these conclusions can be drawn with considerable confidence: 1. Only one species contributes to the absorbance at a given isosbestic point. 2. The equilibrium of this species is not appreciably affected by temperature changes. 3. The only manner in which isosbestic points can be generated is for the absorptivity of one species at a given wave length to be linearly dependent on temperature, at least to a good approximation.[4] 4. Multiplication of a family of absorption spectra generated at temperatures $t_1$, $t_2$, $t_3$, . . . $t_n$ by the corresponding factor $(1 + \gamma t_n)/(1 + \gamma t_1)$, to a good approximation, only shifts and does not destroy the isosbestic points which have resulted in the original generation.

NOTE ADDED IN PROOF.—Since the foregoing paper was submitted for publication, Cohen and Fischer have concluded in a paper entitled "Isosbestic Points" (J. Chem. Soc.,

(4) It is possible that $\epsilon_i(\lambda) = \epsilon_i^0(\lambda)\exp h(\lambda)t$; in the approximation of $h(\lambda)t \ll 1$, it would thus assume the form given in eq. 11.

3044 (1962)) that whenever absorbing components are related linearly, isosbestic points are not confined to two-component systems. It is hoped that the foregoing paper will clearly show that although possible in principle, it is exceedingly unlikely that isosbestic points will arise from multi-component absorbing systems, even when they are linearly related, especially when more than one isosbestic point occurs.

Cohen and Fischer are correct in stating that systems producing isosbestic points are characterized by only one degree of freedom. At constant temperature two absorbing components are allowed, provided they are linearly related. When temperature is varied, there are no compositional degrees of freedom and only one absorbing component is allowed. Presumably, then, variation of total pressure on a system containing only one absorbing component could give rise to isosbestic points.

# SECONDARY REACTIONS IN CONTROLLED POTENTIAL COULOMETRY. II. SECONDARY ELECTRODE REACTIONS

BY ALLEN J. BARD AND JASPAL S. MAYELL

*Department of Chemistry, The University of Texas, Austin 12, Texas*

*Received April 23, 1962*

Controlled potential coulometric experiments in which the product of the primary electrode reaction undergoes secondary chemical reactions involving the formation of an electroactive species are considered. A mathematical treatment of the effect of these secondary reactions upon $n_{app}$, the apparent number of faradays per mole of electroactive material, and upon current–time behavior, is given. The use of controlled potential coulometric data for the determination of the number of electrons involved in each electrode reaction, for the elucidation of the over-all reaction mechanism, and for the estimation of the rate constants of the intervening chemical reactions, is described, and several examples are given.

## Introduction

Controlled potential coulometric electrolysis, a technique for studying electrode reactions, is mainly used for the determination of $n$, the number of faradays per mole of electroactive substance consumed, and for the production of macro amounts of electrolysis products. When secondary chemical reactions occur, non-integral $n$-values are sometimes found, and by examination of the variation of $n$ with such variables as concentration and stirring rate, information about the mechanism of the electrode reaction can be obtained. In a previous communication[1] the effects of secondary chemical reactions between the product of the primary electrode reaction and the original electroactive species, or secondary reactions leading to the regeneration of the electroactive species, were discussed. This paper discusses cases in which the product of the primary electrode reaction undergoes reactions leading to the occurrence of additional electrode reactions, and the effect of these secondary electrode reactions upon $n$, and upon the variation of the electrolysis current with time. The use of controlled potential coulometric data for the determination of the number of electrons involved in the electrode reactions, for the elucidation of the over-all mechanism of the electrode reaction, and

(1) D. H. Geske and A. J. Bard, *J. Phys. Chem.*, **63**, 1057 (1959).

for the estimation of the rate constants of the intervening chemical reactions, is described.

**Classification.**—The four general cases are classified according to the behavior of the reaction intermediate, R. The primary electrode reaction is represented as

$$C \pm ne^- \longrightarrow R$$
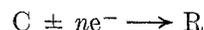
where C is the electroactive material and R is the soluble primary product of the electrode reaction. In the reactions below, A, B, P, $R_2$, Y, and Z represent electrolytically inert materials and the applied potential is such that all electrode reactions occur without activation polarization.

**Case I. R' Undergoes a Single Secondary Pseudo-first Order Reaction and an Electrode Reaction.**—

$$R \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} R'$$

$$R' + Z \longrightarrow P$$

$$R' \pm ne^- \longrightarrow Y$$
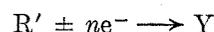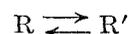
**Case II. R' Undergoes a Single Second-order Reaction and an Electrode Reaction.**—

$$R \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} R'$$

$$2R' \longrightarrow R_2$$

$$R' \pm ne^- \longrightarrow Y$$

**Case III. R Undergoes Parallel Pseudo-first Order Secondary Reactions, One of Which Produces an Electroactive Species.—**

$$R + Z \longrightarrow R' + B$$

$$R + A \longrightarrow P$$

$$R' \pm ne^- \longrightarrow Y$$
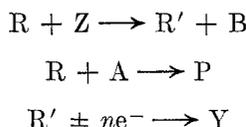
**Case IV. R Undergoes Parallel Secondary Reactions; a Second-order Reaction and a Pseudo-first Order Reaction Which Produces an Electroactive Species.—**

$$R + Z \longrightarrow R' + A$$

$$2R \longrightarrow R_2$$

$$R' \pm ne^- \longrightarrow Y$$
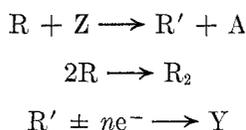
Variations of these cases, two of which are discussed later, can be treated by suitable modification of the procedure outlined below.

## Mathematical Treatment

**General Considerations.**—The assumptions and conditions of this treatment are the same as those previously described.[1] The current, $i$, taken as a positive quantity, is related to the rate of consumption of C and the rate of the production of Y by

$$i = -n_1 FV[\mathrm{d}(C)/\mathrm{d}t] \text{ electrode reaction } +$$

$$n_2 FV[\mathrm{d}(Y)/\mathrm{d}t] \text{ electrode reaction} \quad (1)$$

where $F$ is the faraday, $V$ is the total volume of the solution, and $(C)$ and $(Y)$ are the concentrations of species C and Y, respectively. The rates of concentration change under limiting current conditions are

$$[\mathrm{d}(C)/\mathrm{d}t] \text{ elec. rxn. } = -p(C) \quad (2)$$

$$[\mathrm{d}(Y)/\mathrm{d}t] \text{ elec. rxn. } = p(R') \quad (3)$$

where $p$ is a constant, depending upon the prevailing mass transfer conditions, electrode area, solution volume and cell geometry,[1] and is assumed to be the same for both electrode reactions. Combination of (1), (2), and (3) yields

$$i = n_1 FVp(C) + n_2 FVp(R') \quad (4)$$

The apparent number of electrons per mole of electroactive materials, $n_{app}$, is determined experimentally, and is defined as

$$n_{app} = \frac{\int_0^t i \, \mathrm{d}t}{FV[(C_i) - (C)]} \quad (5)$$

where $(C_i)$ is the initial concentration of C. The notation $n^0_{app}$ refers to evaluation of $n_{app}$ at the completion of the electrolysis, where $(C)$ approaches zero

$$n^0_{app} = \frac{\int_0^\infty i \, \mathrm{d}t}{FV(C_i)} = \frac{Q}{FN} \quad (6)$$

where $N$ is the number of moles of C, and $Q$ is the amount of electricity consumed in coulombs.

Since C is only involved in the primary electrode reaction, the equation

$$(C) = (C_i)e^{-pt} \quad (7)$$

holds in all cases.

**Case I.**—The intermediate R changes to $R'$ before undergoing the competing reactions

$$R' + Z \xrightarrow{k_1} P \quad (8)$$

$$R' \pm n_2 e^- \longrightarrow Y \quad (9)$$

The production of $R'$ is assumed to be rapid enough so that the rate of this reaction does not enter into the over-all kinetics of the reaction. When $k_1$ is either very large or very small, integral values of $n^0_{app}$ are obtained. For $k_1 \approx 0$, the reaction is composed of two succeeding electrode reactions, and $n^0_{app} = n_1 + n_2$, while when $k_1$ is large, $n^0_{app} \approx n_1$. For the purposes of this discussion Z is assumed present in large excess, so that (8) is a pseudo-first order reaction, with $k_1' = k_1(Z)$. The system is described by the equation

$$\mathrm{d}(R')/\mathrm{d}t = p(C) - k_1'(R') - p(R') \quad (10)$$

Solving (7) and (10), the value of $R'$ as a function of time is obtained

$$(R') = \frac{p}{k_1'} (C_i)e^{-pt} (1 - e^{-k_1't}) \quad (11)$$

Combining (4) and (11) the variation of $i$ with time is obtained

$$i = FpV(C_i)e^{-pt}\left[ n_1 + n_2 \frac{p}{k_1'} (1 - e^{-k_1't}) \right] \quad (12)$$

The log current *vs.* time plots in Fig. 1 indicate that the observed deviation from linearity is only slight. Integration of eq. 12 with respect to time, and introduction into (6) yields

$$n^0_{app} = n_1 + n_2[1/(1 + \lambda)] \quad (13)$$

where $\lambda = k_1'/p$. Variation of $n^0_{app}$ with $\lambda$, shown in Fig. 2, indicates that non-integral values of $n^0_{app}$ will be obtained for a range of $\lambda$ of $10^{-2}$ to $10^2$. For this reaction scheme, $n^0_{app}$ is independent of changes in $(C_i)$.

The modification of Case I, where the production of $R'$ is kinetically controlled

$$R \xrightarrow{k_1} R' \quad (14)$$

with no competitive secondary reaction, may be treated in a similar manner. The equations describing the system are

$$\mathrm{d}(R)/\mathrm{d}t = p(C) - k_1(R) \quad (15)$$

$$\mathrm{d}(R')/\mathrm{d}t = k_1(R) - p(R') \quad (16)$$

Solving (7), (15), and (16) yields

$$(R') = \frac{k_1 p(C_i)}{(k_1 - p)^2} [(k_1 - p)te^{-pt} -$$
$$e^{-pt} + e^{-k_1 t}] \quad (17)$$

and

$$i = pFV(C_i) \left\{ n_1 e^{-pt} + \frac{n_2 k_1 p}{(k_1 - p)^2} \times \right.$$
$$\left. [(k_1 - p)te^{-pt} - e^{-pt} + e^{-k_1 t}] \right\} \quad (18)$$

Variations of $\log i$ with $t$ for several values of $k_1$ is shown in Fig. 3. Under all conditions $n^0{}_{app} = n_1 + n_2$.

**Case II.**—The intermediate R changes to R' before undergoing the competing reactions

$$2R' \xrightarrow{k_1} R_2 \quad (19)$$

$$R' \pm n_2 e \longrightarrow Y \quad (20)$$

The limits of $n^0{}_{app}$ for very large and very small $k_1$'s are the same as in Case I. The production of R' is given by

$$d(R')/dt = p(C) - p(R') - k_1(R')^2 \quad (21)$$

Combining (21) with (7), a second degree equation in $(R')$ and $t$ which cannot be solved in closed form is obtained. This equation also results as a special case of the reaction scheme in case IV, and results of the numerical solution of this equation will be discussed in that section.

**Case III.**—R reacts in two parallel chemical reactions, and an electroactive substance is produced in one of these

$$R + Z \xrightarrow{k_1} R' + B \quad (22)$$

$$R + A \xrightarrow{k_2} P \quad (23)$$

$$R' \pm n_2 e^- \longrightarrow Y \quad (24)$$
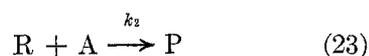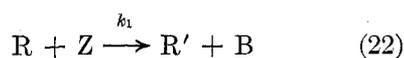
This treatment assumes Z and A are present in large excess, so that reactions 22 and 23 are pseudo-first order reactions, with $k_1' = k_1(Z)$ and $k_2' = k_2(A)$. When the ratio of $k_1'/k_2'$ is large, $n^0{}_{app}$ is essentially $n_1 + n_2$, while when $k_1'/k_2'$ is small, $n^0{}_{app} \approx n_1$. The system is described by the equations

$$d(R)/dt = p(C) - (k_1' + k_2')(R) \quad (25)$$

$$d(R')/dt = k_1'(R) - p(R') \quad (26)$$

Combining (25) and (7) and solving for $(R)$ yields

$$(R) = \frac{p(C_i)}{(k_1' + k_2' - p)} [e^{-pt} - e^{-(k_1' + k_2')t}] \quad (27)$$

Substituting (27) and (26), and solving for $(R')$, gives

$$(R') = \frac{k_1' p(C_i)}{(k_1' + k_2' - p)^2} \times$$
$$e^{-pt} [e^{-(k_1' + k_2' - p)t} + (k_1' + k_2' - p)t - 1] \quad (28)$$
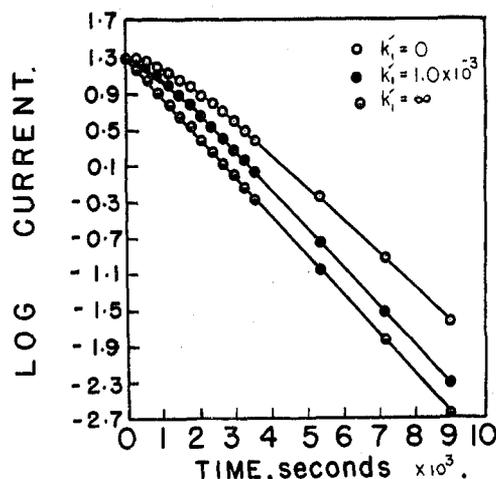


Fig. 1.—Case I: $\log i$ vs. $t$ at different values of $k_1'$, calculated for $V = 0.2$ l., $p = 10^{-3}$ sec.$^{-1}$, $(C_i) = 1.0$ m$M$, and $n_1 = n_2 = 1$.
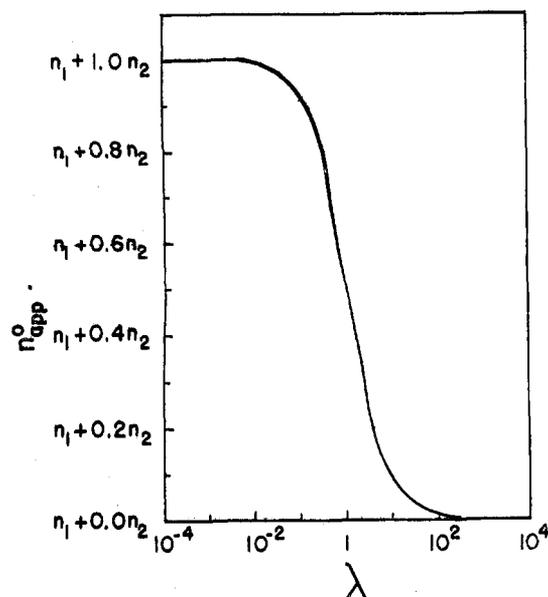


Fig. 2.—Case I: variation of $n^0_{app}$ with $\lambda$.

and, from (4)

$$i = pFV(C)e^{-pt} \left[ n_1 + \frac{n_2 k_1' p}{(k_1' + k_2' - p)^2} \times \right.$$
$$\left. [e^{-(k_1' + k_2' - p)t} + (k_1' + k_2' - p)t - 1] \right] \quad (29)$$

The variation of current with time for several values of $k_1'$ and $k_2'$ is shown in Fig. 4. Combination of (29) and (6) yields

$$n^0{}_{app} = n_1 + n_2[1/(1 + \lambda')] \quad (30)$$

where $\lambda' = k_2'/k_1'$. Equation 30 is the same form as (13), and variation of $n^0{}_{app}$ with $\lambda'$ can be observed from Fig. 2, if $\lambda$ is replaced by $\lambda'$.

**Case IV.**—R reacts in two parallel chemical reactions, one a second-order reaction and the other a pseudo-first order reaction generating an electroactive species.
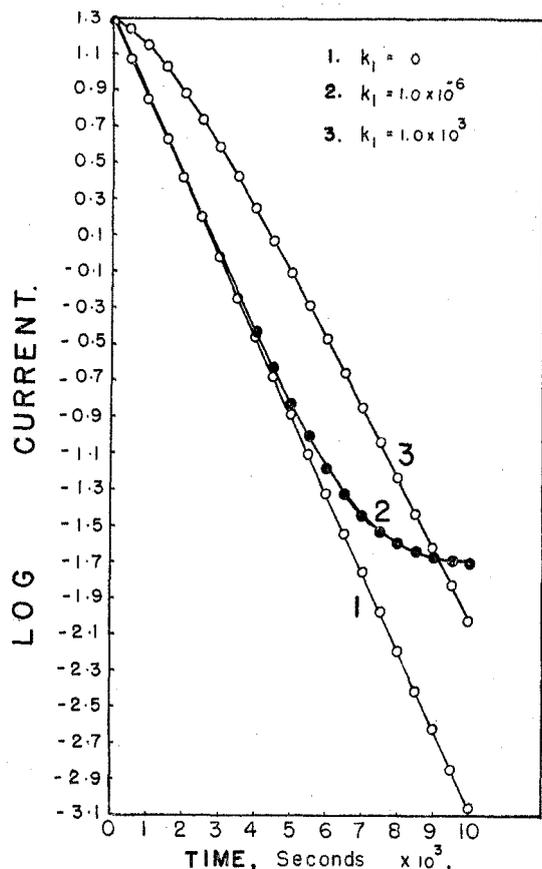
Fig. 3.—Case I: log $i$ vs. $t$ at different values of $k_1$ calculated for $V = 0.2$ l., $p = 10^{-3}$ sec.$^{-1}$, $(C_i) = 1.0$ m$M$, and $n_1 = n_2 = 1$.

$$R + Z \xrightarrow{k_1} R' + B \qquad (31)$$

$$2R \xrightarrow{k_2} R_2 \qquad (32)$$

$$R' \pm n_2 e^- \longrightarrow Y \qquad (33)$$
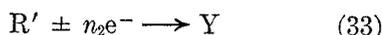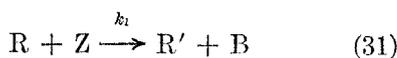
The system is described by the equations

$$d(R)/dt = p(C) - k_1'(R) - k_2(R)^2 \quad (34)$$

$$d(R')/dt = k_1'(R) - p(R') \qquad (35)$$

where $k_1' = k_1(Z)$, $Z$ being assumed present in large excess. Combination of (24) and (7) yields

$$d(R)/dt = p(C_i)e^{-pt} - k_1'(R) - k_2(R)^2 \quad (36)$$

It was not possible to obtain a closed-form solution of eq. 36. Numerical solutions were obtained with the aid of a CDC 1604 computer employing a program based on the Adams-Moulton and Runge-Kutta methods. The values of $(R)$ as a function of time for several values of $k_1'$ and $k_2$ are shown in Fig. 5. Combination of (4), (6), and (7) yields

$$n^0{}_{app} = n_1 + \frac{n_2 p}{(C_i)} \int_0^\infty (R')dt \qquad (37)$$

and solving (35)

$$\int_0^\infty (R')dt = \frac{k_1'}{p} \int_0^\infty (R)dt \qquad (38)$$
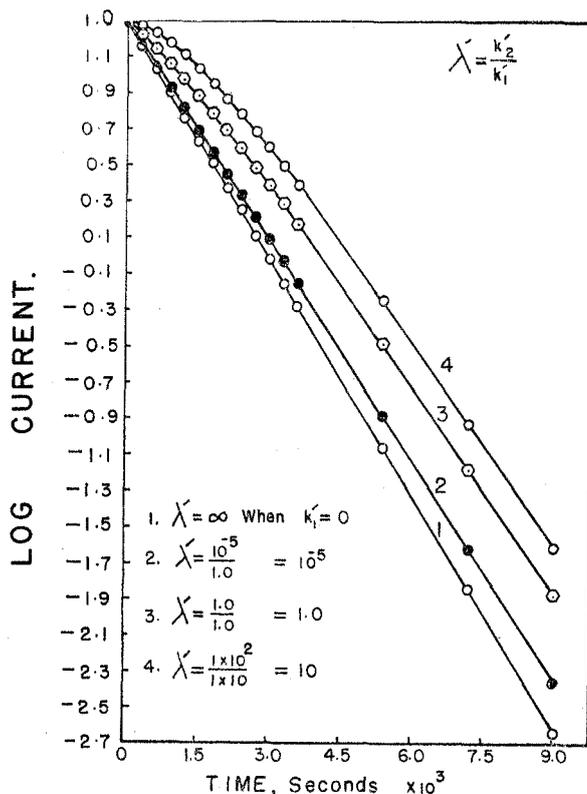


Fig. 4.—Case III: log $i$ vs. $t$ at different values of $k_2'/k_1'$ calculated for $V = 0.2$ l., $p = 10^{-3}$ sec.$^{-1}$, $(C_i) = 1.0$ m$M$, and $n_1 = n_2 = 1$.
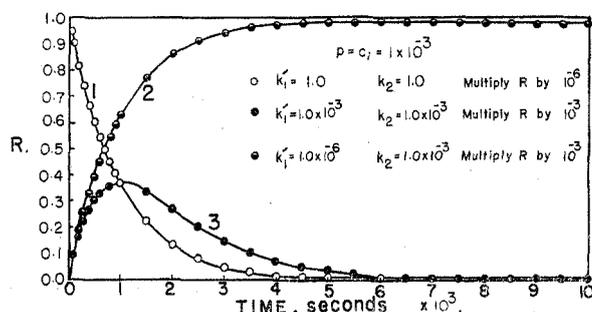


Fig. 5.—Case IV: variation of $(R)$ with $t$ at different values of $k_1'$, $k_2$, $p$, and $C_i$.

The values of $\int_0^\infty (R)dt$ were obtained by graphical integration of $(R)$ vs. time plots, and values of $n^0{}_{app}$ for different values of $k_1'$ and $k_2$ are shown in Fig. 6. Although the behavior of $(R)$ with time is different for the same value of the ratio $k_1'/k_2$, for different individual values of $k_1'$ and $k_2$ (compare curves 1 and 3, Fig. 5), the area under curves of the same $k_1'/k_2$, when multiplied by $k_1'/(C_i)$, are the same, so that the curves in Fig. 6 depend only upon the ratio of the rate constants.

The variation of the current with time was calculated for several values of $k_1'$ and $k_2$ by solving eq. 35 for $(R')$, using values of $(R)$ obtained from the numerical solution of (36), and introducing them into (4). The current–time curves in Fig. 7 depend upon the individual values of $k_1'$ and $k_2$, rather than their ratio.

## Discussion

The rate constants for the secondary chemical reactions in the preceding schemes can be determined from (1) the behavior of the electrolysis current with time, (2) the variation of $n^0_{app}$ with $p$ and $(C_i)$, and (3) the relative quantities of products formed. The current-time behavior in general does not give sufficient information to allow the prediction of reaction mechanisms or the estimation of rate constants. In all cases the current decays to background level, and the slight curvature of log $i$-$t$ curves, although indicative of kinetic complications, is not significant enough to allow differentiation between the cases. Moreover, curvature of log $i$-$t$ curves may result in even simple electrode reactions if the potential of the electrode is not maintained at the mass-transfer limiting region. However current-time curves do allow differentiation between these cases and catalytic reactions[1] (reactions involving the regeneration of the original electroactive substance by a chemical reaction following the electrode reaction), in which case the current decays to a constant value larger than the background current.

Differentiation among the four cases under study here can be most easily accomplished by observing the variation of $n^0_{app}$ with $(C_i)$, $p$, and solvent. In case I, $n^0_{app}$ is independent of $(C_i)$, but varies with $p$. In case III, $n^0_{app}$ is independent of both $(C_i)$ and $p$. Cases II and IV are indicated when $n^0_{app}$ is dependent upon both $(C_i)$ and $p$. Differentiation between these two cases may sometimes be accomplished by changing the solvent or supporting electrolyte (the usual reactants in the secondary chemical reaction), since case IV involves reaction with a second substance while case II does not. Variation of $n^0_{app}$ with temperature will sometimes be a useful diagnostic aid.[2] The analysis of products obtained in controlled potential coulometry is certainly an important aid for deducing reaction mechanisms. Quantitative analysis of these products should lead to reinforcement of the $n^0_{app}$ data. In some cases this data alone may be useful in estimating rate constants, especially when $n^0_{app}$ data is difficult to obtain, (e.g., when an appreciable background current is present).

The range of rate constants accessible for evaluation by these methods depends upon the particular case. Taking $p$ to be adjustable between $10^{-1}$ and $10^{-4}$ sec.$^{-1}$, then for case I, $k_1'$ in the range of 1 to $10^{-5}$ sec.$^{-1}$ will lead to non-integral values of $n^0_{app}$. For case II, the range of $k_1$ is between $10^{-1}$ and $10^{-7}$ sec.$^{-1}$, for usual concentrations. For cases III and IV only a ratio of rate constants can be obtained. This ratio may be between $10^{-2}$ and $10^2$ for case III, and between $10^{-4}$ and 1 (depending upon $(C_i)$) for case IV. For very large rate constants, the theoretical model may not apply, even if the ratio of rate constants may still appear in the accessible range, since most of the chemical reaction will occur very close to the electrode surface and the homogeneous concentration of intermediate assumed in this treatment will not be obtained. Although qualitatively similar results will be observed in such cases, the calculated

(2) J. S. Mayell and A. J. Bard, to be submitted for publication.
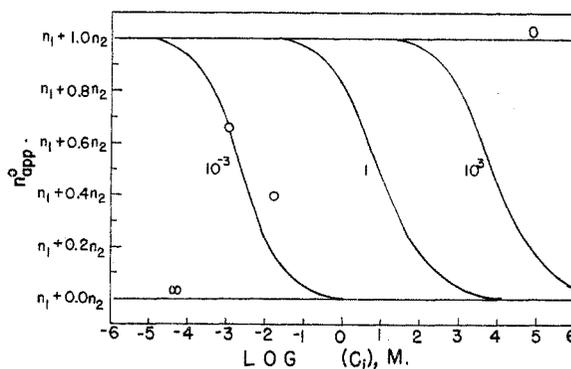


Fig. 6.—Case IV: variation of $n^0_{app}$ with log $(C_i)$ at different values of $\lambda = k_1'/k_2$. O, experimental points obtained for electroreduction of benzyldimethylanilinium bromide at $-35°$ in acetonitrile.
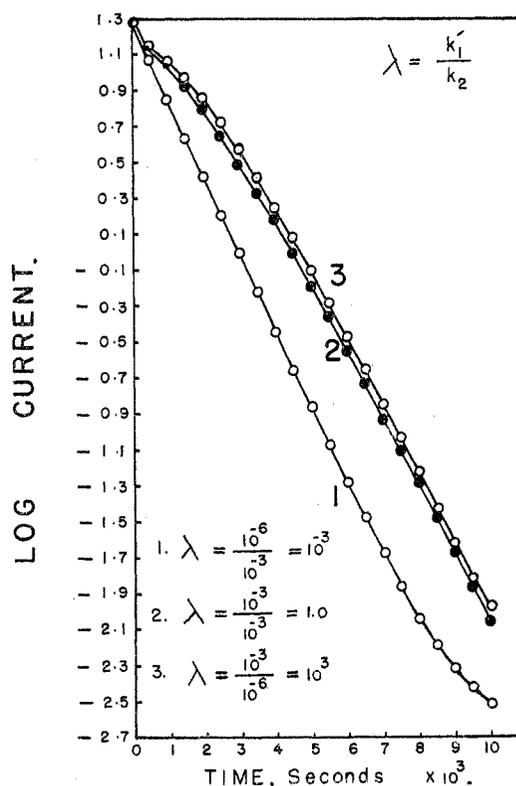


Fig. 7.—Case IV: log $i$ vs. $t$ at different values of $k_1'$ and $k_2$ calculated for $V = 0.2$ 1., $p = 10^{-3}$ sec.$^{-1}$, $(C_i) = 1.0$ m$M$, and $n_1 = n_2 = 1$.

numerical value of $k_1'/k_2$ may be significantly in error.

Examples of reaction schemes illustrated by the preceding cases will often be found in electrode reactions of organic substances. Frequently the product of the electrode reaction is a free radical which may couple with another radical, react with the solvent, or undergo further electrode reactions. Although the electroreduction of the potassium salt of 2-carboxybenzaldehyde (I) has not been studied by controlled potential coulometry, the products of the electrode reaction are said to be hydrodiphthalyl (II) and phthalide (III).[3,4] A

(3) V. M. Rodionow and V. V. Levchenko, J. Gen. Chem. U.S.S.R., 6, 1563 (1936).

possible reaction mechanism leading to these products and corresponding to case II involves the reactions



(39)

(I)



(40)



(II)



(42)



(43)

(III)
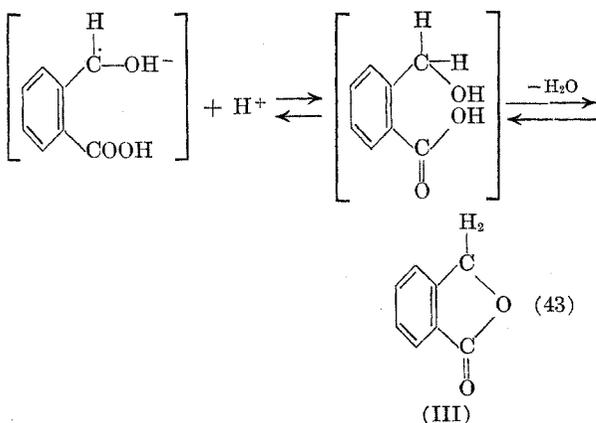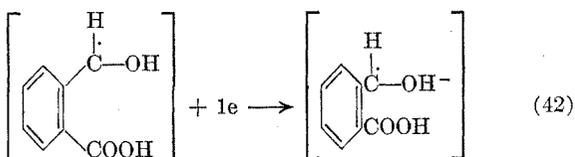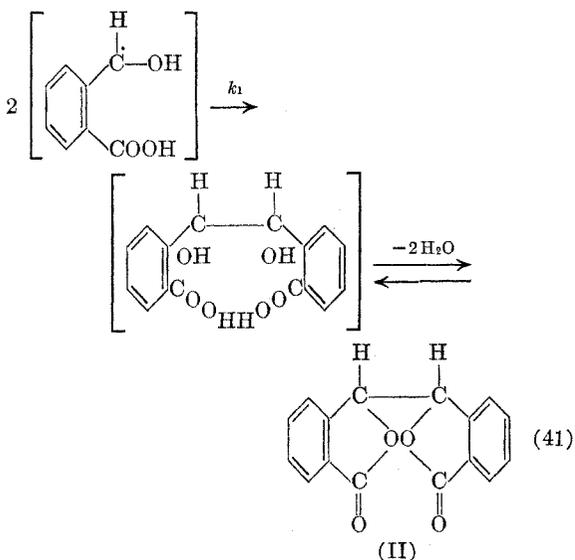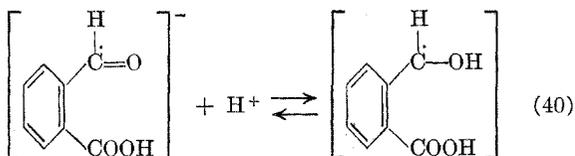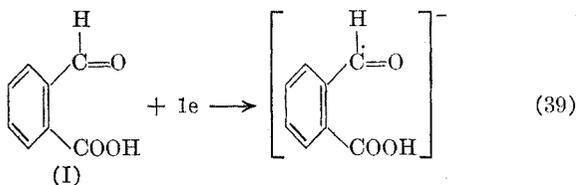
The electrooxidation of hydrazine at a platinum electrode, recently discussed by Karp and Meites,[5,6]

(4) M. J. Allen, "Organic Electrode Processes," Chapman and Hall, London, 1958, p. 71.
(5) S. Karp, M.S. Thesis, Polytechnic Institute of Brooklyn, 1960.
(6) S. Karp and L. Meites, J. Am. Chem. Soc., 84, 906 (1962).
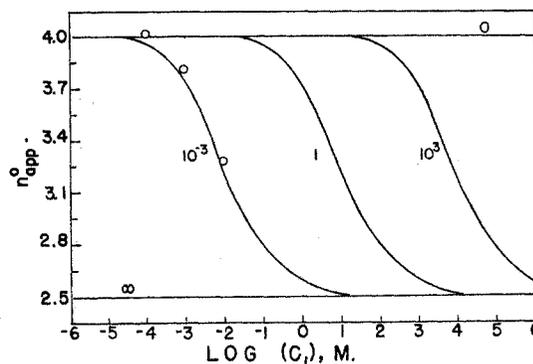
Fig. 8.—Variation of $n_{app}^0$ with log $(C_i)$ for modification of case II for different values of $p/k_1$: O, experimental points from results of Karp and Meites for electrooxidation of hydrazine, in 0.05 $F$ $H_2SO_4$.

is related to case II. The mechanism proposed by these authors for dilute sulfuric acid solutions is essentially

$$N_2H_4 - 2e \longrightarrow N_2H_3^+ + H^+ \quad (44)$$

$$N_2H_3^+ \rightleftharpoons N_2H_2 + H^+ \quad (45)$$

$$^1/_2(2N_2H_2 \xrightarrow{k_1} NH_3 + HN_3) \quad (46)$$

$$^1/_2(HN_3 - 1e \longrightarrow H^+ + {}^3/_2N_2) \quad (47)$$

$$N_2H_2 - 2e \longrightarrow N_2 + 2H^+ \quad (48)$$
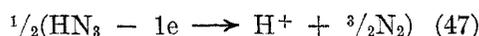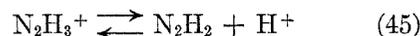
The previous treatment of case II requires modification before application to this reaction scheme because of reaction 47. The treatment is very similar to that given previously and the result is[7]

$$n^0_{app} = n_1 + n_2 + \frac{p(n_3 - n_2)}{(C_i)} \int_0^\infty (R') \, dt \quad (49)$$

where $n_1$, $n_2$, and $n_3$ are the number of electrons involved in (44), (47), and (48), respectively. The values of the integral in (49) are the same as those determined numerically in case IV. The results for the variation of $n^0_{app}$ with $(C_i)$ for the case of hydrazine $(n_1 = 2, n_2 = 1/2, n_3 = 2)$ is shown in Fig. 8, with the experimental points given by Karp and Meites.[5,6] The proposed mechanism does fit the expected coulometric behavior and yields a value of $p/k_1$ of about $10^{-3}$.

This work was prompted by results obtained in the electroreduction of benzyldimethylanilinium bromide.[2] On the basis of controlled potential coulometry as well as polarographic and other data, the following mechanism, corresponding to case IV, was proposed

$$\begin{array}{c} CH_3 \quad + \\ C_6H_5CH_2-N-C_6H_5 + 1e \longrightarrow \\ CH_3 \end{array}$$

$$\begin{array}{c} CH_3 \\ C_6H_5CH_2\cdot + C_6H_5N: \quad (50) \\ CH_3 \end{array}$$
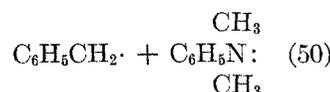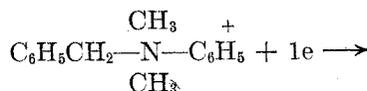
(7) J. S. Mayell, Ph.D. Thesis, The University of Texas, 1962.

$$C_6H_5CH_2\cdot + H_2O \text{ (or } CH_3CN) \xrightarrow{k_1}$$

$$C_6H_5CH_3 + OH\cdot \text{ (or } CH_2CN\cdot) \quad (51)$$

$$C_6H_5CH_2\cdot + C_6H_5CH_2\cdot \xrightarrow{k_2}$$

$$C_6H_5CH_2CH_2C_6H_5 \quad (52)$$

$$OH\cdot \text{ (or } CH_2CN\cdot) + 1e \longrightarrow$$

$$OH^- \text{ (or } CH_2CN^-) \quad (53)$$
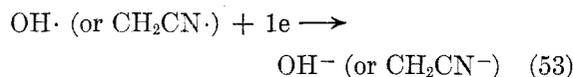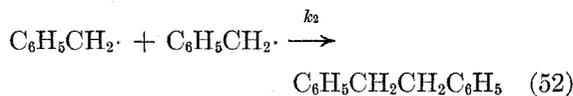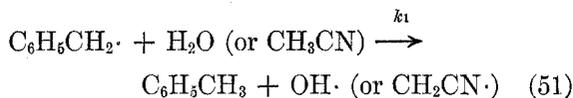
Some experimental points obtained during the controlled potential coulometric reduction of benzyldimethylanilinium bromide are plotted in Fig. 6, and indicate a ratio of rate constants for reactions 51 and 52 of about $10^{-3}$. Details of this work will be presented elsewhere.[2]

Because controlled potential coulometry allows the unequivocal determination of $n^0_{app}$, independent of estimations of diffusion coefficients, electrode areas, and transfer coefficients, it is a valuable adjunct to other electrochemical methods in the determination of mechanisms of electrode reactions. Often, to be sure, several possible reaction schemes will lead to the same over-all behavior, and in these cases, actual observation of the reaction intermediates by such techniques as electron paramagnetic resonance spectroscopy and visible or ultraviolet spectrophotometry is necessary.

---

# VAPOR PRESSURE STUDIES OF SULFUR TRIOXIDE AND THE WATER–SULFUR TRIOXIDE SYSTEM[1]

BY J. H. COLWELL[2] AND G. D. HALSEY, JR.

*Department of Chemistry, University of Washington, Seattle 5, Washington*

The vapor pressures of liquid and $\gamma$-SO$_3$ (trimeric form, m.p. 16.86°) have been determined in an all-glass apparatus. The vapor pressure of the so-called $\beta$-SO$_3$, which is only formed in the presence of $>10^{-5}$ mole fraction of water, also is reported. Vapor pressure and melting point studies of the H$_2$O–SO$_3$ system are reported in the range of 0.8 mole fraction SO$_3$ upward. The solutions so formed solidify at constant temperature to form a solid solution of the same composition as the melt. A syneresis upon standing for several weeks was observed in the 0.999 mole fraction SO$_3$ sample.

## Introduction

In the gas[3] and liquid[4] phases, SO$_3$ has been shown, by spectroscopic studies, to be an equilibrium mixture of monomer and trimer. Liquid SO$_3$ freezes at 16.8° to an ice-like solid ($\gamma$-SO$_3$) which has been shown by X-ray diffraction studies[5] to be entirely trimeric. There are two other solid modifications of SO$_3$, $\alpha$- and $\beta$-SO$_3$, which are high polymers. $\alpha$-SO$_3$ is an amorphous appearing solid and $\beta$-SO$_3$ consists of needle-like crystals.

Crystals of $\beta$-SO$_3$ occur only when small quantities of water are present in samples of SO$_3$. One may assume that these crystals consist of polysulfuric acid molecules and several investigators through the years have proposed that $\beta$-SO$_3$ is a hydrate,[6-8] which amounts to the same thing.

Smits and Schoenmaker[9] found the vapor pressure of mixtures of liquid and $\beta$-SO$_3$ to be the same

as that of pure liquid SO$_3$. Furthermore, they[10] found that by careful distillation, the liquid could be removed from such samples, which left the $\beta$-SO$_3$ apparently unaffected. The vapor pressure of this form was lower than that of liquid SO$_3$, but above 31° the $\beta$-SO$_3$ slowly melted to a liquid having the same vapor pressure as pure liquid SO$_3$. From this observation it was concluded that $\beta$-SO$_3$ was a more stable form below 31°, and that water acted only as a catalyst for the transformation from liquid to $\beta$-SO$_3$.

In the present study, the vapor pressures of liquid, $\beta$-, and $\gamma$-SO$_3$ were redetermined; the vaporization process of $\beta$-SO$_3$ was studied; and the vapor pressures and melting points of the H$_2$O–SO$_3$ system from 80 to 99.9 mole % SO$_3$ were determined systematically.

## Experimental

SO$_3$ was obtained by degassing 20% fuming H$_2$SO$_4$. This was accomplished by bubbling helium through the acid while heating at 120–140° under reduced pressure and condensing the evolved SO$_3$ in a liquid nitrogen trap. The SO$_3$ then was distilled under vacuum several times to remove any H$_2$SO$_4$ carried over. These distillations were conducted at 23–25° with the vapor being condensed at 20°. Samples obtained in this way consisted entirely of liquid SO$_3$ with no needles of the $\beta$-form appearing upon standing. The samples of SO$_3$ used by several other investigators were "dried" with P$_2$O$_5$. It has been reported,[9] however, that such samples exhibited abnormally high vapor pressures. This phenomenon was reinvestigated[11] and attributed to the

(1) This research was partially supported by the Air Force Office of Scientific Research of the Air Research and Development Command.

(2) Eastman Kodak Company Fellow, 1959–1960. Based in part on a thesis submitted by Jack H. Colwell in partial fulfillment of the requirements for the Ph.D. degree at the University of Washington, 1961.

(3) R. W. Lovejoy, J. H. Colwell, D. F. Eggers, Jr., and G. D. Halsey, Jr., *J. Chem. Phys.*, **36**, 612 (1962).

(4) H. Gerding and W. J. Nijveld, *Rec. trav. chim.*, **59**, 1206 (1940).

(5) R. Westrik and C. H. MacGillavry, *ibid.*, **60**, 794 (1941).

(6) R. Weber, *Pogg. Ann.*, **159**, 313 (1876); *Ber. deut. chem. Ges.*, **19**, 3185 (1886).

(7) A. Berthoud, *Helv. Chim. Acta*, **5**, 513 (1922).

(8) V. R. Grau and W. A. Roth, *Z. anorg. allgem. Chem.*, **188**, 123 (1930).

(9) A. Smits and P. Schoenmaker, *J. Chem. Soc.*, **125**, 2554 (1924).

(10) A. Smits and P. Schoenmaker, *ibid.*, 1108 (1926).

(11) J. H. Colwell, Ph.D. Thesis, University of Washington, 1961.