

be estimated from the following considerations. Slater<sup>7</sup> has derived the following equation from the equation of state for a solid at absolute zero and a Taylor's series expansion of the Morse equation

$$\gamma = \frac{ar_e}{2} + \frac{1}{3} \quad (6)$$

where  $r_e$  is the equilibrium distance between atoms, and  $a$  is the constant coefficient in the exponents of

(7) J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 452 ff.

the Morse equation. It is further shown<sup>7</sup> that values of  $r_e$  and  $a$  for several elements are about the same in the solid as in the diatomic state. Values of  $\gamma$  (eq. 6) for the solids agree with the values from the respective diatomic molecules, within 20%. Now if  $\gamma$  is computed from tabulated values of  $a$  and  $r_e$  for diatomic oxygen,  $\gamma$  takes the value 1.94 which is only 5% higher than 1.84 found in these experiments. The magnitude and constancy of the  $\gamma$  from these experiments is consistent with the fundamental ideas of the solid-state model.

## EVALUATION OF THE EFFECT OF SECONDARY REACTIONS IN CONTROLLED POTENTIAL COULOMETRY

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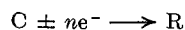
Controlled potential coulometry is an effective tool in studying electrode reactions. When a primary electrode reaction is followed by a secondary chemical reaction which regenerates or consumes the electroactive material, the apparent number of faradays per mole of reactant is in general a function of experimental variables. This paper presents a mathematical treatment of several reaction schemes in which secondary reactions occur. A method for evaluating the true  $n$ -value as well as the kinetic parameters of the secondary chemical reaction is given.

### Introduction

Electrolysis at controlled potential is an experimental technique which is widely employed in the study and elucidation of electrode reactions. Experimental determination of  $n$ , the number of faradays per mole of electroactive material, yields the data which allows prediction of the primary electrode reaction products. This is of particular importance in the treatment of organic substances where  $n$  may be larger than three or four. The principles and methodology of controlled potential electrolysis have been thoroughly reviewed by Lingane.<sup>1</sup>

The interpretation of coulometric data is straightforward when integral  $n$  values are obtained. Non-integral  $n$  values will in general be obtained when there are secondary chemical reactions between the product of the electrode reaction (or substances derived from the primary product) and the original electroactive species, or when there are secondary chemical reactions leading to the regeneration of the electroactive substance. This paper presents a mathematical treatment for several of these cases. This work is intended to serve as a guide for the determination of the true  $n$ -value as well as for the evaluation of kinetic parameters from coulometric data.

**Classification.**—It is convenient to classify the possible reaction schemes in terms of the behavior of the reaction product, R. The electrode reaction is represented as



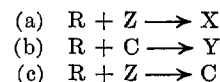
where C is the electroactive material and R is the soluble primary product of the electrode reaction. It is assumed that only a single electrode reaction occurs, thus induced reactions are not treated here.

(1) J. J. Lingane, "Electroanalytical Chemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 222.

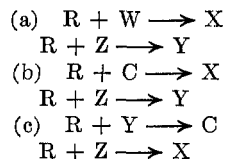
In the reactions below, W, X, Y, and Z represent electrolytically inert materials.

**Case I. R Undergoes No Further Reaction.**—This case, which is most frequently encountered, involves only integral values of  $n$ ; the characteristics of the current-time curves have been derived and verified by Lingane.<sup>2</sup> Under these circumstances, R is the experimentally observed reaction product.

**Case II. R Undergoes a Single Secondary Reaction.**—



**Case III. R Undergoes Parallel Secondary Reactions.**—



Cases IIa and IIIa are essentially identical to Case I, except that the final product is different from the primary electrode reaction product. Cases IIb, IIc, IIIb and IIIc are similar in that experimental  $n$ -values will in general be non-integral and dependent upon some experimental parameters such as  $(C_i)$ , the initial concentration of electroactive material. Cases IIc, IIIf and IIIc are derived under the restrictive assumption of  $(Z)$  being large enough that  $d(Z)/dt \approx 0$ .

Other cases, such as the occurrence of three parallel reactions or the formation of the reactive intermediate R from a slow chemical reaction following the electrode reaction, can be treated by

(2) Ref. 1, pp. 225-229.

suitable modification of the procedure outlined below.

**Mathematical Treatment. General Considerations.**—Controlled potential coulometry is usually performed in a stirred solution with the electrode maintained at a potential such that a single electrode reaction occurs. The potential of the electrode is chosen so that the rate of the reaction given in equation 1



is controlled by the rate of mass transfer of C from the bulk of the solution to the electrode. Under these conditions, the rate of the reverse reaction is considered negligible.

The current  $i$  is given by equation 2

$$i = nFm[(C) - (C_0)] \quad (2)$$

where  $F$  is the faraday,  $(C)$  is the concentration of C in the bulk of the solution,  $(C_0)$  is the concentration at the electrode surface, and  $m$  is a constant dependent on prevailing mass-transfer conditions. Under conditions of the Nernst diffusion layer treatment<sup>3</sup>  $m$  is  $AD/\delta$ , where  $A$  is the area of the electrode,  $D$  is the diffusion coefficient of C, and  $\delta$  is the thickness of the "diffusion layer." More recent studies<sup>4</sup> have defined  $m$  in terms of several hydrodynamic parameters.

When limiting current conditions prevail,  $(C_0) \simeq 0$ , equation 2 becomes

$$i = nFm(C) \quad (3)$$

Current, taken as a positive quantity, is related to the rate of consumption of C by

$$i = -nFV \left( \frac{d(C)}{dt} \right)_{\text{elec. rxn.}} \quad (4)$$

where  $V$  is the total volume of the solution and the minus sign is affixed because  $(d(C)/dt)_{\text{elec. rxn.}}$  is a negative quantity. Combining (4) and (3) gives the rate of concentration change caused by the electrode reaction

$$\left( \frac{d(C)}{dt} \right)_{\text{elec. rxn.}} = -p(C) \quad (5)$$

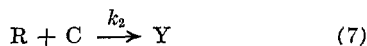
where  $p = m/V$ .

The apparent number of electrons per mole  $n_{\text{app}}$  is determined experimentally and is defined as

$$n_{\text{app}} = \frac{\int_0^t i dt}{FV[(C_i) - (C)]} \quad (6)$$

The following assumptions have been made in the derivations given below—(a) the electrolysis solution is homogeneous except for the solution at the electrode surface, the "diffusion layer," (b) volume of the electrolysis solution is large in comparison with that of the "diffusion layer," (c) where chemical equations are written, any equilibrium is displaced far to the right.

**Case IIb.**—The occurrence of a single secondary reaction consuming C



will lead to integral values of  $n_{\text{app}}$  when  $k_2$  is either very large or very small. The symbol  $n_{\text{app}}$  refers

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

(4) See e.g., B. Levich, *Acta Physicochim. U.R.S.S.*, **17**, 257 (1942).

to evaluation of  $n_{\text{app}}$  at completion of the electrolysis where  $(C)$  approaches zero. Similar superscript notation is used below for  $(R)$ ,  $(X)$  and  $(Y)$  with the same meaning. For  $k_2 \simeq 0$  the reaction is essentially identical with Case I and  $(R^0) = (C_i)$  and  $n_{\text{app}}^0 = n$ . When  $k_2$  is large,  $(R^0) \simeq 0$  and  $n_{\text{app}}^0 = n/2$ . The evaluation below is applicable for intermediate  $k_2$  values.

The system is described by the equations<sup>5</sup>

$$\frac{d(C)}{dt} = -p(C) - k_2(R)(C) \quad (8)$$

$$\frac{d(R)}{dt} = p(C) - k_2(R)(C) \quad (9)$$

Dividing (8) by (9) and solving for  $(C)$  with  $(R) = 0$  at  $t = 0$ , letting  $k_2/p = \gamma$ , gives

$$(C) = (C_i) + (R) + \frac{2}{\gamma} \ln [1 - \gamma(R)] \quad (10)$$

It is convenient to evaluate  $n_{\text{app}}$  by noting that

$$\int_0^t i dt = nFm \int_0^t (C) dt \quad (11)$$

From equations 9 and 11

$$\int_0^t i dt = nFm \int_{R=0}^R \frac{d(R)}{p - k_2(R)} = -\frac{nFV}{\gamma} \ln [1 - \gamma(R)] \quad (12)$$

Substitution of (12) into (6) along with (10) gives

$$n_{\text{app}} = \frac{n}{2} \left\{ 1 - \frac{(R)}{(R) + \frac{2}{\gamma} \ln [1 - \gamma(R)]} \right\} \quad (13)$$

An implicit relation for  $(R^0)$  as a function of  $(C_i)$  and  $\gamma$  is obtained from (10).

$$(R^0) + (C_i) = -\frac{2}{\gamma} \ln [1 - \gamma(R^0)] \quad (14a)$$

A similarity was noted between the  $n_{\text{app}}^0$ -( $C_i$ ) dependences of Case IIb and IIIb and it was found that equation 14a could be approximated by

$$(R^0) \simeq \frac{1}{2\gamma} \ln [2\gamma(C_i) + 1] \quad (14b)$$

Evaluation of  $n_{\text{app}}^0$  can be done by appropriate combination of (13) and (14a) giving the alternate expressions

$$n_{\text{app}}^0 = \frac{n}{2} \left[ 1 + \frac{(R^0)}{(C_i)} \right] \quad (15a)$$

$$n_{\text{app}}^0 = -\frac{n}{\gamma(C_i)} \ln \left[ 1 - \gamma(C_i) \left( \frac{2n_{\text{app}}^0}{n} - 1 \right) \right] \quad (15b)$$

The approximate explicit form is

$$n_{\text{app}}^0 \simeq \frac{n}{2} \left\{ 1 + \frac{1}{2\gamma(C_i)} \ln [2\gamma(C_i) + 1] \right\} \quad (15c)$$

It is evident from examination of equation 14a that  $(R^0) \leq 1/\gamma$ . Equations 14a and 15a,b predict the expected values of  $n_{\text{app}}^0$  for very large and very small values of  $\gamma$ , i.e.,  $n_{\text{app}}^0 = n/2$  and  $n_{\text{app}}^0 = n$ , respectively.

(5) The total rate of concentration change is of C

$$\frac{d(C)}{dt} = \left[ \frac{d(C)}{dt} \right]_{\text{electrode}} + \left[ \frac{d(C)}{dt} \right]_{\text{rxn.}} \quad (7)$$

$$\left[ \frac{d(C)}{dt} \right]_{\text{rxn.}} = -k_2(C)(R)$$

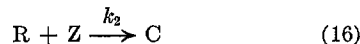
Combination of these equations with (5) gives (8). Equation 9 is derived in a similar manner.

Figure 1 shows the variation of  $n_{app}^0$  with  $(C_i)$  at several values of  $\gamma$ . It can be seen that variation of  $n_{app}^0$  with  $(C_i)$  will take place at usual concentrations, only when  $10^4 > \gamma > 1$ . Consideration of the experimental  $n_{app}^0$  values allows evaluation of  $\gamma$ .

Evaluation of  $\gamma$  can also be done from data for  $(R^0)$  or  $(Y^0)$  as a function of  $(C_i)$  by means of equation 14a.

It was not possible to obtain closed-form solutions for  $(C)$  and  $(R)$  as a function of  $t$ . Numerical solutions of differential equations 8 and 9 were obtained with the aid of the IBM 650 computer. It was found that  $(C)/(C_i)$  was a function of the parameters  $\gamma(C_i)$  and  $pt$ . Representative solutions are shown in Fig. 2. Deviations in linearity of the  $\log(C)/(C_i)$  vs.  $pt$  plot occur only in the early part of the electrolysis.

**Case IIc.**—A single secondary reaction regenerating C



is the case recently treated mathematically by Meites and Moros<sup>6</sup> under the assumption of a first-order regenerative reaction. The presentation below arrives at the same conclusions as those of Meites and Moros, but the results are expressed somewhat differently to allow comparison with the other three cases in this paper. The system is described by equations 17, 18 and 19

$$\frac{d(C)}{dt} = -p(C) + k_2(R)(Z) \quad (17)$$

$$\frac{d(R)}{dt} = p(C) - k_2(R)(Z) \quad (18)$$

$$(R) = (C_i) - (C) \quad (19)$$

For purposes of this discussion  $(Z)$  will be assumed to be present in large excess so that  $d(Z)/dt \approx 0$ .

Combining (17) and (19) and solving for  $(C)$  with the initial condition  $(C) = (C_i)$ ,  $t = 0$ , gives

$$(C) = (C_i) \left[ \frac{\gamma' + e^{-p(1+\gamma')t}}{1 + \gamma'} \right] \quad (20)$$

where  $\gamma' = k_2(Z)/p$ .

It is evident from equation 20 that at large values of  $t$

$$(C) = \frac{\gamma'(C_i)}{1 + \gamma'} \quad (21)$$

and hence  $(C)$  can approach zero only when  $p \gg k_2(Z)$ . Thus evaluation of  $\gamma'$  can be done by determining  $(C)/(C_i)$  *in situ* when the current reaches a steady value.

Solution for  $n_{app}$  is conveniently done by combination of (17), (19) and (11)

$$n_{app} = n \left[ \frac{1}{1 + \gamma'} + \frac{p\gamma't}{1 - e^{-p(1+\gamma')t}} \right] \quad (22)$$

It is of interest that  $n_{app}$  is independent of  $(C_i)$ , but is time dependent. Variation of  $n_{app}$  with time under ordinary experimental conditions will be noted only when  $\gamma' \geq 0.1$ .

**Case IIb.**—This case concerns the parallel competitive secondary reactions

(6) L. Meites and S. A. Moros, *Anal. Chem.*, **31**, 23 (1959).

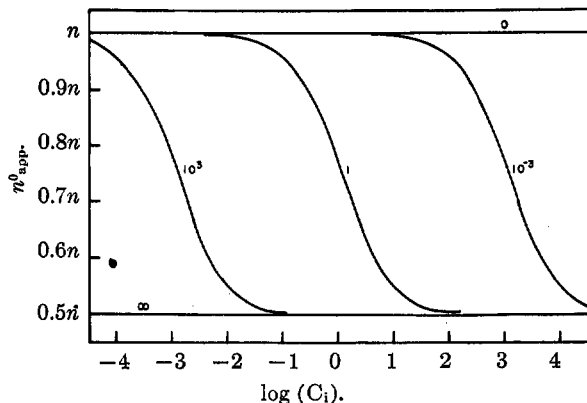


Fig. 1.—Case IIb: dependence of apparent number of faradays per mole,  $n_{app}^0$  vs.  $\log(C_i)$ ; data for various values of  $\gamma$ , liter mole<sup>-1</sup>.

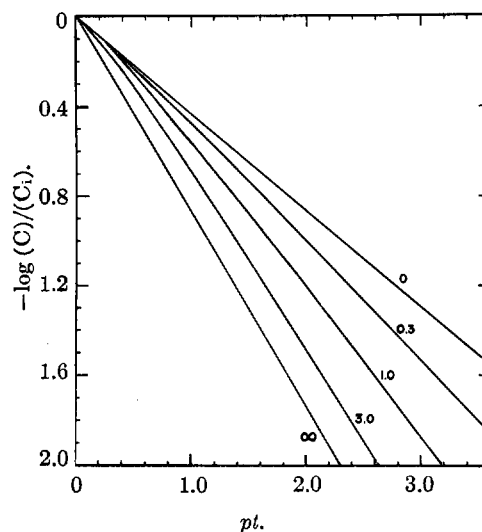
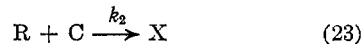


Fig. 2.—Case IIb: variation of  $-\log(C)/(C_i)$  vs.  $pt$  plot with variation of  $\gamma(C_i)$ . Values of  $\gamma(C_i)$  given on plot.



and is described by equations 25 and 26

$$\frac{d(C)}{dt} = -p(C) - k_2(C)(R) \quad (25)$$

$$\frac{d(R)}{dt} = p(C) - k_2(C)(R) - k_3(Z)(R) \quad (26)$$

Assuming the concentration of  $Z$  is so large that it remains essentially constant throughout the reaction, and making the stationary state assumption  $d(R)/dt \approx 0$

$$(R) = \frac{p(C)}{k_2(C) + k_3'} \quad (27)$$

where  $k_3' = k_3(Z)$ .

Introducing (27) into (25) and solving for  $(C)$  under the initial conditions  $(C) = (C_i)$  at  $t = 0$ , gives

$$(C) = \frac{(C_i)e^{-2pt}}{2K(C_i) + 1} [K(C_i) + \{K^2(C_i)^2 + [2K(C_i) + 1]e^{2pt}\}^{1/2}] \quad (28)$$

where  $K = k_2/k_3'$ .

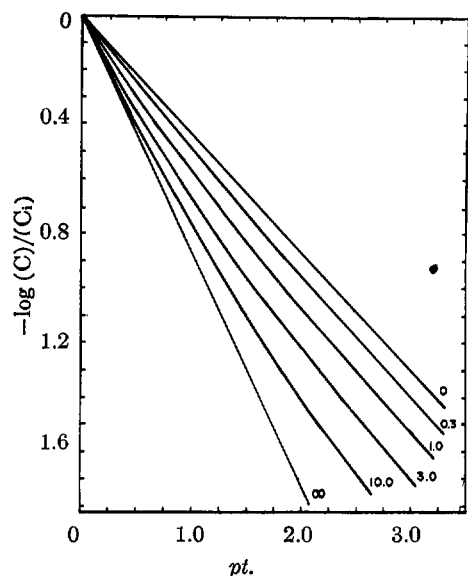


Fig. 3.—Case IIIb; variation of  $-\log(C)/(C_i)$  vs.  $pt$  plot with variation of  $K(C_i)$ . Values of  $K(C_i)$  given on plot.

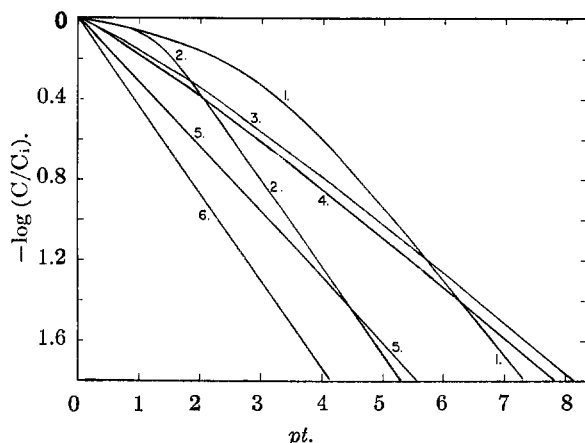


Fig. 4.—Case IIIc: numerical computation of  $-\log(C)/(C_i)$  vs.  $pt$ : 1,  $(C_i) = 4$  mM,  $(Y_i) = 8$  mM,  $K' = 1000$  liter mole<sup>-1</sup>; 2,  $(C_i) = 10$  mM,  $(Y_i) = 10$  mM,  $K' = 1000$  liter mole<sup>-1</sup>; 3,  $(C_i) = 1$  mM,  $(Y_i) = 2$  mM,  $K' = 1000$  liter mole<sup>-1</sup>; 4,  $(C_i) = 8$  mM,  $(Y_i) = 16$  mM,  $K' = 100$  liter mole<sup>-1</sup>; 5,  $(C_i) = 2$  mM,  $(Y_i) = 4$  mM,  $K' = 100$  liter mole<sup>-1</sup>; 6,  $K' = 0$ .

The current decay follows the expression [from (3) and (28)]

$$i = \frac{nFm(C_i)e^{-2pt}}{2K(C_i) + 1} [K(C_i) + \{K^2(C_i)^2 + [2K(C_i) + 1]e^{2pt}\}^{1/2}] \quad (29)$$

This expression can be compared with the equivalent expression for case I<sup>2</sup>

$$i = nFm(C_i)e^{-pt} \quad (30)$$

As  $K \rightarrow 0$ , (Case IIa), equation 29 becomes identical with (30). As  $K$  approaches infinity, equation 29 becomes

$$i = nFm(C_i)e^{-2pt} \quad (31)$$

since  $C$  reacts with  $R$  as soon as it is formed.

Figure 3 shows typical current-time curves for this case. For  $K(C_i)$  values larger than approximately twenty, a  $\log[(C)/(C_i)]$  vs.  $t$  plot is not useful in evaluating  $K$ . In the suitable range of values  $K$  can be evaluated from current-time data

and independent evaluation of  $p$  by appropriate solution of eq. 29.

Solution for  $n_{app}$  is done by combination of (25), (27) and (11)

$$n_{app} = \frac{n}{2} \left\{ 1 - \frac{1}{2K[(C_i) - (C)]} \ln \left[ \frac{2K(C) + 1}{2K(C_i) + 1} \right] \right\} \quad (32)$$

and

$$n_{app}^0 = n \left\{ \frac{1}{2} + \frac{1}{4K(C_i)} \ln [2K(C_i) + 1] \right\} \quad (33)$$

It can be seen that  $n_{app}^0 = n$  at  $K = 0$ , and  $n_{app}^0 = n/2$  as  $K \rightarrow \infty$ , as would be expected from the reaction scheme.

The variation of  $n_{app}^0$  with  $(C_i)$  is approximately the same as that shown in Fig. 1 for Case IIIb, where  $K$  values in liter mole<sup>-1</sup> are substituted for values of  $\gamma$ . Variation of  $n_{app}^0$  with  $(C_i)$  takes place at usual concentrations only when  $K > 1$  liter mole<sup>-1</sup>.

At the completion of the electrolysis the concentrations of  $X$  and  $Y$  are

$$(X^0) = \frac{1}{4K} \{2K(C_i) - \ln [2K(C_i) + 1]\} \quad (34)$$

$$(Y^0) = \frac{1}{2K} \ln [2K(C_i) + 1] \quad (35)$$

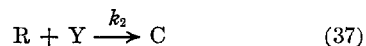
Experimental determination of these quantities provides an alternate method of evaluating  $K$ .

The stationary state assumption used in the treatment requires that  $R$  be very small at all times, or that

$$k_2(C) + k_3' \gg p(C) \quad (36)$$

Thus the range of  $k_2$  and  $k_3'$  that can be examined using this derivation depends upon the experimental choice of  $p$ .

**Case IIIc.**—The "catalytic" reaction scheme



is described by the equations

$$\frac{d(C)}{dt} = -p(C) + k_2(R)(Y) \quad (39)$$

$$\frac{d(R)}{dt} = p(C) - k_2(R)(Y) - k_3'(R) \quad (40)$$

$$\frac{d(Y)}{dt} = -k_2(R)(Y) \quad (41)$$

where  $k_3' = k_3(Z)$ , *i.e.*,  $Z$  is present in much larger quantity than  $C$  or  $Y$ .

Writing the stationary state approximation for  $(R)$ , *i.e.*,  $d(R)/dt \approx 0$

$$(R) = \frac{p(C)}{k_2(Y) + k_3'} \quad (42)$$

substituting it into (39) and (41) and solving the two equations gives

$$(C_i) - (C) = \frac{k_3'}{k_2} \ln \left( \frac{Y_i}{Y} \right) \quad (43)$$

where  $(Y_i)$  is the initial concentration of  $Y$ .

It is not possible to obtain an explicit expression for  $(C)$  as a function of time. Numerical computation for a number of cases, Fig. 4, showed that  $(C)/(C_i)$  is a function of  $pt$ ,  $(Y_i)$ ,  $(C_i)$ , and  $K'$ , where  $K' = k_2/k_3'$ . It is seen from Fig. 4 that in all cases the slope of the  $\log(C)/(C_i)$  vs.  $pt$  plot is

smaller than when no catalytic regeneration occurs.

Evaluation of  $n_{app}$  is done by substituting (42) into (41), integrating, and substituting into (11). The resulting expression is substituted into (6) along with (43) to give

$$n_{app} = n \frac{\left[ (Y_i) - (Y) + \frac{1}{K'} \ln \frac{(Y_i)}{(Y)} \right]}{\frac{1}{K'} \ln \frac{(Y_i)}{(Y)}} \quad (44)$$

At the completion of the electrolysis where (C) approaches zero, evaluation of  $(Y^0)$  from (43) and substitution into (44) gives

$$n_{app}^0 = n \left\{ 1 + \frac{(Y_i)}{(C_i)} [1 - e^{-K'(C_i)}] \right\} \quad (45)$$

The dependence of  $n_{app}^0$  on  $(Y_i)/(C_i)$  and  $K'$  is depicted in Fig. 5.

If  $(Y_i)$  is large in comparison to  $(C_i)$

$$(C) = (C_i) e^{-pt/(K''+1)} \quad (46)$$

where  $k_2' = k_2(Y_i)$  and  $K'' = k_2'/k_3'$ , then

$$n_{app}^0 = (K'' + 1)n \quad (47)$$

### Discussion

At first examination the reaction schemes for Cases IIb and IIIb appear highly unlikely. It is indeed true that the limitation of electrolytic inertness imposed on W, X, Y, Z suggests that the indicated reaction schemes will be found only infrequently. Most frequent application of the derivations for Cases IIb and IIIb probably can be made to organic species, for instance in a coupling reaction between R and C. In this case the oxidation (or reduction) of the product of the secondary reaction could well occur at a more oxidizing (or reducing) potential than the primary electrode reaction. This present paper was prompted by an experimental study of the electro-oxidation of the tetraphenylborate ion in acetonitrile, an example of Case IIb.<sup>7</sup>

The variation of  $n$ -values for the reduction of picric acid with initial concentration<sup>8</sup> may be an example of Case IIb or IIIb. Meites and Meites suggest that the dependence of  $n$  on the original concentration of picric acid is caused by a competition between further electroreduction of a partially reduced intermediate and a chemical rearrangement of the intermediate. The data also could be explained in terms of Case IIb or IIIb. Numerous examples of catalytic electrode reactions, corresponding to case IIc or IIIc have been investigated by polarographic techniques.<sup>9</sup> For example, in the presence of hydroxylamine, titanium(III), from the electroreduction of titanium(IV), is chemically oxidized to titanium(IV) by hydroxylamine. Moros and Meites<sup>10</sup> made a coulometric study of the reduction of manganese(II) to manganese(I) in cyanide media and concluded that water was reduced by manganese(I), an example of case IIc. These same authors<sup>6</sup> report evidence showing that the reduction of vanadium(IV) to vanadium(II) involves catalytic currents or induced currents or both.

(7) D. H. Geske, *THIS JOURNAL*, **62**, 1062 (1959).

(8) L. Meites and T. Meites, *Anal. Chem.*, **28**, 103 (1956).

(9) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 108 ff.

(10) S. A. Moros and L. Meites, unpublished, see ref. 6.

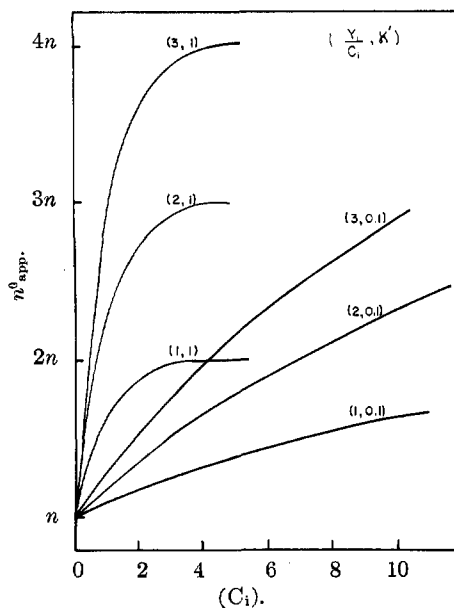


Fig. 5.—Case IIIc: dependence of  $n_{app}^0$  on  $(Y_i)/(C_i)$  and  $K'$ .

The preceding treatment points to three alternate methods for determining kinetic rate constants (or ratios of rate constants) of the secondary chemical reactions. The three types of useful information are current-time data, variation of  $n_{app}^0$  with  $(C_i)$  or  $t$ , and quantitative analysis of the solution. Selection of the most appropriate method will depend on the peculiar characteristics of each case. In cases IIb and IIIb the true  $n$ -value may be evaluated directly by extrapolation of  $n_{app}^0$  data to low  $(C_i)$ , or by extrapolation of  $n_{app}^0$  values to high  $(C_i)$  values where  $n_{app}^0 = n/2$ . In case IIc an extrapolation of  $n_{app}$  to zero time gives the true  $n$ -value, while in case IIIc,  $n_{app}^0$  is obtained by extrapolation to zero  $(C_i)$ .

The range of values of rate constants accessible for evaluation by methods indicated above depends upon the particular case. In case IIb the range is dependent on the value of  $p$ , which would ordinarily range from  $10^{-1}$  to  $10^{-4}$  sec.<sup>-1</sup>, hence limiting  $k_2$  to  $10^{-4}$  to  $10^3$  liter mole<sup>-1</sup> sec.<sup>-1</sup>. For case IIIb the ratio of rate constants  $K$  could be obtained over the range 1 to  $10^4$  from  $n_{app}^0$ - $(C_i)$  data.

Whereas treatment of catalytic cases by voltammetric techniques is feasible for values of  $k_2(Z)$  larger than  $0.1$  sec.<sup>-1</sup>, controlled potential coulometry is concerned with somewhat slower catalytic reactions. In case IIc,  $\gamma'$  can range from approximately  $10^{-1}$  to 10, thus giving a range of  $k_2(Z)$  of  $10^{-5}$  to 1 sec.<sup>-1</sup>.

The accessible range of  $K'$  values for case IIIc depends on  $(Y_i)$ . Since  $K'$  is a ratio of rate constants, independent measurement of one of the constants is necessary for absolute evaluation of the other.

Single secondary reactions too rapid for treatment by cases IIb and IIc may be made accessible by purposely introducing a competing parallel reaction and treating the system by case IIIb or IIIc.

Experimental elucidation of an electrode reaction

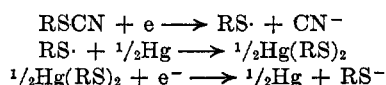
where secondary reactions occur certainly must include solution analysis. Clearly, the electrochemical data are extremely useful and in certain circumstances may furnish kinetic data which otherwise would be difficult to obtain. It should be noted that where some estimate of diffusion coefficient is available the true  $n$ -value for a reaction may be obtained from polarographic and chronopotentiometric data. Since  $n_{app}^0$  is dependent on  $p$  at a particular ( $C_i$ ) value in cases IIb and IIc and is independent of  $p$  for cases IIIb and IIIc an experimental means is at hand for distinguishing parallel and single secondary reactions.

This treatment has assumed that limiting current conditions are in force at the electrode throughout the electrolysis. Thus potentiostats whose voltage output is so inadequate that limiting current conditions are not attained until the electrolysis has proceeded for some time, cannot be used in an experimental study based on the mathematical expressions derived above.

The expressions derived can be applied with minor modifications to millicoulometric determinations,<sup>11</sup> where only a part of the electroactive

material is consumed.

Non-integral  $n$ -values alone are not a sufficient condition for concluding that the case under consideration is one of the cases discussed here. Higher order secondary reactions, induced reactions,<sup>6</sup> competing secondary electrode reactions or other complex reaction schemes can also result in non-integral  $n$ -values. For example, Lanza, *et al.*,<sup>12</sup> report an  $n$  of 1.26 in the millicoulometric reduction of phenyl and benzyl thiocyanate. The postulated reaction scheme was



The  $n$ -value was explained by the authors as caused by the loss of mercuric mercaptide through diffusion away from the dropping mercury electrode.

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## THE ELECTROOXIDATION OF THE TETRAPHENYLBORATE ION; AN EXAMPLE OF A SECONDARY CHEMICAL REACTION FOLLOWING THE PRIMARY ELECTRODE PROCESS

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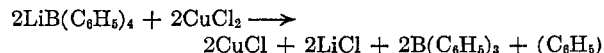
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Voltammetric and chronopotentiometric studies with platinum electrodes have shown that tetraphenylborate ion in acetonitrile solution undergoes a two-electron oxidation. Controlled potential coulometric data for  $n_{app}^0$ , the apparent number of faradays per mole, varied from 1.02 to 1.8 over the concentration range  $1.0 \times 10^{-2}$  to  $8.9 \times 10^{-5}M$ . This variation indicated that a secondary chemical process was consuming tetraphenylborate ion. A reaction scheme is proposed in which the products of the primary electrode process are biphenyl and diphenylboronium ion. A secondary reaction between tetraphenylborate ion and hydrogen ion, which is generated by reaction of diphenylboronium ion with the solvent system, produces benzene and triphenylboron. Solution analysis data are presented in support of the proposed reaction scheme. Reasonable agreement was found between the experimental dependence of  $n_{app}^0$  on the concentration of tetraphenylborate ion and that calculated on basis of the rate of the secondary reaction and the electrode parameter.

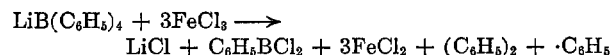
In the decade since the preparation of lithium tetraphenylborate by Wittig, *et al.*,<sup>1</sup> a voluminous literature has accumulated on the chemistry of the tetraphenylborate ion (TPB). Nearly two hundred literature references are listed in recent bibliographies.<sup>2</sup> The bulk of the work has been concerned with application of TPB as an analytical reagent for various cations, including potassium.

This present study was prompted by the observation that TPB could be electrolytically oxidized at a platinum electrode in anhydrous acetic acid, *N,N*-dimethylformamide and acetonitrile. The work reported below was done employing acetonitrile as solvent.

A number of preliminary studies of the homogeneous chemical oxidation of TPB have been made under diverse conditions. The reaction



has been reported in ether solution.<sup>3</sup> Spier<sup>4</sup> developed an oxidimetric method for determination of potassium in which precipitated potassium TPB was treated with acidic ceric ammonium nitrate at 92°. One mole of potassium TPB consumed 72 equivalents of ceric ion, whereas total oxidation of TPB to boric acid, carbon dioxide and water would require 120 equivalents. Razuvaev and Brilkina<sup>5</sup> heated anhydrous ferric chloride and potassium TPB in acetone "on the water-bath" for 30 minutes. On basis of the analysis of the reaction mixture, this reaction scheme was suggested



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