

## Secondary Reactions in Controlled Potential Coulometry. IV. Reversal Coulometry and Following Chemical Reactions

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## Secondary Reactions in Controlled Potential Coulometry. IV.

### Reversal Coulometry and Following Chemical Reactions

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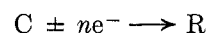
Controlled potential coulometric experiments in which the potential of the working electrode is shifted to reverse the direction of electrolysis are considered. A comparison of the number of coulombs of electricity accumulated during the forward electrolysis,  $Q_f$ , to those accumulated during the reverse electrolysis,  $Q_b$ , allows the determination of rate constants of chemical reactions following the electrode reaction. A mathematical treatment for various first- and second-order chemical reactions is given and several examples are discussed.

#### Introduction

Coulometric methods have been applied to the study of secondary reactions which affect the course of an electrolysis. If the product of the electrode reaction undergoes secondary reactions, such as reaction with the electroactive species or regeneration of the electroactive species by reaction with nonelectroactive material, the electrolysis reaction is perturbed and the measured number of coulombs involved in the electrolysis is different from that expected of the unperturbed reaction. Often anomalies in the current-time curve can be noted. For reactions in which the product of the electrode reaction forms nonelectroactive products, however, no deviations of the forward electrolysis are noted. In this case, if the electrode potential is changed so that the product of the electrode reaction is allowed to undergo a further electrode reaction (most frequently by shifting the potential so that the product, formed by say reduction, is oxidized), a chemical reaction of the product will cause a decrease in the number of coulombs required for the second electrolysis. This technique will be called *reversal coulometry*.

This paper discusses cases in which the product of the electrode reaction undergoes first- and second-order reactions following the electrode reaction. The use of reversal coulometric data for the determination of rate constants of these reactions is also described.

*Classification.* The primary electrode reaction is represented as



where C is the electroactive material and R is the soluble primary product of the electrode reaction. In the reactions below, W, X, Y, and Z represent electrolytically inert materials at the applied potential.

In case I R undergoes no further reaction; and in case II R undergoes a single pseudo-first-order reaction,  $R (+Z) \rightarrow Y$ . R undergoes a single reversible first-order reaction,  $R \rightleftharpoons Z$ , in case III and a single second-order reaction,  $2R \rightarrow Y$ , in case IV. R undergoes parallel pseudo-first-order reaction,  $R (+Z) \rightarrow Y$  and  $R (+W) \rightarrow X$ , and parallel first- and second-order reactions,  $R (+Z) \rightarrow Y$  and  $2R \rightarrow X$ , in cases V and VI, respectively.

#### Mathematical Treatment

*General Considerations.* The assumptions and conditions are the same as those previously described.<sup>1</sup> The electrolysis of species C is carried out under mass transfer controlled conditions until time  $t_1$  when the potential is shifted to one at which R is electrolyzed, but not C. In the discussion which follows it is assumed that C is first reduced to R and then the potential is shifted so that R is oxidized back to C. The treatment of cases in which R is oxidized to another species, or in which the oxidation of both R and C occurs

(1) D. H. Geske and A. J. Bard, *J. Phys. Chem.*, **63**, 1057 (1959); A. J. Bard and J. S. Mayell, *ibid.*, **66**, 2173 (1962.)

upon further electrolysis, involves straightforward extensions of the method.

During the forward reaction, the reduction of C, the electrolysis is unperturbed in all cases, and the current,  $i_t$ , is given by

$$i_t = nFVp(C) \quad (1)$$

where  $F$  is the faraday,  $V$  is the total volume of solution,  $p$  is a mass transfer constant, dependent upon prevailing mass transfer conditions, electrode area, solution volume, and cell geometry,<sup>1</sup> and  $(C)$  is the concentration of species C. The rate of electrolysis of C is

$$d(C)/dt = -p(C) \quad (2)$$

$$(C) = (C_i) \exp(-pt) \quad (3)$$

where  $(C_i)$  is the initial concentration of C. The number of coulombs of electricity consumed in the forward electrolysis,  $Q_f$ , is given by

$$Q_f = \int_0^{t_1} i_t dt = nFV(C_i)(1 - e^{-pt_1}) \quad (4)$$

For a complete electrolysis ( $pt_1$  large)

$$Q_f^0 = nFV(C_i) \quad (5)$$

where the superscript notation denotes completion of electrolysis. At  $t_1$ , R is oxidized and

$$[d(R)/dt]_{\text{elec rxn}} = -p(R) \quad (6)$$

For simplicity,  $p$  and  $n$  for the reverse reaction are assumed to be the same as those for the forward one; the extension to cases involving different  $p$  and  $n$  values follows essentially the same treatment. The current during the reverse electrolysis is

$$i_b = nFVp(R) \quad (7)$$

and

$$Q_b = \int_{t_1}^{t_2} i_b dt = nFVp \int_{(R)_{t_1}}^{(R)} (R) dt \quad (8)$$

where  $Q_b$  is the number of coulombs of electricity consumed in the reverse electrolysis (from  $t = t_1$  to  $t = t_2$ ), and  $(R)_{t_1}$  is the concentration of R at the time  $t_1$ , when the electrolysis direction was reversed. For complete electrolysis

$$Q_b^0 = \int_{t_1}^{\infty} i_b dt = nFVp \int_{(R)_{t_1}}^0 (R) dt \quad (9)$$

No sign distinction is made between the forward or backward electrolysis current or coulombs.

*Case I.* For no secondary reactions involving R, the system is described by the following equations

$$d(R)/dt = p(C) \quad 0 < t < t_1 \quad (10)$$

$$d(R)/dt = -p(R) \quad t > t_1 \quad (11)$$

with the conditions  $(R) = 0$  at  $t = 0$ , and  $(R) = (R)_{t_1}$  at  $t = t_1$ . Combining (3) and (10) and integrating the resulting equation yields an expression for  $(R)$  during the forward electrolysis, and particularly at time  $t_1$

$$(R)_{t_1} = (C_i)[1 - \exp(-pt_1)] \quad (12)$$

For the reverse electrolysis, solving (11), using (12) as an initial condition yields

$$(R) = (C_i) \exp(-pt) [\exp(pt_1) - 1] \quad (13)$$

An expression for  $Q_b$  is obtained by combining (13) and (8) and integrating

$$Q_b = nFV(C_i)(1 - e^{-pt_1})[1 - e^{-p(t_2 - t_1)}] \quad (14)$$

Some special cases are of interest. When  $(t_2 - t_1)$  is large, so that the back electrolysis is carried to completion,  $Q_b^0 = Q_f$ , as expected. When  $(t_2 - t_1) = t_1$ , or the duration of the back electrolysis is equal to that of the forward one

$$Q_b/Q_f = 1 - \exp(-pt_1) \quad (15)$$

Note that in this case the number of coulombs involved in the forward and back electrolyses are not the same since in general  $(R)_{t_1}$  is smaller than  $(C_i)$ , and the current during the back electrolysis is smaller than that during the forward one at corresponding times. Equation 15 can be used to determine  $p$ , as shown in the discussion. The  $p$  determined by this method is the  $p$  characteristic of the reverse reaction.

*Case II.* The intermediate R is consumed by an irreversible first- or pseudo-first-order reaction



where Z is present in large excess and  $k = k'(Z)$ . During the forward electrolysis the change in  $(R)$  is described by

$$d(R)/dt = p(C) - k(R) \quad (17)$$

with the initial condition  $(R) = 0$  at  $t = 0$ . Combining (3) and (17) and solving yields

$$k \neq p \quad (R)_{t_1} = \frac{p(C_i)}{k - p} (e^{-pt_1} - e^{-kt_1}) \quad (18a)$$

$$k = p \quad (R)_{t_1} = p(C_i)t_1 e^{-pt_1} \quad (18b)$$

During the reverse electrolysis

$$d(R)/dt = -(p + k)(R) \quad (19)$$

so that

$$(R) = (R)_{t_1} \exp[-(p + k)(t - t_1)] \quad (20)$$

Combination of (8) or (9) and (20) leads to expressions for  $Q_b$  and  $Q_b^0$

$$Q_b = \frac{nFVp(R)_{t_1}}{p+k} [1 - e^{-(p+k)(t_2-t_1)}] \quad (21a)$$

$$Q_b^0 = nFVp(R)_{t_1}/(p+k) \quad (21b)$$

where  $(R)_{t_1}$  is given by (18a) or (18b). Combination of (21a) and (4) then yields

$$k \neq p \quad \frac{Q_b^0}{Q_t} = \frac{p^2}{k^2 - p^2} \left[ \frac{1 - \exp[(p-k)t_1]}{\exp(pt_1) - 1} \right] \quad (22a)$$

$$k = p \quad Q_b^0/Q_t = pt_1/[2(e^{pt_1} - 1)] \quad (22b)$$

$Q_b^0/Q_t$  varies between 0 and 1 and is a function of  $pt_1$  and  $p/k$ , but not of  $(C_i)$ . A plot of  $Q_b^0/Q_t$ , which can be used in estimating  $k$ , is shown in Fig. 1.

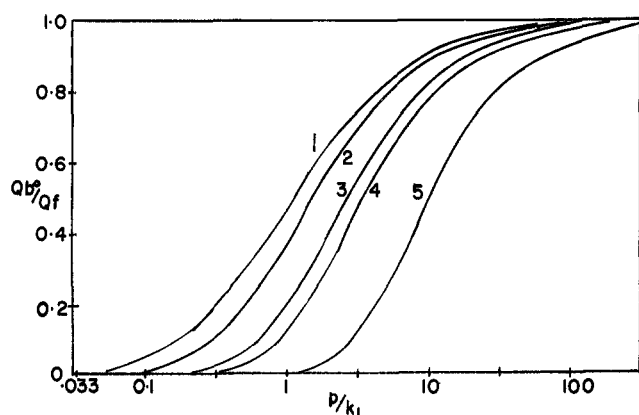


Figure 1. Case II: variation of  $Q_b^0/Q_t$  with  $p/k_1$  at various values of  $pt_1$  (or % electrolysis): (1) 0.1 (9.5%), (2) 0.51 (40%), (3) 1.6 (80%), (4) 2.3 (90%), (5) 6.9 (99.9%).

For slow reactions, a waiting period between the forward and back electrolysis, from  $t_1$  to  $\tau$ , can be used. During this waiting period

$$d(R)/dt = -k(R) \quad (23)$$

$$(R) = (R)_{t_1} \exp[-k(t - t_1)] \quad (24)$$

so that

$$(R)_\tau = (R)_{t_1} \exp[-k(\tau - t_1)] \quad (25)$$

where  $(R)_{t_1}$  is given by (18). Using  $(R)_\tau$  in (21) will yield appropriate expressions for  $Q_b$  and  $Q_b^0$ .

*Case III.* The intermediate R is consumed by a reversible first-order reaction



During the forward reaction the system is described by the equations

$$d(R)/dt = p(C) - k_f(R) + k_b(Z) \quad (27)$$

$$d(Z)/dt = k_f(R) - k_b(Z) \quad (28)$$

with the initial condition,  $(R) = (Z) = 0$ , at  $t = 0$ . From the stoichiometry of the reaction and (3)

$$(R) = (C_i) - (C) - (Z) = (C_i)[1 - \exp(-pt)] - (Z) \quad (29)$$

Combining (28) and (29) and solving for  $(Z)$  yields

$$(Z) = \frac{k_f(C_i)}{\kappa(\kappa - p)} \{ \kappa(1 - e^{-pt}) - p(1 - e^{-\kappa t}) \} \quad (30)$$

where  $\kappa = k_f + k_b$ . Combining (29) and (30) yields a value of  $(R)_{t_1}$ .

$$(R)_{t_1} = (C_i) \left\{ [1 - k_f/(\kappa - p)](1 - e^{-pt_1}) + [k_f p/\kappa(\kappa - p)](1 - e^{-\kappa t_1}) \right\} \quad (31)$$

During the reverse electrolysis

$$d(R)/dt = -(p + k_f)(R) + k_b(Z) \quad (32)$$

$$d(Z)/dt = k_f(R) - k_b(Z) \quad (33)$$

with the condition,  $(R) = (R)_{t_1}$  and  $(Z) = (Z)_{t_1}$ , at  $t = t_1$ . Solving (32) and (33) simultaneously (e.g., by the Laplace transform method) yields

$$(R) = \frac{(R)_{t_1}}{2} [e^{-(a-b)\tau} + e^{-(a+b)\tau}] + \frac{G}{2} [e^{(a-b)\tau} - e^{-(a+b)\tau}] \quad (34)$$

where

$$a = (p + k_f + k_b)/2, \quad b^2 = a^2 - pk_b, \quad \tau = t - t_1$$

and

$$G = \{ k_b(C_i)[1 - \exp(pt_1)] - a(R)_{t_1} \}/b$$

Combining (4), (8), and (34) and integrating yields

$$\frac{Q_b}{Q_t} = 1 - [2k_b(C_i)(1 - e^{-pt_1})]^{-1} \{ (a+b)[(R)_{t_1} + G]e^{-(a-b)\tau_1} + (a-b)[(R)_{t_1} - G]e^{-(a+b)\tau_1} \} \quad (35)$$

where  $\tau_1 = t_2 - t_1$ . At long  $\tau_1$ ,  $Q_t = Q_b^0$  since the reaction is reversible. The variation of the current during the reverse electrolysis can be obtained by combining (7) and (34) and in general will follow the behavior previously described by Bard and Solon<sup>2</sup> (see eq. 36 in ref. 2).

(2) A. J. Bard and E. Solon, *J. Phys. Chem.*, **67**, 2326 (1963).

Case IV. The intermediate R is consumed by a second-order (coupling) reaction



During the forward reaction the system is described by the equation

$$d(R)/dt = p(C) - k_2(R)^2 \quad (37)$$

with  $(R) = 0$  at  $t = 0$ . Combination of (3) and (37) yields

$$d(R)/dt = p(C_i)e^{-pt} - k_2(R)^2 \quad (38)$$

This equation is essentially that treated by Chien,<sup>3</sup> and by using the transformations

$$(R) = (1/k_2u)(du/dt) \quad (39)$$

$$\tau = \exp(-pt) \quad (40)$$

the following equation is obtained

$$\tau^2 u'' + \tau u' - \kappa \tau u = 0 \quad (41)$$

where  $u''$  and  $u'$  are the second and first derivatives of  $u$  with respect to  $\tau$ , respectively, and  $\kappa = k_2(C_i)/p$ . This is a Bessel's equation whose solution is<sup>4</sup>

$$u = c_1 I_0(2\sqrt{\kappa\tau}) + c_2 K_0(2\sqrt{\kappa\tau}) \quad (42)$$

where  $c_1$  and  $c_2$  are constants and  $I_m$  and  $K_m$  are modified Bessel functions of the first and second kind, respectively, of order  $m$ . Using (39) and the initial condition finally yields an equation for  $(R)$  at time  $t_1$

$$(R)_{t_1} = \frac{(C_i)x \beta' K_1(x) - I_1(x)}{2\kappa \beta' K_0(x) + I_0(x)} \quad (43)$$

where

$$\beta' = I_1(2\sqrt{\kappa})/K_1(2\sqrt{\kappa}) \quad (44)$$

$$x = 2\sqrt{\kappa} \exp(-pt_1/2) \quad (45)$$

During the reverse electrolysis

$$d(R)/dt = -p(R) - k_2(R)^2 \quad (46)$$

and  $(R) = (R)_{t_1}$  at  $t = t_1$ . Solving (46) yields

$$(R) = \frac{Ap \exp[-p(t - t_1)]}{k_2 \{1 - A \exp[-p(t - t_1)]\}} \quad (47)$$

where

$$A = k_2(R)_{t_1}/[k_2(R)_{t_1} + p] \quad (48)$$

Using (8) or (9) and (48) yields

$$Q_b = (nFVp/k_2) \ln \{1 + [k_2(R)_{t_1}/p][1 - e^{-p(t_2-t_1)}]\} \quad (49a)$$

$$Q_b^0 = (nFVp/k_2) \ln \{1 + k_2(R)_{t_1}/p\} \quad (49b)$$

and combination of (4), (43), and (49b) gives

$$Q_b^0/Q_t = \ln \{(Bx/2 + 1)/(1 - e^{-pt_1})\} \quad (50)$$

where

$$B = \frac{\beta' K_1(x) - I_1(x)}{\beta' K_0(x) + I_0(x)} \quad (51)$$

Values of  $Q_b^0/Q_t$  were computed as functions of the dimensionless parameters  $p/k_2(C_i)$  and  $pt_1$  using a CDC 1604 computer and an original function subroutine for the various modified Bessel functions. The results of these calculations, shown in Fig. 2, allow the determi-

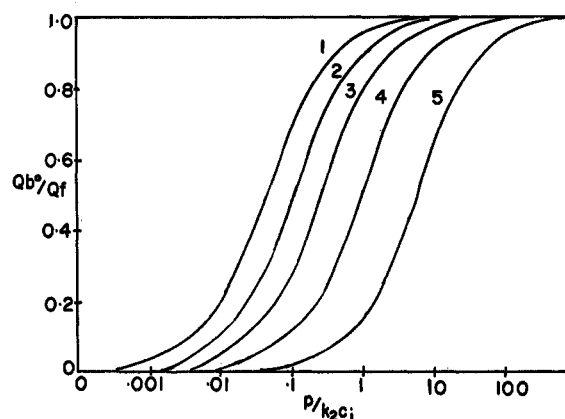


Figure 2. Case IV: variation of  $Q_b^0/Q_t$  with  $p/k_2(C_i)$  for various values of  $pt_1$  (or % electrolysis): (1) 0.1 (9.5%), (2) 0.22 (20%), (3) 0.51 (40%), (4) 1.6 (80%), (5) 6.9 (99.9%).

nation of  $k_2$ . Note that a second-order (coupling) reaction can be distinguished from a first-order one by the dependence of  $Q_b^0/Q_t$  upon  $(C_i)$  at a given value of  $pt_1$ .

The extension of this case to include a waiting period from  $t_1$  to  $\tau'$  follows exactly as in case II, with

$$d(R)/dt = -k_2(R)^2 \quad (52)$$

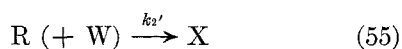
$$(R)_{\tau'} = (R)_{t_1}/[1 + k_2(R)_{t_1}(\tau' - t_1)] \quad (53)$$

where  $(R)_{t_1}$  is given by (43). Using  $(R)_{\tau'}$  in place of  $(R)_{t_1}$  in (49) will yield appropriate expressions for  $Q_b$  and  $Q_b^0$ .

Case V. The intermediate R is consumed by parallel first- or pseudo-first-order reactions.

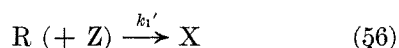
(3) J. Chien, *J. Am. Chem. Soc.*, **70**, 2256 (1948.)

(4) F. B. Hildebrand, "Advance Calculus for Engineers," Prentice-Hall, Englewood Cliffs, N. J., 1949, p. 167.



where Z and W are present in large excess and  $k_1 = k_1'(Z)$  and  $k_2 = k_2'(W)$ . The general form of the equations governing the electrolysis in this case are the same as those in case II, so that the final equation for this case can be obtained by replacing  $k$  by  $(k_1 + k_2)$  in (22).

*Case VI.* The intermediate R is consumed by parallel reactions, a pseudo-first-order reaction and a second-order (coupling) reaction.



where  $k_1 = k_1'(Z)$ . During the forward reaction the system is described by the equation

$$d(R)/dt = p(C) - k_1(R) - k_2(R)^2 \quad (58)$$

with  $(R) = 0$  at  $t = 0$ . Combination of (3) and (58) yields

$$d(R)/dt = p(C_i)e^{-pt} - k_1(R) - k_2(R)^2 \quad (59)$$

The analytical solution of this equation generally follows the treatment of Weller and Berg.<sup>5</sup> It is solved using the same transformation as in case IV, eq. 39 and 40, which transforms (59) to

$$\tau^2 u'' + (1 - m)\tau u' - \kappa \tau u = 0 \quad (60)$$

where  $m = k_1/p$  and  $\kappa = k_2(C_i)/p$ . The solution of this Bessel equation is<sup>4</sup>

$$u = \tau^{1/2m} Z_m(2\sqrt{\kappa\tau}) \quad (61)$$

where

$$Z_m(x) = c_1' J_m(x) + c_2' J_{-m}(x) \quad (62)$$

for nonintegral values of  $m$ , and

$$Z_m(x) = c_1 J_m(x) + c_2 Y_m(x) \quad (63)$$

for integral values of  $m$ ,  $J_m$  and  $Y_m$  are Bessel functions of the first and second kind, respectively, of order  $m$ , and  $c_1$ ,  $c_2$ ,  $c_1'$ , and  $c_2'$  are constants. The use of (39) and the initial condition finally yields an equation for  $(R)$  at time  $t_1$ .

$$(R)_{t_1} = (C_i)x B'/2 \quad (64)$$

where

$$x = 2\sqrt{\kappa} \exp(-pt_1/2) \quad (65)$$

$$B' = \frac{\beta' J_{m-1}(x) - J_{-(m-1)}(x)}{\beta' J_m(x) + J_{-m}(x)} \quad (66a)$$

$$\beta' = J_{-(m-1)}(2\sqrt{\kappa})/J_{m-1}(2\sqrt{\kappa}) \quad (66b)$$

for nonintegral values of  $m$ , and

$$B' = \frac{\beta J_{m-1}(x) - Y_{m-1}(x)}{\beta J_m(x) - Y_m(x)} \quad (67a)$$

$$\beta = Y_{m-1}(2\sqrt{\kappa})/J_{m-1}(2\sqrt{\kappa}) \quad (67b)$$

for integral values of  $m$ .

During the reverse electrolysis

$$d(R)/dt = -(p + k_1)(R) - k_2(R)^2 \quad (68)$$

with  $(R) = (R)_{t_1}$  at  $t = t_1$ . This equation is of the same form as (46) so that the solutions for  $Q_b$  and  $Q_b^0$  are the same as (49) with  $p$  in the natural logarithm term replaced by  $(p + k_1)$ . This result, with (4) and (64), yields

$$Q_b^0/Q_t = \ln [B'x/2(1 + m) + 1]/\kappa(1 - \exp[-pt_1]) \quad (69)$$

where  $B'$ ,  $x$ ,  $m$ , and  $\kappa$  are defined as before. Inspection of (69) shows that  $Q_b^0/Q_t$  is a function of the dimensionless parameters  $p/k_2(C_i)$ ,  $k_1/p$ , and  $pt_1$ . Rather than use (69) to solve for values of  $Q_b^0/Q_t$ , however, it was more convenient to solve (58) numerically using a CDC 1604 computer and employing a slight modification of a library program based on a Runge-Kutta and Adams-Moulton procedure.<sup>6</sup> Typical results of these calculations are shown in Fig. 3.

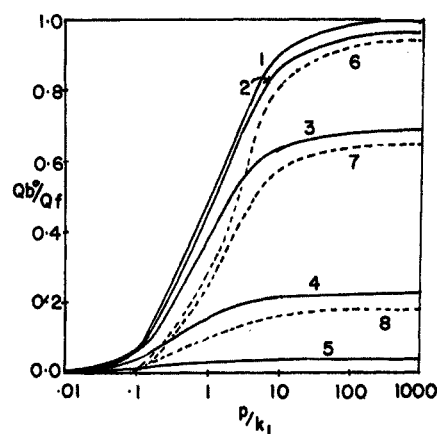


Figure 3. Case VI: variation of  $Q_b^0/Q_t$  with  $p/k_1$  for various values of  $p/k_2(C_i)$ : (1) and (6) 10 or larger, (2) and (7) 1, (3) and (8) 0.1, (4) 0.01, (5) 0.001; —,  $pt_1 = 0.1$ ; - - - - -,  $pt_1 = 1.0$ .

(5) K. Weller and H. Berg, *Ber. Bunsenges. Physik. Chem.*, **68**, 33 (1964).

(6) J. L. Raney and G. J. Lastman, D2 UTEX RKAMPDP, Computation Center, the University of Texas, UTD2-02-003 (1964).

## Results and Discussion

Reversal coulometry in the absence of complicating chemical reactions was tested by studying the reduction of ferricyanide ion at a platinum electrode, followed by the oxidation of the formed ferrocyanide ion, and the reduction of iron(III) in an oxalate medium at a mercury electrode, followed by the oxidation of the iron(II). In both cases reduction was carried out for a time,  $t_1$ , followed by a change in the electrolysis potential to one at which oxidation of the iron(II) species would occur. The oxidation was also carried out for  $t_1$  sec. The value of  $p$  was calculated from the measured value of  $Q_b/Q_f$  using (15). Note that for an electrolysis with no complicating chemical reactions, a time delay between the reduction and oxidation does not affect the results. Values of  $p$  determined by this method were compared to those obtained from the current decay curves during the oxidation. Results of these experiments, given in Tables I and II, indicate that reversal coulometry may be a rapid and simple method of determining  $p$  values.

**Table I:** Reversal Coulometry in Absence of Side Reactions: Reduction and Oxidation in a Solution Initially Containing 25.2 mmoles of  $K_3Fe(CN)_6$  in ca. 6.5 ml. of 1 M HCl at a Platinum Electrode<sup>a</sup>

$t$ , sec.	$Q_b/Q_f$	$p \times 10^2$ , sec. <sup>-1</sup>	
		Calcd. <sup>b</sup>	Oxdn
30	0.294	1.14	1.44
60	0.476	1.08	1.29
100	0.667	1.10	1.12
150	0.815	1.12	1.15
Complete electrolysis	...	...	1.13

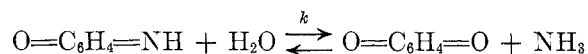
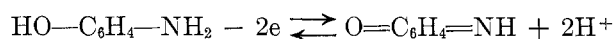
<sup>a</sup> Reduction potential = -0.3 v. vs. s.c.e.; oxidation potential = +0.5 v. vs. s.c.e. <sup>b</sup> Calculated from eq. 15. <sup>c</sup> Calculated from current decay curve for oxidation.

**Table II:** Reversal Coulometry in Absence of Side Reactions: Reduction and Oxidation of a Solution Initially Containing 25.0 mmoles of Iron(III) in ca. 6.5 ml. of 0.5 M  $H_2SO_4$  and 0.2 M  $K_2C_2O_4$  at a Mercury Pool Electrode<sup>a</sup>

$t_1$ , sec.	$Q_b/Q_f$	$p \times 10^2$ , sec. <sup>-1</sup>	
		Calcd. <sup>b</sup>	Oxdn. <sup>c</sup>
30	0.214	0.80	...
50	0.322	0.78	0.70
100	0.494	0.69	0.72
150	0.634	0.66	0.71

<sup>a</sup> Reduction potential = -0.44 v. vs. s.c.e.; oxidation potential = -0.04 v. vs. s.c.e. <sup>b</sup> Calculated from eq. 15. <sup>c</sup> Calculated from current decay curve for oxidation.

The electrooxidation of *p*-aminophenol (PAP) at a platinum electrode was used to test reversal coulometry with a following chemical reaction. The oxidation of PAP in aqueous solution has been studied by several electrochemical techniques<sup>7</sup> and has been shown to occur as follows



The reaction was studied by oxidizing PAP at 0.7 v. vs. s.c.e. for  $t_1$  sec., determining  $Q_f$ , and then shifting the potential to reduce the imine completely and determining  $Q_b^0$ . The value of  $p$  was calculated using either the decay curve during the forward electrolysis or the formula [obtained from (4) and (15)]

$$p = -t_1^{-1} \ln(1 - Q_f/Q_f^0) \quad (70)$$

Values of  $p/k$  were determined from graphs such as Fig. 1, and values of  $k$  calculated. The results given in Table III show good agreement among the calculated  $k$  values (values calculated assuming a second-order following reaction give much poorer agreement). The average value of  $k$ ,  $1.11 \times 10^{-2}$  sec.<sup>-1</sup>, for the hydrolysis of benzoquinoneimine in 0.99 M  $H_2SO_4$  at 25.9° is in fair agreement with the value recently obtained<sup>8</sup> in 1.02 M  $H_2SO_4$  at 25.0°,  $0.74 \times 10^{-2}$  sec.<sup>-1</sup>.

**Table III:** Reversal Coulometry with Following First-Order Chemical Reaction. Oxidation and Reduction in Solution Initially Containing Varying Amounts of *p*-Aminophenol (PAP) in 6.5 ml. of 0.99 M  $H_2SO_4$  at a Platinum Electrode<sup>a</sup>

Amount of PAP, $\mu$ moles	$Q_b^0/Q_f$	$p \times 10^2$ , sec. <sup>-1</sup>	$k \times 10^2$ , sec. <sup>-1</sup>
8.05	0.180	0.94	1.11
22.5	0.175	0.88	1.11
39.2	0.160	0.63	1.12

<sup>a</sup> Oxidation potential = 0.70 v. vs. s.c.e.; reduction potential = 0.50 v. vs. s.c.e.; temperature 25.9°,  $t_1$  150 sec.

The technique of reversal coulometry was also used in the study of the electroreduction of riboflavin in a dimethyl sulfoxide medium,<sup>9</sup> a system which also apparently involves a following first-order reaction.

(7) A. C. Testa and W. H. Reinmuth, *Anal. Chem.*, **32**, 1512 (1960); H. B. Herman and A. J. Bard, *ibid.*, **36**, 510 (1964), and references contained therein.

(8) S. R. Christenson and F. C. Anson, *ibid.*, **36**, 495 (1964).

(9) S. V. Tatwawadi and A. J. Bard, to be submitted for publication.

Reactions corresponding to cases IV and VI are common in electrochemistry, especially where the product of the electrode reaction is a free radical. For example, the electroreduction of ketones in a nonprotonating solvent occurs by a one-electron reduction to a ketyl radical, which can react by either a first-order reaction to form an alcohol or by a second-order coupling to form a pinacol,<sup>5</sup> and which should follow the characteristics of case VI.

### Experimental

The controlled potential coulometric apparatus for reactions at a platinum electrode was the "high speed"

type,<sup>10</sup> equipped with a voltage-to-frequency coulometer and a Wenking potentiostat. Reversal was accomplished by switching a new potential into the potentiostat using a double-pole, double-throw switch; the coulometer was read immediately before switching. Ultrasonic stirring in the high speed cell was not used. For reduction at a mercury cathode, a two-compartment cell with a mercury pool electrode was employed.

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(10) A. J. Bard, *Anal. Chem.*, **35**, 1121 (1963).

## The Thermodynamic and Physical Properties of Beryllium Compounds. VI.

### The Heat of Formation of Beryllium Nitride<sup>1</sup>

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The decomposition pressures of solid  $\text{Be}_3\text{N}_2$  to  $\text{Be}(\text{g})$  and  $\text{N}_2(\text{g})$  over the temperature range 1450–1650°K. have been determined by the torsion effusion technique. From the data obtained in this research and available thermodynamic properties of the species involved, a third-law value of  $\Delta H_{f,298}$  for  $\text{Be}_3\text{N}_2(\text{s})$  has been found to be  $-140.3 \pm 1.5$  kcal./mole.

### Introduction

The heat of formation of  $\text{Be}_3\text{N}_2$  was first measured calorimetrically by Neumann, Kroger, and Haebler<sup>2</sup> by the direct nitridation of beryllium metal, and was reported to be  $-133.4 \pm 0.6$  kcal./mole. In 1934, Neumann, Kroger, and Kunz<sup>3</sup> reported a value of  $-135.3$  kcal./mole, determined by combustion calorimetry. In 1958, Apin, Lebedev, and Nefedova<sup>4</sup> obtained a value of  $-135$  kcal./mole from a study of the explosive reaction of beryllium powder with trimethylenetrinitramine. More recently, Gross<sup>5</sup> has obtained a value of  $-138.5$  kcal./mole from a calorimetric study of the reaction of beryllium with ammonia.

The entropy of  $\text{Be}_3\text{N}_2$  at 298°K. was estimated by Kelley<sup>6</sup> to be 12 e.u. More recent heat capacity

(1) This research was supported by the Air Research and Development Command of the United States Air Force.

(2) B. Neumann, C. Kroger, and H. Haebler, *Z. anorg. allgem. Chem.*, **204**, 81 (1932).

(3) B. Neumann, C. Kroger, and H. Kunz, *ibid.*, **218**, 379 (1934).

(4) A. Ya. Apin, Yu. A. Lebedev, and O. I. Nefedova, *Zh. Fiz. Khim.*, **32**, 819 (1958).

(5) P. Gross, Fulmer Research Inst., Ltd. (Great Britain), Report No. 163/11, Contract AF 61(052)447, March 31, 1963.

(6) K. K. Kelley, U. S. Bureau of Mines Bulletin 407, U. S. Govt. Printing Office, Washington, D. C., 1937.