

which occurs, the particles in the fresh colloid may actually have grown almost to their ultimate size during the period of deaeration and current measurement. In particular this is expected in the case of the more dilute colloid system since fairly large concentrations of  $\text{Ag}(\text{CN})_2^-$  were employed in these experiments. In the experiments with the more concentrated fresh colloid, a small amount of wool violet was added. This dye is adsorbed on the surface of the colloid particles thereby decreasing the magnitude of the surface available for the reaction. This would also be expected to lead to smaller values for  $k_z$ . Saturation of the surface with wool violet eliminates completely the kinetic current. This effect is illustrated in Table IV.

TABLE IV  
EFFECT OF WOOL VIOLET 6BN ON THE KINETIC CURRENT

Added wool violet (mg./ml.)	$i_k$ ( $\mu\text{amp.}$ )
0.020	7.88
.040	7.55
.100	5.70
.200	0.30
.400	0.00

At a level of 0.04 mg./ml. wool violet, the effect is small but not insignificant and would account in part for the unexpected agreement of the values of  $k_z$  for the more concentrated fresh colloid and the dialyzed colloid.

It is of interest to calculate an approximate value for the heterogeneous rate constant from the derived value of the pseudo rate constant and the specific surface of the dialyzed colloid. The experimentally derived rate constant is related to the heterogeneous rate constant  $k_h$  by the equation

$$1000k_z = k_h A \quad (16)$$

Kolthoff and Bowers<sup>4</sup> found, from radioactive bromide exchange experiments, that 5% of the silver bromide in a dialyzed colloid is present in the surface. Using this value and taking the thickness of one layer of silver bromide as 2.9 Å., values of  $5.1 \times 10^7 \text{ cm.}^2/\text{mole}$  for the surface area of the dialyzed colloid and  $1.6 \times 10^{-2} \text{ cm./sec.}$  for the heterogeneous rate constant are obtained.

**Dependence of the Kinetic Current on the Height of Mercury.**—At low ratios of dicyanide argentate-(I) to colloidal silver bromide, the kinetic current was found to be independent of the head of mercury. However, as the ratio was increased, a large dependence was observed. Since  $\alpha$ , according to either the reaction layer concept or the more rigorous equation, is independent of  $h$  whereas  $\beta$ , according to the assumptions made in the derivation of equation 10, is directly proportional to the height of mercury, these observations are in qualitative agreement with the theory presented. Values of  $\beta$ , as a function of  $h$ , can be calculated from the currents obtained at various heights of mercury by making use of equation 5 and assuming  $\alpha$  to be constant. When this was done and plots of  $\log h$  vs.  $\log \beta$  made, straight lines having the slopes indicated in Table V were obtained.

TABLE V  
VALUES OF  $\Delta \log h / \Delta \log \beta$

System	$[\text{Ag}(\text{CN})_2^-]$ (mmoles/l.)	$[\text{AgBr}]$ (moles/l.)	$\alpha$	$\frac{\Delta \log h}{\Delta \log \beta}$
Fresh colloid	0.307	0.0196	60.3	0.95
Fresh colloid	.565	.00250	24.4	1.10
Dialyzed colloid	.588	.0189	51.0	0.97

These results are in good agreement with the assumptions made in the derivation of equation 10.

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## Voltammetric Membrane Electrodes. II. Current-Potential Curves of Reversible and Irreversible Electrode Processes<sup>1</sup>

BY RICHARD C. BOWERS AND ARTHUR M. WILSON<sup>2</sup>

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Current-potential curves for reversible and irreversible electrode processes, at the voltammetric mercury membrane electrode (V.M.M.E.), are quantitatively interpreted by assuming that a linear concentration gradient is established fairly rapidly within the membrane diffusion layer. Experimental results for the reduction of thallos and nickel ion and for the reduction and oxidation of the *p*-benzoquinone-hydroquinone couple are given. The criteria of reversibility at membrane electrodes are discussed.

### Introduction

In a previous publication,<sup>3</sup> it was pointed out that the limiting currents observed at a voltammetric membrane electrode indicate that the membrane provides a well-defined diffusion layer when the electrode is placed in a stirred solution. Due to the finite thickness of the membrane, a linear con-

centration gradient within the membrane is established fairly rapidly. Current-potential curve equations derived on the basis of the Nernst diffusion layer concept<sup>4</sup> are therefore expected to be quantitatively obeyed at this type electrode. The present paper presents a theoretical treatment, based on this concept; and an experimental study of current-potential curves for reversible and irreversible processes occurring at the voltammetric mercury membrane electrode (V.M.M.E.).

(1) Based on the dissertation of Arthur M. Wilson in partial fulfillment of the requirements for the Doctor of Philosophy, 1958.

(2) Toni-Gillette Fellow, 1956-1957; Du Pont Teaching Fellow; 1957-1958.

(3) R. C. Bowers and A. M. Wilson, *THIS JOURNAL*, **80**, 2968 (1958).

(4) W. Nernst, *Z. physik. Chem.*, **47**, 52 (1904).

### Theoretical

For purposes of discussion, the types of electrode processes can be classified as reversible and irreversible. In the former, it is assumed that the electrode reactions are sufficiently rapid so that electrochemical equilibrium is attained at the electrode surface. Under these conditions, the relative concentrations of the oxidized and reduced species at the electrode surface is governed by the Nernst equation. The characteristics of irreversible waves, on the other hand, are determined by the rate of the electrode reaction as well as by the rate of diffusion.<sup>5</sup> Reversible processes at a mercury electrode can be classified further according to whether the reduced species forms an amalgam with the mercury or is soluble in the aqueous (membrane) phase.

In the following treatment, it will be assumed that a linear concentration gradient is established within the membrane. This condition is attained after a short time of electrolysis at constant potential. Although this assumption is not strictly valid for potential scan experiments, the deviation is probably small at slow rates of potential scan.

**Current-Potential Curves of Reversible Processes. Case I. Oxidized and Reduced Species Soluble in the Aqueous (Membrane) Phase.**—The treatment of this case is identical to Delahay's<sup>6</sup> treatment of current-potential curves for reversible processes in stirred solutions. At the steady state, the concentrations of the oxidized and reduced species at the electrode surface can be expressed as functions of the current and it can be shown that

$$E = E^0 + \frac{RT}{nF} \ln \frac{f_0 D_R}{f_R D_0} + \frac{RT}{nF} \ln \frac{i_{1,c} - i}{i - i_{1,a}} \quad (1)$$

where  $f_0$  and  $f_R$  are the activity coefficients and  $D_0$  and  $D_R$  are the diffusion coefficients of the oxidized and reduced species, respectively and  $i_{1,c}$  and  $i_{1,a}$  are the cathodic and anodic limiting currents, respectively.<sup>7</sup> For an electrode process involving hydrogen ions, such as the *p*-benzoquinone-hydroquinone couple, an appropriate term containing the hydrogen ion activity must be added to equation 1.

#### Case II. Reduced Species Soluble in Mercury.

—Although a true steady state is not attained under these circumstances, it will be assumed that a linear concentration gradient is established within the membrane when electrolysis is carried out at constant potential. The equation for the concentration of the oxidized species is then

$$C_{0(x)} = Ax + B \quad (2)$$

where  $A$  and  $B$  are functions of time. The concentration of the reduced species in the mercury is dependent upon the rate of deposition and subsequent diffusion away from the surface and its concentration is governed by Fick's second law. The concentrations of the oxidized and reduced species at the electrode surface, as a function of

time, can therefore be obtained by solving these two equations simultaneously with the initial conditions;  $C_{0(x,0)} = C_0^0$  and  $C_{R(x,0)} = 0$  and the boundary conditions;  $C_{0(1,t)} = C_0^0$ ,  $C_{R(\infty,t)} = 0$ ,

$$D_0 \left( \frac{\partial C_0}{\partial x} \right)_{x=0} + D_R \left( \frac{\partial C_R}{\partial x} \right)_{x=0} = 0$$

and

$$(C_0/C_R)_{x=0} = a_{Hg} f_R / f_0 \exp \left[ \frac{nF(E - E_a^0)}{RT} \right]$$

In the last boundary condition,  $a_{Hg}$  is the activity of mercury in the amalgam and  $E_a^0$  is the standard potential for the reduction of metal ion into the amalgam. This boundary value problem can be solved using the Laplace transformation<sup>8</sup> and one obtains

$$i/i_l = \exp \gamma^2 \operatorname{erfc} \gamma \quad (3)$$

where  $i_l$  is the limiting current and  $\gamma$  is given by

$$\gamma = \frac{a_{Hg} f_R D_0}{f_0 l} \sqrt{\frac{t}{D_R}} \exp \left[ \frac{nF(E - E_a^0)}{RT} \right] \quad (4)$$

**Current-Potential Curves for Irreversible Processes.**—The Nernst diffusion layer concept has been used by Eyring and co-workers<sup>5</sup> and Tanaka and Tamamushi<sup>9-11</sup> in order to interpret irreversible polarographic waves. In our case, this treatment is rigorous. In the case of a totally irreversible electrode reaction, the rate of the backward reaction is negligible and the equation of the current can be written as<sup>6</sup>

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

where  $k_f^0$  is the heterogeneous rate constant for  $E = 0$ ,  $\alpha$  is the transfer coefficient and  $n_a$  is the number of electrons involved in the rate-determining step. By expressing the concentration of the oxidized species at the electrode surface as a function of the current it can be shown that

$$E = \frac{RT}{\alpha n_a F} \ln \frac{k_f^0 l}{D} + \frac{RT}{\alpha n_a F} \ln \frac{i_l - i}{i} \quad (6)$$

and

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{k_f^0 l}{D} \quad (7)$$

### Experimental

**Reagents.**—1.0 *M* solutions of recrystallized reagent grade potassium nitrate were used as supporting electrolyte in all experiments except in the studies of the *p*-benzoquinone-hydroquinone system. In these experiments, phosphate buffers, prepared from reagent grade chemicals and made 1.0 *M* in potassium ion were used. Stock solutions of thallos chloride were prepared from recrystallized thallos chloride. Nickel chloride solutions were made from reagent grade  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and standardized by precipitation of the nickel ion with dimethylglyoxime.<sup>12</sup> The stock solutions of *p*-benzoquinone and hydroquinone were prepared daily from twice sublimed Merck practical grade *p*-benzoquinone and recrystallized Mallinkrodt "photopurified" hydroquinone.

(8) For details of the solution see: A. M. Wilson, Ph.D. Thesis, Northwestern University, 1958.

(9) N. Tanaka and R. Tamamushi, *Bull. Chem. Soc. Japan*, **22**, 187 (1949).

(10) R. Tamamushi and N. Tanaka, *ibid.*, **22**, 227 (1949); **23**, 110 (1950).

(11) N. Tanaka and R. Tamamushi, *Sbornik Mezinarod. Polarog. Sjezdu Praze*, 1st Congr., 1951, Pt. I, Proc., 486-534.

(12) H. H. Willard and H. Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1943.

(5) H. Eyring, L. Marker and T. C. Kwok, *J. Phys. Colloid Chem.*, **53**, 1453 (1949).

(6) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishing Co., Inc., New York, N. Y., 1954, Chapter 9.

(7) The cathodic current is considered positive and the anodic current negative.

**Mercury Membrane Electrode.**—The electrode employed has been described in a previous publication.<sup>3</sup> The cellophane employed for the membrane was donated by E. I. du Pont de Nemours and Company.

**Apparatus.**—A jacketed cell was used in order to maintain a constant temperature of  $25.0 \pm 0.1^\circ$  in all experiments. The solutions were stirred using a magnetic stirrer. All solutions were deaerated with Linde H. P. nitrogen. Current-potential curves and current-time curves were recorded with a Sargent Model XXI polarograph, the pen response being approximately four seconds full scale. The potential setting on the polarograph was calibrated using a Leeds and Northrup potentiometer prior to recording each current-potential or current-time curve.

## Results and Discussion

**Current-Potential Curves of Reversible Processes. Case I. Oxidized and Reduced Species Soluble in the Aqueous (Membrane) Phase.**—The *p*-benzoquinone-hydroquinone couple has been shown to be reversible at the dropping mercury electrode<sup>13</sup> and it was chosen as an example of a reversible system in which both the oxidized and reduced species are soluble in the aqueous phase. Steady state diffusion currents were attained fairly rapidly with this couple and plots of  $\log(i_{l,c} - i)/(i - i_{l,a})$  vs. potential gave straight lines. The experimental results are summarized in Table I.

TABLE I  
CURRENT-POTENTIAL CURVE CHARACTERISTICS OF THE *p*-BENZOQUINONE-HYDROQUINONE COUPLE

$C$ (mM)		$l \times 10^2$ (cm.)	<i>p</i> H	$E_{1/2}$ , v. vs. S.C.E.	$\frac{\Delta E}{\Delta \log \frac{i_{l,c} - i}{i - i_{l,a}}}$
$C_6H_4O_2$	$C_6H_6O_2$				
0.00	0.332	7.50	7.29	0.047	0.038
1.615	1.615	7.50	7.29	.042	.037
1.635	0.327	7.50	7.29	.039	.036
2.38	2.38	29.6	7.29	.039	.040
					.033
2.38	2.38	7.50	6.91	.059	.037

<sup>a</sup> Two distinct straight line segments observed.

Although no serious deviation from equation 1 is observed, it is seen that the slopes of the  $\log(i_{l,c} - i)/(i - i_{l,a})$  vs. potential plots deviate considerably from the theoretical value of 0.0296. In fact with the thicker membrane, two distinct slopes were observed. In addition, the half-wave potential appears to be slightly dependent upon the relative concentrations of *p*-benzoquinone and hydroquinone. On the other hand, the shift in half-wave potential with *p*H is very nearly that expected and the half-wave potential is essentially independent of the membrane thickness. These observations suggest that this couple is not totally reversible at this electrode. In such a case, the rates of the electrochemical reactions as well as the rates of diffusion of the oxidized and reduced species govern the current-potential curves. In contrast to totally irreversible processes, however, the rate of the backward reaction cannot be neglected and the equation describing this intermediate case is rather involved.<sup>6</sup> Additional experiments with this couple are in progress.

**Case II. Reduced Species Soluble in Mercury.**—At potentials between  $-0.30$  and  $-0.60$  v. vs. S.C.E., the diffusion current due to the re-

(13) L. J. Smith, I. M. Kolthoff, S. Wawzonek and P. M. Ruoff, *THIS JOURNAL*, **63**, 1018 (1941).

duction of thallos ion decayed continuously with time as predicted by equations 3 and 4. At potentials more negative than  $-0.60$  v. vs. S.C.E. (limiting current region) a steady-state current was attained.

The quantity  $\gamma/\sqrt{t}$ , defined by equation 4, can be evaluated from a plot of  $\exp \gamma^2 \operatorname{erfc} \gamma$  vs.  $\gamma^{14}$  and experimental values of  $i/i_1$  at various times. Within experimental error, the value of  $\gamma/\sqrt{t}$  is found to be constant at a constant potential. Typical results are shown in Table II.

TABLE II  
VALUES OF  $\gamma$  AND  $\gamma/\sqrt{t}$  AT  $-0.500$  V. vs. S.C.E.  
 $l = 9.85 \times 10^{-3}$  cm.,  $0.625 \times 10^{-3} M Ti^{2+}$ ,  $i_1 = 11.1 \mu\text{amp.}$

$t$ (sec.)	$i$ ( $\mu\text{amp.}$ )	$\gamma$	$\gamma/\sqrt{t}$
40	8.6	0.240	3.79
80	7.9	.320	3.58
120	7.5	.380	3.47
160	7.1	.445	3.52
200	6.8	.490	3.48
240	6.6	.530	3.42
320	6.2	.615	3.44

By rewriting equation 4 in the form

$$E = E^0_a + \frac{RT}{nF} \ln a_{H_2} + \frac{RT}{nF} \ln \frac{f_o D_R^{1/2}}{f_R D_o} + \frac{RT}{nF} \ln \frac{\gamma}{\sqrt{t}} \quad (8)$$

it becomes apparent that a plot of  $\log \gamma/\sqrt{t}$  should yield a straight line having a slope of  $0.0591/n$ . (at  $25^\circ$ ). This was found to be true (Fig. 1). In addition, when  $\gamma/\sqrt{t} = 1$

$$E(\gamma/\sqrt{t} = 1) = E^0_a + \frac{RT}{nF} \ln a_{H_2} + \frac{RT}{nF} \ln \frac{f_o D_R^{1/2}}{f_R D_o} \quad (9)$$

This potential is analogous to the half-wave potential at the dropping mercury electrode since its value is dependent on the oxidation-reduction potential of the metal ion being reduced and the diffusion coefficients of the oxidized and reduced species. A comparison of equation 9 with the analogous equation for the half-wave potential at the dropping mercury electrode<sup>15</sup>

$$E_{1/2} = E^0_a + \frac{RT}{nF} \ln \frac{a_{H_2} f_o D_R^{1/2}}{f_R D_o^{1/2}} \quad (10)$$

indicates that

$$E(\gamma/\sqrt{t} = 1) = E_{1/2(D.M.E.)} - \frac{RT}{nF} \ln \frac{D_o(m)}{D^{1/2}_{o(w)} l} \quad (11)$$

Here  $D_o(m)$  and  $D_o(w)$  are the diffusion coefficients of the ion in the membrane and aqueous solution, respectively.

A summary of the current-potential curve characteristics for the reduction of thallos ion at this electrode is given in Table III.

The agreement between theory and experiment is excellent.

**Current-Potential Curves for an Irreversible Process.**—Strassner and Delahay<sup>16</sup> have studied the electrode kinetics of the irreversible reduction of hexaquinonickel ion at the dropping mercury

(14) See for example, H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, p. 373.

(15) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Chapter XI, Interscience Publishing Co., Inc., New York, N. Y., 1952.

(16) J. J. Strassner and P. Delahay, *THIS JOURNAL*, **74**, 6232 (1952).

TABLE III  
CURRENT-POTENTIAL CURVE CHARACTERISTICS OF  
THALLOUS ION  
 $0.625 \times 10^{-3} M \text{ TlCl}; 1.0 M \text{ KNO}_3$

$\times 10^3$ (cm.)	$\frac{\Delta E}{\log \gamma/\sqrt{i}}$	$E(\gamma/\sqrt{i} = 1)$ v. vs. S.C.E. Obsd.	Calcd. (eq. 11) <sup>a</sup>
9.85	0.580	-0.416	-0.418
29.6	0.0605	-0.392	-0.389

<sup>a</sup>  $E_{1/2}$  of thallos at D.M.E. = -0.475 v. vs. S.C.E.<sup>15</sup>  
 $D_{o(m)} = 2.0 \times 10^{-5} \text{ cm.}^2/\text{sec.}; D_{o(m)} = 4.7 \times 10^{-6} \text{ cm.}^2/\text{sec.}$

electrode. It was therefore of interest to employ this ion in order to verify the equations for totally irreversible processes.

It was found that constant potential electrolysis of nickel ion at the V.M.M.E. did not yield a steady-state current as might be expected. Rather, the current increased gradually after the initial rapid decrease. This rise in current is attributed to a decrease in the overpotential for the evolution of hydrogen. This results from a fairly rapid accumulation of nickel at the mercury surface. In order to prevent the evolution of hydrogen, mercuric ion was reduced simultaneously with the nickel ion. A bulk concentration of mercuric ion equal to twice that of nickel was sufficient to prevent any appreciable evolution of hydrogen and steady-state currents were readily attained. As predicted by equations 6 and 7, plots of  $\log(i_i - i)/i$  vs. potential yielded straight lines and the half-wave potential was shifted to more positive values when the membrane thickness was increased. The results are given in Table IV.

TABLE IV  
CURRENT-POTENTIAL CHARACTERISTICS OF NICKEL ION  
 $0.854 \times 10^{-3} M \text{ Ni}^{++}, 1.90 \times 10^{-3} M \text{ Hg}^{++}, D_{\text{Ni}^{++}} = 0.92 \times 10^{-5} \text{ cm.}^2/\text{sec.}$

$l \times 10^3$ (cm.)	$E_{1/2}$ (v. vs. S.C.E.)	$\alpha n \alpha$	$k^{\text{of}}$ (cm./sec.) vs. S.C.E.	$k^{\text{of}}$ (cm./sec.) vs. N.H.E.
9.85	-1.082	0.328	$0.9 \times 10^{-10}$	$2.1 \times 10^{-9}$
29.6	-1.002	0.320	$1.2 \times 10^{-10}$	$2.3 \times 10^{-9}$

The agreement between the values of  $\alpha n \alpha$  and  $k^{\text{of}}$  at the two different thicknesses is very good.

It is of interest that the above values of  $\alpha n \alpha$  and  $k^{\text{of}}$  correspond fairly closely with the values for these quantities reported by Stassner and Delahay<sup>16</sup> in the case of hexaquinonickel ion reduction at the dropping mercury electrode in the presence of 0.01% gelatin. Actually they found that as the gelatin concentration is increased, the value of  $\alpha n \alpha$  as well as the value of the free energy of activation for the electrode process decreased. Apparently the cellophane membrane effects the electrode kinetics of the reduction of hexaquinonickel ion in a manner similar to gelatin, the change in  $\alpha n \alpha$  and in the heterogeneous rate constant being in the same direction and of the same order of magnitude in the two cases. According to Strassner and Delahay,<sup>16</sup> the effect of gelatin on the electrode kinetics can be ascribed to either the adsorption of the gelatin on the mercury drop or to a complexation of the nickel ion by gelatin. In our case, it seems unlikely that an interaction

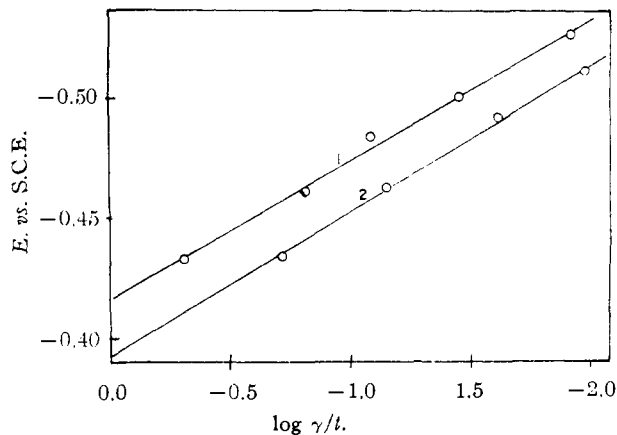


Fig. 1.—Variations of  $\log \gamma/\sqrt{i}$  with potential; potential corrected for  $iR$  drop across cell;  $0.625 \times 10^{-3} M \text{ TlCl}, 1.0 M \text{ KNO}_3$ ; (1)  $l = 9.86 \times 10^{-3} \text{ cm.};$  (2)  $l = 29.6 \times 10^{-3} \text{ cm.}$

between the cellophane membrane and the mercury surface, similar to the adsorption of gelatin, on the mercury would occur. On the other hand, an interaction (complexation) between nickel ions and the functional groups of the cellophane is expected.<sup>3</sup>

### Conclusions

The present investigation indicates that current-potential curves of electrode processes occurring at voltammetric membrane electrodes can be interpreted quantitatively by assuming a linear concentration gradient within the membrane diffusion layer.

The following criteria of reversibility at this electrode can be stated. In a totally irreversible process, a pronounced shift toward more positive potentials (in the case of cathodic processes) upon increasing the membrane thickness is observed. The half-wave potential for a completely reversible process, where both the oxidized and reduced species are soluble in the aqueous (membrane) phase, is independent of the membrane thickness and a plot of  $\log(i_{i,c} - i)/(i - i_{i,a})$  vs. potential yields a straight line of theoretical slope,  $0.059/n$ . Amalgam formation by the reduced species, in reversible reductions of simple metal ions, prevents the attainment of steady-state currents except on the limiting current region.

From the results of the study of the reduction of the hexaquinonickel ion, it is concluded that the electrode kinetics of this process are effected by an interaction between the nickel ions and functional groups present in the cellophane membrane. The *p*-benzoquinone hydroquinone couple does not appear to be totally reversible at the voltammetric mercury membrane electrode when cellophane is used as the membrane. The treatment of reversible reductions of ions of metals which are soluble in mercury is rather involved, however in the case of thallos ion reduction, excellent agreement between theory and experiment is obtained.

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