

## AN EXAMINATION OF THE STEADY-STATE KINETICS OF CONSECUTIVE AND PARALLEL ELECTRODE REACTIONS

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The influences of consecutive and parallel reactions on overall kinetics were compared and a mechanism was proposed explaining the values of Tafel slopes for anodic dissolution of copper in solutions of sulphuric and perchloric acids.

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This work was prompted by a desire to find possible simple explanations for the 40 to 50 mV range of Tafel slopes observed for the anodic dissolution of copper in aqueous sulphuric acid and also the approximately 60 mV Tafel slope observed over some 3 decades (hysteresis free) for the anodic dissolution of copper in aqueous perchloric acid<sup>1</sup>.

Because of the often limited number of decades of current over which reliable, precise measurements can be made, it was desired to express as generally as possible the degree of curvature which could be expected in semilogarithmic graphs of current versus potential for various idealized mechanisms involving two simultaneously current-determining reactions. This becomes especially important in those cases where the limiting Tafel slopes are possibly not very different, for example 40 mV and 60 mV. Under these conditions pseudo-Tafel behaviour can be observed in the transition region, and means of investigation are required. The literature is concerned largely with the limiting Tafel lines because of their diagnostic properties<sup>2-7</sup> and with consecutive single-electron transfer reactions.

### THEORETICAL

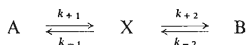
Provided 1. the stoichiometric numbers are identical (which usually means that intermediates do not interact), 2. the limiting rates of diffusion of bulk solution species involved in reaction with intermediates are very much greater than the rate of reaction, 3. only the forward component of current is considered and 4. the intermediates do not diffuse away from the electrode at a significant rate, then the steady-state current associated with two consecutive electrode reactions can usually (some

exceptions are given later) and conveniently be written in the reciprocal form

$$i^{-1} = (nFY_1)^{-1} + (nFY_2)^{-1} \quad (1)$$

$Y_1$  and  $Y_2$  are mechanistic dependent functions of potential of constant "b-value" ( $b_1$  and  $b_2$ , respectively; the limiting Tafel slopes) defined for any function  $X$  by,  $b_X = \partial E / \partial \log_{10} X$ ;  $n$  is the total number of electrons transferred for one overall chemical act and  $E$  is the electrode potential. When there is a preceding equilibrium,  $Y_1$  and  $Y_2$  both contain a factor  $v^{-1}K^{1/\nu}$ ;  $\nu$  is the stoichiometric number of the two simultaneously rate determining steps and  $K$  is the equilibrium constant of the preceding equilibrium. This has no effect on the form of the equations deduced. These results follow readily from the Christiansen expression<sup>5-9</sup> of the consequence of the steady-state principle, but may of course be written down from first principles. The effects of diffusion of reactants and products are regarded as eliminated at this stage. Diffuse double-layer and ohmic potential drop effects are also regarded as eliminated.

In the case of the simple reaction:



$$i^{-1}nFA = k_{+1}^{-1} + k_{-1}(k_{+1}k_{+2})^{-1}.$$

Here  $A$  represents the reactants and  $A$  the appropriate activity term.  $k_{+2}$  and/or  $k_{-1}$  may contain a factor equal to the bulk concentration of some reactant. Also, by comparison with equation (1).

$$b_1^{-1} = b_{k_{+1}}^{-1}; \quad b_2^{-1} = b_{k_{+1}}^{-1} + b_{k_{+2}}^{-1} + |b_{k_{-1}}^{-1}|$$

If the reaction is preceded by an equilibrium  $\sum a_1 A_1 \rightleftharpoons \sum b_2 B_2 + \nu A$  i.e. the overall reaction is  $\sum a_1 A_1 + \sum a_2 A_2 \rightleftharpoons \sum b_1 B_1 + \sum b_2 B_2$ , then

$$i^{-1}(n/\nu) F(\prod [A_1^{a_1} / \prod [B_2^{b_2}]^{1/\nu} = k_{+1}^{-1} K^{-1/\nu} + k_{-1}(k_{+1}k_{+2})^{-1} K^{-1/\nu},$$

where  $B_2$  represents a product formed prior to the "rate-determining reaction" and  $A_2$  represents a reactant not involved until after the "rate-determining reaction". This equation is of the same form as equation (1).

By application of elementary kinetic principles and the definition of a rate-determining step, it can be shown that

$$(i_+/i_-)_\eta = \exp(nF\eta/\nu RT), \quad (2)$$

where  $\nu$  refers as before to the rate determining sequence of steps,  $\eta$  is the over-

potential and  $i_+$  and  $i_-$  are the forward and backward components of the current (when the backward component is not considered  $i$  is written for  $i_+$ ). This equation applies to any number of parallel reactions taken together provided  $\nu$  and the products are the same in each case.

Combining this result with equation (1) we have for the net forward current

$$i^{-1} = [(nFY_1)^{-1} + (nFY_2)^{-1}] [1 - \exp(-nF\eta/\nu RT)]^{-1}. \quad (3)$$

This is a generalized form of the particular equation (6'') given by Vetter<sup>3</sup>;  $|b_1| > |b_2|$  and  $b_1$  and  $b_2$  have as yet unspecified values including possibly  $\infty$ .

$Y_2$  may involve a diffusion from the electrode to the bulk of the solution. This case can be included in this analysis if the equivalent diffusion layer thickness ( $\delta$ ) can be regarded as constant and the corresponding rate constant in  $Y_2$  simply replaced by  $D/\delta$  ( $D$  is the diffusion coefficient of the diffusing species).

The restrictions on stoichiometric numbers and the requirement of a high rate of diffusion of bulk species which react with intermediates, follow from the need for  $b_1$  and  $b_2$  to be constants. These are severe restrictions but are very common and also inherent in the earlier related derivations for the special case of two single-electron-transfer consecutive steps given by Vetter<sup>2,3</sup> and examined further by Hurd<sup>4</sup>. As explained later, useful semiquantitative results follow even when the stoichiometric number is not the same for the two steps.

No restriction is placed on  $n$ , and the distribution of the  $n$  electrons between the steps exerts its influence through  $b_1$  and  $b_2$ . This is the result of the fact that while electrode reactions may be chemically in "series" or in "parallel", their currents are always additive but not necessarily equal.

The current due to two simple, independent parallel reactions can then be very conveniently represented by  $i = n_1FY_1 + n_2FY_2$ ;  $n_1$  and  $n_2$  are the values of  $n$  for the respective parallel paths.

## DERIVATIONS AND RESULTS

### *The Consecutive Case*

We define  $r = Y_2/Y_1$  and a scale of potential ( $\Delta$ ) such that  $\Delta = 0$  at  $r = 1$ . The subscript zero will indicate  $\Delta = 0$ . Thus  $r_0 = (Y_2/Y_1)_0 = 1$ .

We have,

$$\log_{10} Y_2 = \log_{10} Y_{2,0} + (\Delta/b_2) \quad (4)$$

so that,

$$r = \text{antilog}_{10} \left( \frac{\Delta}{b_2} - \frac{\Delta}{b_1} \right). \quad (5)$$

From equation (1) by differentiation and substitution for  $Y_2/Y_1$ , we have,

$$\frac{1}{b} = \frac{1}{b_1} + \frac{1}{b_2} - \frac{1}{1+r} \left( \frac{1}{b_1} + \frac{r}{b_2} \right),$$

giving

$$b = (1+r) b_1 b_2 / (r b_2 + b_1) \quad (6)$$

or

$$r = b_1(b - b_2) / b_2(b_1 - b), \quad (7)$$

and

$$b_0 = 2b_1 b_2 / (b_1 + b_2). \quad (6a)$$

Further, equation (1) may be written,

$$nF/i = (1+r)/Y_2.$$

Taking logarithms and substituting for  $\log_{10} Y_2$  from equation (4),

$$\log_{10} i = (A/b_2) - \log_{10} (1+r) + \log_{10} nFY_{2,0}. \quad (8)$$

Replacing  $nFY_{2,0}$  by  $2i_0$  and writing  $I_c = i/2i_0$  (the subscript c indicating consecutive) we have,

$$\log_{10} I_c = (A/b_2) - \log_{10} (1+r). \quad (9)$$

Incidentally, the full expression for the net forward current is in view of equation (3),

$$\log_{10} i = (A/b_2) - \log_{10} (1+r) + \log_{10} 2i_0 + \log_{10} [1 - \exp(-nF\eta/RT)]. \quad (10)$$

### The Parallel Case

$$i = n_1 F Y_1 + n_2 F Y_2.$$

We define  $r = n_2 Y_2 / n_1 Y_1$  so that as for the consecutive case we have,

$$r = \text{antilog}_{10} [(A/b_2) - (A/b_1)],$$

$$b = (1+r) b_1 b_2 / (b_2 + r b_1), \quad (11)$$

$$r = b_2(b_1 - b) / b_1(b - b_2), \quad (12)$$

$$b_0 = 2b_1 b_2 / (b_1 + b_2). \quad (11a)$$

Also, since  $i = n_1 F Y_1 (1 + r)$ ,

$$\log_{10} I_p = (\Delta/b_1) + \log_{10} (1 + r), \quad (13)$$

where,  $I_p = 2i/i_0$  and the subscript p indicates parallel reactions.

Incidentally, if the products are identical and  $v$  is the same, the full expression for the net forward current is, in view of equation (2),

$$\log_{10} i = (\Delta/b_1) + \log_{10} (1 + r) + \log_{10} (i_0/2) + \log_{10} (1 - \exp(-nF\eta/vRT)). \quad (14)$$

Inspection of equations (6) and (11) reveals:

$$b \text{ (parallel reactions; } r = m) = b \text{ (consecutive reactions; } r = m^{-1}).$$

By definition,  $r \text{ (at } \Delta) = r^{-1} \text{ (at } -\Delta)$  so that,

$$b \text{ (parallel reactions; at } \Delta) = b \text{ (consecutive reactions; at } -\Delta)$$

and one set of results serves for both reaction types.

By taking idealized values of  $b_1$  and  $b_2$  (at 25°C:  $\infty$ , 237, 118.4, 59.2, 47.4, 39.5 mV, etc) general idealized graphs and tables of  $b$  versus  $\Delta$  and also  $\log_{10} I_p$  and  $\log_{10} I_c$  versus  $\Delta$  have been drawn (5 mV intervals in the interval  $\Delta = \pm 150$  mV). Fig. 1 shows the general relationship between  $\log_{10} I_p$  and  $\log_{10} I_c$ . Figs 2 and 3 illustrate how even with a considerable change in  $b$ , pseudo-Tafel behaviour can be observed in some cases over more than two decades of current. In those cases where a compari-

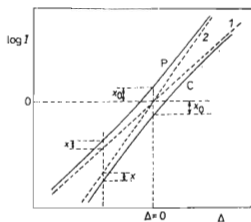


FIG. 1

Diagrammatic Relationship of  $\log I_p(P)$  and  $\log I_c(C)$  to  $\Delta$

$x = \log_{10} (1 + r)$ ;  $x_0 = \log_{10} 2$ ; 1  $\log_{10} Y_1 n_1 F$  (i.e.  $\Delta/b_1$ ) vs  $\Delta$ ; 2  $\log_{10} Y_2 n_2 F$  (i.e.  $\Delta/b_2$ ) vs  $\Delta$ .

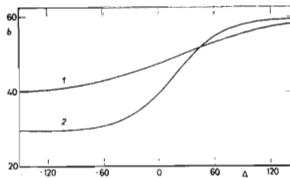


FIG. 2

Consecutive Reactions

1  $b_1 = 59.2$  mV,  $b_2 = 39.5$  mV; 2  $b_1 = 59.2$  mV,  $b_2 = 29.6$  mV.

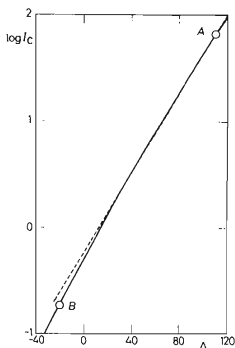


FIG. 3

Consecutive Combination of Terms  $b_1 = 59.2$  mV,  $b_2 = 39.5$  mV

Dashed line  $b = 53$  mV, A  $b = 56.2$ , B  $b = 45.6$  mV.

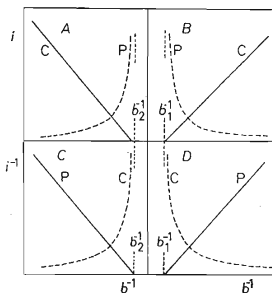


FIG. 4

Diagrammatic Representation of  $i$  and  $i^{-1}$ , resp. vs  $b^{-1}$  Curves

C Indicates consecutive, P parallel reactions.

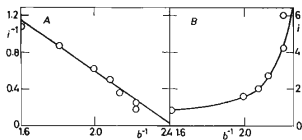


FIG. 5

Anodic Dissolution of Polycrystalline Copper at 337 mV and 25°C

Influence of addition of 1M-H<sub>2</sub>SO<sub>4</sub> to 1M-HClO<sub>4</sub>, 50–200 mV/s, single or double potential sweeps from c. 30 μA/cm<sup>2</sup> anodic.  $i$  in mA/cm<sup>2</sup>,  $b$  in 0.1 V. A cf. Fig. 4C, B cf. Fig. 4A.

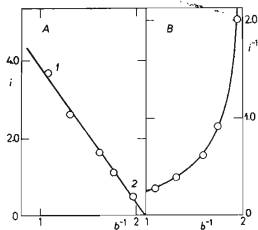


FIG. 6

Anodic Dissolution of Polycrystalline Iron at -300 mV in an acetate buffer at 25°C

Influence of solution composition 1 pH 3.98, 2 pH 2.98,  $i$  in mA/cm<sup>2</sup>,  $b$  in 0.1 V (permission of Bech-Nielsen<sup>12</sup>)

son is possible, the results for the consecutive case are of course similar to those of Vetter<sup>2,3</sup> and Hurd<sup>4</sup>. However, Hurd's computer solutions considered small intervals of potential only in the region of  $\eta = 0$  with the result that the interesting transition region when  $\eta \gg 0$  only contained one or two point solutions. Hurd was led to the impression of a true Tafel region at higher potentials and a pseudo-Tafel region at lower potentials, the slope in the pseudo-Tafel region depending on the ratio of the exchange-currents of the steps of the process. The form of the semilogarithmic current-potential curve is, as shown above by equations (9) and (13), quite independent of the ratio of the exchange-currents except in so far as this defines the magnitude of  $\eta$  and consequently how much of the undistorted curve can be observed; this distortion would however provide limited extended pseudo-linearity in the parallel reaction case not considered by Hurd. Conway<sup>10</sup> considered the influence of potential on consecutive and parallel reactions and gave diagrams similar to Fig. 1. except that only the limiting slopes were considered. He has also stated<sup>11</sup> that there is a smooth transition between the two limiting Tafel regions over a small potential range. This statement must be recognized as a relative one (Fig. 2 and 3), being true only in those cases where a small potential range corresponds with several times the smaller of the limiting  $b$ -values (as is the case considered in Conway's original paper<sup>10</sup>). Actually, for  $r$  to change from 10 to 0.1,  $\Delta$  must change by  $2b_2/[1 - (b_2/b_1)]$ , (compare reference<sup>5</sup>; this corresponds with a change in  $b^{-1}$  from  $b_1^{-1} + [(b_2^{-1} - b_1^{-1})/11]$  to  $b_2^{-1} - [(b_2^{-1} - b_1^{-1})/11]$ . However, this does not give a very helpful guide to the expected degree of curvature of Tafel plots as illustrated in Fig. 3.

The case of two rate determining steps with different values of  $\nu$  cannot be treated in this simple manner. However, a semiquantitative picture of the behaviour can be obtained by considering the limiting combinations which in this case correspond to different combinations of  $b_1$  and  $b_2$ . For example, the current for the simple Volmer-Tafel mechanism ( $H^+ \rightleftharpoons H$ ;  $2H \rightarrow H_2$ ) may be written,  $i^{-1} = (nFY_1)^{-1} + (nFY_2)^{-1}$  where  $Y_2^1 = [H] Y_2$ . It is readily found that (at 25°C) at low potentials  $b_2^1 = 29.6$  mV and  $b_1 = 118.4$  mV whereas at high potentials  $b_1 = 118.4$  mV and  $b_2^1 = 47.4$  mV. In this way convenient limits are placed on the rate of transition in those cases where the stoichiometric numbers of the steps differ. Suitable combination gives a surprisingly accurate estimate of the behaviour in the transitional region.

It is not suggested that these curves can be used in a diagnostic manner but because of their generality they should be very useful for quick semi-quantitative tests and curve fitting. The computer programmes are very easily changed to give results for any selected pairs of  $b$ -values.

In view of the pseudo-Tafel behaviour possible for some combinations of  $b$ -values, it is desirable to be able to predict the relationship between current and its associated  $b$ -value at a constant potential. We suppose that either  $Y_1$  or  $Y_2$  (not both) can be varied at constant potential by for example changing solution composition or electrode surface state; the mode of variation of the  $Y$ -term will be immaterial.

The consecutive case. By rearranging equation (1) and substituting for  $Y_2$ ,

$$i = nFY_1 \left( \frac{r}{1+r} \right).$$

From equation (7)

$$\frac{r}{1+r} = \frac{b_1(b-b_2)}{b_2(b_1-b) + b_1(b-b_2)} = \frac{b_1(b-b_2)}{b(b_1-b_2)}.$$

For the case of  $Y_1$  constant, these equations lead at once to

$$i = A_1 - (A_1 b_2/b),$$

where  $A_1$  is a constant (Fig. 4A). When  $Y_2$  is constant,

$$i = (A_2 b_1/b) - A_2,$$

where  $A_2$  is another constant (Fig. 4B).

The parallel case. Supposing  $Y_1$  is constant, we have

$$i = n_1 F Y_1 (1+r)$$

and substituting for  $(1+r)$  from equation (12),

$$i^{-1} = A_3 - (A_3 b_2/b),$$

where  $A_3$  is a constant (Fig. 4C). In the case when  $Y_2$  is constant, we obtain,

$$i^{-1} = (A_4 b_1/b) - A_4$$

( $A_4$  is a constant; see Fig. 4D).

These results are not to be regarded as providing fully diagnostic tests but as providing conditions which must be fulfilled if such mechanisms are postulated; limiting unobservable  $b$ -values may sometimes be estimated.

Tentative applications of these results have been made in connection with the anodic dissolution of copper<sup>11</sup> and the anodic dissolution of iron<sup>12</sup>. Some results treated in this way are given in Figs 5 and 6.

A special, possibly rather important case where the above treatment fails is that where reaction and simultaneous surface diffusion of an intermediate occur. By



adapting earlier solutions<sup>13-15</sup> of this problem it can be shown that this can give rise to apparently linear Tafel lines over many decades of current and also to idealized but anomalous limiting Tafel slopes such as 240 mV and 47.5 mV (at 25°C); the latter may be of significance with regard to the anodic dissolution of copper in aqueous sulphuric acid. The 47.5 mV limiting law arises from surface diffusion not of metal ad-species as contemplated earlier by many authors but from surface diffusion of a cuprous species; the  $b$ -value for the anodic current is then given by, (Fig. 7)

$$\frac{1}{b} = \frac{1}{39.5} - \frac{1}{237} \left[ 1 - \frac{2u}{\sinh 2u} \right] \quad (15)$$

(at 25°C, where  $b_u = 237$  mV). The 60 mV Tafel slope observed in aqueous perchloric acid<sup>1</sup> may be a result of slow surface diffusion of cuprous ions from crystal steps (where equilibrium between the lattice and a cuprous ad-species is postulated) and widely spaced active centres for further oxidation. Cathodic experiments with a rotating-disc electrode in aqueous perchloric acid indicate a slow step prior to charge-transfer or widely spaced active centres<sup>1</sup> according to the model of Nagy, Horanyi and Vertes<sup>16</sup>.

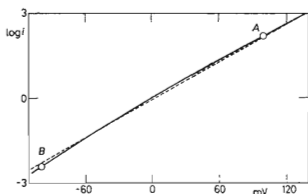
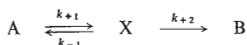


FIG. 7

Effect of Surface Diffusion (Constant Coefficient) of  $\text{Cu}^+$  on Anodic Tafel Plot  
Dashed line linear approximation, A  $b = 47.1$ , B  $b = 40.2$  mV.

Another situation where the above treatments may have to be modified is that where coverage of the electrode by an intermediate is not  $\ll 1$ . For the reaction



and when the coverage of the electrode by B is constant or  $\ll 1$ , the expression for the current is of the form

$$i^{-1} = (nFY_1)^{-1} + (nFY_2)^{-1} + (nFY_3)^{-1}. \quad (16)$$

However, in those cases where the coverage by  $X$  is  $\ll 1$ ,  $b_{k+1} = b_{k+2}$  or  $b_{k+1} = \infty$ , equation (16) reduces to equation (1) (reaction order will be complicated in some cases).

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#### REFERENCES

1. Reeve J. C.: Unpublished results.
2. Vetter K. J.: *Z. Naturforsch.* 7a, 328 (1952).
3. Vetter K. J.: *Z. Naturforsch.* 8a, 823 (1953).
4. Hurd R. M.: *J. Electrochem. Soc.* 109, 327 (1962).
5. Bockris J. O'M.: *J. Chem. Phys.* 23, 817 (1956).
6. Green M., Robinson P. H.: *J. Electrochem. Soc.* 106, 253 (1959).
7. Nord H., et al.: *Acta Chem. Scand.* 15, 300 (1961).
8. Christiansen J. A.: *Advan. Catalysis* 5, 311 (1953).
9. Christiansen J. A.: *Z. Physik. Chem. (Frankfurt)* B33, 145, (1936); B37, 374 (1937).
10. Conway B. E.: *Trans. Royal Soc. Canada* 54, Series III, Section II, 19 (1960).
11. Conway B. E.: *Electrode Processes*, p. 110. Ronald Press, New York 1965.
12. Bech-Nielsen G.: Unpublished results.
13. Lorenz W.: *Z. Elektrochem.* 57, 382 (1953).
14. Fleischmann M., Thirsk H. R.: *Electrochim. Acta* 2, 22 (1960).
15. Damjanovic A., Bockris J.O'M.: *J. Electrochem. Soc.* 110, 1035 (1963).
16. Nagy F., Haranyi G., Vertes G.: *Acta Chim. Acad. Sci. Hungary* 34 (1). 35 (1962).