

the specific conductance to the concentration  $c$  in equivalents per liter. Consequently

$$\Lambda \sim \sum \gamma_i u_i \quad (1)$$

where  $\gamma_i$  is the fraction of the ions of species  $i$  which actually contribute to transport of charge at a given concentration. The Debye-Hückel-Onsager theory assumes that  $\gamma_i$  equals unity and ascribes the decrease of  $\Lambda$  with increasing concentration to a decrease in mobility arising from the electrostatic forces between the ions. The mobility is found to be

$$u_i = (u_i^0 - \Delta u_i) (1 + \Delta X/X) \quad (2)$$

where  $u_i^0$  is the limiting mobility at infinite dilution,  $\Delta u_i$  is the electrophoretic counter-velocity<sup>12,13</sup> of the solvent and  $\Delta X$  is the braking relaxation field<sup>14,15</sup> which an ion creates by its motion. The asymmetry in the atmosphere of a moving ion also produces a virtual osmotic force  $\Delta P$  which slightly increases conductance,<sup>9</sup> and finally a correction must in general be made for the increase in static viscosity of the solution due to the presence of the ions.<sup>5</sup> Since both  $u_i^0$  and  $\Delta u_i$  are inversely proportional to viscosity, (2) becomes

$$u_i = (u_i^0 - \Delta u_i)(1 + \Delta X/X + \Delta P/X)/(1 + Fc) \quad (3)$$

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