

minimum in the TC vs. concentration isotherm (21)—correctly describes the data obtained. However, it seems unlikely that so many compounds would show maxima or minima in nitrogen but none of them would do so in Ar or CO<sub>2</sub>, while they do give positive and negative responses in these gases.

One possible alternative explanation is that a concentration gradient is established in the cell as a result of thermal diffusion between the cell wall and the hotter filament. This could result in a transfer of thermal energy across the gradient, the so-called Dufour effect (?). If so, it should be possible to eliminate this effect by increasing the turbulence in the cell. Preliminary investigation with such a cell indicates that this is so.

The lack of W peaks and the low cost of CO<sub>2</sub> suggest that it would be a better carrier gas than nitrogen for preparative work (and possibly even some analytical work). Some workers have reported collecting samples in CO<sub>2</sub> by freezing it to dry ice (9). Also, the wide variation in response values (positive and negative) might be useful for qualitative analysis of pure compounds. Further work with CO<sub>2</sub> and other carrier gases of low TC is planned.

#### ACKNOWLEDGMENT

The authors thank Floyd Fredricks for obtaining some of the data.

#### LITERATURE CITED

- (1) Bennett, L. A., Vines, R. G., *J. Chem. Phys.* **23**, 1587 (1955).
- (2) Bohemen, J., Purnell, J. H., *J. Appl. Chem.* **8**, 433 (1958).
- (3) Dal Nogare, S., Juvet, R. S., Jr., "Gas Liquid Chromatography," p. 192, Interscience, New York, 1962.
- (4) Dreisbach, R., compiler, "Physical Properties of Chemical Compounds," 3 Vols., American Chemical Society, Washington, D. C., 1955, 1959, 1961.
- (5) Hansen, R. S., Frost, R. R., Murphy, J. A., *J. Phys. Chem.* **68**, 2028 (1964).
- (6) Harvey, D., Morgan, G. O., in "Vapor Phase Chromatography—London, 1956," p. 74, D. H. Desty, ed., Academic Press, New York, 1957.
- (7) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids," p. 522, Wiley, New York, 1954.
- (8) Hoffmann, E. G., *ANAL. CHEM.* **34**, 1216 (1962).
- (9) Hornstein, I., Crowe, P., *Ibid.*, **37**, 170 (1965).
- (10) Jamieson, C. R., *J. Chromatog.* **3**, 464, 494 (1960); **4**, 420 (1960); **8**, 544 (1962); **15**, 260 (1964).
- (11) Keppler, J. G., Dijkstra, G., Schols, J. A., in "Vapour Phase Chromatography—London, 1956," p. 222, D.

- H. Desty, ed., Academic Press, New York, 1957.
- (12) Keulemans, A. I. M., Kwantes, A., Rijnders, G. W. A., *Anal. Chim. Acta* **16**, 29 (1957).
- (13) Littlewood, A. B., "Gas Chromatography," pp. 329–33, Academic Press, New York, 1962.
- (14) Madison, J. J., *ANAL. CHEM.* **30**, 1859 (1958).
- (15) Messner, A. E., Rosie, D. M., Argabright, P. A., *Ibid.*, **31**, 230 (1959).
- (16) Panson, A. G., Adams, L. M., *J. Gas Chromatog.* **2**, 164 (1964).
- (17) Pauschmann, H., *Z. Anal. Chem.* **203**, 16 (1964).
- (18) Purcell, J. E., Ettore, L. S., *J. Gas Chromatog.* **3**, 69 (1965).
- (19) Purnell, H., "Gas Chromatography," p. 286, Wiley, New York, 1962.
- (20) Rothman, A. J., Bromley, L. A., *Ind. Eng. Chem.* **47**, 899 (1955).
- (21) Schmauch, L. J., Dinerstein, R. A., *ANAL. CHEM.* **32**, 343 (1960).
- (22) Smith, B. D., Bowden, W. W., *Ibid.*, **36**, 82 (1964).
- (23) Spencer, H. M., *J. Am. Chem. Soc.* **67**, 1858 (1945).
- (24) Stuve, W., in "Gas Chromatography—1958," p. 178, D. H. Desty, ed., Academic Press, New York, 1958.
- (25) Verzele, M., *J. Chromatog.* **15**, 482 (1964).
- (26) Williams, A. F., Murray, W. J., *Talanta* **10**, 937 (1963).

RECEIVED for review April 7, 1965. Accepted July 22, 1965. Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 3, 1965.

# Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics

RICHARD S. NICHOLSON

Chemistry Department, Michigan State University, East Lansing, Mich.

► The theory of cyclic voltammetry has been extended to include electron transfer reactions which are described by the electrochemical absolute rate equation. Results of theoretical calculations made it possible to use cyclic voltammetry to measure standard rate constants for electron transfer. Thus, a system which appears reversible at one frequency may be made to exhibit kinetic behavior at higher frequencies, as indicated by increased separation of cathodic and anodic peak potentials. The standard rate constant for electron transfer is determined from this peak potential separation and frequency. The method provides an extremely rapid and simple way to evaluate electrode kinetics. The reduction of cadmium is used as an illustration.

DURING RECENT years a number of methods have been developed for the measurement of electrode reaction kinetics. In one sense, some of

these determine electrode reversibility indirectly by measuring the apparent standard rate constant for electron transfer from only cathodic (or anodic) polarization. In a few cases both cathodic and anodic polarization give consistent results (13). Many of the relaxation techniques developed for fast reactions have the disadvantage that small amplitude perturbations are used, and consequently differences or changes in mechanisms are not easily detected.

A method which overcomes this disadvantage and at the same time gives a direct estimate of reversibility is cyclic triangular wave voltammetry. Thus, the presence of homogeneous reactions in the mechanism is readily detected, and interpretation of results usually is simple. A direct estimate of electrode reversibility is provided, because the potentials at which oxidation and reduction occur are observed directly. For example, at low frequencies it may be possible with a given system that electrochemical equilibrium always is maintained at the electrode

surface. Under these conditions the separation of cathodic and anodic peak potentials is about  $60/n$  mv., and the reaction is reversible.

Clearly for this case no kinetic information about the electron transfer reaction can be obtained. However, if frequency is increased sufficiently, a point may be reached at which the kinetics of electron transfer become competitive with the rate of potential change. Under these conditions it may be possible to study the kinetics of the electrode reaction, and the separation of peak potentials should be a measure of the standard rate constant for electron transfer. Thus, at least in principle, one can estimate standard rate constants simply by observing cyclic polarograms on the oscilloscope, and then increasing the triangular wave frequency until the separation of peak potentials becomes greater than  $60/n$  mv. The standard rate constant then should be a calculable function of frequency at this peak potential separation. Unfortunately, there is no *a priori* way

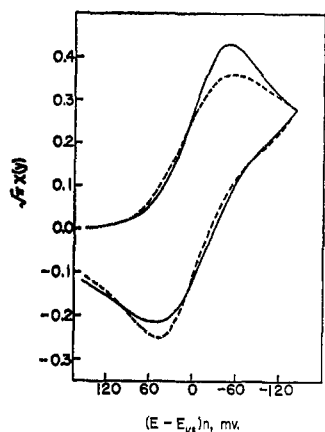


Figure 1. Cyclic polarograms showing effect of charge transfer coefficient,  $\alpha$

—  $\psi = 0.5; \alpha = 0.7$   
 .....  $\psi = 0.5; \alpha = 0.3$

to make this correlation because effects of concentration polarization can be treated only by mathematical analysis of the mass transport processes. Such an analysis is not available for the present case, and consequently applications of these ideas using cyclic voltammetry have been limited to simple statements that a given system appears to be reversible or irreversible (7, 10).

In the study of electrode reaction mechanisms, it often is useful to be able to obtain experimentally a rapid estimate of electron transfer rates. Because this appeared to be possible with cyclic voltammetry in the way just described, we have attempted a theoretical treatment of the problem which includes the effects of concentration polarization. Our primary objective was to determine if cyclic voltammetry could be used to provide rapid and reasonably accurate determinations of standard rate constants for electron transfer. Thus, the theoretical correlations between peak potentials, standard rate constant, and rate of potential scan have been emphasized, although other correlations are possible. A serious limitation of this approach would result if peak potential separations depended also on the charge transfer coefficient,  $\alpha$ . This would require an independent measure of  $\alpha$ , and make the method of little use in terms of the stated objectives. However, through proper selection of conditions, peak potential separations become nearly independent of  $\alpha$ .

Because there is neither theoretical nor experimental advantage to considering more than one cycle of the applied triangular wave, theoretical calculations have been limited to this case. Consideration also has been restricted to the case of *in situ* generation of the reduced form of the couple under investigation. This actually has two

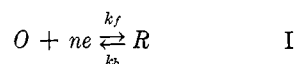
advantages. First, it reduces by one the number of independent variables in the theoretical calculations. Second, it has the experimental advantage of not requiring preparation of amalgams of known concentration for the study of reductions at mercury electrodes.

The method described can be applied to systems in which homogeneous chemical reactions precede or follow electron transfer provided such reactions are either rapid or slow compared to the standard rate constant for electron transfer. The cases in which these conditions are not met are easily detected from the form of the experimental current-voltage curves (11).

The reduction of cadmium is used as an illustration of the method developed here. Application to other systems is in progress and will be reported elsewhere.

### THEORY

We assume the following mechanism:



There  $k_f$  and  $k_b$  are heterogeneous rate constants of the electron transfer, and are assumed to be functions of potential as expressed through the electrochemical absolute rate equation. The time dependence of electrode potential is the form of an isosceles triangle. System I is assumed to be initially in equilibrium. Both  $O$  and  $R$  are to be soluble either in the electrode or solution phase.

To account for concentration polarization, diffusion to a plane electrode is assumed to be the only source of mass transport. Mathematical formulation of this problem follows

$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} \quad (1)$$

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} \quad (2)$$

$$t = 0, x \geq 0$$

$$C_O = C_O^*; C_R = C_R^* \quad (3)$$

$$t \geq 0$$

$$\lim_{x \rightarrow \infty} C_O = C_O^*; \lim_{x \rightarrow \infty} C_R = C_R^* \quad (4)$$

$$t \geq 0, x = 0$$

$$D_O \frac{\partial C_O}{\partial x} + D_R \frac{\partial C_R}{\partial x} = 0 \quad (5)$$

$$D_O \frac{\partial C_O}{\partial x} = k_f C_O - k_b C_R \quad (6)$$

Undefined terms have their usual significance (11).

With the electrochemical absolute rate equation, Equation 6 can be transformed to

$$D_O \frac{\partial C_O}{\partial x} = k_s e^{-\frac{\alpha n F}{RT} (E - E^\circ)} \times \left[ C_{O_x=0} - e^{\frac{n F}{RT} (E - E^\circ)} C_{R_x=0} \right] \quad (7)$$

There  $E$  is the electrode potential;  $E^\circ$  is the standard potential;  $k_s$  is the standard rate constant at  $E = E^\circ$ ;  $\alpha$  is the transfer coefficient; and the remaining terms have their usual significance.

The potential in Equation 7 for the first scan (reduction) of the triangular wave takes the form

$$E = E_i - vt \quad (8)$$

and for the second scan (oxidation)

$$E = E_i + vt - 2v\lambda \quad (9)$$

Here,  $E_i$  is the initial equilibrium potential,  $v$  is  $dE/dt$ , and  $\lambda$  is the period of the triangular wave.

If Equations 7, 8, and 9 are combined the result is

$$D_O \frac{\partial C_O}{\partial x} = k_s (C_O^*/C_R^*)^{-\alpha} [S_\lambda(t)]^{-\alpha} \times (C_{O_x=0} - (C_O^*/C_R^*) S_\lambda(t) C_{R_x=0}) \quad (10)$$

The function  $S_\lambda(t)$  is defined as

$$S_\lambda(t) = \begin{cases} e^{-at} & t < \lambda \\ e^{at} - 2a\lambda & t > \lambda \end{cases} \quad (11)$$

where

$$a = nFv/RT \quad (12)$$

Equation 10 is the final form of boundary condition 6.

By application of Laplace transform methods the above boundary value problem can be converted to the following dimensionless linear integral equation with variable coefficients

$$\frac{\chi(y) [\gamma (C_O^*/C_R^*) S_{a\lambda}(y)]^\alpha}{\psi} = 1 - S_{a\lambda}(y) - \int_0^y \frac{\chi(z) dz}{\sqrt{y-z}} - \gamma (C_O^*/C_R^*) S_{a\lambda}(y) \int_0^y \frac{\chi(z) dz}{\sqrt{y-z}} \quad (13)$$

To make Equation 13 dimensionless the following substitutions and changes of variable were made:

$$\gamma = (D_O/D_R)^{1/2} \quad (14)$$

$$y = at \quad (15)$$

$$\chi(y) = D_O \frac{\partial C_O}{\partial x} / C_O^* \sqrt{\pi a D_O} \quad (16)$$

$$\psi = \gamma^\alpha k_s / \sqrt{\pi a D_O} \quad (17)$$

For large values of  $\psi$  (large  $k_s$  or small  $v$ ) Equation 13 becomes independent of  $\psi$  and  $\alpha$  and reduces to the

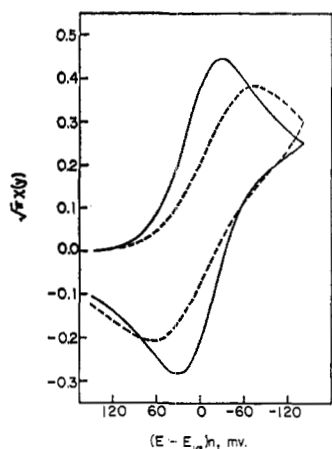


Figure 2. Cyclic polarograms showing effect of charge transfer parameter,  $\psi$

—  $\psi = 7.0; \alpha = 0.5$   
 .....  $\psi = 0.25; \alpha = 0.5$

corresponding equation for reversible (Nernstian) electron transfer (11). Likewise, as  $\psi$  approaches zero, Equation 13 approaches the case for totally irreversible electron transfer (11). The intermediate case, which is of interest here, is described completely by Equation 13.

#### Solution of Integral Equation.

Equation 13 cannot be solved analytically. Although a solution in the form of an infinite series can be obtained, series solutions for more than one-half cycle become hopelessly complicated. The only practical approach, therefore, which for the present case can be applied without loss of generality, is numerical evaluation. We have used a method described previously (11). Several other methods also are possible, and apparently the method used by DeVries and VanDalen (6) involves less computational time for comparable accuracy (5).

Solutions of Equation 13 were independent of values of  $\gamma(C_O^*/C_R^*)$  provided  $\gamma(C_O^*/C_R^*)$  was greater than  $e^{6.5}$ . This corresponds to the experimental fact that if  $R$  is absent initially and the voltage scan is begun at potentials anodic of the polarographic wave, current-voltage curves are independent of the exact initial potential selected. All calculations have been performed using  $\gamma(C_O^*/C_R^*) = e^{6.5}$ .

With this simplification it was possible to calculate numerically current-voltage curves. These curves depended on three variables,  $\psi$ ,  $\alpha$ , and  $\lambda$ . It has been shown previously that  $\lambda$  affects only the anodic wave, and that there the effect on anodic peak potentials is quite small (11). This is particularly the case when switching potentials close to the cathodic peak are avoided [ $(E_\lambda - E_{1/2})_n > 90$  mv.]. All calculations reported here are based on a value of  $(E_\lambda - E_{1/2}) = 141/n$  mv. Thus,

calculated current-voltage curves could be interpreted on the basis of only two variables,  $\psi$  and  $\alpha$ .

**Results of Calculations.** When  $\psi$  becomes sufficiently large ( $k_s$  large, or  $\nu$  small), current-voltage curves calculated from Equation 13 are independent of the kinetic parameters  $\psi$  and  $\alpha$ . For this case results are identical to ones obtained previously where the electron transfer was assumed to be Nernstian (11). This limit occurs when  $\psi > 7$ , which is in good agreement with calculations of Matsuda and Ayabe (8).

When  $\psi < 7$ , the current-voltage curves are dependent on both the values of  $\psi$  and  $\alpha$ . For sufficiently small  $\psi$  ( $k_s$  very small or  $\nu$  very large), the back reaction for electron transfer is unimportant, and the processes for oxidation and reduction can be treated separately as the totally irreversible case. Thus, results calculated from Equation 13 for  $\psi = 0.001$  agree exactly with previous calculations in which electron transfer was assumed to be totally irreversible (11). This also is in agreement with calculations of Matsuda and Ayabe (8).

For intermediate values of  $\psi$  (a region sometimes referred to as quasi-reversible), the form of the current-voltage curves depends markedly on the exact values of  $\psi$  and  $\alpha$ .

The dependence on  $\alpha$  is shown in Figure 1 where curves for two values of  $\alpha$  and  $\psi = 0.5$  are compared. Generally, the results are as expected, and  $\alpha$  affects the symmetry of the curves in two ways. For  $\alpha < 0.5$ , the cathodic peak is more rounded than the anodic peak. This broadening also results in a lowering of peak height. For  $\alpha > 0.5$ , the converse holds.

The second effect involves a slight displacement of the waves along the potential axis. For example, as  $\alpha$  decreases, the cathodic peak is displaced cathodically. At least for the data used to construct Figure 1, the effect is slight. Moreover, as the cathodic peak shifts cathodically with decreases of  $\alpha$ , the anodic peak also shifts cathodically. Therefore, in terms of differences of peak potentials,  $\Delta E_P$ , changes in  $\alpha$  tend to cancel. Thus, values of  $\Delta E_P$  for the present case are nearly independent of  $\alpha$  in the range  $0.3 < \alpha < 0.7$ . The extent to which this holds depends on the exact value of  $\psi$ . Naturally, as  $\psi$  increases the approximation becomes increasingly good. Thus, for  $\psi = 0.5$  ( $\Delta E_P$  ca.  $105/n$  mv.), there is about a 5% variation of  $\Delta E_P$  for  $\alpha$  changing from 0.3 to 0.7. For  $\psi < 0.5$  the variation is greater, and causes about a 20% change of  $\Delta E_P$  for  $\psi = 0.1$ . However, for this case the curves have deviated considerably from the reversible case ( $\Delta E_P$  ca.  $200/n$  mv. compared with  $60/n$  mv. for the reversible case).

The dependence on  $\psi$  of theoretical current-voltage curves is shown in

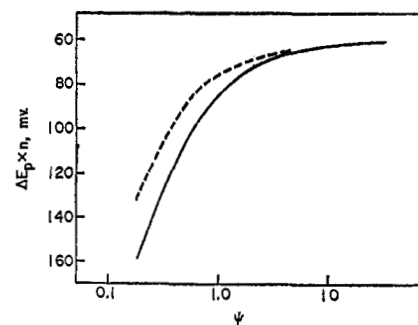


Figure 3. Working curve showing variation of peak potential separation with  $\psi$

—  $\psi$  is defined by Equation 17  
 .....  $\psi$  is defined by Equation 18

Figure 2 where curves for two values of  $\psi$  and  $\alpha = 0.5$  are compared. The curve for  $\psi = 7$  corresponds (within about 1%) to the reversible case and is independent of  $\alpha$ . As  $\psi$  decreases two effects can be distinguished from Figure 2. Both cathodic and anodic peaks are lowered, and both waves appear drawn out—i.e., they occur over a wider potential range. Thus, the cathodic wave is shifted cathodically and the anodic wave is shifted anodically. This naturally results in an increased separation of cathodic and anodic peak potentials.

The exact variation of peak potentials with  $\psi$  is shown in Figure 3, and the data used to construct Figure 3 are in Table I. In Figure 3  $\Delta E_P \times n$  ( $n$  is the number of electrons) is plotted as a logarithmic function of  $\psi$ . Data for Figure 3 were obtained using  $\alpha = 0.5$ , but from the previous discussion the curve of Figure 3 is nearly independent of  $\alpha$ . As would be expected the curve approaches linearity for small  $\psi$  [see Equation for peak potential of irreversible waves (11)]. In this region  $\Delta E_P$  is markedly dependent on  $\alpha$ .

Table I. Variation of Peak Potential Separations with Kinetic Parameters for Cyclic Voltammetry

$\psi^a$	$\Delta E_P \times n,^b$ mv.
20	61
7	63
6	64
5	65
4	66
3	68
2	72
1	84
0.75	92
0.5	105
0.35	121
0.25	141
0.1	212

<sup>a</sup> See Equation 17.

<sup>b</sup> For  $\alpha = 0.5$ .

It should be noted that the theoretical curves of Figure 2 could correspond either to two different systems having different electron transfer rates—and observed at the same scan rate—or to the same system observed at two different scan rates. This is exactly the behavior anticipated in the discussion at the beginning and provides the basis of using cyclic voltammetry to estimate electron transfer rates. Figure 3 gives quantitatively the relationship between peak potentials, scan rate, and electron transfer rate.

To use Figure 3 in this way a scan rate is selected which gives an experimental  $\Delta E_p$  in the useful range of Figure 3. From the experimental  $\Delta E_p \times n$ , the corresponding value of  $\psi$  is obtained from Figure 3. If scan rate is known,  $k_s$  can be calculated from Equation 17. Actually, to apply Equation 17 rigorously  $\gamma^\alpha$  also must be known. However, except for the unusual case of very large differences between  $D_o$  and  $D_R$ , the quantity  $\gamma^\alpha$  is very near unity, regardless of  $\alpha$ .

Although the useful working range of Figure 3 is fairly restricted, this is not a serious limitation, especially if rough estimates of  $k_s$  are all that is required. This is so because the wide range of scan rates normally available with cyclic voltammetry allows simple experimental selection of any  $\Delta E_p$  for measurements.

The upper limit of rate constants that can be determined experimentally by the above procedure is discussed in a later section.

#### APPLICATION OF THEORY TO REDUCTION OF CADMIUM

To evaluate the method described above a model system is required for which the mechanism and kinetic parameters are well known. The extensive investigations on cadmium, which have been made previously using a variety of techniques, appeared to make cadmium a logical choice. However, the compilation by Tanaka and Tamamushi of kinetic data (14) shows a considerable variation of both standard rate constants and charge transfer coefficients for cadmium when determined by various workers. Nevertheless, cadmium was considered the best model system available, and therefore it was used to test the theoretical calculations.

#### EXPERIMENTAL

**Apparatus.** The circuit was essentially the same as described previously (10). All measurements were made with a three-electrode potentiostatic circuit, using a single Philbrick Model SK2-V operational amplifier (G. A. Philbrick Researches, Inc. Boston, Mass.). To improve rise-time

and increase current capabilities, a Philbrick Model K2-BJ booster amplifier was used in series with the potentiostat. The bandwidth of the potentiostat was adjusted for the solution used to provide optimum rise-time and stability. To do this the ideas of Booman and Holbrook were used (1, 2). A good quality commercial potentiostat (e.g., Wenking Potentiostat, Brinkmann Instruments, Westbury, N. Y.) presumably could be used in place of the potentiostat just described.

Two different signal generators were used, and both proved adequate. One was constructed from operational amplifiers and has been described previously (10). The other was an Exact Model 255 function generator (Exact Electronics, Inc., Hillsboro, Ore.), which proved useful and versatile.

The detector was a Tektronix Model 536 oscilloscope provided with a Polaroid camera attachment (Tektronix Type C-12). The vertical input was always a Type D plug-in preamplifier. This could be operated in the differential mode and permitted use of a floating load resistor in the potentiostatic circuit (10). To measure scan rates for the function generator constructed from operational amplifiers, a Type T plug-in preamplifier was used for the horizontal input of the oscilloscope. With the Exact function generator, scan rates could be dialed directly with an accuracy of  $\pm 2\%$  and this proved to be a considerable advantage over the other signal generator. To measure peak potential separations a Type H plug-in preamplifier was used for the horizontal input of the oscilloscope. The horizontal axis then was driven by the cell potential, and peak potential separations could be measured with an accuracy of about  $\pm 2$  mv.

The cell assembly has been described previously (10).

**Materials.** Solutions were prepared from cadmium sulfate (Baker A. R.) and anhydrous sodium sulfate (Baker A. R.). The concentrations were: cadmium sulfate, ca.  $2 \times 10^{-4}M$ ; sodium sulfate, 1.0 M. The exact cadmium concentration was not determined. Measurements were made in a constant temperature room at ambient temperatures of 23° to 25° C.

#### RESULTS AND DISCUSSION

Both one-cycle and multi-cycle (steady state) experiments were run and as would be expected the differences between  $\Delta E_p$  for the two methods were of the order of experimental error. Nevertheless, data reported here are for one-cycle experiments to conform to theoretical calculations. For all experiments an initial potential of  $-0.370$  volt vs. S.C.E. was used, and the amplitude of the triangular wave always was 300 mv.

Results for reduction of  $2 \times 10^{-4}M$  cadmium in 1.0M sodium sulfate are summarized in Table II. To convert experimentally determined values of  $\psi$

Table II. Determination with Cyclic Voltammetry of  $k_s$  for Reduction of Cadmium

$v$ , volt/sec.	$\Delta E_p$ $\times n$ , mv.	$\psi^a$	$k_s^b$ , cm./sec.
48.0	94	0.70	0.25
60.0	98	0.61	0.25
90.0	108	0.48	0.24
120.0	115	0.41	0.23

<sup>a</sup> Determined from Figure 3; see Equation 17.

<sup>b</sup>  $2 \times 10^{-4}M$  cadmium sulfate, 1.0M sodium sulfate.

to  $k_s$ , the diffusion coefficients of Okinaka (12) were used. A value of  $\alpha$  equal to 0.25 also was used. Although no effort was made to determine  $\alpha$  accurately, the value of 0.25 was estimated by comparing with theory the symmetry and shape of cathodic and anodic waves for cadmium. The calculated value of  $k_s$  is fairly insensitive to variations of  $\alpha$ , as already mentioned.

The values of  $k_s$  in Table II agree reasonably well with some other workers (14). The disagreement with others (12, 14) is not entirely explained. The apparent rate constant does change some with different supporting electrolytes. For example, we find  $k_s$  equal to about 0.6 cm./sec. in 2M perchloric acid. The value in sulfuric acid is slightly higher. In addition, electrodes are subject to an aging effect noted by Delahay (3, 4). We also observe this decrease of apparent rate constants with time, but the effect in our solutions is not as great as Delahay found (about a factor of two change in  $k_s$  for the first 20 minutes quiescence).

The upper limit of rate constants that can be determined by the above method appears to be set by a combination of factors. First, in the measurement of peak potential separations, uncompensated ohmic potential losses are a serious source of error. Thus, for the rapid scan rates required to study fast electrode reactions, peak currents become fairly large and even relatively small solution resistances can introduce serious error. Moreover, the effects of uncompensated  $iR$  drop qualitatively are very similar to kinetic effects (9). This is amply illustrated by Figure 3 where the dashed curve is a plot of data calculated previously for the effect of  $iR$  losses on cyclic voltammetry (9). The definition of the horizontal axis ( $\psi$ ) of Figure 3 for this case should be (9):

$$\psi = 1/(nF/RT)nFA \times (\pi a D_o)^{1/2} C_o^* R_u \quad (18)$$

Thus, the variation of peak potential separation with scan rate is quite similar for the two cases.

The effect of ohmic potential losses can be minimized in three ways. First,

relatively concentrated electrolytes of high conductivity can be used to reduce the total cell resistance. Second, with a three-electrode potentiostat placement of the Luggin capillary probe in close proximity with the working electrode serves to compensate for a majority of the total cell resistance [see Booman and Holbrook for the exact relationship (2)]. Third, relatively low concentrations of electroactive material can be used to keep total cell currents small. This latter approach is limited, however, by charging current. Thus, at high scan rates charging current may become an appreciable fraction of the total cell current, especially when low concentrations of electroactive material are used.

For the cadmium system investigated here a concentration of 2 to  $5 \times 10^{-4}M$  appeared to be optimum for low cell currents without excessive charging current contributions. Maximum peak currents were of the order of 0.2–0.3 ma. Total solution resistance (ca. 20 ohms)

measured by peak potential shifts on moving the Luggin probe more than 10 radii from the working electrode agreed with values calculated from the conductivity of the solution (2). By careful placement of the Luggin probe the uncompensated resistance was estimated to be 3 to 4 ohms (2), so that maximum ohmic potential losses were of the order of 1 mv.

The upper limit of rate constants measurable with cyclic voltammetry therefore depends on several factors. The most important of these is probably conductivity of the solution under investigation. With electrolytes of reasonably high conductivity, it should be possible to measure rate constants as large as 1 to 5 cm./sec.

#### LITERATURE CITED

- (1) Booman, G. L., Holbrook, W. B., *ANAL. CHEM.* **37**, 795 (1965).
- (2) *Ibid.*, **35**, 1793 (1963).
- (3) Delahay, P., Trachtenberg, I., *J. Am. Chem. Soc.* **80**, 2094 (1958).

- (4) Delahay, P., *J. Chim. Phys.* **54**, 369 (1957).
- (5) DeVries, W. T., Free University, Amsterdam, The Netherlands, private communication, 1965.
- (6) DeVries, W. T., VanDalen, E., *J. Electroanal. Chem.* **8**, 366 (1964).
- (7) Galus, Z., Lee, H. Y., Adams, R. N., *Ibid.*, **5**, 17 (1963).
- (8) Matsuda, H., Ayabe, Y., *Z. Elektrochem.* **59**, 494 (1955).
- (9) Nicholson, R. S., *ANAL. CHEM.* **37**, 667 (1965).
- (10) Nicholson, R. S., Shain, I., *Ibid.*, p. 190.
- (11) *Ibid.*, **36**, 706 (1964).
- (12) Okinaka, Y., *Talanta* **11**, 203 (1964).
- (13) Selis, S. M., *J. Phys. Chem.* **68**, 2538 (1964).
- (14) Tanaka, N., Tamamushi, R., *Electrochem. Acta* **9**, 963 (1964).

RECEIVED for review June 28, 1965. Accepted August 3, 1965. Presented in part at the Division of Analytical Chemistry, 150th Meeting ACS, Atlantic City, N. J., September 1965. Work supported in part by the United States Army Research Office—Durham under Contract No. DA-31-124-ARO-D-308. Other support was received from the National Science Foundation under Grant No. GP-3830.

# Polarography of Lead(II) in Aqueous Hydrofluoric Acid (1 to 12M) with a Dropping-Mercury Electrode of Teflon

HELEN P. RAAEN

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

► The polarographic behavior of  $Pb^{+2}$  ( $\sim 0.03$  to  $0.8mM$ ) in aqueous HF (1.00 to 12.00M) was studied with a D.M.E. of Teflon. The polarographically usable potential span for 12.00M HF is about +0.4 to  $-1.0$  volt vs. S.C.E.; for 1.00M HF, the limit extends to about  $-1.2$  volts. Within this span only one polarographic wave for  $Pb^{+2}$  exists; it is for the polarographically reversible 2-electron-change reduction  $Pb^{+2} \rightarrow Pb^0$ . The  $E_{1/2}$  values determined are  $-0.380$  (for 1.00M HF) to  $-0.370$  (for 12.00M HF)  $\pm 0.003$  volt vs. S.C.E.; the values are not affected by change in  $Pb^{+2}$  concentration. The wave is of excellent form and is usable for both qualitative and quantitative purposes. The relation of  $i_d$ , and also of  $(di/dt)_{max}$ , to  $Pb^{+2}$  concentration is linear; plots of these variables pass through the origin. With increase in HF concentration from 1.00 to 12.00M, no change occurs in the number of lead waves, shape of the wave, polarographic reversibility of the reduction, or  $n$ ; the  $i_d$  decreases slightly; and the  $E_{1/2}$  becomes about 10 mv. more positive.

THE DROPPING-MERCURY electrode of Teflon (DuPont) has been described (8), and its operation in noncorroding media was investigated (9, 10). A review was given (8) of the polarography—done before the D.M.E. of Teflon was developed—of substances in liquid hydrofluoric acid and in aqueous acid fluoride media.

The polarography of lead in acid fluoride media has been studied to a limited extent. West, Dean, and Breda (11) obtained a well-defined wave for lead in 0.5M  $Na_2F_2$  [sic]–0.01% gelatin solutions of pH 1.1 to 2.75 that contained considerable amounts of nitric acid added to dissolve the lead fluoride precipitate; the solutions therefore contained lead nitrate and slightly dissociated hydrofluoric acid. The polarography of lead, as  $PbF_2$ , in liquid hydrofluoric acid was investigated briefly by Clifford (2). Mesaric and Hume (7) used polarography to study lead fluoride complexes and their solubilities; the solutions they studied were 1mM in  $Pb^{+2}$ , up to 0.7M in  $F^-$ , and of 2M ionic strength adjusted by adding  $NaClO_4$ . With a D.M.E. of Teflon, Headridge and associates studied the

polarographic behavior of the ions of a number of elements, including lead, in 0.1M  $NH_4F$ –0.1M HF (4) and polarographically determined molybdenum in niobium-base alloys using 0.5M HF–0.5M  $H_2SO_4$  as supporting medium (5).

With the D.M.E. of Teflon, the polarographic characteristics of  $Pb^{+2}$  in aqueous hydrofluoric acid solutions have now been studied in some detail. The data given herein are the first polarographic data reported for  $Pb^{+2}$  in aqueous solutions of reasonably high HF concentration and that contain no other added constituents—e.g., a salt to contribute ionic strength or a maximum suppressor.

#### EXPERIMENTAL

**Reagents. Standard Solutions of  $Pb^{+2}$  in Aqueous HF.** A quantity of lead fluoride,  $PbF_2$ , (B & A purified grade) calculated to give 1mM solution was added to an aqueous solution of HF (1.00, 4.00, 8.00, or 12.00M). After maximum dissolution the solution was filtered to remove undissolved  $PbF_2$ . The  $Pb^{+2}$  concentration of the filtered solution was determined by a separate analysis in which HF was removed from test portions by fuming